

**Referee: J. Rudolph (Referee #2):**

**Comments:** The paper presents an interesting example for the use of isotope ratio measurements to gain insight into complex atmospheric reaction systems, here the formation of nitric acid and nitrate from NO<sub>x</sub>. Overall the paper is well written, the experimental work and interpretation solid and the subject (particle formation by oxidation of primary atmospheric pollutants is relevant for air quality. I also appreciate that the authors openly explain that isotope ratio studies in complex systems can only provide constraints (here given as range of possible contributions to nitrate formation) and that additional information is required to fully understand the magnitude of contributions from different individual reaction pathways. Consequently, I recommend publication although the authors need to address some questions and uncertainties in more detail before the paper should be accepted for publication.

*A: Thanks very much for your comments. We reply to your comments one by one as follows. One point needs to be addressed here is that we have removed section 3.4 from the manuscript due to that we are unable to explain the variations of  $\delta^{15}\text{N}(\text{NO}_3^-)$  well so far.*

**Comments:** 1. May main concern is that the paper does not consider the photolysis of NO<sub>2</sub> during daytime. Although this reaction is included in Figure 1 (R3), it is not considered in the excess oxygen calculation. During daytime the reaction sequence  $\text{NO}_2+h\nu\Rightarrow\text{NO}+\text{O}$   $\text{O}+\text{O}_2\Rightarrow\text{O}_3$   $\text{NO}+\text{O}_3\Rightarrow\text{NO}_2+\text{O}_2$  (R1) will result in a steady state which can (depending on photon flux and ozone concentration) be established within several minutes. This will result not only in an isotope exchange for N between NO and NO<sub>2</sub> (Chapter 3.4.3) but also for O between NO<sub>x</sub>, O<sub>2</sub> and O<sub>3</sub>. In contrast to this at night R1 is a one-way street. I do not know to which extent the daytime “recycling” of NO from NO<sub>2</sub> photolysis will impact the excess oxygen ratio in NO<sub>2</sub> and NO (and consequently in nitrate) or the <sup>15</sup>N isotope ratio. Nevertheless, this is something that needs to be explained and discussed and potentially may change the interpretation of the isotope ratio measurements.

*A: Thanks for your comment. The work of (Michalski et al., 2014) shows that, in both the light and dark simulations of NO<sub>x</sub>-O<sub>2</sub>-O<sub>3</sub> system, the  $\Delta^{17}\text{O}$  values between NO<sub>2</sub> and NO were essentially equal within  $\pm 0.1\%$ . In this case, the final  $\Delta^{17}\text{O}$  value of NO<sub>2</sub> depends on the relative importance of O<sub>3</sub> oxidation in NO<sub>2</sub> production rates rather than photolysis. However, since simulation conditions have*

difference with the ambient conditions, future work should study whether or not photolysis alone can induce large diurnal difference in  $\Delta^{17}O(NO_2)$  at ambient conditions. As for the  $^{15}N$  isotope ratio, previous studies suggest N isotope exchange equilibrium between NO and  $NO_2$  play an important role in  $\delta^{15}N$  of NO,  $NO_2$  and atmospheric nitrate (Savarino et al., 2013; Freyer et al., 1993). Equation (6) suggest the partitioning of  $^{15}N$  between NO and  $NO_2$  depends on the relative concentration of  $NO_2/NO_x$  and the temperature-dependent isotope exchange constant. During the daytime, when NO and  $NO_2$  coexist in  $NO_x$  cycling, the N isotope exchange between NO and  $NO_2$  can influence their individual  $\delta^{15}N$  (Freyer et al., 1993). At night, however, as NO is oxidized into  $NO_2$  without photolysis, NO concentrations can be near zero when  $O_3$  concentrations are high. In this case,  $NO_2$  can reflect  $\delta^{15}N$  of local  $NO_x$  sources, that's  $NO_2/NO_x$  approaches 1 and  $[\delta^{15}N(NO_2) - \delta^{15}N(NO_x)]$  approaches 0 in Eq. (6). According to the work of (Walters et al., 2016), the lifetime of Leighton cycle reactions and  $NO_x$  exchange can be comparable, therefore, the isotopic exchange between NO and  $NO_2$  will be a mixture of these processes. The isotopic exchange associated with the  $NO + O_3$  reaction and  $NO_2$  photolysis has yet to be determined, so it will be a subject of future study. Due to that we are unable to explain the variations of  $\delta^{15}N(NO_3^-)$  well, we have removed section 3.4 from the manuscript.

**Comments:** 2. The authors use several approximations and comparisons with published results (e.g. for estimating NO, the contribution of specific pathways of nitrate formation etc.). The validity of applying these published results for this study will depend on pollution levels, degree of impact of local sources, contribution from processed polluted air masses and so on and therefore may not be directly applicable to the cases studied here. This needs to be explained and discussed in more detail.

**A:** Thanks for your suggestions. We are very sorry that some key species are not observed during our sampling period. When we use approximations to get their values, we try our best to let the approximations be reasonable or applicable for our cases. The estimate of  $\alpha$  based on calculated  $HO_2$  and  $RO_2$  concentrations belongs to the first kind. Our estimated  $\alpha$ , based on calculated  $HO_2$  and  $RO_2$  concentrations, is in the range of possible  $\alpha$  values that directly derived from observed  $\Delta^{17}O(NO_3^-)$  (Fig. 5) and is similar to the values determined in other mid-latitude areas (Michalski et al., 2003; Patris et al., 2007). So our estimated  $\alpha$  on the base of calculated  $HO_2$  and  $RO_2$  should be reasonable. Besides, the subsequent estimate of fractional contribution of different nitrate formation pathways, which is based on estimated  $\alpha$  and observed  $\Delta^{17}O(NO_3^-)$ , is a range but not a specific value. This range should

*be representative for the real situation. We have removed section 3.4, interpretation of  $\delta^{15}\text{N}(\text{NO}_3^-)$  variations, from the manuscript.*

**Comments:** 3. The various values (e.g. rate constants, excess isotope ratios in Table 2, estimates of [NO] from [CO]) used in the calculations will have uncertainties, which will add uncertainty to all quantitative results. This needs to be evaluated in more detail.

*A: Thanks for your comment. It's true that various values used in the calculations have uncertainties, and therefore add uncertainty to all quantitative results. However, as stated in the last answer, the estimated fractional contribution of different nitrate formation pathways is a range but not a specific value.*

**Comments:** 4. Subchapter 3.4.1: Indeed, the impact of deposition on  $^{15}\text{N}$  is difficult to estimate. The argument that the impact of partitioning between gas and PM is minor since both  $\text{HNO}_3$  and nitrate are collected on the filter is not convincing. Deposition rates for  $\text{HNO}_3$  and nitrate differ and will be highly variable depending on the situation. If the  $^{15}\text{N}$  isotope ratios for PM nitrate and gas phase  $\text{HNO}_3$  differ, differences in deposition rates will change the isotope ratio for the sum of  $\text{HNO}_3$  and nitrate.

*A: Thanks for your comment. Indeed, the impact of deposition on  $^{15}\text{N}$  is difficult to estimate during long range transport. In the present study, however, our sampling site is in megacity Beijing, which is the source region for  $\text{NO}_x$  and atmospheric nitrate. So the impact of deposition on our observed  $\delta^{15}\text{N}(\text{NO}_3^-)$  should be minor, especially when considering that no rains were observed except for a very small snow. We agree with your comment that deposition rates for  $\text{HNO}_3$  and nitrate differ. However, when considering the relatively short time of both  $\text{HNO}_3$  and nitrate from being produced to being collected in our sampling site, we doubt that differences in deposition rates will not change the isotope ratio for the sum of  $\text{HNO}_3$  and nitrate as much as that observed in remote areas (Geng et al., 2014). Again, we have removed section 3.4 from the manuscript.*

**Comments:** 5. Chapter 3.4.3: This chapter neglects the  $\text{NO}+\text{O}_3$  and  $\text{NO}_2+h\nu$  cycle (see above). Furthermore  $f_{\text{NO}_x}$  (in Eq. 6) is based on [NO] values calculated from measured [CO] and  $[\text{NO}_2]$  and consequently the calculated values for  $[\delta^{15}\text{N}(\text{NO}_2) - \delta^{15}\text{N}(\text{NO}_x)]$  are in reality a non-linear function of the  $[\text{NO}_2]$  and [CO] concentrations. Thus Figure 7a is a plot of  $\delta^{15}\text{N}(\text{NO}_3^-)$  versus a non-linear function

of  $[\text{NO}_2]$  and  $[\text{CO}]$ . Not sure how to interpret this, but obviously  $[\text{NO}_2]$  and  $[\text{CO}]$  will vary for different sources with different  $^{15}\text{N}$  values. In order to be of value for the reader there needs a more detailed discussion than “should therefore be interpreted with the consideration of atmospheric contexts”. The discussion of  $\delta^{15}\text{N}(\text{NO}_3^-)$  should be combined into one chapter discussing the different factors that may influence  $\delta^{15}\text{N}(\text{NO}_3^-)$ . Due to the complexity of the various factors influencing  $\delta^{15}\text{N}(\text{NO}_3^-)$  the attempt to discuss individual contributions separately does not work well. A revised version considering these specific problems will merit publication.

*A: Thanks very much for your comments. The influence of Leighton cycle on  $^{15}\text{N}$  can be summarized into the isotopic exchange constant  $K$  in Eq. (6) (Freyer et al., 1993). However, since the  $K$  value used in our study is determined from  $\text{NO}/\text{NO}_2$  mixture without considering the influence of Leighton cycle (Walters et al., 2016), we truly neglects the  $\text{NO}+\text{O}_3$  and  $\text{NO}_2+h\nu$  cycle. According to the work of (Walters et al., 2016), the lifetime of Leighton cycle reactions and  $\text{NO}_x$  exchange can be comparable, therefore, the isotopic exchange between  $\text{NO}$  and  $\text{NO}_2$  will be a mixture of these processes. The isotopic exchange associated with the  $\text{NO} + \text{O}_3$  reaction and  $\text{NO}_2$  photolysis has yet to be determined, so it will be a subject of future study. Due to that we are unable to explain the variations of  $\delta^{15}\text{N}(\text{NO}_3^-)$  well, we have removed section 3.4 from the manuscript.*

## **Details**

General: Often a values are given as  $(xyz\pm abc)$ , it is not always clear whether the  $\pm$  indicates the error of the mean or the standard deviation.

*A: Thanks for your reminding. The  $\pm$  indicates the standard deviation and it has been illustrated in the manuscript in line 17 and 141.*

Correlations: If I understand correctly, the authors present  $r$  and not  $r^2$ .  $R$  values of 0.5 or so correspond to  $r^2$  of 0.25, a very weak correlation. These low  $r$  values need a more critical discussion of their meaning. It maybe that even a weak correlation has statistical validity. However, it has to be remembered that for  $r=0.5$ ,  $r^2=0.25$ , which means that only 25% of the observed variability can be explained by a linear dependence between dependent and independent variable.

*A: Thanks for your comments. These **low  $r$  values** is not discussed for their meaning in the present manuscript.*

The authors use “wine colored” in several figure captions. Dark red would be better.

*A: Thanks for your suggestion. The “wine colored” has been changed into “dark red” throughout the manuscript.*

53: . And once formed

*A: Thanks for your suggestion. We have corrected this error in line 53.*

76: Sampling site

*A: Thanks for your suggestion. We have corrected this error in line 74.*

78: Super site set by..

*A: Thanks for your suggestion. We have corrected this mistake in line 76.*

81: About 10 km to our sampling site

*A: Thanks for your suggestion. We have corrected this mistake in line 79.*

88, 94: Insoluble substances were filtered (removed by filtration?)

*A: Removed by filter membrane.*

90: When determine the...

*A: Thanks for your suggestion. We have corrected this mistake in line 88.*

90: precision by our

*A: Thanks for your suggestion. We have corrected this mistake in line 88.*

95: which were decomposed from

*A: Thanks for your suggestion. We have corrected this mistake in line 93.*

110, 111 and other lines: is respectively

*A: Thanks for your suggestion. We have corrected this mistake.*

130: at the same time

*A: Thanks for your suggestion. We have corrected this error in line 127.*

133, 134: I assume weighted averages are meant. I understand the meaning and rationale for concentration weighted oxygen excess, but I am not sure what production rate weighted means.  $\alpha$  is a ratio with the total NO<sub>2</sub> production rate in the denominator, consequently the production rate weighted average for  $\alpha$  would be some kind of average for the nominator, that is  $k[\text{NO}][\text{O}_3]$ . This requires more clarification and explanation.

*A: Thanks for your comment. The production rate weighted  $\alpha$  is calculated by*

$$\frac{\sum k_{R1}[\text{NO}][\text{O}_3]}{\sum(k_{R1}[\text{NO}][\text{O}_3]+(k_{R2a}[\text{NO}][\text{HO}_2])+(k_{R2b}[\text{NO}][\text{RO}_2])}$$

*for PD of each haze event.*

164: samples

*A: Thanks for your suggestion. We have corrected this error in line 160.*

251: a small snow lasted for..

*A: Thanks for your comment. We have removed this part for the manuscript.*

258: ..it has been proposed that atmospheric nitrate that resulting from heterogeneous uptake of N...

*A: Thanks for your comment. We have removed this part for the manuscript.*

262: Don't present similar trends..

*A: Thanks for your comment. We have removed this part for the manuscript.*

518: is set by

*A: Thanks for your suggestion. We have corrected this error in line 444.*

551: . And

*A: Thanks for your suggestion. We have corrected this error in line 471.*

## **Reference**

- Freyer, H. D., Kley, D., Volz - Thomas, A., and Kobel, K.: On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen, *J. Geophys. Res. Atmos.*, 98, 14791-14796, 1993.
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- Michalski, G., Scott, Z., Kabling, M., and Thiemens, M. H.: First measurements and modeling of  $\Delta^{17}\text{O}$  in atmospheric nitrate, *Geophys. Res. Lett.*, 30, 2003.
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