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

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

Anonymous Referee #1

Winton et al report observations of the nitrogen isotopic composition of nitrate in Antarctic (DML) in the atmosphere, snow "skin layer", and depth profiles in snow pits. They use these observations combined with a snow chemistry model to understand what controls the variability in the nitrogen isotopes and nitrate concentrations and to assess the utility of such observations in ice cores as a proxy for past surface UV radiation. They conclude that although photolytic driven recycling and loss of reactive nitrogen is what determines the nitrate isotopes and abundances at this location, that variability in parameters such as snow accumulation rate have a large enough impact on the nitrogen isotopes so as to preclude the influence of variability in surface UV in determining the nitrogen isotopic composition of snow nitrate.

We agree that variability in the snow accumulation rate precludes the use of using the δ^{15}N-NO$_3^-$ composition as a surface UV proxy in the short-term. However, longer-term UV trends may be inferred from ice cores at the site taking into account or constraining factors masking the UV-impact such as e-folding depth and accumulation rate.

The observations and model-based interpretation are robust and important as it would be useful to have a paleo-UV proxy. As the authors state, it is important to assess the sensitivity of nitrogen isotopes at particular locations in order to determine its usefulness as a proxy for any given process. Unfortunately, the paper is frustrating to read because it is it so repetitive and spends so much time on introductory material throughout the manuscript that it is hard to find the actual interpretation of the results. It is as if the authors are afraid to state their interpretation. I suggest moving (and condensing) the introductory material that is spread throughout the manuscript (especially in section 4) to the introduction and making sure that the actual interpretation is presented up front instead of hidden. Because of this, it's sometimes hard to determine if the results support their conclusions. The paper as is reads as a first or second draft, not a final manuscript ready for submission for publication. This is particularly evident in the conclusions, which is not even written in paragraph form.

We agree with the reviewer that too much background information is spread throughout the discussion rather than the introduction. We have condensed and moved the most relevant material to the introduction. Overall, we have revised the manuscript to provide better clarity on our interpretation of the results and conclusions.

Additional comments:

I find the concept of the number of times nitrate is recycled difficult to wrap my head around. Does this mean that each molecule of nitrate is recycled on average three times before being archived? Is this averaged over the depth of the photic zone? I would imagine some molecules (like those that are close to the surface in summer) are recycled more than others, so that there is actually some distribution of recycling events on a molecule per molecule basis so as to average around the number 3. Is this interpretation correct? I suggest elaborating on this in the methods section.

The number of recylings is the "average number of recyclings" undergone by the archived nitrate, i.e., below the zone of active photochemistry. Recycling includes the following processes: the combination of NOx production from nitrate photolysis in snow, venting to the air above the snowpack and subsequent atmospheric re-oxidation of NO_x to form atmospheric nitrate, the deposition (dry and/or wet) of a fraction of the product, and the export of another fraction (Erbland et al., 2015). In TRANSITS, there is a tracer/counter called CYCL, which, in a given box (snow layer or atmosphere), represents the average number of recyclings undergone by nitrate in that box. The CYCL value for primary nitrate is set to 0, and CYCL variables in the boxes are incremented by 1 each time NO_2 molecules cross the air-snow interface. The average number of recyclings is calculated as a mass weighted average of the CYCL values of the 52 snow layers (representing one week of snowfall) which are archived below 1 m over the course of 1 year, in order to average out any seasonal variability.

The average number of recyclings undergone by the archived nitrate at our study site in Dronning Maud Land (DML) is 2 for the last layer before leaving the photic zone, which means that, on average, the archived nitrate at DML has undergone 2 recyclings (i.e., loss, local re-oxidation, deposition). Erbland et al. (2015) notes that this number of recyclings represents an average value for the archived nitrate. Considering individual ions in the archived nitrate, the number of recyclings could be variable as some ions may have travelled through the entire snowpack zone of active photochemistry without being recycled, while some underwent many recyclings.

We have expanded the explanation of the number of recycling's in the methodology (lines 337-345) as follows:

Modified text: "TRANSITS calculates the average number of recyclings undergone by the archived NO_3^-, i.e., below the zone of active photochemistry. In TRANSITS, the average number of recyclings undergone by NO_3^- in a given box (snow layer or atmosphere) is represented by a tracer (or counter) called CYCL. The CYCL value for primary NO_3^- is set to 0, and CYCL variables in the boxes are incremented by 1 each time NO_2 molecules cross the air-snow interface. The average number of recyclings is calculated as a mass weighted average of the CYCL values of the 52 snow layers (representing one week of snowfall) which are archived below 1 m over the course of 1 year, in order to average out any seasonal variability. Erbland et al. (2015) notes that the number of recyclings represents an average value for the archived NO_3^-, i.e., considering individual ions in the archived NO_3^-, the number of recyclings could be variable as some ions may have travelled through the entire snowpack zone of active photochemistry without being recycled, while some underwent many recyclings."

Second paragraph of the introduction: It seems strange to say that the primary sources of nitrate are transport of nitrate from the stratosphere and transport of alkyl nitrates in the troposphere without mentioning transport of inorganic nitrate in the troposphere. Where is the evidence that inorganic nitrate is not transported in the troposphere to Antarctica? A model study suggests that it is certainly possible (Lee et al., 2014). Also, soil NOx should be mentioned as a NOx source in the troposphere.

We have added the transport of inorganic nitrate (fossil fuel combustion, soil, and lightning) and referenced Lee et al. (2014) in lines 53-56 as follows:

Modified text: "Primary sources of reactive nitrogen species to the Antarctic lower atmosphere and snow pack include the sedimentation of polar stratospheric clouds (PSC) in late winter (Savarino et al., 2007) and, to a minor extent, advection of oceanic methyl nitrate (CH_3NO_3) and peroxyacyl nitrates (PAN) (Jacobi et al., 2000;Jones et al., 1999;Beyersdorf et al., 2010), in addition to tropospheric transport of inorganic NO_3^- from lightning, biomass burning and soil emissions (Lee et al., 2014)."

Page 2 lines 61 – 62: Reprase to: "Model results from Zatko et al. (2016) suggest that…"

Done

Page 4 line 116: Are you referring to skin layer nitrate here? Since you are measuring nitrate in three different locations, you should always be specific about which location you are talking about and not just say "nitrate".

No, we are referring to ice core nitrate as mentioned in the sentence. We have added "ice core nitrate" for clarity.

Page 4 line 128: Perhaps you should say that you are referring to the e-folding depth of the snow photic zone, UV radiation, or something less vague.

Done

Page 5 line 157: If you remove the word "While" from the beginning of this sentence it will be grammatically correct.

Done

Page 8 line 259: By "lower" do you mean "shallower"? Lower could also mean deeper, so it would be better to use words like deeper and shallower when referring to the depth in the snow beneath the surface.

"Lower" has been replaced with "shallower".

Section 2.7: It seems quite important to state what value you assume for the N-isotopic composition of primary nitrate, before it is impacted by photolysis.

The $\delta^{15}N$-NO_3^- value of primary nitrate is set to 19 ‰ as estimated by Savarino et al. (2007). This value is reported in Table S3.

Page 12 line 371: "values" of what? Concentration? Isotopes? Both? Since you measured more than one thing you need to be specific.

We have added $\delta^{15}N$-NO_3^- values to this sentence.

Page 13 Section 3.5: You should probably note that gas phase HNO3 and particulate nitrate have different dry deposition rates.

Agreed, we have noted this in lines 418-419 as follows:

Modified text: "Although gas phase HNO_3 and particulate NO_3^- have different dry deposition rates…"

Section 3.6: I think you should elaborate on the difference between the actual (from photolysis) and apparent fraction factor. The latter is lower than the actual due to recycling. Also, related

to this, can the difference between the actual and apparent fractionation factor be used to calculate fractional loss?

We have discussed the difference in lines 88-91. We found that the single loss Raleigh model does not work well at sites with an annual signal in δ^{15}N-NO$_3^-$, and therefore suggest that at DML it is not useful for calculating fractional loss. The text was modified as follows:

Modified text: "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."

Page 15 line 455: Is this at DML?

Yes, the Weller et al. (2004) study is at DML. We have added "at DML" for clarity.

Page 15 line 459: Which results? Concentration? Isotopes? Both?

Both. We have added "NO$_3^-$ mass concentrations and δ^{15}N-NO$_3^-$" to the sentence.

Page 15 lines 472 – 473: Does the model simulate the influence of hoar frost and diamond dust on nitrate deposition? The way this sentence is written it seems that it does, but this is surprising to me as I didn't think the model was a meteorological/snow model that calculated such things. It seems that you are saying that diamond dust and hoar frost explain the difference between the model and the observations, and that the model has these things but they didn't happen in reality.

No, the model does not simulate the influence of hoar frost and diamond dust on nitrate deposition. We suggest that the difference between the simulated and observed nitrate concentrations in the skin layer is due to a sampling artefact where we are diluting the high nitrate concentrations of diamond dust and hoar frost observed in new deposition. We have modified the sentence in lines 564-566 as follows:

Modified text: "Here, extremely high concentrations of NO$_3^-$ from new deposition from diamond dust and hoar frost are also found. In summary, it is likely that we do not measure such high NO$_3^-$ mass concentrations in hoar frost and diamond dust in the skin layer because of sampling artefacts or blowing snow, which can dilute or remove the diamond dust and hoar frost."

Section 4.2: This is a perfect example of the section 4 having lots of introductory material without any results. The entire first paragraph reads like an introduction except for the very last sentence. However, the very last sentence of the first paragraph is not specifically supported by your observations. By the time I finished the 5 pages of section 4.2, I have no idea what you learned or what you are concluding from your new observations.

Section 4.2 has been condensed to 2 pages and the interpretation of results clarified.

Section 4.1: Again, I have no idea what you are concluding in this section.

We conclude that overall our nitrate conclusion measurements agree well with the literature and that the simulated results from TRANISTS match our observations with the exception of

the skin layer concentrations. We provide possible reasons for this difference, and have modified Section 4.1 for clarity.

Page 17 line 540: "is no exception" to what?

We have deleted "is no exception".

Page 18 lines 547 – 551: It seems that if you are collecting both gas and particulate phase nitrate that you cannot conclude that sea salt promotes conversion of HNO3 to nitrate. I'm sure that it does, however, I don't see how your observations provide evidence of this.

We agree and have removed this section.

Page 18 lines 558-559: I suggest rephrasing this as "…Dome C where the underlying snowpack is the dominant… skin layer via photolytic recycling and redeposition.

Done

First paragraph of section 4.3: Need a reference for this statement.

Section of text has been removed.

Page 20 line 617: It could also be transported away as nitrate, not just NO2.

We have added nitrate to the sentence.

Page 21 line 648: "The contribution to what? of natural sources"

The "contribution of nitrate from natural sources" has been added to the sentence.

Page 21 lines 659-660: If you say that denitrification causes O-isotopes to increase, then you need cite a paper that provides evidence of this. However, I would delete this sentence since this paper does not address O-isotopes.

Agreed, we have delete the sentence.

Page 22 line 690: How was the apparent fractionation factor calculate? There should be an equation for this in the methods section.

Please see equation 7 in the methods in section 3.6.

Page 22 line 706: are these FNO2 values a daily mean, a daily maximum?

The model estimates are mean values for the 1-14 January 2017 period as stated in line 465.

Page 24 lines 742 – 746: What is the difference between the grain size and impurity concentrations at these two locations? The N-isotopes may be sensitive to something, but if that something shows no significant difference between these two locations than it won't be able to explain the differences in Nisotopes.

As far as we are aware, at Dome C and DML, there are only published values of major ions in the snow pack in the top 30 cm which is the depth relevant for influencing the e-folding depth. For example, in the top 30 cm of the snow pack nitrate concentrations at Dome C are ~75 ppb (Frey et al., 2009) while they are ~55 ppb at DML (this study). Insoluble dust concentrations are higher at DML than Dome C in the Holocene (Delmonte et al., 2019), while no black carbon data is available at DML for comparison. There is considerate variability in the snow grain size

across Antarctica (Brucker et al., 2010). In particular, wind crust layers which occur in the snowpack have larger grain sizes and these have been observed at Dome C (France et al., 2011).

Based on the available data, we don't have a clear understanding of why the e-folding depth is lower at DML. Station pollution is less than at Dome C (Helmig et al., 2020), thus it is unlikely related to black carbon. However, other impurities are deposited in DML snow due to the closer proximity to marine sources. Snow grain sizes may be smaller, which will increase scattering, at DML than Dome C (Brucker et al., 2010). The larger e-folding depth at Dome C is in part due the presence of windcrust layers which comprise larger grain sizes. Sensitivity studies show that nitrate impurities have only a small contribution on the e-folding depth compared to scattering by snow grains which dominate (Chan et al., 2015;France et al., 2011;Zatko et al., 2013). Further work is required to determine why the e-folding depth is lower at DML. We have discussed this in lines 692-700 as follows:

Modified text: "The e-folding depth depends on the density and grain size of snow crystals, and the concentration of impurities. In terms of published values, impurity concentrations are generally higher at DML, for example dust and major ion concentrations (Delmonte et al., 2019;Legrand and Delmas, 1988), due to proximity to marine sources. Yet station pollution is greater at Dome C (Helmig et al., 2020), and thus the lower e-folding depth is unrelated to black carbon concentrations. Furthermore, there is considerate variability in snow grain size across Antarctica. The larger e-folding depth in windcrust layers at Dome C is due to larger grain sizes in those layers (France et al., 2011). Snow grain size may be smaller at DML, which will increase scattering (Brucker et al., 2010), but further work is required to confirm if this is the dominate factor influencing the lower e-folding depth at DML. Sensitivity studies show that NO_3^- impurities make a small contribution to the e-folding depth compared to scattering by snow grains which dominate (France et al., 2011;Chan et al., 2015;Zatko et al., 2013)."

Page 25 lines 786-787: The e-folding depth is 20 years yet the nitrate is archived after 5-6 years. This seems conflicting. Why is nitrate archived when it is still in the photic zone?

Weller et al. (2004) determine archived nitrate as the typical mean concentrations representative for the last 100 years. We have deleted the e-folding time of 20 years from sentence.

Page 25 lines 792 and 796: Are you referring to observed or modeled values here?

Observed values. We have added "observed" sentence.

Page 25 line 807: Snow optical properties are part of what determines the depth of the photic zone, so it seems weird to mention these two things separately here as if they aren't related.

We have deleted snow optical properties.

Page 26 Line 821: "lower" than what?

Lower than the base case profile. We have added "base case" to the sentence.

Page 28, last sentence of section 4.5.3: Explicitly state here why the sensitivity is greater at Dome C than at DML.

Done

Page 28 line 899: What would cause a change in the e-folding depth?

The e-folding depth could change due to a change in dust or black carbon concentrations (which are light absorbing impurities) or a change in the snow morphology in a particular snow layer. This has been added to lines 843-844 as follows:

Modified text: "The e-folding depth could change over time due to higher or lower dust or black carbon concentrations or a change in the snow grain size in a particular snow layer."

Page 29 line 919: What does "unpicking" mean in this context? Perhaps choose a better word.

Unpicking been replaced with disentangling.

Page 29 line 931: This is percent. Should it be permil?

Yes, percent symbols have been changed to permil symbols.

Figure 1 caption: State the difference between HiVol 2 and 3.

Done.

Figure 2: The boxes in this figure are totally unclear to me. What are the gray boxes trying to convey?

The box a) is in insert of the Kohnen Station and boxes b) and c) our inserts of our two sampling sites at the station. We have edited the caption to make this clearer.

Figure 4: Mark the seasons (e.g., shade winter) in c) and f). It's hard to see the seasonal cycles.

We have shaded the seasons in panel c) and updated the caption. The snow pit in Frey et al. (2009) was not dated and thus we cannot shade the seasons for Dome C.

Figure 4: Why does the x-axis scales to all the way to 1500 and 300 when the observations are much lower than this? The axes should be scaled by the range of the data.

We deliberately chose to keep the x-axis the same for each plot rather than scaling by the range of the data. This is so the reader can see the difference in concentration and isotopic values between the atmosphere, skin layer and snowpack profiles and between the two sites. In particular, we wanted to highlight the denitrification of the snowpack from enriched values in the snow pits to depleted values in the atmosphere.

Figure 5: Why is "recycling factor" listed as a process occurring below the snow photic zone? How is "tropospheric input" different from "net lateral advection"?

We have moved recycling to encompass the atmosphere and snow boxes. We have renamed net lateral advection to tropospheric input.

Figure 7: Why are these values for accumulation rates chosen as sensitivity studies in the model? What is the base case that you are changing each parameter around?

The justification for the range of accumulation rates used in the sensitivity study can be found in section 4.5.1.

The base case is explained in section 4.5 and in the caption, we refer the reader to that section.

Figure 8: This is showing the change in TCO around what value?

We used present day TCO values that were used in all our calculations. These values vary weekly and can be found the supplement (Table S3). For each week, a constant amount of ozone (e.g. 100 DU) was added or subtracted from these values. We have added this information to the caption and text in lines 816-817 as follows:

Modified text: "For each week, a constant amount of ozone (e.g. 100 DU) was added or subtracted from these present day values."

References

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