We thank the reviewer for their supportive and constructive comments on the manuscript. We feel that the paper has been improved by the review process. Below, we address each of the reviewer's specific and technical line-by-line comments. The reviewer comments are in black text, while the responses are in *blue italics* and new text added to the manuscript is in blue.

Specific comments from Reviewer 1:

Line 18: Here in the abstract authors mention that the major NOx source in low latitude region is lightning based on d15N, whereas in line 299-305 they conclude that the possible NOx source includes other natural sources such as biomass burning and soil emission. Biomass burning and soil microbes can supply NOx with d15N of -7 to 12 ‰ (Fibiger and Hastings, 2016) and -60 to -14 ‰ (Miller et al., 2018), respectively. Thus it would be difficult to rule them out from possible sources based solely on d15N. The abstract should be corrected to be consistent with discussion.

*The abstract has been edited to be consistent with the discussion of potential sources at the low latitudes as follows: "*Based on δ^{15}N-NO_3^-, the dominating primary NO_x sources were likely a combination of lightning, biomass burning and/or soil emissions at the low latitudes, as well as oceanic alkyl nitrates and snowpack emissions at the mid and high latitudes, respectively.*"*

Line 94-95: Theoretical mechanistic of non-mass dependent isotope signature in ozone is thought to originate from the stabilization step of asymmetric molecules of excited ozone (O3*), as mentioned in Ireland et al. (2020) and initially proposed by Heidenreich and Thiemens (1986). It is not believed to be associated with photochemistry. Please revise the explanation accordingly.

*The explanation of the origin of the non-mass dependent isotope signature in ozone has been revised as follows: "*Non-mass dependent fractionation occurs in the troposphere and is thought to originate from asymmetric molecules of excited ozone (O_3*) that lose excess energy via stabilisation to product O_3 (Heidenreich & Thiemens, 1986; Ireland et al., 2020).*"*

Line 103: "a lack of exchange of O atoms with O3" is not correct expression because formation of nitrate is not equilibrium reaction, unlike the case of isotopic exchange between H2O and OH. I suggest rephrasing to "increased contribution from other oxidants".

*A lack of exchange of O atoms with O3, has been rephrased to "*increased contribution from other oxidants*".*

Line 166: The authors report that field blanks represented 32% and 59% of the NO3- on sample filters in winter and spring respectively. While they corrected concentration measurements for these field blanks, there is no mention about corrections of isotopic measurements. To mitigate the potential impact of blanks, it is common to collect an excessive amount of nitrate relative to the blank on each filter, or to measure isotopic compositions of the blanks to correct those of samples (e.g., Savarino et al., 2007). But in this manuscript, authors conducted ~24 hours sampling to obtain higher temporal resolution, which resulted in small nitrate loadings on the filters. What is source of the field blanks, and would it be possible to discount the significant impact on isotopic signatures?

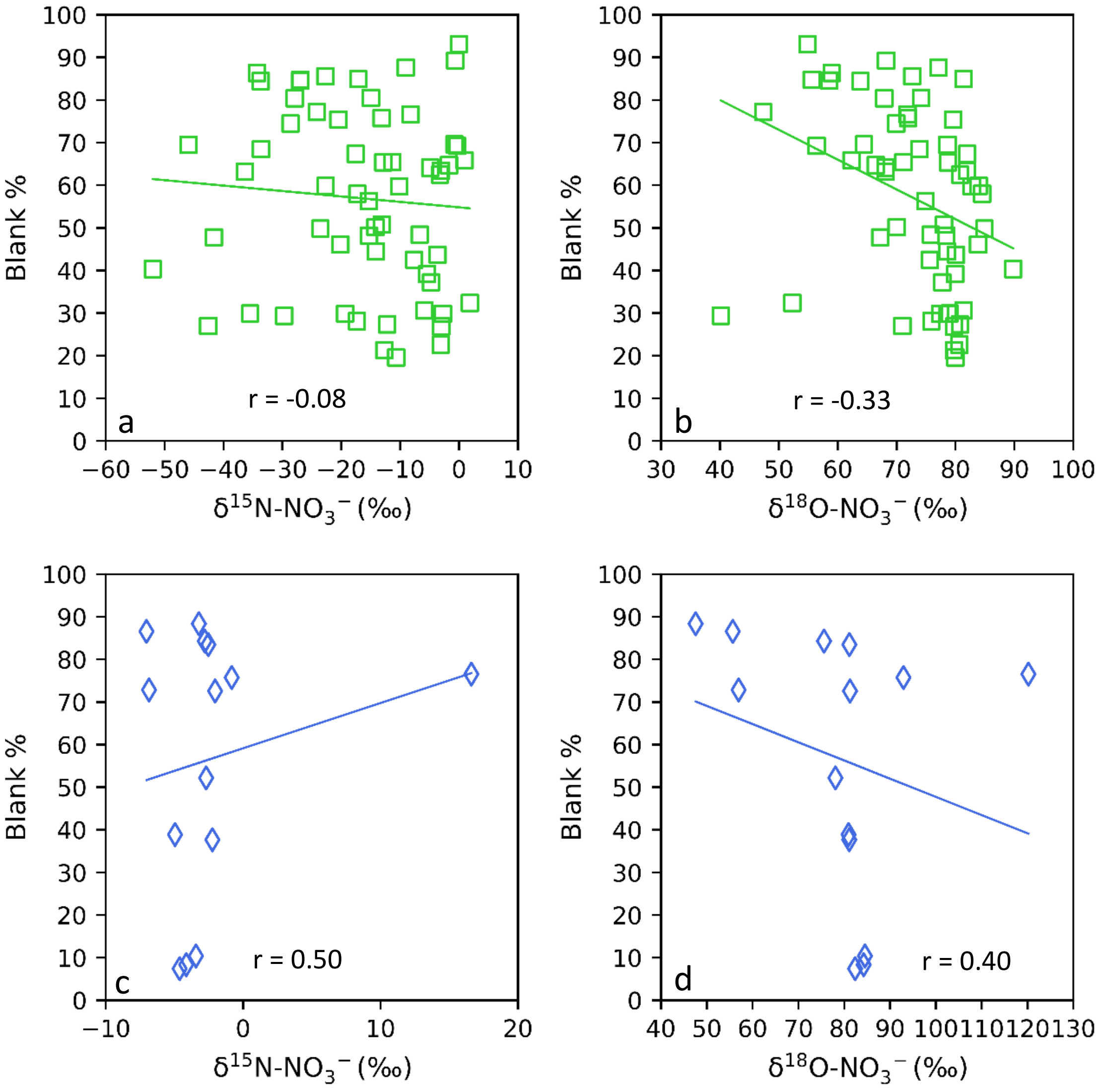
Is it possible to assume isotopic signatures of the blanks? Even if not, the potential impact and the assumption made for the later interpretation should be carefully addressed.

The amount of nitrate on each stage of the field blank filters is roughly similar (e.g., average of 214 and standard deviation of 41 nmols per filter across stages 1 through 4). The spring and winter sample concentrations are much lower than the summer concentrations, therefore the percentage contribution of the blank to the total signal is larger in spring and winter. In order to facilitate a seasonal comparison, it was important to not increase the number of sampling hours too much from summer to winter to spring. The blank extract concentrations were all less than 1.5 μM, therefore we did not have enough volume to measure the isotopic composition directly.

In evaluating the potential sources of the blank, we concluded that it was unlikely to have a vastly different $\delta^{15}N$ *than the sample nitrate for several reasons. First, and importantly, in the figures below the percent contribution of the blank vs.* $\delta^{15}N$*- and* $\delta^{18}O\text{-}NO_3^-$ *for spring and winter show no significant relationship indicating that the measured signal is not being driven by a blank. Second, the sodium and chloride values are not unusually high in the blank filters, which lead us to conclude that there was no contamination with seawater. There is also not an unusually high value for sulfate, which makes us confident that ship stack emissions are not the source of the blank.*

Finally, the coarse mode $\delta^{15}N$ *is a mass weighted average of stages 1 through 4 for each filter deployment. As a result, samples where the blank is a high proportion of the total signal result in low sample nitrate concentrations, and that stage will then have a relatively low influence on the resulting mass weighted average d15N. If the blank was greater than the sample concentration for a given stage that value was not used in the mass weighted average* $\delta^{15}N$*.*

*This is now noted in section 2.2.2: "*It is important to note that given the low [NO_3^-] of the field blanks (< 1.5 μM), no isotopic analysis could be performed on the blank filters and therefore the blank was not subtracted from the isotope results. However, we note that there was no relationship found between the blank percent contribution and $\delta^{15}N$- or $\delta^{18}O\text{-}NO_3^-$ for spring and winter. This indicates that the measured signal is not driven by the blank contribution.*"*



The blank percentage of sample (Blank %), versus $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in spring (a and b, respectively) and winter (c and d, respectively).

Line 200: Is 72-hour AMBT enough to trace NOx source? I would expect any references or discussion to certify the lifetime of nitrate for 72-hours.

Estimates for the atmospheric lifetime of nitrate in the atmosphere range from about 3 to 5 days (Lu et al., 2021). The spatial uncertainty associated with the location of HYSPLIT generated air mass back trajectories increases the further back in time they are used. It was therefore necessary to use the most conservative time frame, while still ensuring that the lifetime of nitrate in the atmosphere is accounted for. Therefore, a lifetime of 3 days was chosen. In certain cases, i.e., at the lower latitudes near coastal Southern Africa, some 120 day air mass back trajectories were analysed to ensure that even for the upper range of nitrate atmospheric lifetime estimates, no continental influence was experienced near South Africa. In the case of the mid and high latitudes, using 120 hour air mass back trajectories made no difference to the interpretation of the results and thus it was decided to use the most conservative air mass back trajectory path length.

*We have now included references in the methods section 2.3 where the nitrate lifetime is stated, and explained why we used the lower estimate of the nitrate lifetime range for plots of air mass history, as follows: "*Model estimates of the atmospheric lifetime of NO_3^- range from approximately three to five days (Lu et al., 2021). AMBTs become increasingly uncertain the further back in time they are used (Sinclair et al., 2013). To minimize this uncertainty, the shortest possible AMBTs are generated while still accounting for the lifetime of NO_3^- (i.e., 72-hours). Daily 120-hour AMBTs computed for the duration of each voyage were additionally computed (Fig. SX), to confirm that even when utilising the maximum estimate for NO_3^- atmospheric lifetime, no continental influence from southern Africa is expected.*"*

We have also included an additional supplementary figure which shows 120 hour AMBTs computed for each hour of every voyage, to confirm the lack of influence from continental Southern Africa.

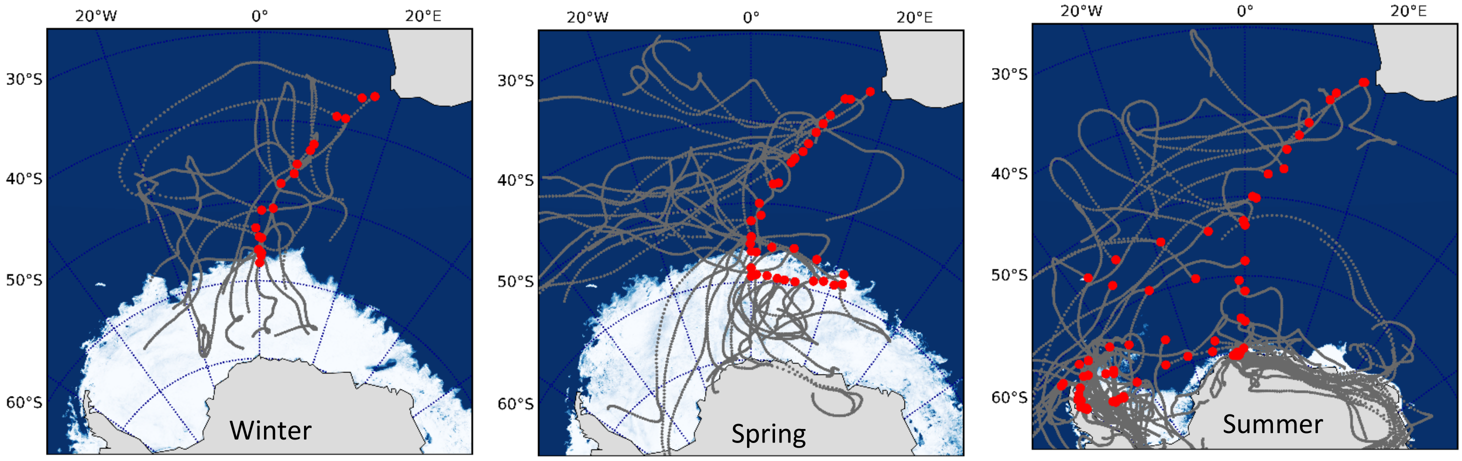


Figure S6. 120 hour AMBTs (grey) computed for each hour of the research voyage conducted in winter, spring and summer respectively. Red circles denote the location of the ship at each hour and represent the cruise track.

Line 256: I did not see any discussion about potential influence of isotopic fractionation on d15N through NOx oxidation, even though authors points to it in the introduction (Line 81-83). To appropriately convey the limitations of their approach appropriately, I believe the authors need to address how they assumed minimal or negligible influence by isotopic fractionation in their interpretation.

We agree with reviewer 1 that some explanation of why we assume minimal or negligible isotopic fractionation during NO_x oxidation is required. In remote environments where Ozone concentrations largely exceed NO_x concentrations (such as open ocean environments), NO_x isotopic exchange occurs at a much slower rate than the Leighton Cycle reactions, such that little to no equilibrium isotope fractionation is expressed, and the $\delta^{15}N$ of nitrate is assumed to reflect the $\delta^{15}N$ of the NO_x source (Walters et al., 2016).

*This explanation is now included in the text as follows: "*In remote environments where O_3 concentrations largely exceed NO_x concentrations, as is the case for the remote Southern Ocean, NO_x isotopic exchange occurs at a much slower rate than the Leighton Cycle reactions. Therefore, little to no equilibrium isotope fractionation is expressed, and the $\delta^{15}N$ of NO_3^- is assumed to reflect the $\delta^{15}N$ of the NO_x source (Walters et al., 2016).*"*

Line 391: What is meant by “prior work” here? I perceive that the authors are assuming that the influence of isotopic fractionation on d18O through NOx oxidation is insignificant, and therefore d18O-NO3- directly reflects d18O of oxidants. This is an important point to interpret D17O vs d18O plots later. I would suggest including references or discussion to support this assumption.

*Here we are making the assumption that the $\delta^{18}O$ of various oxidants are known and directly reflected in the formation of nitrate. Previous studies similarly make the same assumption, and these studies are now cited in the text. The text has been updated to: “*These differences allow us to qualitatively assess NO and NO_2 oxidation chemistry involving contributions by various oxidants. Similarly to previous work conducted in the Southern Ocean MBL and in Antarctica (Walters et al., 2019; Shi et al., 2021), we make the assumption that oxidant $\delta^{18}O$ values are known and directly represented in the NO_3^-.*”*

Line 416 and Figure 6: I am confused by the apparent inconsistency in the isotopic composition of ozone as reported in the text and plotted in the figure. While the text states “a δ18O of ~114 to 138‰”, the O3-endmember is plotted around d18O of ~110‰ in Figure 6. I am unsure of how the authors employed the lowest value of possible variation in d18O of ozone. In case of D17O, ozone end-member is estimated to be 37 to 39‰ based on experimental studies determining transferring factors of O3-term to products for NO + O3 (Savarino et al., 2008) and NO2 + O3 (Berhanu et al., 2012). Would it be possible to do similar calculation for d18O? Or, is there another reason for d18O of ~110‰ in Figure 6?

We thank the reviewer for alerting us to this error. The O3-endmember should be plotted around a $\delta^{18}O$ of ~114‰, not 110‰. This figure has now been corrected.

Technical comments:

I would suggest combining Figures 2, 3, and 5 so readers can refer to information of concentration, d15N, and d18O of each sample at once.

Both reviewers have recommended that we combine figures 2, 3 and 5, with the second reviewer suggesting that we include Figure S3. As such, we have created a single figure with 4 panels as seen below.

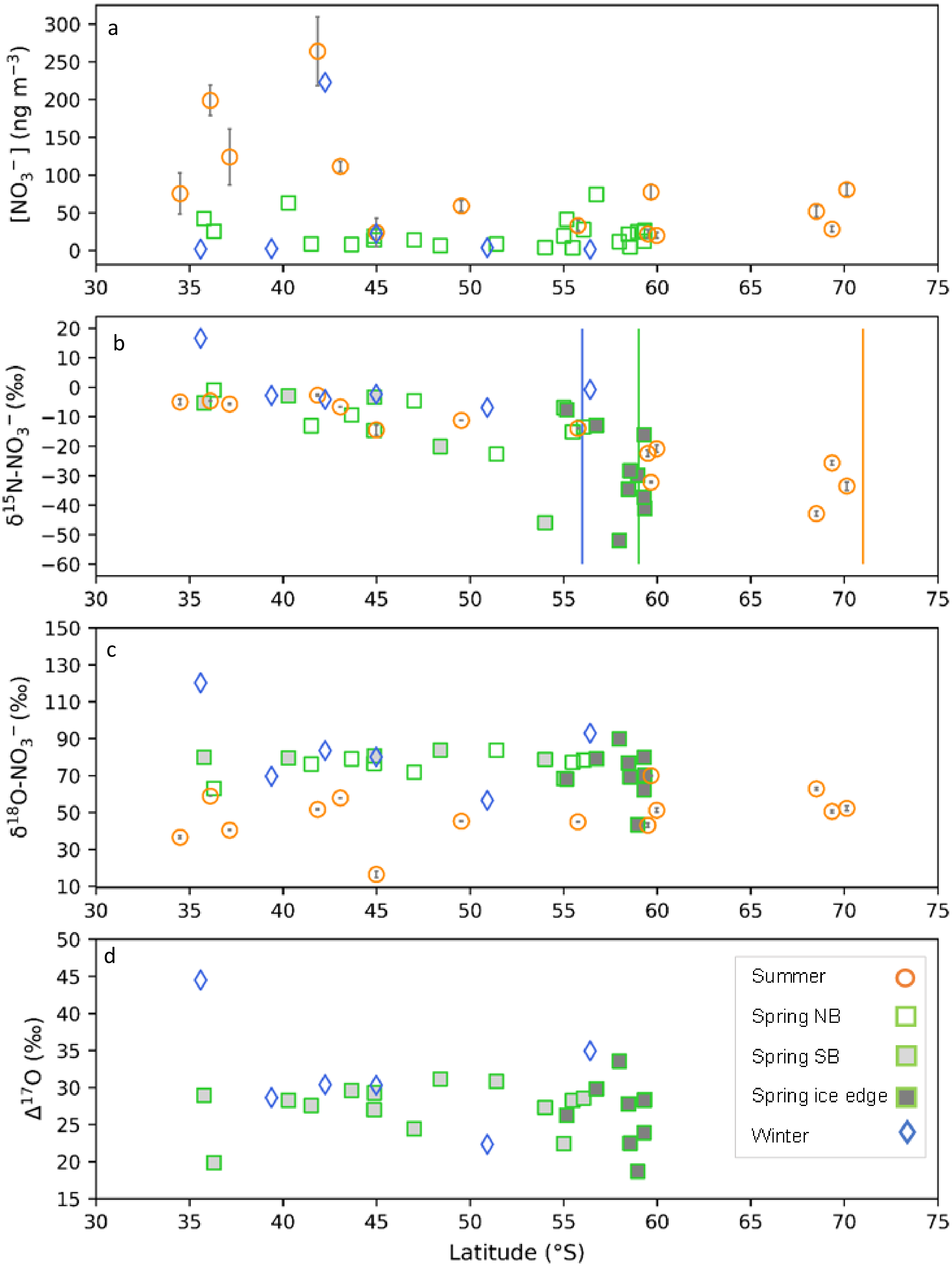


Figure 2. The average coarse mode (> 1 µm) atmospheric nitrate concentration [NO$_3^-$] (ng m^{-3}) (a), weighted average δ^{15}N of atmospheric nitrate (δ^{15}N-NO$_3^-$ (‰ vs. N$_2$)) (b), δ^{18}O of atmospheric nitrate (δ^{18}O-NO$_3^-$ (‰ vs. VSMOW)) (c) and Δ^{17}O of atmospheric nitrate (Δ^{17}O-NO$_3^-$ (‰)) (d) as a function of latitude (° S). Winter, spring and summer are denoted by blue diamonds, green squares, and orange circles, respectively. For the summer data, where error bars (± 1 SD) are not visible, the standard deviation is smaller than the size of the marker. Spring data are separated into northbound (NB), southbound (SB) and ice edge legs by clear, light grey

and dark grey fills, respectively for panels b-d. Vertical lines indicate the approximate location of the sea ice edge in summer (orange), winter (blue) and spring (green), identified visually using satellite derived sea ice concentration obtained from passive microwave sensors AMSR2 (Advanced Microwave Scanning Radiometer 2; Spreen et al., 2008)

Line 22, 261, and 488: The term “stratospheric NOx” sounds not proper. Nitrogen is transported from the stratosphere in the form of nitrate or nitric acid, not NOx. I would suggest rephrasing as “stratospheric nitrate”.

In all instances, the term “stratospheric NO_x*” has been rephrased to* “stratospheric NO_3^-*”.*

Line 68: “from” -> “form”.

This grammatical error has been corrected.

Line 142: I presume “exceed 0 m s-1” is “exceed 1 m s-1”.

“> 0 m s^{-1}*” has been replaced with* “> 0.5 m s^{-1}*”, the lowest wind speed recorded by the data logger.*

Line 156-195: Section 2.2.1 Isotopic analysis includes description of sea water sampling and its nitrite concentration measurement. To improve the construction, I suggest dividing section 2.2 to three small sub-sections as:

Line 157-170 -> 2.2.1 Concentration analysis

Line 171-190 -> 2.2.2 Isotopic analysis

Line 192-195 -> 2.2.3 Sea water sampling and nitrite concentration analysis

Section 2.2 has been separated into 3 subsections to improve the constructions of the section (i.e., 2.2.1 NO_3^- *concentration analysis, 2.2.2 Isotopic analysis and 2.2.3 Sea water sampling and* NO_2^- *concentration analysis).*

Line 168: “(Sect. 2.3)” should be matched with the appropriate section number.

Sect. 2.3 has been updated to the appropriate section number, Sect. 2.2.2.

Line 206: A sentence “During…Southen Ocean.” is not necessary.

This sentence has been removed.

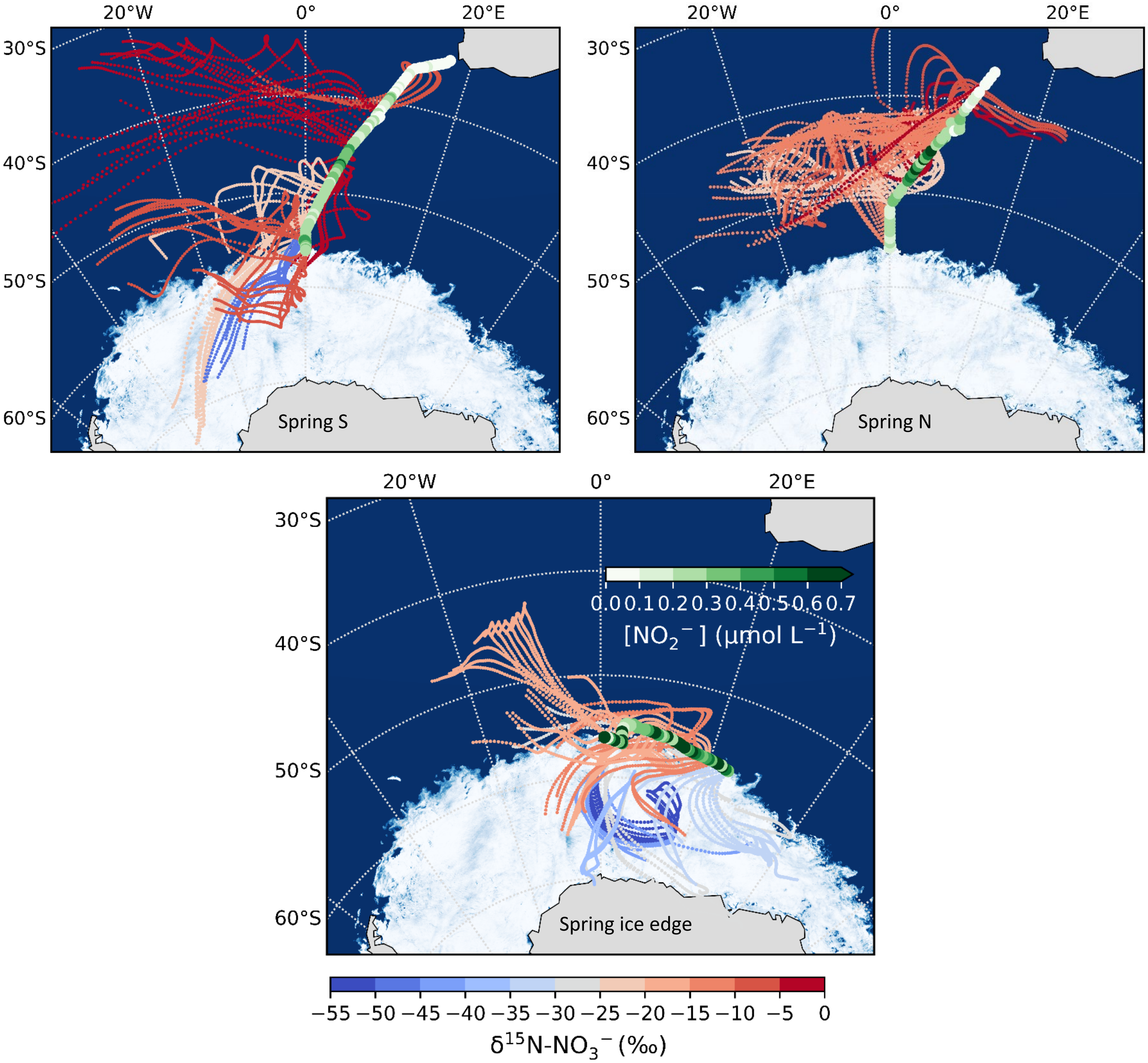
Line 221: “ice edge transect (d)” and “northbound voyage (e)” may be reversed. I see

Figure 1e shows ice edge transect voyage.

This error has been corrected. Each panel of Figure 1 now includes a descriptive label e.g., ‘Spring S*’ to denote the season and southbound leg.*

Line 335, Figure 4: The ranges of colorbars for d15N-NO3 and [NO2-] are consistent among three panels so one for each parameter is enough. I would suggest leaving three maps as is and placing two colorbars below the panel c.

Seeing as the scale of all colour bars are the same in Figure 4, only 2 will be included below panel C to avoid repetition. The updated figure is included below.



Line 438: “δ18O-H2O(v) (= -13.6 ± 1.5‰)” is inconsistent with “(-13.9 ± 1.4‰)” in Line 420. Correct either.

The $\delta^{18}O\text{-}H_2O_{(v)}$ value in line 438 has been corrected so that it matches the value in line 420 (-13.9 ± 1.4‰), which is the right value.

Line 444: “d18O” -> “δ18O”

This has been corrected.

Citations that were not in the original manuscript:

The below citations have now been included in the manuscript.

Fibiger, D. L.; Hastings, M. G. (2016) First Measurements of the Nitrogen Isotopic Composition of NOx from Biomass Burning. *Environ. Sci. Technol. 50* (21), 11569–11574.

https://doi.org/10.1021/acs.est.6b03510.

Heidenreich JE III, Thiemens MH. (1986) A non-mass-dependent oxygen isotope effect in the production of ozone from molecular oxygen: the role of symmetry in isotope chemistry. *J. Chem. Phys.* 84:2129–36, https://doi.org/10.1063/1.450373

Miller, D. J.; Chai, J.; Guo, F.; Dell, C. J.; Karsten, H.; Hastings, M. G. (2018) Isotopic Composition of In Situ Soil NOx Emissions in Manure-Fertilized Cropland. *Geophysical Research Letters*, *45* (21), 12,058-12,066. https://doi.org/10.1029/2018GL079619.

Savarino, J.; Bhattacharya, S. K.; Morin, S.; Baroni, M.; Doussin, J.-F. (2008) The NO+O3 Reaction: A Triple Oxygen Isotope Perspective on the Reaction Dynamics and Atmospheric Implications for the Transfer of the Ozone Isotope Anomaly. *J. Chem. Phys. 128* (19), 194303. https://doi.org/10.1063/1.2917581.