

The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen across Antarctica in a global chemical transport model

Zatko et al. [2015]

Responses to Reviewer 1:

Thank you for all of these thoughtful and helpful comments and suggestions. These suggestions, along with suggestions from Reviewer 2, have led us to now refer to the modeled snowpack as “idealized”, largely because we agree that this study is based on several assumptions about the spatial variability of snow physical and optical properties. As mentioned in our responses to Reviewer 2, the goal of this research is to investigate the potential spatial variability in the flux of snow-sourced NO_x associated with snow nitrate photolysis along with the recycling, loss, and spatial redistribution of nitrogen across Antarctica, an environment in which observations of these parameters over large spatial scales are difficult to obtain. This modeling study is used to perform sensitivity studies aimed to guide future lab and field campaigns. We have clearly stated this goal in the abstract and also in the last paragraph of the introduction.

The phrase ‘comparable to observations’ is used frequently to compare a large range of result from the model to the very limited observations available across the Antarctic continent, and overall a strong case is not made that the model is comparable.

We have removed all references of model-measurement agreement in the manuscript although observations are still overplotted where available.

Sensitivity of the model’s parameters are tested for the calculation of the average flux of NO_x from the snow, and the model is most sensitive to the quantum yield and fraction assumed for nitrate that is “photolabile”. However, the sensitivity of the calculations is not tested for wet and dry deposition parameterizations, accumulation rate, and boundary layer height, which should all be expected to be very important.

Thank you for these suggestions. In a sense, accumulation rate is varied when concentrations of black carbon (C_{BC}) are changed because snow accumulation rate influences the flux of snow-sourced NO_x (F_{NO_x}) through its impacts on C_{BC} and thus the depth of the snow photic zone. Snow nitrate concentrations are also somewhat influenced by accumulation rate, so changes in snow nitrate concentrations also reflect changes in snow accumulation rate. Although we have not directly changed the rates of wet and dry deposition, we have performed sensitivity studies where only dry deposited nitrate (instead of total nitrate) is photolabile (see section 3.2). Unfortunately, we have not performed sensitivity studies where boundary layer heights are varied because arbitrary variation in the model boundary layer height would lead to inconsistent model physics and thus may give an inaccurate estimate

of the impact of boundary layer height on the transport and redistribution of snow-sourced NO_x .

In some ways this simulation highlights to me a great deal that we lack in terms of understanding of photochemistry in and above snow-covered surfaces.

We hope that the results of our sensitivity studies will give readers a sense of which parameters influence snow-sourced NO_x the most. Many of these parameters are uncertain, such as the concentration of photolabile nitrate, which is one of the most influential parameters for F_{NO_x} . Since these parameters are very important for snow-sourced NO_x , we hope that this study echoes other studies that have called for further field and laboratory studies aimed to better quantify the fraction of total nitrate that is photolabile.

This paper could be significantly improved upon if more detailed comparisons were made at sites such as South Pole and Dome C, where a great deal of data exists (for the environment) in terms of surface snow concentration, gas phase concentrations, and boundary layer conditions. Then the model would be much more believable for scaling up to the entire continent.

Thank you for this suggestion. In an earlier version of this manuscript, we compared boundary layer nitrate and ozone mixing ratios to modeled mixing ratios of these species. Modeled mixing ratios of nitrate and ozone are to a large degree dependent upon the height of the model boundary layer. Unfortunately, it is difficult to determine how well modeled boundary layer heights compare to observations because observations often span a large range at many stations (see Table 1 below for more detail). Additionally, other photochemical reactions in the snowpack that influence oxidant concentrations in the polar boundary layer (e.g., photolysis of H_2O_2 , production of reactive halogens) that are not included in the model at present will impact NO_3^- , HNO_3 , and O_3 through oxidant cycling reactions. Although we have not compared modeled boundary layer mixing ratios to observations in the manuscript, we have calculated factor increases in NO_x , NO_3^- , O_3 , OH for a model run with snow photochemistry compared to a model run without snow photochemistry in order to demonstrate how this one snow photochemical reaction alone (photolysis of snow nitrate) impacts, in a relative sense, the mixing ratios of NO_3^- , HNO_3 , OH , and O_3 .

Additionally, more careful comparisons with specific sites where isotopic data is available in the snow and in the atmosphere would also help to more fully evaluate the model and whether it is worth considering the quantified results in the paper.

We unfortunately do not simulate atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ in the model and also cannot simulate vertical profiles of $\delta^{15}\text{N}(\text{NO}_3^-)$ in the snow since the model does not contain an explicit snow-column model. We are unsure of other ways to more carefully compare observed isotopic data to available model output from this study besides comparing modeled and observed $\delta^{15}\text{N}(\text{NO}_3^-)$ below the photic zone. Fortunately, these observations cover a large range of snow accumulation rates,

which is the predominate factor governing its variability across the Antarctic continent.

Specific comments:

P18972, L14-15: This is a very big assumption. Laboratory, field, and box modeling studies all suggest that a very small portion of nitrate can explain the fluxes of NO_x out of the snow at South Pole and Summit (Greenland). Further, several studies suggest that a significant portion of the photolyzed nitrate products remain in the aqueous phase. Indeed, using isotopes of nitrate in laboratory and field studies, there are multiple suggestions of in situ reactions requiring water (or something isotopically similar) in the reformation of nitrate following photolysis (McCabe et al., Frey et al., Erbland et al., Shi et al., - all already cited in this paper) and this is likely happening in the snow (as opposed to in the boundary layer). How is it that these studies, or what they suggest, should be ignored in this context?

The fraction of snow nitrate that is photolyzed in the model is limited by the use of a low quantum yield ($\phi=0.002$ [Chu and Anastasio, 2003]) and by the assumption that only dry-deposited nitrate is available for photolysis. These limit the fraction of total nitrate in the snow that is photolyzed in this study. Using this approach, there is order-of-magnitude agreement between modeled and measured snow-sourced NO_x. In contrast, using the quantum yield presented in Zhu et al. [2010] results in an overestimate of modeled F_{NO_x} by 3 orders of magnitude. The recombination of the NO_x photoproducts in the condensed phase has been observed in the references cited above, and will influence lab- and field-based estimates of the quantum yield.

The recombination effects within ice grains suggested in Erbland et al. [2013] will lower the flux of snow-sourced NO_x and influence oxygen isotopes, although nitrogen isotopes are not influenced by this 'cage effect'. There are uncertainties in the amount of NO_x that is trapped within the ice grain. Erbland et al. [2015] suggest that 15% of NO_x experiences cage effects, but this fraction is an estimate and there are large uncertainties associated with the amount of NO_x that experiences recombination chemistry.

Nitrate that has been wet deposited to the snow likely has a higher probability of being trapped in the ice grain (and thus experience 'cage effects' or 'recombination chemistry') compared to dry deposited nitrate, although there may be some diffusion of nitrate in the snow grain after deposition. We have assumed that all wet deposited nitrate is unavailable for photolysis. We now specifically discuss recombination chemistry in the manuscript in section 2.1.3 in light of the potential influence that this process has on modeled snow-sourced NO_x fluxes.

P18974, L26 – P18975, L9: The phrase “likely from the redistribution of nitrate resulting from photolysis and subsequent recycling” is a major conclusion from this work and it is therefore inappropriate to state this here

unless it is referenced in some way to other work that provides evidence for this.

There is evidence that nitrate concentrations vary considerably across the Antarctic ice sheet (for example for ITASE plus individual smaller scale studies) There is evidence that nitrate is much more concentrated in the top 2 cm of snow than below. But to what depth? The remainder of the “photic-zone depth” is very loose terminology here, since later the model will be used to calculate e-folding depths. If the concentrations in the surface snow are an artifact of nitrate redistribution than it seems that the model would be better compared with atmospheric concentrations (aerosols, fresh snow) than snow concentrations alone. Further, this would make the scaling below (P18975, L20-25) based upon dry versus wet deposition much more acceptable if the simulated results were similar to observations in the atmosphere.

We have removed the phrase ‘likely from the redistribution of nitrate resulting from photolysis and subsequent recycling’ from this paragraph.

Nitrate concentration profiles generally show an enhancement in the top several centimeters of snow and then a sharp decrease to a stable equilibrium value throughout the remainder of the snow column, which in the vast majority of cases is at least as deep as 1 e-folding depth of UV actinic flux. In this manuscript, the full photic zone (3 e-folding depths of UV actinic flux) is used to calculate fluxes of NO_x from the snow. Since nitrate concentrations in the top 2 cm are enhanced by a factor of 6 compared to nitrate concentrations below, nitrate concentrations are decreased by an equal amount from the full photic zone (3 e-folding depths of UV actinic flux) for mass balance. Later in the manuscript, specifically when τ_z is calculated, an ‘effective’ photic zone depth is used (1 e-folding depth of UV actinic flux) because 87-91% of snow-sourced NO_x is produced within the top 1 e-folding depth.

For reasons stated above, it is difficult to interpret the model-measurement agreement for boundary layer mixing ratios. Through various sensitivity studies, we have explored the implications for snow-sourced NO_x on our assumptions about both snow nitrate concentration and the assumption that only dry deposited nitrate is photolabile (see section 3.2.).

P18976, L1-9: It does indeed seem unnecessary for a global model to include a liquid like region and distribute nitrate based upon this since there is still a fair amount of uncertainty regarding this within the laboratory based literature. It is clear from the Thomas et al. study (and studies by Boxe et al. such as ACP, 2008 and J. Phys. Chem. A., 2005) that the flux of NO_x from the snow in different places can be accounted for by only photolyzing a very small percentage of the nitrate in the snow, because it is concentrated in the LLR. This is an important distinction from blowing away/recycling all of the nitrate in the photic zone. This is a critical point that needs to be better evaluated in the context of whether it is worthwhile to even consider the simulated results as having any bearing in the real world if it cannot reconcile this. In other

words, parameterizing the loss of nitrate from snow may be necessary at this scale, but this does not mean that work suggesting a great deal of nitrate is reformed within the snow (see comments above also) or that the loss of nitrate is minor compared to the bulk nitrate concentration in snow when including a LLR can be ignored.

Thank you for this comment, as well as the related comment above. As also mentioned above, we have used the quantum yield from Chu and Anastasio [2003] and additionally have only assumed that dry-deposited nitrate is available for photolysis. In these ways, only a fraction of the total nitrate in the snow is photolyzed in this study over the course of a year and there is at least order-of-magnitude agreement between modeled and measured snow-sourced NO_x when taking this approach. The modeling studies mentioned above represent calculations for a single location, and thus are able to “tune” their model to produce the desired results for that single location (e.g., Thomas et al. [2011] need to assume that only 6% of snow nitrate is photolabile to match observations at Summit). Since we do not have observations at every grid box in the model, we need to make more process-based assumptions about the fraction of snow nitrate that is photolabile. There are essentially no laboratory or field based observations of the fraction of nitrate that is photolabile that allow us to examine the validity of our assumptions about this parameter. Hence, we perform sensitivity simulations that effectively change this fraction (changing the quantum yield, removing the dry-deposition limitation) to evaluate the importance of these assumptions.

As mentioned above, Thomas et al. [2011] find that only 6% of the nitrate in snow must be photolyzed to match modeled and observed NO mixing ratios in the boundary layer. In this study, there are places where a similar fraction of nitrate in snow is photolabile (e.g., 10-15% around the coasts, Figure 3c), and the fluxes of NO_x calculated in these region are on the order of $10^8 \text{ molec cm}^{-2} \text{ s}^{-1}$, which is the same order of magnitude as most snow-sourced NO_x flux observations.

We have added discussion about recombination chemistry and nitrate concentrations in the LLR into the manuscript in sections 2.3.1. In regions where wet deposition is dominant, we feel that we are attempting to take recombination chemistry into account (albeit crudely).

P18977, section 2.3.1. There is a great deal of uncertainty associated with the assumptions made in this section. Several aspects of the assumptions are tested via sensitivity studies. But it is critical to better understand how sensitive the calculations are to the amount of deposition taking place in the model (wet versus dry, total deposition overall). Further it is also very important to test sensitivity to accumulation rate as this should be very important for how long nitrate remains in the photic zone. Studies that directly work to quantify accumulation rate are limited and often fraught with the difficulty of dealing with blowing snow, drafting, density changes etc. So a simple comparison with a few values that “seem” to fit the model is weak at best, and it should be understood how important this parameter is to

determining simulated values. Finally, changes in boundary layer height should be tested for sensitivity. In section 3.4., the authors are dismissive about comparing the model to observed boundary layer heights, as they vary over a large range and don't agree well. How important is this? A priori I would expect this to play a very important role in determining how much of this NO_x is transported away versus recycled and "re"deposited locally, which applies to all of the results computed in this work.

Thank you for these suggestions. It is true that we have not performed sensitivity studies varying wet and dry deposition, boundary layer height, or snow accumulation rate specifically. At least two of these parameters (snow accumulation rate and the fraction of wet versus dry deposition of nitrate) have considerable spatial variability in the model, allowing us to examine their influence without the need for arbitrary changes. The biggest influence that the snow accumulation rate will have on F_{NO_x} is via its impacts on snow black carbon and nitrate concentrations, and we have performed sensitivity studies varying both of these parameters. Although we have not directly changed the relative rates of wet and dry deposition, we have performed sensitivity studies where only dry deposited nitrate influences snow-sourced NO_x. We have not performed sensitivity studies where boundary layer heights are varied because changes in boundary layer height would lead to inconsistencies with model physics (e.g., temperatures, winds). It would be difficult to associate changes in our results solely with changes in the boundary layer height, and interpretation of arbitrary changes in boundary layer height may be misleading due to associated inconsistencies in model physics as described above.

Below is a table that shows observed boundary layer heights compared to monthly-averaged model boundary layer heights for several stations in Antarctica. Unfortunately it is difficult to tell how well the boundary layer is represented in the model because there is such a large range of observed boundary layers at many locations. The observations are generally averaged value over the course of the measurement period. Several observations span the full range of diurnal values, and these observations have been noted in the table below.

Table 1. Observed and modeled boundary layer heights in Antarctica

Location	Observed BL (m)	Modeled BL (m)	References
Neumayer	10-300 (summer)	460 (Dec) 285 (Jan) 300 (Feb)	Handorf [1996] Konig-Langlo et al. [1998] Davis et al. [2004] Weller et al. [1999]
South Pole	50-600 (Dec-Jan) 200-375 (Mar-Nov) 100-300 (Mar-Aug) 25-300 (Nov-Dec)	50 (Dec,Jan,Feb) 40-45 (Mar-Nov)	Oncley et al. [2004] Travouillon et al. [2008] Neff et al. [2008]
Dome C	0-300 m (summer, with diurnal variation) 10-300 m (summer, with diurnal variation) 25-40 m (winter)	65 (Jan) 50 (Feb) 40 (Mar-Oct) 50 (Nov) 104 (Dec)	King et al. [2006] Lawrence et al. [2004] Trinquet et al. [2008] Casanta et al. [2014]
Halley	200-300 (summer) 40-110 (summer) 200-400 (winter) 50-150 (winter)	190 (Jan) 270 (Feb) 200 (Mar) 160 (Apr) 125 (May) 80 (Jun) 170 (Jul) 120 (Aug)	King et al. [2006] Jones et al. [2008] Jones et al. [2006] Anderson [2003]
Kohnen	200-500 (Nov-Dec, diurnal variation)	80 (Nov) 130 (Dec)	Kodama et al. [1989]

P18979, L22-23: How, on the timescale of ice cores (e.g., glacial/interglacial cycles) would it ever be assumed that factors that influence snow photochemistry would remain the same? The fraction lost from year to year seems like it would be highly variable, not “stable from year to year”. In fact, snowpit profiles from Antarctica (studies cited here such as Rothlisberger, Frey, Dibb, Shi) show quite a significant amount of variability in concentration with depth.

Over the timescales of ice cores, we would definitely expect there to be changes in many parameters that would influence snow photochemistry, such as changes in snow accumulation rates with climate or changes in the concentration of light-absorbing impurities. However, over the number of years that nitrate remains in the photic zone (up to 7.5 years in Antarctica in the present day), these parameters remain relatively constant. f can be calculated for present-day snow and for glacial-period snow separately, using an appropriate number of years that nitrate remains in the photic zone for each period. In this study, we are focusing on the present climate.

P18982, L15-20: It needs to be made clear here and in several other places what below 2 cm means. To what depth is the model calculating over? To what depth is being compared to with the observations? Below surface could be to 3km!, please quantify this here and in table 2 and in the figure captions.

Why is it that a constant concentration is assumed? Above, there is direct discussion of the evidence for variability in nitrate concentrations at the surface. Justification should be made as to why it is important to use a constant concentration.

Please report concentration (or actually, it's mass fraction when reported as ng/g) in consistent units

Why are only ITASE measurements compared here? The isotope results are seemingly compared with more data, but those studies must all have concentration data available also. Given the much more limited data on the East Antarctica Ice Sheet, it seems worthwhile to compare with Frey, Erbland, and Shi transect concentration data as well.

Thank you for suggesting that we make the depth terminology “below 2 cm” more clear throughout the manuscript. Throughout the manuscript (sections 2.1.3., Table 1, Figure 3 caption, Figure 4 caption) we have clarified “below 2 cm” to mean “from 2-cm depth to the bottom of the photic zone (z_{3e})”. In Table 2 and Table 3 we now use the variable “[NO_3^-]_{bot}”, which has been clearly defined in Table 1.

We have assumed spatially constant concentrations of nitrate across Antarctica ([NO_3^-]_{bot} = 60 ng g⁻¹, [NO_3^-]_{bot} = 360 ng g⁻¹). Although there is a wide range of multi-year, sub-surface snow nitrate concentrations measured across Antarctica during the ITASE campaign [Bertler *et al.*, 2005], there is not a clear spatial pattern associated with these observations. Although we use constant snow nitrate concentrations across Antarctica, a number of sensitivity studies are performed to investigate the impact of snow nitrate concentration on snow-sourced NO_x. In sensitivity studies, snow nitrate concentrations are halved and doubled, the nitrate enhancement factor is varied from 1 to 10, and it is assumed that all nitrate is photolabile (see section 3.2.). We have now slightly rearranged the beginning of section 2.1.3. and added two sentences to explain why we use constant nitrate concentrations across Antarctica.

Erbland *et al.* [2015] and Shi *et al.* [2014] provided snow nitrate concentration data in tabular form and we have now included this data in Figure 3d and have updated the text and figure caption accordingly.

P18986: At the top and bottom of this page there are important disagreements with Davis *et al.* (2000) and Erbland *et al.* (2015), and both seem to be dismissed as “varying approaches”. Why are the calculated values so different? Given the understanding the authors believe they are developing from the sensitivity studies, what most likely explain the difference in results?

Thank you for addressing this issue. While this manuscript was in the review process, we have had some discussions with Joël Savarino and Joseph Erbland about how to best calculate NRF_{τ_z} in light of the reviews of their paper, which at the time was in the review stages in ACPD. We have now removed NRF_{τ_z} from the manuscript and compared our calculated NRF_{yr} (now just NRF) with the NRF values calculated in Erbland et al. [2015] and Davis et al. [2008]. The reason that NRF_{τ_z} was not valid is because although loss of nitrate occurs throughout the snow photic zone, the recycling happens mainly at the surface via re-deposition of snow-sourced NO_x . Our modeled NRF_{yr} (not just NRF) values are similar in magnitude to the NRF values reported in Erbland et al. [2015] and Davis et al. [2000]. We have outlined changes made to the nitrogen recycling part of this manuscript in the “Letter to the Editor” and have copied this information below. The last paragraph in section 3.3. has also been updated to reflect this change and compares the NRF values from these different studies.

Excerpt from “Letter to the Editor”:

Removal of NRF_{τ_z} from manuscript

Joël Savarino and Joseph Erbland (LGGE, France) have recently used a snow chemistry column model to investigate nitrogen recycling between the air and snow at Dome C, Antarctica (manuscript was in review in ACPD at the time of writing). Conversations with them, initiated by a reviewer of their manuscript, convinced all of us that NRF_{yr} (not NRF_{τ_z}) represents the total number of nitrogen recyclings between the air and snow archived in ice cores. We have decided to remove NRF_{τ_z} from our manuscript and have changed NRF_{yr} to simply NRF . In sum, it is not necessary to multiply NRF by τ_z to calculate the degree of recycling archived in ice-core records because the majority of recycling happens in the first year after deposition to the ice sheet. Most of the recycling occurs between the air and the snow surface layer (\sim top 2 cm) because snow-sourced HNO_3 is re-deposited only to the surface layer. In contrast, loss of nitrate occurs throughout the snow photic zone. Model-estimates of nitrogen recycling at Dome C in Erbland et al. [2015] (4 recycling events) and in this study (9 recycling events) are now more similar in magnitude. The difference (4 versus 9) may be due to the assumption in Erbland et al. that 20% of snow-sourced nitrate is transported away via katabatic winds ($f_{exp} = 0.2$). We are able to calculate f_{exp} in our modeling framework, and we calculate that 25% of snow-sourced nitrate is transported away at Dome C ($f_{exp} = 0.25$), which is slightly larger than the assumption in Erbland et al. Larger values of f_{exp} will lead to larger loss of snow nitrate, which may also lead to a larger number of recycling events via transport and redeposition of snow-sourced NO_x throughout East Antarctica. Additionally, the NRF values calculated for East Antarctica ($NRF=6-10$) are within the uncertainty of NRF values estimated by Davis et al. [2008]. These comparisons are further described in section 3.3.

Since NRF_{τ_z} is now removed from the manuscript, we have moved the discussion of τ_z to later in the manuscript because τ_z is needed to calculate f . Additionally, in

section 3.6., f is now compared to NRf across Antarctica instead of NRf_{τ_z} , which leads to a different relationship between spatial patterns of nitrogen recycling and photolysis-driven loss of snow nitrate. This relationship is discussed in the text, but the change does not significantly alter our conclusions.

Figure 7 now shows only NRf and Figure 9 now shows τ_z in addition to f and $\delta^{15}\text{N}(\text{NO}_3^-)$. We have moved τ_z into Figure 9 because τ_z is still used to calculate f and is no longer used to estimate the degree of nitrogen recycling (NRf_{τ_z}). Figure 10 now shows NRf vs. f instead of NRf_{τ_z} vs. f . Instead of separating the data into East and West Antarctica, we have separated the data by the number of years that nitrate remains in the snow photic zone.

P18988, L11 and L19-20: What does sub-photic zone mean? What depth range is this? Why not compare with surface observations (i.e. some mean of the top few cm (or a mean of the model calculated photic zone for each observation point. The comparison here seems not justified or worse, artificially constructed. Furthermore, on line 20 it is suggested that the ice core measurements are representative of observations “well below the snow photic zone”. But, upon deposition, the snow nitrate was exposed to light (before it was archived in the “sub-photic zone”). Better terminology is needed here to help the reader understand what is being referred to and why this is an important comparison to make. Unless it is an instant in time below the photic zone, the nitrate is not necessarily lacking in influence of exposure to photolytic processing. In fact, here and below, it seems important to consider comparing with atmospheric observations – i.e. the primary signal that is then processed in the surface snow – rather than that that has already been photolytically altered.

Sub-photic zone is the depth in snow below the bottom of the photic zone, which is any depth interval below 3 e-folding depths of UV actinic flux in this study. Below this depth, ~95% of the radiation has been attenuated.

The $\delta^{15}\text{N}(\text{NO}_3^-)$ calculated in this study represents snow below the photic zone (below 3 e-folding depths of actinic flux) because it is indicative of the loss of snow nitrate over the total time that it spent in the snow photic zone. When nitrate is buried below the snow photic zone, no more photolysis or alteration of $\delta^{15}\text{N}(\text{NO}_3^-)$ occurs; hence, the $\delta^{15}\text{N}(\text{NO}_3^-)$ (referred to as asymptotic $\delta^{15}\text{N}(\text{NO}_3^-)$ in Erbland et al. [2013]) is further unaltered and is preserved in the ice-core record. The chemical and physical properties of snow within the photic zone are used to estimate what the enrichment in $\delta^{15}\text{N}(\text{NO}_3^-)$ would be in ice cores at depths below the photic zone (below Z_{3e}).

Since we have not incorporated a detailed snow chemistry column model into GEOS-Chem, we are unfortunately not able to simulate vertical profiles of $\delta^{15}\text{N}(\text{NO}_3^-)$ in snow or calculate surface $\delta^{15}\text{N}(\text{NO}_3^-)$ values. Since we are only able to calculate $\delta^{15}\text{N}(\text{NO}_3^-)$ values in this study that are relevant for ice-cores or snow that is below

the photic zone, we compare our modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ values with $\delta^{15}\text{N}(\text{NO}_3^-)$ observations from snow below the photic zone, which is a region without snow photochemistry.

P18988, L25-26: “The modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ values are generally higher than observations, however, boundary layer $\delta^{15}\text{N}(\text{NO}_3^-)$ observations are negative over much of Antarctica (Erbland et al., 2013; Frey et al., 2009; Morin et al., 2009; Savarino et al., 2007), making modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ values biased high by up to 40%”. A few questions here. What is being compared? Snow nitrate $\delta^{15}\text{N}(\text{NO}_3^-)$ values to snow nitrate $\delta^{15}\text{N}(\text{NO}_3^-)$ values, atmosphere to atmosphere, or snow to atmosphere? The link between the negative atmosphere values and the model being biased high is not making sense here to me. In addition, “over much of Antarctica” is a stretch – the Erbland and Frey studies include atmospheric observations at Dome C, Savarino at DDU and Morin in the Weddell Sea. 3 sites hardly count as over much of Antarctica, given it’s size. Still, it seems important to compare, at those sites, the model versus observations in the atmosphere to better constrain the simulation.

Thank you for asking us to clarify whether we are discussing atmospheric or snow $\delta^{15}\text{N}(\text{NO}_3^-)$ values in this sentence. We are comparing modeled and observed sub-photoc zone/ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ values here, not atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ values. We have updated this sentence as shown below:

“The modeled enrichments in ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ values are generally higher than the sub-photoc zone $\delta^{15}\text{N}(\text{NO}_3^-)$ observations presented in Figure 9c, however, boundary layer $\delta^{15}\text{N}(\text{NO}_3^-)$ observations are negative over much of Antarctica [Erbland et al., 2013, Frey et al., 2009, Morin et al., 2009, Savarino et al., 2007], making modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ values biased high by up to ~40‰ since we assume that the $\delta^{15}\text{N}$ of atmospheric nitrate (NO_3^- and HNO_3) deposited to the snow surface is always equal to 0‰”.

In the equation used to calculate enrichments in ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ (equation 11), the $\delta^{15}\text{N}$ of NO_3^- in the atmosphere is required. In this way, atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ influences the value of ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$. We have set the atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ in equation 11 equal to 0 because we only examining the impacts of snow nitrate photolysis on enrichment in ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$. Where observations of atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ are available in Antarctica, the measured values are generally negative (up to -40‰). Since we have set $\delta^{15}\text{N}(\text{NO}_3^-)$ equal to 0, rather than a negative number, this leads to the high bias in ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ that was mentioned in the text.

We have removed the terminology “over much of Antarctica”. This sentence now reads: “The modeled enrichments in ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ values are generally higher than the sub-photoc zone $\delta^{15}\text{N}(\text{NO}_3^-)$ observations presented in Figure 9c, however, boundary layer $\delta^{15}\text{N}(\text{NO}_3^-)$ observations are negative in both coastal [Morin et al., 2009, Savarino et al., 2007, Wagenbach et al., 1998] and continental [Erbland et al.,

2013, Frey et al., 2009] Antarctica, making modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ values biased high by up to $\sim 40\%$.”

Due to the lack of a snow chemistry column model, we are unable to simulate atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ in the model and thus cannot compare this model output to observations.

P18990, L3-6: Two aspects of the $\delta^{15}\text{N}(\text{NO}_3^-)$ work should be tested for sensitivity. How sensitive are the results to the photolytic fractionation factor? How sensitive are the results to the initial starting values of 0% . Berhanu et al.’s laboratory study is much better developed than previous work, but the results therein (and the companion paper by Meusinger et al.) look nothing like what is suggested in the model here. For instance, in the laboratory study the e-folding depth is only a few to several centimeters (or less) and the amount of nitrate lost is fairly minimal even given long exposure times. In addition, the Frey et al. (2009), Erbland et al. (2013), and Shi et al. (2015) work suggest that the apparent fractionation factors, base on snowpits in the field, vary considerably (Frey et al. report -49.8 and -71.0 for field based snow, and theoretically predict -44.8 ; Shi et al. report values from -93.1 to -50.2 for the apparent fractionation factor at low accumulation sites in the 0 - 20 cm depth and higher values at the higher accumulation sites; Erbland et al. report -74.3 to -40.0 for Dome C, Vostok, and similar sites, higher values again for higher accumulation sites). The field based values reflect a number of processes, even if they are dominated by photolytic loss. Still, the balance of evidence suggests that sensitivity to the photolytic fractionation factor should be tested within a fairly wide range (or at least at much more negative values too).

For the last sentence here, can an example be show as to how $\delta^{15}\text{N}$ could be used to estimate the degree of recycling and loss for a different point in time than present? What values need to be known to perform this calculation? Do constant conditions need to be assumed over time (e.g., concentration, deposition, LAI, overhead sun, etc)? Looking at figure 10, how would one know the f value for their site if the nitrate is heavily processed?

Additionally my read of this section is that field work is needed to better understand the atmospheric isotopic values across Antarctica, both in terms of what might be primary input and what is secondary formation over the continent because of snow emissions of NO_x . Depending on the results of the suggested sensitivity analyses above this may be worth including in the conclusions as a focus of future work as well.

Changes in the photolytic fractionation factor and air $\delta^{15}\text{N}(\text{NO}_3^-)$ both influence ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ values considerably. We assume air $\delta^{15}\text{N} = 0\%$ in this study as we are only examining the enrichment in snow $\delta^{15}\text{N}(\text{NO}_3^-)$ due to photolysis. The magnitude of the fractionation factor will certainly impact our calculations of the enrichment in snow $\delta^{15}\text{N}(\text{NO}_3^-)$ due to photolysis, though it will not impact our

calculations of other parameters in this study (e.g., F_{NO_x} , f , and NRF). We have varied the photolytic fractionation factor from -90‰ to -10‰ and found that ice-core $\delta^{15}N(NO_3^-)$ by increases by a factor of 2 and decreases by a factor of 5, respectively, across Antarctica. We have added the following sentence to the end of section 3.5.:

“The modeled ice-core $\delta^{15}N(NO_3^-)$ values resulting from the photolysis-driven loss of snow nitrate are sensitive to the fractionation constant (ϵ). The fractionation constant is varied over the full range of values reported in Erbland et al [2013], Frey et al., [2009], and Shi et al. [2014]; an ϵ of -90‰ increases $\delta^{15}N(NO_3^-)$ by a factor of 2 and an ϵ of -10‰ decreases $\delta^{15}N(NO_3^-)$ by a factor of 5 across Antarctica.”

Thank you for suggesting that we provide an example of how $\delta^{15}N(NO_3^-)$ could be used to estimate the degree of recycling and loss for a different point in time than the present. In section 3.6. we now discuss which values must be known to perform this calculation (e.g., snow accumulation rate and light-absorbing concentrations in snow) and how these parameters may change under different climate scenarios.

We agree that more measurements of atmospheric isotopic values across Antarctica would be incredibly valuable.

P18890, L19-21: The pattern is suggested to be dependent about the patterns of snow accumulation rate and LAI across the continent, yet the sensitivity to accumulation rate is not tested, and the sensitivity to LAI is limited so why is this so important to the pattern?

In this study, the spatial pattern of F_{NO_x} is dependent on the spatial patterns of LAI in snow, and the spatial patterns of LAI are dependent on snow accumulation rate. The spatial pattern is also dependent on the fraction of photolabile nitrate, which we have now included in this section as well (thank you for bringing this to our attention).

This part of the text now reads: “The modeled spatial pattern of the flux of snow-sourced NO_x is determined by the patterns of light-absorbing impurity concentrations in snow and the fraction of photolabile NO_3^- across Antarctica. The spatial pattern of light-absorbing impurities is strongly influenced by snow accumulation rates and the spatial pattern of photolabile NO_3^- in the model is influenced by the amount of wet deposited NO_3^- compared to total deposited NO_3^- across Antarctica. Snow NO_3^- concentrations were kept constant for this simulation; however, spatial variations in snow NO_3^- concentrations would also influence the spatial pattern of F_{NO_x} across Antarctica.”

P18991, L10: Not clear how a conclusion can be drawn about preservation in the coastal region when the model is limited in it’s ability to reproduce observations in the region. While the reason for this limitation is explained in the paper, how can conclusions be drawn about what the modeling is producing if there is no way to verify its realism?

Thank you very much for this comment. We have removed this sentence from the conclusions.

Technical Comments/corrections:

P18964, L5: nitrate photolysis is not a direct source of ozone, remove mention of this in the ().

Ozone has been removed from these parentheses.

P18964, L5: I disagree with the use “disturbs the preservation of NO₃⁻ in ice cores”. It needs to be clear here that nitrate photolysis changes what is preserved or changes what is ultimately archived in the snow such that ice cores may not reflect a primary atmospheric signal (or loading). The phrase as it is now (and later in the text) implies that nitrate can be affected after it is preserved, and I do not understand the term “disturbs” in this context.

We have changed this sentence to: “Nitrate (NO₃⁻) photolysis in snow provides a source of oxidants (e.g., hydroxyl radical) and oxidant precursors (e.g., nitrogen oxides) to the overlying boundary layer, and alters the concentration and isotopic (e.g., δ¹⁵N) signature of NO₃⁻ preserved in ice cores.”

We have also made similar updates in the introduction and in section 2.3.

P18965, L13: Levy et al. 1999 is one of the few modeling studies that actually shows the temporal and spatial dependence of the NO_x lifetime against loss. Be more specific here in terms of what is relevant to this study – eg. mid to high southern latitudes where the lifetime is typically longer than only a day, especially in winter.

We have changed this sentence to include the NO_x lifetimes in polar regions as presented in Appendix A5 of Levy et al. [1999]. The sentence now reads: “Oxidation to form nitrate (HNO₃/NO₃⁻) is the main sink for NO_x in the troposphere [Logan, 1983], and the lifetime of NO_x against oxidation to nitrate is 1-3 days in polar regions [Levy et al., 1999]”.

P18965, L15: There are much more recent studies that are relevant here than Logan 1983. For instance, Xu, Penner et al. suggest the global average lifetime of nitrate (particulate and HNO₃) is about 5 days.

Thank you for bringing this more recent paper to our attention. This sentence now reads: “NO₃⁻ is lost from the atmosphere through dry and wet deposition to the Earth’s surface, and has an atmospheric lifetime of roughly 5 days [Xu and Penner, 2012].”

P18965, L19: So as not to confuse the reader later replace “recycles” with “returns” (ie this is only speaking to the atmospheric impact and not the recycling back to snow nitrate).

We have replaced “recycled” with “returns” in this sentence.

P18967, L13: In the above equation, everything is listed as in the aqueous phase. It needs to be clear here that NO₂ and NO can then be lost to the gas phase and THEN pumped out of the snowpack.

The sentence below E1 and E2 now reads: “The aqueous phase NO₂ produced in E1 is can be transferred to the gas phase and subsequently transported into the interstitial air [Boxe *et al.*, 2005] and then released to the atmosphere.”

P18967, L15-16: The local abundance of NO_x is also dependent upon how much NO_x is transported away from the site. If you look at any of the studies referenced here in terms of NO_x fluxes, almost none of them understand the NO_x budgets at individual locations.

In this sentence, we are specifically addressing the relative abundance of NO and NO₂, not the total local abundance of NO_x. We agree that the local abundance of NO_x is subject to local transport patterns.

P18968, L4: Please remove the use of the phrase “disturbs the preservation”. See above comments in the abstract, and consider that this process makes what is preserved not necessarily reflect atmospheric loading of nitrate.

We have removed this phrase and the sentence now reads: “The photolysis of snow NO₃⁻ and subsequent recycling between the air and snow alters the concentration and isotopic (e.g., δ¹⁵N) signature of NO₃⁻ that is ultimately preserved in polar ice sheets, which hampers the interpretation of ice-core NO₃⁻ records [Wolff *et al.*, 2008].”

P18968, L19: Given the timescale of the model simulations in this study, this sentence is a bit iffy. While the model is compared with some ice core data, this seems to be because the data is limited not because the model is actually being aimed at reconstructing ice core δ¹⁵N.

One of the major goals of this modeling study is to calculate ice core δ¹⁵N in the present climate, which is explained in more detail in some of the comments above. Since this is a main goal of our work, we would like to keep this sentence in the manuscript.

P18974, L12: Some justification as to why a value from coastal Alaska is applicable to the Antarctic ice sheet should be made here (even if the insoluble material plays a small role in the results).

We have added a phrase to the end of the sentence starting with “To our knowledge..”. This sentence now reads: “To our knowledge, observations of soluble light-absorbing impurities in Antarctic snow are unavailable. We use soluble LAI observations from the Arctic to provide a general estimate of the importance of soluble LAI in polar snow.”

P18978, L4: This fits with the earlier assumption that the photolabile nitrate is located closer to the surface. The range of % NO_x produced is different here than in the caption of Figure 1.

In this section of the text, we mention that 87-91% percent of snow-sourced NO_x is produced in the top 1 e-folding depth. In Figure 1, we mention that 30-65% of the snow-sourced NO_x is produced in the top 2 cm of snow. In this study, the top e-folding depths of UV actinic flux extends below the top 2 cm of snow.

P18981, L13: Suggest moving “Fig. 3” into the () so as not to cause confusion with Figure 3 of this paper.

Thank you for this suggestion. We have moved Fig. 3 into the parentheses.

P18984, L25: “peroxyacl” is a misspelling.

Thank you for catching this misspelling. We have corrected it in the latest version of the manuscript.

Figure 1: Why does it appear that nitrate formed locally is deposited, snowed upon, and then photolyzed to NO_x ? Not that % snow-sourced NO_x in the top 2 cm is different here than in the text.

As mentioned in the comments above, the % in the Figure 1 caption refers to the top 2 cm and the % in the text refers to the top 1 e-folding depth. This has been made more explicit in the figure caption.

In Figure 1, F_{PRI} represents long-range transport of nitrate and input from the stratosphere and F_R represents the nitrate that has been photolyzed in the snow, exported as NO_x into the boundary layer, and then re-deposited back to the snow. To illustrate that not all of the nitrate formed in the atmosphere is re-deposited to the original site of photolysis, we have now added another arrow to simulate transport of nitrate away from the original site of NO_x emission from snow.

Figure 3: Why not also compare with surface snow concentrations (rather than just $[\text{NO}_3^-]_{bot}$ scaled by F_p)

The snow nitrate concentration measurements that have been included in Figure 3d are sub-surface snow nitrate concentration measurements. For consistency, we have compared these observations to $[\text{NO}_3^-]_{bot}$. Due to the rapid decrease of snow nitrate concentrations in the top 2 cm, observations of “surface” snow nitrate concentrations are difficult to interpret, as some observations represent the average over the top 2 cm, while other represent observations in the surface skin layer (~ 1 mm).

Figure 6a and 6b are not particularly useful; the ratios in c and d are much more helpful for understanding how much difference this can make.

Figures 6a and 6b show where F_{NO_x} has been set to 0 in these sensitivity studies, which is helpful for quickly visualizing how much recycled nitrate is present in regions where F_{NO_x} has been set to 0. For example, although F_{NO_x} is set to 0 across West Antarctica, Figure 6d shows that some recycled nitrate is still present in West Antarctica.

Figure 9a: It seems the figure caption here should be rephrased. I find it very confusing to look at negative values as a fraction of nitrate lost by photolysis. In the model it seems it should be possible to account for or track how much nitrate is lost and then how much nitrate is deposited to the site as a result of secondary formation on the continent from snow-sourced NO_x. Maybe then the fraction of nitrate that is the result of photolytic processes (i.e. some amount is lost + some amount is returned as result of snow-sourced NO_x becoming nitrate) could be quantified and illustrated, rather than just a fraction that is lost (which again does not actually describe what is pictured).

Thank you for this comment. The variable, f , described in this study is used to calculate the amount of nitrate lost (or gained) from the snow associated with snow nitrate photolysis. We have decided to change the sign of equation 9 (E9) so that negative f values now represent loss of nitrate from the snow and positive f values represent gain of nitrate to the snow. We have rephrased the figure caption and also the description of this figure in the text (section 3.5) to reflect these changes. Since negative f values now represent net loss of snow-sourced nitrate, equation 11 (E11) has been slightly altered to reflect this sign change.

Figure 10: Can the sizes of the text on the axes and in the equations be made larger? They are difficult to read now and will be worse if resized for a different format

The text size in Figure 10 has been made larger.

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