Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-334-RC2, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric $\delta^{17}O(NO_3^-)$ reveals nocturnal chemistry dominates nitrate production in Beijing haze" *by* Pengzhen He et al.

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Received and published: 25 June 2018

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 NOx. 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. i) May main concern is that the paper does not consider the photolysis of NO2 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 NO2+hv=>NO+O O+O2=O3 NO+O3=>NO2+O2 (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 NO2 (Chapter 3.4.3) but also for O between NOx, O2 and O3. 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 NO2 photolysis will impact the excess oxygen ratio in NO2 and NO (and consequently in nitrate) or the 15N isotope ratio. Nevertheless, this is something that needs to be explained and discussed and potentially may change the interpretation of the isotope ratio measurements. ii) 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 nor be directly applicable to the cases studied here. This needs to be explained and discussed in more detail. iii) 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 evaluated in more detail. iv) Subchapter 3.4.1: Indeed, the impact of deposition on 15N is difficult to estimate. The argument that the impact of partitioning between gas and PM is minor since bot HNO3 and nitrate are collected on the filter is not convincing. Deposition rates for HNO3 and nitrate differ and will be highly variable depending on the situation. If the 15N isotope ratios for PM nitrate and gas phase HNO3 differ, differences in deposition rates will change the isotope ratio for the sum of HNO3 and nitrate. v) Chapter 3.4.3: This chapter neglects the NO+O3 and NO2+hv cycle (see above) Furthermore f NOx (in Eq. 6) is based on [NO] values calculated from measured [CO] and [NO2] and consequently the calculated values for (δ15N(NO2)- δ15N(NOx)) are in reality a

non-linear function of the [NO2] and [CO] concentrations. Thus Figure 7a is a plot of δ15N(NO3-) versus a non-linear function of [NO2] and [CO]. Not sure how to interpret this, but obviously [NO2] and[CO] will vary for different sources with different 15N 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 δ15N(NO3-) should be combined into one chapter discussing the different factors that may influence δ15N(NO3-). Due to the complexity of the various factors influencing δ15N(NO3-) the attempt to discuss individual contributions separately does not work well.

A revised version considering these specific problems will merit publication.

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.

Correlations: If I understand correctly, the authors present r and not r2. R values of 0.5 or so correspond to r2 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, r2=0.25, which means that only 25% of the observed variability can be explained by a linear dependence between dependent and independent variable.

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

53: . And once formed

76: Sampling site

78: Super site set by..

81: About 10 km to our sampling site

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

90: When determine the. . .

90: precision by our

95: which were decomposed from

110, 111 and other lines: is respectively

130: at the same time

133, 134: I assume weighted averages are meant. I understand the meaning and rational for concentration weighted oxygen excess, but I am not sure what production rate weighted means. α is a ratio with the total NO2 production rate in the denominator, consequently the production rate weighted average for α would be some kind of average for the nominator, that is k[NO][O3]. This requires more clarification and explanation.

164: samples

251: a small snow lasted for..

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

262: Don't present similar trends..

518:is set by 551: . And

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