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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 #2

Received and published: 30 January 2018

General Comments: This manuscript presents new data on the isotopic composition of atmospherically-derived nitrate (NO3-). Specifically, the authors have analyzed the oxygen mass-independent signature (Δ17O) and the nitrogen stable isotope ratio (δ15N) of wet and dry (size and phase resolved) atmospheric nitrate deposition at two locations (rural and urban) in Japan to assess spatial/temporal sources and processing of atmospheric nitrate. The authors found similar Δ17O values of wet deposited atmospheric nitrate at both the rural and urban sites indicating similar NOx oxidation pathways involved in its formation. However, significant differences in Δ17O were found in dry deposition, in which lower values were observed in the urban setting that the authors have concluded to be the result of a larger contribution from peroxy radical

oxidation of and/or OH oxidation of NO2. These results suggest that wet deposited nitrate tends to be the result of long range transport while dry deposited nitrate is the result of local NOx oxidation. While the explanations of Δ17O aren’t novel, particularly observed seasonal variations, and do not add to our understanding of temporal variabilities in Δ17O of nitrate, observed Δ17O differences in size and particle resolved nitrate is interesting and may be of interest to the ACP community. I think the possibility of using Δ17O to understand the spatial variabilities in NOx oxidation and transport is particularly intriguing. However, I found the discussion of Δ17O and δ15N (almost no explanation of δ15N drivers) to be lacking, and the provided explanations are often ad hoc rather than supported by experiment or theory. I would like to see a more detailed interpretation of these values (specific comments are below). Additionally, I have some concerns about the collection techniques for phase-resolved nitrate. Once the interpretation of these values is improved and a more thorough evaluation of methodologies is provided, I would recommend for this manuscript for publication.

Specific Comments:

Comment 1: Figure 1 – How were the arrow weights and font size determined to represent the relative oxidation pathway significance? Are these sizes qualitative or quantitative (to scale) based on empirical data or model results?

Comment 2: Section 2.1- Air-mass back-trajectories (seasonal) would be useful to understand the potential influence of transported "dry" nitrate (HNO3(g) + NO3-) at these two sampling sites. This seems to be especially important at the rural location since it is remotely populated.

Comment 3: Lines 127 – 129. It is my understanding that filter pack methods are not an optimal way to provide nitrate phase speciation because of the potential for bias resulting from p-NO3- volatilization. While this may not impact the Δ17O of p-NO3- (as mentioned in text Lines 138 - 143) it could contribute to a Δ17O bias to the collected HNO3(g). How confident are the authors that actual p-NO3- and HNO3 speciation was achieved? As long as all “dry” NO3- was collected using the filter pack method, a Δ17O comparison between dry and wet NO3- seems plausible but comparing Δ17O between phase of nitrate (i.e. HNO3(g) vs p-NO3-) does not seem to be suitable utilizing this collection technique.

Comment 4: Section 2.2 (General) – Please provide more details about the collection technique. No mention of field blanks, replicate precision, and breakthrough limits was provided. These all could contribute to collection artifacts that may influence Δ17O (field blank) and δ15N values. I am particularly concerned about how well-preserved d15N-NO3- was for the long-sampling times due to breakthrough limits of the filters and NO3- volatilization.

Comment 5: Lines 158 – 160 – Samples were calibrated to working lab standards with a δ18O range of 1.1 an 22.4 per mil; however, atmospheric nitrates have elevated δ18O values that are typically larger than 65-per mil and upwards of 100 per mil. I'm concerned about this low calibration range because NO2- analysis by azide often induces an oxygen exchange effect (although correctable), but the low standard δ18O values might dampen this effect as compared to a δ18O standard with a much higher value. Additionally, no mention of how Δ17O was calibrated was provided. Do the working lab standards have a Δ17O > 0? If not, how might this impact the samples' calibrated values?

Comment 6: Lines 164-166 – How might accounting for nitrite contributions impact the reported analytical precision? There are uncertainties in both the concentrations and isotope values for nitrite and (nitrate+nitrite), thus the samples with significant nitrite amounts should have a reported precision that accounts for this propagated error. Additionally, while analytical precision for the working lab standards was provided, how might the propagation of collection, extraction, and analytical uncertainties contribute to the reported error in the Δ17O and δ15N values?

Comment 7: Lines 201 – 204 -I think it would be helpful to define “coarse” and “fine”

particulate nitrate in the methods section (near Lines 134-138). Based on the method description, “coarse” appears to be particles >10 μm and “fine” is < 10 μm. I think this is important to define because “fine” PM in the literature commonly refers to <2.5 μm.

Comment 8: Lines 199-222 – Interestingly, a Δ17O difference is found between coarse and fine p-NO3- at both the rural and urban sites. Can the authors provide a plausible explanation for why this difference is observed rather than only point out the difference?

Comment 9: Section 3.1 (General) – Much of the Δ17O explanations are ad hoc. How do the measured atmospheric nitrate Δ17O values compare to the modeled predictions (Alexander et al., ACP 2009)? How does the explanation that lower Δ17O values in dry deposited NO3- in urban areas is driven by peroxy radicals or OH chemistry, compare to Δ17O model predictions in NO2 and nitrate (Morin et al., ACP, 2011)? Additionally, can the authors provide a further description about differences between Δ17O of dry and wet deposited nitrate in the urban location? Particularly, how might in-cloud nitrate formation impact wet Δ17O? (either HNO3 absorption or is there potential for N2O5 hydrolysis that may elevated in-cloud nitrate Δ17O relative to local HNO3(g)+p-NO3-)? Assuming that below cloud nitrate is effectively scavenged during precipitation events, the urban in-cloud nitrate may have elevated Δ17O relative to wet deposited nitrate at the rural location. Is this true and can the authors suggest the source (rural vs urban) and/or oxidation regime of the in-cloud nitrate?

Comment 10: Section 3.2 (General) The discussion of δ15N is very limited in scope. Are the seasonal variations observed in δ15N possibly associated with differences in NOx emission sources and/or seasonal changes in NOx oxidation efficiencies? What are the expected δ15N values based on NOx emission sources for the sample sites and how do they correspond to the measured values in atmospheric nitrate.

Comment 11: Lines 259 – 264 – Correlations are often found between δ15N and Δ17O, which is interesting. Can the authors provide an explanation about the driving forces behind this relationship? Is this a connection between emission sources and oxidation chemistry or is this relationship primarily driven by the NOx oxidation regime?

Comment 12: Section 3.4 (General) – The authors discussion about accounting for dry Δ17O in urban water-shed regions for assessing nitrate processing in environmental waters is interesting, but this is based on one urban location. How applicable is the differences in Δ17O of dry and wet deposited nitrate to all urban regions for assessing urban water-shed nitrate processing?

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