G. Michalski (Referee #3):

Comments: A very interesting and exciting dataset. I think the manuscript would do well with some significant revisions.

A: Thanks very much for your comments. We reply to your comments one by one in the following part. 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 $\delta^{15}N(NO_3^-)$ well so far.

Comments: 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 $\Delta^{17}O$ value NO_2+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 $\Delta^{17}O$ of 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 O_3 $\Delta^{17}O$ 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 O_3 $\Delta^{17}O$ had "insignificant variation" 28 ‰ - 23 ‰, if one considers ~20% variation insignificant.

4. Lab experiments have clearly noted an O_3 $\Delta^{17}O$ temperature dependence.

5. NO_X photochemical equilibrium experiments (Michalski et al., 2013) a higher terminal atoms value transfer and Vicars noted that $\Delta^{17}O(O_3)$trans. in the range of 38–44‰ fits data.

6. Even assuming a fixed value of O_3 $\Delta^{17}O$ 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.

A: Thanks for your comment. The value of 24.85α and 24.85α + 13.66 in line 114 is respectively the $\Delta^{17}O$ value NO_2+OH and $NO3+HC$ pathway (Table 1). To be clear for readers, we have added "By

using the $\Delta^{17}O$ assumptions for different pathways in Table 1 and the definition $f_{R6} + f_{R7} + f_{R8} + f_{R9} + f_{R10} = 1$, Eq. (1) is further expressed as:" in line 110 before Eq. (2). And to be consistent with the significant digit of our assumption ($\Delta^{17}O(O_3) = 26$ ‰), "24.85" and "13.66" have been changed into "25" and "14" respectively throughout the manuscript. We have learned that observed $\Delta^{17}O$ values spanned largely in the work of (Krankowsky et al., 1995) and (Johnston and Thiemens, 1997) during the preparation of our manuscript. However, (Vicars and Savarino, 2014) questioned in their paper that "In the study of Krankowsky et al. (1995), no correlation was found between the $\delta^{17}O$ and $\delta^{18}O$ values of ozone, suggesting that the large degree of variability observed for $\Delta^{17}O$ is an artifact resulting from statistical scatter of the individual d measurements. These results are therefore not inconsistent with the hypothesis that the tropospheric value of $\Delta^{17}O(O_3)$ is constant. However, the data of Johnston and Thiemens (1997) reveal a systematic variation in the relationship between $\delta^{17}O$ and $\delta^{18}O$, with data from three different sites aligning on different slopes in a three-isotope plot. The authors of this study concluded that the observed variations resulted from differences in ozone transformation pathways between the three sites and suggested that measurements of the triple-isotope composition of ozone could therefore be useful in constraining the tropospheric ozone budget. This conclusion was later questioned by Brenninkmeijer et al. (2003), who argued that the differences in slope were not statistically significant and suggested that they were related to analytical bias." In addition, $\Delta^{17}O(O_3) \approx 26$ ‰ from the observations of (Vicars and Savarino, 2014) and (Ishino et al., 2017) compare quite well in terms of average value: 25 ± 11 ‰ and 26 ± 5 ‰ for the studies of Krankowsky et al. (1995) and Johnston and Thiemens (1997) respectively, and the observations of (Vicars and Savarino, 2014) and (Ishino et al., 2017) are more recent publications, so we prefer $\Delta^{17}O(O_3)$ values reported by (Vicars and Savarino, 2014) and (Ishino et al., 2017). The assumption that $\Delta^{17}O(O_3) \approx 26$ ‰ is also adopted by (Chen et al., 2016). It's true that lab experiments have clearly noted an O_3 $\Delta^{17}O$ temperature dependence. However, as (Vicars and Savarino, 2014) summed in their paper, "the experimentally determined dependency of $\Delta^{17}O(O_3)$ on the pressure of ozone formation suggests a relatively small decrease of only ~2 ‰ for an increase in pressure from 500 to 760 Torr (0.7 to 1.0 atm) (Morton et al.,1990; Thiemens and Jackson, 1990); and temperature dependency studies suggest an increase in $\Delta^{17}O$ of only ~5 ‰ for an increase in ozone formation temperature from 260 to 320 K (Morton et al., 1990; Janssen et al., 2003). For these reasons, it is often assumed that $\Delta^{17}O(O_3)_{bulk}$ in the troposphere exhibits no more than a 1–2 ‰ level of variability under standard*

surface conditions". Nevertheless, we noted that both (Vicars and Savarino, 2014) and (Ishino et al., 2017) uses the nitrite-coated filter technique in their studies, future studies may need other technique to verify whether $\Delta^{17}O(O_3)$ is truly constant in the surface atmosphere.

Comments: 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

A: Thanks for your comment. We realized that we are unable to explain $\delta^{15}N(NO_3^-)$ data well so far, and thus removed section 3.4 from the manuscript.

Comments: Line 200: "To estimate the specific α value, chemical kinetics in Table 2 and Eq. (3) were used. Specific α is estimated to range from 0.86 to 0.97 with a mean of (0.94±0.03)". The coefficients used to estimate HO_2 has significant uncertainties (again r2= ~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 $RO_2 = 0.7HO_2$ must be significant and site specific. The validity of this assumption in the context of extreme haze needs to be discussed.

A: Thanks for your comment. As we all know, there are some similarities between Tokyo and Beijing, e.g., both of them are in the East and both of them are megacities, which increases the possible applicability of using the regression. In the regression, the HO_2 concentration is related with O_3 concentration (Kanaya et al., 2007), and we expect HO_2 concentration should be related with O_3 concentration too in Beijing as both HO_2 and O_3 are photochemical products whether or not in haze. Meanwhile, in the same season, the HO_2 concentration observed in Beijing (Liu et al., 2012) is generally comparable with that reported by (Kanaya et al., 2007) in Tokyo. If we double the estimated HO_2 and RO_2 concentrations, the calculated α would be 0.89±0.05. If we halve the estimated HO_2 and RO_2, the calculated α would be 0.97±0.02. Both of these two situation will not change the importance of nocturnal chemistry reported in the manuscript. As for $RO_2 = 0.7HO_2$, it's the general value reported in the literature (Liu et al., 2012; Elshorbany et al., 2012; Mihelcic et al., 2003). Neither double nor halve the value will change the importance of nocturnal chemistry reported in the manuscript (α = 0.92±0.04 and 0.95±0.02 respectively). In addition, Our estimated α, based on calculated HO_2 and RO_2 concentrations, is in the range of possible α 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 α on the base of calculated HO_2 and RO_2 should be reasonable.

Comments: "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.

A: Thanks for your reminding. We have changed the reference into an earlier one, i.e., (Liang et al., 1998).

Comments: 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 aerosol surface area was determined if that was part of the scheme? "1-h averaged mixing ratios of observed surface CO, NO_2, SO_2 and O_3 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_2, RO_2, 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 (O3, NO_2,)? This section was entirely too vague for anything useful to be inferred about the accuracy of predicted NO3 or N2O5 mixing ratios.

A: Thanks very much for your comments. The MCM model (version 3.3) we used is the standard one from the website (http://mcm.leeds.ac.uk/). The model includes heterogeneous reactions. However, we have no aerosol surface data as input. The 1-h averaged mixing ratios of observed surface CO, NO_2, SO_2 and O_3 and estimated NO is used to initialize the model and these mixing ratios are updated every 12 hours. The model is set to output one dataset per hour. We did not adjust the photolysis to account for haze, so the model predicted HO_2 and RO_2 is expected to be higher than the real value. In fact, the average of model predicted HO_2 during the sampling period (including day and night) is 1.35 ppt,

higher than our estimated value (0.88 ppt) by ~50%. Therefore we used the estimated value rather than the model predicted HO₂ in our calculation due to that the estimated value is based on observed O₃ concentration. There also exist gaps between the measured O₃, NO₂ and predicted O₃, NO₂ (17 and 31 ppb vs 26 and 23 ppb respectively). This may due to that photolysis was not adjusted and the emission of NO_X was not considered during modeling. Since we use the standard MCM model only to get nocturnal radicals (N₂O₅ and NO₃), the unadjusted photolysis may be not a major factor influencing predicted NO₃ or N₂O₅ mixing ratios. In addition, the variation trend of predicted NO₃ and N₂O₅ is a more useful information than the specific concentration in our study, which possibly deduce the risk of using this model in the present study.

Comments: "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 15N variations in atmospheric nitrate.

A: Thanks for your reminding. This reference has been replaced by (Freyer, 1991).

Comments: 254 "The quartz filter used here is thought to collect both particulate nitrate and gaseous HNO3" this statement needs better justification by citing filter pack studies. This is particularly true in Beijing where NH4NO3 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 NH4NO3.

A: Thanks very much for your reminding. We realized that the exact nature of the nitrate species collected during sampling using fiber filters has always been an area of some debate due primarily NH₄NO₃ and thus removed the statement from the manuscript.

Comments: Isotopic fractionations associated with nitrate formation pathways. These (Photolysis and KIE effects in NOy) 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?

A: Thanks for your comment. It's true that isotopic fractionations associated with nitrate formation

pathways are largely unknown, so we decided to remove the entire section 3.4 from the manuscript. As for our observation, $\delta^{15}N(NO_3^-)$ is generally high (7.4±6.8 ‰), however, we do not know whether it is related to nitrate formation pathways. The $\delta^{15}N(NO_3^-)$ data is open for you if you are interested in haze in China.

Comments: 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 Y data is not a measurement of the δ15N 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.

A: Thanks for your comment. We uses the 12h-averaged temperature to calculate this. We cannot know how much the uncertainty of NO estimation influences the relationship between $\delta^{15}N(NO_3^-)$ and $[\delta^{15}N(NO_2) – \delta^{15}N(NO_X)]$, so we removed the entire section 3.4 from the present manuscript.

Comments: 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/NO2 ratios. Was the a correlation between $\delta^{15}N$ and f_{NO2}? The exchange section should discuss in terms of Freyers and Walters et al. papers that measured $\delta^{15}N$ values of ambient NO$_2$.

A: Thanks for your comment. I have no idea why the correlation is better in residential heating season, perhaps due to that source emission in residential heating season is more stable, leading to other factors, e.g., isotopic exchange, being more important for the trend of $\delta^{15}N(NO_3^-)$. Again, we removed the entire section 3.4 from the present manuscript.

Comments: "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 maybe 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 ?

A: Thanks very much for your suggestions. It's true that coal combustion and vehicles are the most important emissions in Beijing and its surrounding regions. We are sorry that we have not found better N inventory for Beijing, perhaps Qiang Zhang in Tsinghua University have the last inventory for Beijing.

Comments: 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.

A: Thanks for your comments. There is no correlation between $\Delta^{17}O$ and $\delta^{15}N$ (Fig. 4f), so we did not further discuss their relationship. The $\delta^{18}O$ is highly positively correlated with $\Delta^{17}O$ ($R^2 = 0.9$, data not shown), which means it may have almost the same implications with $\Delta^{17}O$, and thus we did not present the data of $\delta^{18}O$ but $\Delta^{17}O$ in the manuscript.

Reference

Chen, Q., Geng, L., Schmidt, J. A., Xie, Z., Kang, H., Dachs, J., Cole-Dai, J., Schauer, A. J., Camp, M. G., and Alexander, B.: Isotopic constraints on the role of hypohalous acids in sulfate aerosol formation in the remote marine boundary layer, Atmos. Chem. Phys., 16, 11433-11450, 2016.

Elshorbany, Y. F., Kleffmann, J., Hofzumahaus, A., Kurtenbach, R., Wiesen, P., Brauers, T., Bohn, B., Dorn, H. P., Fuchs, H., and Holland, F.: HOx budgets during HOxComp: A case study of HOx chemistry under NOx‐limited conditions, J. Geophys. Res., 117, 2012.

Freyer, H. D.: Seasonal variation of 15N/14N ratios in atmospheric nitrate species, Tellus B, 43, 30-44, 1991.

Ishino, S., Hattori, S., Savarino, J., Jourdain, B., Preunkert, S., Legrand, M., Caillon, N., Barbero, A., Kuribayashi, K., and Yoshida, N.: Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate, and ozone at Dumont d'Urville, coastal Antarctica, Atmos. Chem. Phys., 17, 3713-3727, 2017.

Johnston, J. C., and Thiemens, M. H.: The isotopic composition of tropospheric ozone in three environments, J. Geophys. Res. Atmos., 102, 25395-25404, 1997.

Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H.,

Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO2 radical concentrations during the winter and summer of 2004, J. Geophys. Res., 112, 2007.

Krankowsky, D., Bartecki, F., Klees, G., Mauersberger, K., Schellenbach, K., and Stehr, J.: Measurement of heavy isotope enrichment in tropospheric ozone, Geophys. Res. Lett., 22, 1713-1716, 1995.

Liang, J., Horowitz, L. W., Jacob, D. J., Wang, Y., Fiore, A. M., Logan, J. A., Gardner, G. M., and Munger, J. W.: Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, J. Geophys. Res. Atmos., 103, 13435-13450, 1998.

Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L., Stickel, R., Liao, J., Shao, M., Zhu, T., and Zeng, L.: Summertime photochemistry during CAREBeijing-2007: ROx budgets and O3 formation, Atmos. Chem. Phys., 12, 7737-7752, 2012.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of Δ17O in atmospheric nitrate, Geophys. Res. Lett., 30, 2003.

Mihelcic, D., Holland, F., Hofzumahaus, A., Hoppe, L., Konrad, S., Müsgen, P., Pätz, H. W., Schäfer, H. J., Schmitz, T., and Volz‐Thomas, A.: Peroxy radicals during BERLIOZ at Pabstthum: Measurements, radical budgets and ozone production, J. Geophys. Res., 108, 2003.

Patris, N., Cliff, S. S., Quinn, P. K., Kasem, M., and Thiemens, M. H.: Isotopic analysis of aerosol sulfate and nitrate during ITCT‐2k2: Determination of different formation pathways as a function of particle size, J. Geophys. Res. Atmos., 112, 2007.

Vicars, W. C., and Savarino, J.: Quantitative constraints on the 17O-excess (Δ17O) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitrite-coated filter technique, Geochim. Cosmochim. Acta, 135, 270-287, 2014.