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Atmospheric
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Discussions

Interactive comment on “The influence of snow grain size and impurities on the vertical profiles of actinic flux and associated NO$_x emissionsontheAntarcticandGreenlandicesheets''byM.$

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The manuscript presented by Zatko et al. can be divided into three parts: (1) some new measurements of black carbon (BC) concentrations in the snow at Summit, Greenland and Dome Concordia, Antarctica, (2) the development of a parameterization for vertical profiles of the actinic flux in the snowpack in the UV an visible range taking into account BC and other absorbers, (3) the estimation of the transport and chemical lifetimes of NOx in the firn air produced by photolysis inside the snow. Part (1) is a useful addition to the currently limited information on BC concentrations in the snow in polar regions. It especially points out the importance of the station activity on measured

concentrations close to the stations. This has an important impact on the correct determination of BC in the snow in future studies in Greenland and Antarctica and on the impact of BC on photochemical reactions observed close to stations. Part (2) possibly provides a useful tool for further studies of the impact of snow photochemistry in large scale models although the potential application remains somewhat obscure to me (see major comment below). However, the approach used in part (3) is inconsistent and in my opinion cannot be published in the current form. For the transport of NOx from the snowpack to the atmosphere, the authors consider two processes: diffusion and wind-pumping. Based on available parameterizations for these processes the authors obtain lifetimes for NOx due to the transport to the atmosphere called ïĄťescape. This approach would make sense if the NOx concentrations in the firn air would always be higher than in the ambient air. However, as described on p. 15761f the authors need to assume profiles of NOx (and other trace gases) for the calculation of the chemical lifetimes. They used observed ambient concentrations scaled to the actinic flux at 305 nm. This leads to an exponential decrease of NOx concentrations in the firn air (p. 15769, l. 28f). By the way the few available firn air measurements of NO and NO2, but also of other reactive trace gases indicate that this is normally not the case [e.g. Jacobi et al., 2004; Helmig et al., 2009]. Nevertheless, as a result of the assumed profile all transport processes would lead to a downward flux of NOx deeper into the snow and no NOx would ever escape the snowpack meaning that the calculated ïĄťescape becomes useless for NOx. In a second approach, the authors use profiles for NOx comparable to those obtained in a previous modeling study at Summit [Thomas et al., 2011]. In this case NO shows a maximum somewhere between 5 and 10 cm depth, while NO2 remains constant throughout the snowpack. Such a profile causes a similar problem regarding the direction of the fluxes. In this case only the firn air above the NOx maximum contributes to an upward flux leading to an escape of NOx from the firn air to the atmosphere. At depths below the maximum, the NOx flux should again be directed downwards into the snow making the escape of NOx from this region impossible. Although I am not an expert in that field I believe that at least in the atmosphere mechanisms for counter-gradient fluxes exist. Possibly the wind-pumping mechanism can cause such a counter-gradient fluxes? But that needs to be verified and discussed in detail. In any case, the diffusion mechanism will certainly lead to a direction of the NOx flux according to the gradient. Thus, even if the wind-pumping may help to transport the NOx from deeper layers to the ambient air, the diffusion would in any case cause a flux in the different direction. Moreover, equation (30) can be regarded as an integrated initial NOx production rate in the snow, but not as flux out of the snowpack because reactions in the condensed phase of the snow can already reduce the fraction of NOx that is transferred to the adjacent firn air. In summary, with an exponential decrease of NOx in the firn air the escape to the atmosphere is only possible with the assumption of a counter-gradient flux, which is in my opinion highly uncertain. Assuming a profile with an NOx maximum at a certain depth constrains the snow layer from which the NOx can escape to the depth of this maximum. However, this maximum is not well constrained by field measurements, only by the modeling study of Thomas et al. for conditions at Summit. Due to the different conditions that can impact the NOx profile (like e-folding depths!) I doubt that the simulated profiles at Summit can directly be applied to conditions in Antarctica as was done by the authors. Overall, I recommend that the authors remove part (3) from the manuscript (also because I find that their calculations of the chemical lifetimes of NOx in the firn air are very uncertain). In my opinion, part (1) and (2) can constitute a reasonable manuscript acceptable for publication after considering the further comments below. If the authors want to retain part (3), I find it only publishable if these estimates are limited to Summit with the constrains described above for the NOx flux. In this case the authors may rely on the simulated firn air profiles from the Thomas et al. paper.

Major comments:

Introduction: The Introduction is not well written and contains several smaller and bigger formal and organizational errors. In my opinion NO2 cannot be considered as an oxidant (p. 15746, l. 7). The preservation of H2O2 in ice cores depends on physical processes and accumulation [McConnell et al., 1998; Hutterli et al., 2003], if snow photochemistry plays a role for the preservation of organics remains to be shown (p. 15746, l. 14-15). The definitions of actinic flux and e-folding depth (p. 15747, l. 15-16 and p. 15748, l. 7-8) are not well placed. Lines 1-3 on page 15747 repeat the authors' view of the NOx-HNO3 cycling in the snow-atmosphere system already described at the beginning of the same paragraph. By the way, this is one major point the manuscripts tries to address by comparing the NOx lifetimes due to transport and potential chemical reactions inside the firn air (chapters 2.4 and 3.4), while the introduction already gives the final view of the authors. If and how much of the NOx will be emitted to the atmosphere before it is oxidized to HNO3 remains rather uncertain (see comment above). The description starting on P. 15747, l. 22 of the results of the calculations presented by Wolff et al. (2002) using the now revised absorption coefficients of ice can be much shortened since the cited field measurements also indicate that the obtained e-folding depth were underestimated. First measurements of HULIS in arctic snow are now available [Voisin et al., 2012] (p. 15748, l. 22-23). The description of the collection and analysis (p. 15748, l. 24ff) can be shortened because it is repeated in more detail in paragraph 2 (where it belongs!).

The authors only provide a rough comparison of their results with the measurements by France et al. [2011] at Dome C. However, the available measurements are much more detailed. For example, France et al. [2011] provide observed wavelength-dependent e-folding depths for different snow types. Are these reproduced by the proposed parameterizations using reasonable assumptions about the snow grain size? Similarly, at Summit measurements of the nitrate photolysis rates were performed within the snowpack using actinometry [Peterson et al, 2002; Qiu et al, 2002]. How do these measurements compare to the proposed parameterization and the Monte-Carlo based simulations by Peterson et al. [2002]? A more detailed comparison of the simulated actinic flux profiles and nitrate photolysis rates is certainly necessary to underline the validity of the proposed parameterization.

According to the authors one of the major motivations for this study was the intention to provide a parameterization for the calculation of actinic fluxes and nitrate photolysis rates in the snowpack that can be included in global models (p. 15749, l. 6ff; p. 15754, l. 23ff; p. 15755, l. 13f; p. 15775, l.7ff). However, this statement remains quite imprecise throughout the manuscript. As far as I know most land-surface schemes that are used in global models to represent snow and snow properties do not generate grain size or black carbon concentrations in the snow. Both are crucial variables that are needed for the proposed parameterization. On the other hand the NCAR Community Land Model CLM has been used [e.g. Flanner and Zender, 2006; Flanner et al., 2009] to estimate the impact of BC in the snow on regional and global climate. But to do so they integrated their snow radiation scheme SNICAR in the CLM. As a result, CLM combined with SNICAR delivers full radiative profile in the simulated snowpack making a new parameterization obsolete. Possibly, the authors have the application in other models in mind, but they should clearly state for which kind of land surface schemes or models their parameterization can be useful.

Minor comments:

On p. 15769, l. 3ff the authors state that the variability in sastrugi dimensions are most important for the escape of NOx from the firn air saying also that the impact of the variability of the other parameters are negligible. Please give the range of values used for the other parameters for these tests. For example, the tortuosity of the snow shows a considerable variability and has at the same time a strong impact on the diffusion coefficient of NOx.

The authors assume that all of the nitrate in the snow at South Pole and Dome C is introduced by dry deposition (p. 15764, l. 5f). This is quite unrealistic. Although measurements are very limited, Dibb et al. [2004] demonstrated that at South Pole a newly accumulated surface snow layer showed higher nitrate concentrations than observed in the previous surface layer before. The authors should revisit their assumptions about the fraction of dry and wet deposition of nitrate in Antarctica.

P. 15764, l. 21: The ratio of BC at Summit and Dome C is rather two than three.

P. 15764, l. 23ff: The higher BC concentrations in the snow at Summit could also be caused by a more efficient deposition.

P. 15766, l. 12: Figure 3b shows only the dependence of the actinic flux in the presence of BC, but not nonBC.

P. 15766, l. 22: z = 50 cm instead of 500 cm?

Table 1: From which depth ranges were the samples? I also recommend to give the same information for each sample in a separate table as supplementary material.

Figures 2 to 6: In theses figures the scale of the depths ranges from ∼100 to 300 cm. If the figures are not deleted in a revised manuscript I recommend to make this scale uniform (for example using 200 cm as a bit more than 3 times the largest e-folding depths).

Figure 3b: The actinic flux with BC = 0 is smaller than in the presence of 0.3 ppb or 0.6 ppb BC? This can not be correct.

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