

## ***Interactive comment on*** “The influence of snow grain size and impurities on the vertical profiles of actinic flux and associated

**NO<sub>x</sub> emissions on the Antarctic and Greenland ice sheets”** by M. C. Zatko et al.

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Zatko\_ACP\_2012\_211 Response to Eric Wolff’s (Reviewer 2) comments:

Dr. Wolff, thank you for your helpful comments. Please see our responses to each of your comments below.

Major Comments: R2C1a: 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).

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In the submitted paper, more emphasis was placed on BC compared to nonBC in snow simply because the concentration of BC in the snow can be quantified, but the concentration of nonBC in the snow cannot be quantified. Only the contribution of absorbance of nonBC can be quantified. Therefore, we have added various statements throughout the text to emphasize the fact that nonBC dominates absorption in the UV and near-visible wavelength regions (section 3.1, 3.3, 3.6, conclusion). We have reworded the second to last sentence in section 3.3 to include the influence of nonBC on  $z_e$  and have changed Figure 3B to emphasize the importance of nonBC on absorption.

R2C1b: 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.

You are correct that an increase in nonBC towards the station is the only explanation for our calculated  $e$ -folding depths. Although we cannot currently quantify the concentration of nonBC material in snow as mentioned above, the fraction of nonBC absorption ( $f_{\text{nonBC}}$ ) increases and the concentration of BC (CBC) decreases with increasing distance from the station. The maximum change in the fraction of absorption by BC or nonBC from  $\lambda=298\text{--}345$  nm between snow near and 11 km away from Dome C station is 13% while the corresponding change in BC concentration is 42%. While we cannot quantify the concentration of nonBC ( $C_{\text{nonBC}}$ ), we can infer that the station is a source of both BC and nonBC because the change in the  $f_{\text{nonBC}}$  is smaller than the change in CBC. Although nonBC always dominates absorption in the UV, our

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measured Ångström exponents indicate that nonBC absorption is even more important than BC absorption away from the station than near the station because the Ångström exponents are higher in remote snowpacks. This suggests that both BC and nonBC concentrations are decreasing away from the station (since  $f_{\text{nonBC}}$  changes less drastically than  $f_{\text{BC}}$ ), but that  $f_{\text{BC}}$  is decreasing at a faster rate compared to  $f_{\text{nonBC}}$ . We have added discussion about the spatial trends in BC and nonBC into section 3.1 and the conclusion.

R2C2: 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.

In the paper we discuss the relationship between e-folding depth and  $\text{NO}_x$  flux, noting that there will be a proportionally lower flux of  $\text{NO}_x$  in regions with shorter e-folding

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depths. The e-folding depths are shorter in snowpacks near the station because of increased impurity concentrations compared to more remote snowpacks. Thank you for taking this conclusion one step further and suggesting the presence of a strong horizontal gradient and flux of NO<sub>x</sub> towards the stations. To our knowledge, the horizontal gradient in the flux of NO<sub>x</sub> has not been measured in high resolution at any polar region within a 20 km radius surrounding the station. Assuming that most nitrate is removed from the snow by photodenitrification, more nitrate should be present in the top 2 cm of snowpacks away from stations due to the increased post-depositional processing that results from an increased flux of NO<sub>x</sub> from the snow. Also, nitrate buried in the snow should be enriched in  $\delta^{15}\text{N}$  in remote snowpacks compared to near-station snowpacks, following thinking similar to Frey et al. [2009]. However, the magnitude of the impact on the  $\delta^{15}\text{N}$  and also the nitrate concentration profile will depend on accumulation rate, and thus on location. Also, it is unclear whether or not station activities enhance the local concentration of nitrate and modify the  $\delta^{15}\text{N}$ . Before such measurements are performed, the effects of accumulation rate and station activities on the  $\delta^{15}\text{N}$  and nitrate concentration profiles in snow should be calculated with a 1-D model in order to estimate the magnitude of the effect, which is beyond the scope of this paper.

Minor Comments: R2C3: Equation 4. A is defined in  $\text{m}^2\text{s}^{-2}$ , while L is defined in  $\text{ug}\cdot\text{cm}^{-2}$ . With these units, C<sub>BC</sub> would be in units of [10 mg/g], a factor 10<sup>7</sup> from what is claimed. I am guessing that the derived C<sub>BC</sub> are right (they look right) so there must be a scaling constant in the equation (alternatively use SI units and save yourself the anguish!).

Thank you for catching the unit inconsistencies in the equations in sections 2.2 and 2.3. In my MATLAB script, I use cgs units for all variables. Originally I reported the variables in the units that are typically used in the radiative transfer community, but now I report all variables in cgs units in the Methods section. However, in the Results (section 3) and Conclusion (section 4) sections, I refer to variables such as grain size

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and BC concentration in the units used commonly in the radiative transfer community (e. g.  $\mu\text{m}$  and  $\text{ng g}^{-1}$ ).

R2C4: 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.

In equation 6, optical depth is meant to be dimensionless, as mentioned in section 2.1, paragraph 1. I have now included “absorption” before “optical depth” in an attempt to make this point more clear in section 2.1, paragraph 5.

R2C5: Equation 10: Again,  $K_{\text{ext}}$  is defined as in  $\text{cm}^2 \text{E}^{-1}$  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!

Please see response to R2C3.

R2C6: Page 15760, line 13, spelling of Burkholder.

The spelling of Burkholder is now corrected (section 2.4, paragraph 6).

R2C7: 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.

We now no longer use dry and wet deposition to estimate the amount of nitrate available for photolysis in the snow due to the uncertainties surrounding the issue. Based on your recommendation, we now calculate a “potential”  $\text{NO}_x$  flux (see section 3.5),

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where we assume that all nitrate in the snow is available for photolysis.

R2C8: 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: : :”.

The phrase “and a plausible range of values for the variables for the variables considered (Tables 3)” has been included between “for a given  $\lambda$ ” and “impurity” in last paragraph of section 3.3. The range of values used can be found in the Figure 3 legends.

R2C9: 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.

Thank you for reminding us that Rothlisberger et al. [2000] contains nitrate profiles. We had been using results from Frey et al. [2009], but will now also include the 800  $\mu\text{g kg}^{-1}$  value reported in Rothlisberger et al. [2000]. Using a maximum nitrate concentration of 800  $\mu\text{g kg}^{-1}$  in the top 2 cm of snow at Dome C results in a  $\text{NO}_x$  flux of  $1.7\text{E}9 \text{ molec cm}^{-2} \text{ s}^{-1}$  in snowpacks at least 11 km away from Dome C station and  $1.2\text{E}9 \text{ molec cm}^{-2} \text{ s}^{-1}$  in snowpacks near the station, which are a factor of 1.3-1.4 larger than when a maximum nitrate concentration of 330  $\mu\text{g kg}^{-1}$  was used. The contribution of the top 2 cm of snow to the total flux of  $\text{NO}_x$  from the snow increased by 15.8% in snow away from the station and by 17% in snow near the station when a maximum nitrate concentration in the top 2 cm of 800  $\mu\text{g kg}^{-1}$  is used instead of 330  $\mu\text{g kg}^{-1}$ . These updates have been incorporated into section 3.5.

R2C10: 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.

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We have removed the sentences previously on page 15773, line 22 and page 15774, line 3 in the original manuscript and have replaced “above  $3z_e$ ” with “closer to the snow surface than  $3z_e$ ” in the paragraph 3 of the conclusion of the updated manuscript. Results of sensitivity studies have revealed that if the concentrations of BrO and OH in the snowpack are increased dramatically ( $10^{-9}$  mol mol<sup>-1</sup>),  $\tau_{\text{chemical}}$  becomes shorter (more efficient) than  $\tau_{\text{escape}}$  (now only  $\tau_{\text{wind pumping}}$ ) at depths closer to the surface than  $3z_e$ .

R2C11: Fig 3b. How can 0 ppb (black) be in the middle? Please correct this. Figure 3b: This figure has been corrected. A value of 1.42 ng g<sup>-1</sup> was accidentally used instead of 0 ng g<sup>-1</sup>.

R2C12: Fig 3d, there is no inset as promised in the caption. Figure 3d: Thank you for noticing that the inset has not been included. The inset is now present.

R2C13: Fig. 4: the colours for windpumping and escape are indistinguishable, please use different colours.

Figure 4: Figure 4 has now been removed based upon comments from Hans-Werner Jacobi.

R2C14: 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 photolyzed 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)

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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.

Thank you very much for your thoughts on this issue. We agree that assuming an exponential decay of NO and NO<sub>2</sub> in the snow is not appropriate. Given the uncertainty in snowpack NO<sub>x</sub> profiles, we have removed diffusion from our analysis and assume that wind pumping is the only mechanism for removing NO<sub>x</sub> from the snow (although diffusion is likely important in reality). Also, we now limit our NO<sub>x</sub> lifetime analysis to Summit. The chemical profiles calculated in the Thomas et al. [2011] study suggest that the concentration of NO<sub>2</sub>, NO, BrO, and OH are higher in the snow compared to the atmosphere until a depth of 20-30 cm. The profiles suggest that diffusion towards the atmosphere from the snow occurs above the depth of the peak concentration (20-30 cm), which is roughly 1-2 e-folding depths depending on snowpack impurity concentration. Including diffusion in addition to wind pumping will further reduce the escape lifetime if the concentration in the snowpack is greater than in the overlying atmosphere. However, even without diffusion, wind pumping of NO<sub>x</sub> from the snowpack to the atmosphere is still dominant compared to NO<sub>x</sub> decay to HNO<sub>3</sub> when base-case conditions are assumed for variables used to calculate the wind pumping and chemical lifetimes (see Table 3 and Table 4). Our NO<sub>x</sub> lifetime comparison results remain qualitative, although we assume that the wind pumping lifetime is shorter than the chemical lifetime at Dome C and South Pole in order to calculate the potential flux of NO<sub>x</sub>. We have discussed these issues in the last paragraph of section 3.4.

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