We appreciate both Reviewers' helpful comments and suggestions that significantly improve our manuscript's readability. Specifically, we have improved our figures as suggested by Reviewer # 1. For example, in our original manuscript, figures had small text that was very difficult to read, so we have enlarged the text size on axes, titles, and legends for all figures. We also have removed repetitive axes and legends for clearer visualization in the revised manuscript. Further, we have reorganized section 3.3 as suggested by Reviewer # 2. For example, in the original manuscript, section 3.3 contained information about the comparison between calculated and simulated $\Delta(^{17}O)$ and $\delta(^{18}O)$, which was quite hard to follow. However, in the revised manuscript, we have broken up section 3.3 into sections 3.3 and 3.4. This newly organized section helps streamline our discussion. According to this organization, the order of the figures was also changed in the revised manuscript based on the new flow. These changes do not alter the interpretations and the major findings of this work. Overall, these changes have led to the improvement of the presented manuscript. A point-by-point response to all reviewer comments is provided below.

Reviewer #1:

General comments:

In this paper, the authors use both field observations and modelling to examine the controls on temporal variability of oxygen isotopes in atmospheric nitrate. They find that the seasonal changes in nitrate isotopes are related to the formation chemistry pathways. Using oxygen isotopes as a tracer of past chemical origin has been studied some before for $\Delta^{17}O$ but less so for $d^{18}O$ in nitrate, so it is interesting to see their investigation with $d^{18}O$ added here. They find evidence from the oxygen isotopes that formation pathways are more different than expected for HNO_3 vs pNO3. They investigate this further with their modeled results.

Overall, my comments are minor. I found that the paper is generally written well and is methodologically sound. The authors do a good job explaining their methods in details and providing plenty of statistical values to support their results and discussion. The amount of work and effort put into producing the data and considering its interpretation is clearly evident. The writing and discussion can be rather dense at times, particularly when discussing model results and comparing isotopic values. This isn't necessarily a bad thing, as it is providing valuable information for people concerned with atmospheric chemistry modeling and nitrogen oxide dynamics. However, it could improve the readability to a broader audience if the dense sections of the discussion were supplemented with some broader summarizing or restating statements that make sure the main point is made clear and understood.

Response: Thank you for your helpful comments and suggestions, which have significantly improved the readability of our manuscript. We have addressed the raised points and revised the manuscript according to these suggestions. Below is a point-by-point response to the raised comments.

Specific comments:

Comments: This perhaps goes toward my primary suggestion, which is that it is not entirely evident what the broader impact and implications of the findings are to a non-specialist. Do these findings change our prior understanding of how nitrate is being formed? What do they lead us to think differently about atmospheric chemistry and nitrate going forward? Does the dominance of specific pathways tell us any new information about the local atmospheric chemistry? Are these results just specific to the local area, or is there reason to think that they have broader significance? Anything that can link the dense results into more easily graspable concepts would help the reader (particularly those outside of the nitrogen oxide chemistry community) better understand why these are interesting and intriguing findings. This would be a nice wrap up paragraph or small section of the discussion before the conclusion, just to give kind of a "greatest hits of the discussion" all presented in one place clearly.
Response: Thank you for your helpful suggestions. We made additions to the revised manuscript to highlight the broader significance of our findings. Specifically, we have added a wrap-up paragraph in the discussion section before the conclusion on Page 16, Lines 482-492 that points out the significance of GEOS-Chem for overpredicting nitrate formation via N_2O_5 heterogeneous reactions, "Overall, the observed differences in the oxygen isotopic composition of HNO_3 and pNO_3, the observed relationships of $\delta(^{18}O)$ and $\Delta(^{17}O)$ in the different nitrate phases, and the significant mismatch with the global model base case challenge our current representation of nitrate chemistry in atmospheric chemistry models. Generally, the GEOS-Chem $\Delta(^{17}O)$ simulations were biased high relative to observations, indicating the over-incorporation of O_3 during nitrate formation. The largest discrepancies in the model-observation comparisons, particularly for pNO_3, occur in winter. Our optimized chemistry, constrained by the observed $\delta(^{18}O)$ and $\Delta(^{17}O)$, suggested that the heterogenous production of nitrate via N_2O_5 chemistry is currently significantly overestimated. While our focus is on the northeastern US, an area of important environmental change due to regulated emissions reductions, this finding has implications for the global modeling of atmospheric nitrate and oxidation chemistry".

Further, we have added broader significance in the conclusion that addresses the importance of our findings for oxidation chemistry in the troposphere on Page 17, Lines 506-514, "Additionally, this finding has important implications for predicting oxidation chemistry in the atmosphere. For instance, the production of nitrate via heterogeneous hydrolysis of N_2O_5 represents a radical termination process, such that a much-reduced importance of this reaction could yield more radical chemistry with an impact on oxidant concentrations. Indeed, an important mechanism for converting NO_x to atmospheric nitrate could affect controlling the oxidizing efficiency, which directly influences the atmospheric oxidation budget and many atmospheric pollutants' (notably greenhouse gases) lifetime in the atmosphere. Thus, better constraining their chemistries and feedbacks is crucial to understanding atmospheric nitrate production pathways and its connection to atmospheric oxidation chemistry".

Comments: The bulk of my comments are focused on the figures. While most of the plots are fairly clear in their structure, they often had text that was very difficult to read, and I'm sure this will be a problem if they are printed in a final manuscript without changes. In many cases, duplicate axes and legends could be removed to increase space, but some figures may need more consideration as to how to become legible. The map figure (Fig 1) is also particularly lacking, especially relative to the otherwise high quality of this manuscript.

Response: We appreciate the comments on the figures. For Figure 1, we know that the previous version of the map lacked contextual information and scales, so we added scale, geographic coordinates, and legend in the revised manuscript (see specific comment and response below). Additionally, we agree that some axes and legends were repetitive and hard to read, so we have simplified and enlarged axes and legends and broken up some Figures for clearer visualization in the revised manuscript. For example, we have broken up Figure 4 into Figure 4 and Figure 5 and Figure 7 into Figure 7 and Figure 9. In the original version, Figure 4 and Figure 7 contain information about $\Delta(^{17}O)$ and $\delta(^{18}O)$ values of HNO_3 and pNO_3 by the CASTNET sites that were quite complicated to follow. In the revised manuscript, Figure 4 and Figure 7 only include $\Delta(^{17}O)$ information of HNO_3 and pNO_3 and Figure 5 and Figure 8 are only for $\delta(^{18}O)$ information of HNO_3 and pNO_3. In addition, based on your suggestion, we increased the axes and legends text size in Figures 4, 5, 7, and 9. We also removed repetitive axes and legends in Figures 4, 5, 7, and 9. Further, the $\delta(^{18}O)$ correlation of Figure 7 in the original version was merged with Figure 9 since they contain the same information about $\delta(^{18}O)$.

Additionally, we have reorganized section 3.3 as suggested by Reviewer #2 and the order of figures was also changed in the revised manuscript. For example, the pie chart (Figure 6 in the original manuscript) was moved to Figure 8 in the revised manuscript. Overall, breaking up the figures in this way and reorganization of section 3.3 improve the readability of the manuscript.

Technical comments

Comment: The method of writing $d^{18}O$ and $\Delta^{17}O$ with parenthesis as $d(^{18}O)$ and $\Delta(^{17}O)$ is unusual and not standard. This not only comes across as slightly odd, but in my opinion reduces readability by adding more "clutter" to the text. And overall, the sheer number of parentheses used throughout makes reading difficult. In many cases, they seem unnecessary. For example, at 332: **$\Delta(^{17}O)$ value ((39±2) ‰; ..citation)** could be **$\Delta^{17}O$ value (39±2 ‰; …citation)** which is more readable. Use of parenthesis like $\delta(^{18}O, O_3{}^{*})$ instead of the more standard $d^{18}O_{O3*}$ or $d^{18}O(O_3*)$ makes it more difficult to understand and bulkier to read.

Response: Thank you for these comments. This notation follows IUPAC recommendations for any quantity symbol, including isotope deltas, to enclose labels in parentheses, and this was the recommended notation by the editor. Thus, we did not make these suggested notation changes.

Comment: At some times in the abstract and throughout, the term significant/significance is used to describe a result, but it isn't clear whether this is referring to statistical significance or not. In some cases, perhaps consider rewording to remove any ambiguity.

Response: Thank you for these comments. In the revised manuscript, we use significant/significance when dealing only with statistical significance. Other than that, we have reworded ambiguous words using similar meanings. For example, we have replaced 'significantly' to 'notably' on Page 9, Line 271 in the revised manuscript. Further, we have replaced 'significantly' to 'dramatically' on Page 15, Line 433 and 'significant' to 'critical' on Page 18, Line 523 in the revised manuscript.

Comment: The use of nitrate vs. NO_3^- is inconsistent throughout. It seems to shift from nitrate to NO_3^- in the methods, and then shift back to just nitrate.

Response: Thank you for pointing this out. We have replaced NO_3^- with nitrate in the method section to be consistent in the revised manuscript.

Comment: 14: First sentence is worded unwieldy with "by high population density, high emissions density and degraded air quality and acid rain"

Response: Thank you for pointing this out. We have corrected the sentence on Page 1, Lines 14-15, as follows, "The northeastern US represents a mostly urban corridor impacted by high population and fossil-fuel combustion emission density. This has led to historically degraded air quality and acid rain that has been a focus of regulatory-driven emissions reductions."

Comment: 18: "Oxygen isotope deltas" is odd phrasing. Perhaps just "oxygen isotopic ratios"? I did a search for this term and the only result on the internet that came back was for this preprint.

Response: Thank you for this comment. Since we are referring to δ, the correct terminology is isotope deltas which was the recommended terminology provided by the editor. Thus, no change was made in reference to this comment.

Comment: 23: pNO_3?

Response: Thank you for pointing out this typo. We have corrected it as pNO_3 on Line 23 in the revised manuscript.

Comment: 72: Subject verb agreement

Response: Thank you for pointing this out. We have corrected "has" to "have". This change was made on page 3, Line 72, in the revised manuscript.

Comment: 150: This is a long paragraph, and might benefit from being split.

Response: Thank you for the comment. The paragraph was split into two paragraphs in section 2.3.

Comment: 153: Perhaps add the citation as a reference instead of a link here
Response: We have added the citation for the GEOS-Chem model description instead of a link on Page 6, Lines 156-159 as, "The GEOS-Chem global model of atmospheric chemistry (Bey et al., 2001; Walker et al., 2012; 2019) was utilized to track the production of NO_2 and HNO_3 at the CASTNET sites and further to model the oxygen isotopic deltas (e.g., $\delta(^{18}O)$ and $\Delta(^{17}O)$) following a previous framework (Alexander et al., 2020)."

Comment: 193: Space missing I think here between O_3 and O_3^*
Response: Thank you for pointing this out. We have made this correction on Page 7, Line 205.

Comment: 212: The water isotope assumed to be -6, but this would vary seasonally. Between GNIP and USNIP, we have good records of the seasonal variability of water isotopes in precipitation. I'm not sure how much this would impact your modelling results, but if any substantial oxygen exchange is occurring between water and nitrogen oxides, it could explain some of the model discrepancy between observed values and the modelled values. For example, the $d^{18}O_{NO3}$ values in winter are lower than predicted by the model, but this would be a time when $d^{18}O_{precip}$ values are often < –15 ‰ in New York, for example, and much lower than the –6 ‰ included in your model.
217: We have direct water vapor isotopic measurements from eastern N America (https://doi.org/10.1038/sdata.2018.302). Similar to the liquid water comment above, these also vary dramatically with seasons (usually with vapor varying even more than precipitation, since the dry winter air can be very isotopically light when there is no precipitation).
Response: Thanks for raising this point. It is indeed true that $\delta(^{18}O)$ values of H_2O significantly vary depending on latitudinal effects, longitudinal effects, and altitude effects (Michalski et al., 2012). However, in our model optimization, changes in $\delta(^{18}O)$ of H_2O values scarcely impacted $\delta(^{18}O)$ of nitrate. Rather, variabilities of $\delta(^{18}O)$ of O_3 and OH values, likely driven by temperature and pressure, were the main levers to change the $\delta(^{18}O)$ significantly. Given the lack of sensitivity to the $\delta(^{18}O)$ of H_2O, we adopted a typical mid-latitude value of -6 ‰ as our reference value. For future online modeling of $\delta^{18}O$ values, we will consider incorporating direct water vapor isotope measurements, and we appreciate your comment.

We have also addressed these sentences in the revised manuscript for clarification on Page 15, Line 436-439, "A typical mid-latitude value (-6 ‰) of $\delta(^{18}O, H_2O)$ was selected in this study. We note that the $\delta(^{18}O, H_2O)$ will vary seasonally; however, the calculated $\delta(^{18}O)$ value of nitrate was insensitive to this value because of the relatively minor role that H_2O contributes to O atoms of atmospheric nitrate.

Comment: 332: Notably? Instead of notable, perhaps
Response: Thank you for pointing this out. We have changed the wording to "notably" on Page 12, Line 345 in the revised manuscript.

Comment: Figure 1. This map is extremely basic and lacks any contextual information that could help us understand the study region better. There is no scale, or geographic coordinates, or legend. The projections clearly differ between the two maps, but there's no way to determine what matches what because there is no spatial referencing. Also, this means that the area covered in the box at left doesn't match the extent covered in the inset (the box would need distorted and angled to accurately pair up with the inset). A map that includes features that directly impact the study would be immensely beneficial, such as one showing local urban areas, land use, transportation routes. And even though Canada is directly upwind of these sites, the country doesn't exist on the inset map.

Response: Thank you for this comment, and we have updated the map based on your feedback. For example, in the revised manuscript, we are using the same projections for the map of the United States (left) and CASTNET sampling sites (right) in Figure 1. We have included Canada in the map as well. Further, we have added scale, legends, and coordinates. The map also indicates major cities (urban areas) and highway routes.

Comment: Fig 4. I like the data presentation here, but the text and labels are impossible to read without zooming in 300%. Many of the axes and labels are repeated across plots, so perhaps you could eliminate axes labels for many and use the saved space to increase label size.

Response: Thanks again for these suggestions. We have updated the plot in Fig 4 based on your suggestions. For example, we have removed the repetitive axes and labels and increased the font size in the plot. Further, we have broken up Figure 4 into Figure 4 and Figure 5 for clearer visualization. In the original version, Figure 4 contained information about $\Delta(^{17}O)$ and $\delta(^{18}O)$ values of HNO_3 and pNO_3 by sites. In the revised manuscript, Figure 4 now only includes $\Delta(^{17}O)$ values of HNO_3 and pNO_3, and Figure 5 is for $\delta(^{18}O)$ values of HNO_3 and pNO_3, which have helped improve our manuscript.

Comment: Fig 6. Just for consideration, in many cases a bar plot can get across the point of a pie chart more clearly and more effectively. Humans are bad at judging relative angular sizes, but much better at comparing relative heights in a bar plot. It might help get the point here across better. But not a required revision from me.

Response: Thank you for the suggestion. We tried to make a bar chart as recommended, but we found that the bar chart was difficult to interpret for seasonal differences. We thought the pie chart did this more effectively. We now labeled the sections of the pie chart with percentages (%) to reduce confusion regarding the dominant formation pathways and their temporal differences. Again, Figure 6 in the original manuscript was moved to Figure 8 in the revised manuscript since we have reorganized section 3.3.

Comment: Fig 7. Again, the small multiples approach is good, but there is a lot of individual text on them that is impossible to read and thus it is hard to understand what the overall story the reader is supposed to get from this plot. Eliminating axes and perhaps moving the regression information to a table would help.

Response: Thank you for the suggestions. In the revised manuscript, we have increased the font sizes and removed the repetitive axes in the plot. We have removed individual text, which was repetitive, and put linear regression only in the plot. Further, we have broken up Figure 7 into Figure 7 and Figure 9 for clearer visualization. In the original version, Figure 7 contained information about $\Delta(^{17}O)$ and $\delta(^{18}O)$ values of HNO_3 and pNO_3 by site; in the revised manuscript, Figure 7 only includes $\Delta(^{17}O)$ values of HNO_3 and pNO_3, and Figure 9 is for $\delta(^{18}O)$ values of HNO_3 and pNO_3. Further, Figure 9 in the original version was merged with Figure 11 as Figure 9 in the revised manuscript since they contain the same information about $\delta(^{18}O)$.

Reviewer #2:

GENERAL COMMENTS:

The authors investigate the atmospheric nitrate formation pathways, along a highly populated urban corridor, using $\Delta^{17}O$ and $\delta^{18}O$ in weekly sampled nitric acid (HNO_3) and particulate (pNO_3) nitrates, collected by EPA from three CASTNET sites of Northeastern USA, from December 2016 to Dec 2018. They employ the GEOS-Chem model to verify the production pathways of atmospheric nitrate using their nitrate concentrations and $\Delta^{17}O$ and $\delta^{18}O$ results. They find that the model overestimates the concentrations by 2 or 3 times; and generate isotopic values closer to reality for warm months relative to cold months. They explain these discrepancies between modeling and observations by the model inflating the heterogeneous N_2O_5 hydrolysis production of HNO_3 and pNO_3.

In general, the article is well written, well organized, and scientifically sound, and undeniably deserves publication in ACP. The required changes for publication are of moderate level.

MAIN CONCERNS:

In terms of structure and content, the article would be optimized if: a) the authors presented their objectives and working hypothesis at the end of the introduction (see below); and b) the section on results and discussion was better organized (see below). They could better articulate their main contribution n the basis of these clear objectives.

Regarding the science, some parts of the interpretation need to be expanded. A first aspect regards the mechanisms invoked to control the seasonal concentration and isotope patterns. These concentration and isotope changes with seasons are clear and likely combined, and their controlling factors should be discussed together while explaining both observations (see below). The performance of their model changes with seasons as well. Are all seasonal observations linked to the same mechanisms? This should be clearly discussed (better wrapped up). A second aspect is regarding the δ^{18}O values of O_3 and O_2/RO_2/HO_2 that are obtained/suggested to optimize their model outputs (Table 2). The validity of such values for describing natural systems should be better supported.

Response: Thank you for your constructive feedback, comments, and suggestions, which have helped improve our manuscript. We have addressed the raised points and revised the manuscript according to these suggestions. Below is a point-by-point response to the reviewer's comments.

SCIENCE:

Comment: Lines 32-33 The authors should rephrase as there is no δ^{15}N values presented in the manuscript. The abstract should summarize the content of the current article in terms of data.
Response: Thank you for pointing this out. We have removed reference to $\delta(^{15}N)$ in the revised abstract.

Comment: Lines 146-147 – The authors should only present the significant digits of the deviations estimated for Δ^{17}O values using USGS34 and USGS35, that at the unit, i.e., 1 and 2‰, respectively. The presentation of their results should conform to that deviation as the first digit after the dot does not mean anything (1.1 and 2.4‰).
Response: Thank you for pointing this out. We have updated the sentence on Page 6, Lines 151-153 in the revised manuscript, "USGS34 ($\sigma(\delta(^{18}O))$ = 0.5 ‰ (n = 21); $\sigma(\Delta(^{17}O))$ = 1 ‰ (n = 26)); USGS35 ($\sigma(\delta(^{18}O))$ = 0.4 ‰ (n = 27); $\sigma(\Delta(^{17}O))$ = 2 ‰ (n = 26)), and IAEA-N3 ($\sigma(\delta(^{18}O))$ = 0.3 ‰ (n = 23))."

Comment: Sub-section 2.3 The confidence interval of the estimated pNO_3 and HNO_3 concentrations should be provided so that the readers can judged by themselves if the departures between measured and modeled concentrations are significant or not.
Response: Thank you for this suggestion. However, the model only produces a single monthly average value. We utilize a Normalized Mean Bias calculation to best represent comparisons between the model and observations (as has been used previously in published literature, e.g., Heald et al., *ACP*, **2012**). We have clarified this by defining the Normalized Mean Bias (*B*) as an equation (Eq. 1 in the revised manuscript on Page 7, Lines 182-186.

Comment: Lines 253-255, 261-262 and Figure 3 (1) The reader can only disagree with the statement that the overestimation by model is for the entire year. In fact, the model does not overestimate the pNO_3 concentration of the warm months or the HNO_3 of the cold months, at all sites (Fig. 3). (2) What is the confidence interval on the modeled concentrations? It would be useful to indicate it on each graph.

Response: Thank you for these comments, and in the revised manuscript, we added descriptions regarding the seasonality in the model comparison with observations of nitrate concentrations. Overall, the model overestimates tNO_3 across the two-year period for the considered sites. This is because modeled HNO_3 was significantly overestimated during the summer season, while the modeled pNO_3 was overestimated for the entire year with a much greater discrepancy in the winter season. For clarification, we have rephrased on Page 9, Lines 265-267 as follows: "However, there are significant seasonal model biases for the HNO_3 and pNO_3. The model significantly overestimates pNO_3 during the winter (3-9 times) and overestimates HNO_3 during the summer (2-3 times)."

Comment: Section 3.2 What are the uncertainties (or confidence intervals) on the isotopic outputs of the models?

Response: Thanks again for this suggestion. However, the model does not produce uncertainties or confidence intervals for its output of $\Delta(^{17}O)$. There is undeniable uncertainty related to the simulated chemistry/emissions/transport, but it is not possible to estimate these impacts individually on the modeled $\Delta(^{17}O)$ uncertainty as the calculation of $\Delta(^{17}O)$ is completed "offline" after the emissions, chemical transformations and transport have taken place. Thus, we evaluate the model's ability to represent oxidation chemistry and simulate $\Delta(^{17}O)$ relative to observations by calculating the Normalized Mean Bias.

Comment: Lines 312-313 This observation is true for the cold periods only. The $\Delta(^{17}O)$ pNO_3 minus $\Delta(^{17}O)$ HNO_3 difference becomes practically nil or negative during the warm months (Fig. 4). This is combined with the fact that pNO_3 concentrations are low during warm months. The explanatory text (lines 315-322) does not present an interpretation for these seasonal observations.

Response: Thanks again for this feedback, and in the revised manuscript, we have made clarifications on the $\Delta(^{17}O)$ differences between pNO_3 and HNO_3. First of all, Lines 312-313 was meant to describe 1:1 relation plot between $\Delta(^{17}O)$ and $\delta(^{18}O)$ (Figure 5 in the original manuscript), not Figure 4, but we referenced the incorrect Figure in the original version of the manuscript. In the revised manuscript, we have made this correction, and Figure 5 was moved to Figure 6.

Throughout the entire year, we observed significantly higher values for $\Delta(^{17}O, pNO_3)$ than $\Delta(^{17}O, HNO_3)$ that is indicated in Fig 6 in the revised manuscript. The difference between $\Delta(^{17}O, pNO_3)$ and $\Delta(^{17}O, HNO_3)$ was larger in the cold season than in the warm season. For example, on average, $\Delta(^{17}O, pNO_3)$ was (5.1±2.6 ‰) higher than $\Delta(^{17}O, HNO_3)$ during the cold months, while $\Delta(^{17}O, pNO_3)$ was (2.7±4.7 ‰) higher than $\Delta(^{17}O, HNO_3)$ during warm months. Thus while the magnitude of the $\Delta(^{17}O)$ difference between pNO_3 and HNO_3 exhibited seasonality, overall, $\Delta(^{17}O, pNO_3)$ was always higher than $\Delta(^{17}O, HNO_3)$. We have updated these statements in the revised manuscript on Page 11, Lines 324-327.

Comment: Line 335 The two isotopic groups overlap noticeably, they have the same slope as mentioned and similar ranges, and they practically have similar intercepts (within error margin). Samples of the two matrices with upper right values contain more O_3 than the other samples, clearly. Is it rigorous to suggest that more O_3 is incorporated in pNO_3?

Response: Thank you for this comment. $\Delta(^{17}O)$ is a unique signature of O_3, and other oxidants except for O_3 have $\Delta(^{17}O)$ of near 0 ‰. The $\Delta(^{17}O)$ value of the transferable O atom of O_3 has been observed to be around 39±2 ‰ (Vicars and Savarino, 2014), so the main contribution of high $\Delta(^{17}O)$ values is related to O_3 reactions. When we compare $\Delta(^{17}O)$ and $\delta(^{18}O)$ of pNO_3 and HNO_3, $\Delta(^{17}O)$ values of pNO_3 are clearly higher than HNO_3. Since the only oxidant with $\Delta(^{17}O) > 0$ is O_3, it is a valid and rigorous suggestion that pNO_3 had more O_3 incorporation than HNO_3.

Comment: Line 349 In line with the statements, the reference to Figure 6 must be to 6a? The statement is true only for that panel of results.

Response: Thank you for pointing these out. Since the pie charts exist as 1 panel in the Figure, it doesn't need to be divided by letters, so we have removed the letters in the Figure in the revised manuscript. This change is reflected in the revised Figure 8.

Comment: Lines 352-355, and 360-362 Do the authors refer to the Base GEOS-Chem only or to the two versions of the model (base and optimized GEOS-Chem) ? Overall, the performance of the models (the fit with isotopic observations) is not uniform. Depicting it with the average residuals does not fully reflect the reality. In 50% of the reported cases, the quality of the fits varies seasonally. To explain in detail, at all sites, the model fits better during warm months than during cold ones for: the Base model $\Delta(^{17}O)$ and $\delta(^{18}O)$ outputs for HNO_3, and the two models $\delta(^{18}O)$ outputs for pNO_3.

Response: Thank you for your feedback. The lines mentioned in the comment refer to the base case GEOS-Chem only. The 1st and 2nd paragraphs in section 3.3 in the original manuscript dealt with calculated $\Delta(^{17}O)$ and $\delta(^{18}O)$ using the base GEOS-Chem model only. We know that the model's performance varies with season, so we reported each residual between observed and calculated oxygen isotopic compositions in the plot in the manuscript (i.e., Fig 4 in the original manuscript). Overall, the model showed lower residuals during warmer months than during cold ones indicating that the model performance was better during the warm seasons. This makes sense in that the over-production of N_2O_5, which dominates in colder months, is the main cause of the mismatch between the model and observations.

For clarification, we have added a table that summarizes the residuals of the base and optimized GEOS-Chem by season in the revised manuscript (see Table 2). Further, we have added some sentences explaining the residuals' seasonal differences in the revised manuscript.

First, the new sentence on Page 12, Lines 362-364 is as follows: "Calculated $\Delta(^{17}O)$ based on GEOS-Chem output reproduced the observed temporal variations well **(Figure 4)**, although the model better captured the lower observed $\Delta(^{17}O)$ during warmer months versus the higher values observed in the cooler months (**Table 2**)."

Secondly, the new sentence on Page 13, Lines 378-380 is as follows: "After optimization, the residuals between observed and calculated $\Delta(^{17}O)$ dramatically decreased (**Figure 4),** especially in the cold season **(Table 2**)."

Lastly, the new sentence on Page 14, Lines 414-416 is as follows: "Still, as with $\Delta(^{17}O)$, the calculated $\delta(^{18}O)$ showed far more disagreement with observations during cooler months than warmer months (**Table 2**)."

Residuals		**$\Delta(^{17}O, HNO_3)$**	**$\Delta(^{17}O, pNO_3)$**	**$\delta(^{18}O, HNO_3)$**	**$\delta(^{18}O, pNO_3)$**
Base GEOS-Chem	Annual	4.1 ‰	2.3 ‰	15.5 ‰	15.9 ‰
	Cold	6.2 ‰	1.7 ‰	23.1 ‰	20.4 ‰
	Warm	2.0 ‰	2.8 ‰	7.9 ‰	11.4 ‰
Optimized GEOS-Chem	Annual	2.0 ‰	1.7 ‰	6.2 ‰	10.4 ‰
	Cold	2.3 ‰	1.4 ‰	5.7 ‰	13.2 ‰
	Warm	1.8 ‰	2.0 ‰	6.7 ‰	7.7 ‰

Comment: Lines 367-368 Indeed. As suggested above, what are the uncertainties on the isotopic outputs of the models?

Response: Thanks again for raising this point; however, there are no confidence intervals for the model output. Please refer to similar comments and our responses above.

Comment: Line 368 Please indicate which biases.

Response: Thank you for this comment. The biases in that sentence refer to the errors in the chemical mechanisms in GEOS-Chem. For clarification, we have updated the sentence on Page 14, Lines 413-414 in the revised manuscript as follows: "Additionally, uncertainties in the gas-phase and aerosol scheme related to tNO_3 production in GEOS-Chem could account for the discrepancy."

Comment: Lines 395-403 The text should be clarified and smoothed as there is no isotopic data on Figure 6. Instead, Figure 6 serves as basis for the interpretation of the previously presented seasonal changes in $\Delta^{17}O$ and $\delta^{18}O$ values in terms of pathways.

Response: Thank you for your comment. We have removed the mention of the isotope data in the paragraph to keep the focus on the fractional pathway results.

Comment: Line 419 Replace initial by well known.
Response: Thank you for the suggestion. We have made this correction on Page 15, Line 443 in the revised manuscript.

Comment: Lines 419-422 Ok, So what? Please explain. How such a value (11‰) can exist?
Response: Thank you for this comment. The oxygen isotopes of HO_2 and RO_2 were not directly measured in the previous studies, but it was assumed that O_2 is incorporated into nitrate via the oxidation of NO by peroxy radicals formed from O_2 reactions with H and organic radicals (Michalski et al., 2012). Thus, we assumed in this study that the $\delta(^{18}O)$ of HO_2 and RO_2 values could directly reflect $\delta(^{18}O)$ of O_2 (23 ‰), assuming that there is no isotope exchange during the reactions. However, the optimization predicts a value of only 11 ‰, which could be related to the isotope effect associated with NO + RO_2/HO_2. Our optimization would suggest that RO_2/HO_2 singly substituted with ^{18}O (e.g., $R^{18}O^{16}O$, $H^{18}O^{16}O$) reacts slower than the ^{16}O isotopologues (e.g., $R^{16}O_2$ or $H^{16}O_2$). Therefore, this value could be applicable for $\delta(^{18}O)$ of HO_2 and RO_2 values considering the isotope effect during the reactions. We have added these sentences in the revised manuscript for clarification on Page 15, Lines 446-449.

Comment: Lines 430-435 As in the former question, how such a value (89.9‰) can exist? Lowering by 20‰ as calculated by Walter and Michalski (2016) does cover such a change as the one proposed here. Please explain how the value is credible.
Response: The optimization predicts a value of 89 ‰ for $\delta(^{18}O, O_3)$, which is lower than our assumed value (e.g., 126 ‰). Note that the observations of Vicars and Savarino (2014) suggest a standard deviation of ~13 ‰ based on their measurements across a range of latitudes in the Atlantic Ocean. While the optimized value is still lower than the limited observations suggest, only the isotope effect for the NO + O_3 reaction is known. Other reactions with NO_y species (e.g., NO_2+O_3) have not been directly studied for their potential isotope effects. Furthermore, equilibrium isotope effects between N_2O_5, NO_2, and NO_3 could result in mass-dependent fractionation of $\delta(^{18}O)$, as well. Still, the elevated $\delta(^{18}O, O_3)$ value compared to other oxidants is consistent with our expectations. We have updated this content in the revised manuscript for clarification on Page 16, Line 462-468.

Comment: Lines 456-457 The referred article is not yet published (but cited in the discussion, which is fine), and this is a conclusion which should directly derive from the data set presented in the manuscript. It is better advised to present conclusions based on the current set of data.
Response: Thank you for your comment. We have removed the referenced article in the conclusion in the revised manuscript.

FORM:

Comment: The last paragraph of the introduction (lines 93-99) presents the main findings of the study, is that a format encouraged by ACP? In a classical scientific manner, the readers would appreciate reading the objectives of the research and the working hypothesis advanced by the authors. It is suggested here that lines 93-99 be replaced by the objectives of the research, with possibly the hypothesis posed by the authors prior to conducting their research.
Response: Thank you for your comment. We have updated the last paragraph of the introduction with the hypothesis and motivation in the revised manuscript on Page 4, Lines 91-103 as follows: "The northeastern US remains an important region to monitor due to historically degraded air quality by NO_x emissions and negative atmospheric nitrate deposition impacts on sensitive ecosystems. Changes in oxidation chemistry and chemical feedbacks associated with nitrate production and deposition have important implications for predicting air quality improvements and informing policy recommendations. In this study, using the Clean Air Status and Trends Network (CASTNET) samples, we explored spatiotemporal differences in HNO_3 and pNO_3 concentrations and production mechanisms in the northeastern US over two years. Based on these observations, we aimed to better constrain the mismatch in modeled predictions of atmospheric nitrate chemistry in the northeastern US. This is the first study to quantitatively evaluate the triple oxygen isotope composition from observations and model simulations in the northeastern US. The comparison with the combination of $\Delta(^{17}O)$ and $\delta(^{18}O)$ values, and both gaseous and particle phases of nitrate, provide a significant advance in our ability to probe the representation of oxidation chemistry in atmospheric chemistry models."

Comment: Lines 324-327 These two sentences should be merged as they are partly repetitive.
Response: Thank you for your comment. Since the 1st sentence is repetitive, we have removed that sentence on Page 12, Line 338 in the revised manuscript.

Comment: Section 3.3 For the reader, the text of this section is hard to follow as it jumps from Figure 6, to Figure 7 then back to 4, back to 7, then to 6. The issue does not simply relate to the references to figures, but to the way the train of thoughts is presented from examining the agreements between model and observation at a given site, then going to the spatial limitation of the modeling... The section needs reorganization: a simple way would be to first discuss Fig. 4, then 6 and then 7, highlighting the key observations and wrapping up with the integrated interpretation at the end.
Response: Thank you for the comment. We have reorganized section 3.3 based on your suggestions. Originally, section 3.3 contained information about the comparison between calculated and simulated $\Delta(^{17}O)$ and $\delta(^{18}O)$, but we have broken up section 3.3 into sections 3.3 and 3.4. In the revised manuscript, section 3.3 only contains information about $\Delta(^{17}O)$, and section 3.4 is for $\delta(^{18}O)$. This newly organized section helps streamline our discussion. According to this organization, the order of the figures was also changed in the revised manuscript based on the new flow. For example, the pie chart (Figure 6 in the original manuscript) was moved to Figure 8 in the revised manuscript. Further, we have broken up Figure 4 into Figure 4 and Figure 5 and Figure

7 into Figure 7 and Figure 9 in the revised manuscript for clearer visualization. Overall, these changes significantly improve the readability of our manuscript.

Comment: Lines 330-351 For coherence, the observations based on the data of 6b and 6c should be presented before jumping to Figure 7.

Response: Thank you for the comment. In the revised manuscript, based on your previous recommendation, we have reorganized the structure of section 3.3, so the order of figures, including Figures 6 and 7, was changed in the revised version. The flow and figure references were also changed based on the new organizational structure. We have described each Figure in detail in the revised manuscript in sequential order.

Comment: Lines 445-446 What is the reference for the δ^{15}N study? We understand that there is a companion article to be published in ACP that is different from the former study.

Response: The reference that we mentioned in Lines 445-446 is our companion paper. The companion paper (acp-2022-621) is about the nitrogen isotope compositions of the same samples in this work. This article focuses exclusively on oxidation chemistry using oxygen isotopes, while the companion paper primarily focuses on precursor sources of nitrate using nitrogen isotopes across the northeastern US, but also presents oxidation chemistry constraints based upon the $\delta(^{15}$N). We think it is important that readers know of both studies.

Comment: Line 467 Replace 'better' by 'improved'.

Response: Thank you for the suggestion. We have replaced it as 'improved' on Page 18, Line 522.

OTHER Specific points:

Comment: Lines 72-79 (and all text) - why carry parentheses when using the Delta notation? Most scientists using isotopes do not. Makes the notation heavy without justification or need.

Response: Thank you for these comments. The standard notation for any quantity symbol is to enclose labels in parentheses, and was the recommended notation format from the editor. Thus, we did not make these notation changes.

Comment: Line 77 – remove Oxygen from parenthesis, as it is clear that the reference material is for O measurements.

Response: Thank you for the suggestion and we have made this change in the revised manuscript on Line 77.

Comment: Line 101 change police of 2. M

Response: We are not exactly sure of the meaning of this comment, but we have changed the alignment of this subsection heading in the revised manuscript on Page 4, Line 106.

Comment: Line 102 write 'Sample collection at CASTNET sites'

Response: Thank you for the suggestion. Since we didn't deal with the detailed sample collection method in the manuscript, we just thought that it is better to keep the title as CASTNET Samples.

Comment: Line 114 write 'analyses' instead of analysis, because the term refers to different analyses

Response: Thank you for the suggestion. We have updated based on the suggestion on Page 5, Line 119.

Comment: Line 141 replace is by was, for coherence with the rest of the sentence.

Response: Thank you for the suggestion. We have updated based on the suggestion on Page 5, Line 146.

Comment: Line 149 add 'modeling' to this title

Response: Thank you for the suggestion. We have updated based on the suggestion on Page 6, Line 155.

Comment: Line 151 replace 'to' by 'and' or 'to model' by 'using' (?); replace isotope by values.

Response: Thank you for the suggestion. We have updated the sentence on Page 6, Lines 156-159 as follows: The GEOS-Chem global model of atmospheric chemistry (Bey et al., 2001; Walker et al., 2012; 2019) was utilized to track the production of NO_2 and HNO_3 at the CASTNET sites and further to model the oxygen isotope deltas (e.g., $\delta(^{18}O)$ and $\Delta(^{17}O)$) following a previous framework (Alexander et al., 2020).

Comment: Line 176 add 'from model outputs' to this title

Response: Thank you for the suggestion. We have updated it based on the suggestion on Page 7, Line 188.

Comment: Line 229 remove 's' from discussion

Response: Thank you for the suggestion. We have updated based on the suggestion on Line 241 in the revised manuscript.

Comment: Lines 285-286 rephrase (, 'which were or are' instead of 'were'?); there is a word missing.

Response: Thank you for pointing out this typo. We have added 'which' in the sentence on Page 10, Line 297.

FIGURES:

Comment: Figure 6 The three model outputs presented in (a) are for

Response: We are not exactly sure of the meaning of this comment, but we have added more detailed descriptions in the caption of that Figure. Again, the original Figure 6 was moved to Figure 8 in the revised manuscript since we have reorganized section 3.3.

Reference

Heald, C. L., Collett Jr, J. L., Lee, T., Benedict, K. B., Schwandner, F. M., Li, Y., Clarisse, L., Hurtmans, D. R., Van Damme, M., and Clerbaux, C.: Atmospheric ammonia and particulate inorganic nitrogen over the United States, Atmospheric Chemistry and Physics, 12, 10295–10312, 2012.

Michalski, G., Bhattacharya, S. K., and Mase, D. F.: Oxygen isotope dynamics of atmospheric nitrate and its precursor molecules, in: Handbook of environmental isotope geochemistry, Springer, 613–635, 2012.

Vicars, W. C. and Savarino, J.: Quantitative constraints on the ^{17}O-excess (Δ^{17}O) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitrite-coated filter technique, Geochimica et Cosmochimica Acta, 135, 270–287, 2014.