

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-622

Anonymous Referee #2

Referee comment on "Nitrate chemistry in the northeast US – Part 2: Oxygen isotopes reveal differences in particulate and gas-phase formation" by Heejeong Kim et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-622-RC2>, 2022

GENERAL COMMENTS

The authors investigate the atmospheric nitrate formation pathways, along a highly populated urban corridor, using $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 on 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 $\delta^{18}\text{O}$ values of O_3 and $\text{O}_2/\text{RO}_2/\text{HO}_2$ that are obtained/suggested to optimize their model outputs (Table 2). The validity of such values for describing natural systems should be better supported.

SCIENCE

Lines 32-33 The authors should rephrase as there is no $\delta^{15}\text{N}$ values presented in the manuscript. The abstract should summarize the content of the current article in terms of data.

Lines 146-147 – The authors should only present the significant digits of the deviations estimated for $\delta^{17}\text{O}$ 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‰).

Sub-section 2.3 The confidence interval of the estimated pNO_3 and HNO_3 concentrations should be provided so that the readers can judge by themselves if the departures between measured and modeled concentrations are significant or not.

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.

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

Lines 312-313 This observation is true for the cold periods only. The $\delta^{17}\text{O}$ pNO_3 minus $\delta^{17}\text{O}$ 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.

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 ?

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.

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 $\hat{\Delta}^{17}O$ and $\delta^{18}O$ outputs for HNO_3 , and the two models $\delta^{18}O$ outputs for pNO_3 .

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

Line 368 Please indicate which biases.

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 $\hat{\Delta}^{17}O$ and $\delta^{18}O$ values in terms of pathways.

Line 419 Replace initial by well known.

Lines 419-422 Ok, So what? Please explain. How such a value (11‰) can exist?

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.

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.

FORM

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.

Lines 324-327 These two sentences should be merged as they are partly repetitive.

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.

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

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

Line 467 Replace 'better' by 'improved'.

OTHER Specific points

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.

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

Line 101 change police of 2. M

Line 102 write 'Sample collection at CASTNET sites'

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

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

Line 149 add 'modeling' to this title

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

Line 176 add 'from model outputs' to this title

Line 229 remove 's' from discussion

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

FIGURES

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