

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.

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.

Line 150-151. State the specific Tisch Environmental filter used along with its surface area.

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

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 cm^2 reference in line 172) and if this is the case it should be included in the methods section to avoid confusion. Later the authors state that “The pooled standard deviation (Sp) of four repeated sample measurements for $[\text{NO}_3^-]$ 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.

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.

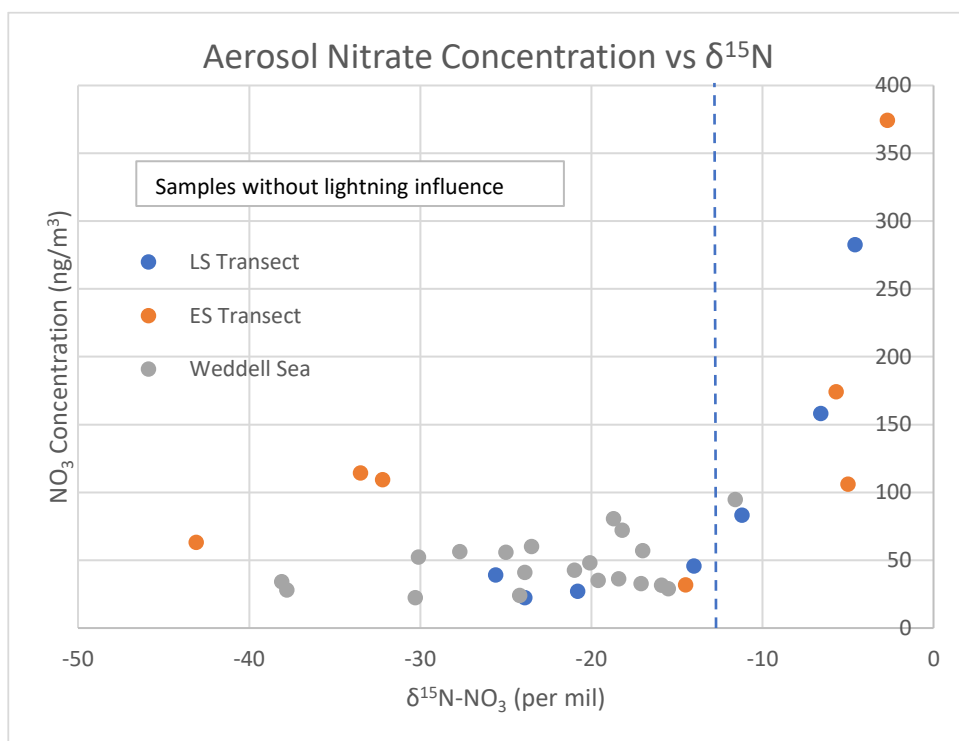
Lines 195-197. For each filter deployment, the authors weighted the isotopic values of the size fractions based on the mass of nitrate in the fractions. This seems very reasonable and it simplifies the data

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.

Lines 198-200. Why were only nitrite concentrations measured in seawater (what about nitrate)? Also, it seems like isotopic measurements of ocean water NO_2 and or NO_3 would be useful for the later discussion surrounding RONO_2 as a source of atmospheric N.

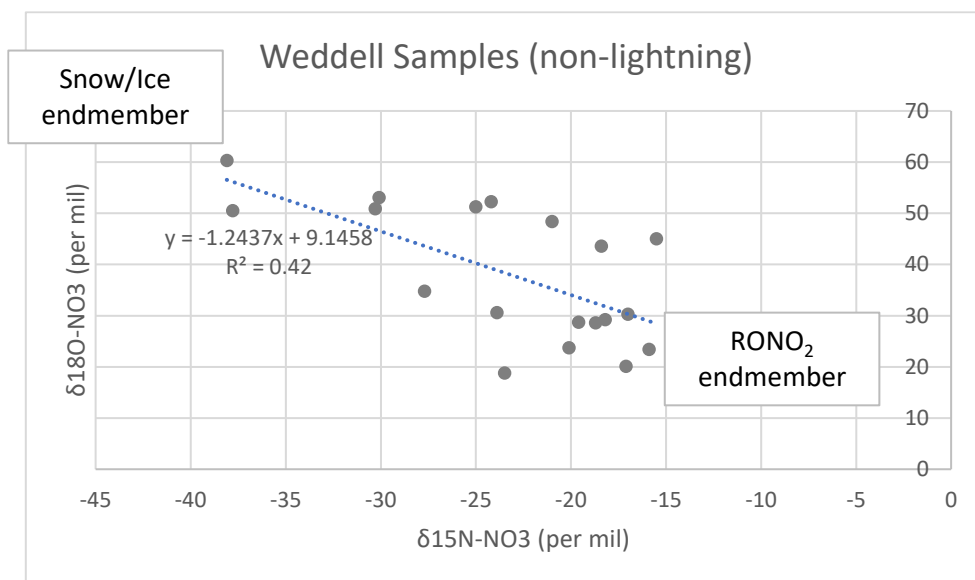
Lines 217-219. State the latitudinal range of values used in the comparison of Weddell Sea and transect samples.

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.



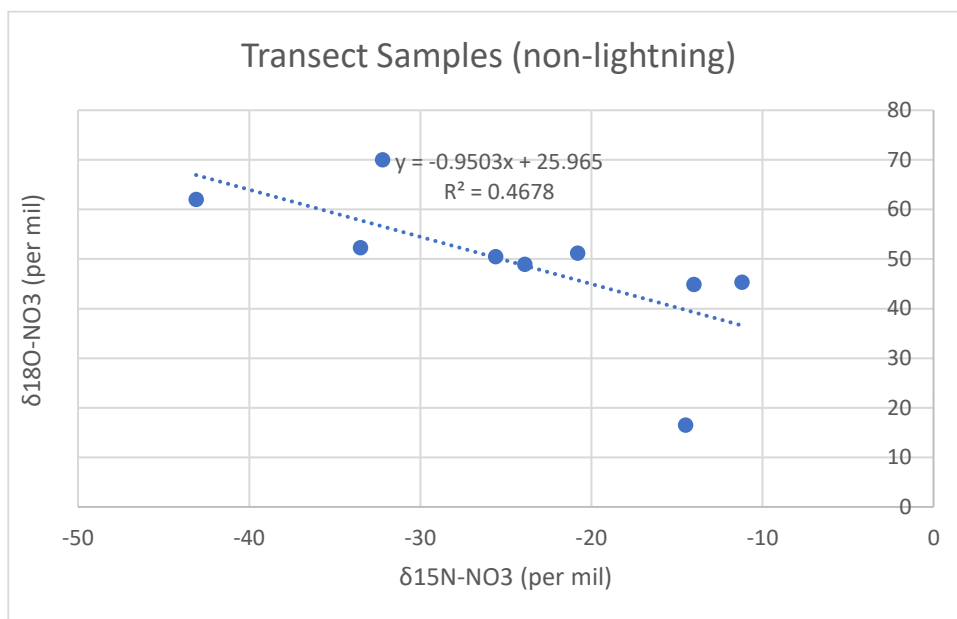
This figure clearly shows a strong relationship exists between nitrate concentration and $\delta^{15}\text{N}$ with the highest concentrations found in samples with the $\delta^{15}\text{N}$ near zero per mil. This finding supports the hypothesis that NO_x produced by lightning is an important source of NO_3 aerosol in the Southern Ocean, especially in the latitude 30-40 degree band.

Using this plot, one can delineate samples without any clear influence from lightning ($\delta^{15}\text{N} < -12$ per mil). Looking at only samples without lightning influence, I then plotted dual-isotope graphs ($\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$) for the Weddell Sea and Transect datasets to see if there were any relationships detectable. Typically, dual isotope plots can be used to infer two endmember mixing dynamics in systems where fractionation is not important.



There is a significant linear relationship between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the Weddell Seas samples, strongly suggesting two endmember mixing dynamics are at play. One could assign one endmember with $\delta^{15}\text{N}$ of $\sim +15$ per mil and $\delta^{18}\text{O}$ of $\sim +25$ per mil which corresponds to the hypothesized RONO₂ endmember discussed in the paper. A second endmember with relatively high $\delta^{18}\text{O}$ ($\sim +70$ per mil) and relatively low $\delta^{15}\text{N}$ (~ -40 per mil) can be defined and corresponds to the snow/ice source discussed in the paper.

A linear relationship was also observed between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ for Transect samples.



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.

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

Line 255. How is lifetime defined?

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

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

Line 281. Delete word “therefore”.

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

Line 299. Remove word “previously”.

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

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 NO₃ 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 RONO₂ 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 RONO₂ 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 (NO₂ 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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ of -22 +/- 7.5 per mil based on what we know about the substrates and reactions that produce it.

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