Reply to the review of Anonymous Referee #3

We would like to thank Reviewer #3 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.

Berhanu et al. conduct a field experiment to examine the relative impacts of physical and photochemical loss of snow nitrate at Dome C on nitrate concentrations and isotopic composition. The experimental design is innovative as it is the first to attempt to study this issue by replicating actual field conditions, but at the same time this limits their ability to uniquely distinguish between different processes. The authors need to adequately discuss these limitations. Although they do, the paper is so poorly organized, and contains many confusing and ambiguous statements, that it is difficult to follow their discussion and even rationale. Therefore it is difficult for me to effectively evaluate the scientific integrity of this manuscript.

The term "shape of the incoming light flux" and "shape of the solar actinic flux" is ambiguous, especially in the abstract. Perhaps use "spectral distribution" instead.

Now changed with spectral distribution

The manuscript says that the Python code for correcting for blank effects and isotopic exchange is in the supplement, but I don't see it there.

Yes, this code was not applied to the dataset presented in this manuscript as we had enough sample amounts. Hence, this sentence is now removed from the manuscript.

Page 33056 Lines 10-13: Here you say that the loss of nitrate is comparable for both snowpits, and also say that the loss was larger for the UV pit. Are they the same or is one pit different from the other in terms of nitrate fractional loss? This is important If they have the same amount of loss than this warrants discussion, as one would e xpect the UV pit to experience much more loss of nitrate if indeed UV photolysis is the dominant loss process as you claim.

We agree with the reviewer, this section is confusing. What we meant was that for the first 7 cm, the relative change of nitrate are comparable for the snow pits (note that the natural snow surface also decreases during the same period), despite being influenced by the different processes (UV and non-UV). We think this resulted primarily from the effect of mixing in these top layers with input flux of nitrate from the surrounding area (either through snow drift events or dry/wet deposition of HNO_3) (please see reply to reviewer 4 for detailed explanation of the reasons). Thus, it is logical that both pits show a similar trend between 0-7 cm since the same process influences these layers. Below 7cm depth, the difference between the two fields is clear. There, the UV pit shows a larger loss, in agreement with a stronger sink resulting from a stronger photolysis.

Page 33058 Lines 1-7: You refer to figure 9 to discuss results from both pits, but figure 9 only shows results from one pit.

The reference to Figure 9 in the old manuscript is only given as an illustration of the good correlations obtained for late collections, not to emphasis any difference between the two pits. This figure is now excluded in the revised manuscript, but a table is provided (Table 2) with derived slopes (fractionations), correlation coefficient (r^2-values) and their significance (p-values). The text has been revised.

Page 33058 Lines 12-20: Again, the discussion here refers to figure 10 to discuss results from both pits, but figure 10 only shows results from the UV pit.

We have now included the results from the Control pit as well and shown in Figure 12 of the new manuscript. The text has been revised.

Page 33060 Line 8: Convergence between what? Between the two pits? Between samples at different depths in one or more pits?

This term "convergence" refers to all surface samples from the different batches (mainly UV#2-UV#6 and Control#4-Control#6) pointing towards similar f and $\delta^{15}N$ values. We have now modified this sentence as: "An interesting observation was the convergence in both the nitrate concentration and $\delta^{15}N$ values among the surface snow samples from the different batches".

Page 33060 Line 13: Where do these d15N values come from?

These $\delta^{15}N$ values refer to the converging value of the surface snow samples of the snow pits as given two lines before. We have also added the phrase "…as can be seen in Figures 3 and 5", so that the reader can easily understand from where these numbers are obtained.

Page 33060 Lines 20-23: Could this be important in both pits? Even if there is <u>no photolytic loss of nitrate in the control pit</u>, could nearby snow-sourced NOx/nitrate could be transported and deposited to the surface of the control pit?

In the whole manuscript, we have not concluded "no photolytic loss" for any of the pits. What we observe is a weaker photolytic loss for the control field. Regarding the dry deposition of HNO_3 on snow, the reviewer is right that indeed dry deposition may take place on both pits, as both are "open" to the surrounding atmosphere. As mentioned previously, this may mask the effect of pure photolysis, complicating interpretation of results obtained from the top layers within the framework of the experimental setup, i.e. to reveal the isotopic effect induced by UV radiation alone. This is the reason why the first top cm samples were not included in the quantification of the photolysis effect.

A discussion of the mismatch between the laboratory and field results
should be placed all together, not scattered throughout sections 4 and 5.

We have made a step wise comparison between the results from this study and what has been done in previous studies.

- First part compared the apparent isotopic fractionations with the ones obtained by Frey et al., 2009 and Erbland et al., 2013.
- Second part compares these apparent isotopic fractionations with the laboratory study by Berhanu et al., 2014 which is more relevant for purely photolytic isotopic fractionation under controlled conditions
- The third part computes isotopic fractionations using the ZPE-shift approach from Frey et al., 2009 considering the plexi-plates transmittance and compares with what was obtained by Frey et al., 2009.

This material is all in one section (section 4.1.1. in the new manuscript) but in different paragraphs. We have provided a summary of the comparison within a single paragraph in the conclusion section. We are satisfied with the current structure.

Page 33064 Lines 28-30: I don't see how you can exclude physical processes such as evaporation from either pit. Therefore you have not minimized (or even reduced) physical loss in the UV pit.

We have not stated anywhere in the manuscript that physical loss is excluded. We rather stated that because the plexi-plates may trap heat, evaporation might even be enhanced. The idea of using two identical fields with only the solar radiation modified for one of them was precisely done to account for any other processes such as physical loss. We are fully aware of this mechanism and the experimental setup was carefully designed to reveal the UV effect. The fact that at depth the fractionation factors are consistent with the apparent fractionation found on natural snow pits, and consistent with the laboratory UV experiment and theoretical modeling of UV fractionation, and finally consistent with the design of the UV and Control field experiment, is convincing enough that we have concluded that UV photolysis is the process fractionating nitrate. Assuming that the control and UV fields are subjected to the same "physical processes", then the difference between the two experimental pits should converge to a pure UV fractionation. However, we cannot guarantee that the control experiment is totally free of photolysis. This is why we always used the term apparent fractionation factors for the fractionations observed in the different experiments. The bottom line is that there is a significance difference between the Control and UV pits, and this difference is due to the increased photolysis rate in the UV field.

Page 33064 Lines 17-19: "clearly pointing the radiations" is not grammatically correct.

This phrase is now changed to "…clearly indicating that this cage effect phenomena is induced by presence of UV radiation"

Page 33064 Lines 21-24: I'm confused. Did this study conclude -59.9 or -67.9? If both, what's the difference? If only one, where does the other one come from?

The value -59.9 ‰ refers to the average value derived for the depth dependence isotopic farctionations (values shown in Figure 12 of the new manuscript), obtained by binning all the snow pits data for a given depth. In other words, it is a time independent depth average.

The value -67.9 ‰ is derived as the average of $^{15}\varepsilon$ values obtained from each sampling event (UV#2, UV#3, and so on…) , in other words a depth independent time average.

Note that the uncertainty associated with each values made these two quantifications indistinguishable. We have rewritten the text to make the origin of the numbers more clear.

Page 33066 Lines 10-15: I don't understand why you would say that -67.9 is representative only of photolytic processes when you were not able to remove physical loss.

This value represents one of the best estimates so far obtained in determining the nitrogen isotopic fractions in the field associated with photolysis.

The uncertainty on the numbers is clearly derived and discussed. The difference in isotopic fractionations pits (-55.8 ‰) should represent the purely photolytic isotopic fractionation for two main reasons:

- the isotopic fractionations derived for the UV-pit (excluding surface snow samples) is mainly due to photolysis with a minor contribution from physical release
- In contrast, the values obtained for the control pit (again excluding surface samples) have a minor contribution from photolysis with significantly different isotopic fractionation. Here, we would like to stress that the derived isotopic fractionations for each sampling event of the control pit are consistent with stronger correlation coefficients and significance (see Table 2 in the new manuscript).

Hence, it will be reasonable to take the difference between the isotopic fractionations derived between the UV-pit (-67.8 ‰) and the control pit (-12.0 ‰), as we expect the physical release to have a similar impact in both pits whereas the change in the UV-pit is mainly associated with photolysis. However, the effect of physical release may not be exactly the same in both pits as well as minor photolysis might be present.

Interestingly the purely photolytic value (-55.8 ‰) is in good agreement with what has been observed in a laboratory study (-47.9 ‰) (Berhanu et al., 2014) and theoretically calculated (-48 ‰) (Frey et al., 2009).

This is now explained in the revised manuscript and the sentence noted by the reviewer (Page 33066 Lines 10-15) has been removed.

Page 33066 Line 21: Replace "short" with "shallow".

Revised

Figures: Symbols and colors should be consistent from figure to figure throughout for each (e.g., "control#0" should be the same in each figure. It's also helpful to have the line and the symbol the same color.

All figures have been redrawn with consistent symbols and colors.

Figure 5: It's not top and bottom but right and left. The profiles suggest re-deposition to the surface. Is this discussed in the manuscript?

The revised figures are arranged in accordance with the caption.

We do not understand how from the isotope profiles such conclusion can be deduced. It can also be interpreted as a mixing process with surrounding nitrate (drifted snow or dry HNO_3 deposition) and snow nitrate from the snow pit. As briefly discussed previously and with reviewer 4, because the top layers are inevitably in contact with the surrounding environment and thus integrate many processes, we choose not to focus on these mixed layers in this manuscript, which would have required a special focus and a very different sampling strategy to really understand the dynamic of these mixed layers. We think that is beyond the scope of our manuscript.

Figure 7: Use consistent labeling. Is there a difference between control-0 and control#0?

No difference and now control-0 is replaced with control#0

Figure 10 caption: Which sampling events specifically? Even the first one? Where does the -50 to -70 permil range come from? Provide references in the caption.

All sampling events except UV#0 and Control#0 are taken into account to draw the depth dependence of the fractionation. At a given depth, all sampling events were binned and from the relative change in concentration and isotopes, the fractionations were derived. The range -50 to -70 shown by the shaded region is selected visually.

This is now included in the figure caption of Figure 12 (in the new manuscript) as "…this region is shaded for visual reference".

Figure 12: Define the triangle symbols in caption. Why is one a line while the others are discrete symbols?

All are now discrete symbols.

References

Berhanu, T. A., Meusinger, C., Erbland, J., Jost, R., Bhattacharya, S. K., Johnson, M. S., and Savarino, J.: Laboratory study of nitrate photolysis in Antarctic snow. II. Isotopic effects and wavelength dependence, J Chem Phys, 140, Artn 244306
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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.

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