

Line 114 it is unclear to what the coefficients 24.85 and 13.66 mean or where they are derived. As someone versed in the field, and some information on line 26, I can surmise this is the  $\Delta^{17}\text{O}$  value  $\text{NO}_2+\text{OH}$  pathway, but this is in no way clear to the non-specialist. There are host of assumptions that go into this number that are not explained and have uncertainties that are not being propagated through. Six points on this are

1. From the text there is the assumption that the  $\Delta^{17}\text{O}$  of  $\text{O}_3$  is essentially a fixed value of 26‰, which is by no means codified in the literature, despite the some who would hope so because it makes the data analysis less problematic.
2. Johnston et al. and Krankowsky et al. observed  $\text{O}_3$   $\Delta^{17}\text{O}$  values that spanned 18.8‰ to 41‰ with a standard deviation of 4.8‰.
3. Two papers by the Savarino group using a different method arrive at values close to 26‰ with smaller variations of 1 and 1.6‰. Their Antarctic paper noted  $\text{O}_3$   $\Delta^{17}\text{O}$  had “insignificant variation” 28 ‰ - 23 ‰, if one considers ~20% variation insignificant.
4. Lab experiments have clearly noted an  $\text{O}_3$   $\Delta^{17}\text{O}$  temperature dependence.
5.  $\text{NO}_x$  photochemical equilibrium experiments (Michalski et al., 2013) a higher terminal atoms value transfer and Vicars noted that  $\Delta^{17}\text{O}(\text{O}_3)_{\text{trans.}}$  in the range of 38–44‰ fits data.
6. Even assuming a fixed value of  $\text{O}_3$   $\Delta^{17}\text{O}$  value of 26‰, one cannot increase significant (24.85) digits by division/multiplication.

The authors should note these conflicting assumptions and how these assumptions would influence their interpretations of reaction pathways.

NO was derived CO mixing ratios derived from observations in winter Beijing (Lin et al., 2011). The correlation coefficients for this relationship are .76 and .82, which means there is some uncertainty in the derived NO. How would this impact the author’s results

Line 200: “To estimate the specific  $\alpha$  value, chemical kinetics in Table 2 and Eq. (3) were used. Specific  $\alpha$  is estimated to range from 0.86 to 0.97 with a mean of (0.94±0.03)”. The coefficients used to estimate HO<sub>2</sub> has significant uncertainties (again  $r^2 = \sim 0.7$ ) and the regression itself is are not universal but are valid for Tokyo. No discussion on whether this would hold in an extreme haze event in Beijing. Likewise the uncertainty of  $\text{RO}_2 = 0.7\text{HO}_2$  must be significant and site specific. The validity of this assumption in the context of extreme haze needs to be discussed

“lifetime of atmospheric nitrate is typically on the order of days (Vicars et al., 2013)” I doubt that Vicars was the first to determine the lifetime of nitrate in the atmosphere. Further the lifetime is significantly dependent on precipitation frequency so if there was no rain during the collection period the lifetime of nitrate is significantly longer, though it does not change the authors point.

138 “We use the Master Chemical Mechanism “ This requires an entire discussion section. MCM is a gas phase mechanism. Were heterogeneous reactions included? Based on what uptake scheme? How was aerosol surface area determined if that was part of the scheme? “1 h-averaged mixing ratios of observed surface CO, NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub> and estimated NO” what does this mean? Did you initialize the model with these mixing ratios? Or did you correct the model to match these hourly? Or did you run the model hourly? What length of spin-up do you use? How was photolysis adjusted to account for haze? This model predicts things like OH<sub>2</sub>, RO<sub>2</sub>,

NO...how does the model prediction compare with your estimation of these key compounds that we parameterized by your isotope scheme, but not measured? How does it predict things that were measured over time ( $O_3$ ,  $NO_2$ )? This section was entirely too vague for anything useful to be inferred about the accuracy of predicted  $NO_3$  or  $N_2O_5$  mixing ratios.

“variation of atmospheric  $\delta^{15}N(NO_3^-)$  can be interpreted by the following four processes (Vicars et al., 2013)” again please give credit where credit is due, Freyer used this scheme 20 years before Vicars to investigate  $^{15}N$  variations in atmospheric nitrate.

254 “The quartz filter used here is thought to collect both particulate nitrate and gaseous  $HNO_3$ ” this statement needs better justification by citing filter pack studies. This is particularly true in Beijing where  $NH_4NO_3$  is a major component of PM and loss by volatilization could also be occurring. Vicars, like myself (2003), limited this assumption to coastal sampling where seas salt buffering was present and noted that “the exact nature of the nitrate species collected during sampling using glass fiber filters has always been an area of some debate due primarily  $NH_4NO_3$ .”

Isotopic fractionations associated with nitrate formation pathways. These (Photolysis and KIE effects in  $NO_y$ ) are largely unknown and the discussion should reflect that. Walters ab initio paper indicates IF equilibrium is dominant the more oxidized compounds should have higher  $^{15}N$ . Is this consistent with observations?

275 “Where  $K$  is the isotopic exchange constant of  $N$  between  $NO$  and  $NO_2$ , which is temperature-dependent ..” It is not clear if the authors are using temperature to calculate this daily, if so what temperature? Average? Day and night average? Clearly this equation is very dependent on fraction of  $NO_2$ , which is based on  $NO$  estimations that also have uncertainty, which should be discussed and represented on the y-axis error bar on figure 7. That caption should emphasize the  $\delta^{15}N$  data is not a measurement of the  $\delta^{15}N$  of ambient  $NO_x$  (Freyer, Walters) but a calculation. It would also seem that since the authors are presenting  $\delta^{15}N$  in ‰, that the RHS of Eq. 6 will need to be multiplied by a factor of 1000.

279 “the correlation is better in residential heating season ... especially in residential heating season.” mechanistic, why would this so? The authors seem to imply residential heating is promoting exchange when its likely  $NO/NO_2$  ratios. Was there a correlation between  $\delta^{15}N$  and  $fNO_2$ ?

The exchange section should discuss in terms of Freyers and Walters et al. papers that measured  $\delta^{15}N$  values of ambient  $NO_2$

“Influence of  $NO_x$  emissions.” This section could be greatly expanded, there has been a lot of recent work by the Elliot, Hastings, and Michalski groups of  $^{15}N$  sources. While coal may be dominant in the surrounding regions, automobiles and diesel trucks in Beijing must be significant, particularly during stagnant conditions. Is there a better  $N$  inventory for Beijing itself?

I did not see any discussion about any (or lack thereof) correlation between  $\delta^{18}O$ ,  $\Delta^{17}O$  and  $\delta^{15}N$ . If they are completely decoupled then that would argue for source effects, if there is some covariation, then exchange/chemistry could be the main process.