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Interactive comment on "Spatial variations in snowpack chemistry and isotopic composition of NO$_3^-$ along a nitrogen deposition gradient in West Greenland" *by* Chris J. Curtis et al.

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RESPONSES TO REVIEWER2

In response to comments from both reviews posted, we have added a new introduction and discussion based on additional relevant literature as suggested by the reviewers. We take the point that there is scope for confusion in our use of the term "gradient" given that the geographically central Kellyville sites represent one end of the data points in terms of deposition and isotopes. However our results show that there are very few significant differences between the two inland regions (KV, IS) while both differ from the coastal snowpack in the same direction (higher δ15N and Δ17O; lower

nitrate concentrations etc). We will therefore amend our title and heading accordingly to reflect instead the comparison of coastal with inland sites rather than implying a linear gradient.

RC2.1 Comparison with seasonal snowpack at Summit

We maintain that we do provide a comparison with seasonal snowpack at Summit as this forms a key part of our argument about the importance of postdepositional processing (see Discussion Section 4.1 where we cite numerous studies which measured recent firn and seasonal snowpack on the Greenland ice sheet and elsewhere, including Fibiger et al 2016). We thank Reviewer 2 for drawing our attention to the fact that our $\Delta17O$ data are remarkably similar to those of Kunasek et al (2008) from snowpits at Summit, who found $\Delta17O$ ranging from 22.4 ‰ in summer (compare our study where summer rainfall = 20.6-23.1 ‰ to 33.7 ‰ in winter (30.8-34.4 ‰ in our seasonal snowpack). We further note that our data are very similar to those from Alert, Canada and Barrow, Alaska reported in Morin et al (2008, 2012).

Furthermore, in Section 4.3.3 we specifically compare seasonal snowpack from Summit with our data and indeed cite the $\delta15N$ value of -10 ‰ from the Hastings et al (2004) study (p17, L18). Like Reviewer 2, we were also struck more by the similarities between our seasonal snowpack and the winter/spring data from Summit snow, and further attribute differences between our seasonal snowpack (winter only) and ice core records with the fact that ice cores resolved annually include much less depleted summer precipitation; p17 lines 26-7). Hence we agree with the reviewer, and in fact do argue, that there is little evidence for spatial differences in the nitrate isotopic composition of the falling snow across the "gradient" (coast to ice sheet) but that there are spatial differences in how the snowpack nitrate is processed – hence the gradient or spatial pattern is one of differential postdepositional processing linked to snowpack accumulation and other climatic factors. However, to clarify the comparisons we will subdivide the discussion into comparisons with seasonal snow and comparisons with ice core records. The relevance of comparisons with ice core records (rather than just

modern snowpack) relates to the wider scope of our project looking at N deposition and isotopic composition as drivers of change in palaeolimnological records.

RC2.2 Postdepositional processing (with new section for Introduction)

We thank the reviewers for drawing our attention to the additional and more recent literature on postdepositional processing – particularly since we feel that it strengthens our interpretation of the data.

NEW TEXT: The processing of nitrate in deposited snowpack, termed postdepositional processing, occurs at the air-snow interface and may entail losses and in situ cycling of nitrate, with different impacts on both net deposition fluxes and isotopic fractionation depending on their relative importance (Frey et al., 2009; Geng et al., 2015; Fibiger et al., 2016). Nitrate may be released back to the atmosphere by desorption and evaporation as HNO3, often termed 'physical' losses (Mulvaney et al., 1998; Berhanu et al., 2015), or by photolysis (sometimes referred to as photodenitrification) (Frey et al., 2009). Photolysis of snowpack nitrate by UV radiation produces NOx, which may then undergo various processes which differ in relative importance depending on local conditions. NOx may be; 1. re-emitted from the snowpack and transported away from the area, depending on wind speed; 2. redeposited by dry deposition; 3. reoxidised back to nitrate and redeposited (re-adsorption or dissolution) (Frey et al., 2009). Erbland et al. (2015) define "nitrate recycling" as the net effect of nitrate photolysis (producing NOx), following atmospheric processing and oxidation to form atmospheric nitrate, and the local redeposition (wet or dry) and export of products. Recycling may also include redeposition of directly emitted HNO3 (Erbland et al., 2013). Hence both physical and photolytic processes may lead to effective net losses of nitrate from the snowpack if products are transported away from the location, but a proportion may be recycled and hence does not result in net removal from the snowpack, although such recycling can progressively modify isotopic signatures of the nitrate. Photolysis is associated with large fractionation of both N (15ÆŘ between -48 and -56 ‰ and O (18ÆŘ = -34 ‰ which both tend to increase δ15N and δ18O in the remaining snowpack nitrate if the

NOx produced is removed from the system (Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2015; Geng et al, 2015). In situ recycling of nitrate can also reduce $\delta 18O$ and $\Delta 17O$ due to oxygen isotope exchange with water (Frey et al., 2009; Shi et al., 2015), which has a different isotopic signature from atmospheric oxidants. This means that the negative 18ε is not expressed in the residual snow nitrate and, in fact, the apparent overall oxygen isotope fractionation can be positive (between 9 and 13 ‰ Berhanu et al., 2015). However, the depth-integrated $\delta 15N$ remains constant if there is no net loss of nitrate, hence $\delta 15N$ is deemed a more reliable indicator of net postdepositional losses than oxygen isotopes (Geng et al., 2015; Zatko et al., 2016). Much smaller (only slightly negative) fractionation constants for other processes have been derived, e.g. physical release of nitrate (evaporation) but studies in the Antarctic by Erbland et al. (2013) found different experimental values at different temperatures and hence these factors are not generally transferable to regions with differing climatic regimes.

Antarctic studies have generally found photolysis to be the dominant driver of nitrate remobilisation and isotopic fractionation, while acknowledging that physical processes could play a greater role in coastal and other regions (Erbland et al., 2013; Berhanu et al., 2015). Erbland et al (2013, 2015) working in Antarctica found that fractionation in $\delta 18O$ and $\Delta 17O$ through nitrate loss and recycling was much less pronounced than $\delta 15N$ and either slightly positive or not significantly different from zero. Similar results for $\Delta 17O$ were also found experimentally by McCabe et al. (2005) and Berhanu et al. (2015). Erbland et al (2013) suggested that the small fractionation factors for $\delta 18O$ and $\Delta 17O$ in their coastal Antarctic snowpack could indicate a greater role for physical nitrate release, which does not entail oxygen exchange. Zatko et al. (2016) demonstrated that recycling of snow nitrate in Greenland, where nitrate spends a much shorter time in the photic zone, is much less than in Antarctica. They assumed that wet deposited nitrate is more likely to be embedded in the interior of snow grains whereas dry deposited nitrate on the grain surface should be more photolabile, so that in situ recycling is also a function of the form (wet vs dry) of nitrate deposited. New discussion:

role of postdepositional processing in isotopic differences between regions Since post-depositional processing occurs primarily in the photic zone of the snowpack (modelled values from 6-51cm in Greenland in the study of Zatko et al., 2016), a larger proportion of the snowpack at the inland sites must be exposed to such processing during spring, while much deeper snowpack at the coast will retain a greater proportion of unprocessed nitrate. Although dust inputs are likely to be greater at the inland sites, potentially reducing the depth of the snow photic zone, the much smaller snowpack and greater wind redistribution suggests a much greater potential overall for postdeposition processing through UV exposure and wind removal of photolysis or evaporative products than at the coast (cf. Frey et al., 2009). Frey et al (2005) found that at wind speeds of less than 3 m s-1 (as found at our coastal sites) the effects of wind-pumping were less important than diffusion; while our inland regions experience higher mean annual wind speeds of 3.6 (Kellyville) and 4.0 (ice sheet) m s-1. Furthermore, several studies of both modern snowpack and ice core nitrate (e.g. Geng et al, 2015) attribute differences in nitrate δ15N to differences in snow accumulation rate, which is consistent with results of our study showing a less-transformed snowpack nitrate signal at the coast. Frey et al. (2009) also highlighted the importance of surface and wind-driven sublimation processes in the enrichment of insoluble chemical species and the removal of volatile species. Their study, like ours, indicated smaller nitrate transformations from snowpack in higher accumulating areas at the coast compared with inland, and the analysis of Zatko et al (2016) in both Antarctica and on the Greenland ice sheet found that enrichment of snowpack nitrate was greatest in areas with the lowest accumulation rates – consistent with our data from seasonal snowpack. The modelling study of Zatko et al (2016) also indicates that up to 100% of snowpack nitrate deposition in SW Greenland is primary deposition, rather than recycled. Our data, if we assume that coastal snowpack nitrate most closely represents regionally deposited precipitation nitrate, indicate an enrichment in δ15N of 3.8 ‰ at the ice sheet and 5.6 ‰ at Kellyville, while Δ17O is 3.0 ‰ higher at the ice sheet and 3.6 ‰ higher at Kellyville, relative to coastal snowpack. The lack of a concomitant decrease in δ18O for inland snowpack

C5

suggests the postdepositional enrichment in δ15N may be due primarily to net losses from snowpack rather than in-situ recycling. Slightly higher mean values of δ18O at inland locations, while not significant, are also suggestive of fractionating losses, rather than in situ recycling which would be expected to reduce δ18O. Given that δ15N shows an increase without a concomitant decrease in Δ17O, nitrate loss rather than recycling would appear to be the dominant process at inland sites, which is consistent with the presence of a much smaller, more sublimated and wind-redistributed snowpack inland which favours removal and transport of photolytic and evaporative products rather than in situ recycling.

If the much higher δ15N values inland do indeed reflect a much greater impact of postdepositional processing on the much smaller snowpack, then it follows that the initial snowpack deposition of nitrate may have been larger, but has subsequently been reduced by photolysis and evaporation, while coastal snowpack more faithfully records the initial atmospheric inputs of nitrate.

NEW TEXT - CONCLUSIONS FOR OUR STUDY

We conclude that at our inland regions, but especially at Kellyville, lower precipitation and snowpack accumulation in combination with higher wind speeds enhances both photolytic and physical (sublimation & evaporative) losses of snowpack nitrate. Since we see a significant enrichment in δ15N but not in δ18O (inland mean values are higher, but not significantly different from the coast) we suggest that in situ recycling is less important than net losses through photolysis and wind removal of NOx. Physical losses would also lead to δ15N and δ18O enrichment of remaining snowpack nitrate without affecting Δ17O. However, we find significantly higher Δ17O at our inland sites compared with coastal sites, in combination with higher δ15N, but no difference in δ18O. The higher Δ17O found in the inland regions must therefore reflect a greater role for the O3 oxidation pathway as the source of snowpack nitrate, compared with the coastal sites.

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RC2.3 Pollutant source regions

While we do of course acknowledge that there may be major differences in pollutant source regions across Greenland, in particular from the coast to the interior, the spatial scope of our study is very small relative to the size of the ice sheet and the modelled gradients shown by Zatko et al (2016). Hence we would argue that while differential source regions cannot be ruled out, our study areas are actually very close to each other relative to distances from source regions. Perhaps the most striking result is the similarity of our coastal isotopic data (both δ15N and Δ17O in seasonal snowpack but also in the summer rain samples) with studies much further afield including snowpack at Summit on the ice sheet, and atmospheric nitrate at Alert, Canada and Barrow, Alaska (Hastings et al., 2004; Kunasek et al., 2008; Morin et al., 2012; Fibiger et al., 2016). Hence it seems unlikely that differences in source region are a plausible explanation for the spatial differences in the isotopic signatures of deposited snow observed in our study.

The modelling study of Zatko et al (2016) also shows an increase in the proportional loss of nitrate through photolysis moving inland from the coast towards the ice sheet. While not directly applicable due to the lack of permanent snow cover in our study transect, their modelled enrichment of ice-core nitrate would be in the range 1-5 ‰ for the inland regions of our study and zero at the coast (Fig 11d in Zatko et al., 2016), which is entirely consistent with our findings in the seasonal snowpack.

RC2.4 Deposition estimates

Our new introductory text explaining the basis for the study should clarify why we feel it important to derive at least a first approximation of total deposition fluxes. We acknowledge that the lack of rainfall samples precludes an accurate assessment of deposition inputs but argue that we can suggest probable bounding values (min, max) with some caveats, given that rainfall represents about 50 % of total annual precipitation. Since the sparse rainfall chemistry data suggest that concentrations may differ from snow-

pack by 0.57-1.63x for nitrate, 1.42-1.72x for ammonium and 0.91-1.39% for sulphate, we will add deposition uncertainty estimates on the assumption that our rainfall data are representative of total rainfall chemistry.

Other Arctic studies of seasonal atmospheric nitrate have generally indicated lower summer concentrations than spring, when maxima are generally seen (e.g. Morin et al., 2012), although Dibb et al (2007) found nitrate maxima in June snowpack. Comparing our assumed snowpack accumulation period of October to March, the monthly data of Dibb et al (2007) show mean values over this period which are very close to the annual means presented for Summit. Hastings et al (2004) found mean nitrate concentrations were highest in spring and summer, while Burkhart et al (2004) found no clear seasonality.

Reviewer 2 Detailed comments:

RC2.5 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.

Response: Text will be reworded accordingly.

RC2.6 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.

Response: Additional introductory text has been provided and contrasting text reworded.

RC2.7 Methods, page 3, line 23 - assume 100 m should be 100 cm?

Response: No, 100 m is correct, this figure is our spacing of snowpack depth measurments around the catchment transects.

RC2.8 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?

Response: $\delta(15N)$ and $\delta(18O)$ values were determined using the standard denitrifier method with N2O as analyte gas (Casciotti et al. 2002). $\Delta(17O)$ was determined using the thermal decomposition method with O2 as analyte gas (Kaiser et al. 2007). $\delta(15N)$ values have been corrected for isobaric interference of N217O (Kaiser & Röckmann, 2008), using the $\Delta(17O)$ measurements. The standard deviations represent analyses in duplicate. As stated in section 2.3, we used 10 nmol of NO3– for isotopic analyses.

RC2.9 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.

Response: By homogenous we meant evenly distributed on the flat lake ice surface, compared with the patchy snow cover on catchment slopes. We will re-word accordingly. We agree that we may not be comparing the same snow and propose adding new text in the Discussion as follows:

It is possible that the snow accumulated on lake ice is of a different age mix than that sampled on catchment slopes, due to differential removal and redeposition during wind redistribution. Since higher concentrations of most ions were recorded in lake-ice snowpack (significant for nitrate at the coast and Kellyville) it may be hypothesized that postdepositional losses of nitrate are enhanced in snow on catchment slopes. Such a mechanism is also supported by the isotope data whereby terrestrial snowpack has generally higher $\delta15N$ than lake ice snowpack, suggesting postdepositional enrichment. It is not possible to determine how snow has been redistributed in the current study (and in fact would be extremely difficult to measure in practice), but the consistent pattern for all lake catchments in all regions does suggest a common process operating

across the study region.

RC2.10 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, than the explanation of ammonium sulfate deposition as a "cause" of higher concentration on the coast (page 12) does not make sense.

Response: We did consider the possibility of biogenic sources of ammonium from seabird colonies, since these sites are all 2-3 km from the coast, but we have no recent data and older records indicate only very small colonies (20 pairs) within 10 km and the only sizeable colony of several hundred pairs is around 100 km away (Boertman et al., 1996). To our knowledge there are no major seabird colonies in the vicinity of the coastal sites.

We state on p12 (line 16) that NH4+ (17 mol ha–1 a–1) and non-seasalt SO42– (22 mol ha–1 a–1 as $\frac{1}{2}$ SO42–) are similar in charge equivalent terms; we have already accounted for the sea-salt excess (from sea-spray aerosols) of sulfate (total SO42– is more than 4x nssSO42–). The high correlation between NH4+ and nssSO42– in coastal snowpack suggests they are largely co-deposited. We therefore stand by our assertion that (NH4)2SO4 aerosols could contribute to the higher loads of NH4+ and SO42– at the coast.

RC2.11 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).

Response: We have added additional discussion of the Fibiger and Kunasek papers – thank you for the suggestion. We stated in line 25 that the discussion of a possible role for ODEs is speculative, but other major ions certainly do indicate a much greater marine influence at the coast. Given the additional discussion of the $\Delta 17O$ data above we acknowledge that other factors could also affect the relative importance of different oxidants at the coast relative to inland regions. We do though feel that we should at least suggest possible mechanisms for the differences in $\Delta 17O$ observed. We have added additional text on comparing the seasonal snowpack from Summit, specifically for $\Delta 17O$ data. We have also added additional justification for comparing with ice core data.

RC2.12 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.

Response: We agree there is scope for confusion and will remove this sentence.

RC2.13 Page 14, line 16: What is Fibiger and Hastings (2016)? It is not included in the reference list.

Response: We have added the missing reference to the reference list (see below).

RC2.14 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 Zatko et al. modeling study could give some context here as well. One possibility not considered here could also be that snow sourced emissions of NOx from the interior result in deposition of nitrate along the coast with a low d15N value reflecting the large photolytic fractionation.

Response: We do not have data for the prevailing transport patterns to either the coastal or inland locations, but we briefly discuss this issue in Section 4.3.1. A detailed discussion on this topic is beyond the scope of this paper, but we suggest to add the following text:

Kahl et al (1997) argue that trajectories to Summit on the ice sheet are similar to Dye 3 in south Greenland (Davidson et al., 1993), and that in winter, 94% belong to westerly transport patterns (in fact moving from SW coastal zones NE onto the ice sheet). Geng et al (2014) assume the dominance of N American pollutant sources at Summit. For our sites in SW Greenland it appears that similar long-range source areas would apply. Alternative approaches (lake sediment records of Pb isotopes) have indicated that European sources are also important contributors to pollution across the region (Bindler 2001a, b), while the modelling study of Zatko et al. (2016) suggests that our study region is an area of wind convergence with air flow mainly from the interior down to the coast. Hence there is no clear indication in the literature of the key local source regions affecting our study areas, but some evidence that coastal and inland areas are likely to be exposed to similar long-range sources. It is an interesting suggestion that snow-sourced (photolytically released) emissions from the interior with low δ15N could contribute to low snowpack δ15N in our study, but such a process alone would not explain the higher δ15N values at Kellyville compared with those closer to the ice sheet and at the coast; we would still have to invoke postdepositional processing.

While we believe we have convincing evidence (in terms of precipitation, snow accumulation, wind speed, temperature etc) for increased postdepositional processing inland, we have no evidence to suggest there are likely to be major differences in source re-

gions for our study areas – especially given the similarities between isotopic signatures and concentrations in the coastal snowpack and from winter snowpack at Summit, and the location of our inland sites between the coast and the ice sheet. Our proposed 'gradient' of increased postdepositional processing moving inland from the coast is also entirely consistent with the modelling study of Zatko et al. (2016). See new text above under "Pollutant source regions"

RC2.15 Page 14, line 32: remove "while", the latter part of the sentence supports the former part.

Response: word removed

RC2.16 Response: Page 15, line 12: what is gas phase aerosol NO3-? and what is this assumption here of the difference in 15N based upon?

Response: As above – will add word "gas phase and aerosol", with several new supporting references added.

RC2.17 Section 4.3.2: the terminology throughout the manuscript needs to better reflect the difference between post-dep loss versus recycling of nitrate.

Response: Will be done, as per new text and revisions provided above.

RC2.18 Page 16, line 20: While Geng et al. do assert this it is based upon an assumption about the NOx 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.

Response: We will remove this sentence.

RC2.19 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.

Response: Thanks for the correction. Morin et al.'s study was at Alert, Canada and

they compared with Summit data. We have amended the text accordingly. As pointed out, they are also reporting coastal data albeit from much further north. We have also added discussion of the later paper by Morin et al (2012) comparing data from Alert and Barrow (Alaska). We are again struck by the similarities with our own coastal data, indicating much larger scale regional similarities in nitrate isotopic composition and strengthening our argument about postdepositional processing as the most likely driver of spatial differences in our study.

Additional references to be added to the manuscript and cited above:

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Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2017-140/bg-2017-140-AC2-supplement.pdf

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