Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1071-AC1, 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.

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Received and published: 27 March 2018

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?

Reply: The sizes are qualitative as we will indicate in a revised legend of Fig. 1.

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

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since it is remotely populated.

Reply: Our sampling sites in Rishiri and Sapporo are only 200 km apart and are both located on the Sea of Japan side of Hokkaido prefecture. The sites were chosen so that their air-mass back-trajectories are similar for daily and longer time scales. We will revise the text to clarify this point.

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.

Reply: We appreciate this helpful suggestion. In prior work we observed a minor amount of HNO3 volatilization from particulate nitrate at our sites using the filter-pack method (Noguchi et al., 2009). Since the primary aim of our present study is to quantify the D17O difference between wet and dry deposition (and not the D17O difference between HNO3 gas and particulate nitrate) we have decided to move Figs. 3c-f and 5c-d (which display the gaseous and particulate data) from the main body of the manuscript to the supplemental material. We will also remove the statistical analyses and text concerning the comparison the particle and gas data, and we will state in the body of the manuscript that HNO3 volatilization may bias interpretation of the measured isotopic values of gaseous and particulate nitrate (although not the comparison of course vs. fine particles). These changes will allow us to focus our interpretation and discussion on differences in the concentrations and isotopic values of wet and dry deposition (which are not affected by potential volatilization, as the reviewer notes).

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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 $\Delta17O$ (field blank) and $\delta15N$ 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.

Reply: The samples were collected using the standard operating method of EANET (Acid Deposition Monitoring Network in East Asia) as we will indicate in the revised manuscript. We will add details about the filter blanks, replicate precision and breakthrough limits to the revised manuscript. As stated above to response to comment #3, because of the potential impact of NO3 volatilization we will no longer report the differences in d15N between particulate and gaseous nitrate.

Comment 5: Lines 158 – 160 – Samples were calibrated to working lab standards with a $\delta18O$ range of 1.1 an 22.4 per mil; however, atmospheric nitrates have elevated $\delta18O$ 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 $\delta18O$ values might dampen this effect as compared to a $\delta18O$ standard with a much higher value. Additionally, no mention of how $\Delta17O$ was calibrated was provided. Do the working lab standards have a $\Delta17O > 0$? If not, how might this impact the samples' calibrated values?

Reply: Besides running standards for routine calibration to check/calibrate both fractionations and oxygen exchanges, we also measured USGS34 ($\delta18O$ = -27.9‰ and $\Delta17O$ = -0.1‰ and USGS35 ($\delta18O$ = +57.5‰ and $\Delta17O$ = +21.6‰ at least every month to check instrument linearity. We will revise the text to clarify our methods of isotopic analysis.

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?

Reply: For all samples (at both sites), the maximum nitrite/nitrate ratios in the samples were 28.6%, 13.3%, and 7.4% for coarse particles, fine particles, and gas, respectively. Therefore, the maximum extents of d15N corrections for the limited number of dry deposition samples with nitrite concentrations > 5 % of the total nitrite plus nitrate concentrations were 1.1, 0.2, and <0.1‰ respectively, and the maximum extents of D17O corrections were 5.7, 3.1, and 0.4‰ respectively. Therefore, we conclude that the potential bias in the isotopic values of dry deposition was much smaller than the errors assumed in the final total isotopic values of dry deposition (around ±2.5‰ for d15N and ±3‰ for D17O). We will add these details to the revised manuscript. 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.

Reply: Done.

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?

Reply: We will add text to state that we interpret the lower values of D17Ofine than D17Ocoarse to indicate that D17Ofine is more influenced by local sources (produced within the boundary layer of urban area) than D17Ocoarse, which is more supplied through long-range transport (produced in free troposphere).

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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?

Reply: We will revise the text to indicate that the D17O values of wet and dry deposition at Rishiri (and D17O values of wet deposition at Sapporo) are consistent with the model predictions in Alexander et al. 2009 in which most of nitrate is produced in the background, free tropospheric air. The D17O values of dry deposition in Sapporo were lower, so we concluded that nitrate formation paths within the boundary layer of the urban area (Sapporo) were somewhat different from those predicted by the model. We now cite Morin et al. 2011 to support our explanation of lower D17O values being driven by peroxy radicals and/or OH. Formally modeling our D17O results, and also addressing the additional questions the reviewer poses, would require us to input/change the parameters in such models. However, we did not measure many of the variables that such models require since they were beyond the scope of the present study. We plan to make such comprehensive observations in Sapporo (and the other urban areas, if possible) in the future.

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

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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.

Reply: We will add text to indicate that we interpret variation in d15N to be primarily controlled by the NOx oxidation efficiencies rather than sources. This hypothesis is supported by the higher d15N in dry deposition (supplied from local sources) than in wet deposition (supplied via long range transport), especially at Sapporo. Probably because of 15N-enrichment in NO2 than in NO (Freyer, 1991), residual NOX becomes depleted in 15N during partial removal of NOX as nitrate in troposphere so that nitrate supplied via long range transport has lower δ15N values than that supplied from local sources. Furthermore, nitrate supplied via long-distance transport in summer (higher removal efficiency) showed lower d15N than nitrate supplied via long-distance transport in winter (lower removal efficiency).

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?

Reply: As discussed above, we will add text to clarify that we interpret variation in D17O as primarily controlled by the oxidation paths of NOx and variation in d15N as primarily controlled by NOx oxidation efficiencies. The correlations between D17O and d15N likely reflect their common control, i.e. the rate of the NO2 + OH reaction.

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?

Reply: We don't know how applicable the difference between D17O values of nitrate in dry and wet deposition are in other urban settings, and we attempted to be intentionally cautious in the text to avoid over extrapolating our results to other settings. Please also note that the difference between D17Owet and D17Ototal (=D17Owet + D17Odry) was only 1.9‰ in the urban site (Sapporo), because wet deposition was the major portion of total deposited nitrate. Therefore, D17Owet could be use to approximate D17Ototal if larger error were allowed for D17Ototal (e.g. ±2‰ or more). The difficult cases will be semi-closed, highly polluted urban sites where the major portion of nitrate comes from local sources. To predict D17Ototal of such urban sites in future studies, we think it will be necessary to increase the number of observations to accurately parameterize Δ17Ototal. We will revise the text to incorporate these points.

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