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## Comment on tc-2021-92

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Community comment on "Impacts of the photo-driven post-depositional processing on snow nitrate and its isotopes at Summit, Greenland: a model-based study" by Zhuang Jiang et al., The Cryosphere Discuss., <https://doi.org/10.5194/tc-2021-92-CC1>, 2021

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I think it is critically important that the authors do more to compare with the larger body of isotopic measurements of nitrate in the snow and atmosphere at Summit, Greenland. The conclusions drawn here focus on the loss and recycling of nitrate when the model can just as well explain the observations based on a change in the primary nitrate isotopic signal rather than photolytic redistribution of nitrate in the snow. A number of works from my research group on surface snow and snowpack at Summit, Greenland have all concluded that photolytic loss OR recycling cannot explain the observations presented in those studies. If the model here is indeed correct, this is an opportunity then to re-interpret those conclusions. Or better constrain the model and present stronger evidence-based conclusions. Simply put – the model has multiple tuning options to improve agreement between predictions and observations, but can it actually explain what's observed at Summit?

### Spatial heterogeneity

First and foremost, the issue of spatial heterogeneity in the isotopic composition of snowpits and surface snow mean that comparing with a single year of observations and suggesting that everything can be explained is not appropriate. I understand the purpose of the study here is to focus on the loss of nitrate from within the photolytic zone and the model then suggests that much of this snow-sourced NO<sub>x</sub> is re-deposited as nitrate at the surface. Hence the interest in using the surface snow observations we published in Jarvis et al. (2009). However, there are additional observations that could be compared with to better understand if the need for photolysis in the model is actually correct. For starters, Fibiger et al. (2016) present observations of d15N, d18O and D17O in surface snow and in atmospheric nitrate for two years (2010 and 2011) in the spring (May/June). Both the surface snow observations and the atmospheric observations should be compared with the model predictions. Jarvis et al (2009) also includes atmospheric observations that are neglected here.

Additionally, it is inappropriate to compare the range in surface values to the range found in snowpits and suggest that this represents real change in the isotopes (lines 65-85; ~line 240) – again there is significant spatial heterogeneity to contend with and the comparison with observations should be an envelope or a distribution and not a single line. Furthermore, it appears that one year of surface snow values is being compared to

an averaged snowpit from a different year? Again, spatial AND temporal heterogeneity could easily explain a big portion of this difference (if not all). Also, the “higher” values in the snowpit than in surface snow neglect the fact that it is possible that there is also local contamination of the snow by the presence of the field camp/field work – this is well discussed and direct evidence for the isotopic values associated with this potential source are given in Fibiger et al. (2016).

### **Fpri assumptions**

The assumptions of the values for Fpri (both concentration and isotopically) need to be better justified. The Fibiger et al. (2016) surface snow isotope data ALL fall within a 3-end member plot (see Figure 8 in that paper) that are suggested to represent the primary nitrate signatures (this includes D17O data from Fibiger et al. (GRL, 2013) as well). Why not use these end-members as an a priori assumption/test? Why assume surface snow values when authors of the current work have argued in other papers that even the top few cm misrepresents what is happening in the very surface layer of the snow? It is stated in this paper that the Fpri assumptions could be underestimates – which directly agrees with the values presented in Fibiger et al. So again, why not use these values compared to the constant 0 and 30 per mil assumptions for d15N and D17O, respectively. In fact, if the highest endmember values for D17O found in Fibiger et al (2016) (39 per mil) were used for D17O primary it likely would much better fit the seasonal D17O observations than the model currently does! This offers much in the way of better constraining our understanding of nitrate in snow at Summit that weakens the current manuscripts as presented.

### **D17O mismatch**

A critical point is that the model cannot match the D17O observations. The authors note that a primary signal therefore must be important in driving the seasonality. Yet, the global chemical modeling results of Alexander et al. (2020) do not match the D17O observations at Summit either, and GEOS-Chem does not include exchange with the snow/post-depositional processing of nitrate. Why not discuss these results compared to the understanding trying to be made locally here? With neither a chemical transport model nor a box model matching the results our understanding clearly has a long way to go and there is an important opportunity for the authors to make an advance here. For instance, the key point in the beginning is that post-depositional processing does not significantly affect D17O. What is significant? The GEOS-Chem model simulations predict the seasonality of D17O well but overestimates the values; would the 2.1 per mil decrease here because of recycling help to resolve much of this over-estimation? If it does, isn't that significant? The lack of significance seems to be related to the fact that 2.1 per mil is much different than the 9 per mil difference seen in the observations, but the co-authors of this work have used changes as small as 2 per mil to argue for significant changes in atmospheric oxidation pathways in other environments. In fact, in the spring surface snow alone the median D17O values between 2010 and 2011 change by ~3 per mil (Fibiger et al., 2013) – which again can reflect spatial and temporal heterogeneity OR differences in chemistry between years (both of which are not considered in this study).

### **Other fractionation effects**

The authors discuss re-formation of nitrate in the snow – does this induce an isotopic effect on d15N? It should be addressed that re-formation within the snow that impacts D17O should also impact d15N (and d18O) as well.

The potential for loss via evaporation/volatilization of nitrate should also be considered (Shi et al., Isotope fractionation of nitrate during volatilization in snow: A field investigation in Antarctica. *Geophys Res Lett.* 46(6):3287-3297. 10.1029/2019GL081968,

2019)

### **The conclusion of 21% loss**

The key conclusion of the manuscript is that “as much as 21% of nitrate is lost”. In the model the majority of this nitrate is not actually lost – it’s redistributed. And the model better explains the seasonality based on a primary signal change. On net, more like 2% of nitrate is actually lost and this agrees with what Fibiger et al (2016)’s observational study based on isotopes found and what Thomas et al. (2011)’s modeling study based on gas phase and snow concentrations of a variety of species found. Quoting here from the discussion section of Fibiger et al (2016): “Previously, it was thought that local recycling of NO<sub>3</sub> might be important at Summit [Jarvis et al., 2009; Kunasek et al., 2008]. If this were true, however, there should be some connection between local gas phase concentrations and the isotopes of NO<sub>3</sub> in the snow. If HNO<sub>3</sub> were formed locally and deposited by cloud-to-ground scavenging of NO<sub>3</sub> in the snow (Figure 1, arrows d and g), then BrO concentrations above 1 pptv should be influencing NO<sub>3</sub> in the snow [Kunasek et al., 2008; Morin et al., 2007] via reactions (R6) through (R9). In particular, we expect that when BrO is high, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of nitrate would also be high, as BrO retains the anomalous isotopic signature of the O<sub>3</sub> from which it is derived. The local signal, if important, should be present in the snow as the lifetimes of NO and HNO<sub>3</sub> at Summit are only a few hours. This is evident in the atmospheric HNO<sub>3</sub> and NO concentrations at Summit, as both approach zero at low solar zenith angle. This is evidence that there is some loss or recycling of NO<sub>3</sub> from the snow in Greenland [Honrath et al., 1999], but as noted above, as little as 2% of NO<sub>3</sub> loss from the snow can account for observed NO<sub>x</sub> concentrations above the snow [Thomas et al., 2011]. This photolysis of NO<sub>3</sub> to NO<sub>x</sub> has a significant influence on local NO<sub>x</sub> concentrations and the  $\delta^{15}\text{N}$ -HNO<sub>3</sub> in the atmosphere at Summit, but appears small enough to not have a significant effect on the residual NO<sub>3</sub> in the snow. If photolysis of NO<sub>3</sub> to NO<sub>x</sub> followed by deposition of locally formed HNO<sub>3</sub> (Figure 1, arrows a, c, and d) was having a strong influence on the NO<sub>3</sub> in the snow, we would expect that snow NO<sub>3</sub> concentrations would reflect NO and HNO<sub>3</sub> atmospheric concentrations. There was, however, no connection found between the local concentrations of BrO, NO, or NO<sub>y</sub> and any of the isotopes of NO<sub>3</sub> or [NO<sub>3</sub>]. This lack of relationship was found using 3, 5, and 12 h back averages of the gas phase data, from each time point that a snow sample was taken, accounting for potential variations in the lifetime of NO<sub>x</sub> against deposition as NO<sub>3</sub>. This indicates that local chemistry, either through recycling of NO<sub>3</sub> or local conversion of NO<sub>x</sub> to NO<sub>3</sub>, is not influencing the NO<sub>3</sub> preserved in the snow. This lack of relationship is true both across each season and over shorter timescales within.” In the end, our work has suggested that photolytic loss and recycling may be taking place but it represent a very small portion of the overall nitrate in the snow. The authors of present student should be obliged to provide clear evidence as to why this conclusion is not justified.

An approach that truly considers past work and challenges/reconsiders previous interpretations, based on a robust comparison between the model and observations, is needed and not provided in this manuscript. Rather, model results are presented that 1) show that the isotopic composition of preserved nitrate is quite sensitive to the assumed signature in nitrate when first deposited, and 2) suggest that photolysis of nitrate may significantly modify the seasonal profile in  $\delta^{15}\text{N}$  if enough of the nitrate in the snow is photolyzed. The authors assert that the seasonal variation in the isotopic composition of deposited nitrate is too poorly constrained to consider that it might be preserved largely unaltered (our conclusion from multiple prior studies), and conclude that the observed seasonal pattern is created by post-depositional photolysis (their assumption at the outset, neglecting prior peer-reviewed work).