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Comment on acp-2021-487

Anonymous Referee #2

Referee comment on "Oxidation pathways and emission sources of atmospheric particulate nitrate in Seoul: based on $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ measurements" by Saehee Lim et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-487-RC2>, 2021

In this study by Lim et al., the authors measured the D17O and d15N of atmospheric nitrate particulates in Seoul, Korea during two different seasons and used this isotopic information to understand the oxidation formation pathways of atmospheric nitrate and to source partition NOx emission sources. The basic rationale is to estimate the relative fractions of the three major nitrate oxidation pathways using the conservative D17O tracer and then use these fractions, along with the relevant nitrogen isotope effects (mostly derived from theoretical calculations), to re-construct the original d15N of ambient NOx. This isotope effect-corrected d15N-NOx signal can then be combined with d15N-NOx source signatures to source partition local NOx emissions. While I found this research important and timely, and that the analysis and discussions related to the D17O of nitrate are thorough and convincing, there are multiple flaws and ambiguities in the discussion of the d15N data.

First, nitrogen isotope effects that are important for the conversion of gaseous NOx to particulate nitrate are not clearly discussed and treated during the data analyses and discussion. The first of those is the nitrogen isotope effect for the Leighton NOx cycle. The authors used a lumped isotope effect of 1.018 to represent the combined kinetic and equilibrium isotope effect for the photochemical NO-NO2 cycling. However, this value was determined by simultaneous d15N-NO2 and d15N-NOx in a very different atmospheric environment (in terms of NOx concentration, NO-to-NO2 ratio, and O3 concentration; i.e., Julich Germany) (Freyer et al., 1993). How this value is representative to the study site of this work is unknown. More importantly, this value is an annual average, without considering temperature effects. A following laboratory study confirming this value (Li et al., 2020) was also conducted at room temperature. Because seasonal temperature fluctuations likely have strong effects on nitrogen isotopic fractionations in the atmosphere (Walters and Michalski, 2015), these impacts need to be acknowledged and considered during the nitrogen isotope data correction. This is a particularly important issue for this study as the temperature effects are expected to manifest to different extent in the data collected during the summer and winter seasons.

It is also not clear how the isotope effect for the NO₂-OH oxidation was represented during the data analysis. In several places, the authors claimed that this step exerts no isotope effect; in some other places, a small isotope effect of -3 permil was mentioned (e.g., Line 182-184). The empirical and/or theoretical grounds for these deductions were not sufficiently stated.

Furthermore, the isotope effect for the conversion from gaseous HNO₃ to particulate nitrate was completely ignored. A previous study found that the isotope effect for this gas-to-solid conversion step dominated the variability of atmospheric nitrate aerosols, was dependent on aerosol pH, and can be potentially as large as 22 permil (Geng et al., 2014).

In general, I found more work is needed to better consider the large uncertainties surrounding the nitrogen isotope effects during the d¹⁵N data correction. While some of these uncertainties have been mentioned in this manuscript, failures to incorporate these uncertainties into the NO_x source partitioning invalidates the partitioned results. Consequently, these results should be deemed only qualitative, but not quantitative. In this sense, a thorough sensitivity analysis, like the one used to treat NO_x source signatures, is required to tackle these uncertainties associated with the nitrogen isotope effects.

Minor comments:

[1] 87-89: The mention of negative fractionation effect here is very confusing. First, you need to define what a positive (or normal) isotope effect is and then to assign either a positive or a negative sign to indicate positive/negative isotope effects.

[2] 172-179: Throughout the manuscript, it is not clear how this A factor was derived using in situ data and used to correct d¹⁵N data.

[3] 182-184: this sentence is difficult to follow. Did you assume no fractionation during NO₂-OH oxidation or use -3 permil for this step? Need more clarifications.

[4] 264: I understand these source endmembers were presented somewhere else in the paper. But to ease readability, I would suggest including several sentences or a table here to summarize or contrast the different δ¹⁵N ranges.

Reference:

Freyer, H.D., Kley, D., Volz, Thomas, A. and Kobel, K., 1993. On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen. *Journal of Geophysical Research: Atmospheres*, 98(D8), pp.14791-14796.

Li, J., Zhang, X., Orlando, J., Tyndall, G. and Michalski, G., 2020. Quantifying the nitrogen isotope effects during photochemical equilibrium between NO and NO₂: implications for δ¹⁵N in tropospheric reactive nitrogen. *Atmospheric Chemistry and Physics*, 20(16), pp.9805-9819.

Walters, W.W. and Michalski, G., 2015. Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules. *Geochimica et Cosmochimica Acta*, 164, pp.284-297.

Geng, L., Alexander, B., Cole-Dai, J., Steig, E.J., Savarino, J., Sofen, E.D. and Schauer, A.J., 2014. Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change. *Proceedings of the National Academy of Sciences*, 111(16), pp.5808-5812.