Reply to editor's comments

We would like to thank Dr. Thorsten Bartels-Rausch for his constructive comments and positive ideas to further improve this manuscript. Here, we provided a point by point reply (written in red) to his comments (written in black).

Overall, I think that the manuscript can be more quantitative and that important data and details from the supplement can be included in the text to tackle the concerns raised by the referee. Let me try to summarize the main issues that I still see with the revised manuscript:

- A more careful and quantitative analysis of the fraction of snow at the surface that is impacted by mixing with the surrounding snow. I think it was not so much questioned that you remove data points from the snow surface, but it was questioned whether this should be done at 2, 7 or 12 cm. A quantitative argumentation for example based on Fig. 5 looks like a good idea to me. Throughout the manuscript, it is still difficult to understand which threshold you used and why.

In lines 384-399 we have stated briefly that as a first approach we have divided the snow pit into two regions i.e., at 7 cm depth. This division is based on the nitrate concentration and $\delta^{15}N$ profiles shown in Figs 3 and 5 and kind of a general first approach. However, looking into the details of $\delta^{15}N$ results, such general data exclusion led to an artefact and we used the $\delta^{15}N$ signal to exclude specific data points. With such an approach, for UV#0-UV#3 only data points between 0-2 cm were removed while data points between 0-6 cm depth were removed in case of UV#4 - UV#6 (section 4.1.1). We have also stated that exclusion of more data points in case of the late collected samples is due to longer exposure time of these samples to the mixing process.

Our main difficulty resides in the fact that there is no clear threshold since the mixing layer is heterogeneous in space and time, and thus exclusion of mixed snow depends on the sampling site and time. As mentioned before, the consistency of the data was the criteria used. This is explained in the text and we don't see how we can better improve the description.

o Maybe use dashes lines in Figure 3 and 5 to indicate the sections of each data set individually, as opposed to the shaded area.

As the suggested by the editor we have now removed the shaded region and replaced it with two dashed line representing the two thresholds: 0-2 cm for samplings #0-#3 and 0-6 cm for the remaining samplings. To keep consistency, the shaded region is also removed from the similar figures in the supplementary materials. We have removed the shaded region in figures 7 and 8 as there is no clear trend in the profiles with sampling and using dashed lines will not add any information but will rather make the figure confusing.

o Clarify the importance or use of the 7 cm threshold that is mentioned in the text. Or, omit stating or using it, when you decide that the individual thresholds are better.

As mentioned above, the 7 cm threshold is deduced from the general profiles in nitrate concentration and $\delta^{15}N$ values. Exclusion of all data at this depth was chosen as a first approach to keep consistency in removing same depth data among samplings as well as ensuring the remaining data points are in accordance with Rayleigh type processes. However, having a close look at these measurements only some of the data points were inconsistent with a Rayleigh treatment, and hence we have applied the individual thresholds approach based on the $\delta^{15}N$ values.

As suggested by the editor, we have now added in the text that the 7 cm threshold is used as a first approach to identify the mixing zone and later a new approach based on individual thresholds was used (section 4.1.1.).

o Was the snow that fluffy that it could mix with surrounding snow at the top few cm?

The experimental snow was a wind-blown snow and was not hardened snow throughout the study period (This is added to the manuscript experimental section lines 147-148). However, there was a fluffy snow on top which we usually remove before sampling based on the wooden marks which show the surface level of the experimental pit.

• Based on the referee comments, the choice of C0 is not straightforward. I have to admit that I also do not fully understand that choice. Could you give more details about the problem with the calibration?

Still, all measurements of the same time (so, each number in the plots) were done with the same calibration? So, discussing UV#0-Control#0 vs. UV#1-Control#1 etc. should still be possible? Results and conclusions from that traditional analysis might add important information to the manuscript. I feel it is not enough to assume that there was no change in the amount of nitrate in that depth [of C0] (lines 255 ff). Can you justify this based on your data and some statistics?

The issue regarding the calibration shift is briefly given in the replies to reviewers (please see reply to reviewer 2 on page 2) as well as in the main text. It may not be clear enough when we stated measurements of the same batch is conducted at the same time. We tried to measure most of the samples of a given pit of a specific batch (for e.g., UV#1) at once but not all the samples from both pits. Usually, it is one full batch of a specific pit samples and about half of the other pit samples, which are usually measured. Some samples were also remeasured in a different batch or measured together with other type of snow samples. Again here we would like to state that the choice of nitrate concentration at a depth of 25-30 cm as C_0 was not the intention of this study. However, considering the above-mentioned issues as well as referring to the $\delta^{15}N$ values at this depth, we strongly believe that samples from such depth can be considered as zone of minor photolytic effect and consequently chosen as C_0. There is now a body of evidence from recent publications (Erbland et al., 2012, Frey et al., 2009, France et al., 2011, Berhanu et al., 2014) that support our approach. The decrease of concentration at depth simply doesn't make sense at all and it is physically unsustainable. The only rational explanation is a hiatus during the calibration. In fact, taken C_0 as the asymptotic value at depth make more sense in term of the Rayleigh treatment because it is only the relative loss that should be taken. In theory, the concentration is unnecessary, arbitrary unit could also have been used.

Another difficulty in such approach is difference in depth as sampling exactly at the same depth during a given sampling event is impossible (with at least ±1 cm shift)

- Figure 3: Could you indicate the photolytic zone for your snow? Could you indicate the times of the samples 0-6 in the caption (as noted in table 1 of the supplement). I further suggest showing all data in these figures and not just a selection.

In my opinion, determining accurately the photic zone is not straight forward. The zone of active chemistry where we can see a change in $\delta^{15}N$ from Fig 3 can go all the way down to 30 cm. Previous field studies determined a photic zone of about 50 cm (3 times the e-folding depth) (France et al., 2011) for typical Dome C snow, which probably has a different snow optical properties than the experimental snow.

The times of sampling are already in the figure caption and stated as …*the numbers denote the sampling events, which were carried out at 10-day intervals from 02/12/2011 to 30/01/12.*

Again here as we have also stated in the replies to the reviewers the choice of showing only even numbered sampling events in the main MS is to avoid data cluttering and simplifies the explanation in the results and discussion sections. We still believe that adding these extra values doesn't improve in any way the data interpretation. The reader can always refer to the supplementary documents if he needs a global view of the data. This is a common practice and we don't understand why there is so much focusing on this point.

Minor Things:

- Experimental Section: Could you add a description about the snow. Was it fluffy? Did it settle or harden during your experimental time; did it else change its optical appearance? Do you have any means to give estimates of the density (like from volume of molten sample vs. snow sample).

The surface snow seemed to be settling with time but was not hardened. For example during sampling it was not very difficult to sample few centimeters of snow but it was also not so soft.

Regarding density, we do not have any other means to calculate it. Based on years of experience in the field, snow was more like faceted grains (Gallet et al., 2011) so density around 225 kg/m3 to 330 kg/m3.

We have now added the sentence …As the snow density was not measured, its value can be estimated to be about 225 kg m^{-3} to 330 kg m^{-3} based on its faceted grains like structure (Gallet et al., 2011) to the Experimental section.

Can you estimate the photolytic zone for your snow? Or in other words, is it valid to compare to compare to light transmission measurements at Dome C (line 179 ff).

Refer to reply above but because we used natural snow grain, we are confident that the comparison is valid and this approach is the best we could do.

- The definition of isotope ratio line 68 and 72 do not match

We have now removed the delta terms in line 68 to avoid the definition mismatch.

- Line 296: “could still have been”, you observed such drifts, no need for conjungtive.

Now it is changed to “was deposited”

- Figure 10 and text 459 ff: I had difficulties relating the text and figure 10. Why, for example, is 0-7 cm excluded for all samples, when in the response to the referee you mention that for some samples 0-2 cm is excluded (page 7)? Also, I don not see “progressively more negative (data) over time” in Figure 10. Does this not look like a stable plateau?

Figure 10 shows the determined nitrogen isotopic fractionations under the three cases: (1) Control samples (2) UV samples excluding all 0-7 cm depth samples between, and (3) same as (2) but here samples are excluded based on $\delta^{15}N$ (individual thresholds approach for e.g. 0-2 cm depth for UV#0-3).

The progressively more negative isotopic fractionations refer to case 2 where we have discarded all samples at 0-7 cm depth (shown in red squares). Accordingly with time $\delta^{15}N$ changes from -20 ‰ to about -60 ‰, in contradiction with the stable plateau stated by the editor (Also refer to the replies above).

- Could you comment in the conclusions, why you see a change in isotope ratio driven by photolysis, but no change in concentration.

At first, we would like to clarify that there are changes both in concentration and isotopic ratios driven by photolysis. However, the signals associated with these changes are different. While mass loss seems to be smaller stronger signal change is observed in $\delta^{15}N$ and this is a direct consequence of the high fractionation factor of the photolysis process. A small change in concentration is translated into a high variation of isotope ratios. This is now included in the conclusion section (lines 620-624).

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, Doi 10.1063/1.4882899, 2014.

Erbland, J., Vicars, W. C., Savarino, J., Morin, S., Frey, M. M., Frosini, D., Vince, E., and Martins, J. M. F.: 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, 6403-6419, DOI 10.5194/acp-13-6403-2013, 2013.

Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J. M. F.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, Atmos Chem Phys, 9, 8681-8696, DOI 10.5194/acp-9-8681-2009, 2009.

France, J. L., King, M. D., Frey, M. M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A., and Savarino, J.: Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, Atmos Chem Phys, 11, 9787-9801, DOI 10.5194/acp-11-9787-2011, 2011.

Gallet, J. C., Domine, F., Arnaud, L., Picard, G., Savarino, J.: Vertical profile of the specific surface area and density of the snow at Dome C and on a transect to Dumont D'Urville, Antarctica - albedo calculations and comparison to remote sensing products, The Cryosphere, 5(3), 631-649, doi: 10.5194/tc-5-631-2011.