

# ***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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First, the authors should show  $\delta^{18}\text{O}$  data along with  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ . Importantly,  $\delta^{18}\text{O}$  of deposition nitrate has long been measured and reported in the literature to infer atmospheric  $\text{NO}_x$  chemistry and tracing nitrate deposition in terrestrial ecosystems. Reporting both  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  has been modeled for the photochemical cycling between  $\text{NO}$ - $\text{NO}_2$ - $\text{O}_3$  (e.g., Michalski et al., Atmos. Chem. Phys., 14, 4935-4953, 2014). In Michalski et al. (2014), at a photochemical equilibrium with

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O<sub>3</sub>,  $\delta^{18}\text{O}$ -NO<sub>x</sub> was estimated to have a value of  $\sim 117\%$ . Therefore, the measured  $\delta^{18}\text{O}$  in this study should be used as an independent line of evidence for partitioning formation pathways of deposition nitrate (e.g., O<sub>3</sub> vs. RO<sub>2</sub> for NO<sub>2</sub>; O<sub>3</sub> vs. OH for HNO<sub>3</sub>).

Reply: We will add  $\delta^{18}\text{O}$  data to the figures, as requested.

Second, more data interpretations are needed for the measured  $\delta^{15}\text{N}$ . Admittedly, a variety of chemical and physical processes can alter  $\delta^{15}\text{N}$  of deposition nitrate from original source  $\delta^{15}\text{N}$ -NO<sub>x</sub>. However, this study seems represent a unique case in which NO<sub>x</sub>-NO<sub>3</sub>- photochemical pathways can be constrained by  $\Delta^{17}\text{O}$  (and potentially  $\delta^{18}\text{O}$ ) and study design (urban vs. rural). For example, if the measured dry nitrate deposition were from local sources, as constrained by lower  $\Delta^{17}\text{O}$ , how would the measured relatively higher  $\delta^{15}\text{N}$  of dry deposition in the urban site reflect local NO<sub>x</sub> emission sources? Using passive samples for  $\delta^{15}\text{N}$ -NO<sub>2</sub> analysis along a highway, Redling et al. (2013, Biogeochemistry, 116, 261-274) found that most vehicle-sourced NO<sub>x</sub> deposited in near road environment and was associated with a  $\delta^{15}\text{N}$  of -5 to 5%. Therefore, I would recommend the authors to better relate interpretation of the measured  $\delta^{15}\text{N}$  to the growing literature on  $\delta^{15}\text{N}$ -NO<sub>x</sub> source signatures.

Reply: We will expand our discussion of the  $\delta^{15}\text{N}$  data as requested by both reviewers. In addition, in our revisions we will better relate interpretation of our  $\delta^{15}\text{N}$  data to the  $\delta^{15}\text{N}$ -NO<sub>x</sub> literature, as suggested. As discussed in response to comment #10 from reviewer #2 we interpret that variation in  $\delta^{15}\text{N}$  is primarily controlled by the NO<sub>x</sub> oxidation efficiencies; therefore, the winter high  $\delta^{15}\text{N}$  values are likely close to source  $\delta^{15}\text{N}$  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  $\Delta^{17}\text{O}$ , and the controls on variation in  $\delta^{15}\text{N}$  values of nitrate (NO<sub>x</sub> emission sources and/or seasonal changes in NO<sub>x</sub> oxidation efficiencies) have been debated since 1960s. Therefore, although we are able to use our  $\Delta^{17}\text{O}$  data to help constrain interpretation of our  $\delta^{15}\text{N}$  data, we don't view the  $\Delta^{17}\text{O}$  data as conclusive regarding how to interpret the  $\delta^{15}\text{N}$  data.

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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  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  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  $\text{D}_{17}\text{O}_{\text{wet}}$  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  $\delta^{15}\text{N}$  are highly inter-related so that I am looking for

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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  $\mu\text{mol/L}$ . 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-NO<sub>3</sub> 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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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-1071>, 2018.

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