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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Deposition, recycling and archival of nitrate stable isotopes between the air-snow interface: comparison between Dronning Maud Land and Dome C, Antarctica" *by* V. Holly L. Winton et al.

Anonymous Referee #2

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

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ronmental conditions (i.e. accumulation rate, snowfall timing, and e-folding depth).

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

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

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

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

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

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

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

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

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

It is stated that the poorly constrained "quantum yield of NO3- photolysis in natural snow" yields a flux of NOx that is 50 times too high. Can this not be tested in TRANSITS? And shouldn't this affect the TRANSITS results as well and not just the estimated calculations here? Finally, consider better comparing with Zatko et al., 2016 throughout the discussion – the equations used here are very similar to that paper and that work does in fact quantify the recycling despite the line later that only two studies have done so and then Zatko's work is compared with.

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

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

Technical comments:

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

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

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

Line 34: TOC should be TCO

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

Line 57: J should be (J)

Line 64: add a comma after Greenland

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

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

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

Line 300: followed should be follows

Line 303: add the word in after changes

Line 370: remove and before archived

Line 398: as a year round does not make sense

Line 457: inter-decadal should be interannual

Line 475: Fig 5 should not be cited here

Line 490: remove are

Line 530: up taken should be taken up

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

Line 566: rephrase “form of nitrogen to skin layer”

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

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

Line 643-653: I have serious issues here with the interpretation of previous literature. First and foremost, the assumption that anthropogenic emissions of NOx are positive in d15N and natural emissions are negative in d15N is false and not up to date. Recent work shows that vehicle emissions are, in fact, negative in d15N (Miller et al.,

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

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

Line 698: add an before annual

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

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

less photolysis than expected is really very interesting.

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

Line 855: depending ON the timing

Line 902: due TO photolysis-driven

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

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

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

Line 922: resulting IN an enrichment

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

Line 945: THE ground

Figure 3: how is the data averaged here?

Figure 4: x-axis on right side is misspelled

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

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

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