

***Interactive comment on “The influence of snow grain size and impurities on the vertical profiles of actinic flux and associated  $\text{NO}_x$  emissions on the Antarctic and Greenland ice sheets” by M. C. Zatko et al.***

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This paper is a quite technical and comprehensive attempt to study some of the factors that determine the photochemically-induced flux of  $\text{NO}_x$  from polar snowpacks. It combines some useful new measurements of black carbon with existing optical data to make inferences about the depth profile of actinic fluxes in snowpack, and the factors to which those profiles are sensitive. This provides some important insights about the fact that measurements near stations may not be representative of the wider polar plateau, and a potential to parameterise actinic flux in firn for large scale models. It then assesses the assumption used in previous studies that most  $\text{NO}_x$  produced in

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shallow firn escapes from the snowpack. This has been a long-standing assumption in snow photochemical studies: the discussions in this paper, and the qualitative result (yes, it does escape) are important for progressing the field, even though they do point out some issues (some raised in the paper, some not) that need further study. Overall, I therefore think the paper is a very worthy contribution to ACP. It is quite a hard read in places, and I think there are some detailed technical issues that need resolving, but overall I would recommend publication after moderate revision (I have labelled it as major revision because some significant thinking is required, not because I think there are substantial problems).

After completing my review, I read the second review by Jacobi, and I will add some thoughts about his main point.

I have two larger scale comments on the paper, and then some technical issues:

1. Role of BC and nonBC. At several points in the paper it is clear that nonBC is more important as an absorber in the UV (the part responsible for snow photochemistry) than BC. From Table 1,  $f_{\text{nonBC}}$  is 86–89% of the UV absorption both at, and away from, the station. I am therefore wondering why there is so much emphasis on BC in the text and tables (for example, Table 5). If it is true that the e-fold depth at Dome C is roughly half compared to its value away from the station then, from the data in Table 1, this must imply that the reason for this is a change in nonBC, not a change in BC, and yet this is barely discussed. In fact, on page 15768, line 5 and around, the paper specifically claims that the change in  $z_e$  is due to an increase in BC, but this is impossible with the data we are given: if BC in the clean sector at Dome C is responsible for 11% of the UV absorption, then (making crude assumptions) increasing it by a factor 3 only increases absorption by a factor  $(0.89+3*0.11)=1.22$ , not by a factor 2. Furthermore,  $f_{\text{nonBC}}$  would reduce to 67%, whereas it is given as 86%, which can only be achieved by a large increase in  $C_{\text{nonBC}}$ . Please think this through and explain what is happening here.

2. There are some interesting implications of the suggestion that the e-fold depth is much shorter at the stations than away from them, and these should be explored in the paper. Firstly this would suggest a flux from the snowpack a factor 2 higher outside the station area compared to inside the station vicinity, and therefore a strong horizontal gradient and flux around the stations. If this has not been observed then the paper should suggest experiments that should be done to observe it. Furthermore if it is asserted, as this paper does, that the main agent of nitrate loss from the snowpack is through photochemistry rather than re-volatilisation, then this should be occurring at double the rate outside the station vicinity. This should easily be discernable in concentrations of remaining nitrate below the photochemical zone. A simple test of whether this is true is therefore to measure the concentration profiles over the top metre at different distances from the station: a clear change in the concentration profile away from the station would support the assertion, whereas (unless other processes not normally considered are taking place) lack of such a trend would suggest that there is a problem with the ideas about trends in absorbers, or about the assumption that photolysis dominates the nitrate loss. Roughly speaking, if the e-fold depths increases by a factor 2, then the  $\ln(\text{concentration})$  profile should also shift by a factor 2, implying substantially lower concentrations below the photoactive zone (which of course is deeper), and a different profile within the zone. The authors should discuss this.

#### Detailed comments

Equation 4.  $A$  is defined in  $\text{m}^2$ , while  $L$  is defined in  $\mu\text{g}\cdot\text{cm}^{-2}$ . With these units,  $C_{BC}$  would be in units of  $[10 \text{ mg/g}]$ , a factor  $10^7$  from what is claimed. I am guessing that the derived  $C_{BC}$  are right (they look right) so there must be a scaling constant in the equation (alternatively use SI units and save yourself the anguish!).

Equation 6:  $T$  is said to be an optical depth which makes me expect units of length. But it only makes sense with the other equations (eg equation 12) if it is dimensionless (no units). Perhaps you mean it to be a relative optical depth as in Fig 1. Anyway again this needs checking.

Equation 10: Again,  $K_{\text{ext}}$  is defined as in  $\text{cm}^{-1}$  in line 16 of page 15752, but cannot be if  $r_e$  is in  $\mu\text{m}$  unless there is a scaling constant.

I have not checked all the equations but I strongly urge you to check them all with your co-authors again. While you may actually have done your calculations with the correct numbers, if you place these incorrectly scaled equations in the literature someone else will end up doing it wrong!

Page 15760, line 13, spelling of Burkholder.

Page 15764, first few lines. This estimate of wet vs dry deposition is not very robust since I am fairly sure GEOSCHEM does not take account of some of the processes for uptake of nitrate on cold surfaces that we believe occur. I think one should probably simply say that the calculations assuming all nitrate is on the surface represent an upper limit of what photolysis is possible.

Page 15767, lines 13-15. Of course the question of which parameters most affect the actinic flux depend on the range of possible values that is assessed. You need to say “suggest that, for a given  $\lambda$ , and a plausible range of values for the variables, impurity. . .”.

Page 15772, line 24. Where does the suggestion come from that the concentration in the top 2 cm is higher at SP than DC? Values of 800  $\mu\text{g}/\text{kg}$  have been reported regularly near the surface at Dome C (eg Rothlisberger et al 2000). Please specify what your data refer to.

Page 15773, line 22 and several following places (including page 15776, line 1): your use of “above 3  $z_e$ ” is ambiguous. You must mean at depths greater than 3  $z_e$ , whereas “above” (vertically) implies the opposite. Please make this clear.

Fig 3b. How can 0 ppb (black) be in the middle? Please correct this.

Fig 3d, there is no inset as promised in the caption.

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Fig. 4: the colours for windpumping and escape are indistinguishable, please use different colours.

I finally turn to the Jacobi comment. Of course he is right that, as soon as the concentration is highest at the surface, diffusion will not remove NO<sub>x</sub> from the snowpack. However, I don't think this is as severe a restriction as he believes, as long as this calculation is treated as a qualitative answer to the question: does most of the photolysed NO<sub>x</sub> escape? Firstly, wind-pumping dominates diffusion to about 30 cm (> 1 e-folding depth), and would dominate over chemical loss to around 2 e-folding depths. Thus, if there was no diffusion at all, "most" of the produced NO<sub>x</sub> would escape. Secondly, it is obvious that the exponential gradient assumed in some of the chemical calculations cannot be maintained: both diffusion and windpumping will flatten the gradient at the top, while the NO<sub>2</sub>/NO ratio (increasing with depth) will also create a flattening or reversal of any gradient. The diurnal cycle (except at SP) will also create night-time reversals of the gradient in NO<sub>2</sub> (if production nearly stops, the NO<sub>x</sub> from the day is there at depth while nearer the surface it has been removed): in that case, diffusion will be important from any depth where the diffusion lifetime is of order several hours. I agree that it is glib to assume such an exponential profile, and the authors will need to discuss this issue, but in practice I think they will be able to argue that the escape lifetime is shorter than the chemical lifetime over most of the photochemically active zone. There are of course huge uncertainties (because of lack of data) in the chemical lifetime, so this conclusion should remain firmly qualitative.

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