Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1071-AC2, 2018

Interactive comment on "Triple oxygen isotopes indicate urbanization affects sources of nitrate in wet and dry atmospheric deposition" *by* David M. Nelson et al.

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Received and published: 27 March 2018

First, the authors should show δ18O data along with δ15N and Δ17O. Importantly, δ18O of deposition nitrate has long been measured and reported in the literature to infer atmospheric NOx chemistry and tracing nitrate deposition in terrestrial ecosystems. Reporting both δ18O and Δ17O may not only better connect this study to the literature, but also can serve as an additional constraint on chemical pathways of nitrate formation. For example, coupled δ18O and Δ17O has been modeled for the photochemical cycling between NO-NO2-O3 (e.g., Michalski et al., Atmos. Chem. Phys., 14, 4935-4953, 2014). In Michalski et al. (2014), at a photochemical equilibrium with

O3, δ18O-NOx was estimated to have a value of âĹij117‰Ṫherefore, the measured δ18O in this study should be used as an independent line of evidence for partitioning formation pathways of deposition nitrate (e.g., O3 vs. RO2 for NO2; O3 vs. OH for HNO3).

Reply: We will add d18O data to the figures, as requested.

Second, more data interpretations are needed for the measured δ15N. Admittedly, a variety of chemical and physical processes can alter δ15N of deposition nitrate from original source δ15N-NOx. However, this study seems represent a unique case in which NOx-NO3- photochemical pathways can be constrained by Δ17O (and potentially δ18O) and study design (urban vs. rural). For example, if the measured dry nitrate deposition were from local sources, as constrained by lower Δ17O, how would the measured relatively higher δ15N of dry deposition in the urban site reflect local NOx emission sources? Using passive samples for δ15N-NO2 analysis along a highway, Redling et al. (2013, Biogeochemistry, 116, 261-274) found that most vehicle-sourced NOx deposited in near road environment and was associated with a δ15N of -5 to 5‰Ṫherefore, I would recommend the authors to better relate interpretation of the measured δ15N to the growing literature on δ15N-NOx source signatures.

Reply: We will expand our discussion of the d15N data as requested by both reviewers. In addition, in our revisions we will better relate interpretation of our d15N data to the d15N-NOx literature, as suggested. As discussed in response to comment #10 from reviewer #2 we interpret that variation in d15N is primarily controlled by the NOx oxidation efficiencies; therefore, the winter high d15N values are likely close to source d15N values, such as produced by the combustion of fossil fuels for heat production and/or in vehicles. However, the focus of our manuscript is in D17O, and the controls on variation in d15N values of nitrate (NOx emission sources and/or seasonal changes in NOx oxidation efficiencies) have been debated since 1960s. Therefore, although we are able to use our D17O data to help constrain interpretation of our d15N data, we don't view the D17O data as conclusive regarding how to interpret the d15N data.

Third, I found that the analytical perspective of this manuscript is not adequately described. In particular, deposition samples were collected in 2009, whereas it is not clear when these samples were measured for isotopes. It has been reported in the literature that during prolonged sample storage (i.e., a few months), nitrite concentrations may decrease, leading to sporadic and haphazard δ15N and δ18O of nitrate at lower nitrate concentrations when the proportion of nitrite was relatively high (Granger et al., 2008, Limnol. Oceanogr., 53(6), 2533-2545). Nitrite can be unstable, even when frozen, so spontaneous decomposition of nitrite to nitric oxide and re-oxidation of nitric oxide to nitrate may cause dilute/change N and O isotopes of initial nitrate. Has any quality control been conducted to assess effects of prolonged sample storage on isotopic analysis?

Reply: Concentration analyses were performed within a few months after each sample was collected, and isotopic analyses were done in 2011 for the samples of Sapporo and in 2013 for the samples of Rishiri. All of the samples were archived under refrigeration at the Hokkaido Research Organization. Prior to isotopic analysis of the archived samples, we re-analyzed concentrations of both nitrate and nitrite and verified the differences were less than 10% than the concentrations measured within a few months of sample collection. Furthermore, both the weighted-average and variation range of D17Owet determined in this study for the samples taken in 2009 coincided with those determined in 2006-07 in the same station (Tsunogai et al., 2010). As a result, while the oxygen isotope exchange reaction between nitrite and water must reach to the isotope exchange equilibrium during the storage, the influence of both deterioration and contamination were minimum for nitrate. We will add these details to the revised manuscript.

Finally, I am not opposed to combining results and discussion sections. However, I think that this paper would be improve with some reorganization. As presented, I think the combination of results and discussion is not justified, as discussions on oxidation pathways, transport distance, and δ15N are highly inter-related so that I am looking for

some larger and integrated explanation/description about the presented data.

Reply: We have separated the results and discussion as suggested.

Specific comments: Line 148-150: what were precision and detection limit of the IC measurements?

Reply: The precision was 1.6% for concentration and the detection limit was 0.03 μmol/L. We will add this information to the revised manuscript.

Line 159: d18O of the used working standards were significantly lower than d18O of atmospheric nitrate. Would this overrange affect the precision on d18O determination? And what standards were used for D17O calibration?

Reply: This comment was address in response to comment #5 from reviewer #2.

Line 163: What was the propagated error on d15N-NO3 when nitrite was present? Line 165: It would be nice to show the pH range of the collected wet deposition here.

Reply: This comment was address in response to comment #6 from reviewer #2. The pH values ranged from 4.65 to 5.29 at Sapporo and from 4.51 to 5.02 in Rishiri, and we will add this information to the revised manuscript.

Line 202: What mechanism was causing this D17O offset between coarse and fine particles? Please elaborate.

Reply: This comment was address in response to comment #8 from reviewer #2.

Line 259-260: This positive correlation between d15N and D17O worth further discussion. What mechanism was invoked here? Please elaborate.

Reply: This comment was address in response to comment #11 from reviewer #2.

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