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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Global inorganic nitrate production mechanisms: Comparison of a global model with nitrate isotope observations" *by* Becky Alexander et al.

Anonymous Referee #2

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Review of Alexander et al.

This work is a modeling study focused on the formation of atmospheric nitrate. Based upon the oxygen isotopic composition of nitrate, specifically D17O, the authors utilize the model to quantify the different production pathways of atmospheric nitrate. D17O is a useful tracer for this purpose because it is sensitive to oxidation pathways mediated by ozone or oxygen atoms from ozone. Overall this study represents an update to an earlier 2009 study by the same lead author, because the global atmospheric chemistry model used (GEOS-Chem) has had considerable updates to its chemistry since the earlier work. Because this represents a follow on to an earlier study, in some ways, the work is not as novel. Still, it makes an interesting contribution to field and is certainly a benchmark by which other isotopic modeling studies of its kind will be compared. There are a number of issues in the manuscript that should be addressed and several suggestions that the authors should take into consideration before publishing the work.

Abstract: revisit the abstract after incorporating comments from all reviewers. Additionally, clarify the percentages of the different pathways – one page 2 lines 2-4 it, at first read, appears as if you are only talking about 41% + 41% + 6%. It would be useful to keep in mind 1) that the isotopic composition from ozone does not appear as certain as presented, and 2) that the global compilation of observations is still heavily biased towards the northern mid-latitudes. In the sentence ending on line 11, I suggest adding "on a global scale." at the end of the sentence.

Page 3, line 2: double check the wavelength and provide a reference (e.g., JPL); if memory serves this should be <400 nm.

Page 3, lines 11-15: citations should be provided for each of these pathways, or at least something that sums this up.

Page 3, line 17: It does not make sense to cite Alexander et al., 2009 here. The global lifetime is not presented in that work, nor is it expressly calculated in this current manuscript, which it should be. Note below too that there are a variety of statements in the manuscript that are inconsistent with this broad statement here, which also may or may not represent the lifetime actually found in GEOS-Chem.

Page 3, line 21: add "For example" before "the photolysis of NO3- in snow grains. . ."

Page 5, lines 5-12. This is a major suggestion – please introduce here a clear distinction between the bulk ozone isotopic value versus the terminal isotopic value. This distinction was not made well in Alexander et al 2009 – was 35‰ (O3)bulk or (O3)trans? Similar for Michalski et al. This is a critical distinction that comes up later in the manuscript. Further discussion and review of the differences in these assumptions amongst studies would be a useful addition to this manuscript. Otherwise, the reader is left feeling that there is a much wider gap in knowledge than suggested in the current study.

The language regarding new O3 observations “around the globe” needs to be expanded upon and clarified. Three studies, using the same technique and largely averaging over vast stretches of the globe do not equal “around the globe”.

This is a minor point, but please do consider that, while the newer observations are certainly more consistent than previous work, a detailed look at the methodology in Vicars et al. (RCM, 26, 1219-1231) shows that VERY large corrections are necessary for this method to yield the appropriate D17O(O3) results. It would behoove the authors of the current manuscript to consider whether they want to hang their hat on the absolute certainty of this new technique before it is, at the very least, used by other groups in laboratory and field studies.

Page 6, line 13: In Figure 1, NO2 is not shown to react with HO2. This should be OH?

Page 7, lines 21-23. Transport of NO3- is not considered in the model, such that the results will reflect the “locally” produced NO3-. Here it is suggested that this will make” little difference in polluted regions where most nitrate is formed locally.” Evidence for this – from the model and/or from the literature – need to be included here. At first glance, this is inconsistent with the statement in the introduction that the average lifetime is 3 days.

Furthermore, as highlighted later, the actual results from the model do not agree well enough with observations to assume that the lack of transport is not important. Can the authors further comment on the potential bias this might cause, particularly for regions where long-range organic nitrate transport would be important?

Page 9, line 7: please further explain this equation, I simply do not understand it. Why is 0.25 simply added?

Page 9, line 19: the measurement work for D17O(O3) does present error (i.e. analytical reproducibility and differences from the average when combining all measurements “across the globe”). This should be expressly stated here. Further, this uncertainty should be discussed in the results and discussion in terms of how sensitive the final products are to the fact that D17O(O3) can vary by a couple of per mil.

Page 10, lines 1-2: It probably should be noted that many of the observations compared with are precipitation nitrate, and therefore not only representative of the surface. Perhaps here is could be stated how many datasets compared with represent surface aerosol collection versus precipitation? How important is this in the disagreement between the observations and model?

Page 11, line 15 and line 25: Is the Δ17O(O3) on the order of 25‰ representative of the bulk or transferrable component of O3? Again, a careful discussion of bulk versus terminal is warranted in this manuscript and should be made clear throughout when referring to the isotopic composition that is actually transferred to nitrate ultimately.

Page 11, lines 15-18: How much does the D17O(nitrate) increase? Can you elaborate further on this point about the increase in modeled nitrate due to increased importance of O3 in NOx cycling (85%) compared to the earlier 80%? Does this increase play a larger role than the post-NO2 reactions?

Page 12, lines 5-14: This section should also include comment on why observations of D17O have found lower values than produced by the model.

Page 12, line 7-14: This discussion is strange. The Savarino et al, 2007 work comes before the updated and much more certain (according to this manuscript) observation of D17O(O3). The error in Δ17O(O3*) has been reported to be 39+/-2 per mil, which seems to indicate that a tropospheric value as high as 41‰ could be possible. Further, Savarino’s later work (Vicars and Savarino, 2014 cited in the manuscript! and comments of Savarino himself in presentations and in discussions on ACPD) in fact negates this conclusion suggesting that the photolysis and reformation of stratospheric ozone that enters the troposphere should reset the tropospheric ozone to local values (see discussion of this in Fibigier et al., JGR, 2016). Values near 40 per mil have also been observed in Greenland – by a different research group using different techniques – so it seems highly improbable that the values near 40 per mil simply cannot exist. Please update and reframe this discussion based upon more recent work and consider also acknowledging the observations in Greenland such as (Fibiger et al, JGR-Atmos., 121, 5010 5030, 2016) and references therein.

Page 12 Lines 18-20: A more detailed comparison between modeled values and values observed in mid-latitudes should be made. The model results do not match well with results in Princeton despite the authors claims. In fact, the model matches better with La Jolla than with Princeton, so it is not clear why La Jolla is highlighted here. Point to figure comparisons more specifically here (ie Figure #'s).

The time series comparisons overall are not nearly as impressive as the global, bunched, comparison. What needs to be done in the community to get this more right? The time series speak to a lot of inconsistency in making local assumptions. For instance, there are important differences in model vs obs in the winter/spring of Princeton, Mt. Lulin, and La Jolla (and this likely speaks to the fact that local versus transported nitrate could be important); and then the fall values at Princeton, Mt. Lulin and Cape Verde are all not captured at all. More care should be taken and a more full discussion of the model/obs comparison should be done.

Page 12-13: It would be useful to summarize here what impact the model uncertainties reported in the other works has on D17O(NO3-). Nowhere in the current work is the model compared to NOx or nitrate observations – only the isotopic composition of nitrate. So at least framing what uncertainties are important for consideration and the type of impact they would have on D17O(NO3-) seem important here.

Page 13, lines 9-11 and line 27-28: I am not clear here why the uncertainty in the gamma(N2O5) is not considered here? E.g., the work by Bertram and Thornton (Atmos. Chem. Phys., 9, 8351–8363, 2009) and Tham et al. (Atmos. Chem. Phys., 18, 13155–13171, 2018) that suggest uptake coefficients range a lot from 0.001-0.035 and 0.005-0.039, respectively. How much uncertainty in D17O(NO3-) would changes in this parameter yield?

Page 16, Section 4.2: it should be made clear here why the "standard" simulation is used for this on not the cloud chemistry simulation, the latter is treated as if it is the state of the art through the rest of the manuscript.

This section (and the previous) is really interesting. The authors should consider adding in figures of change in D17O(NO3-) based on the sensitivity studies. The emphasis is placed on gas phase chemistry changes in the figures, which is interesting, but since the paper is really about D17O(NO3-) it seems a missed opportunity to show some change in D17O. This is especially important in that the comparison with the time series observations (Figure 6) is underserved in the manuscript and makes the model seem much more uncertain. Regional digestion might speak to why they are such inconsistencies in seasonality at several stations in the mid-lats OR it might speak to how much difference in D17O is not captured by not having transported nitrate. Furthermore, future observational studies that compare with this work will be 1) better served, 2) this work will be more cited, and 3) this will advance the community forward in terms of our understanding of atmospheric chemistry based upon D17O (i.e. where we understand it and where we don't!).

Page 16, lines 26-28: Globally, the D17O of nitrate remains relative unchanged from 2000 to 2015 emissions, but nitrate is not globally mixed. A more detailed regional analysis again would be really interesting here. For example, how does decreased NOx emissions impact the modeled D17O (and oxidation chemistry) and how does increased NOx emissions alter D17O in China? What are the implications for future observations?

Page 17, Conclusions: I again stress that the authors should make a full discussion of bulk versus transferred isotopic anomaly and the implications of previous assumptions. While it is compelling that the global model agrees better with the updated bulk and transferred value (and note that the transferred values reported by Vicars have an uncertainty of 2 per mil!), the global model still only explains 51% of the variance and the time series plots by location show important and significant disagreements. In other words, it is not a convincing assumption that because the global agreement is better with 25 per mil as the bulk that the observations are correct.

As suggested above, having some discussion of regionality and figures of change in D17O(NO3) based upon the sensitivity studies would be useful, especially for observational work to compare with the model results and make progress on our understanding of key oxidation pathways.

This is minor, but it might be useful to acknowledge key assumptions in the work here and acknowledge what important steps forward are needed. Otherwise I imagine there will be a paper in another 10 years that will tell us “actually now we really know even better what we’re doing” in atmospheric chemistry models. For instance, some key assumptions include: nitrate is locally produced; transported NO3- is not considered/treated nor is there any acknowledgement of how much of a difference this could make (see time series diffs!); NO emitted at night contains one-half its original O and one-half from local oxidant; the D17O(NO2) is calculated using 24-hour production rates [this is an improvement over earlier work but also means the production rates are out of sync with the nighttime versus daytime calculations]; model is compared with observations based on surface only.

Page 18, line 11: NO2+HO2 again? This not happening in the model correct?

Table 1: define A or refer directly to equation in text.

Figure 1: Consider that comparison (in the text) to the NO oxidation branching ratios of Alexander et al., (2009) would be interesting to allow for an understanding on how model updates have changed the modeled branching ratios with implications for D17O.

Please make D’s symbols in the fig caption.

Figure 2: Adding an image of the D17O of NO2 would be interesting too.

Figure 5: I’m not sure +/- 50% is really appropriate for this figure (also these are not identified in the figure caption). If the model were more than +/-25% off we could consider it completely not in the right world! It might be interesting to add the best fit line from Alexander et al. (2009) to compare with present study. References for the observational studies should be explicit in the figure or make a table and refer to that table.

Figure 6: Again, it might be interesting to compare the time series with a what was predicted by the 2009 model. Reference for the observations need to be made. Delta should be a symbol. Why are there more than one observational point for DDU?

Figure 7: Gammas should be symbols.

Figure 9: this is not particularly useful – it is exactly described in the text, could be moved to supplement.

Figure 10: Not sure “acidity-dependent yield” is how it is referred to in the main text? It is difficult to see these figures in this format. For Figs 7-11 I found myself wanting to understand how much change in D17O there would be associated with different regions.

Supplement: Which simulation is used to produce Figure S1? Probably should make this explicit for all figures, or at least when it is NOT the cloud chemistry simulation. Is it possible to extend the color bar? It is difficult to digest since so much of the globe ends up close to 2 days.

Figure S2-S6: suggest including a more complete caption stating that this is . . . then same as. . .or for comparison with Figure...

Figure S5 caption is incorrect?

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