

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

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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 ($\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$) of depositional nitrate, as well as their temporal variations. Interestingly, they find that $\Delta^{17}\text{O}$ of dry nitrate deposition at the urban site was lower than $\Delta^{17}\text{O}$ of urban wet deposition and $\Delta^{17}\text{O}$ 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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NO_x 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 ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) in deposition studies.

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 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 NO - NO_2 - O_3 (e.g., Michalski et al., Atmos. Chem. Phys., 14, 4935-4953, 2014). In Michalski et al. (2014), at a photochemical equilibrium with O_3 , $\delta^{18}\text{O}$ - NO_x 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_3 vs. RO_2 for NO_2 ; O_3 vs. OH for HNO_3).

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_x . However, this study seems represent a unique case in which NO_x - NO_3 - 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_x emission sources? Using passive samples for $\delta^{15}\text{N}$ - NO_2 analysis along a highway, Redling et al. (2013, Biogeochemistry, 116, 261-274) found that most vehicle-sourced NO_x 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_x 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 $\delta^{15}\text{N}$ 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?

Finally, I am not opposed to combining results and discussion sections. However, I think that this paper would be improved 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 $\delta^{15}\text{N}$ 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: d^{18}O of the used working standards were significantly lower than d^{18}O of atmospheric nitrate. Would this overrange affect the precision on d^{18}O determination? And what standards were used for D^{17}O calibration?

Line 163: What was the propagated error on $\text{d}^{15}\text{N}\text{-NO}_3$ 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 D^{17}O offset between coarse and fine particles? Please elaborate.

Line 259-260: This positive correlation between d^{15}N and D^{17}O worth further discussion. What mechanism was invoked here? Please elaborate.

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