

Interactive comment on “Global inorganic nitrate production mechanisms: Comparison of a global model with nitrate isotope observations” by Becky Alexander et al.

Greg Michalski (Referee)

gmichals@purdue.edu

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The discussion on A 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 $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ 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

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NO₂ “cloud chemistry” at night and HNO₃ production early morning when O₃ levels are low due to nighttime titration.

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? 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 $\delta^{17}\text{O}(\text{O}_3) = 26 \pm 1\%$ 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 ones wants to acknowledge that something we do not understand is going on with either tropospheric O₃ $\Delta^{17}\text{O}$ dynamics or their measurements.

Also they might include Wang et al. for some additional south American data <https://www.sciencedirect.com/science/article/pii/S0016703714001811?via%3Dihub>

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