Reply to the review of Anonymous Referee #1

We would like to thank Reviewer #1 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.

This manuscript presents an interesting attempt to better understand the impact of UV light on the preservation, and isotopic modification, of nitrate in snow at Dome C. A pair of experimental snow pits was created from drifted snow that was manually homogenized, then a plexiglass filter was used to largely exclude UV from one of the pits, with a transparent plexiglass plate above the other pit to replicate any impacts due to wind pumping, greenhouse effect, etc. Both pits were sampled about every 10 days (7 times total), yielding depth profiles of both the concentration of nitrate and its isotopic composition. Analysis focuses primarily on the loss of nitrate mass and the enrichment of N-15 in the nitrate remaining in the snow over the ⇠2-month long experiment.
The main conclusions are that UV photolysis of nitrate is the primary factor causing both loss of nitrate mass and strong preferential release of N-14 from the snow at low accumulation sites in east Antarctica like Dome C. Of particular interest is the derived "apparent N-15 fractionation" of -68 =/- 12 permil in the pit exposed to UV compared to -12 +/- 2 permil in the pit where most of the UV photons were excluded. The authors suggest that this fractionation may be a better value to use in models than previously published estimates based on both field and lab studies. This may be correct, or it may be a matter to be debated by the experts, but I agree that the isolation study clearly demonstrates that UV photolysis is the dominant process changing the N isotopic composition of nitrate lingering in the photic zone of snow at Dome C.
On the other hand, it is far less clear that photolysis is the main process causing loss of nitrate from the snow. In both of the pits most of the nitrate that is lost comes from the near surface layers (0-5 cm in some cases, more like 0-12 in others, authors suggest 0- 7 cm as the zone where non-photolytic processes may have complicated their results). The authors state that "In general, the loss of nitrate in the top 7 cm was comparable for both the control and UV samples;" (pg 33056, lines 10 and 11) and based on Figure 3 in the manuscript and Figure 2 in the supplemental material I fully agree. However, the sentence quoted above continues: "the loss was larger for those samples exposed to solar UV relative to the control samples." This assertion seems to reflect what they hoped to see, rather than what the data revealed. The authors also suggest that in the pit exposed to UV there is continued minor loss (up to 25 %) between 7 and 20 cm while in the control pit no more than 20% is lost from any layer below 5 cm. But, Figure 2 in the supplemental material shows that for the profiles sampled 20 Jan in the pit not exposed to UV about 60% of the nitrate appears to have been lost from sample plotted at 6 cm and about 50% from the one just below, with > 20% lost as deep as 12 cm.

As already mentioned in our replies to the other reviewers, strong indications (unrealistic "mass loss" with corresponding isotope fractionation, convergence of the surface concentration and isotope values to the surrounding snow, observed drifted snow on each field with variable pattern (up to 20 cm thick), impossible to stop gaseous dry deposition, etc.) show that the first 7 cm should be viewed as a mixed layer between the experimental snow and surrounding snow, through both wet and dry mixing. Because surrounding snow has a lower nitrate concentration, mixing gives the false impression of an apparent mass loss. Thus this layer should be treated with caution, and the observed decrease in concentrations is not necessarily the consequence of mass loss. We agree that the original manuscript was not enough clear on this point. We hope that it is clear in the new version. Our reply regarding the excess nitrate in the UV pit follows below.

Note that mine are “eyeball” estimates that could be refined if I had the data. If the authors want to assert that there truly is more nitrate lost from the UV pit (overall, or in certain depth ranges) they should quantify such statements.

We think that the figures plotting *f* vs isotopic values, the level of ^{15}N fractionation between the two fields, even the concentration profiles taking into account the hiatus in standard are clear enough to show a significant difference in mass loss between the two experiments (e.g. no *f* change in the control at 20 cm depth, more than 10 % for the UV). The Rayleigh treatment of the data is another way of showing this difference. Again here we are mainly talking about observations below the 7 cm threshold. Saying that, it does not mean that there is no change in the control field but the change is significantly different than the UV pit.

Granted, given the surprising variability in measured nitrate concentrations near the bottom of both pits (which should have been, and in fact is assumed to be, constant) (see Figure 1 in supplement) it will be hard to show statistically significant differences. Bottom line, I urge the authors to stick with claiming that UV photolysis causes most of the change in N-15/N-14, and back off the mass loss claim.

Given the experimental complexity and caveats in the field study, indeed it is difficult to show a significant mass loss at the deepest levels of these pits without taking account the hiatus in the concentration measurements. In our effort to show the original data, we did not choose to display the corrected concentration profiles. Saying that, we agree with the reviewer that mass loss is more blurry than the isotope data. In fact, the isotope profiles clearly show that the control pit is not subjected to radical isotope change, an indication that either the concomitant variation of concentration should be minimum or that the fractionation associated this variation is small; basically the conclusion of the manuscript.

This is probably the most important example, but I find that the authors are kind of sloppy throughout the manuscript, making poorly substantiated claims, and sometimes making mildly contradictory claims in different passages. In the list of

minor edits below further examples will be noted. First, I will raise an example where I feel important details are just omitted.
Given that there is a section 2.4 on Experimental precautions, I was very surprised that so few details were provided in section 2.1 regarding how the sample profiles were collected 7 different times from a 200 x 100 cmˆ2 area without disturbing the snow left behind. It is stated that each sample included 500-1000 g of snow, and near the surface the sampling depth interval appeared to be 2 cm. Assuming density of 0.3 g/cc, the surface area of the top several samples would have to be a little more than 800 cmˆ2. Noting that 7 such profiles were collected from each of the experimental pits, by the end of the season nearly 30% of the homogenized snow would have been removed (at least in the near surface layers). (It also seems likely that the act of sampling would disturb snow around the profile to some extent, so how was this minimized and/or mitigated?) The vertical pipes created by each profile would seem likely to modify air/heat/NOx exchange if left open, so I assume they were backfilled, but what was the source of the fill? Clearly, it would be fortuitous if the fill material closely matched what was removed (in terms of the evolving depth profiles of microphysics and also nitrate concentrations and isotopes), so what precautions were taken to ensure that subsequent profiles were not modified by earlier sampling events?

The reviewer has raised some very important points which requires clarification in the manuscript.
We have now reorganized sections 2.1 and 2.4. To answer the reviewer's questions samples were collected 7 times at a 10-day frequency. Mostly, we have sampled 300-600 g snow and in a few cases about 1 kg of snow was sampled. A gap of 10 cm undisturbed snow was left in between each sampling location so that the nearby snow profiles remain unaffected. Every time after sampling, the vertical pipes were filled with natural snow (Note that this natural snow is not same as the homogenized drifted snow). In our protocol, we opted for open fields to minimize other perturbations (heat, accumulation of NOx, not allowing air snow exchange etc), the limitation of this strategy is a possible exchange of matter with the surrounding area by wind pumping, drifted snow, dry deposition etc. Thus even if we had refilled the vertical pipe with initial snow, exchange, wind pumping dry deposition would not have stopped, as it occurs in a natural field. Observing is disturbing, something unavoidable. The question is if the perturbation is large enough to disturb the photodinitrification. We took all possible precautions to limit these perturbations. As noted by the reviewer, the % of surface sampling was small, we refilled the sample volume. The distance between sample locations (10 cm) is believed to be sufficient to limit light backscattering change but ultimately what should be viewed is the different behavior between the two fields, as it can reasonably be assumed that at the statistical level both fields are disturbed by the same processes except that UV photolysis is magnified in one of the two fields.

A couple of additional minor quibbles in this section: given Figure 1 in the supplement, do you really think that the precision of the nitrate concentration measurements was better than 3% (pg 33051, line 19)? I think that would imply that the 1450 ppb in the bottom 5 cm should always have been in the range 1400 – 1500 ppb.

After reviewing all the replicates of the standard measurements, the stdev is actually closer to 5 %. This has been corrected in the new manuscript. We would like also to mention that 5 % is precision not accuracy and thus does not take into account any offset as mentioned before. In fact, for a given profile, the variation of concentration of the last 10 cm is in the precision range.

Was it possible to sample the profiles with the plexiglass plates in the frames, or did they need to be re- moved? If the latter, how long was the control pit exposed to full sun each time (and was it near mid day and peak actinic flux)?

The plexi plates were removed from their frames for the length of sampling (1h maximum) mostly in the morning (10 a.m. local time). Considering the characteristic time of the photolysis process (week if not months, note that after two months of experiment, the isotope composition were still far from reaching the observed natural field isotope fractionation at 10 cm 20 ‰ vs 150 ‰ for artificial and natural respectively) so that just time of sampling is very short in comparison of the characteristic time.

I note that a 1000 g snow sample will not fit into a 2-L Whirl-Pack bag unless the density is greater than 0.5, which seems implausibly high for depths < 30 cm, especially for experimental snow that was ground just before the experiment. I am also confused by the need for such large samples, given the complications noted in paragraph above (i.e., it would have seemed desirable to collect smaller samples to minimize disturbance). Authors state that they wanted to ensure > 100 nmol nitrate per sample for the full isotope analyses, but the lowest concentration in any single sample (Fig 1 in supplement) was > 3 nmol/g, suggesting samples of 35 g would have been adequate (vast majority of samples had concentrations > 6 and prob- ably 2/3 were over 16 nmol/g). Not sure what the authors are talking about when they mention some of the samples had “initial nitrate concentrations of about 1.5 nmol/ml” but even such clean snow would have > 100 nmol in a 70 g sample.

We needed to collect enough samples for replicate isotopic measurements in case of failure during the process. Our procedure is scaled for a few hundreds of ml of samples (as most of the time it is natural snow that we are processing). We agree that we could have sampled less snow, but could not have reduced disrupting the snow as a minimum size for a snow pit is required to sample comfortably (size of tools and hands, width to reach the bottom, etc.).

Here are a list of additional, mostly minor, comments keyed to page/line #.

33046/14-15 as noted above, if you want to claim more mass loss in the UV pit, need to make the comparison more quantitative. Based on current text, I would not put this statement in the abstract.

This sentence is now removed from the abstract

33046/23-24 related comment, not sure that photolysis established as dominant for mass loss, so suggest just claiming it dominates N fractionation.

Corrected accordingly.

33047/10 Mayewski and Legrand, 1990 is not a great citation given context of this sentence. They claimed that nitrate at South Pole was not impacted by post-depositional processing.

We have changed this reference to Legrand, M. R., and S. Kirchner (1990), Origins and variations of nitrate in south polar precipitation, *J Geophys Res*, *95*(D4), 3493-3507.

33047/14 Not sure the Summit references belong in a sentence talking about low accumulation sites. Maybe change the early part to say "is problematic at most sites on the polar ice sheets, where…"

The sentence has been modified as suggested by the reviewer.

33047/24-27 confusing sentence, especially the part defining R (which is not anywhere else) Was an equation in an earlier draft that included R?

This comment is correct; indeed a sentence was missing which has now been added to the manuscript:
"Stable isotope ratios (R) ($n(^{18}O)/n(^{16}O)$, $n(^{17}O)/n(^{16}O)$ and $n(^{15}N)/n(^{14}N)$) are expressed as isotopic enrichments/depletion ($\delta^{18}O$, $\Delta^{17}O$ and $\delta^{15}N$) relative to a reference where $\delta = (R_{spl}/R_{ref}) - 1$, and R represents the elemental $^{17}O/^{16}O$, $^{18}O/^{16}O$, or $^{15}N/^{14}N$ ratio in the sample or reference material.".

33047/27 don't need both "in for" here

Corrected.

33048/19-22 Confused by this sentence, and how it relates to suggestion that Blunier et al., 2005 measured too low a fractionation in lab study using broad band light source. Seems that the fractionation would need to get more negative in UV to reconcile with field estimates (including yours in this paper) but I think sentence implies opposite.

The reason why Blunier et al., 2005 measured too low fractionations is due to exposing the snow to short wavelength UV (down to 200 nm). This will lead to less negative or even positive fractionations. In the laboratory study (Berhanu et al., 2014) we have shown this case, and stated that with filters appropriate to Dome C, the laboratory shows close agreement with the field.

33049/17 should “wider” be “wide”?

It is now corrected

33050/5 on page 33055 state that the mean nitrate in the two pits was 1431 and 1478 ppb, so I would say 1450 here (rather than 1600)

It is now corrected.

33053/19 delta in this line should not be the fractionation factor, since you are already using delta for the isotope ratio values in Eqn 1. Blunier et al. used alpha, so perhaps that is a good precedent.

We don’t understand the reviewers point here. The Rayleigh fractionation line can be given either as a power law of α or ε since α-1 = ε. The Rayleigh equation written R/R0 = f^(α -1), the ln of this law gives our equation 1 and the slope, α -1 or ε.

33054/15-21 Not clear how you use the natural pits to estimate fractionation. If same analysis as above, how is initial concentration constrained (needed for f)? In fact, as noted later (in sections 3.4 and 4.1.3), I am not sure if you do end up using natural pits.

This section is modified and as noted by the reviewer it was meant to be from the two snow pits (not natural snow pits).

33057/4-6 Sentence could be more precise. The 8-14 ‰ values are always in the top sample (0-2 cm, not 0-7) and for UV2 this is the max (it is not decreasing to this value). Could add UV1 also if the range was 5-14 permil.

The turn towards the surface value took place within the top 0-7 cm but the value 8-14 ‰ is at the surface. Even UV#2 showed a turn from a δ^{15}N value of 14.9 ‰ to 12.5 ‰. We have changed the surface level to 0-2 cm from 0-7 cm.

33058/section 3.4 Not clear how the values in Fig 10 were derived. Are they based on Rayleigh plots for each depth, with points for sampling events 1-6? Note, here it seems that Fig 10 is based on the UV pit (not natural pits).

Yes, figure 10 is based on the UV exposed pit. By using f and δ^{15}N obtained from samples collected at similar depth, we have derived fractionations using Rayleigh plots for that depth.

33059/6 Again, not convinced by claim for more loss in UV pits.

Please refer to previous comments as well as comments to other reviewers.

33061-62/first paragraph of 4.1.1 If you want to subjectively pick which samples to include and which to leave out, you need to explicitly tell the reader which ones stayed for each pit. Also, if you are going to do this for the UV pit, seems you may be obliged to also do it for the control. I do not think this will change the overall story, but including the region where f and the isotopes are changing fast will probably give larger fractionation for that pit as well. Would be better if you could define objective criteria to identify near surface samples that do not fit assumptions, and apply to both pits.

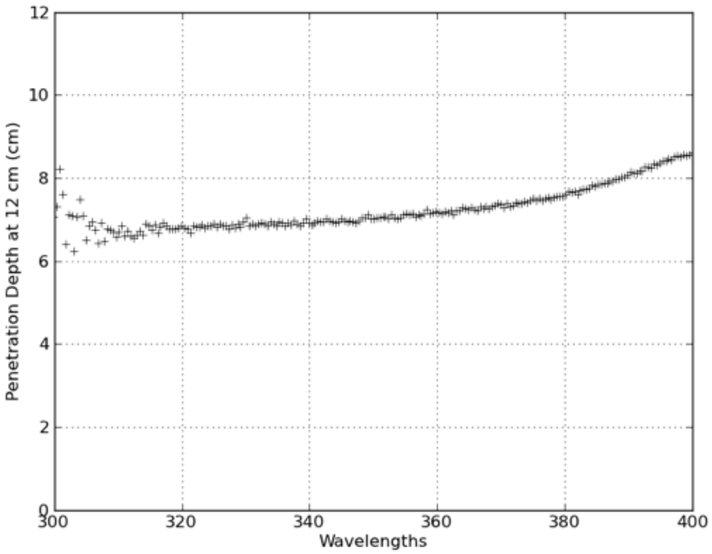
In section 4.1 we stated that some of the surface snow samples were excluded due to the strange profile in the $\delta^{15}N$ pattern opposite to what is observed below 7 cm depth. As simply disregarding values below 7 cm depth will introduce an artefact, we have used the change in $\delta^{15}N$ as a tracer so that any data point within 0-7 cm depth with $\delta^{15}N$ shifting to lower values than its following depth was excluded. In case of UV#4-UV#6, this is the region where non-photolytic processes are taking part significantly and all samples between 0-7 cm were excluded. In case of UV#0 to UV#3, only samples at 0-2 cm depth were excluded. This is in agreement with an increase of mixing (with surrounding environment) with time. As time passes, the top layers are increasingly impacted by the mixing effect. The only rational criteria to eliminate layers (we should keep in mind that drifted snow was not evenly distributed on the field) are therefore based on the isotopic composition trends which should always increase with time, the opposite is a sign of mixing with local nitrate that possesses, like our starting isotope composition, always a relatively low value.
This procedure is applied for both control and UV-exposed samples. In section 4.1.1 we have stated that samples from the surface to where $\delta^{15}N$ starts to shift to more negative values were excluded. In the conclusion section 33067/3-5, we have also stated that there might be an error introduced while excluding some of the top layer points where the photolysis effect is significant.

33062/20 What do you mean about comparisons between center and edge? Does this mean that even more profiles than 7 were collected (see long comment about sampling details above)? Even if you just mean that some of the 7 profiles were close to the edge of both the experimental snow and plexiglass while others were near center, this should have been detailed in section 2.1.

As we have repeatedly stated we had 7 sampling events. However, the total field size is much bigger than for only 7 samplings. Some samples were at the edge of the plate and some at the center. During high solar zenith angle, a portion of UV might directly find the control pits and we expect more direct contact with the edge samples than center samples. But we have not observed any systematic bias associated with the location of sampling, an indication that the residual photolysis had a minor effect. We now believe that most of the change observed on the control experiment is probably the result of physical processes.

33064-33065/section 4.1.3 Where does the -60 value come from? Is this not the average of the points in Fig 10? Confusing to compare this value to -68 “from the ex- perimental UV exposed pit” since Fig 10 is from that pit. My impression was that the -68 came from adjusted values based on each profile (Fig 12 and third column in Table 2) while Fig 10 came from looking at constant depth bins over time from UV1-6. Any case, this is confusing.

Yes, as stated by the reviewer the value -59.9 ± 24.7 ‰ is calculated as the average of the points in Fig 10. The value -67.9 ± 12.0 ‰ is the average of the individual samplings (UV#0 to UV#6). The comparison was made to show that the isotopic fractionations are both time and depth independent because as demonstrated in the laboratory experiment (Berhanu, et al., 2014), the only important parameter to change the fractionation factor (as cross section are intrinsic properties of the molecule and quantum yield is assumed to be the same) is the spectral distribution of the radiation and how it convolves with the cross section. In other words, reducing or increasing the spectral distribution of the incoming light by the same factor for all wavelengths does not change the fractionation factor. For UVs in the range of interest, energy is reduced by a factor almost independent of wavelength (Warren et al., 2006; France et al., 2011) which can also be seen from the figure below (Libois Q., personal communication). Therefore it is logical to see no dependence with time or depth. This is the same argument used to say that only physical processes or a mix of physical and photolysis processes impact the control experiment but can’t be only a photolysis effect.



33065/7-8 you say that Berha al closely

matched

33065/7-8 here you say that Berhanu et al closely matched Dome C irradiance, but on 33063/8-11 and again just below (33066/7) you say that the lab study could not match natural light field. Suspect the filtered lab light was pretty close, maybe close enough (probably not the main reason for disagreement).

The lab study closely matched the field light conditions. But there are many other issues including snow optical properties and non-photolytic processes which are also different in both studies. Complication in the top layer sample measurements from multiple processes may have also impacted the determined isotopic fractionations in the field.

33066/16-18 Not sure I saw where the results from the natural pits were shown and described before this. See comment above from 33064-33065.

This is now corrected.

References

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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.

Warren, S. G., Brandt, R. E., and Grenfell, T. C.: Visible and near-ultraviolet absorption spectrum of ice from transmission of solar radiation into snow, Appl Optics, 45, 5320-5334, Doi 10.1364/Ao.45.005320, 2006.

Reply to the review of Anonymous Referee #2

We would like to thank Reviewer #2 for his/her useful suggestions and detailed comments which we have addressed briefly below. For clarity, we keep the reviewer's comments in black while our response is in red font.

General comments:

This work is an interesting contribution in the growing body of work on nitrate, nitrate photolysis, and the isotopes of nitrate, particularly at Dome C. An experiment was done in the field at Dome C utilizing two snowpits with manually homogenized snow, with one pit covered with a plexiglass plate that allows UV light and another that limited UV exposure.
The snowpits were then sampled over ∼two months to characterize and compare the behavior and expected isotopic fractionation for δ15N, δ18O and Δ17O of nitrate exposed and not exposed to UV light. The purpose of the experiment provides an interesting field test of the isotopic fractionation associated with photolytic loss to compare with the same groups laboratory experiments. The primary conclusion of the work is that photolysis is the primary driver of loss of nitrate based on comparison of derived apparent isotope fractionation factors in the field to that derived in the prior laboratory experiment (Berhanu et al., 2014) and in theoretical calculations (Frey et al., 2009). This conclusion is valid, but may be overstated based on the data and data reduction presented. The subject matter overall should be of interest to the ACP community. The manuscript needs a good deal of revision to be acceptable for publication.

The primary purpose of this work is to evaluate apparent isotope fractionation factors for photolytic loss of nitrate in the field. In the Data Reduction section of the paper, the authors use a Rayleigh-type formulation to calculate the isotope fractionations based upon the amount of loss of nitrate in experimental profiles that were exposed to UV light over time. The nitrate fraction, or fraction of nitrate remaining in the snow, is calculated from the ratio of the final nitrate concentration (C) compared to the initial nitrate concentration in the snow (Co). The authors use the average concentration measured at 25-30 cm as Co to compare with the concentrations at other depths in each profile. I do not understand this choice. The expectation would be that the amount of loss of nitrate would change with depth as the light is attenuated (and in fact they assume that 25-30 cm is sufficient to justify negligible loss but this is not entirely justified – see comments below). Why not use the profile collected at time zero, i.e. the first sampling and compare each sampling at the same depth to the original first profile to gauge the amount of loss of nitrate?

As stated by the reviewer, the primary goal of this experimental study was to understand the change in nitrate mass and isotopic composition associated with solar UV by comparing the time evolution of nitrate in each snow pit relative to Control#0 and UV#0. This approach would have also been simpler if we can calculate f simply from the amount of nitrate at time t (i.e. C) to C_0 for each pit. However, we were unable to follow this approach as explained in detail in the manuscript associated with the shift in the nitrate standards during concentration measurements. This led to nitrate concentration greater than the concentration at the beginning of the experiment in deep layers (for e.g., about 200 ppb below 25 cm in Control#6). This issue can be further illustrated by looking at the nitrate concentration measurements in Fig S.1. Accordingly, below about 15 cm depth in the control samples, the nitrate concentration seems fairly stable within each batch, however, different concentration values are measured for each (approx.1200 ppb to 1700 ppb) independent of the sampling period. Here, there is no loss of nitrate depending on depth as the profile observed for surface samples. This is a clear indication that it is not a process associated mass loss or gain but a simple shift, probably due to a calibration issue between measurement sessions. As such shift will lead to an artefact between profiles with wrong implication, we have applied another strategy where we assumed the mass loss or isotopic fractionation is minor (Not absent!) between 25-30 cm depth, and we used the average nitrate concentration at this depth as the C_0. With this approach, the trend expected from a Rayleigh fractionation process is established, further validating the followed approach. The calibration issue is further demonstrated by the very stable isotope ratios (Fig S3) obtained at depth across samplings of the control experiment. The stability of the $\delta^{15}N$ measured below 10 cm is a strong indication that the actual concentration observed at depth within the snow pits is an artifact.

They suggest that the depths of samples across different profiles may or cannot be exactly the same. In this case, it would make most sense to group the profiles based on depth intervals such as 0-5 cm, 5-10cm, 10-15cm, etc. In this case an average concentration value from the control and from UV#0 at each depth interval would be Co, and measured concentration averaged over the number of samples collected in that interval could be compared (i.e. the 3 datapoints between 0-5cm in profile 1 would be compared against the average concentration in the control between 0-5cm). I do not see why it is relevant to calculate the amount of nitrate re- maining near the surface or at 10 cm or at 15 cm against what is happening at 25-30 cm across all profiles at all times. In fact, there is a lot of heterogeneity across the profiles in each pit in terms of concentrations at 25-30 cm, suggesting that negligible loss is not necessarily accurate. Additionally, some of the profiles have higher concentrations that the control or UV#0 in the 25-30 cm interval.

The need for calculating nitrate remaining (f) with respect to nitrate conc at 25-30 depth is twofold: to avoid the artefact arising from the use of incorrect standard concentrations and for later determination of isotopic fractionations (for e.g., $^{15}\varepsilon$). If all the control samples showed no change in nitrate mass and isotopic composition then a direct comparison between the two pits at similar depth may be practical. The shift in concentration is discussed briefly above. Regarding suitability in isotopic fraction calculations, averaging delta values (for e.g., $\delta^{15}N$) is not practical as their values range between -10 to +40 ‰ and averaging will lead to wrong interpretation. As the process is not at steady state (i.e. the snow is denitrified after sampling), stacking or binning the different samplings by depth interval is an incorrect procedure.

Finally, the conclusions regarding lack of change of the epsilon values with depth should be checked by verifying comparison of samples across similar depth intervals rather than comparing all profiles against a single depth interval.

This is a very important point. We could not compare samples across similar depth as we had a single data point at a given depth and time. But it will be very useful to conduct future studies on the depth dependence of isotopic fractionations by sampling across similar depth at a given time. Further, conducting such sampling at different times will further illustrate if the isotopic fractionations change over time. However, it should be noted that such experimental design requires a bigger pit size as it requires more samples, which is not practical with the present experimental setup.

The description of the data reduction does not appear to be true in the supplemental figures. There seems to be miscalculation and/or missing data, although admittedly the figures are hardly readable. First and foremost the data included in the figures should be reported somewhere (I thought this was a requirement of ACPD/ACP?). Second, the figures must be adjusted to be readable, the symbols and lines should be consistent and carried through all figures rather than changing with each figure (this again makes it very difficult to follow the discussion). It should be justified in the text as to why only the even profiles are chosen to be shown in the text while all data is shown in the supplement. (I believe that it should be possible to format the figures such that all profiles can be shown in a way that is readable.) From what I can tell there seems to be disagreement between figures S1 and S2 in terms of the calculations described in the Data Reduction section. For example UV#6 in Fig S1b nitrate concentration is reported to 23 cm, then in Fig S2b the UV#6 profile extends all the way to 30 cm. If the nitrate concentration only extends (or was only measured) to 23 cm how can the fraction of loss be calculated below this depth? In the control pit most profiles have concentrations higher than #0 (even at 25-30cm) but the f values are nearly equal – why? There are number of other inconsistencies between the supplementary figures and text figures of the concentration compared to fraction of nitrate suggesting the authors should recheck these calculations/figures/data.

The reviewer points out some important considerations that have resulted in revisions throughout the manuscript.

Following the reviewers' advice, we have now included the data as supplementary material.

We have also redrawn the above mentioned figures for better readability and consistency.

The choice of presenting only even samplings in the main text is simply for visual purposes. Showing all the data would only clutter the figures without improving communications. This is now explained in the main text of the new manuscript.

The figures have been redrawn so as to avoid ambiguity, and have consistency in color and labeling.

Regarding the reference concentration to be used for *f*, we believe it is associated with a calibration offset, as explained above. Instead, we used the concentration at depth of each profile as the reference starting concentration for that profile, since all these samples were quantified with the same calibration curve. Because the deep samples are barely photolyzed as demonstrated by the small change in $\delta^{15}N$, as well the small change in nitrate concentration, we assumed that the concentration between 25-30 cm depth represents the starting concentration, C_0.

At a few points in the manuscript the authors mention that "below 50 cm, the photolysis of nitrate becomes negligible. . .(France et al., 2011)" (p.33051). For the data reduction it is assumed that at 25-30cm negligible loss of nitrate would occur. There needs to be more discussion surrounding this point.

As stated below 50 cm negligible photolysis takes place, based on light penetration measurements. However, at 30 cm depth, the photolysis rate is low enough that during the period of the experiment, this layer can be considered as undisturbed as demonstrated by the $\delta^{15}N$ composition matching the starting composition closely. Thus, the values are used for normalizing f. In other words, in nature, snow at 30 cm depth has been exposed to at least 4 summer seasons or 4 times 3 months of continuous photolysis starting from the surface while the UV pit snow in this experimental study was exposed to only 2 months of photolysis at a fixed depth, namely a very small fraction of the UV dose endured by the natural snow. Taking 20 cm as the depth characteristic of UV penetration in snow (France et al. 2011), the relative dose received by the 30 cm experimental snow with respect to natural snow can be calculated as:

$$2x\{\exp(-30/30)\} / (3x\{1+\exp(-10/20)+\exp(-20/20)+\exp(-30/30)\}) = 7\ \%$$

i.e. a small fraction of the natural snow.

(An additional side note here that the average concentration at 25-30 cm is near 1400 ppb while the original snow on p.33050 had a concentration of near 1600ppb; and there is considerable heterogeneity across concentrations in each pit at 25-30 cm suggesting that something may in fact be changing at this depth).

The amount 1600 was measured from three snow samples taken from the homogenized experimental snow on 02 December 2011 at the beginning of the experiment on ppb is associated with the shift in concentration of the standard as mentioned above. We have corrected the original snow nitrate amount to 1450 ppb, the average concentration between 25-30 cm depth for UV#0 and Control#0.

The conclusion of the current manuscript (and previous work in the group) is that photolysis is the dominant control on changes in δ15N of nitrate. Yet, Frey et al., 2009 and Erbland et al., 2013 show changes in δ15N that occur below 50 cm. Between 30 and 60 cm one of the pits in Frey et al. shows a δ15N increase of more than 150 ‰. Several of the Erbland et al. inland pits show increasing δ15N over the entire depth range of 40cm. How is it possible that δ15N continues to show similar changes below 50 cm if photolysis is the main control and is negligible at this depth?

In previous publications by Fey et al (2009) and Erbland et al (2013), changes in δ^{15}N occurring below 50 cm were described. It should be noted that these changes occur in natural snow pits at 50 cm depth, which implies about 7 years old snow at Dome C (with an accumulation rate of about 7 cm of snow/yr). Of course at these depths, δ^{15}N values as high as 150 ‰ can be observed as the snow was exposed to photolysis and recycling for a couple of years and then eventually buried by the new snow layers which will undergo the same process. However, this experimental study is based on a single season study and higher δ^{15}N values are expected and actually observed at the surface, but not at 30 cm depth. Below 50cm, δ^{15}N records the value below the photic zone. Variations below that zone represent variations in parameters that control the photolytic rate and the starting composition (e.g., accumulation, snow fall δ^{15}N signal, nitrate concentration, solar radiation, atmospheric UV transparency and variations to exposure to UV). There is no reason to expect a constant δ^{15}N value after 50 cm even if photolysis has stopped.

Consider too that the France et al. reference may not be entirely appropriate here. The e-folding depths (eFDs) from France et al. were measured at 350 and 400 nm only; as illustrated in Frey et al. 2009 the peak in the spectral absorption curve for nitrate is 305 nm and calculated j value is centered around 320 nm and is very low at 350 nm and above. The modeled eFD for 305 nm from Zatko et al. 2013 for remote Dome C snow is 18-22 cm, suggesting that about 37% of the light is left to penetrate below 22 cm. This distinction in the possibility of light reaching to 25-30 cm and possibly deeper than 50 cm is very important for the design of the data reduction in this paper.

The modeled eFD for 305 nm from Zatko et al., 2013 for remote Dome C snow is actually very close to France et al., 2011 (20 cm for hoar layer) despite that the measurements and the model are at two different wavelengths. In a personal communication, France provided data below 350 nm, down to 314 nm and show constant eFD down to 314 nm, so the eFD is not really an issue as there is a common acceptance for 20 cm for clean snow. The main difference, as explained before, lies in the time of exposure, not the eFD. As demonstrated before, in such short time experiments, we can assume that at 30 cm, nitrate is practically unprocessed. Giving the size of the snow reservoir and the small loss, we can reasonably consider this layer as our starting composition, which is further demonstrated by the stable δ^{15}N signals. Note also that if the light penetration can go further than 50 cm (which we never opposed), the actinic flux is reduced by orders of magnitude at this depth and concentrations of nitrate never converge to zero as some of the nitrate are locked in the crystal matrix. Finally studying 30 cm, 50 cm, or even 1 m does not change the interpretation as long as the selected depth is enough to show the fractionation trend. However, going deeper increases the vulnerability to processes that may have nothing to do with a photolysis process. Fluctuations at depth, beyond a reasonable nitrate photolysis depth (e.g. 3x eFD) can indeed be the result of non-steady state surface processes (e.g. accumulation, ozone layer, source of nitrate, temperature, etc).

It is unacceptable to mention an artifact in the data as part of the supplement and conclusions alone. The potential for the problem in the concentration data to affect all of the results needs to be better elucidated in the main text. In fact, in the methods section there is no mention of reproducibility for the concentration measurements based on the data shown here, only based on previous work. It should be directly addressed why and how there may be an artifact in concentration data. This should also then be considered in terms of the error associated with the calculation of the fractionation factors, which depend on the concentration measurements. Some type of error propagation should be possible to account for how much error this artifact in concentration data might introduce to the Rayleigh model based calculations. The use of standard deviation across the calculated results may not be a realistic measure of the range that is possible given the larger errors on concentration than is suggested in the main text.

The issue/artifact with the concentration rests on standard calibration error (e.g. dilution error), which is a systematic error that results in an offset of concentration between analysis sessions but not within a session. Such an error, based on ground observation (e.g. stable concentration and isotope compositions at depth or conformity with the Rayleigth treatment) is easily corrected using our procedure (note that Rayleigh treatment requires relative losses not absolute ones) and does not introduce additional error.

Pre-concentration of samples appears to be a standard technique within this group. However, more discussion of the method should be included.

Lines 20-25 p. 33052 suggest that standards were treated identically to samples, but it is not clear if they were also subjected to the pre-concentration method. Are the reference materials such as the USGS35, 34, 32 run through this method as well to verify that it does not change the isotopes? Is the same NaCl that was used for the pre-concentrating of samples used to make the matrix of the reference materials? The corrections for the isotope data say they are included the Supplement, but they are not.

The preconcentration step was not applied to the standards because such identical treatment turned out to be unnecessary. When we set up our method, this IT test was performed and did not show any significant difference beyond the reported uncertainty in the absence of such treatment. Note also that this is a standard procedure (Silva et al., 2000), and since recovery of ions from the resin is always very close to 100 %, no fractionation is observed. NaCl used to elute and prepare the matrix is different (never tested but reference product is always coming from the same manufacturer), however, the water used between samples and standards should be and is the same, as the water isotopic composition has a great importance due to a small oxygen isotopic exchange with some intermediate nitrogen compounds during bacteria digestion.

Regarding the corrections script in the supplementary materials, they were not provided as we have not used them at the end. They were meant for samples with very low nitrate conc. such as natural snow pits (samples below 30 cm depth), which are not presented in this manuscript and this sentence is removed from this manuscript now.

I do appreciate that a field experiment of this type makes for many factors beyond one's control. But the manuscript fails to really put together a coherent picture and explanation for the data, yet in the abstract and conclusions are very firm about proof for photolytic loss of nitrate being the dominant process at Dome C. A few concerns surrounding this issue include that significant amounts of loss of nitrate in the top 10 cm take place in both pits – so in the case where UV light is allowed to penetrate and in the case when it is limited. While some of the explanations offered may account for this partly, it is really difficult to accept that a similar mass loss is seen in both pits that must be explained by photolytic loss in just one snowpit. The authors make the case that the isotopic fractionation is so different for the two pits, despite the similar mass loss, and this needs to be revisited based on the above suggestions regarding how to evaluate the fractionation factors relative to the control profiles at similar depths rather than by comparing with a single depth. It also would be important to consider changes in calculated epsilon with time for each pit. While both experimental pits show similar mass loss near the surface, over time differences in their behavior are very apparent and this likely could be made clear by looking at fractionation of δ^{15}N at a given depth interval and whether it changes in a consistent way over time that is different between the two pits. This may help to provide a better avenue for explaining the differences between the pits. Without a better understanding of what could have caused such similar loss, the importance of photolysis is overstated.

Firstly, we would like to clarify that photolysis is not absent in the control pits but reduced, and this issue become very complicated in case of surface snow samples.

It is also very important to consider the isotopic measurements (δ^{15}N), which show a clear difference between the two pits (but not to consider only the concentration measurements).

However, reviewers 3&4 also raised this issue and we have extensively explained the reasons why the first 7 cm should be taken with caution. The reviewer can refer to these replies. In a few words, the apparent losses observed in the first cm are the results of surface processes that have nothing to do with photolysis but with drifted snow, temperature effect, dry deposition and so on. The decrease is apparent because mixing with surrounded snow that contains less nitrate amount gives an apparent decrease of concentration. We do not think that such first layers should be interpreted in any way. It is just a mixed layer unavoidable in an open system as our set up. Deeper, the snow is completely isolated from the surrounding snow, and the expected trend is clearly observable (small loss for control, large loss for UV).

At depth we are unable to distinguish a pure physical loss (e;g. desorption) or a mix between physical and residual photolysis for the control experiment. Unfortunately, a "pure" photolysis fractionation factor cannot be deduced from a simple subtraction, taking the control experiment as the reference. Note also that deltas are not additive quantities and cannot be subtracted without taking into account mass balance. Conversely, fractionation factors are additive quantities, so if control should be used as a reference it is the difference between $^{15}\varepsilon_{app}$ (UV) and $^{15}\varepsilon_{app}$ (control) that should be applied.

In the figures (but not the text), the authors suggest that they are ignoring the top 7 cm because the lack of an understanding for the big loss in the control pit but at the same time suggest that they only rule out some of the data based on δ15N. What data is ruled in (or out) and how? And why? This must be explained in the text.

This question is not easy to answer because the interference/mixing produced by the drifted snow is not evenly distributed within and between each field. There is no threshold depth from which we can rationally exclude data. Exclusion of data points in this range depend how badly they fit the expected model (Rayleigh model), in a same way as outliers are excluded. The reviewer should understand that the only purpose of filtering this mixed layer is to better constrain the first sampling experiments where losses at depth are weak making the Rayleigh treatment unreliable without taking into account undisturbed samples from the first cm. The criteria to keep or exclude the data in the mixed layer is based on aberrant behavior (δ^{15}N increase with decreasing depth or said in other words less fractionated for more sun exposure). In case of UV#4-UV#6, this is the region where non-photolytic processes are taking part significantly and all samples between 0-7 cm were excluded. In case of UV#0 to UV#3, only samples at 0-2 cm depth were excluded. Note that as time move on, more samples are excluded, in agreement with longer interference time with the surrounding snow.
This procedure is applied for both control and UV-exposed samples. In section 4.1.1 we have stated that samples from the surface to where δ^{15}N starts to shift to more negative values were excluded. In the conclusion section 33067/3-5, we have also stated that there might be an error introduced while excluding some of the top layer points where the photolysis effect is significant.

The amount of loss observed in the field is very different than that calculated in Frey et al. 2009 and that found in the laboratory experiments. This should be discussed.

The amount of loss is dependent on the amount and duration of exposure to solar UV (for field experiments) or the actinic flux of UV light and wavelength region.

In case of the laboratory experiments loss of nitrate is higher when strong UV is allowed to reach the snow (for e.g. in case of 280 nm filter than 320 nm filter) (Berhanu et al., 2014). Also, the solar spectrum has little resemblance with a Xe UV lamp, therefore it is almost impossible to compare rate of loss between different set up. In addition if the exposure at a fixed wavelength was longer loss will be higher (low f values) and vice/versa. However, it does not change the isotopic fractionation value since δ^{15}N scales with *f*, maintaining constant isotopic fractionation (ε). This is the beauty of ε, it is independent of δ and loss, it is a parameter that characterizes a process, not quantities, equivalent to a kinetic rate for a chemical reaction.

At several points in the manuscript the authors suggest that they cannot interpret the δ18O and Δ17O data, but then do discuss it. The mentions of not discussing this data should be deleted since the data is shown and discussed, even if it is not yet understood. In several of the works by this group the possibility of "cage effects" that lead to re-oxidation of snow-sourced NOx to nitrate in situ is invoked to explain the lowering of δ18O and (possibly) Δ17O. This is never connected to the understanding based on the δ15N. Comparison amongst the theoretical values (Frey), laboratory values (Berhanu) and the field values (this study) is used to suggest that this all speaks consistently to an understanding of the fractionation associated with photolysis as the primary driver of nitrate loss. Yet the theoretical values are calculated based on simple (one-way, single process) loss of nitrate alone, and no influence of secondary formation.

We write that we will not discuss specific trends or values for δ^{18}O and (possibly) Δ^{17}O. In order to avoid confusion, we have now rephrased such sentences. Regarding the cage effect, this process is "buried" into the quantum yield of dissociation. Isotopic fractionations of ^{15}N occurs only when dissociation is effective. If the products go back to reactants there is no isotopic effect for ^{15}N. It would be the same for oxygen isotope if there were no isotopic exchange in the meantime. To have an effect on ^{15}N, the cage effect should have a preference for ^{14}N or ^{15}N, which is something we did not consider.

In the laboratory experiments, nitrogen gas is specifically used to blow away photolysis products to limit secondary formation in the gas phase, but my guess is this would not necessarily limit the so-called cage effects. In the field, neither the secondary reformation in the gas phase nor the in situ "cage effect" is controlled for. So how does this all influence the fractionation for δ15N amongst the studies and why is this effect on δ18O and Δ17O not important for δ15N?

See previous comment for the cage effect. Nitrogen gas in lab experiment is indeed used to evacuate the photolysis products, not to control the cage effect, which is under the control of ice crystal lattice (2.75 Angstroms between oxygen atoms), a mean free path equivalent to 222 atmospheres! Regarding the reformation in the gas phase within the snow pack, we have followed conclusions of the work studying flux NO_x emissions from snow and vertical HNO_3 gradient measurements that either neglect or assume a small internal recycling, while most of NOx being emitted to the atmosphere (Honrath et al., 2002; Davis et al., 2008; Frey et al., 2013).

On page 33057, it is suggested that no real differences or trends are detected in the oxygen isotope data. I disagree. In Figure 5, the UV pit Δ17O is consistently lower for much of the profiles compared to #0 (especially below 10 cm). This is not the case in the control pit (all profiles overlap and there is no distinguishable pattern). This appears to be significant (especially when compared with the differences/patterns in δ15N that are invoked as truly significant and robust). While there is variability in Δ17O in the #0, only the values at the surface and 5 cm are not significantly different and the top 7 cm is largely being ignored in the manuscript anyhow. The lowering of Δ17O in the UV pit seems consistent with the hypothesis that re-oxidation of photolysis products in "the cage" leads to exchange with a low Δ17O (low δ18O) source, does it not? It is not clear why this difference in Δ17O should be ignored.

We appreciate the reviewer for pointing out such trends such as in UV#5. However, this is a specific case and it is inconsistent with what he proposes as re-oxidation followed by the cage effect and subsequent lowering of Δ^{17}O. If it was truly the case, we expect Δ^{17}O of UV#6 would have been consistently lower, or UV#4 to be higher (which is not always true). Hence, drawing such conclusion will be incorrect, as we do not observe a consistent pattern in such a profile but we do not deny the possibility that there is trend but difficult to see due to very small changes in Δ^{17}O values.

Regarding the difference between the UV and Control pits over all Δ^{17}O differences, indeed we agree with the reviewer that more variability is present in the case of UV-exposed pit than the Control pit samples, implying "the cage effect", as mentioned by the reviewer and which is already present in the manuscript.

Throughout the manuscript is should be consistently clear that the fractionation factors are apparent. In some cases the subscript "app" is used and this should be applied throughout the manuscript, including the abstract and supplement.

We have now adopted the subscript "app" throughout the new manuscript.

The inconsistency in using app emerges from the design of the experiment (expected to derive purely photolytic fractionation factors) and the observation where part of the non-photolytic processes are at least minimized.

Specific comments:

-L17, p33046: would suggest using the subscript "app" to be clear that the fractionation values are derived as "apparent isotopic fractionations"

The subscript "app" is now added

-L1, pp33048: SMOW = Standard Mean Ocean Water

It is now corrected

-Methods section: I think the details regarding the potential artifact in the concentration data must be discussed in the methods section. The mention of the concentration methods, pre-concentration methods, etc. should be part of another or separate section – it doesn't make sense to have this as part of the Experimental Design.

We wanted and would like to keep the possible artefacts in the experiment in the discussion section as we need to show the results before discussing what can possibly happen on the surface snow nitrate. The only tools we have to verify indded there are additional processes are the conc and isotopic measurements.

The section regarding the experimental design is now reorganized.

-For the Experimental Design it seems important to include more details about how the snowpit was sampled. If a hole was a dug in order to sample "a wall" of snow, was this hole then backfilled? If it was left open this seems like it would radically change the wind-pumping, allow for a lot of drift, and/or allow for more radiation from the side – all of which could potentially contribute to the large changes seen near the surface in the experimental pits. If the snowpits were refilled between sampling time so there wasn't a large hole al- lowing for significantly more drift, wind-pumping or more radiation from the side, then how was snow added? By shoveling?

Reviewer 1 also raised this question and it is discussed there. A section regarding this issue is now included in section 2.2.

Was density of the snow measured? This snow would likely be compacted and a significant change in density might explain some difference in the amounts of loss seen in the field compared to that in earlier work at Dome C or in the laboratory experiments. In other words, how might the change in density for the experimental pits influence the results seen?

All of this is to say, more details are needed in how sampling was completed. It also might be worth moving Figure 11 and presenting it as part of the Methods section to fully explain the experimental setup and conditions to consider in understanding the results and discussion.

No, we have not measured density of the snow but again what is important here is to look the difference of behavior between control and UV fields. While density is an important parameter for light penetration, both fields should have close density profile.

p 33050: How was transmittance determined? Why is transmittance for the non-UV plate not shown for below 310 nm? It almost appears as if the values are increasing again below 330 nm and 305 nm is the peak in nitrate absorption so this could be really important.

It was measured as a ratio between incoming solar light below the plexi plate (I) to light on top of plexi (I0).

Sometimes light reflected back by snow might lead to a transmittance greater than one.

This is due to back scattering of light and the position of the probe when scanning incoming and transmitted light – not perfectly the same position and orientation for incoming and transmitted light, producing inconsistent absorption spectrum at very low radiation flux.

For the control plates, the transmittance was zero or negative at shorter wavelengths, which is due to insufficient light reaching the detector, and thus introducing a lot of noise in measurement.

-L9, p33051: why is data only shown to 30cm if samples were collected to 50cm? What does the data below 30 cm show?

Data below 30 cm are from natural snow pits, not part of the homogenized snow. We have analyzed a couple of samples at this depth and found low nitrate concentrations and high δ^{15}N as expected from natural pits of similar depth.

-L19, p 33051: Does this reproducibility of concentration measurements from previous studies hold up based on replicates measurements in this study?

Based on replicate standards measurement, we have calculated the precision to be within 5 %.

-L16, p33052: Is 900 degrees C correct here? Kaiser et al only use 780C and other studies report values closer to 800C.

Yes we use 900 degrees. By experience we know that the recorded temperature depends on the exact location of the probe. We don't know where it is located for other groups, in our case, it is in contact with the quartz tube that holds the gold tube in the oven.

-L20-25, p 33052: What is Dome C water? Is this melted snow that contains ions or is this melted snow that is purified or something else?

Dome C water is melted snow that passed through a milipore purification unit. It does not contain any ions.

-p33052-33053: Were any replicate samples run? How do these standard deviations compare to that based upon the reference materials replicates that are run many times?

Standard deviations were obtained from standards (4 types and 4 of each=16 standards at least), which were measured during analysis of every batch.

These are the average of the standard deviations of standards measured in each batch. Based on these replicates, the standard deviation is estimated at around 5% (300-1000 ppb), and 10% (10-300 ppb). Samples measurements were not duplicated giving the number of analysis to conduct in such short period of time (>1000). However, from extensive experience in using such systems, we are confident that stdev of standards are a good estimate of the stdev of samples.

-L2, p33053: What is an average uncertainty?

Within each batch, the standards are measured 2-3 times. The overall accuracy of the method is estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials and their expected values. The reduced stdev can be seen as an average standard deviation. However, we agree with the reviewer that the wording is incorrect and it is now changed to "overall accuracy".

-Data reduction section: In this section use of the "app" subscript is appropriate and useful. Please use this throughout the manuscript when referring to apparent isotope fractionation values.

This subscript is now used.

-L18-20, p33054: I do not understand what this means –are these different days of collection? Or the same profile sub-sampled? If there are 4 samples averaged then why are there not error bars denoting the standard deviation associated with this averaging? Please better explain this.

Yes, these samples are taken over a 10-day interval with sampling events at similar depth. The error bars are given in Fig. 12 of the new manuscript.

-p33056: Throughout this section the language needs to be much more precise. In the figure it really looks like loss is only "significant" to 17 cm, yet here it says it is signifi- cant to 20cm, then below it's not significant or ceases below 25 cm yet the difference between the UV#0 and UV#6 is as large here as the difference between UV#0 and other profiles at 20 cm. Then from 28-30cm all of the profiles show a decrease? why? What is "significant"? Please go through this section more carefully and quantitatively justify the choices of what is significant, what is robust, etc.

In the new manuscript, we have rewritten this paragraph and excluded terms like "minor" and "significant", and instead used actual *f* values to express nitrate loss quantitatively.

The 28-30 cm depth, the bottom of our experimental pit, is the depth where the new higher nitrate containing experimental snow and natural snow come in contact with each other. Please look carefully at Figure 3 (and Fig 1 of supplementary materials), we do not see any sample showing a decrease at 28 cm. It is rather at 30 cm depth where Control#6 and UV#6 for examples show a decrease. Considering the fact that sampling depth is not very precise and densification of the experimental snow with time, this decrease is an indication that we might have sampled part (even few mm) of the low nitrate containing natural snow leading to a decrease in *f* from 1 at 28 cm to 0.95 at 30 cm.

Why are only even #'s shown in these figures? (this needs to be justified in the text)

Please see comments to Reviewer 1 (It is for clarity, the additional lines would add clutter without communicating additional meaning).

-L1, p33058: How is "robust" defined? Some type of table showing regressions, R2 values and significance (p values) for all samples sets should be shown somewhere (right now it is only shown for UV#6 in the figure). And R2 values should be included in Table 2.

They are now included

L20, p33058: The 18e and 17E data ARE presented in the manuscript! Rephrase this.

We have now removed this sentence.

L20-23, p33060: This should lead to less loss, not more loss. And this should be true for only the experimental pits and not the natural surface snow (which is not the case shown in Figure 4 and Figure 6). This should be reconsidered.

Considering the reviewers comment as well as the lifetime of NO_x of few hours, we have rephrased this sentence.

L6-7, p33060: "tops of snow pits were covered with the plexi-plates" This seems a bit of an inconsistent statement with earlier comments in the paper. The plates were 9 cm above the snow and snow is not necessarily perfectly vertical at all times. Also, is all of the deposition expected to be wet-only?

To rephrase, yes plates were placed on vertical stands at about 20 cm above the surface. It is also true that snow fall is not always in vertical position and dry deposition of HNO_3 is not blocked by the plate. However, we agree that this sentence may be confusing and we have rewritten as follows “snowfall was not observed during the sampling period; therefore, wet deposition of nitrate via snowfall is excluded. However, dry deposition of HNO_3 is still possible even with the plates in palce” in the new manuscript.

L15, p33061: This is a strange and incorrect title. Maybe “Nitrogen isotopic fractionation: 15eapp” (where the 15 is superscript and the app is subscript)

Corrected

L5-8, p33062: Here and in the tables the Frey et al. values should be directly taken from the manuscript, not averaged or rounded.

These values were given by Frey et al. and the values in the text and the values given in the table are not exactly the same. This can be verified from the manuscript by Frey et al.2009. We have reported the values given in the text.

L9-10, p33063: It is interesting however that the laboratory results were similar to the theoretical values in Frey et al. 2009, which used the TUV model that is very similar to the actual spectral actinic flux.

L6, p33064: “sample UV#3” – this is not really a sample, but a mean of samples or a profile or ?

UV#3 is a batch of samples at different depth. It is now corrected in the new manuscript.

L5-15, p33065: It seems important to note that the laboratory study was only a 12 cm column, and loss was only observed in the top 5 cm – so this is very different than what is observed in the field and not a big depth range to make such significant reaches in terms of conclusion in line 12-13.

While the thickness of the snow involved in the process can be different as it depends on the light source flux, time of exposure and other experimental settings, the process is the same, denitrification of snow by UV light. Thus, we believe that the depth-independence of the isotopic fractionation is a robust observation based on lab experiments, and now not only field observations but also by theoretical consideration as UV absorption in snow is almost independent of wavelength (all UV’s are attenuated by the same factor), and thus does not change the convolution between absorption cross-section and radiation spectrum, which is the main driver for the fractionation factor. This is also confirmed by a recent study modeling snow denitrification (Erbland et al., 2015).

p33065-33066: Again it is very important to label all of the epsilon values as apparent (i.e., “app”).

All are now labelled as “app”

L26, p33066: you might consider including density in this list of physical properties as well.

It is now included

L5-8, p33067: see general comments, but this artifact needs to be clearly addressed in the manuscript and it’s potential influence on the calculated epsilon values needs to be quantified.

Technically, what we meant was not more of an artifact rather the possibility of underestimation of the isotopic fractionations while excluding all samples at 0-7 cm depth (the photic zone). As briefly stated in section 4.1.1 in the new manuscript, excluding partly or all samples within this 0-7 cm depth have a significant difference in the derived isotopic fractionations.

Overall the quality of the tables and figures is very poor.

Table 2: The text must explain how δ15N is used to identify “external processes” and therefore what data is excluded versus included. Why is sampling 1 not included here? It is not clear which columns belong to which headers.

Table 2 is re-arranged. However, why #0 and #1 are not included is already clearly stated in the text. To repeat it here, due to an insignificant change in nitrate mass and isotopic composition, the linear fits for samples #0 and #1 from both pits were only weakly correlated, and are not discussed.

Table 3: The values reported in the table are not the values reported in Frey et al. (e.g., -49.8 not -50.0, etc.). If reporting to one decimal place then this should be reported exactly and not rounded.

Again here, these numbers are given in Frey et al 2009 page 8686 right column.

Table 4: again, these are not the exact values that appear in Frey et al. Here 6.0 +/-2.1 should be 8.8 +/- .2.1! Please copy both values correctly.

Again here, Please refer to Frey et al 2009 and the years (DC04 or DC07 pit)

Figure 1: why is transmittance below 310 nm not included for the non-UV plate? Why are there values above 1 for transmittance?

Please see above.

Figure 2: It may be worth mentioning on the figure itself that the 2 nm shift has been applied for clarity.

It is now included.

Figure 3: Why is only some data shown and not all profiles? “unexposed to solar UV” is an overstatement as discussed in the manuscript (transmittance is not zero, some light comes in when the sun is low, etc.) – perhaps say “reduced UV exposure.” The shading in Figure 3 should be used consistently (i.e. in Figs 5, 7, and 8 as well).

Again see above.

We have now used the term “reduced UV exposure”.

The figures are now modified.

Figure 4 and Figure 6: These data do not fit well with the overall explanations provided in the text. The surface snow in the experimental pits seems to have been largely influenced by “external processes” and unnatural drifting, scouring, sublimation. If these external factors are so important for explaining the top 7 cm behavior in the experiment pit, why does the surface snow in the experimental pits compare so well with natural snow?

The comparison between “natural surface snow” and “experimental surface snow” is precisely to show that surrounding snow might have been mixed with the experimental snow, and thus the isotope and concentration values converged to the natural snow instead of following steady denitrification process.

Figure 5: there is no top and bottom panels.

The figure and its caption is now modified

Can the formatting in Figure 3 and 5, be similar and consistent in Figure 7 and 8 (this includes the look of the plots and the symbols and lines).

It is formatted accordingly in the new manuscript

Figure 9: This is an important figure/result. Some of the numbers are difficult to read. The relationships (including R2 and p values) shown in this example should be reported for all profiles, not just the one. This would work well as a table in the text or supplement.

We have included a table for all profiles now as Table 2 in the new manuscript

Figure 10: The text emphasizes over and over that samples were not necessarily taken at the same depth in each sampling event, so why is that stated here? Please see general comments about the calculations. It would make much more sense to be using depth intervals and including all of the data within those depth intervals. Also the epsilon is not “measured” between -50 to -70 ‰ (this range includes theoretical and laboratory experiment).

Figure 11: Suggest moving this earlier. It would make the gray shading in the data

plots make more sense and would set the stage for the discussion of results.

This figure is now moved earlier in the new manuscript

Figure 12: The text needs to explain what data points were identified and how based on the δ15N. Why is the dashed line a line and not individual points? The way that this figure and the text reads, it suggests that data was chosen to dismiss the observed trend in 15e, which may in fact be real!

We have now included the Points in Figure 10 of the new manuscript.

Figure 13: The text is very dismissive of the δ18O and Δ17O data. And the R2 shown in Figure 9 for Δ17O is 0.07 (and what is the p value? Is this significant at all?), meaning that less than 7% of the variability is explained by this relationship. Thus, showing Figure 13 is not really appropriate or legitimate when the data is not treated or explained robustly.

We have now excluded figure 13 from the manuscript.

Supplement.

The figures in the supplement overall are extremely poor. The symbols, colors, and lines (including the weight of individual profile lines) should all be used consistently. Figure 1 has an incomplete figure caption or no figure caption; Figure 3 does not even include numbers on the y-axis; using thicker lines for some profiles draws attention to only certain profiles, and should be avoided. The supplement does not include the isotope data corrections and description as suggested in the text.

The supplementary material has been revised.

The overall carelessness in the manuscript and supplement undermines the quality of the data and undermines the legitimacy of the manuscript overall.

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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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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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 NOx 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 δ^{15}N values with the top layers converging to δ^{15}N ≈ 10 ‰, 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
- ± 1-2 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 δ^{15}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 δ^{15}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 δ^{15}N is lower (more negative) than the subsequent deeper and 0-2 cm depth for UV#0-UV#2Same 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.

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