Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1071-RC2, 2018

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #3

Received and published: 2 February 2018

In the paper, "Triple oxygen isotopes indicate urbanization affects sources of nitrate in wet and dry atmospheric deposition," Nelson et al. present a compelling data set of wet and dry deposition samples collected at two rural and urban sites in Japan. Both of these two sites received nitrate deposition from local (short-distance transport) and regional (long-distance transport) sources, although presumably in different magnitude. They present comprehensive information in speciation and isotopic compositions (δ15N and Δ17O) of depositional nitrate, as well as their temporal variations. Interestingly, they find that Δ17O of dry nitrate deposition at the urban site was lower than Δ17O of urban wet deposition and Δ17O of dry and wet deposition in the rural site, indicating that dry nitrate deposition in the urban site largely resulted from local

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NOx emission sources. Overall, the data set presented in this manuscript is timely and important. However, I just think more comprehensive analysis could be done using the existing data set, which may provide important implications for using all three isotopic tracers of nitrate (δ15N, δ18O, Δ17O) in deposition studies.

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 $\sim$117‰. Therefore, 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).

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‰. Therefore, I would recommend the authors to better relate interpretation of the measured δ15N to the growing literature on δ15N-NOx source signatures.

Third, I found that the analytical perspective of this manuscript is not adequately de-

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scribed. 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?

Finally, I am not opposed to combining results and discussion sections. However, I think that this paper would be improve with some re-organization. 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.

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

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?

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.

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

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

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