

Reviewer comments in bold, author responses in plain text.

**Abstract: revisit the abstract after incorporating comments from all reviewers.**

We have revised the abstract in response to reviewer #3 and to your comments below.

**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%.**

We added “individually” in this section of the abstract to clarify that 6% is not the sum of all the other pathways but represents the maximum contribution from each individual pathway. The sentence now reads:

“All other nitrate production mechanisms *individually* represent less than 6% of global nitrate production near the surface, but can be dominant locally.”

**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.**

The phrase “on the global scale” has been added to the end of the abstract as suggested.

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

Correct, this has been changed to 398 nm based on the IUPAC recommendation.

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

*Atkinson* [2000] sums this up nicely and has been cited.

**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.**

The *Park et al.* [2004] reference has been cited here instead. We have also added the following sentence to the end of the first paragraph of section 3:

“In the model, the global, annual mean lifetime of NO<sub>x</sub> in the troposphere against oxidation to nitrate is about 1 day; about 50% of this loss is from the reaction of NO<sub>2</sub> + OH. NO<sub>x</sub> loss from N<sub>2</sub>O<sub>5</sub> becomes more important near the surface where aerosol surface area is relatively high. The global, annual mean lifetime of nitrate in the troposphere against wet and dry deposition to the surface is about 3 days.”

**Page 3, line 21: add “For example” before “the photolysis of NO<sub>3</sub><sup>-</sup> in snow grains. . .”**

Done. Thanks for this suggestion.

**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‰ (O<sub>3</sub>)<sub>bulk</sub> or (O<sub>3</sub>)<sub>trans</sub>? 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.**

We added here that we are referring to the bulk isotopic composition of ozone. The sentence now reads:

“Previous modeling studies showed good agreement with observations of  $\Delta^{17}\text{O}(\text{nitrate})$  when assuming *that the bulk oxygen isotopic composition of ozone* ( $\Delta^{17}\text{O}(\text{O}_3)$ ) is equal to 35‰.”  
Later in the manuscript (methods section) we present the distinction between bulk and terminal O-atom isotopic composition, where we define the terminal O-isotopic composition as  $\Delta^{17}\text{O}(\text{O}_3^*)$ , as has been done in previous publications. Throughout the manuscript, we have changed the “\*” symbol from a superscript font to regular font so it is easier for the reader to see. We also redefine the  $\Delta^{17}\text{O}(\text{O}_3)$  symbol in the conclusions section.

**The language regarding new O<sub>3</sub> 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”.**

Good point. The wording “around the globe” has been removed from the introduction. We double checked and this is the only time this term was used in the manuscript.

**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 D<sup>17</sup>O(O<sub>3</sub>) 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.**

Thank you for this comment. Reviewer #3 also had this same concern. We have changed the following sentence:

“Reduction in uncertainty in the value of  $\Delta^{17}\text{O}(\text{O}_3)$  enables improved interpretation of  $\Delta^{17}\text{O}(\text{nitrate})$  as an observational constraint for the relative importance of nitrate formation pathways in the atmosphere.”

to:

“These new observations of  $\Delta^{17}\text{O}(\text{O}_3)$ , combined with improved understanding and hence more comprehensive chemical representation of nitrate formation in models, motivates an updated comparison of observed and modeled  $\Delta^{17}\text{O}(\text{nitrate})$  as an observational constraint for the relative importance of nitrate formation pathways in the atmosphere.”

We have also changed wording on the value of  $\Delta^{17}\text{O}(\text{O}_3)$  in the abstract, introduction, and conclusions so as not to imply that there is no remaining uncertainty in its value.

**Page 6, line 13: In Figure 1, NO<sub>2</sub> is not shown to react with HO<sub>2</sub>. This should be OH?**

I assume you are referring to the reaction  $\text{NO} + \text{HO}_2$  to form  $\text{HNO}_3$ ? This is a termolecular reaction that is in competition with the bimolecular reaction  $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ . The branching between the termolecular and bimolecular reactions is such that less than 1% proceeds via the termolecular pathway. Hence, the termolecular reaction is often ignored. However, since it is included in the GEOS-Chem chemical mechanism, I show it in Figure 1. Figure 1 shows that this reaction is negligible. Kinetic data for these reactions can be found in IUPAC. We have added the following sentence to the methods section:

“The reaction of  $\text{NO} + \text{HO}_2$  can also form  $\text{HNO}_3$  directly, although the branching ratio for this pathway is  $< 1\%$  (Butkovskaya et al., 2005).”

**Page 7, lines 21-23. Transport of NO<sub>3</sub><sup>-</sup> is not considered in the model, such that the results will reflect the “locally” produced NO<sub>3</sub><sup>-</sup>. 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.**

This is difficult to quantify without comparing model simulations with and without transporting the isotopic tracers. One would expect the highest bias in regions without a local source of  $\text{NO}_x$ , i.e., where all nitrate is formed elsewhere and transported to remote locations. Conversely, one would expect less bias in regions with strong local sources of  $\text{NO}_x$  and hence nitrate production. However, since we do not quantify this bias, I changed “little” to “less”. The sentence now reads:

“This should make *less* difference in polluted regions where most nitrate is formed locally.”

**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?**

Long-range transport of organic nitrates such as PAN would effectively represent a local source of  $\text{NO}_x$  to remote regions upon decomposition to  $\text{NO}_x$ . Any other source of  $\text{NO}_x$  that is effectively recycled, such as the photolysis of nitrate on snow grains, would also represent a local source of  $\text{NO}_x$  and reduce the model bias resulting from lack of transport. To that end, we have further modified the previously mentioned sentence to the following to show that polluted areas are not the only regions where one might expect local source of  $\text{NO}_x$  to dominate the source of nitrate:

“This should make less difference in polluted regions where most nitrate is formed locally, or for example in polar regions in summer when photochemical recycling of nitrate in the snowpack represents a significant local source of  $\text{NO}_x$  at the surface.”

We note that we don't state that transport is not important for simulating  $\Delta^{17}\text{O}(\text{nitrate})$  at any particular location. Our approach without transporting the isotopic tracers will reflect the full range of calculated  $\Delta^{17}\text{O}(\text{nitrate})$  on the global scale for any particular isotopic assumption. To be sure not to unintentionally imply that lack of transport is not a concern, we have modified this sentence to the following:

“Although lack of transport of the isotope tracers hinders direct comparison of the model with observations at any particular location, this approach will reflect the full range of possible modeled  $\Delta^{17}\text{O}(\text{nitrate})$  values for the current chemical mechanism, which can then be compared to the range of observed  $\Delta^{17}\text{O}(\text{nitrate})$  values around the globe.”

In addition, we have elaborated on the potential role of lack of transport at particular locations in our extended discussion of comparison of the model with the locations shown in Figure 6.

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

The value of 0.25 is a result of our low-end assumption of  $A_{\text{night}} = 0.5$ , and that half of nitrate formed during the nighttime originates from NO emitted during that same night. The equation now reads:

“ $A_{\text{low}} = 0.5A + 0.5A_{\text{night}}$ , where  $A_{\text{night}} = 0.5$ ”

**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.**

I think you are referring here to the standard deviation of the  $\Delta^{17}\text{O}(\text{O}_3)$  observations, which is 1‰. This leads to an uncertainty of less than 1.5‰ in the calculated values of nitrate. We hesitate to add discussion of error bars based on this observed standard deviation (beyond stating it in the manuscript) because we don't want to suggest this represents a significant contribution to uncertainty in modeled values of  $\Delta^{17}\text{O}(\text{nitrate})$ . Indeed, some (see reviewer #3) suggest that these observations are biased low on the order of 5‰. To represent the full range

of likely possible  $\Delta^{17}\text{O}(\text{O}_3)$  values, we also show a comparison of model results to observations when assuming a value of  $\Delta^{17}\text{O}(\text{O}_3)$  that is at the high end (35‰) of the possible range based on observations, laboratory studies, and model simulations. This figure is shown in the SI (Fig. S6).

**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 it 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?**

We changed this sentence:

“We focus on model results near the surface because these can be compared to observations; currently only surface observations of  $\Delta^{17}\text{O}(\text{nitrate})$  are available.”

to:

“We focus on model results near the surface (below 1 km) because these can be compared to observations; currently only surface observations of  $\Delta^{17}\text{O}(\text{nitrate})$  are available. We note that two observation data sets (from Bermuda (Hastings et al., 2003) and Princeton, NJ (Kaiser et al., 2007)) are rainwater samples and thus may represent nitrate formed aloft. However, since cloud water peaks on average near 1 km altitude in the MERRA2 meteorology used to drive GEOS-Chem, our model sampling strategy should capture the majority of the influence of clouds on nitrate formation.”

**Page 11, line 15 and line 25: Is the  $\Delta^{17}\text{O}(\text{O}_3)$  on the order of 25‰ representative of the bulk or transferrable component of  $\text{O}_3$ ? 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.**

We clarify in this sentence that we are referring to the bulk isotopic composition of ozone.

**Page 11, lines 15-18: How much does the  $\Delta^{17}\text{O}(\text{nitrate})$  increase? Can you elaborate further on this point about the increase in modeled nitrate due to increased importance of  $\text{O}_3$  in  $\text{NO}_x$  cycling (85%) compared to the earlier 80%? Does this increase play a larger role than the post- $\text{NO}_2$  reactions?**

A back of the envelope calculation suggests that calculated  $\Delta^{17}\text{O}(\text{nitrate})$  would need to increase between 7 - 13.5‰ in order to explain why we got good agreement assuming a bulk ozone isotopic composition of 35‰ in the 2009 paper compared to only needing to assume 26‰ in the present paper. The value of 13.5‰ is from the difference between 35‰ and 26‰ (9‰) times 1.5. The upper limit (13.5‰) is assuming that all O-atoms come from ozone ( $A = 1$  and all nitrate from R2). The lower limit is assuming a lower end value of  $A = 0.4$  (from Figure 2) and all nitrate forms from R1. The actual difference is between these two end members, suggesting a difference on the order of 10‰. On average, the increase in the value of  $A$  from 0.80 to 0.85 would result in a difference of  $0.05 * 39‰ = 2‰$ . This suggests, that on average,

the main difference is due to the increase in R2, R4, R5, and R6, although there is likely some temporal and spatial variability. We have added the following sentence to address this: “An increase in the average  $A$  value from 0.80 to 0.85 would tend to increase the calculated  $\Delta^{17}\text{O}(\text{nitrate})$  on the order of 2‰ ( $0.05 \times \Delta^{17}\text{O}(\text{O}_3^*)$ ), suggesting that the increase in the relative importance of the terminal reactions R4, R5, R6, R8, and R10 explains the majority of the difference between the results presented here compared to Alexander et al. (2009).”

**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.**

We have added the following sentence to this paragraph:

“However, observations of  $\Delta^{17}\text{O}(\text{nitrate})$  in autumn and winter in Beijing suggest much higher values ( $30.6 \pm 1.8\text{‰}$ ) than was measured at Mt. Lulin ( $15 - 30\text{‰}$  in winter). A potential reason for the model overestimate of the observed values at Mt. Lulin could be qualitatively explained by transport of nitrate formed in the free troposphere to this high altitude location, where the high  $\Delta^{17}\text{O}(\text{nitrate})$  producing pathways (R4-R8) should be negligible due to minimal aerosol surface area for heterogeneous chemistry.”

**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  $\Delta^{17}\text{O}(\text{O}_3^*)$  has been reported to be  $39 \pm 2$  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).**

It is important here to differentiate between transport of ozone versus nitrate from the stratosphere to the troposphere. Indeed, transport of ozone from the stratosphere to the troposphere would not retain its stratospheric isotopic signature for very long (on the order of 3 hours as suggested by Michalski et al. [2014]). Here we are referring to the transport of nitrate (not ozone) that was formed in the stratosphere and deposited to the surface. However, I do agree that the range in the observed values of  $\Delta^{17}\text{O}(\text{O}_3^*)$  of 2‰ certainly allows for a value of 41‰ for nitrate formed within the troposphere assuming a  $\Delta^{17}\text{O}(\text{O}_3^*)$  value at the upper end of the range and that all O-atoms of nitrate originate from ozone ( $A = 1$  and all nitrate forms from R2 and/or R5). Although this is not outside the realm of possibility for nitrate formed in the Antarctic troposphere during winter, it does seem unlikely that all nitrate in wintertime in Antarctica formed locally. Since there are no known local source of  $\text{NO}_x$  in the Antarctic winter, there must be a significant amount of nitrate formed at lower latitudes (where there is some sunlight and 41‰ would thus be unlikely) and transported to Antarctica. We have added the following to the discussion:

“As previously noted in Savarino et al. (2007), the maximum observed  $\Delta^{17}\text{O}(\text{nitrate})$  value ( $40.6\text{‰}$ ) is not possible given our isotope assumption for the terminal oxygen atom of ozone

( $\Delta^{17}\text{O}(\text{O}_3^*) = 39\text{‰}$ ); however, it is theoretically possible given the 2‰ uncertainty in observed  $\Delta^{17}\text{O}(\text{O}_3^*)$ . A value of  $\Delta^{17}\text{O}(\text{nitrate}) = 41\text{‰}$  is possible if  $\Delta^{17}\text{O}(\text{O}_3^*) = 41\text{‰}$  and all oxygen atoms of nitrate originate from ozone ( $A = 1$  and all nitrate forms from R2 and/or R5). Although this may be possible for nitrate formed locally in the Antarctic winter due to little to no sunlight, lack of local  $\text{NO}_x$  sources during Antarctic winter makes it unlikely that all nitrate observed in Antarctica forms locally. Long-range transport from lower latitudes and/or the stratosphere likely contributes to nitrate observed in Antarctica during winter (Lee et al., 2014).”

**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.**

A look at Fibiger et al. [2016] suggest values up to about 30‰, not 41‰. There’s a mention of 39‰ but this is an end-member extrapolation, not an observed value. Am I missing something? It would be nice to include this data set in the model-observation comparison; however, I cannot seem to find the actual data on the JGR web site or mention of where I can find it in the manuscript.

**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.**

Originally we focused on the largest discrepancies, i.e., the largest overestimates (Mt. Lulin) and the largest underestimates (polar winter). We have added additional discussion of the discrepancies at all of the other locations shown in Figure 6 to this section.

“The model compares better to the mid-latitude locations close to pollution sources (La Jolla and Princeton), although the model overestimates wintertime  $\Delta^{17}\text{O}(\text{nitrate})$  in Princeton, NJ, USA by up to 6‰ and underestimates winter time  $\Delta^{17}\text{O}(\text{nitrate})$  in La Jolla, CA, USA by up to 4‰. The model overestimate at Princeton during winter could be due to the fact that these are precipitation samples and not ambient aerosol samples, and thus may reflect nitrate formed at altitudes higher than we are sampling in the model. The underestimate at La Jolla, CA could be

due to underestimates in reactive chlorine chemistry in the model, which would tend to increase  $\Delta^{17}\text{O}(\text{nitrate})$  by increasing nitrate formation by the hydrolysis of halogen nitrates (R6) in this coastal location. The model underestimates the  $\Delta^{17}\text{O}(\text{nitrate})$  observations at Cape Verde in late summer/early autumn by up to 6‰ (Savarino et al., 2013). Comparison with results from the steady-state model employed in Savarino et al. (2013) suggests that the low bias could be due to an underestimate of nitrate formation via  $\text{NO}_3 + \text{DMS}$  (R2). The steady-state model in Savarino et al. (2013) agreed with observations when R2 represented about one-third of total nitrate formation. The model results presented here have R2 representing about 15% of total nitrate formation in this season. An underestimate of the relative importance of R2 could result from a model underestimate of atmospheric DMS abundances.”

We note that this added discussion of discrepancies at particular locations and times is speculative. A thorough comparison of the model with observations at individual locations would benefit from using the meteorology of the specific year of the observations (we ran only for the years 2015 and 2000) and a higher spatial resolution. The goal here is to present a comparison of all of the observations at once yielding a global perspective. This approach facilitates examination of isotopic assumptions in a way that comparisons at one location do not.

**Page 12-13: It would be useful to summarize here what impact the model uncertainties reported in the other works has on  $\text{D}17\text{O}(\text{NO}_3^-)$ . Nowhere in the current work is the model compared to  $\text{NO}_x$  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  $\text{D}17\text{O}(\text{NO}_3^-)$  seem important here.**

We have an entire section (section 4) following this section (section 3) devoted to discussion of model uncertainties utilizing several sensitivity studies. If you feel that something is missing from this section please specify.

It’s true that we don’t compare the model to observations of  $\text{NO}_x$  and nitrate concentrations. Concentrations are dependent on many factors such as emissions, chemistry, transport and deposition, all of which have their own uncertainties. The advantage of  $\Delta^{17}\text{O}(\text{nitrate})$  is that it is mainly sensitive to chemistry, and thus provides a metric to assess  $\text{NO}_x$  chemistry in models in a way that concentration observations cannot.

**Page 13, lines 9-11 and line 27-28: I am not clear here why the uncertainty in the  $\gamma(\text{N}_2\text{O}_5)$  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  $\text{D}17\text{O}(\text{NO}_3^-)$  would changes in this parameter yield?**

The “cloud chemistry” model as presented here utilizes the Bertram and Thornton parameterization. As described in section 2,  $\gamma_{\text{N}_2\text{O}_5}$  is calculated in the model as a function aerosol water content, chemical composition, and temperature and thus does vary over the



range you describe. This would be better addressed in a paper comparing modeled and observed  $\Delta^{17}\text{O}(\text{nitrate})$  at a location and time period when the  $\text{N}_2\text{O}_5$  pathway is dominant. Indeed, we are examining the importance of heterogeneous reactions in general for nitrate formation and  $\Delta^{17}\text{O}(\text{nitrate})$  at a location (Beijing) where heterogeneous chemistry is likely very high. This is a paper in preparation.

That said, we do examine the impact of the changing importance of the  $\text{N}_2\text{O}_5$  pathway on  $\Delta^{17}\text{O}(\text{nitrate})$  by comparing our “standard” and “cloud chemistry” simulations. The cloud chemistry simulation results in an increase in  $\Delta^{17}\text{O}(\text{nitrate})$  over the standard simulation due to the increase in the  $\text{N}_2\text{O}_5$  pathway (compare Figure 5 and Figure S3) as a result of adding  $\text{N}_2\text{O}_5$  hydrolysis in clouds.

**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.**

We decided to highlight the cloud chemistry simulation as it is the state of the science. However, this new cloud chemistry parametrization is very new, and is not yet included in any models (it is only now being implemented into the public version of GEOS-Chem). Thus, all the sensitivity simulations were performed against the standard simulation of the model. The conclusions drawn in the sensitivity simulations described in section 4.2 (hydrolysis of organic nitrates) and section 4.3 (photolysis of aerosol nitrate) should not change with the addition of cloud chemistry, as the cloud chemistry does not impact either of these reactions and the sensitivity simulations suggests that these uncertainties do not significantly impact the calculated  $\Delta^{17}\text{O}(\text{nitrate})$  nor the conclusions.

**This section (and the previous) is really interesting. The authors should consider adding in figures of change in  $\text{D17O}(\text{NO}_3^-)$  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  $\text{D17O}(\text{NO}_3^-)$  it seems a missed opportunity to show some change in  $\text{D17O}$ . 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  $\text{D17O}$  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  $\text{D17O}$  (i.e. where we understand it and where we don't!).**

I made and considered adding figures showing the change in calculated annual-mean  $\Delta^{17}\text{O}(\text{nitrate})$  for each of the sensitivity simulations described in section 4. I decided not to show these figures because while the change in the *annual mean*  $\Delta^{17}\text{O}(\text{nitrate})$  is small, the change in a particular month or time of year can be significantly larger. I was thus afraid that

showing the change in the annual mean  $\Delta^{17}\text{O}(\text{nitrate})$  would imply that  $\Delta^{17}\text{O}(\text{nitrate})$  is not very sensitive to nitrate production mechanisms, which is not the case. I could show Figures 5 and 6 for each sensitivity simulation, which would not hide details that the annual mean hides. I currently show these figures only for the “standard” and “cloud chemistry” simulations (Figures S3 and S4 compared to Figures 5 and 6). This (difference between cloud chemistry and standard simulations) is the largest difference between sensitivity simulations (the difference between the other sensitivity simulations is smaller, as discussed in section 4). If the editor wishes, I can add these additional figures (this would add 6 figures to the SI). But again, the differences will be smaller than what is already shown.

**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?**

Please see the reply above. This point is addressed in the text in section 4.2, which examines the impact of changing NOx emissions from 2000 to 2015 on nitrate formation pathways and  $\Delta^{17}\text{O}(\text{nitrate})$ . The manuscript states:

“Relatively small changes (< 10%) in nitrate formation pathways yield small changes (< 2‰) in modeled annual-mean  $\Delta^{17}\text{O}(\text{nitrate})$  between the year 2000 and 2015, differences in  $\Delta^{17}\text{O}(\text{nitrate})$  over shorter time periods may be larger.”

**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.**

We have rephrased our conclusions (and abstract and introduction) to avoid suggesting that the  $\Delta^{17}\text{O}(\text{O}_3)$  value is now well known. A thorough analysis of why the new observations of  $\Delta^{17}\text{O}(\text{O}_3)$  may be incorrect is beyond the scope of this paper and would only be speculative. This issue is best addressed by a group other than the Savarino group repeating these nitrate-coated-filter measurements or utilizing another technique to measure  $\Delta^{17}\text{O}(\text{O}_3)$  for comparison.

**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.**

Please see previous responses to this point.

**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.**

Hopefully our understanding of atmospheric chemistry will improve every 10 years!

**For instance, some key assumptions include: nitrate is locally produced; transported NO<sub>3</sub>- 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(NO<sub>2</sub>) 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.**

These assumptions and their impact on calculated  $\Delta^{17}\text{O}(\text{nitrate})$  are all addressed explicitly in the manuscript. All of what is suggested in this comment is related to not transporting the isotopic tracers of NO, nitrate, and everything in between. We acknowledge up front in the manuscript that we don't transport the isotope tracers and discuss how this will lead to discrepancies, particularly at locations without local NO<sub>x</sub> sources. In order to quantify the effect at any particular location we would need to transport the tracers, which we do not do here due to the computational expense. However, as stated in the manuscript, the approach we use here will give the full range of calculated  $\Delta^{17}\text{O}(\text{nitrate})$  values in the model which can be compared with observations. We think this is still quite useful for e.g., examining isotopic assumptions (for example, compare Figure 5 with Figure S5).

**Page 18, line 11: NO<sub>2</sub>+HO<sub>2</sub> again? This not happening in the model correct?**

Please see previous reply to this point.

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

Done.

**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.**

The text compares the global mean (80% versus 85% for NO + O<sub>3</sub>). In Alexander et al. (2009), the rest (20%) is from NO + HO<sub>2</sub>/RO<sub>2</sub>. In the current version we also have NO + XO, which is small.

The symbols disappeared after uploading to ACPD. I will resolve this issue with the final version.

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

Good suggestion since other groups are trying to measure this. I've added this figure to the SI (Figure S5).

**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.**

I'm not sure what you mean here by +/- 50%. I think that showing a best fit line for data from another study that is not shown on the plot would be confusing to the reader. References to the observations are in the text as stated in the figure caption. Adding the reference list to the figure caption would make a long figure caption, but I'm happy to do this if the editor thinks it's appropriate.

**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?**

The problem with what you suggest is that I cannot just use the data shown in the figures from the 2009 paper on this plot because different isotopic assumptions were made in the different studies, making the comparison misleading. There were 2 year-long observation campaigns at DDU (Savarino et al. (2007) and Ishino et al. (2017) and I have shown each as separate data points. Both of these studies are referenced in the text.

**Figure 7: Gammas should be symbols.**

Again, symbols disappeared somewhere between uploading and publication. I'll fix all symbols in the final version.

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

Agreed, it is now in the SI.

**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.**

The acidity dependent yield is shown in Figure 9 (not 10), which was the previous comment and is now moved to the SI.

As far as the change in  $\Delta^{17}\text{O}(\text{nitrate})$  for the sensitivity simulation, please see my response in previous comments.

**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.**

It is the “cloud chemistry” simulation. I’ve noted this in the figure caption. I chose to saturate the color bar at 2 days because extending the color bar makes it difficult to see the regions with lifetimes shorter than 1 day. It is the regions with the shorter lifetimes that are important for this part of the discussion, so I wanted to make sure they are clear.

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

These have all been changed except for Figure S5. I don’t want the different isotopic assumption made in this figure to get lost in a long figure caption.

**Figure S5 caption is incorrect?**

This has been fixed. It is the same as Figure 5, not S1.