We thank the reviewers for taking the time to read and comment on our paper. Please find below our responses below to all four reviewers. **Reviewer comments are in bold**, author responses in plain text.

Reviewer #1:

The authors present an interesting analysis of oxygen isotopes in nitrate as a constraint on global chemistry. They consider the main processes, the role of a variety of interesting more minor ones and conclude that N2O5 and OH driven processes are about equal contributors to the global average nitrate source.

I recommend publication as is.

Thank you for your positive comments.

Reviewer #2:

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_x in the troposphere against oxidation to nitrate is about 1 day; about 50% of this loss is from the reaction of NO_2 + OH. NO_x loss from N_2O_5 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 NO3- 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‰ (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.

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 $\Delta^{17}O$(nitrate) when assuming *that the bulk oxygen isotopic composition of ozone* ($\Delta^{17}O(O_3)$) 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 $\Delta^{17}O(O_3*)$, 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 $\Delta^{17}O(O_3)$ symbol in the conclusions section.

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”.

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 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.

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 $\Delta^{17}O(O_3)$ enables improved interpretation of $\Delta^{17}O$(nitrate) as an observational constraint for the relative importance of nitrate formation pathways in the atmosphere.”
to:
“These new observations of $\Delta^{17}O(O_3)$, combined with improved understanding and hence more comprehensive chemical representation of nitrate formation in models, motivates an updated comparison of observed and modeled $\Delta^{17}O$(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 $\Delta^{17}O(O_3)$ in the abstract, introduction, and conclusions so as not to imply that there is no remaining uncertainty in its value.

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

I assume you are referring to the reaction NO + HO_2 to form HNO_3? This is a termolecular reaction that is in competition with the bimolecular reaction $NO + HO_2 \rightarrow NO_2 + OH$. 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 NO + HO_2 can also form HNO_3 directly, although the branching ratio for this pathway is < 1% (Butkovskaya et al., 2005).”

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.

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 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 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 NO_x to remote regions upon decomposition to NO_x. Any other source of NO_x that is effectively recycled, such as the photolysis of nitrate on snow grains, would also represent a local source of 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 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 NO_x at the surface."

We note that we don't state that transport is not important for simulating Δ^{17}O(nitrate) at any particular location. Our approach without transporting the isotopic tracers will reflect the full range of calculated Δ^{17}O(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,wWe 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 Δ^{17}O(nitrate) values for the current chemical mechanism, which can then be compared to the range of observed Δ^{17}O(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_{night} = 0.5, and that half of nitrate formed during the nighttime originates from NO emitted during that same night. The equation now reads:

"$A_{low} = 0.5A + 0.5A_{night}$, where $A_{night} = 0.5$"

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 $\Delta^{17}O(O_3)$ 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 Δ^{17}O(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 $\Delta^{17}O(O_3)$ values, we also show a comparison of model results to observations when assuming a value of $\Delta^{17}O(O_3)$ 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 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?

We changed this sentence:

"We focus on model results near the surface because these can be compared to observations; currently only surface observations of Δ^{17}O(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 Δ^{17}O(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 _17O(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.

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 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?

A back of the envelope calculation suggests that calculated Δ^{17}O(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 Δ^{17}O(nitrate) on the order of 2‰ ($0.05 \times \Delta^{17}O(O_3^*)$), 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 Δ^{17}O(nitrate) in autumn and winter in Beijing suggest much higher values (30.6±1.8‰) than was measured at Mt. Lulin (15 – 30‰ 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 Δ^{17}O(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 _17O(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).

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 $\Delta^{17}O(O_3^*)$ of 2‰ certainly allows for a value of 41‰ for nitrate formed within the troposphere assuming a $\Delta^{17}O(O_3^*)$ 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 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 $\Delta^{17}O$(nitrate) value (40.6‰) is not possible given our isotope assumption for the terminal oxygen atom of ozone ($\Delta^{17}O(O_3^*)$ = 39‰); however, it is theoretically possible given the 2‰ uncertainty in observed $\Delta^{17}O(O_3^*)$. A value of $\Delta^{17}O$(nitrate) = 41‰ is possible if $\Delta^{17}O(O_3^*)$ = 41‰ 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 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 Δ^{17}O(nitrate) in Princeton, NJ, USA by up to 6‰ and underestimates winter time Δ^{17}O(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 Δ^{17}O(nitrate) by increasing nitrate formation by the hydrolysis of halogen nitrates (R6) in this coastal location. The model underestimates the Δ^{17}O(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 NO_3 + 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 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.

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 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 $\Delta^{17}O$(nitrate) is that it is mainly sensitive to chemistry, and thus provides a metric to assess 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(N2O5) is not considered here? E.g., the work by Bertram and Thornton (At-mos. 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?

The "cloud chemistry" model as presented here utilizes the Bertram and Thornton parameterization. As described in section 2, γ_{N2O5} 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 $\Delta^{17}O$(nitrate) at a location and time period when the N_2O_5 pathway is dominant. Indeed, we are examining the importance of heterogeneous reactions in general for nitrate formation and $\Delta^{17}O$(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 N_2O_5 pathway on $\Delta^{17}O$(nitrate) by comparing our "standard" and "cloud chemistry" simulations. The cloud chemistry simulation results in an increase in $\Delta^{17}O$(nitrate) over the standard simulation due to the increase in the N_2O_5 pathway (compare Figure 5 and Figure S3) as a result of adding N_2O_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 $\Delta^{17}O$(nitrate) nor the conclusions.

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!).

I made and considered adding figures showing the change in calculated annual-mean Δ^{17}O(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* Δ^{17}O(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 Δ^{17}O(nitrate) would imply that Δ^{17}O(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 Δ^{17}O(nitrate). The manuscript states:
"Relatively small changes (< 10%) in nitrate formation pathways yield small changes (< 2‰) in modeled annual-mean Δ^{17}O(nitrate) between the year 2000 and 2015, differences in Δ^{17}O(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 $\Delta^{17}O(O_3)$ value is now well known. A thorough analysis of why the new observations of $\Delta^{17}O(O_3)$ 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 $\Delta^{17}O(O_3)$ 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 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.

These assumptions and their impact on calculated $\Delta^{17}O$(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_x 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 $\Delta^{17}O$(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: NO2+HO2 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_3). In Alexander et al. (2009), the rest (20%) is from NO + HO_2/RO_2. 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 $\Delta^{17}O$(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.

Reviewer #3:

The discussion on A values on page 8 has a serious flaw, namely it ignores the rapid isotopic exchange between NO and NO2 (Sharma) and N2O5. This means that the _17O = 0 NO emitted at night does not have to be oxidized into NO2 to dilute NO2_17O value, but can simply exchange with existing NO2. Likewise, nighttime equilibrium NO3+NO2< ! N2O5 would ultimately incorporate additional ozone into NO2.
In other words there is a serious limitation to the counting oxidations and ignoring the exchanges during the nighttime. It probable that that at night isotope exchange equilibrium results in _17O of NO = NO3 = NO2 This in turn would impact HONO _17O and NO2 "cloud chemistry" at night and HNO3 production early morning when O3 levels are low due to nighttime titration.

Thank you for this point. I do think it's important that we discuss this isotopic exchange in the manuscript; however, it won't impact our isotopic assumptions. Isotopic exchange between NO and NO_2 may increase $\Delta^{17}O(NO)$, but it will decrease $\Delta^{17}O(NO_2)$ by the same amount (isotopic mass balance). Similarly, isotopic exchange between NO_2 and NO_3 (via the N_2O_5 intermediate) may increase $\Delta^{17}O(NO_2)$, but it will decrease $\Delta^{17}O(NO_3)$ by the same amount. So our assumed value of N_2O_5 won't change, and thus the calculated value of $\Delta^{17}O$(nitrate) from N_2O_5 hydrolysis (R4) won't change. Remember, this is a global model so we aren't keeping track of individual molecules but are making assumptions about the bulk isotopic composition within a grid box. Of course, atmospheric measurements also represent a bulk quantity. We have updated our discussion of $\Delta^{17}O(NO_x)$ during the daytime versus the nighttime in the introduction and methods sections and added appropriate references.

The other serious limitation is the treatment of the ozone _17O value. It is well known that _17O and _18O in ozone is a strong function of temperature and pressure. The choice of Vicars (Over cryogenic collection studies) because of the apparent constant _17O values is because these were all surface measurements at effectively the same pressure and a narrow temperature range. It is unlikely O3 being recycled above the boundary layer will have a 26 per mil _17O. How much nitrate is formed in the mixed layer versus free troposphere?

I don't see how this matters. You say in your 2014 paper in ACP that ozone transported from the stratosphere into the troposphere won't retain its stratospheric isotopic signature because the isotopic lifetime of ozone is short in the troposphere due to rapid ozone photolysis and reformation. Why would this be any different for ozone transported from the free troposphere to the boundary layer?

Also the authors have chosen to ignore our Atmos. Chem. Phys., 14, 4935–4953, 2014 paper where we showed the pressure and temperature dependence in NO2 _17O values in equilibrium with O3 as a function of temperature and pressure that demonstrates this effect. A lot hinges on the validity of "Recently, much more extensive observations of ïA¸Dˇ 17O(O3)

using a new technique (Vicars et al., 2012) show ïA¸Dˇ 17O(O3) = 26 ± 1‰ around the globe (Vicars et al., 2012;Ishino et al., 2017b;Vicars and Savarino, 2014), and suggest that previous modeling studies are biased low in ïA¸Dˇ 17O(nitrate) (e.g., Alexander et al. (2009)), which would occur if the model underestimated the relative role of ozone in NOx chemistry.”

These are nearly all clean marine boundary layer measurements and simply ignoring the Johnston and Krankowsky cryogenic collection is polluted urban environments seems to be cherry picking the data. Likewise our experimental NO2 _17O values match well with that predicted by the T and P dependence of O3 formation experiments (i.e Thiemens, Mauersberger group). This is not the first paper to ignore these unpleasant contradictions. It seems no ones wants to acknowledge that something we do not understand is going on with either tropospheric O3 _17O dynamics or their measurements.

I initially neglected any discussion of the potential uncertainty in the $\Delta^{17}O(O_3)$ observations using the nitrite coated filter technique as it has yet to be specifically shown that there are problems with this. However, I see your point that this also has yet to be replicated by other groups. Another reviewer also had this same issue. I have now have modified some wording and added some additional discussion so as not to place too much certainty in this value of $\Delta^{17}O(O_3)$ = 26‰. Wording changes are in the abstract, introduction, and conclusions.

Your 2014 paper should have been cited in the original manuscript and we have added this citation in several locations in the revised manuscript.

Also they might include Wang et al. for some additional south American data
https://www.sciencedirect.com/science/article/pii/S0016703714001811?via%3Dihub

Thanks for this suggestion. It would be great to include this in Figure 5; however, the data is not provided in the paper or in the supplement (it is only plotted). Due to the low spatial resolution of the model, including this data would add one data point to Figure 5. The $\Delta^{17}O$(nitrate) observations from this paper represent a 3.5 year mean value.

Specific comment:

Certainly this is a comprehensive modelling study on global inorganic nitrate production mechanisms with a major aim of investigating how they affect global oxygen isotopic composition of nitrate. A state-of-the-art model (GEOS-Chem) is used in this study. Here what I want to address is the role of reactive halogens (BrO, ClO or IO) on the formation of nitrate. As mentioned in the manuscript, the hydrolysis of halogen nitrates (XNO3, where X=Br, Cl, or I) is an important pathway for the inorganic nitrate formation, particularly in marine boundary layer, where open ocean sea spray serves as a large source of inorganic halogens. Basing on their modelling integrations, the authors conclude that halogens is not important and only accounts for ~6% of the global (<1 km) nitrate production. The dominant processes

are reaction of NO2+OH and hydrolysis of dinitrogen pentoxide (N2O5), each accounting for 41% of the production respectively.

However, in an early tropospheric global model (p-TOMCAT) bromine study (Yang et al., 2005, Figure 12c), what they derived is just opposite: A month-long integration (March) shows that BrNO3 hydrolysis reaction can cause a net reduction of lower tropospheric NOx (=NO+NO2) by 40-80% at latitudes >50S in the Southern Hemisphere and by 20-60% at latitudes >70N in the Northern Hemisphere, though the reduction in the tropical regions is very small (<1%) (due to very lower BrO simulated and relatively higher OH concentrations). Note that this modelling work did include any sea ice sourced bromine source (an additional bromine source to the polar troposphere apart from sea spray and short-lived halocarbons). Thus the actual contribution from halogens could be even higher than the result shown in the paper. Then my question is why these two global models give such a big different result of the bromine-related NOx reduction (or HNO3 production)? Please discus about it and supply more information such as surface layer BrO from the GEOS-Chem model form comparison. To help diagnose which halogen dominate, please supply each individual contribution (from Br, Cl and I) or tell clearly which halogen dominates the nitrate formation.

A detailed description of the reactive bromine (and iodine) chemistry in the version of the model used in this study can be found in Sherwen et al., ACP, 2016. We have not made any further modifications to the reactive halogen chemistry for this paper. There is no conflict between this work and Yang et al. (2005). Both Yang and Sherwen show that halogens have a large impact on NO_x levels in the remote marine atmosphere. However, NO_x levels and nitrate production in these regions are small regardless of the halogen chemistry, so halogens (XNO_3 hydrolysis) have a modest impact on global nitrate production, as shown here.

Sherwen et al. (2016) compared model results with and without reactive halogen chemistry. They found that the global, annual tropospheric NO_x burden decreased by 3.1% due to NO_x loss from the hydrolysis of XNO_3. $ClNO_3$ and $BrNO_3$ hydrolysis were approximately equal contributors, while INO_3 was minor. I cannot find a similar value for the impact of reactive halogens on global, annual tropospheric NO_x in Yang et al. (2005) for direct comparison. Yang et al. (2005) state that $BrNO_3$ hydrolysis accounts for up to 60-80% of NO_x loss at high latitudes, but it is much smaller (a few percent) at low latitudes. Figure 18 in Sherwen et al. (2018) suggests a similar spatial pattern, with NO_x reductions up to ~80% in the high latitudes, and much smaller impacts in the low latitudes. Based on this, the results from these two models do not seem inconsistent. The Sherwen et al. (2016) results are also consistent with previous studies (Long et al., 2014; von Glasow et al., 2004; Parrella et al., 2012; Schmidt et al., 2016).

Sherwen et al. (2016) found that the model underestimates the tropospheric BrO column in high latitudes, especially in the southern hemisphere (see Figure 9 from Sherwen et al. (2016)). This is mentioned in the manuscript as a possible explanation for why the model underestimates $\Delta^{17}O$(nitrate) at high latitudes.

In addition, the values shown in Figure 3 of the manuscript really puzzle me. The annual fraction of HNO3 formation from the oxidation of NOx in the troposphere below 1km altitude from the 'XNO3+H2O' is almost at same level as the 'NO2+OH' and 'N2O5+H2O' reactions. Why their global integration numbers are so different, e.g. by almost an order of magnitude, 6% vs 41%? Please explain it.

Figure 3 shows the *fractional* importance of nitrate production pathways. XNO_3 hydrolysis is a dominant nitrate production pathway relative to the other pathways over the remote oceans in the mid to high latitudes. However, NO_x emissions are pretty small in these regions, so that the contribution to total, global nitrate production in these remote oceanic regions is small. In the main (anthropogenic) NO_x source regions, the NO_2 + OH and N_2O_5 hydrolysis pathways dominate local nitrate production, resulting in these reactions being dominant globally.

Although previous studies have not specifically reported the importance of XNO_3 hydrolysis for nitrate production (they focus instead on the importance for NO_x loss), Sherwen et al. (2016) state that the rate of nitrate production from XNO_3 hydrolysis proceeds at a rate of 10% of NO_x loss though the NO_2 + OH pathway. This seems consistent with results from the present study that NO_2 + OH is 41% of global nitrate production near the surface and XNO_3 hydrolysis is about 6%. We have added the following sentence to section 3:

"Although XNO_3 hydrolysis is the dominant nitrate formation pathway over the remote oceans (Figure 3), its contribution to total, global nitrate production is relatively small due to small local NO_x sources in these regions."

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Global inorganic nitrate production mechanisms: Comparison of a global model with nitrate isotope observations

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Abstract. The formation of inorganic nitrate is the main sink for nitrogen oxides (NO_x = NO + NO_2). Due to the importance of NO_x for the formation of tropospheric oxidants such as the hydroxyl radical (OH) and ozone, understanding the mechanisms and rates of nitrate formation is paramount for our ability to predict the atmospheric lifetimes of most reduced trace gases in the atmosphere. The oxygen isotopic composition of nitrate ($\Delta^{17}O$(nitrate)) is determined by the relative importance of NO_x sinks, and thus can provide an observational constraint for NO_x chemistry. Until recently, the ability to utilize $\Delta^{17}O$(nitrate) observations for this purpose was hindered by our lack of knowledge about the oxygen isotopic composition of ozone ($\Delta^{17}O(O_3)$). Recent and spatially widespread observations of $\Delta^{17}O(O_3)$ ~~have greatly reduced this uncertainty~~, and ~~allow for~~motivate an updated comparison of modeled and observed $\Delta^{17}O$(nitrate) and a reassessment of modeled nitrate formation pathways. Model updates based on recent laboratory studies of heterogeneous reactions renders dinitrogen pentoxide (N_2O_5) hydrolysis as important as NO_2 + OH (both 41%) for global inorganic nitrate production near the surface (below 1 km altitude). All other nitrate production mechanisms individually represent less than 6% of global nitrate production near the surface, but can be dominant locally. Updated reaction rates for aerosol uptake of NO_2 result in significant reduction of nitrate and nitrous acid (HONO) formed through this pathway in the model, and render NO_2 hydrolysis a negligible pathway for nitrate formation globally. Although photolysis of aerosol nitrate may have implications for NO_x, HONO and oxidant abundances, it does not significantly impact the relative importance of nitrate formation pathways. Modeled $\Delta^{17}O$(nitrate) (28.6 ± 4.5‰) compares well with the average of a global compilation of observations (27.6 ± 5.0‰) when assuming $\Delta^{17}O(O_3)$ = 26‰, giving confidence in the model's representation of the relative importance of ozone versus HO_x (= OH + HO_2 + RO_2) in NO_x cycling and nitrate formation on the global scale.

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1. Introduction

Nitrogen oxides (NO_x = NO + NO_2) are a critical ingredient for the formation of tropospheric ozone (O_3). Tropospheric ozone is a greenhouse gas, is a major precursor for the hydroxyl radical (OH), and is considered an air pollutant due to its negative impacts on human health. The atmospheric lifetime of NO_x is determined by its oxidation to inorganic and organic nitrate. The formation of inorganic nitrate (HNO_3(g) and particulate NO_3^-) is the dominant sink for NO_x globally, while formation of organic nitrate may be significant in rural and remote continental locations (Browne and Cohen, 2014). Organic nitrate as a sink for NO_x may be becoming more important in regions in North America and Europe where NO_x emissions have declined (Zare et al., 2018). Uncertainties in the rate of oxidation of NO_x to nitrate has been shown to represent a significant source of uncertainty for ozone and OH formation in models (e.g., Newsome and Evans (2017)) , with implications for our understanding of the atmospheric lifetime of species such as methane, whose main sink is reaction with OH.

NO_x is emitted to the atmosphere primarily as NO by fossil fuel and biomass/biofuel burning, soil microbes, and lightning. Anthropogenic sources from fossil fuel and biofuel burning and from the application of fertilizers to soil for agriculture currently dominate NO_x sources to the atmosphere (Jaeglé et al., 2005). After emission, NO is rapidly oxidized to NO_2 by ozone (O_3), peroxy (HO_2) and hydroperoxy radicals (RO_2), and halogen oxides (e.g., BrO). During the daytime, NO_2 is rapidly photolyzed to NO + O at wavelengths (λ) < ~~424~~ 398 nm. NO_x cycling between NO and NO_2 proceeds several orders of magnitude faster than oxidation of NO_x to nitrate during the daytime (Michalski et al., 2003).

Formation of inorganic nitrate is dominated by oxidation of NO_2 by OH during the day and by the hydrolysis of dinitrogen pentoxide (N_2O_5) at night (Alexander et al., 2009). Recent implementation of reactive halogen chemistry in models of tropospheric chemistry show that formation of nitrate from the hydrolysis of halogen nitrates (XNO_3, where X = Br, Cl, or I) is also a sink for NO_x with implications for tropospheric ozone, OH, reactive halogens, and aerosol formation (Schmidt et al., 2016;Sherwen et al., 2016;Saiz-Lopez et al., 2012;Long et al., 2014;Parrella et al., 2012;von Glasow and Crutzen, 2004;Yang et al., 2005). Other inorganic nitrate formation pathways include hydrogen-abstraction of hydrocarbons by the nitrate radical (NO_3), heterogeneous reaction of N_2O_5 with particulate chloride (Cl^-), heterogeneous uptake of NO_2 and NO_3, direct oxidation of NO to HNO_3 by HO_2, and hydrolysis of organic nitrate (Atkinson, 2000). Inorganic nitrate partitions between the gas ($HNO_3(g)$) and particle (NO_3^-) phases, with its relative partitioning dependent upon aerosol abundance, aerosol liquid water content, aerosol chemical composition, and temperature. Inorganic nitrate is lost from the atmosphere through wet or dry deposition to the Earth's surface with a global lifetime against deposition on the order of 3-4 days (Park et al., 2004) ~~(Alexander et al., 2009)~~.

Formation of inorganic nitrate was thought to be a permanent sink for NO_x in the troposphere due to the slow photolysis of nitrate compared to deposition. However, laboratory and field studies have shown that NO_3^- adsorbed on surfaces is photolyzed at rates much higher than $HNO_3(g)$ (Ye et al., 2016). For example, ~~T~~the photolysis of NO_3^- in snow grains on ice sheets has a profound impact on the oxidizing capacity of the polar atmosphere (Domine and Shepson, 2002). More recently, observations of NO_x and nitrous acid (HONO) provide evidence of photolysis of aerosol NO_3^- in the marine (Reed et al., 2017;Ye et al., 2016) and continental (Ye et al., 2018;Chen et al., 2019) boundary layer, with implications for ozone and OH (Kasibhatla et al., 2018).

Organic nitrates form during reaction of NO_x and NO_3 with biogenic volatile organic compounds (BVOCs) and their oxidation products (organic peroxy radicals, RO_2) (Browne and Cohen, 2014;Liang et al., 1998). Products of these reactions include peroxy nitrates (RO_2NO_2) and alkyl and multifunctional nitrates ($RONO_2$) (O'Brien et al., 1995). Peroxy nitrates are thermally unstable and decompose back to NO_x on the order of minutes to days at warm temperatures. Decomposition of longer-lived peroxy nitrates such as peroxyacetyl nitrate (PAN) can provide a source of NO_x to remote environments (Singh et al., 1992). The fate of $RONO_2$ is uncertain. First-generation $RONO_2$ is oxidized to form second-generation $RONO_2$ species with a lifetime of about a week for the first-generation species with ≥ 4 carbon atoms, and up to several weeks for species with fewer carbon atoms (e.g., days to weeks for methyl nitrate) (Fisher et al., 2018). Subsequent photolysis and oxidation of second-generation $RONO_2$ species can lead to the recycling of NO_x (Müller et al., 2014), although recycling efficiencies are highly uncertain (Horowitz et al., 2007;Paulot et al., 2009). $RONO_2$ can also partition to the particle phase ($pRONO_2$) contributing to organic aerosol formation (Xu et al., 2015). $pRONO_2$ is removed from the atmosphere by deposition to the surface, or through hydrolysis to form inorganic nitrate and alcohols (Rindelaub et al., 2015;Jacobs et al., 2014).

The oxygen isotopic composition ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of nitrate is determined by the relative importance of oxidants leading to nitrate formation from the oxidation of NO_x (Michalski et al., 2003). Observations of the oxygen isotopic composition of nitrate ($\Delta^{17}O$(nitrate)) have been used to quantify the relative importance of different nitrate formation pathways and to assess model representation of the chemistry of nitrate formation in the present day (Alexander et al., 2009;Michalski et al., 2003;Costa et al., 2011;Ishino et al., 2017a;Morin et al., 2009;Morin et al., 2008;Savarino et al., 2007;Kunasek et al., 2008;Savarino et al., 2013;McCabe et al., 2007;Morin et al., 2007;Hastings et al., 2003;Kaiser et al., 2007;Brothers et al., 2008;Ewing et al., 2007) and in the past from nitrate archived in ice cores (Sofen et al., 2014;Alexander et al., 2004;Geng et al., 2014;Geng et al., 2017). Ozone-influenced reactions in NO_x oxidation lead to high $\Delta^{17}O$(nitrate) values while HO_x-influenced reactions lead to $\Delta^{17}O$(nitrate) near zero. Oxidation by XO (where X = Br, Cl, or I) leads to $\Delta^{17}O$(nitrate) values similar to reactions with ozone because the oxygen atom in XO is derived from the reaction $X + O_3$. Therefore, $\Delta^{17}O$(nitrate) is determined by the relative importance of O_3 + XO versus HO_x (= OH + HO_2 + RO_2) in both NO_x cycling and oxidation to nitrate. Although freshly emitted NO will have $\Delta^{17}O$(NO) = 0‰, ~~Due to rapid NO_x cycling during the daytime,~~ NO_x achieves isotopic

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equilibrium during the daytime due to rapid NO_x cycling, ~~and~~ so that its $\Delta^{17}O$ value ($\Delta^{17}O(NO_x)$) is solely determined by the relative abundance of (O_3 + XO) to (HO_2 + RO_2) (Michalski et al., 2003).

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The $\Delta^{17}O$ value of HO_x ($\Delta^{17}O(HO_x)$) is near zero due to isotopic exchange of OH with water vapor (Dubey et al., 1997). Previously, observations of ~~T~~the $\Delta^{17}O$ value of ozone ($\Delta^{17}O(O_3)$) showed a large range (~20 – 40‰) (Johnston and Thiemens, 1997;Krankowsky et al., 1995), in contrast to laboratory and modeling studies suggesting that the range of $\Delta^{17}O(O_3)$ in the troposphere should be narrow (32 ± 2 ‰) (Morton, 1990;Thiemens, 1990). The large range of observed $\Delta^{17}O(O_3)$ values is thought to be due to ~~was until recently not well known due to uncertainties arising from~~ sampling artifacts (Brenninkmeijer et al., 2003) ~~in the earlier measurements (Johnston and Thiemens, 1997;Krankowsky et al., 1995)~~ ~~and~~ Uncertainty in the value of $\Delta^{17}O(O_3)$ has been the largest source of uncertainty in quantification of nitrate formation pathways using observations of $\Delta^{17}O$(nitrate) (Alexander et al., 2009). Previous modeling studies showed good agreement with observations of $\Delta^{17}O$(nitrate) when assuming that the bulk oxygen isotopic composition of ozone ($\Delta^{17}O(O_3)$) ~~=~~is equal to 35‰ (Alexander et al., 2009;Michalski et al., 2003). Recently, much more extensive observations of $\Delta^{17}O(O_3)$ using a new technique (Vicars et al., 2012) consistently show $\Delta^{17}O(O_3)$ = 26 ± 1‰ in diverse locations ~~around the globe~~ (Vicars et al., 2012;Ishino et al., 2017b;Vicars and Savarino, 2014), and suggest that previous modeling studies are biased low in $\Delta^{17}O$(nitrate) (e.g., Alexander et al. (2009)), which would occur if the model underestimated the relative role of ozone in NO_x chemistry. ~~Reduction in uncertainty in the value~~These new observations of $\Delta^{17}O(O_3)$, combined with improved understanding and hence more comprehensive chemical representation of nitrate formation in models, ~~enables improved interpretation~~motivates an updated comparison of observed and modeled ~~of~~ $\Delta^{17}O$(nitrate) as an observational constraint for the relative importance of nitrate formation pathways in the atmosphere. Here, we examine the relative contribution of each nitrate formation pathway in a global chemical transport model and compare the model with observations of $\Delta^{17}O$(nitrate) from around the world.

2. Methods

We use the GEOS-Chem global chemical transport model version 12.0.0 driven by assimilated meteorology from the MERRA-2 reanalysis product with a native resolution of 0.5° x 0.625° and 72 vertical levels from the surface up to the 0.01 hPa pressure level. For computational expediency, the horizontal and vertical resolution were downgraded to 4° x 5° and 47 vertical levels. GEOS-Chem was originally described in Bey et al. (2001) and includes coupled HO_x-NO_x-VOC-ozone-halogen-aerosol tropospheric chemistry as described in Sherwen et al. (2016) and Sherwen et al. (2017) and organic nitrate chemistry as described in Fisher et al. (2016). Aerosols interact with gas-phase chemistry through the effect of aerosol extinction on photolysis rates (Martin et al., 2003) and heterogeneous chemistry (Jacob, 2000). The model calculates deposition for both gas species and aerosols (Liu et al., 2001;Zhang et al., 2001;Wang et al., 1998).

Global anthropogenic emissions, including NO_x, are from the Community Emissions Data System (CEDS) inventory from 1950 – 2014 C.E. (Hoesly et al., 2018a). The CEDS global emissions inventory is overwritten by regional anthropogenic emissions inventories in the U.S. (EPA/NE11), Canada (CAC), Europe (EMEP), and Asia (MIX (Li et al., 2017)). Global shipping emissions are from the International Comprehensive Ocean-Atmosphere Data Set (ICOADS), which was implemented into GEOS-Chem as described in Lee et al. (2011). NO_x emissions from ships are processed using the PARANOX module described in Vinken et al. (2011) and Holmes et al. (2014) to account for non-linear, in-plume ozone and HNO_3 production. Lightning NO_x emissions match the OTD/LIS satellite climatological observations of lightning flashes as described by Murray et al. (2012). Emissions from open fires are from the Global Fire Emissions Database (GFED4.1). Biogenic soil NO_x emissions are described in Hudman et al. (2012). Aircraft emissions are from the Aviation Emissions Inventory Code (AEIC) (Stettler et al., 2011).

Chemical processes leading to nitrate formation in GEOS-Chem have expanded since the previous work of Alexander et al. (2009). Figure 1 summarizes the formation of inorganic nitrate in the current model. In the model, NO is oxidized by O_3, HO_2, RO_2 and halogen oxides (XO = BrO, ClO, IO, and OIO) to form NO_2. The reaction of NO + HO_2 can also form HNO_3 directly, although the branching ratio for this pathway is < 1% (Butkovskaya et al., 2005). NO_2 can form HNO_3 directly from its reaction with OH~~ and HO_2~~ and through hydrolysis on aerosol surfaces. NO_2 can react with XO to form halogen nitrates ($BrNO_3$, $ClNO_3$, and INO_3), which can then form HNO_3 upon hydrolysis (as described in Sherwen et al. (2016)). NO_2 can also react with O_3 to form NO_3, which can then react with NO_2,

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hydrocarbons (HC), and the biogenic VOCs monoterpenes (MTN) and isoprene (ISOP). Reaction of NO_3 with NO_2 forms N_2O_5, which can subsequently hydrolyze or react with Cl^- in aerosol to form HNO_3. Reaction of NO_3 with HC forms HNO_3 via hydrogen abstraction. Reactions of NO_3 are only important at night due to its short lifetime against photolysis. Formation of organic nitrate ($RONO_2$) was recently updated in the model as described in Fisher et al. (2016). Reaction of NO_3 with MTN and ISOP can form $RONO_2$. $RONO_2$ also forms from the reaction of NO with RO_2 derived from OH oxidation of BVOCs. $RONO_2$ hydrolyzes to form HNO_3 on a timescale of 1 hour. Inorganic nitrate partitions between the gas (HNO_3(g)) and particle (NO_3^-) phase according to local thermodynamic equilibrium as calculated in the ISORROPIA-II aerosol thermodynamic module (Fountoukis and Nenes, 2007). HNO_3(g) and NO_3^- are mainly lost from the atmosphere via wet and dry deposition to the surface.

In the "standard" model, hydrolysis of N_2O_5, NO_3 ($\gamma_{NO3} = 1 \times 10^{-3}$), and NO_2 ($\gamma_{NO2} = 1 \times 10^{-4}$) occur on aerosol surfaces only. Uptake and hydrolysis of N_2O_5 on aerosol surfaces depends on the chemical composition of aerosols, temperature, and humidity as described in Evans and Jacob (2005). Recently, Holmes et al. (2019) updated the reaction probabilities of the NO_2 and NO_3 heterogeneous reactions in the model to depend on aerosol chemical composition and relative humidity. Holmes et al. (2019) also updated the N_2O_5 reaction probability to additionally depend on the H_2O and NO_3^- concentrations in aerosol (Bertram and Thornton, 2009). In addition to these updates for hydrolysis on aerosol, Holmes et al. (2019) included the uptake and hydrolysis of N_2O_5, NO_2, and NO_3 in cloud water and ice limited by cloud entrainment rates. We incorporate these updates from Holmes et al. (2019) into the "cloud chemistry" model to examine the impacts on global nitrate production mechanisms. We consider the "cloud chemistry" model as state-of-the science, and as such we focus on the results of this particular simulation. Additional model sensitivity studies are also performed and examined relative to the "standard" model simulation. These additional sensitivity simulations are described in Section 4.

$\Delta^{17}O$(nitrate) is calculated in the model using monthly-mean, local chemical production rates, rather than by treating different isotopic combinations of nitrate as separate tracers that can be transported in the model. Alexander et al. (2009) transported four nitrate tracers, one each for nitrate production by NO_2+OH, N_2O_5 hydrolysis, NO_3+HC, and nitrate originating from its formation in the stratosphere. Since $\Delta^{17}O(NO_x)$ was not transported in the Alexander et al. (2009) model, it was calculated using local production rates, so effectively only one-third of the $\Delta^{17}O$(nitrate) was transported in Alexander et al. (2009). Accurately accounting for transport of Δ^{17}O(nitrate) in the model would require transporting all individual isotopic combinations of the primary reactant (NO), the final product (nitrate), and each reaction intermediate (e.g., N_2O_5), which we do not do here due to the large computational costs. Thus, the model results shown here represent Δ^{17}O(nitrate) from local NO_x cycling and nitrate production. This may lead to model biases, particularly in remote regions such as polar-regions in winter-time when most nitrate is likely transported from lower latitudes or the stratosphere. This should make ~~little~~ 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 NO_x at the surface (Domine and Shepson, 2002). Although lack of transport of the isotope tracers hinders direct comparison of the model with observations at any particular location, ~~T~~this approach will ~~however~~ reflect the full range of possible modeled Δ^{17}O(nitrate) values for the current chemical mechanism, which can then be compared to the range of observed Δ^{17}O(nitrate) values around the globe.

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The Δ^{17}O(nitrate) value of nitrate produced from each production pathway is calculated as shown in Table 1. The value of A in Table 1 represents the relative importance of the oxidation pathways of NO to NO_2 where the oxygen atom transferred comes from ozone (NO + O_3 and NO + XO):

$$A = \frac{k_{O_3+NO}[O_3]+k_{XO+NO}[XO]}{k_{O_3+NO}[O_3]+k_{XO+NO}[XO]+k_{HO_2+NO}[HO_2]+k_{RO_2+NO}[RO_2]} \qquad \text{(E1)}$$

In E1, k represents the local reaction rate constant for each of the four reactions, XO = BrO, ClO, IO, and OIO, and we assume Δ^{17}O(XO) is equal to the Δ^{17}O value of the terminal oxygen atoms of ozone, as described in more detail below. This effectively assumes that the other oxidation pathways (NO + HO_2 and NO + RO_2) yield $\Delta^{17}O(NO_x)$ = 0‰. Although HO_2 may have a small ^{17}O enrichment on the order of 1-2‰ (Savarino and Thiemens, 1999b), the assumption that this pathway yields $\Delta^{17}O(NO_x)$ = 0‰ simplifies the calculation and leads to negligible differences in calculated Δ^{17}O(nitrate) (Michalski et al., 2003). This approach assumes that NO_x cycling is in photochemical steady-state, which only occurs during the daytime. A is calculated in the model as the 24-hour average NO_2 production rate, rather than the daytime average only. As was shown in Alexander et al. (2009), rapid daytime NO_x cycling dominates the calculated 24-hour averaged A value, leading to negligible differences in calculated Δ^{17}O(nitrate) for 24-hour averaged values versus daytime averaged values.

NO_x formed during the day will retain its daytime $\Delta^{17}O(NO_x)$ signature throughout the night due to lack of NO_2 photolysis (Morin et al., 2011), suggesting similar *A* values for the nighttime reactions (R2, R4, R5, R8, and R10 in Table 1). However, NO emitted at night will not undergo photochemical recycling; initially suggesting that NO will retain its emitted $\Delta^{17}O(NO)$ value of 0‰ prior to sunrise. (Sharma et al., 1970;Michalski et al., 2014;Morin et al., 2011) ~~retain its originally emitted isotopic signature ($\Delta^{17}O(NO)$ = 0‰) due to lack of NO_x cycling under dark conditions.~~ Thus, ~~A~~any NO emitted at night and oxidized to NO_2 before sunrise will result in $\Delta^{17}O(NO_2)$ equal to one-half of the $\Delta^{17}O$ value of the oxidant, since only one of the two oxygen atoms of NO_2 will originate from the oxidant. Since HO_x abundance is low at night, ozone will be the dominant oxidant. Thus, NO both emitted and oxidized to NO_2 at night will lead to $A_{night} = 0.5$ (half of the O atoms of NO_2 originate from O_3). Although isotopic exchange between NO + NO_2 (Sharma et al., 1970) and NO_2 and NO_3 via thermal dissociation of N_2O_5 (Connell and Johnston, 1979) will tend to increase $\Delta^{17}O(NO)$ above its emitted value of 0‰, the bulk $\Delta^{17}O$ value of NO_x plus NO_3 system will be lower at night than during the daytime due to the absence of photochemical cycling at night (Michalski et al., 2014;Morin et al., 2011). Since the atmospheric lifetime of NO_x near the surface against nighttime oxidation to nitrate (R2+R4+R5) is typically greater than 24 hours (Figure S1), most nitrate formed during the nighttime will form from NO_x that reached photochemical equilibrium during the previous day. Thus, we use values of *A* calculated as the 24-hour average NO_2 production rate for calculating the $\Delta^{17}O$(nitrate) value of all nitrate production pathways, including those that can occur at night. This is consistent with a box modeling study that explicitly calculated the diurnal variability of $\Delta^{17}O(NO_x)$ and $\Delta^{17}O$(nitrate) suggesting similar (within 5%) values for $\Delta^{17}O$(nitrate) when assuming the NO_x reached photochemical steady-state versus explicit calculation of diurnal variability of $\Delta^{17}O(NO_x)$ and $\Delta^{17}O$(nitrate) (Morin et al., 2011). Using 24-hour averaged *A* values may lead to an overestimate of $\Delta^{17}O$(nitrate) in locations with more rapid nighttime nitrate formation rates such as in China and India (Figure S1). However, even in these locations the lifetime of NO_x against nighttime oxidation is greater than 12 hours, suggesting that over half of nitrate formation at night occurs from the oxidation of NO_x that reached photochemical equilibrium during the daytime. When comparing modeled $\Delta^{17}O$(nitrate) with observations, we add error bars to model values in these locations (Beijing and Mt. Lulin, Taiwan) that reflect the range of possible *A* values for nighttime nitrate formation, with the high end (A_{high}) reflecting 24-hour average *A* values and the low end assuming that half of nitrate formation

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$\Delta^{17}O$(nitrate) for total nitrate is calculated in the model according to:

$$\Delta^{17}O(nitrate) = \sum_{R=R1}^{R10} f_R \Delta^{17}O(nitrate)_R \qquad \text{(E2)}$$

where f_R represents the fractional importance of each nitrate production pathway (R1-R10 in Table 1) relative to total nitrate production, and $\Delta^{17}O(nitrate)_R$ is the $\Delta^{17}O$(nitrate) value for each reaction as described in Table 1. To calculate $\Delta^{17}O$(nitrate), we assume that the mean $\Delta^{17}O$ value of the ozone molecule ($\Delta^{17}O(O_3)$) is equal to 26‰ based on recent observations (Vicars et al., 2012;Ishino et al., 2017b;Vicars and Savarino, 2014). Since the ^{17}O enrichment in O_3 is contained entirely in its terminal oxygen atoms (Vicars et al., 2012;Berhanu et al., 2012;Bhattacharya et al., 2008;Savarino et al., 2008;Michalski and Bhattacharya, 2009;Bhattacharya et al., 2014), and it is the terminal oxygen atom that is transferred to the oxidation product during chemical reactions (Savarino et al., 2008;Berhanu et al., 2012), the $\Delta^{17}O$ value of the oxygen atom transferred from ozone to the product is 50% larger than the bulk $\Delta^{17}O(O_3)$ value. Thus, we assume that the $\Delta^{17}O$ value of the oxygen atom transferred from O_3 ($\Delta^{17}O(O_3^*)$) = 1.5 x $\Delta^{17}O(O_3)$ ~~= 39‰~~, as in previous work (e.g., (Morin et al., 2011)), where $\Delta^{17}O(O_3^*)$ represents the $\Delta^{17}O$ value of the terminal oxygen atoms in ozone. Assuming that $\Delta^{17}O(O_3)$ = 26‰ based on recent observations, this leads to $\Delta^{17}O(O_3^*)$ = 39‰.

3. Results and Discussion

Figure 1 shows the relative importance of the different oxidation pathways of NO to NO_2 and nitrate formation below 1 km altitude in the model for the "cloud chemistry" simulation, with equivalent values for the "standard" simulation shown in parentheses. We focus on model results near the surface (below 1 km) because these can be compared to observations; currently only surface observations of $\Delta^{17}O$(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

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clouds on nitrate formation. The dominant oxidant of NO to NO_2 is O_3 (84-85%). Much of the remaining oxidation occurs due to the reaction with peroxy radicals (HO_2 and RO_2). Oxidation of NO to NO_2 by XO is minor (1%) and occurs over the oceans because the main source of tropospheric reactive halogens is from sea salt aerosol and sea water (Chen et al., 2017;Sherwen et al., 2016;Wang et al., 2018) (Figure 2). In the model, the global, annual mean lifetime of NO_x in the troposphere against oxidation to nitrate is about 1 day; about 50% of this loss is from the reaction of NO_2 + OH. NO_x loss from N_2O_5 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.

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For both the "cloud chemistry" and "standard" simulations, the two most important nitrate formation pathways are NO_2 + OH (41-42%) and N_2O_5 hydrolysis (28-41%) , the latter of which is dominant over the mid- to high-northern continental latitudes during winter where both NO_x emissions and aerosol abundances are relatively large (Figures 1 and 3). The "cloud chemistry" simulation results in an equal importance of nitrate formation via NO_2 + OH and N_2O_5 hydrolysis (both 41%) due to increases in the rate of N_2O_5 uptake in clouds and decreases in the importance of NO_2 hydrolysis, which can compete with N_2O_5 formation at night. In the "standard" model, NO_2 hydrolysis represents an important nitrate production mechanism (12%), but it is negligible in the "cloud chemistry" simulation due to the reduction in the reaction probability (from $\gamma_{NO2} = 10^{-4}$ to $\gamma_{NO2} = 10^{-4}$ to 10^{-8}) in the model, which is supported by laboratory studies (Burkholder et al., 2015;Crowley et al., 2010;Tan et al., 2016). The formation of HNO_3 from the hydrolysis of $RONO_2$ formed from both daytime (NO + RO_2) and nighttime (NO_3 + MTN/ISOP) reactions represents 6% of total, global nitrate formation (Figure 1) and is dominant over Amazonia (Figure 3). $RONO_2$ hydrolysis represents up to 20% of inorganic nitrate formation in the southeast U.S. (Figure 3). This is similar to Fisher et al. (2016) who estimated that formation of $RONO_2$ accounts for up to 20% of NO_x loss in this region during summer, with $RONO_2$ hydrolysis representing 60% of $RONO_2$ loss. Globally, the formation of inorganic nitrate from the hydrolysis of $RONO_2$ is dominated by $RONO_2$ formation from the daytime reactions (3-6%), while the formation of $RONO_2$ from nighttime reactions represents up to 3%. The relative importance of nighttime and daytime $RONO_2$ formation is expressed as a range because precursors to $RONO_2$ that formed from monoterpenes can form from both daytime and nighttime reactions, and these precursors are not separately diagnosed in the model output. HNO_3

formation from NO_3 + HC and the hydrolysis of XNO_3 are small globally (5-6%)~~, but the latter is dominant over the remote oceans (Figure 3)~~. Although XNO_3 hydrolysis is the dominant nitrate formation pathway over the remote oceans (Figure 3), its contribution to total, global nitrate production is relatively small due to small local NO_x sources in these regions.

Figures 4 - 6 show modeled $\Delta^{17}O$(nitrate) for the “cloud chemistry” simulation (the “standard” simulation is shown in Figures S2 – S4). Figure 4 shows modeled annual-mean $\Delta^{17}O$(nitrate) below 1 km altitude ($\Delta^{17}O(NO_2)$ is shown in Figure S5). The model predicts an annual-mean range of $\Delta^{17}O$(nitrate) = 4 – 33‰ near the surface. The lowest values are over Amazonia due to the dominance of $RONO_2$ hydrolysis and the highest values are over the mid-latitude oceans due to the dominance of XNO_3 hydrolysis (Figures 3 and 4).

Figure 5 compares the model with a global compilation of $\Delta^{17}O$(nitrate) observations from around the world. Observations included in Figure 5 include locations where there is enough data to calculate monthly means ~~at each location~~ (McCabe et al., 2006;Kunasek et al., 2008;Hastings et al., 2003;Kaiser et al., 2007;Michalski et al., 2003;Guha et al., 2017;Savarino et al., 2013;Ishino et al., 2017b;Savarino et al., 2007;Alexander et al., 2009;He et al., 2018b). Figure 6 compares the seasonality in modeled $\Delta^{17}O$(nitrate) to the observations where samples were collected over the course of approximately one year (McCabe et al., 2006;Kunasek et al., 2008;Kaiser et al., 2007;Michalski et al., 2003;Guha et al., 2017;Savarino et al., 2013;Ishino et al., 2017b;Savarino et al., 2007;Alexander et al., 2009). In contrast to Alexander et al. (2009), the model does not significantly underestimate the $\Delta^{17}O$(nitrate) observations when assuming a bulk ozone isotopic composition ($\Delta^{17}O(O_3)$) on the order of 25‰ (see Figure 2d in Alexander et al. (2009)). The increase in modeled $\Delta^{17}O$(nitrate) is due to increased importance of O_3 in NO_x cycling (85% below 1 km) compared to Alexander et al. (2009) (80% below 1 km altitude), and an increase in the number and fractional importance of nitrate formation pathways that yield relatively high values of $\Delta^{17}O$(nitrate) (red pathways in Fig. 1). Although XO species themselves are only a minor NO oxidation pathway (1%), the addition of reactive halogen chemistry in the model has altered the relative abundance of O_3 and HO_x (Sherwen et al., 2016) in such a way as to increase the modeled $\Delta^{17}O(NO_x)$. The Alexander et al. (2009) study used GEOS-Chem v8-01-01, which included

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tropospheric nitrate formation from the NO + OH, N_2O_5 + H_2O, and NO_3 + HC pathways only. An increased importance of N_2O_5 hydrolysis (R4) and additional nitrate formation pathways that yield relatively high values of $\Delta^{17}O$(nitrate) (R5, R6, R8, and R10) in the present study also explain the increase in modeled $\Delta^{17}O$(nitrate) relative to Alexander et al. (2009). An increase in the average *A* value from 0.80 to 0.85 would tend to increase the calculated $\Delta^{17}O$(nitrate) on the order of 2‰ (0.05 × $\Delta^{17}O(O_3^*)$), 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). Assuming a value of 35‰ for bulk $\Delta^{17}O(O_3)$ in the model that did not include reactive halogen chemistry or heterogeneous reactions in cloud water produced good agreement between modeled and observed $\Delta^{17}O$(nitrate) in Alexander et al. (2009); however, in the current version of the model this bulk isotopic assumption leads to a model overestimate at nearly all locations (Figure S~~5~~6). The "cloud chemistry" model shows somewhat better agreement with the observations (R^2 = 0.51 in Figure 5) compared to the "standard" model (R^2 = 0.48 in Figure S3). Improved agreement with the observations occurs in the mid- to high-latitudes (Figures 6 and S4) is due to addition of N_2O_5 hydrolysis in clouds (Figures 3 and S6).

The mean $\Delta^{17}O$(nitrate) value of the observations (27.7 ± 5.0‰) shown in Figure 5 is not significantly different from the modeled values at the location of the observations (28.6 ± 4.5‰); however, the range of $\Delta^{17}O$(nitrate) values of the observations (10.9 – 40.6‰) is larger than in the model (19.6 – 37.6‰). As previously noted in Savarino et al. (2007), the maximum observed $\Delta^{17}O$(nitrate) value (40.6‰) is not possible given our isotope assumption for the terminal oxygen atom of ozone ($\Delta^{17}O(O_3^*)$ = 39‰); however, it is theoretically possible given the approximately 2‰ uncertainty in observed $\Delta^{17}O(O_3^*)$. A value of $\Delta^{17}O$(nitrate) = 41‰ is possible if $\Delta^{17}O(O_3^*)$ = 41‰ 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 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). Observed $\Delta^{17}O$(nitrate) > 39‰ (in Antarctica) has been suggested to be due to transport of nitrate from the stratosphere (Savarino et al., 2007), as stratospheric O_3 is expected to have a higher $\Delta^{17}O(O_3)$ value than ozone produced in the troposphere (Krankowsky et al., 2000;Mauersberger et al., 2001;Lyons, 2001). Indeed, the model underestimates the observations

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at Dumont d'Urville (DDU) and the South Pole (both in Antarctica) during winter and spring (Figure 6), when and where the stratospheric contribution is expected to be most important (Savarino et al., 2007). The model underestimate in Antarctica may also be due to model underestimates of BrO column (Chen et al., 2017) and ozone abundance (Sherwen et al., 2016) in the southern high latitudes. The largest model overestimates occur at Mt. Lulin, Taiwan (Figures 5 and 6). Based on nitrogen isotope observations ($\delta^{15}N$), nitrate at Mt. Lulin is thought to be influenced by anthropogenic nitrate emitted in polluted areas of mainland China and transported to Mt. Lulin, rather than local nitrate production (Guha et al., 2017). However, observations of $\Delta^{17}O$(nitrate) in autumn and winter in Beijing suggest much higher values (30.6±1.8‰) than was measured at Mt. Lulin (15 – 30‰ 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 $\Delta^{17}O$(nitrate) producing pathways (R4-R8) should be negligible due to minimal aerosol surface area for heterogeneous chemistry. The model compares ~~well~~ better to the mid-latitude locations close to pollution sources (La Jolla and Princeton), although the model overestimates wintertime $\Delta^{17}O$(nitrate) in Princeton, NJ, USA by up to 6‰ and underestimates winter time $\Delta^{17}O$(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 $\Delta^{17}O$(nitrate) by increasing nitrate formation by the hydrolysis of halogen nitrates (R6) in this coastal location. The model underestimates the $\Delta^{17}O$(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 NO_3 + 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.

4. Model uncertainties

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The uncertainty in the two most important nitrate formation pathways, NO_2 + OH and N_2O_5 hydrolysis, and their impacts on NO_x and oxidant budgets, have been examined and discussed elsewhere (Macintyre and Evans, 2010;Newsome and Evans, 2017;Holmes et al., 2019). The impacts of the formation and hydrolysis of halogen nitrates on global NO_x and oxidant budgets have also been previously examined (Sherwen et al., 2016). Here we focus on three additional processes using a set of model sensitivity studies. First, we examine the importance of the third most important nitrate production pathway on the global scale as predicted by the "standard" model, NO_2 aerosol uptake and hydrolysis, and its implications for the global NO_x, nitrate, and oxidant budgets. Second, we examine the role of changing anthropogenic NO_x emissions over a 15-year period (2000 to 2015) on the relative importance of the formation of inorganic nitrate from the hydrolysis of organic nitrates. Finally, we examine the role of aerosol nitrate photolysis on the relative importance of different nitrate formation pathways. The impact of aerosol nitrate photolysis on NO_x and oxidant budgets has been examined in detail elsewhere (Kasibhatla et al., 2018).

4.1 Heterogeneous uptake and hydrolysis of NO_2

Heterogeneous uptake of NO_2 to form HNO_3 and HONO is the third most important nitrate formation pathway in the "standard" model on the global scale (Figure 1). The reaction probability (γ_{NO2}) measured in laboratory studies ranges between 10^{-8} to 10^{-4} depending on aerosol chemical composition (Lee and Tang, 1988;Crowley et al., 2010;Gutzwiller et al., 2002;Yabushita et al., 2009;Abbatt and Waschewsky, 1998;Burkhart et al., 2015;Broske et al., 2003;Li et al., 2018a;Xu et al., 2018). A value of $\gamma_{NO2} = 10^{-4}$ is used in the "standard" model, which is at the high end of the reported range. A molar yield of 0.5 for both HNO_3 and HONO formation is assumed in the model based on laboratory studies and hypothesized reaction mechanisms (Finlayson-Pitts et al., 2003;Jenkin et al., 1988;Ramazan et al., 2004;Yabushita et al., 2009). However, both the reaction rate and mechanism of this reaction and its dependence on chemical composition and pH is still not well understood (Spataro and Ianniello, 2014).

The "cloud chemistry" simulation uses a reaction probability formulation for aerosol uptake of NO_2 (γ_{NO2}) that depends on aerosol chemical composition, ranging from $\gamma_{NO2} = 10^{-8}$ for dust to $\gamma_{NO2} = 10^{-4}$ for black carbon based on recent laboratory studies (Holmes et al., 2019). The updated NO_2 reaction probability results in a negligible (<1%) importance of this reaction for nitrate formation, compared to 12% contribution in the "standard" model. The "cloud chemistry" simulation significantly increases the fractional importance of N_2O_5 hydrolysis (from 28 to 41%, globally below 1 km altitude) compared to the "standard" simulation, in part due to decreased competition from NO_2 hydrolysis and in part due to increased N_2O_5 hydrolysis in clouds. To evaluate the relative importance of competition from NO_2 hydrolysis and the addition of N_2O_5 hydrolysis in clouds, we perform a model sensitivity study that is the same as the "standard" simulation but decreases the reaction probability of NO_2 hydrolysis on aerosol ($\gamma_{NO2} = 10^{-7}$), without adding N_2O_5 hydrolysis in clouds. Similar to the "cloud chemistry" simulation, using $\gamma_{NO2} = 10^{-7}$ renders NO_2 hydrolysis a negligible nitrate formation pathway, and increases the relative importance of N_2O_5 hydrolysis from 28% to 37%. This suggests that reduced competition from NO_2 hydrolysis is the main reason for the increased importance of N_2O_5 hydrolysis in the "cloud chemistry" simulation, though the addition of heterogeneous reactions on clouds also plays a role.

NO_2 hydrolysis represents a significant source of HONO in the "standard" model simulation; the reduced NO_2 reaction probability from $\gamma_{NO2} = 10^{-4}$ to $\gamma_{NO2} = 10^{-7}$ results in a reduction of HONO below 1 km altitude by up to 100% over the continents, with relatively small (up to 1 ppb) changes in nitrate concentrations (Figure 7). The reduction in the rate of heterogeneous NO_2 uptake leads to reductions in OH where this reaction was most important in the model (over China and Europe) due to reductions in HONO, but leads to increases in OH elsewhere due to increases in ozone (by up to a few ppb) resulting from small increases in the NO_x lifetime due to a reduction in the NO_x sink (Figure 8). Similar changes in HONO are seen when comparing the "standard" and "cloud chemistry" simulation (not shown). Increased importance of N_2O_5 hydrolysis in both the "cloud chemistry" simulation and the simulation without cloud chemistry but with a reduced reaction probability for NO_2 hydrolysis increases modeled annual-mean $\Delta^{17}O$(nitrate) by up to 3‰ in China where this reaction is most important. This improves model agreement with monthly-mean observations of $\Delta^{17}O$(nitrate) in Beijing (He et al., 2018a) (Figures 5 and S3).

The product yields of NO_2 hydrolysis are also uncertain. Jenkin et al. (1988) proposed the formation of a water complex, $NO_2 \cdot H_2O$, leading to the production of HONO and HNO_3. Finlayson-Pitts et al. (2003) and Ramazan et al. (2004) proposed the formation of the dimer N_2O_4 on the surface, followed by isomerization to form $NO^+NO_3^-$. Reaction of $NO^+NO_3^-$ with H_2O results in the formation of HONO and HNO_3. Laboratory experiments by Yabushita et al. (2009) suggested that dissolved anions catalyzed the dissolution of NO_2 to form a radical intermediate X-NO_2^- (where X = Cl, Br, or I) at the surface followed by reaction with NO_2(g) to form HONO and NO_3^-. These experiments described above were performed at NO_2 concentrations much higher than exist in the atmosphere (10 – 100 ppm) (Yabushita et al., 2009;Finlayson-Pitts et al., 2003;Ramazan et al., 2004). A laboratory study utilizing isotopically labeled water to investigate the reaction mechanism suggested that the formation of HONO resulted from the reaction between adsorbed NO_2 and H^+, while the formation of HNO_3 resulted from the reaction between adsorbed NO_2 and OH^-, and did not involve the N_2O_4 intermediate (Gustafsson et al., 2009). Results from Gustafsson et al. (2009) suggest an acidity-dependent yield of HONO and HNO_3, favoring HONO at low pH values. A recent study in the northeast U.S. during winter found that modeled nitrate abundance was overestimated using a molar yield of 0.5 for HONO and HNO_3, and the model better matched the observations of NO_2 and nitrate when assuming a molar yield of 1.0 for HONO (Jaeglé et al., 2018). Particles were acidic (pH < 2) during this measurement campaign (Guo et al., 2017;Shah et al., 2018), which may favor HONO production over HNO_3.

We examine the potential importance of this acidity-dependent yield by implementing a pH-dependent product yield in two separate sensitivity simulations, first using an NO_2 aerosol uptake reaction probability of $\gamma = 10^{-4}$ as in the "standard" simulation and second with $\gamma_{NO2} = 10^{-7}$. The acidity-dependent yield for HONO and HNO_3 formation is based on the laboratory study by Gustafsson et al. (2009). We use aerosol pH calculated from ISORROPIA II (Fountoukis and Nenes, 2007) to calculate the concentration of $[H^+]$ and $[OH^-]$ in aerosol water. The yield of HONO (Υ_{HONO}) from heterogeneous uptake of NO_2 on aerosol surfaces is calculated according to E3:

$$\Upsilon_{HONO} = \frac{[H^+]}{[H^+]+[OH^-]} \qquad \text{(E3)}$$

where $[H^+]$ and $[OH^-]$ are in units of M. The yield of HNO_3 from this reaction is equal to ($1 - \Upsilon_{HONO}$). E3 yields values of Υ_{HONO} near unity for aerosol pH values less than 6, decreasing rapidly to zero between pH values between 6-8 (Figure S8~~9~~). Calculated aerosol pH values are typically < 6 in the model except in remote regions far from NO_x sources (Figure S9~~7~~), favoring the product HONO.

The acidity-dependent yield implemented in the "standard" simulation with $\gamma_{NO2} = 10^{-4}$ increases HONO concentrations by up to 1 ppbv in China where this reaction is most important (Figure 9~~10~~). Fractional increases in HONO exceed 100% in remote locations (Figure 9~~10~~). Increased HONO leads to increases in OH on the order of 10 – 20% in most locations below 1 km altitude, while ozone concentrations increase in most locations by up to several ppbv (Figure 9~~10~~). The exception is the southern high latitudes; likely due to decreased formation and thus transport of nitrate to remote locations. The impact on NO_x and nitrate budgets is relatively minor. The global, annual mean NO_x burden near the surface (below 1 km) increases slightly (+2%) as a result of the decreased rate of conversion of NO_2 to nitrate; the change to the global tropospheric burden is negligible. Annual-mean surface nitrate concentrations show small decreases up to 1 ppbv in China where this reaction is most important in the model; impacts on nitrate concentrations over a shorter time period may be more significant (Jaeglé et al., 2018). The fraction of HNO_3 formed from NO_2 + OH (49%) increases due to increases in OH from the HONO source. The fraction of HNO_3 formation from the uptake and hydrolysis of N_2O_5 also increases (from 28% to 32%) due to reductions in the nighttime source of nitrate from NO_2 hydrolysis. The calculated mean $\Delta^{17}O$(nitrate) at the location of the observations shown in Figure 5 (27.9 ± 5.0‰) is not significantly impacted due to compensating effects from changes in both high- and low-producing $\Delta^{17}O$(nitrate) values. Modeled monthly mean $\Delta^{17}O$(nitrate) in China, where NO_2 hydrolysis is most important increases by ~1‰, but is still biased low by 1-2‰.

Using a combination of both the low reaction probability ($\gamma = 10^{-7}$) and the acidity-dependent yield gives similar results as using $\gamma = 10^{-7}$ and assuming a molar yield of 0.5 for HONO and HNO_3 (not shown). In other words, including a pH-dependent product yield rather than a yield of 0.5 for HONO and nitrate results in negligible differences for oxidants, NO_x and nitrate abundances when the reaction probability (γ_{NO2}) is low.

4.2 Hydrolysis of organic nitrates ($RONO_2$)

Anthropogenic NO_x emissions have been increasing in China and decreasing in the U.S. and Europe (Richter et al., 2005;Hoesly et al., 2018b), with implications for the relative importance of inorganic and organic nitrate formation as a sink for NO_x (Zare et al., 2018). To examine the impacts of recent changes in anthropogenic NO_x emissions for nitrate formation pathways, we run the “standard” model using the year 2000 emissions and meteorology after a 1-year model spin up, and compare the results to the “standard” model simulation run in the year 2015. This time-period encompasses significant changes in anthropogenic NO_x emissions in the U.S., Europe, and China, and encompasses most of the time period of the observations shown in Figures 5 and 6. Total, global anthropogenic emissions of NO_x are slightly lower in the 2000-year simulation (30 Tg N yr^{-1}) compared to the year 2015 simulation (31 Tg N yr^{-1}) due to decreases in North America and Europe, counteracted by increases in Asia (Figure ~~S7~~S10). This leads to increases of less than 10% in the annual-mean, fractional importance of the source of nitrate from the hydrolysis of organic nitrates in the U.S., and corresponding decreases of less than 10% over China (Figure 10~~1~~). Relatively small changes (< 10%) in nitrate formation pathways yield small changes (< 2‰) in modeled annual-mean $\Delta^{17}O$(nitrate) between the year 2000 and 2015, differences in $\Delta^{17}O$(nitrate) over shorter time periods may be larger. Changes in the formation of nitrate from the hydrolysis of $RONO_2$ remains unchanged globally, as increases in the U.S. and Europe and decreases in China counteract one another.

4.3 Photolysis of aerosol nitrate

Observations have demonstrated that aerosol nitrate can be photolyzed at rates much faster than HNO_3(g) (Reed et al., 2017;Ye et al., 2016); however, the magnitude of the photolytic rate constant is uncertain. We examine the implications of this process for global nitrate formation pathways by implementing the photolysis of aerosol nitrate as described in Kasibhatla et al. (2018) into the “standard” model simulation, scaling the photolytic rate constant for both fine- and coarse-mode aerosol nitrate to a factor of 25 times higher than that for HNO_3(g) (Kasibhatla et al., 2018;Romer et al., 2018), with a molar yield of 0.67 for HONO and 0.33 for NO_x production. The global, annual mean NO_x burden near the surface (below 1 km) increases slightly (+2%) as a result of the photolytic recycling of nitrate to NO_x, similar to Kasibhatla et al. (2018). Aerosol nitrate photolysis results in only small impacts on the relative importance of nitrate formation pathways (< 2%) likely due to simultaneous increases in O_3 and OH (Kasibhatla et al., 2018), which in turn yields small impacts on calculated $\Delta^{17}O$(nitrate) at the location of the observations shown in Figure 5 (27.9 ± 5.0‰). Nitrate photolysis itself has minimal impact on $\Delta^{17}O$(nitrate) because it is a mass-dependent process (McCabe et al., 2005).

5 Conclusions

Observations of $\Delta^{17}O$(nitrate) can be used to help quantify the relative importance of different nitrate formation pathways. Interpretation of $\Delta^{17}O$(nitrate) requires knowledge of $\Delta^{17}O(O_3)$~~, which until recently was highly uncertain~~. Previous modeling studies showed good agreement between observed and modeled $\Delta^{17}O$(nitrate) when assuming a bulk oxygen isotopic composition of ozone ($\Delta^{17}O(O_3)$) ~~=~~ of 35‰ based on laboratory and modeling studies (Morton, 1990;Thiemens, 1990;Lyons, 2001). However, recent and spatially widespread observations of $\Delta^{17}O(O_3)$ ~~from around the world~~ have consistently shown $\Delta^{17}O(O_3) = 26 \pm 1$‰, suggesting that models are underestimating the role of ozone relative to HO_x in NO_x chemistry. We utilize a global compilation of observations of $\Delta^{17}O$(nitrate) to assess the representation of nitrate formation in a global chemical transport model (GEOS-Chem), assuming that the bulk oxygen isotopic composition of ozone ($\Delta^{17}O(O_3)$) = 26‰. The modeled $\Delta^{17}O$(nitrate) is roughly consistent with observations, with a mean modeled and observed $\Delta^{17}O$(nitrate) of (28.6 ± 4.5‰) and (27.6 ± 5.0‰), respectively, at the locations of the observations. Improved agreement between modeled and observed $\Delta^{17}O$(nitrate) is due to increased importance of ozone versus HO_2 and RO_2 in NO_x cycling and an increase in the number and importance of nitrate production pathways that yield high $\Delta^{17}O$(nitrate) values. The former may be due to implementation of tropospheric reactive halogen chemistry in the model, which impacts ozone and HO_x abundances. The latter is due mainly to increases in the relative importance of N_2O_5 hydrolysis, with the hydrolysis of halogen nitrates also playing an important role in remote regions.

The main nitrate formation pathways in the model below 1 km altitude are from NO_2 + OH and N_2O_5 hydrolysis (both 41%). The relative importance of global nitrate formation from the hydrolysis of halogen nitrates and hydrogen-abstraction reactions involving the nitrate radical (NO_3) are of similar magnitude (~5%). The formation of nitrate from the hydrolysis of organic nitrate has increased slightly in the U.S. and decreased in China (changes <10%) due to changing NO_x emissions from the year 2000 to 2015, although the global mean fractional importance (6%) remains unchanged as the regional changes counteract one another. Nitrate formation via heterogeneous NO_2 and NO_3 uptake and NO_2 + HO_2 are negligible (<2%). Although aerosol nitrate photolysis has important implications for O_3 and OH, the impacts on nitrate formation pathways are small.

The model parameterization for heterogeneous uptake of NO_2 has significant impacts on HONO and oxidants (OH and ozone) in the model. HONO production from this reaction has been suggested to be an important source of OH in Chinese haze due to high NO_x and aerosol abundances (Hendrick et al., 2014;Tong et al., 2016;Wang et al., 2017), with implications for the gas-phase formation of sulfate aerosol from the oxidation of sulfur dioxide by OH (Shao et al., 2018;Li et al., 2018b). More recent laboratory studies suggest that the reaction probability of NO_2 on aerosols is lower than that previously used in the model. Using an NO_2 reaction probability formulation that depends on the chemical composition of aerosols as described in Holmes et al. (2019) renders this reaction negligible for nitrate formation, and has significant implications for modeled HONO, ozone, and OH. Although uncertainty also exists in the relative yield of nitrate and HONO from this reaction, the impacts of this assumption are negligible when we use these updated NO_2 reaction probabilities. Observations of $\Delta^{17}O$(nitrate) in Chinese haze events during winter (He et al., 2018b) may help to quantify the importance of this nitrate production pathway in a region where the model predicts it is significant.

Author contributions: B.A. designed the study and performed the model simulations and calculations. All other authors provided model code and contributed to writing and analysis.

Data availability: The GEOS-Chem model is available at http://acmg.seas.harvard.edu/geos

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Table 1. Calculated Δ^{17}O(nitrate) in the model for each nitrate production pathway (X = Br, Cl, and I; HC = hydrocarbon; MTN = monoterpene; ISOP = isoprene; $\Delta^{17}O(O_3^*)$ = 39‰). A is defined in equation E1.

	Nitrate formation pathway	**Δ^{17}O(nitrate)**
	Gas-phase reactions	
R1	NO_2 + OH	$\frac{2}{3}A\Delta^{17}O(O_3^*)$
R2	NO_3 + HC	$(\frac{2}{3}A + \frac{1}{3})\,\Delta^{17}O(O_3^*)$
R3	NO + HO_2	$\frac{1}{3}A\Delta^{17}O(O_3^*)$
	Aerosol uptake from the gas-phase followed by hydrolysis	
R4	N_2O_5 + $H_2O_{(aq)}$	$(\frac{2}{3}A + \frac{1}{6})\,\Delta^{17}O(O_3^*)$
R5	N_2O_5 + Cl^-(aq)	$(\frac{2}{3}A + \frac{1}{3})\,\Delta^{17}O(O_3^*)$
R6	XNO_3 + $H_2O_{(aq)}$	$(\frac{2}{3}A + \frac{1}{3})\,\Delta^{17}O(O_3^*)$
R7	NO_2 + $H_2O_{(aq)}$	$\frac{2}{3}A\Delta^{17}O(O_3^*)$
R8	NO_3 + $H_2O_{(aq)}$	$(\frac{2}{3}A + \frac{1}{3})\,\Delta^{17}O(O_3^*)$
R9	$RONO_2$ + $H_2O_{(aq)}$ (where $RONO_2$ is from NO + RO_2)	$\frac{1}{3}A\Delta^{17}O(O_3^*)$
R10	$RONO_2$ + $H_2O_{(aq)}$ (where $RONO_2$ is from NO_3 + MTN/ISOP)	$(\frac{2}{3}A + \frac{1}{3})\,\Delta^{17}O(O_3^*)$

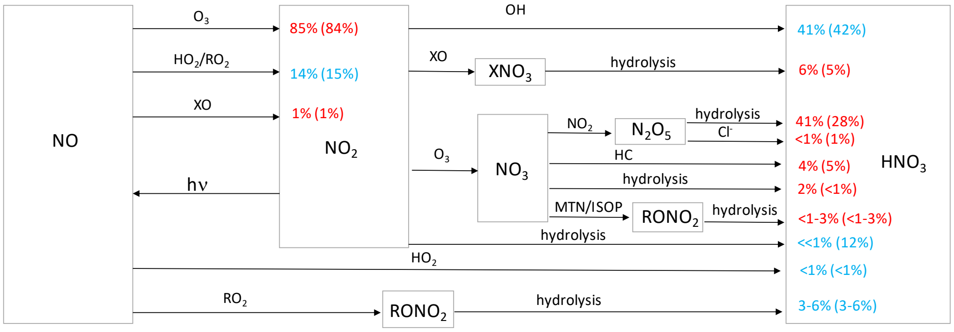

Figure 1. Simplified HNO_3 formation in the model. Numbers show the global, annual mean percent contribution to NO_2 and HNO_3 formation in the troposphere below 1 km for the "cloud chem" ("standard") simulation. Red indicates reactions leading to high $\Delta^{17}O$ values, blue indicates reactions leading to low $\Delta^{17}O$ values. $HO_2 = HO_2+RO_2$; X = Br+Cl+I; HC = hydrocarbons; MTN = monoterpenes; ISOP = isoprene.

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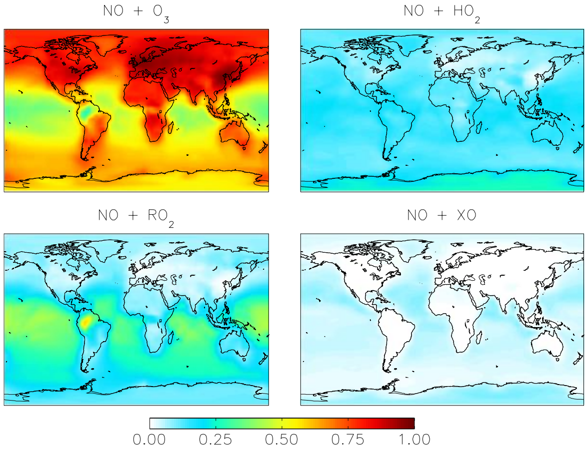

Figure 2. Annual-mean fraction of NO_2 formation from the oxidation of NO in the troposphere below 1 km altitude in the "cloud chemistry" model.

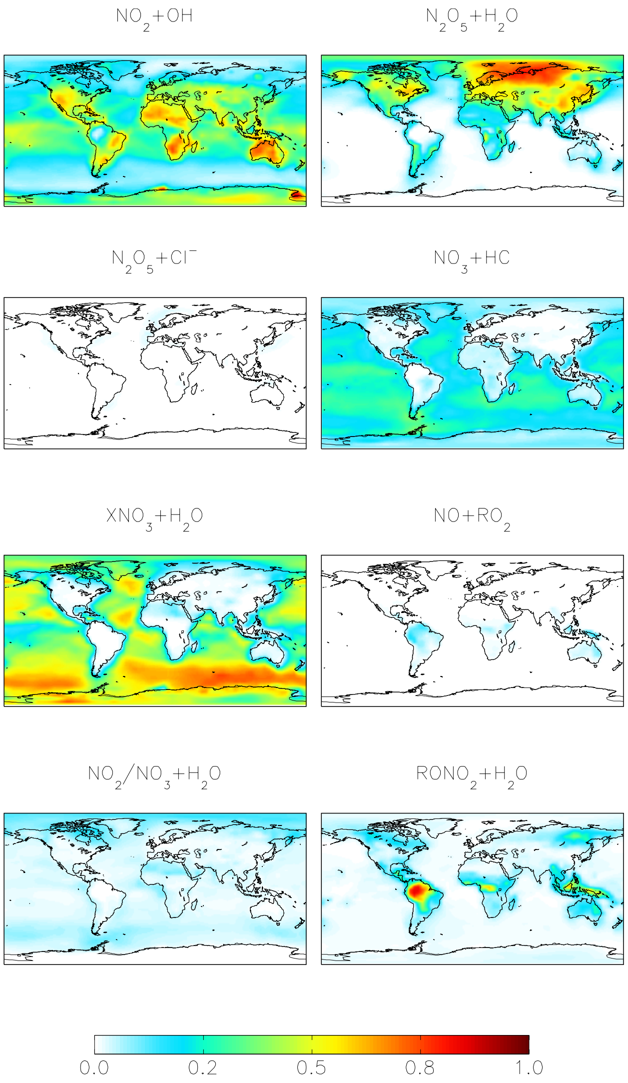

Figure 3. Annual-mean fraction of HNO_3 formation from the oxidation of NO_x in the troposphere below 1 km altitude in the "cloud chemistry" model.

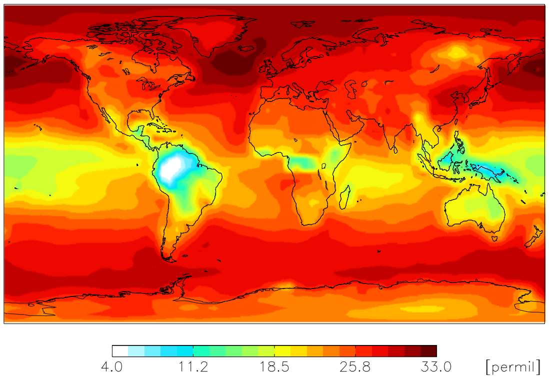

Figure 4. Modeled, annual-mean Δ^{17}O(nitrate) below 1 km altitude for the "cloud chemistry" model.

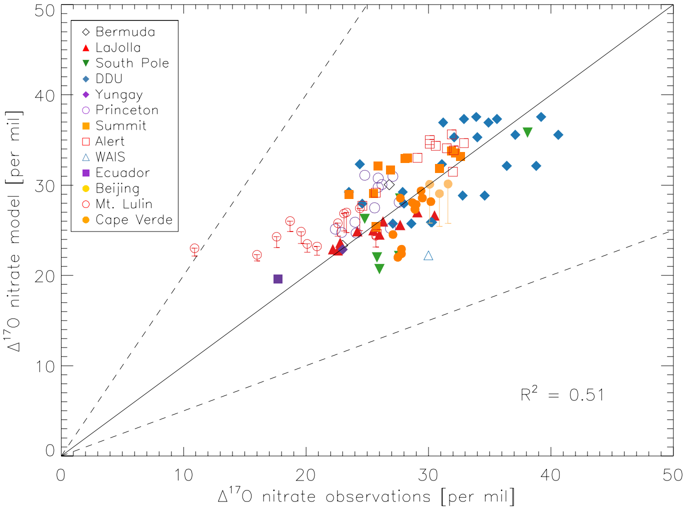

Figure 5. Comparison of monthly-mean modeled ("cloud chemistry") and observed Δ^{17}O(nitrate) at locations where there are enough observations to calculate a monthly mean. References for the observations are in the text. The error bars represent different assumptions for calculated modeled *A* values for nighttime reactions as described in the text. Error bars for Beijing and Mt. Lulin reflect the range of possible modeled *A* values for nighttime reactions as described in the text.

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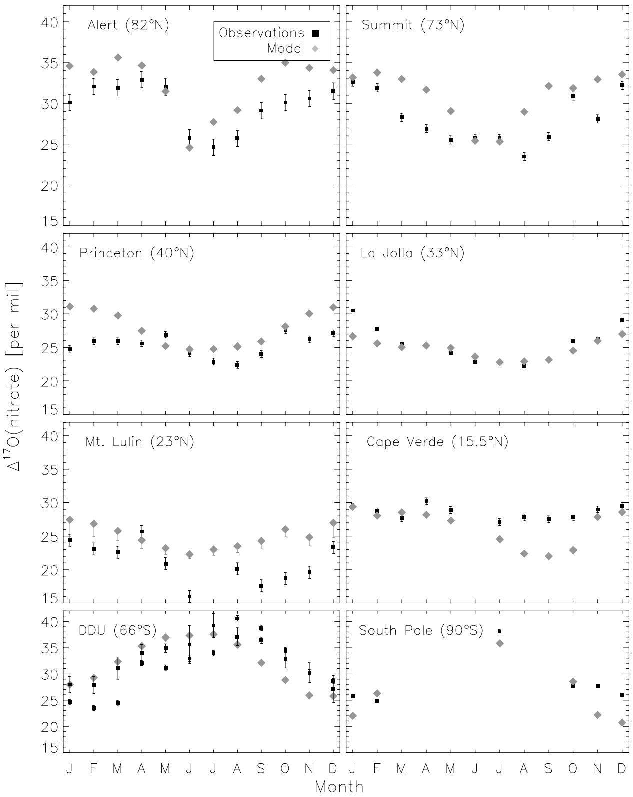

Figure 6. Comparison of monthly-mean modeled ("cloud chemistry") and observed Δ^{17}O(nitrate). Error bars for Mt. Lulin reflect the range of possible modeled *A* values for nighttime reactions as described in the text.

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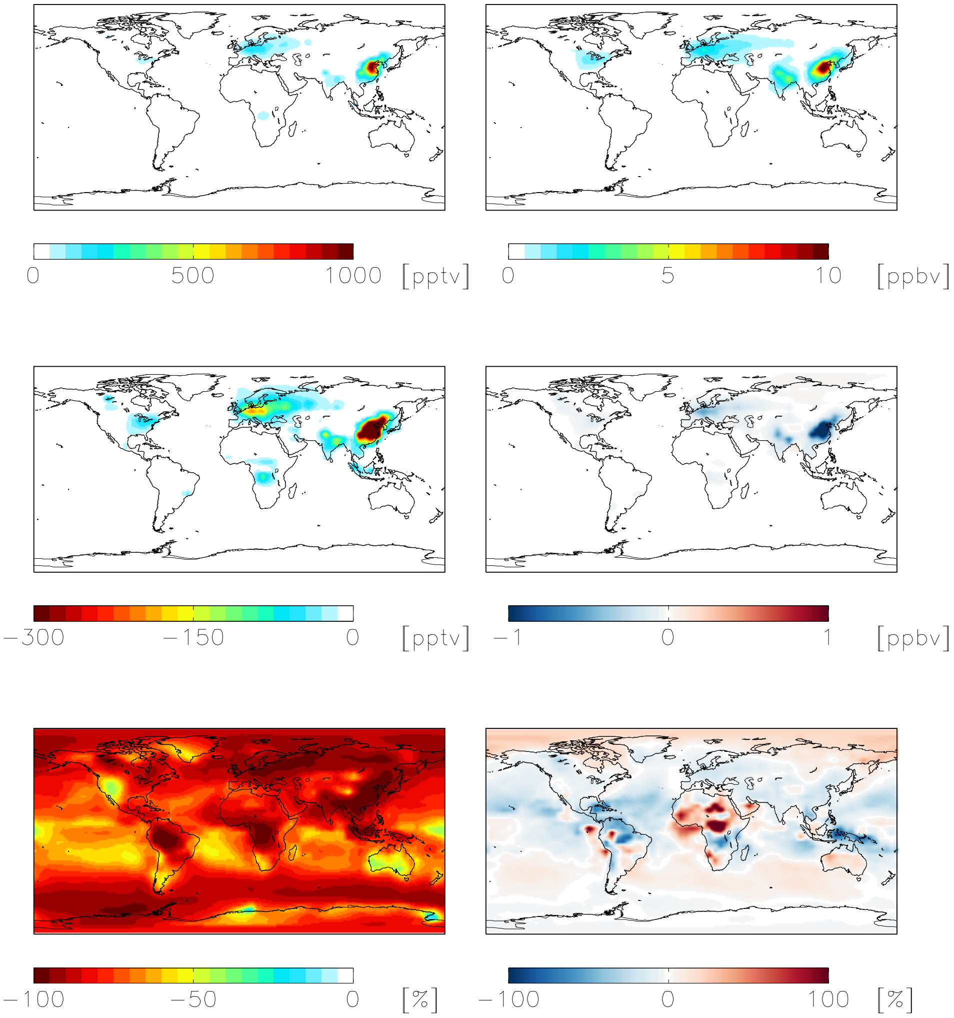

Figure 7. Modeled annual-mean HONO (left) and fine-mode nitrate (right) concentrations below 1 km altitude in the "standard" simulation (top) with $\gamma_{NO2} = 10^{-4}$ for NO_2 hydrolysis. Absolute (middle) and relative (bottom) change in concentrations below 1 km altitude between the "standard" model and the model simulation with $\gamma_{NO2} = 10^{-7}$. Negative numbers represent a decrease relative to the standard simulation.

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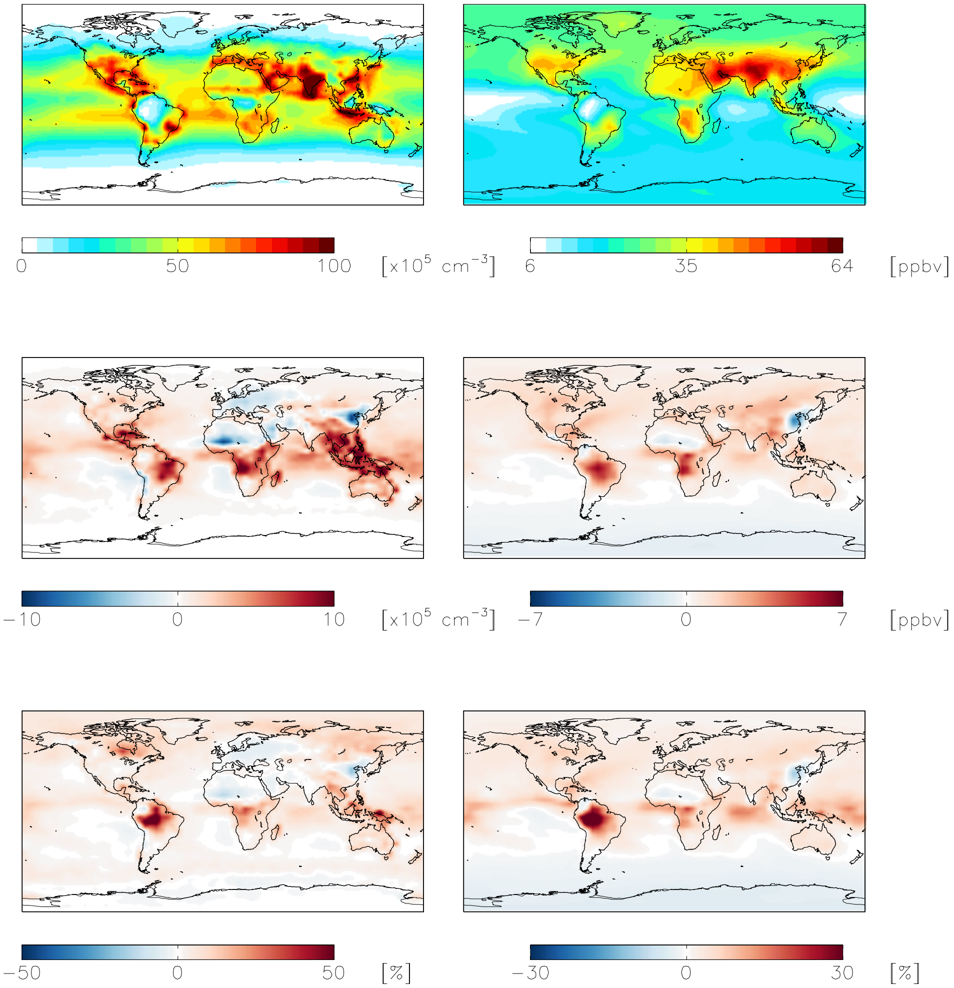
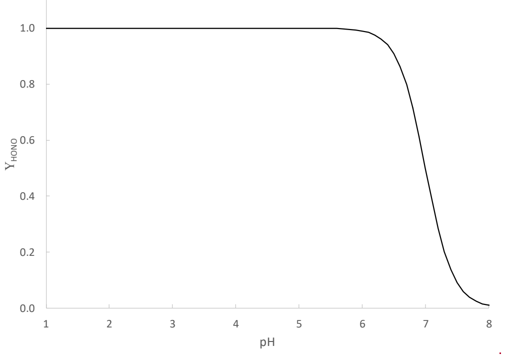


Figure 8. Same as Figure 7 except for OH (left) and ozone (right).



~~**Figure 9.** Calculated yield of HONO from the heterogeneous reaction of NO_2 on aerosol surfaces as a function of pH.~~

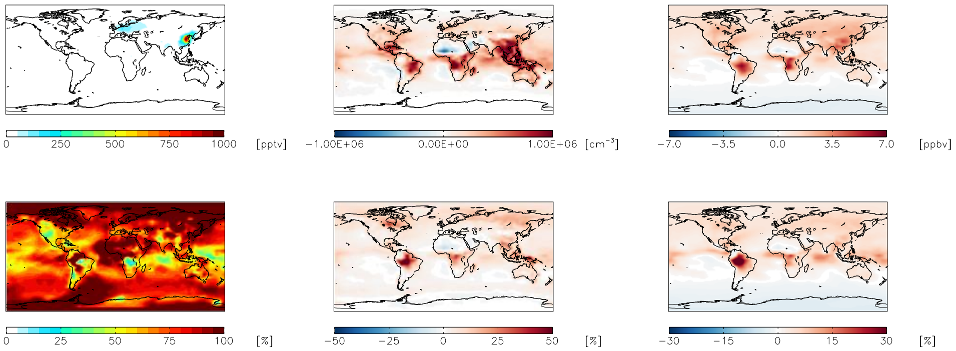


Figure 9~~10~~. Absolute (top) and relative (bottom) change in HONO (left), OH (middle), and ozone (right) concentrations below 1 km altitude between the “standard” model and the model simulation with an acidity-dependent yield from NO_2 hydrolysis. Positive numbers represent an increase relative to the “standard” simulation.

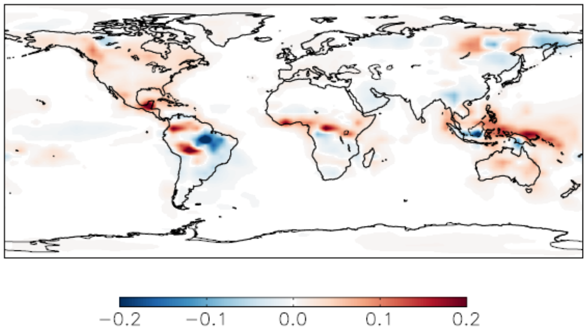


Figure 10~~1~~. Modeled annual-mean difference in the fractional production rate of HNO_3 from the hydrolysis of organic nitrate below 1 km attitude in the year 2015 relative to 2000 (2015 – 2000).