

This manuscript by Michalsk et al provides a framework that calculates the differences in the atmospheric transformation of different N-15 substituted NO_y molecules, i.e., the isotope fractionations caused by the chemical conversions of NO_x to different final products. Despite some weakness in the parameterizations of the fractionation factors which are needed to quantify the reaction rate constant of N-15 substituted molecules, the framework serves as a tool to test the sensitivity of, e.g., δ¹⁵N of atmospheric HNO₃, to the NO-NO₂ cycling and the subsequent conversion pathways of NO₂ to HNO₃. This will be very helpful to understand the variations of atmospheric HNO₃ measured in different environments. Nevertheless, I feel the manuscript needs some more illustrating data/figures to better understand/evaluate the ability of the model as well as the model outputs. In addition, I think the manuscript needs a better proofread, as there are apparently some typo or mislabeling of figure or equation numbers (I will specify later).

My major concerns/comments are as follows:

1. Most of the reaction rate constants of the N-15 substituted molecules in the model were estimated by multiplying the general chemical reaction rate constant by the fractionation factor. This technologically is not a big issue, however, in some specific reactions, I think the authors oversimplified the treatments. Especially, for the case of OH + NO₂ → HNO₃ reaction. The authors considered this is an EIE instead of KIE, as it is a third body reaction that contains two steps: firstly formed an activated *HNO₃, and which can be deactivated to HNO₃ or decompose to NO₂ and OH. The authors stated the first step, OH + NO₂ <-> *HNO₃ is the dominant isotope step and that induces a large fractionation factor. But I don't quite get the point: if this is a EIE process, then during the lifetime of *HNO₃ to HNO₃, would an isotope equilibrium between NO₂ and *HNO₃ be able to fully established? The author should compare the rate of *HNO₃ decomposition, and its rate of collision with M to form HNO₃, if the decomposition rate is orders of magnitude larger than the collision rate to form HNO₃, then the assumption of OH+NO₂ → HNO₃ is an EIE with alpha of 40 permil is valid. Otherwise, the isotope effect caused by this reaction need to be reevaluated, as well as the entire model results as currently in the model this reaction accounts a large fraction of the overall isotope difference from NO_x to HNO₃.

2. The treatment of N₂O₅ hydrolysis: The model doesn't contain aerosol chemistry but considering the importance of N₂O₅ hydrolysis in nighttime HNO₃ production, this has to be involved in the model. The authors treated this as a first order reaction to go directly as $k \cdot [\text{N}_2\text{O}_5] \rightarrow 2\text{HNO}_3$. This is a common method, but in order to get it right (so the isotopes are correct), the authors at least need to compare the production of HNO₃ from this parametrized first-order reaction is realistic, i.e., it will dominate nighttime HNO₃ production and account for a large fraction of total nitrate production in the system. This is because N₂O₅ hydrolysis is a dominant HNO₃ production pathway, contributing to ~ 40 % of total HNO₃ budget which comparable with the OH + NO₂ pathway in the daytime (Alexander et al., 2019 ACP). Unfortunately, from the limited figures in SI, it appears the nighttime HNO₃ production is often flattened in the four simulation cases. If this is true, then the parametrization of the N₂O₅ reaction in the model is probably wrong. P.s., this is one of the reasons that I think more illustrating data/figure needs to be provided. To evaluate the isotope behaves in the model, the chemistry has to be first correctly simulated. So the authors need to first show the day and night HNO₃ production and discuss whether the production close enough to the observations.
3. Mass balance. As a box model, it is a closed system, so mass, as well as isotopes has to be conserved. Otherwise there might be something wrong with the model setup. So I think the authors should show a mass balance figure, with the time evaluation of total N, as well as total N-15 in the model. This is important to evaluate the overall model performance.
4. I am curious why the model predict a large seasonal variations in d¹⁵N of HNO₃ for the case of Tucson city, but in the four case simulations (i.e., urban, rural, forest and marine) there were minimum diurnal cycle in d¹⁵N of HNO₃ especially in the last few days of the simulations. This is strange, as explained by the authors, the relative importance of NO isotope exchange versus Leighton cycle and OH reaction determined the seasonal cycle, but at the same time, won't be the shift of this relative importance from day to night larger than that in the seasonal scale? So why the modeled diurnal cycle is so small compared to the modeled seasonal cycle? In addition, the authors state the Tucson case d¹⁵N HNO₃ was reported as 48 hours simulation result, I wondered what it will look like

if for 4 or 5 days simulation, which is the typical lifetime of atmospheric nitrate. In other words, why picked 48 hours?

5. During the day time, the model result indicates that NO-NO₂ isotope exchange is very small compared to the Leighton cycle and the OH reaction. I just wanted to see more data to prove this, i.e., can the authors compare the rate of exchange versus the reaction rates of the Leighton cycle and OH reaction during the daytime?
6. The last, I suggest to authors to add another case simulation, that in the middle of 5 day simulation, varying the δ¹⁵N of emitted NO from 0 to, e.g., 10 permil, and see how the isotopes of NO_y in the system vary. This will be interesting as in real environment, NO_x emitted from different sources and its isotope vary all the time.

The following are some general comments:

1. P6, line 38-39, this approach has also been mentioned by Bao et al. 2015 (<https://doi.org/10.1016/j.gca.2015.07.038>) and He et al. 2020 (<https://bg.copernicus.org/preprints/bg-2020-120/>).
2. Section 2.3.1, for the sensitivity tests in this and other similar sections, it is unclear how many chemistry are involved. For example, in figure 2, was nighttime chemistry involved? If yes, why δ¹⁵N of HNO₃ stays the same at night but when δ¹⁵N of NO₂ is very low?
3. Section 2.3.1, the second paragraph, the discussion on daytime NO₃ and NO₂O₅, I think this can be made less complicated to just show the mass of these molecules during the daytime, their negligible mass during daytime is the reason of their negligible isotope effects.
4. Section 3.14, what is ε_{plison-48}? If you meant the NO₂ + Oh reaction, won't it be ε₋₃₉?
5. Section 3.3.5, line 35: δ¹⁵N(NO-NO₂) = + 20 ‰, but From Figure 15, I didn't see this 20 per mil difference in early nighttime of 1/2 and 6/2;
6. Same section, line 37: Shouldn't be Jan. 2 and Jun 2?
7. Same section, last sentence: "conditions it requires about 6 hours for NO_x to achieve full isotopic equilibrium", I doubt this. First, Walters et al. paper in GRL 2016 actually shows the exchange is fast. In addition, in this simulations, it seems the δ¹⁵N difference between NO and NO₂ reach the maximum by late night, but this could be a result of mass

balance, i.e., when almost all NO is converted to NO₂, and d15N of NO₂ approaches to zero (the starting value), and by mass balance NO will be very negative. It will be much more helpful to understand this if the fraction of NO overnight can be plotted. This issue also exists for all other case simulations. In addition, the model has continued NO emissions with d15N of zero (not a completely closed system), how does this continued add-up of NO affect the isotopes of the system?

8. P28, Line 35-36: can you pull out the rate of isotope exchange between NO and NO₂, as well as the rate of photolysis and Leighton cycle at daytime and night? it is surprising that at daytime isotope exchange appears to be negligible.
9. P29, Line 11-12, what is SI Fig. X? and there is no OH figure in SI.