

1) We agree that atmosphere should be changed to troposphere. We prefer to keep nitric acid as this term is more often used in atmospheric chemistry than nitrate and there are no neutralization reactions in the model.

2,3) We agree the d should be added to the left hand side, we thought this was done in revision and will be corrected. The mass balance equation is normalized to concentration as is the standard case with isotope mass balance models, which uses mole fractions. This is obvious from a units perspective, since we are calculating $\Delta^{17}\text{O}$ values, including concentration would give molecules/cm³ $\Delta^{17}\text{O}$. The loss term can also be disregarded because in a box model, with no deposition term there is no loss, and nitrate does indeed build up over time, as is seen in figure 1. Of course this is not “reasonable” from an atmospheric perspective, but what the figure shows is that the $\Delta^{17}\text{O}$ values reach a steady state for a fixed set of photochemical conditions, irrespective of the amount of nitrate produced. It is essentially testing the case of nitrate build-up after rain out. The $\Delta^{17}\text{O}_j$ is any mass independent effect in loss reactions, which to the best of our knowledge are all mass dependent so $\Delta^{17}\text{O}_j$ is zero and thus the loss term is zero. As we mention the loss term is only important when multi-dimensions are considered (as in Alexander et al) because transport between boxes would add a new production fraction term (P) based on the amount a of nitrate transported which is a function of the loss in adjacent boxes. In our context the reviewer is incorrect and loss is not a factor in the evolution of $\Delta^{17}\text{O}$ values with time (unless they are suggesting loss rate is non uniform, such as all nitrate produced at night is removed but not that produced during the day...which is illogical). The absence of loss for compounds (such as ozone deposition) is common, indeed the standard practice, in zero dimensional box models.

4) We tested the assumptions about α , about the diurnal differences, which there clearly are since peroxy radicals are not efficiently produced at night. However the key is that α must be weighted by production amount. In continental environments, NO_x is mostly as NO_2 during the day and there is little NO left to oxidize to NO_2 at night, so while α is high, little NO is oxidized. When we tested long term α (summed over course of the run) versus hourly α and mass balance they differed by less than a few tenths of a permil. As we state on page 6936 “It should be noted that α is not fixed in time but will evolve”. In the model α (and HNO_3 branching ratios) are determined hourly, which hold for day or night since it is simply a branching ratio of oxidation, and weighted to the % of NO oxidized (HNO_3) during that hour.

5,6) As we state in the paper, there is simply not enough data to completely reconcile the $\Delta^{17}\text{O}$ in the NO_x system. This is why we used both extremes...All terminal or all bulk. We have not “ignored” anything, but have included as many scenarios as possible, which is the point of the paper. The comment about failing to use Savarino’s terminal experiment as the absolute truth is hypocritical, since they have adopted tropospheric ozone of 25% to balance their model, a value for ozone completely outside that generated the dozens of studies on temperature and pressure effects. Savarino’s experiment is also not representative of the atmosphere because it does not include any effect from NO_2 photolysis, NO_3 production/photolysis, or exchanges that may occur during NO_x cycling.

We do not hold that the model is anything more than a crude predictor to be improved and modified as new data become available. The paper is less about the model being “correct” to test data than it is a first step for using data to correct the model...