

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2022-621

Eva Stueeken (Referee)

Referee comment on "Nitrate chemistry in the northeast US – Part 1: Nitrogen isotope seasonality tracks nitrate formation chemistry" by Claire Bekker et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-621-RC1>, 2022

The authors present new isotopic data and model calculations for atmospheric nitrate phases in the northeastern USA. The results reveal seasonal isotopic patterns in the measured data, which cannot be explained by source variability alone. Instead, the authors propose that the isotopic composition of atmospheric nitrate is significantly impacted by secondary reactions within the atmosphere and that the temporal variability can be explained by changes in the formation pathway.

The manuscript is well written and underpinned by a strong dataset. I'm not an atmospheric chemist and cannot evaluate the model calculations, but as an isotope geochemist I found the paper interesting to read and overall compelling.

My main comment is to better discuss the importance of varying nitrate formation pathways. What causes them to change seasonally, and what can that tell us about the broader environment (either anthropogenic or natural processes)?

Apart from that, I only have a few minor points for clarification (to the non-specialist):

I. 60-61: This sentence needs to be simplified. Maybe write "Accounting for these isotope effects is important when using for $\delta(15N)$ as quantitative tracker..."

I. 85-86: This sampling description is lacking lots of details. Which containers were used? How were the filters applied? How much sample was collected? Please expand this paragraph and provide appropriate references.

I. 93: Perhaps also state that the data agree to within XX%. A 1:1 relationship could also arise if there were a significant but consistent offset between the datasets.

II. 94-95: Does this mean that samples from four weeks were mixed together into one container? Please state this more clearly.

II. 104-105: Name the model of the mass spectrometer. Was the same instrument used to measure D17O?

I. 185: Provide some quantitative comparison here for how high NO_x levels used to be in the past. Otherwise, the reader is left wondering.

I. 228: Better rephrase to "This increase is likely due to a significant heating demand during this period". Please also explain why other reasons can be ruled out, leaving heating (i.e., coal combustion?) as the most likely explanation. NOTE: Later in the discussion it is argued that the observed seasonal variability is caused by secondary fractionation effects rather than source variability. Hence this sentence here should be rewritten. Otherwise, it is very confusing.

I. 229: As above, change to "... possibly due to increased emissions related to electricity generation for cooling". Explain why other reasons can be ruled out. NOTE (same as above): Later in the discussion it is argued that the observed seasonal variability is caused by secondary fractionation effects rather than source variability. Hence this sentence here should be rewritten. Otherwise, it is very confusing.

II. 231-238: How could all these endmembers be calculated so accurately? The introduction mentions isotope data for only soils, liquid fuel combustion, vehicles and coal combustion. How were all these other sources listed here isolated from mixed isotopic signals? Please explain how this was done.

I. 276: parenthesis missing in the equation

I. 285: change fractionation to reaction

I. 289: How low is low? Provide a quantitative threshold, so that one can compare this to the data.

II. 331-332: How are the pathways changing? Please expand briefly.

I. 362: Again, remind the reader here how large this reduction was, in percent.

II. 372-374: What is the importance of knowing the nitrate formation pathway? Can knowledge over the pathway help understand air quality or other parameters? Please expand.

Figure 3: Is there any significance to the nitrate speciation between HNO_3 and particulate? Does that relate back to the nitrate formation pathway as well? This would be helpful to discuss in the manuscript.

Figure 4: Make the y-axes shorter in all plots, so that the data are more spread out.

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