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 δ^{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 δ^{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:

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

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.

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