

Comments on manuscript egosphere-2023-2293, “Incorporating Oxygen Isotopes of Oxidized Reactive Nitrogen in the Regional Atmospheric Chemistry Mechanism, Version 2 (ICOIN-RACM2)”, by Wendell W. Walters et al.

In this paper, Walters et al. presented an isotopic chemical mechanism (ICOIN-RACM2) by incorporating oxygen isotopes into the gas-phase chemical mechanism RACM2. This new isotopic mechanism aims to simulate the oxygen mass-independent fractionation signals ($\Delta^{17}\text{O}$) of atmospheric oxidized reactive nitrogen (NO_y) and odd oxygen species. The authors adopted an isotope-tagging method by explicitly tracking the oxygen atom that was transferred from the terminal of ozone in each molecule. After examining the consistency between the new isotopic mechanism and the original RACM2 mechanism, the authors conducted two case studies by applying 0-D box model simulations. The first is to simulate the $\Delta^{17}\text{O}$ of NO_y in ideal photochemical chamber experiments with different initial conditions, and the second is to simulate the diel cycles of $\Delta^{17}\text{O}$ in a summertime atmosphere. The author concluded that this new mechanism would help advance our understanding of NO_y oxidation chemistry and is expected to be useful for future applications in 3-D CTMs.

Oxygen isotope signals, especially $\Delta^{17}\text{O}$, have been widely used to constrain the oxidation chemistry of atmospheric reactive nitrogen. The novel isotopic tagging chemical mechanism introduced by this study could serve as a useful tool in such studies. I feel the paper is well written and the topic is of great interest for the readership of GMD. However, I have three major concerns on this study:

- (1) The assumption of a constant $\Delta^{17}\text{O}$ of ozone. The author cited the study of Vicars and Savarino et al. (2014) to validate the choice of a constant $\Delta^{17}\text{O}(\text{O}_3)$. I agree that the **average** tropospheric $\Delta^{17}\text{O}(\text{O}_3)$ from multiple observational studies is close to 26 ‰, but there are also significant seasonal cycles in these observations, including the Vicars and Savarino. (2014) study. For example, Savarino et al. (2016) suggested an ~ 10 ‰ variation in $\Delta^{17}\text{O}(\text{O}_3)$ in different seasons at Dome C. Xu et al. (2022) also indicated a >5 ‰ variation in the $\Delta^{17}\text{O}$ of the ozone terminal oxygen in Japan (Xu et al., 2022), which was attributed to a stratospheric intrusion event. These values are already large enough to impact the oxygen MIF transferred to other molecules from ozone. Moreover, it is well known that $\Delta^{17}\text{O}(\text{O}_3)$ is sensitive to both temperature and pressure (Thiemens and Jackson, 1990; Janssen et al., 2003) and that stratospheric ozone has a much greater $\Delta^{17}\text{O}$ than tropospheric ozone (Krankowsky et al., 2007). Therefore, adapting an average value from mostly near-surface observations is a major drawback of the method used in this study and severely limits the extension of the proposed mechanism to 3D CTMs, as the author suggested.
- (2) The ignorance of other processes that could produce OMIF. There are several known chemical processes that can produce extra OMIF, e.g., the $\text{CO}+\text{OH}$ reaction and the HO_2+HO_2 reaction (Röckmann et al., 1998; Velivetskaya et al., 2016), and perhaps additional unknown reactions exist. From my point of view, the isotopic tagging method can hardly handle these effects. The impact of these

processes on the $\Delta^{17}\text{O}$ of atmospheric NO_y could be small but should not be ignored in this study.

- (3) Comparisons with observations to validate the proposed mechanism are lacking. Although the author conducted two different case simulations in this study, it is unclear why these cases were chosen. For the chamber simulations, it looks that the model configurations mimic the chamber experiments in Blum et al. (2023), but why the author didn't compare the model results with Blem et al. (2023)? This would provide the reader with a direct impression about the model performance. I noticed that in Blem et al. (2023), both $\Delta^{17}\text{O}(\text{NO}_2)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ were measured, and the comparison should be straightforward. In addition, the measured $\Delta^{17}\text{O}(\text{NO}_2)$ in Blem et al. (2023) could exceed 40 ‰, which cannot be reproduced by assuming a constant 39.3 ‰ $\Delta^{17}\text{O}$ of terminal oxygen in ozone in this study. The modeled atmospheric $\Delta^{17}\text{O}(\text{NO}_2)$ trend in the latter case was also not consistent with recent observations (see my minor comment below). These simple comparisons suggested the limitations or incompetence of the current mechanism.

Nevertheless, I appreciate much about the effort made by this study, and I look forward to incorporating this new oxygen isotopic mechanism into 3D CTMs in the future. I suggest the author to include direct comparisons with the existing observational data especially the chamber experiments, which would require a redesign of the box model simulations, and the author should make more explanations on the points I mentioned above in the revised manuscript. For these reasons I think a major revision is necessary before the final publication of this manuscript on GMD.

- Minor comments

- I don't understand why the author used to added a parenthesis in the delta notation throughout the text. I suggest the author to follow the most conventional notation by using $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$.
- Lines 47-48: Walters et al., 2018, Blum et al., 2020 and Chai and Hastings, 2018 didn't measure $\Delta^{17}\text{O}$ in their study and are improper citations here.
- Line 59-62: I suggest to rephrase this sentence. Clearly, photochemical equilibrium is no longer held at night because there is no light or photolysis of NO_2 , instead of nocturnal NO emission. I understand the author may want to describe that the freshly emitted NO would dilute the residual $\Delta^{17}\text{O}(\text{NO}_2)$ from the daytime, but the statement seems weird to me.
- Table 1: The $\Delta^{17}\text{O}(\text{RO}_2\text{NO}_2)$ should be $1/2 * \Delta^{17}\text{O}(\text{RO}_2)$ plus $1/2 * \Delta^{17}\text{O}(\text{NO}_2)$.
- Section 2.1: Does the model incorporate the photolysis of particle nitrate? The author mentioned the importance of this process but it's not clear if it is included by the model. In addition, I suggest the author to add a table that describing the reaction mechanism in a supplemental file, otherwise the reader not familiar with the RACM2 mechanism would have to search the model code, which is a rather tough task.
- Figure 1 and Figure 2: I suggest to change the y scales in different subplots.

- Line 201-202: The simulated $\Delta^{17}\text{O}$ of NO was described in this sentence but not shown in the figure. Please add it
- Line 297-298: Another possible explanation for the nonzero $\Delta^{17}\text{O}$ of NO is the isotopic exchange between NO and NO₂. The author should easily test this hypothesis by turning off the NO-NO₂ exchange reaction in the mechanism.
- Line 298-234: While the overall day high and night low trend in $\Delta^{17}\text{O}(\text{NO}_2)$ was reproduced by the model, the simulated **diurnal** $\Delta^{17}\text{O}(\text{NO}_2)$ trend was indeed **not consistent** with the observations in Albertin et al. (2021). Albertin et al. (2021) reported that the maximum $\Delta^{17}\text{O}(\text{NO}_2)$ occurred at noon, while the model suggested a minimum at noon. New observations by Albertin et al. (2024) indicated a similar trend. This point deserves further discussion. Moreover, in Figure 4, the simulated diurnal $\Delta^{17}\text{O}(\text{NO}_2)$ seems to be slightly greater than $\Delta^{17}\text{O}(\text{NO})$, especially in case 20. This is astonishing since both photochemical cycling and isotopic exchanges tend to force them equal. Please explain it.
- Line 235: The discussion of the diurnal trend in $\Delta^{17}\text{O}(\text{HONO})$ needs more attention because the photolysis of p-NO₃⁻ seems to not be included by the model, which is however crucial to the HONO budget in many environments (e.g., (Ye et al., 2016)). This point needs more clarification.
- Line 244-245: While the model results suggested little to no variation in $\Delta^{17}\text{O}(\text{HNO}_3)$, many field observations indicated a clear diurnal trend (Vicars et al., 2013; Zhang et al., 2022). The author hypothesized that this was due to the relatively long chemical lifetime of HNO₃ in the system. However, as previously described in the Methods section, a dilution lifetime of 24 h was applied by the model, so it is unlikely that excessive HNO₃ would accumulate in the system, as shown in Figure 1. The 24 h dilution lifetime is actually lower than the typical HNO₃ lifetime in a realistic atmosphere (3-5 days). Please provide more detailed explanations.
- Line 250: I note that in Morin et al. (2011), the simulated $\Delta^{17}\text{O}(\text{HO}_2)$ was nonzero but close to 1-2 per mil, while in this work, the modeled $\Delta^{17}\text{O}(\text{HO}_2)$ was almost identical to 0 (visually from Figure 2 and Figure 4). The nonzero $\Delta^{17}\text{O}(\text{HO}_2)$ in Morin et al. (2011) was attributed to the OH+O₃ reaction. Does this HO₂ formation pathway significant in this work? This would impact the $\Delta^{17}\text{O}$ of H₂O₂, which is potentially useful for sulfate chemistry.
- Some of the reference citations are not consistent with the Copernicus publication style.

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