

General Comments

In this paper the authors present a very interesting and unique set of data on the isotopic composition of coarse mode atmospheric nitrate in the Southern Ocean marine boundary layer. The data were derived from latitudinal transects as well as sampling near the Weddell Sea and Ronne-Filchner Ice Shelf. The authors combined their isotopic measurements of aerosol nitrate with air-mass back trajectory (AMBT) analysis to determine the major sources of NO_x contributing to nitrate aerosols in the Southern Ocean. The paper is well written, the data are clearly presented, and the conclusions derived from the study are well supported, with the possible exception of the estimated $\delta^{15}\text{N}$ signature of oceanic nitrate emissions (see below). I discuss a couple of potential technical issues with the isotope measurements below. I also think that the authors can do more with their dataset – it seems a little over aggregated. For example, I am curious to know how the relationship between $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ varies in the study and if the different size fractions of aerosol had different N masses and isotopic values.

We thank the reviewer for their constructive comments and support for the manuscript. 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*.

Specific Comments:

Lines 88-131. This is a very nice introduction to the main reactions affecting the isotopic composition of oxidized N in the atmosphere.

Thank you, we appreciate the reviewers' careful read of the manuscript.

Line 150-151. State the specific Tisch Environmental filter used along with its surface area. *As per the reviewer's suggestion, the specific filters used (TE-230-GF; Tisch Environmental) will be stated along with their surface area (119 cm²).*

Line 171. Ultra-clean deionized water is vague. Please state the resistance of the DI water in megaohms.

The resistance of the DI water (18.2 M Ω) will now be stated in the manuscript.

Lines 178-179. I am confused by the presentation of the filter blanks. The text states that the average amount of nitrate on a field-blank filter was 484.7 nmoles or 0.4847 μmoles (also, this value should have a standard deviation accompany it). Since the filters were extracted in 25 ml of DI water, 0.4847 μmoles of nitrate would result in a nitrate concentration of 19.4 $\mu\text{moles/liter}$ which seems very high for a blank. I suspect that only a fraction of the blank filter was extracted in DI (hence the approximately 30 cm² reference in line 172) and if this is the case it should be included in the methods section to avoid confusion.

We agree with the reviewer that the presentation of the filter blanks is confusing in its current form. To clarify, the reviewer is correct in assuming that a fraction of each filter blank (30 cm²) was extracted in 30 mL of DI. For a clearer presentation of the filter blanks, we will instead refer to the blank as a percentage of the total concentration as follows: "Final aerosol [NO₃⁻] were corrected by subtracting the field blanks, which typically represented 35% of total [NO₃⁻] on average."

Later the authors state that "The pooled standard deviation (Sp) of four repeated sample measurements for [NO₃⁻] was 0.3 $\mu\text{mol L}^{-1}$ ". Does this sentence refer to an actual aerosol sample or are the authors referring to the blank filters? If the sentence refers to blank filters, then it seems that only four blanks were run over several weeks of aerosol sampling. For context, the authors should state the range of nitrate values measured in the actual aerosol sample extracts.

The pooled standard deviation (*Sp*) of repeated sample measurements for nitrate refers to 4 actual aerosol samples that were measured in duplicate during the IC run. This was included to give an example of instrument precision for the IC system. As such, we will refer to this value ($0.3 \mu\text{mol L}^{-1}$) as the precision of the instrument as opposed to the pooled standard deviation of repeated sample measurements to avoid confusion.

We will also include the range of nitrate values measured in the actual aerosol sample extracts (1.3 to $27.7 \mu\text{mol/L}$) for context, as per the reviewer's suggestion.

Lines 188-190. I believe it is more common for investigators to use the USGS 32 isotope standard (+180 per mil) and USGS 34 (-1.8 per mil) for calibration of $\delta^{15}\text{N}$ values measured with the microbial denitrifier method. In the present study IAEA N3 (+4.7) was substituted for USGS 32 resulting in a very truncated isotopic baseline for calibration. I wonder if the authors could explain why they chose N3 over USGS 32 and if they think their $\delta^{15}\text{N}$ values are comparable to those in other papers.

While it is true that some studies use USGS32 in addition to USGS34 or IAEAN3, the literature shows a range of isotope standards used for sample correction. Ideally, the standards used (whether it is 2 or 3) have isotopic values that are similar to the upper and lower bounds of the samples analyzed. The dynamic range we observe in $\delta^{15}\text{N-NO}_3^-$ is -43.1 to 2.7‰. Unfortunately, there is no isotopic standard with a low $\delta^{15}\text{N}$ comparable to the negative values observed in this dataset. Given the values observed here, the use of a very high $\delta^{15}\text{N}$ standard such as USGS32 would possibly result in a calibration line whose slope was dictated primarily by an isotopic value that is ~ 220‰ away from the lowest observed value. The slope of the correction line would be heavily influenced by the accuracy of the USGS32 analysis, which would introduce error unnecessarily. In the end, the reference materials used here still make our data comparable with other studies, particularly atmospheric studies.

Lines 195-197. For each filter deployment, the authors weighted the isotopic values of the size fractions based on the mass of nitrate in the fractions. This seems very reasonable and it simplifies the data presentation. However, I am curious if there were any consistent mass or isotopic patterns in the size fractions. I believe a small table and a few lines of text would be quite valuable to readers.

We did not include figures showing the nitrate concentration and isotopic composition of nitrate in each size fraction because there were not clear trends with size. We will however include a table of NO_3^- concentration and $\delta^{15}\text{N-NO}_3^-$ per size fraction in the supplemental material for comparison with other size-segregated aerosol studies. The table that we will include is shown below (Table SX).

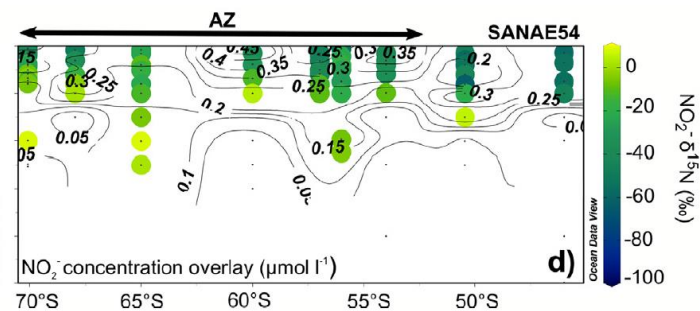
Table SX: The average (Avg) and standard deviation (SD) for atmospheric nitrate concentration ($[\text{NO}_3^-]$ (ng m^{-3})) and nitrogen isotopic composition ($\delta^{15}\text{N-NO}_3^-$) in each aerosol size range: $>7 \mu\text{m}$, 3 to $7 \mu\text{m}$, 1.5 to $3 \mu\text{m}$ and 1 to $1.5 \mu\text{m}$, separated by cruise leg: early summer (ES), Weddell Sea (WS) and late summer (LS).

	$[\text{NO}_3^-]$ (ng m^{-3})						$\delta^{15}\text{N-NO}_3^-$ (‰ vs. N_2)					
	ES Avg (SD)	n	WS Avg (SD)	n	LS Avg (SD)	n	ES Avg (SD)		WS Avg (SD)	n	LS Avg (SD)	n
$>7 \mu\text{m}$	10.7 (17.4)	7	4.1 (4.3)	20	6.9 (6.0)	7	-12.2 (11.2)	6	-14.6 (5.1)	20	-10.4 (2.7)	7
3 to $7 \mu\text{m}$	29.9 (28.9)	7	7.7 (4.9)	20	23.3 (25.7)	7	-18.8 (14.9)	7	-25.8 (9.0)	20	-13.7 (6.0)	7
1.5 to $3 \mu\text{m}$	27.1 (19.3)	7	9.4 (3.6)	20	17.9 (17.7)	7	-20.1 (16.5)	7	-24.5 (6.6)	20	-15.9 (8.3)	7
1 to $1.5 \mu\text{m}$	20.5 (6.4)	7	8.3 (3.4)	20	11.6 (6.0)	7	-19.7 (15.5)	7	-23.0 (7.4)	20	-16.7 (9.5)	7

Lines 198-200. Why were only nitrite concentrations measured in seawater (what about nitrate)? Also, it seems like isotopic measurements of ocean water NO₂ and or NO₃ would be useful for the later discussion surrounding RONO₂ as a source of atmospheric N.

Both seawater nitrate and nitrite concentration measurements were conducted during the research voyage. We only report on surface ocean nitrite concentrations in this manuscript as that is the precursor for alkyl nitrate formation. Modelling studies suggest that oceanic alkyl nitrates can only occur in regions of the ocean that possess non-zero sea surface nitrite concentrations (Fisher et al., 2018). Theory surrounding the aqueous phase chemical formation of alkyl nitrates in the surface ocean suggests no role for sea surface nitrate, therefore its concentration and $\delta^{15}\text{N}$ are not relevant here.

The N isotopic composition of alkyl nitrates in the surface ocean has never been measured, however the $\delta^{15}\text{N}$ of oceanic nitrite can be very low in the Atlantic sector of the Southern Ocean, ranging from -20 to -60‰ (Fripiat et al., 2019), as seen in the figure below taken from Fripiat et al., 2019.



One might assume that alkyl nitrates will have a very low $\delta^{15}\text{N}$ signature as a result. However, to our knowledge there are no studies that investigate the nitrogen isotope fractionation during 1) alkyl nitrate formation in the surface ocean, 2) the flux of alkyl nitrates out of the ocean, and/or 3) the formation of aerosol nitrate from atmospheric alkyl nitrates. As a result, we cannot comment on the extent to which the isotopic composition of alkyl nitrates will reflect the isotopic composition of sea surface nitrite, and this is why we did not include mention of the Fripiat study in our paper.

It should also be noted that the estimated $\delta^{15}\text{N}$ signature that we report for atmospheric nitrate, originating from surface ocean alkyl nitrates, is not necessarily an estimate of the $\delta^{15}\text{N}$ signature of the alkyl nitrate source itself. We address this issue further in the reviewers last point below and detail modifications made to the text to clarify these points.

Lines 217-219. State the latitudinal range of values used in the comparison of Weddell Sea and transect samples.

The latitudinal range of values used in comparison of Weddell Sea and transect samples will be included. The latitudinal range was 56.0 °S to 70.2 °S.

Line 229/Figure 1. Figure 1 is a good overview of the data, but I was curious about how these relationships varied when the data were disaggregated. Fortunately the authors provided a very nice table of data in the Supplemental Materials. Here are some additional graphs that I made with the data that bolster several of the authors hypotheses in the Discussion.

We thank the reviewer for their positive comments on Figure 1 and the supplementary material, as well as their use of figures in support of our hypotheses. We have decided to include the cross plot of atmospheric $[\text{NO}_3^-]$ and $\delta^{15}\text{N}-\text{NO}_3^-$ as a supplementary figure introduced at line 312, to support our hypothesis that the latitudinal gradient in lightning generated NO_x leads to higher $[\text{NO}_3^-]$ and higher $\delta^{15}\text{N}-\text{NO}_3^-$ at the low latitudes. The amended text will read: "Lightning activity at the low latitudes is

also consistent with the higher atmospheric $[NO_3^-]$ observed (Fig. 1A) and is further supported by co-occurring high $[NO_3^-]$ and relatively high $\delta^{15}N-NO_3^-$ values (Fig. SX).”

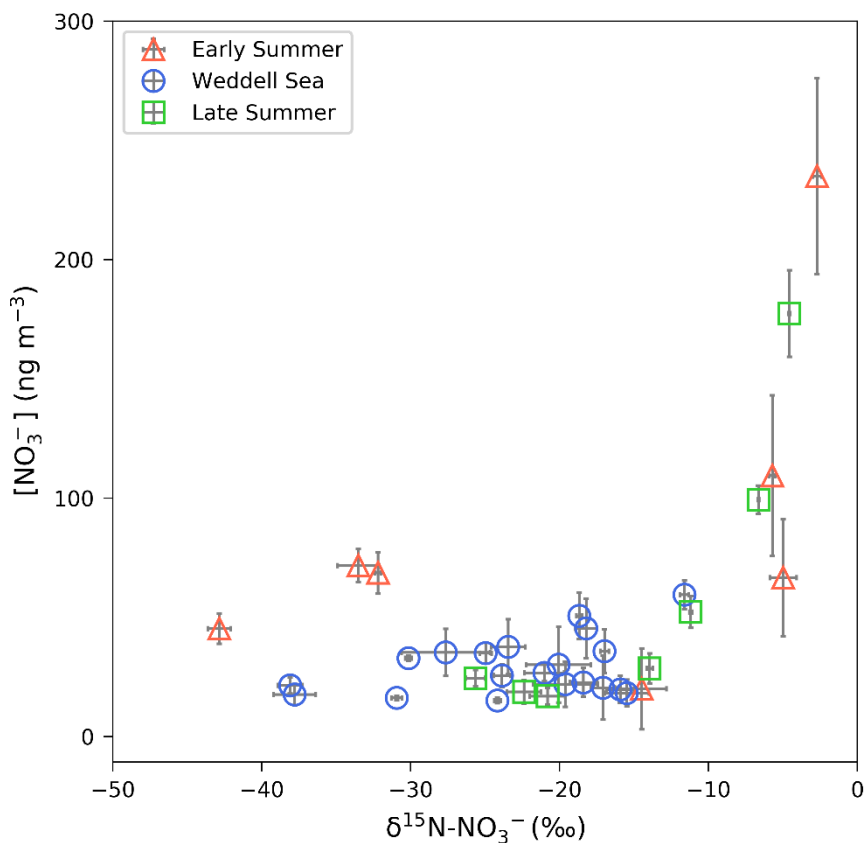


Figure SX. The average (± 1 SD) coarse mode ($> 1 \mu m$) nitrate concentration $[NO_3^-]$ (ng m⁻³), plotted as a function of the weighted average (± 1 SD) $\delta^{15}N-NO_3^-$ (‰ vs. N_2). Early and late summer latitudinal transects are denoted by the red triangles and green squares, respectively. Weddell Sea samples are denoted by blue circles. Where error bars (± 1 SD) are not visible, the standard deviation is smaller than the size of the marker.

Lines 243, 285 and elsewhere. Try to avoid the use of “very”. When stating something is high or low it is probably better to say “relatively high” or “relatively low” based on your ranges of data values.

As per the reviewer’s suggestion, we will avoid using the word “very” when trying to state that something is high/low.

Line 250. It might be useful for readers if you gave a range of NO₃ concentrations in urban airsheds for purpose of comparison.

As per the reviewer’s suggestion, we will include a range of NO₃⁻ concentrations typical of urban airsheds for comparison purposes. The first paragraph of section 4.1 will be edited as follows:

Aerosol NO₃⁻ concentrations were low (< 100 ng m⁻³; Fig. 1A) for most air masses sampled along the latitudinal transect and in the Weddell Sea, consistent with the expectation of minimal influence from anthropogenic NO_x sources. For comparison, NO₃⁻ concentrations in a polluted urban airshed over South Africa can be > 500 ng m⁻³ (Collett et al., 2010).

Line 255. How is lifetime defined?

Lifetime is defined as the amount of time the species (in this case NO_3^-) remains in the atmosphere before being removed.

Lines 265-266. Keeping the units the same might make this comparison clearer.

The units will be kept the same to make the comparison clearer. The sentence will read: “Typical O_3 concentrations observed at coastal sites in Antarctica are on the order of 20 ppbv (Nadzir, et al., 2018), whereas the sum of NO and NO_2 rarely exceeds 0.04 ppbv (Jones, et al., 2000; Weller, et al., 2002; Bauguitte, et al., 2012).

Lines 260-274. The arguments against equilibrium fractionation having a role in the isotopic dynamics of atmospheric NO_x are logical and convincing.

We thank the reviewer for their agreement with our argument in this case.

Line 281. Delete word “therefore”.

The word “therefore” will be deleted.

Line 286. I suggest changing “lightning” to “thunderstorms” and “this mechanism” to “lightning”.

Here we incorrectly reference (Savarino et al., 2007), which makes the sentence unclear. A more appropriate reference (Nesbitt et al., 2016) will be included in the manuscript and line 286 will read: “The latitudinal gradient in lightning NO_x production suggests that lightning NO_x is greatly reduced at high-latitudes (Nesbitt et al., 2016).”

Nesbitt et al., (2016) report global and seasonal distributions of NO_x production by lightning using data from the Optical Transient Detector (OTD), a space-borne lightning sensor that detects lightning flashes. We prefer not to use the word thunderstorms in place of lightning as to avoid confusion, given that some studies assess lightning produced NO_x using the observed distribution of electrical storms and cloud characteristics. In this case we believe using the word “lightning” is more accurate.

Line 299. Remove word “previously”.

The word previously will be removed as per the reviewer’s request.

Line 317. Suggest changing “unlikely to be influenced” to “likely to be less influenced”.

We thank the reviewer for the suggestion but disagree with respect to this change. It will alter the meaning of the sentence and will suggest that snow NO_x is potentially important, which we are explicitly excluding with this sentence. Please also see below.

Section 4.2.2. Based solely on the stable isotope data presented, there does not need to be more than two endmembers to explain the range of $\delta^{15}\text{N}$ values observed in the study: i) near zero per mil lightning source and ii) relatively low, -48 to -56 per mil NO_3 produced from photolysis from snow/ice. However, the authors have combined the isotope data with AMBT to gain better understanding of the atmospheric dynamics during their cruise. This analysis suggests that ocean-derived NO_x , with intermediate $\delta^{15}\text{N}$ (~-22 per mil), could be an important atmospheric source in the mid-latitude samples. They then hypothesize that RONO_2 emissions are a major source of NO_x in the Southern Ocean MBL.

I think this hypothesis needs some beefing up. First, the authors should discuss the accuracy of the AMBTs – are the models reliable in the Southern Ocean? Second, I think the authors should describe the biotic and abiotic processes that generate oceanic RONO_2 and the substrates on which these reactions rely. Third, it would be very useful to discuss both the range of $\delta^{15}\text{N}$ of the substrates (NO_2

and NO₃?) as well as the direction and magnitude of the N fractionations resulting from the production of oceanic RONO₂. While the authors did not measure δ¹⁵N of NO₂ and NO₃ in their study, there are likely other data available from the Southern Ocean to include. Basically, what I'd like to see is if it is reasonable for RONO₂ to have a δ¹⁵N of -22 +/- 7.5 per mil based on what we know about the substrates and reactions that produce it.

We thank the reviewer for their suggestions to strengthen our hypothesis regarding the oceanic RONO₂ source. To address the reviewers comments we will first discuss the accuracy of HYSPLIT modelled AMBTs in the Southern Ocean.

We agree with the reviewer that a discussion of the uncertainty/reliability of HYSPLIT in producing AMBTs is useful considering the extent to which we rely on this AMBTs information to estimate the isotopic signature of aerosol nitrate derived from oceanic alkyl nitrates.

We are aware that HYSPLIT has limitations owing to multiple factors including the spatial and temporal resolutions of the meteorological data used to force the model. The longer the back trajectory is, the less spatial coherency is observed, due to the propagation of error along back trajectories (Sinclair, et al., 2013). This can impact the accuracy of the location of each AMBT computed. According to the literature the spatial uncertainty is estimated to be 15% to 30% of the travel distance because of errors in wind fields (Sarchilli et al., 2011).

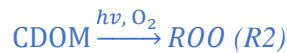
Nevertheless, HYSPLIT is a frequently used tool for assessing air mass origin in the Southern Hemisphere and over Antarctica and is used in all three of the most cited papers for comparison purposes within this manuscript (Morin et al., 2008; Walters et al., 2019; Shi et al., 2021).

Perhaps most importantly with respect to this study, knowing the location of each AMBT with exact precision is not necessary given that we are operating over such large spatial scales. For example, if air masses originate from anywhere north of 43° S they are considered to be influenced by predominantly lightning NO_x. Variation in the path of an AMBT within a zone will not change the percent contribution of the dominant NO_x source in that zone to NO₃⁻, or by extension the δ¹⁵N value that we estimate for NO₃⁻ derived from RONO₂ emissions. The accuracy of AMBTs is perhaps more influential at the high latitudes where we assess contact with sea/continental ice. Even then, if we simply assumed a threshold latitude and suggested that every AMBT located south of 70° is predominantly influenced by snow NO_x emissions, this would not change our results significantly (the δ¹⁵N-NO₃⁻ originating from RONO₂ emissions in this case would be -23.5‰ as opposed to -22‰). However, the northern edge of the sea ice is not uniform with longitude, thus we used the AMBT locations that corresponded with locations of >50% sea ice coverage in an attempt to be more accurate.

Furthermore, our AMBTs are short (72 hours), which alleviates some of the uncertainty caused by the propagation of error along back trajectories, as compared to studies with AMBTs of >5 days. We will add the following to the text to clarify the potential uncertainty associated with the AMBTs, and that this uncertainty is unlikely to influence the estimated δ¹⁵N end member associated with alkyl nitrate emissions: "Using this approach to estimate the δ¹⁵N-NO₃⁻ from oceanic RONO₂ emissions relies heavily on AMBTs generated using HYSPLIT. While HYSPLIT is a frequently used tool for assessing air mass origin in the Southern Hemisphere and over Antarctica (Morin et al., 2008; Walters et al., 2019; Shi et al., 2021), it is important to note that a spatial uncertainty of 15% to 30% of the trajectory path distance can be expected (Sarchilli et al., 2011). AMBTs also become increasingly uncertain the further back in time they are used (Sinclair, et al., 2013). Some of this uncertainty is alleviated by the fact that the AMBTs generated here are relatively short. Additionally, the spatial scale of the low-, mid- and high-latitude zones is large, such that some variation in sample AMBTs will not significantly alter the expected dominant NO₃⁻ source."

Second, a description of reactions leading to oceanic RONO₂ including the substrates of which these rely, are outlined below. In the introduction we outline that although the exact mechanism remains

unclear, experimental evidence suggests that oceanic RONO_2 production occurs via photochemical processes involving the aqueous phase reaction of RO_2 , derived from the photolysis of oceanic dissolved organic matter and NO , derived from seawater nitrite photolysis (Dahl, et al., 2003; Dahl & Saltzman, 2008).



The alkyl nitrate then fluxes out of the ocean into the atmosphere, and either undergoes hydrolysis to form aerosol nitrate or is photolyzed to NO_x , which subsequently forms aerosol nitrate.

The $\delta^{15}\text{N}$ signature of alkyl nitrate is unknown, but the $\delta^{15}\text{N}\text{-NO}_2^-$ measured in the Southern Ocean is very low (Fripiat et al. 2019). However, as mentioned in response to the reviewer above, we do not know the extent to which the $\delta^{15}\text{N}$ signature of nitrite is conserved during the various processes between its formation in the surface ocean and removal as aerosol nitrate. Therefore, based on our data we cannot comment on the $\delta^{15}\text{N}$ of alkyl nitrate itself, or if the value we estimate is consistent with expectations based on surface ocean nitrite $\delta^{15}\text{N}$. We will however clarify this in the text, and include that additional studies are necessary to constrain this value.

We agree with the reviewer that this type of isotopic analysis would be interesting and think that future research regarding the substrates and reactions that produce oceanic RONO_2 , as well as the processes that result in it influencing aerosol nitrate, would be useful to determine whether a $\delta^{15}\text{N}$ value of approximately -22‰ for RONO_2 as a source of aerosol nitrate is reasonable. This is however largely beyond the scope of our study. In light of this, we will not include text outlining the reactions involved in RONO_2 formation in section 4.2.2 to avoid repetition, as this RONO_2 formation mechanism is detailed in the introduction. We will add text to the conclusions suggesting that a mechanistic and isotopic understanding of these processes is needed from future studies as follows: “Additional research is needed to improve our mechanistic and isotopic understanding of surface ocean RONO_2 formation, flux, and conversion to aerosol nitrate in order to constrain the contribution of oceanic RONO_2 emissions to NO_3^- formation in other ocean regions where this source has been invoked, such as the tropical Pacific (Kamezaki et al., 2019).”

Line 467. I suggest replacing “unique” with distinct.

As per the reviewer’s suggestion, this sentence will now read: “Our observations across a large latitudinal gradient of the summertime Southern Ocean MBL suggest it is dominated by natural NO_x sources with distinct isotopic signatures.”