

## Reply to the review of Anonymous Referee #4

We would like to thank Reviewer #4 for his/her useful suggestions and comments which we have addressed briefly below. For clarity, we keep the reviewer's comments in black while our response is in red font.

Nitrate is massively lost from the snowpack to the atmosphere making an interpretation of nitrate concentrations measured in the ice in terms of atmospheric NO<sub>x</sub> difficult if not impossible. The reason for the loss may be desorption or photolysis. This manuscript reports about a field experiment in East Antarctica (Dome C station). The carefully designed experiment compares the evolution of nitrate concentration and its isotopes from homogenized snow with and without UV exposure. The results are consistent with previous experiments and laboratory experiments for the deeper part of the snow mixture. The top layer seems to be affected by various effects. However, the argumentation to exclude this part involves a lot of hand waving. Those results are inconclusive and the experiment needs to be repeated attempting to exclude some of the processes brought up in explaining the inconsistent results of the top layer. This, however, is for another manuscript.

As the reviewer noted here, a good agreement and consistency is observed between previous studies, at least for the snow layers deeper than 7 cm. It is this consistency that let us believe, despite the inherent difficulty to conduct such experiment in the field, that the dataset is exploitable. There is no observation without disturbance, and we have to deal with it. The question that remains is: are the disturbances so significant that they mask the natural processes understudy? In the present case, while the mass concentration change is less pronounced between the two fields (we cannot follow the snow more than what we did for logistical reasons), the isotope variations (see Figure 5 in the revised manuscript) show effects significantly above the uncertainty (mainly because the fractionation factor is large). The aim of the study is to minimize non-photolytic effects in the field and isolate as much as possible the photolytic effect.

The reason to disregard the top 7 cm samples is not the result of some arbitrary decision but is due to the physical conditions of the Antarctic ice sheet. The open field (just roofing) is exposed to (see Fig 9 in the revised manuscript):

- drifting snow unevenly distributed within and between the field (which happened during the experiment),
- side solar exposure for hours during low solar zenith angles (due to the high latitude of the site)
- erosion by wind
- enhanced sublimation induced by the plate cover
- deposition of atmospheric nitrate

There are thus good reasons to believe that the top surface layers are not just exposed to the photolytic process but also other processes that we cannot avoid. We need both field and laboratory studies to understand natural phenomenon- the first are necessarily messy and the second carefully controlled in an "unnatural" way. In this study, completely

enclosed field is unrealizable for practical reasons and would in fact cause more problems (closed system, increase of temperature, absence of equilibrium with surrounding atmosphere, accumulation of gases, etc) beyond solving any of the side effects mentioned above. In fact, an intermediate design was tested some years ago with side plates to overcome low solar zenith angles, but the result was an intolerable accumulation of drifted snow, in addition the system was not able to withstand the wind pressure. Therefore, it is not surprising to see the first top cm not following Rayleigh isotope fractionation processes. In fact, there is a good reason to think that the top cm resembles the surrounding snow despite our effort to protect the top layers. The nature of Antarctic plateau is that if wind is blocked mechanically, drifting snow will accumulate and temperature will change. An open system limits this, but then the surface snow layer is mobile. Figure 4 shows a decreasing trend of concentration in the snow surrounding the fields during the period of sampling, a trend closely followed by the top cm of the fields, independent of the cover type (note that the sampling rate and depth is not the same for the snow pits and the surface snow, i.e. 10 days vs 3 days frequency and 2 cm vs first few mm depths, respectively, generating variability in the comparison). The same is also true for the  $\delta^{15}\text{N}$  values with the top layers converging to  $\delta^{15}\text{N} \approx 10 \text{ ‰}$ , a value close to mean value of the surface snow (Figures 5 and 6). All the processes mentioned above are clearly implicated in the snow nitrate mass and isotopic measurements in the top 7 cm (Figures 3 and 5), which enabled us to divide the snow profile in each pit into two zones (0-7 cm and below 7 cm).

To summarize, because of the following four arguments, we think it is justified to disregard the top cm as this layer does not provide useful information regarding nitrate photochemistry:

- The top cm does not follow a Rayleigh process,
- Visually we could see drifted snow on our fields which was difficult to remove during sampling
- A close match is observed between the snow surface and first cm of snow pits
- $\pm 1\text{-}2$  cm in the sampling depth precision

In contrast, data at depth from immobile snow are physically explainable and in agreement with recent laboratory experiments (Berhanu et al., 2014), global spatial survey (Erbland et al., 2013) and model results (Erbland et al., 2015)

Minor comments:

p. 33047, line 2: It is not true that most deep ice cores are drilled in low accumulation sites. Replace “most” by “many”

It is now replaced

p. 33047, line 14 and in references: Rothlisberger is spelled Röthlisberger

It is now corrected

p. 33047, line 25: “relative to reference” should be “relative to a reference”

It is now corrected

p. 33047, line 27: delete “in”

It is now deleted

p. 22048, line 25: add “and the measurement of Dome C snow from Blunier et al.

It is now added

p. 33060, lines 20-24: This seems rather unlikely. It would require completely still air.

Section 4.1.1: The method to exclude samples seems rather ambiguous. Please illustrate which samples were excluded and be more specific about the criterion. That they do not fit the pattern that you wish to see is not an argument.

This variability is the result of uneven depth of the snow drift on each field. Here, we would like to remind that we have tried to minimize/prevent snow deposition by removing drifted snow on the surface of the two pits regularly (weekly, even daily sometimes). However, it was impossible to keep the surfaces of the two pits 100 % clean from drifted snow. It should be mentioned that at some point the drifted snow could reach thickness of more than 20 cm of hard and stratified snow. We will clarify this point in the text. The “mixing” depth can be easily identified by changes in the chemical and isotopic composition of the samples. As seen in Figure 6 (in the revised version), the top layers (0 – 2 cm) of both pits converge to  $\delta^{15}\text{N}$  of ca. 10 ‰ after 20 days (UV#2 and Control#2), but because the UV field is more fractionated at depth than the control field, the first 7 cm show an opposite trend (increase in  $\delta^{15}\text{N}$  for the control and a decrease for the UV), a strong indication of the mixing effect between the surrounding environment (mass weighted average 12 ‰) and the top snow pit layers. Excluded samples are thus those between 0-7 for UV#4-UV#6, which their  $\delta^{15}\text{N}$  is lower (more negative) than the subsequent deeper and 0-2 cm depth for UV#0-UV#2. Same samples were excluded for the control experiments for consistency.

Figure caption 5 does not fit to the orientation of the profiles in the figure

It is now corrected

## References

Berhanu, T. A., C. Meusinger, J. Erbland, R. Jost, S. K. Bhattacharya, M. S. Johnson, and

J. Savarino (2014), Laboratory study of nitrate photolysis in Antarctic snow. II. Isotopic effects and wavelength dependence, *The Journal of Chemical Physics*, *140*(24), 244305, doi: 10.1063/1.4882899.

Erbland, J., W. C. Vicars, J. Savarino, S. Morin, M. M. Frey, D. Frosini, E. Vince, and J. M. F. Martins (2013), Air-snow transfer of nitrate on the East Antarctic Plateau - Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium in summer, *Atmos. Chem. Phys.*, *13*(13), 6403-6419, doi: 10.5194/acp-13-6403-2013.

Erbland, J., J. Savarino, S. Morin, J. L. France, M. M. Frey, and M. D. King (2015), Air-snow transfer of nitrate on the East Antarctic plateau – Part 2: An isotopic model for the interpretation of deep ice-core records, *Atmos. Chem. Phys. Discuss.*, *15*(5), 6887-6966, doi: 10.5194/acpd-15-6887-2015.