

Interactive comment on “Spatial variations in snowpack chemistry and isotopic composition of NO₃⁻ along a nitrogen deposition gradient in West Greenland” by Chris J. Curtis et al.

Anonymous Referee #2

Received and published: 5 July 2017

I absolutely appreciate that the authors have gone to a great deal of effort to collect unique samples along a climatic gradient in Greenland. However, this manuscript needs a fair amount of work to be of publishable quality. There is a need for more digestion of the data that they have, more updated discussion of the literature surrounding interpretation of isotopes of snowpack nitrate, and a fuller interpretation of the data presented such that conclusions are drawn based upon the evidence presented.

The work presents chemical measurements of snow collected from three different sites in Western Greenland - a coastal site, an inland site, and a further inland site that represents the start of the interior ice sheet. Ionic composition of the snow samples, from

[Printer-friendly version](#)

[Discussion paper](#)



snowpack collections and snow on top of frozen lakes, are discussed in the context of differences in precipitation amount and relative proximity to oceanic (sea salt) sources. The isotopic composition of nitrate is also presented and discussed in the context of sources of atmospheric nitrate and post-depositional processing of snowpack nitrate.

The primary conclusions drawn in the study are focused on the N isotopic composition of nitrate. The authors neglect a fair amount of recent literature on the subject, do not compare and contrast with other work done in Greenland that is relevant, and do not interpret the oxygen isotopes of nitrate. The conclusion that there is a strong gradient in $d_{15}N$ from the margin to the coast is not supported by the evidence presented. This conclusion is based on contrasting the most interior site (-7.5 per mille) to the coastal site (-11.3 per mille). However, the midpoint site has a value higher than the interior site (-5.7 per mille) negating the use of the terminology gradient. Furthermore, there is no comparison with seasonal snowpack at Summit, Greenland (the authors appear to argue that they cannot compare with accumulated snow which I take to mean ice core). Kunasek et al. (JGR, 2008), Hastings et al. (JGR, 2004), and Fibiger et al. (JGR, 2016; GRL, 2013) all present seasonal snow results for the isotopes of nitrate. In fact, the wintertime snowpack at Summit has a mean value similar to the coastal site, i.e. -10 ± 3.2 per mille in Hastings et al. (2004). Further, the more enriched $d_{15}N$ values found in late summer rain at Kellyville and the Ice Sheet also match the snowpack seasonality at Summit (summer = ~ 0 per mille). This makes it highly questionable whether a gradient across the interior of Greenland to the coast can be considered at all. Instead of using a decadal or multi-annual value of -1 per mille from Hastings et al. (2009), the early spring snowpack mean values can be compared with (modern) seasonal snowpack at Summit.

The discussion on post-depositional processing needs to be made much clear in the text. First and foremost, there is no definition of “post-depositional processing”. The manuscript primarily uses this term to mean “loss” of nitrate from the snow, but other times it could represent recycling of nitrate following loss from the snowpack. This

[Printer-friendly version](#)[Discussion paper](#)

needs to be made more clear. In addition, each of the processes discussed - photolysis, volatilization, sublimation - have been discussed in the literature before and at least two of these processes have calculated fractionation factors that could be considered in the discussion (see Frey et al., ACP, 2009). Frey and others have also followed up this earlier work to study photolytic loss in the field and in the laboratory (Berhanu et al., J. Chem. Phys., 2014; Berhanu et al., ACP, 2015; Erbland et al., ACP, 2015 and references therein). The work in Antarctica may or may not be relevant in the manuscript here, but the impact of loss of nitrate from the snow on the isotopes of nitrate is made most clear by the body of work that has been completed at Dome C.

The distinction between post-depositional loss and post-depositional processing is critical. Loss should lead to enrichment of d15N of residual nitrate; pure loss should also lead to enrichment of d18O, however, several studies have shown d18O (and D17O) tend to show decreases when nitrate is lost via photolysis (see lab studies by Berhanu mentioned above, also McCabe et al., JGR, 2005). Erbland et al. (ACP, 2013) suggest that the changes in D17O are negligible; Berhanu et al's field study (ACP, 2015) could not necessarily distinguish the decrease in d18O and D17O b/c of poor precision on the isotope measurements, but the tendency is still observed. Shi et al. (ACP, 2015) do see significant decreases in d18O while d15N of snow nitrate increases with loss of nitrate in low accumulation zones of Antarctica. They explain this as most likely due to recombination effects - i.e. Photolysis of nitrate and reformation of nitrate in situ. This agrees well with the laboratory photolysis experiments of McCabe et al who show decreases in D17O due to recombination. Zatko et al. (ACP, 2016) model the loss and recycling of photolysis nitrate products in Greenland and Antarctica. They assume that any nitrate in the photic zone is photolyzed and lost as NO_x in the gas phase, but this NO_x can be reformed as nitrate and deposited back to the ice sheet. Fibiger et al. (JGR, 2016) give a very nice overview of the different ways in which nitrate can be impacted via loss and/or reformation of nitrate photolysis products. The reformation of nitrate and redeposition would likely change the oxygen isotopes markedly. The d15N should still be enriched given the very large fractionation associated with photolytic loss of nitrate;

but re-deposited nitrate (either in the condensed phase or gas phase) should alter the oxygen isotopic composition compared to the originally deposited atmospheric nitrate. This needs to be addressed in this study. The very high $d_{18}O$ and $D_{17}O$ in this study agree well with the spring results in Fibiger et al. (2016) so I am again struck more by how similar the results are to that found in the interior of the ice sheet than I am with some difference that reveals a supposed gradient across Greenland. Still, the authors should look more closely at the Zatkan modeling results and compare and contrast with the model suggested gradient - I have some reservations about their modeling framework and whether it is at all realistic, but it does discuss the potential for a gradient in post-depositional processing/recycling of nitrate across the ice sheet.

The authors should really look more closely at all of the above studies (most of which are not currently cited) to put their data in better context. In particular, I would suggest comparing and contrasting with seasonal snowpack data from Summit, Greenland; better laying out the potential post-depositional loss vs. recycling mechanisms; interpreting the isotopic data more fully in the context of the possible post-dep processes (i.e. Both $d_{15}N$ and $d_{18}O$, $D_{17}O$); and reconsider whether a gradient actually exists between the coast and ice sheet sites and Summit. At this point, I would argue that their data suggests a lack of a gradient and surprising similarities with seasonal snowpack at Summit, which may actually negate the need for large re-distributions of nitrate suggested in the modeling study of Zatkan.

One additional major comment has to do with the estimates of nitrate deposition on an annual basis. A much clearer discussion on this is needed. Can the rainfall measurements and the snowpack observation be combined to estimate deposition? The scaling up of snowpack that only represents half of the year seems unreasonable given that some of the rainfall samples show higher concentrations than ever found (on average) in the snowpack. How deposition is being defined in the manuscript is also not really clear. And why is this important to quantify (with such large error bars given the scaling)?

[Printer-friendly version](#)[Discussion paper](#)

Finally, there are numerous times in the manuscript where “presumably” or “assumed” are used. This is distracting and also is representative of the fact that much in the manuscript is not evidence based discussion or drawing of conclusions based upon the observations.

Detailed comments:

Introduction, page 2, Line 31 - greater accumulation does not necessarily mean great precipitation rate/amount so this cannot be used as evidence to support a gradient in precipitation. Please clarify this.

Introduction, page 3, Line 4-5 - The Introduction and Abstract contrast in what the primary purpose of this study is/what is being tested. Please clarify.

Methods, page 3, line 23 - assume 100 m should be 100 cm?

Methods, page 4, chemical and isotopic analysis section - Please include a few more details on the isotopic method. Is the gold tube based pyrolysis of N₂O used? How many repeated measures of samples do the std deviations represent (here and for the ion concentrations)? What sample sizes were run for isotopic analysis?

Section 3.4, page 8, line 5: here it is suggested that the snow was homogeneous on the lake surface. This is surprising given the earlier description of the major snow redistribution due to wind. Comparing/contrasting the snowpack and lake ice snow should be done much more carefully. I would argue that it is not at all clear whether these represent the “same” snow in any context.

Section 3.6, page 9: is it possible that the higher NH₄⁺ values at the coast are due to the presence of birds? Several studies in the Arctic (and Antarctic) clearly indicate that bird guano can be a major source of atmospheric ammonia. This would better explain the distinct pattern for nitrate versus ammonium and sulfate. Also, it should be made clear if sulfate is in excess to ammonium. If not, then the explanation of ammonium sulfate deposition as a “cause” of higher concentration on the coast (page 12) does not

Printer-friendly version

Discussion paper



make sense.

Section 4.3, page 13: lines 10-20, need to compare with Fibiger et al. (2016) and Kunasek et al. (2008). Lines 20-29, this is highly speculative, you need more evidence. The “low” end of the D17O is not at all low compared to other measurements of atmospheric nitrate and other measurements of snowpack nitrate. Line 30-35, see comments above but there should be comparisons here with other relevant snowpack data (winter means, early spring surface snow at Summit - Hastings et al. (2004), Kunasek et al. (2008), Fibiger et al. (2016)). It is not as relevant to compare with a decadal or multi-year mean from the ice core in Hastings et al. (2009).

Page 14, lines 1-4: this does not make sense. Here it is being stated as a fact that “nitrate in ice cores reflects Northern Hemisphere pollutants,” yet later it is argued that nitrate in snow in Greenland does represent sources.

Page 14, line 16: What is Fibiger and Hastings (2016)? It is not included in the reference list.

Section 4.3.1: In general this section would be much improved with a discussion of prevailing transport patterns. Would you expect different regions to contribute to the coast versus the interior sites? (For instance, transport studies for Summit and Dye 3 show distinct difference in expected source regions). And again, the discussion here is largely based upon the assumption of a regional gradient, however, it is not clear that a gradient does in fact exist. Further, there should be consideration of meteorological data during the time period of the study, rather than assuming (based on previous work) that the snow represent ~50% of the annual precipitation.

As mentioned above, the Zatzko et al. modeling study could give some context here as well. One possibility not considered here could also be that snow sourced emissions of NO_x from the interior result in deposition of nitrate along the coast with a low d₁₅N value reflecting the large photolytic fractionation.

BGD

Interactive
comment

Printer-friendly version

Discussion paper



Page 14, line 32: remove “while”, the latter part of the sentence supports the former part.

Page 15, line 12: what is gas phase aerosol NO₃-? and what is this assumption here of the difference in ¹⁵N based upon?

Section 4.3.2: the terminology throughout the manuscript needs to better reflect the difference between post-dep loss versus recycling of nitrate.

Page 16, line 20: While Geng et al. do assert this it is based upon an assumption about the NO_x source d¹⁵N values. The more recent work by Walters et al. (already cited here), Fibiger and Hastings (2016) and Miller et al. (JGR, 2017) suggest very different source values than that compiled by Geng et al. making this assumption not valid.

Page 17, line 14: Morin’s study was in coastal Arctic location, not on the ice sheet? Their data should be relevant for comparison to the coastal data here.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-140>, 2017.

Printer-friendly version

Discussion paper

