

## ***Interactive comment on “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” by M. C. Zatko et al.***

**Anonymous Referee #1**

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### General Comments

This work uses a global atmospheric chemistry model to simulate the deposition and photochemical processing of nitrate in snow on the Antarctic continent. The purpose of the study is to quantify the influence of nitrate photolysis on boundary layer chemistry, as well as analyze the photolytic loss of nitrate as NO<sub>x</sub> and secondary oxidation of this snow-sourced NO<sub>x</sub> back to nitrate such that nitrate is redistributed spatially on the Antarctic ice sheet. The model is compared to the few observations that exist in this en-

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vironment, for instance NO<sub>x</sub> fluxes from snow, e-folding depths, nitrate concentrations “at depth”, and the nitrogen isotopic composition of nitrate. The phrase “comparable to observations” is used frequently to compare a large range of results 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. Sensitivity of the model’s parameters are tested for the calculation of the average flux of NO<sub>x</sub> 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.

I have a hard time rating this paper. It is overall well written, in terms of the use of language and organization. In terms of the science, it is difficult to assess how useful this study actually is. I appreciate what the authors are attempting to do, and the subject matter could be of interest to readers of ACP, but the conclusions are based on so many assumptions that it is hard to read either the abstract or conclusions section and feel that we are really gaining. The observational constraints are limited, and the model does not compare all that well with the data that does exist. In multiple cases, the lack of agreement with other studies (observational and modeling) is treated dismissively. I am not entirely sure that the use of a global model in this case is the right tool for this exercise. In other words, if errors were propagated, the quantified values in the abstract would be nonsensical, so how are we really forwarding our understanding? 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. The 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 this 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. Additionally, more careful comparisons with specific sites here isotopic data is available in the snow and in the atmosphere would also help to more fully evaluate

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the model and whether it is worth considering the quantified results in the paper.

#### 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<sub>x</sub> 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?

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 from 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 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.

P18976, L1-9: It does indeed seem unnecessary for a global model to include a liquid

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like region and distribute nitrate based upon this since there is still a fair amount of uncertainty regarding this within the laboratory based literature. However, 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<sub>x</sub> 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 that 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.

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 the 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, drifting, density changes, etc. So a simple comparison with a few values that “seem” to fit with the model is weak at best, and it should be better understood how important this parameter is to determining the simulated values. Finally, changes in boundary layer height should also 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 the NO<sub>x</sub> is transported away versus recycled and “re”deposited

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locally, which applies to all of the results computed in this work.

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.

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 Antarctic Ice Sheet, it seems worthwhile to compare with Frey, Erbland, and Shi transect concentration data as well.

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 significantly different? Given the understanding the authors believe they are developing from the sensitivity studies, what most likely explain the difference in results?

P18988, L11 and L19-20: What does sub-photoc zone mean? What depth range is

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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-photoc 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.

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  $\delta^{15}\text{N}$  values to snow nitrate  $\delta^{15}\text{N}$  values, atmosphere to atmosphere, or snow to atmosphere? The link between the negative atmospheric 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.

P18990, L3-6: Two aspects of the  $\delta^{15}\text{N}$  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

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Meusinger et al.) look nothing like what is suggested by 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, based 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 0-20cm 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 shown 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<sub>x</sub>. 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.

P18990, L19-21: The pattern is suggested to be dependent about the patterns in 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?

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

Technical Comments/corrections

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

P18964, L5: I disagree with the use “disturbs the preservation of NO<sub>3</sub><sup>-</sup> 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.

P18965, L13: Levy et al. 1999 us one of the few modeling studies that actually shows the temporal and spatial dependence of the NO<sub>x</sub> 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.

P18965, L15: There are much more recent studies that are relevant here than Logen 1983. For instance Xu, Penner et al. suggest the global average lifetime of nitrate (particulate and HNO<sub>3</sub>) is about 5 days.

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).

P18967, L13: In the above equations, everything is listed as in the aqueous phase. It needs to be clear here that NO<sub>2</sub> and NO can then be lost to the gas phase and THEN pumped out of the snowpack.

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P18967, L15-16: The local abundance of NO<sub>x</sub> is also dependent upon how much NO<sub>x</sub> is transported away from the site. If you look at any of the studies referenced here in terms of NO<sub>x</sub> fluxes, almost none of them understand the NO<sub>x</sub> budgets at individual locations.

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.

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 data is limited not because the model is actually being aimed at reconstructing ice core  $\delta^{15}\text{N}$ .

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).

P18978, L4: This fits with the earlier assumption that the photolabile nitrate is located closer to the surface. The range of % NO<sub>x</sub> produced is different here than in the caption of Figure 1.

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

P18984, L25: “peroxyacl” is a misspelling

Figure 1: Why does it appear that nitrate formed locally is deposited, snowed upon, and then photolyzed to NO<sub>x</sub>? Note that % snow-sourced NO<sub>x</sub> in the top 2cm is different here than in the text (commented on above).

Figure 3: Why not also compare with surface snow concentrations? (rather than just (NO<sub>3</sub>]<sub>bot</sub> scaled by F<sub>p</sub>)

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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.

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<sub>x</sub>. 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<sub>x</sub> becoming nitrate) could be quantified and illustrated, rather than just a fraction that is lost (which again does not actually described what is pictured).

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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 18963, 2015.

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