

Reviewer comments in bold, author responses in plain text.

The discussion on $\delta^{17}\text{O}$ 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 $\delta^{17}\text{O} = 0$ NO emitted at night does not have to be oxidized into NO₂ to dilute NO₂ $\delta^{17}\text{O}$ 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 $\delta^{17}\text{O}$ of NO = NO₃ = NO₂ This in turn would impact HONO $\delta^{17}\text{O}$ 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 NO₂ may increase $\Delta^{17}\text{O}(\text{NO})$, but it will decrease $\Delta^{17}\text{O}(\text{NO}_2)$ by the same amount (isotopic mass balance). Similarly, isotopic exchange between NO₂ and NO₃ (via the N₂O₅ intermediate) may increase $\Delta^{17}\text{O}(\text{NO}_2)$, but it will decrease $\Delta^{17}\text{O}(\text{NO}_3)$ by the same amount. So our assumed value of N₂O₅ won't change, and thus the calculated value of $\Delta^{17}\text{O}(\text{nitrate})$ from N₂O₅ 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 $\Delta^{17}\text{O}(\text{NO}_x)$ 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 $\delta^{17}\text{O}$ value. It is well known that $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in ozone is a strong function of temperature and pressure. The choice of Vicars (Over cryogenic collection studies) because of the apparent constant $\delta^{17}\text{O}$ 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 $\delta^{17}\text{O}$. 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 $\delta^{17}\text{O}$ 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 $\delta^{17}\text{O}(\text{O}_3)$ using a new technique (Vicars et al., 2012) show $\delta^{17}\text{O}(\text{O}_3) = 26 \pm 1\text{‰}$ 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 $\delta^{17}\text{O}(\text{nitrate})$ (e.g., Alexander et al. (2009)), which would occur if the model underestimated the relative role of ozone in NO_x 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 $\delta^{17}\text{O}$ 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 one wants to acknowledge that something we do not understand is going on with either tropospheric O₃ $\delta^{17}\text{O}$ dynamics or their measurements.

I initially neglected any discussion of the potential uncertainty in the $\delta^{17}\text{O}(\text{O}_3)$ 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 additional discussion so as not to place too much certainty in this value of $\delta^{17}\text{O}(\text{O}_3) = 26\text{‰}$. 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 $\delta^{17}\text{O}(\text{nitrate})$ observations from this paper represent a 3.5 year mean value.