Authors' Response to ACP MS No.: acp-2019-669

We thank the reviewer for the comments and suggestions. In the text below, we outline our responses in blue. Line numbers refer to the revised manuscript.

Anonymous Referee #2

This work present new observations of the isotopic composition of nitrate in atmospheric, skin layer, surface snow and snowpit samples from Dronning Maud Land, Antarctica. The goal of the work is to understand the primary driver(s) of post-depositional processing of nitrate in this environment, based upon a snowpack box model, and determine whether it would be possible to uncover a d15N-nitrate signal that is dependent upon total column ozone. A great deal of work has been done on interpreting the d15N-nitrate in surface snow and the atmosphere at Dome C, and this work seeks to expand the application of similar tools to another site with different environmental conditions (i.e. accumulation rate, snowfall timing, and e-folding depth).

While the data and methods in this work appear sound, and the results are interesting, the manuscript reads as a first draft. With so many authors on this paper, and several who have led work at Dome C, it is surprising how disorganized and filled with typos this work is. Overall, it is difficult to connect the results with the interpretation. Much of the discussion section reads as introduction, and the introduction itself is overly repetitive.

We agree with reviewer, and have reorganised and edited the entire manuscript with particular focus on the introduction and discussion. Please also see our response to referee #1's main comment.

Most critically on the interpretation front, is that the authors must first consider the efolding depth results THEN the results considering changes in the snow accumulation, timing, etc. The model (shown in Figure 7) is simply not at all good enough to draw the conclusions the authors are drawing UNTIL it is shown that with the reduced e-folding depth the model can actually reproduce the observations. This is done as a final step and negates all of the previous discussion that suggests that the model output is robust, and therefore negates the conclusions being drawn.

We agree with the reviewer that the e-folding depth results need to be accounted for before suggesting that the model output fits the observations. We reran TRANISTS with a 5 cm e-folding depth scenario as suggested by reviewer #2. First, we modified the methods section to include a 5 cm e-folding depth scenario (section 2.7 Air-snow transfer modelling). Second, we have added a section on the e-folding depth in the results section (section 3.8 Light attenuation through the snow pack) so the reader can see the observed results of a lower measured e-folding depth at DML upfront. We have also compared the new 5 cm e-folding depth case to the base case in section 3.9 Simulated nitrate mass concentrations and isotopic ratios from TRANSITS modelling. Third, we compare the lower e-folding depth to Dome C and discuss the impact of the lower e-folding depth on post-depositional processes (section 4.3.2.2 Nitrate recycling). Fourth, we have rerun the snow accumulation rate and snowfall timing sensitivity tests with an e-folding depth of 5 cm and modified Figs. 6, 7 and 8 and Table 2 with the new sensitivity test results. An observed e-folding depth of 5 cm was used as it has good fit with observations down to 30 cm depth. In light of the new sensitivity results from TRANSITS, we have reorganised section "4.5 Sensitivity of $\delta^{15}N\text{-}NO_3^-$ to deposition parameters and implications for interpreting ice core records of $\delta^{15}N-NO_3^-$ at DML". Here, we discuss the TRANSITS modelling results by first showing that the base case scenario cannot reproduce the observations and that a reduced e-folding depth is required. Next, we discuss the sensitivity results of a variable snow accumulation rate and snowfall timing with an e-folding depth of 5 cm. With an e-folding depth of 5 cm we are able to reproduce the observations and thus our original conclusions that TRANSITS does a good job are valid.

In section 4.2.3, confidence is built in that TRANSITS can reproduce the seasonal cycle, not at the site here that we are comparing with, but at other sites in Antarctica? This makes no sense.

There are no year-round measurements of atmospheric or skin layer $\delta^{15}N-NO_3^-$ at DML to compare to the TRANSITS seasonality simulations. This section has been rewritten to show that of the available year-round observations and seasonality simulations of atmospheric and skin layer $\delta^{15}N-NO_3^-$ and nitrate mass concentrations in Antarctica, the seasonal pattern is the same at all Antarctic sites. The section has been renamed 4.2.2 Temporal variability of nitrate deposition.

The introduction should be rewritten to better frame where the paper is headed, after the discussion section is reorganized and edited.

Done.

It is well established that photolysis is a major driver of nitrate loss across East Antarctica, between the vast literature at Dome, Erbland's work and Shi's work. At this point, this should be a starting point, not something that is derived step-wise in the manuscript. Furthermore, it would help tighten up and shorten the manuscript. Finally, take a closer look at and include Shi et al., Investigation of post-depositional processing of nitrate in East Antarctic snow: isotopic constraints on photolytic loss, re-oxidation, and source inputs, Atmos. Chem. Phys., 15, 9435–9453, 2015, https://doi.org/10.5194/acp-15-9435-2015.

We agree, and this is reflected in the revised introduction and discussion. In addition, we have cited the Shi et al. (2015) reference in the appropriate places throughout the manuscript, and added the key findings of the paper in lines 137-140 as follows:

Modified text: "Erbland et al. (2013) suggest that NO_3^- loss at the coast reflects both photolysis and evaporation processes, while Shi et al. (2015) proposes that NO_3^- loss at the coast cannot be fully explained by local post-deposition processes and that seasonal cycles in the snowpack reflect stratospheric and troposphere NO_3^- sources during the cold and warm seasons respectively."

The evaporation (volatilization) of nitrate needs more discussion in the introduction. It is stated that that is negligible several times and then, finally, it is explained at lines 680-685 that this is temperature dependent process and THEREFORE not important AT THIS SITE. This should be detailed much earlier on.

As part of the revised introduction, the evaporation of nitrate is discussed in lines 86-98 as follows:

Modified text: "Fractionation constants, which assume a Rayleigh single loss and irreversible process of NO_3^- removal from the snow between phases during evaporation-condensation processes, have been calculated to separate the isotopic signature of evaporation and photolysis processes. As this approach may oversimplify the processes occurring at the air-snow interface, Erbland et al. (2013) referred to the quantity as an “apparent” fractionation constant ($^{15}\varepsilon_{app}$). Thus, the apparent fractionation constant represents the integrated isotopic effect of the processes involving NO_3^- in the surface of the snow pack and in the lower atmosphere. Nitrate evaporation from the snow pack has a $^{15}\varepsilon_{app}$ of ~0 as determined by two independent studies (Erbland et al., 2013;Shi et al., 2019). This indicates that during NO_3^- evaporation, the air above the snow is not replenished and thus there is only a small NO_3^- mass loss. In comparison, fractionation constants associated with laboratory studies and field observations of NO_3^- photolysis are large: $^{15}\varepsilon_{app}$ = -34 ‰ (Berhanu et al., 2014;Meusinger et al., 2014) and -54 < $^{15}\varepsilon_{app}$ < -60 ‰ (Frey et al., 2009;Erbland et al., 2013), respectively. The negative fractionation constant obtained from photolysis implies that the remaining NO_3^- in the skin layer snow is enriched in $\delta^{15}N\text{-}NO_3^-$. In turn, the atmosphere is left with the source of NO_x that is highly depleted in $\delta^{15}N\text{-}NO_3^-$. It follows that evaporation of NO_3^- is negligible on high-elevation Antarctic sites (Erbland et al., 2013;Shi et al., 2019).”

More evidence should be provided that the collection method is robust for representing the isotopic composition of nitrate in the air. The authors state that is “assumed that the atmospheric NO3- collected on glass fibre filters represents the sum of atmospheric particulate NO3- and HNO3 (gas phase)” and then says this is described in Frey et al. (2009). Except Frey et al. makes this exact same ASSUMPTION without providing any evidence that this is the case. Later in this manuscript it is suggested that differences found from earlier work by Weller and Wagenbach may be because different filters were used (Teflon) – which filters are robust? Might the Weller and Wagenbach filters only represent one phase? and if so the authors should understand what the implications of this is for the data comparison.

The glass fiber filters used in this study were employed and tested previously at Dome C, i.e., Frey et al. (2009) do not state an assumption but report evidence from tests with second stage filters. Accordingly, the atmospheric nitrate collected on glass fiber filters represents the sum of atmospheric particulate nitrate ($p\text{-}NO_3^-$) and gaseous nitric acid (HNO_3). The bulk of HNO_3 present in the gas phase adsorbed most likely to aerosols on the filter. This is supported by the observation that second-stage filters (Whatman 41), known to trap HNO_3 quantitatively (Morin et al., 2007), showed either very low nitrate concentrations or none at all.

In section 3.5 and in figure 5, it is never explained what scenario 1 vs scenario 2 is, and where does the 296 for wet deposition come from?

The value for wet deposition (296 pg m^{-2} s^{-1}) in scenario two is calculated using equations 3-5 (total deposition – dry deposition). Scenario one and scenario two are now described in the caption of Fig. 5 and lines 429-443 as follows:

Modified text: “Taking this simple mass balance approach, a schematic of NO_3^- mass fluxes for two scenarios are illustrated in Fig. 5. Scenario 1 is an average annual budget for DML (Fig. 5a). As the atmospheric campaign did not cover an entire annual cycle, we use estimates of atmospheric NO3- fluxes at DML reported by Pasteris et al. (2014) and Weller and Wagenbach (2007) of 43 and 45 pg m^{-2} s^{-1}, respectively, as year round dry deposition fluxes. Due to the linear relationship of ice core NO_3^- mass concentrations with the inverse accumulation, the authors assume that the magnitude of the dry deposition flux is homogenous over the DML region. Mean annual mass concentrations of NO_3^- in our snow pits suggest a total NO_3^- deposition mass flux of 110 pg m^{-2} s^{-1} and therefore a wet deposition mass flux of 65 pg m^{-2} s^{-1}.

However, at relatively low snow accumulation sites where photolysis drives the fractionation of NO_3^- from the surface snow to atmosphere (Frey et al., 2009), it is necessary to take into account the skin layer in the NO_3^- flux budget as this air-snow interface is where air-snow transfer of NO_3^- takes place. In scenario 2, we utilise the available NO_3^- mass concentrations measured in aerosol, skin layer, and snow pits from the ISOL-ICE campaign to estimate the mass flux budget for January 2017 (Fig. 5b). The dry deposition mass flux of atmospheric NO_3^- during January 2017 at DML averages 64 ± 38 pg m^{-2} s^{-1} (Table S5). The NO_3^- mass flux to the skin layer is 360 pg m^{-2} s^{-1}, however only 110 pg m^{-2} s^{-1} of NO_3^- is archived. Considering the active skin layer, only 30 % of deposited NO_3^- is archived in the snow pack while 250 pg m^{-2} s^{-1} is re-emitted to the overlaying atmosphere."

The authors make a claim regarding d18O-NO3- data late in the manuscript (line 660) – this is inappropriate given that none of that data is shown. Further, the claim is that the d18O rises due to denitrification, but there is not previous validity to this statement in the literature.

We have deleted this sentence as this manuscript does not address O-isotopes.

It is stated that the poorly constrained "quantum yield of NO3- photolysis in natural snow" yields a flux of NOx that is 50 times too high. Can this not be tested in TRANSITS? And shouldn't this affect the TRANSITS results as well and not just the estimated calculations here?

We agree that it would be useful to further test the sensitivity of NO_x fluxes to quantum yield in TRANSITS given the large uncertainty of this quantity. However, this has been done previously and we therefore refer to the literature and clarify the statement in lines 471-487 as follows:

Modified text: "It should be borne in mind that the above simple model estimates (Eq. (8)) may significantly underestimate the real emission flux. Previous comparisons of F_{NO2} computed with Eq. (8) and F_{NOx} measured at Dome C showed that observations can exceed model predictions by up to a factor 50 (Frey et al., 2015;Frey et al., 2013). While NO_3^- mass concentrations in snow, the surface actinic flux and e-folding depth were measured at the DML field site, quantum yield of NO_3^- photolysis in surface snow (ΦNO_3^-) was not, but introduces significant uncertainty in the model estimates. Previous lab measurements on natural snow samples collected at Dome C showed ΦNO_3^- to vary between 0.003 and 0.05 (Meusinger et al., 2014). As described above (section 2.6) JNO_3^- used in Eq. (8) was calculated with ΦNO_3^- at -30 ºC (= 2 x 10^{-3}) after Chu and Anastasio (2003), which is near the lower end of the observed range. Thus, up to half of the mismatch between Eq. (8) and Dome C observations can be explained by adjusting ΦNO_3^-. Another factor contributing to larger fluxes and not included in Eq. (8) is forced ventilation.

In the more sophisticated TRANSITS model, Erbland et al. (2015) found that the photolytic quantum yield was one of the major controls on archived flux and primary input flux at Dome C. Erbland et al. (2015) initially used a quantum yield of 2.1 x 10^{-3} at 246 K (France et al., 2011) but it underestimated NO_3^- recycling and overestimated primary NO_3^- trapped in snow. Adjusting the quantum yield to 0.026, within the range observed in the lab (Meusinger et al., 2014), gave more realistic archived $\delta^{15}N\text{-}NO_3^-$ values. However, at Dome C TRANSITS simulated F_{NO2} fluxes were about a factor of 9 - 18 higher than observed F_{NOx}. Erbland et al.

(2015) suggested that the discrepancy could result from the simplifications made in the TRANSITS model regarding the fate of NO_3^- photolysis products."

Finally, consider better comparing with Zatko et al., 2016 throughout the discussion – the equations used here are very similar to that paper and that work does in fact quantify the recycling despite the line later that only two studies have done so and then Zatko's work is compared with.

What we meant to say is that there are only two methods in the literature to quantify the number of recyclings (Erbland et al., 2015;Davis et al., 2008). Zatko et al. (2016) uses the Davis approach. We have edited the section on recycling, stating there are in fact three studies and have included the Zatko et al. (2016) paper in our comparison in lines 671-672 as follows:

Modified text: "Only three studies have attempted to quantify the degree of NO_3^- recycling between the air and snow (Davis et al., 2008;Erbland et al., 2015;Zatko et al., 2016)."

Also Zatko's earlier work (2013) on impurities should be better considered. Later it is attributed to Geng et al. for some reason. Can impurities in the snow not help account for some of the difference in the photolysis results? i.e. difference in impurities in the snow at DML and Dome C could help to account for the significantly lower photolysis rates at DML.

The impact of impurities on e-folding depth is addressed in section 4.3.2.2. Please see response to referee #1 concerning the impact of grain size and impurities on e-folding depth.

The timing and rate of snowfall CANNOT explain the misalignment between the observations and model results (Line 845). The e-folding depth is critical to right FIRST, then test the sensitivity of these other parameters to determine how to make the fit better. Literally none of the model results presented in Figure 7 before the e-folding depth results come close to overlapping with the observations. Also, you should consider having the model results on a different x-axis so that the depth profile, especially for d15N, can be seen. At this point, the idea of seasonality and the possibility of interannual interpretation is difficult to see.

We agree and thank the reviewer for the valuable comment to improve the manuscript. Please see our response to the e-folding depth comment above. We carried out the TRANISTS runs as suggested by referee #1. An e-folding depth of 5 cm has a much better fit with the observations. With the new TRANSITS runs, our conclusions reinforce the importance of accounting for the e-folding depth measurements across Antarctica. Regarding the x-axis on Fig. 7, the new TRANSITS runs with an e-folding depth of 5 cm move the simulated $\delta^{15}N$-NO_3^- values to more negative values. The better fit with the observations means it is much easier to see the interannual variability in the $\delta^{15}N$-NO_3^-. In addition, the seasonal variability is clearly visible in Fig. 4.

Technical comments:

I do my best to point out a lot of simple errors, but it would behoove the authors to take a closer read on the next version of the manuscript.

Line 10: d15N-NO3- should be (d15N-NO3-)

Done.

Line 20: photochemical processes cannot drive the archiving of nitrate; it drives the loss of nitrate or recycling of nitrate from the snow.

“Photochemical processes” has been replaced with “nitrate recycling”.

Line 34: TOC should be TCO

Done.

Line 38: rephrase this line – it appears as if you are suggesting that NO3- is formed from oxidation of N2

Done.

Line 57: J should be (J)

Done.

Line 64: add a comma after Greenland

Done.

Line 97: this is the first use of PSC, spell it out and explain their purpose here

Done.

Line 169-170: the additional skin layer samples for comparison should be represented in the data figures.

The samples representing spatial variability are already plotted in Fig. S6 and Fig 3. To increase visibility of these samples, we have added an error bar representing the spatial variability to Fig. 3. This is considerably lower than the instrumental variability (error bars are smaller than sample points).

Line 219: a references for the seawater ratio (I assume this means sea salt ratio) should be included.

Keene et al. (1986) reference added for the sea salt ratio.

Line 300: followed should be follows

Done.

Line 303: add the word in after changes

Done.

Line 370: remove and before archived

Done.

Line 398: as a year round does not make sense

Done.

Line 457: inter-decadal should be interannual

Done.

Line 475: Fig 5 should not be cited here

Changed to Fig. 7.

Line 490: remove are

This sentence has been removed following the main comments.

Line 530: up taken should be taken up

This sentence has been removed following the main comments.

Line 536: the idea that "NO3- peaks are substantially modified after burial" undermines so much of the current manuscript that suggests that NO3- is archived once buried. Rephrase.

This sentence has been removed following the main comments.

Line 566: rephrase "form of nitrogen to skin layer"

Done.

Line 612: back to THE skin later with a day, or IS transported away

Done.

Line 624-625: see comment above about better explaining the evaportation results; and Shi et al 2019 reflect field conditions, not laboratory conditions.

Section 4.3.1 Evaporation has been removed following the main comments of referees #1 and #2.

Line 643-653: I have serious issues here with the interpretation of previous literature. First and foremost, the assumption that anthropogenic emissions of NOx are positive in d15N and natural emissions are negative in d15N is false and not up to date. Recent work shows that vehicle emissions are, in fact, negative in d15N (Miller et al., 2017, Vehicle NOx emission plume isotopic signatures: Spatial variability across the eastern United States, J. Geophys. Res. Atmos., 122, doi:10.1002/2016JD025877)/ At least three works show that fertilized soil emissions (which are not considered a natural source in emission inventories) are very negatives in d15N (Yu & Elliott, 2017, Novel method for nitrogen isotopic analysis of soil-emitted nitric oxide. Environmental Science & Technology, 51(11), 6268–6278, https://doi.org/10.1021/acs.est.7b00592; Miller et al., 2018, Isotopic composition of in situ soil NOx emissions in manure fertilized cropland, Geophysical Research Letters, 45(21), 12058-12066, https://doi.org/10.1029/2018GL079619.; Li & Wang, 2008, Nitrogen isotopic signature of soil-released nitric oxide (NO) after fertilizer application. Atmospheric Environment, 42(19), 4747–4754. https://doi.org/10.1016/j.atmosenv.2008.01.042.). Geng et al. make the exact same false interpretation that anthropogenic sources are positive and therefore are ruled out in interpretation of a Summit, Greenland core – do not cite this is evidence when it is simply an unwarranted assumption. Finally, please be more precise in the language here – emission sources emit NO (except diesel engines, which can also emit NO2) or you can call it NOx; they do not "have positive d15N-NO3-" values since they do not emit nitrate, it is secondarily formed and subject to partitioning in the atmosphere, which Geng et al. invoke as a major mechanism to explain Greenland ice results, and this is wholly ignored in the current work.

We thank the reviewer for providing additional references concerning the negative isotopic signature of anthropogenic emissions of NO_x. We have edited this section to include the recent work on vehicle NO_x emissions and fertilised soil emissions and provided the references suggested by the reviewer. We have removed the Geng et al. reference which discards anthropogenic nitrate as a potential source to Greenland snow. When referring to the isotopic signature of emission sources, we have replaced $\delta^{15}N\text{-}NO_3^-$ with $\delta^{15}N\text{-}NO_x$. In light of the negative source signature of NO_x emissions, our interpretation that anthropogenic sources do not contribute to the atmospheric $\delta^{15}N\text{-}NO_3^-$ at DML remains unchanged based on i) the well-established literature in which photolysis is the major driver of atmospheric $\delta^{15}N\text{-}NO_3^-$ values over low accumulation sites in East Antarctica (e.g. Frey et al., 2009;Erbland et al., 2015;Erbland et al., 2013;Shi et al., 2015;Shi et al., 2018), and ii) modelling study by Lee et al. (2014) that shows fertilised soil NO_x emissions to Antarctica are minor. We modified the text as follows (lines 637-642):

Modified text: "The $\delta^{15}N\text{-}NO_x$ source signature of the main natural NO_x sources (biomass burning, lightning, soil emissions; $\delta^{15}N\text{-}NO_x <0$ ‰) is lower than anthropogenic NO_x sources, which generally have positive $\delta^{15}N\text{-}NO_x$ values ($-13< \delta^{15}N\text{-}NO_x < 13$ ‰; e.g. (Hastings et al., 2013;Kendall et al., 2007;Hoering, 1957) except in the case of vehicle and fertilised soil NO_x emissions which have negative $\delta^{15}N\text{-}NO_x$ values ($-60< \delta^{15}N\text{-}NO_3^- <12$ ‰; Miller et al. (2017);Yu and Elliott (2017);Miller et al. (2018);Li and Wang (2008). However, a NO_3^- source contribution from fertilised soil NO_x emissions to Antarctica is thought to be minor (Lee et al., 2014)."

Line 690-695: a range of -19 per mil to +12 per mil does not at all "nicely match" with the expected -59 per mil to -16 per mil.

Replaced "nicely match" with "falls within the range".

Line 698: add an before annual

Done.

Section 4.3.3 – seems odd to switch to section i, ii, iii, etc here when earlier subsections are numbered in series (i.e. 4.3.3.1, 4.3.3.2, etc).

Replaced i, ii, iii with 1, 2, 3.

Line 780: Concluding that photolysis is an important driver is not an interesting result given the vast evidence for this throughout the EAIS. The other conclusions are still interesting but this should not be the primary focus. Furthermore, the fact that there is less photolysis than expected is really very interesting.

This section has been removed following the main comments of referee #1.

Line 850-851: Interestingly, Geng et al. 2015 ignores surface snow work at Summit, Greenland to invoke that post-depositional processing can explain everything (Fibiger et al. (2016), Analysis of nitrate in the snow and atmosphere at Summit, Greenland: Chemistry and transport, J. Geophys. Res. Atmos., 121, 5010– 5030, doi:10.1002/2015JD024187; Fibiger et al. (2013), The preservation of atmospheric nitrate in snow at Summit, Greenland, Geophys. Res. Lett., 40, 3484–3489, doi:10.1002/grl.50659.). Here, you are showing that is critical to use surface work to best determine how to interpret ice cores. I suggest you reconsider including comparison with Geng's work here.

Done.

Line 855: depending ON the timing

Done.

Line 902: due TO photolysis-driven

Done.

Line 905: This should reference Zatko et al. not Geng et al.

Done.

Line 913: I strongly disagree with the statement that "TRANSITS doe such a good job of simulating NO-3 recycling in Antarctica" unless you do the e-folding fit first and then explore sensitivities. (I do agree that it is an excellent recommendation to use TRANSITS to assess sites that would be useful for interpreting nitrate isotopic records!)

Please see our response to the e-folding depth comment above. Based on the improved fit of the new sensitivity tests using the e-folding depth of 5 cm, we have kept this statement in the manuscript.

Line 919: unpicking is a strange word here – distinguishing?

Conclusions were rewritten following the suggestion of referee #1. "Unpicking" is no longer used.

Line 922: resulting IN an enrichment

Done.

Line 929: this conclusion would make more sense if the e-folding depth model experiments were done first.

Done.

Line 945: THE ground

Done.

Figure 3: how is the data averaged here?

The RACMO precipitation data is published as daily values. See the data publication for further information https://data.bas.ac.uk/full-record.php?id=GB/NERC/BAS/PDC/01137. The wind data from the AWS is hourly. We have added this to the caption.

Figure 4: x-axis on right side is misspelled

Done.

Figure 5: what is scenario 1 vs 2, this is never explained

This is now explained in text (lines 429-443; see comment above) and in the caption of Fig. 5.

Table 2: Archived should be >30 cm not <30 cm, correct?

Yes, this has been corrected.

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