Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-422-RC3, 2019

Atmospheric Chemistry and Physics Discussions
Open Access

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

Received and published: 17 July 2019

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 Δ17O = 0 NO emitted at night does not have to be oxidized into NO2 to dilute NO2 Δ17O 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 Δ17O of NO = NO3 = NO2 This in turn would impact HONO Δ17O and

Printer-friendly version

Discussion paper

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 Δ17O value. It is well known that Δ17O and δ18O in ozone is a strong function of temperature and pressure. The choice of Vicars (Over cryogenic collection studies) because of the apparent constant Δ17O 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 Δ17O. 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 Δ17O 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 ïĄĎ17O(O3) using a new technique (Vicars et al., 2012) show ïĄĎ17O(O3) = 26 ± 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 ïĄĎ17O(nitrate) (e.g., Alexander et al. (2009)), which would occur if the model underestimated the relative role of ozone in NOx 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 Δ17O 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 Δ17O 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

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-422, 2019.

Printer-friendly version

Discussion paper