**Referee #2**

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 now indicate in the revised legend of Fig. 1 (lines 594-595 of the clean manuscript).*

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.

*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 have revised the text to clarify this point (lines 119-121 of the clean manuscript).*

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 $HNO_3$ 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 $HNO_3$ gas and particulate nitrate) we have moved 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 have also removed the statistical analyses and text concerning the comparison the particle and gas data, and we now state that $HNO_3$ volatilization may bias interpretation of the measured isotopic values of gaseous and particulate nitrate (although not the comparison of course vs. fine particles) on lines 210-212 and 227-228 of the clean manuscript. These changes 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).*

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.

*Reply: The samples were collected using the standard operating method of EANET (Acid Deposition Monitoring Network in East Asia) as now indicate on lines 127-128 of the clean manuscript. We have added details about the filter blanks, replicate precision and breakthrough limits to lines 150-159 and 163-164 of the clean 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 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?

*Reply: Besides running standards for routine calibration to check/calibrate both fractionations and oxygen exchanges, we also measured USGS34 ($\delta^{18}O$ = -27.9‰ and $\Delta^{17}O$ = -0.1‰) and USGS35 ($\delta^{18}O$ = +57.5‰ and $\Delta^{17}O$ = +21.6‰) at least every month to check instrument linearity. We have revised the text to clarify our methods of isotopic analysis (lines 175-185 of the clean manuscript).*

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, ±8‰ for d18O and ±3‰ for D17O). We have added these details to the revised manuscript (lines 191-198 of the clean 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 (line 143 of the clean manuscript).*

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 have added text (on lines 296-299 of the clean manuscript) to state that we interpret the lower values of* $D17O_{fine}$ *than* $D17O_{coarse}$ *to indicate that* $D17O_{fine}$ *is more influenced by local sources (produced within the boundary layer of urban area) than* $D17O_{coarse}$*, which is more supplied through long-range transport (produced in free troposphere).*

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 revised the text (lines 261-268 of the clean manuscript)) 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 (on lines 277 and 283 of the clean manuscript) 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 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 have added text (lines 300-313 of the clean manuscript) 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* $NO_2$ *than in NO (Freyer, 1991), residual* $NO_X$ *becomes depleted in 15N during partial removal of* $NO_X$ *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 have added 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* $NO_2$ *+ OH reaction as we now indicate on lines 314-319 of the clean manuscript.*

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* $D17O_{wet}$ *and* $D17O_{total}$ *(=*$D17O_{wet}$ *+* $D17O_{dry}$*) was only 1.9‰ in the urban site (Sapporo), because wet deposition was the major portion of total deposited nitrate. Therefore,* $D17O_{wet}$ *could be use to approximate* $D17O_{total}$ *if larger error were allowed for* $D17O_{total}$ *(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* $D17O_{total}$ *of such urban sites in future studies, we think it will be necessary to increase the number of observations to accurately parameterize* $\Delta^{17}O_{total}$*. We have revised the text to incorporate these points (lines 339-340 and 354-358 of the clean manuscript).*

**Referee #3**

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 photo- chemical 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 ~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).

*Reply: We have added d18O data to figures 3 and 4, as requested.*

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 high- way, 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.

*Reply: We have expanded our discussion of the d15N data as requested by both reviewers. In addition, in our revisions we have bettered relate interpretation of our d15N data to the d15N-NOx literature, as suggested (lines 322-327 of the clean manuscript). As discussed in response to comment #10 from reviewer #2 we interpret that variation in d15N is primarily controlled by the NOx oxidation efficiencies; therefore, the winter high d15N values are likely close to source d15N 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 D17O, and the controls on variation in d15N values of nitrate (NOx emission sources and/or seasonal changes in NOx oxidation efficiencies) have been debated since 1960s. Therefore, although we are able to use our D17O data to help constrain interpretation of our d15N data, we don't view the D17O data as conclusive regarding how to interpret the d15N data.*

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 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?
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* $D17O_{wet}$ *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 (lines 161-162, 168-170, and 183-185 of the clean 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 δ15N are highly inter-related so that I am looking for 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 µmol/L. We have added this information to the revised manuscript (lines 163-164 of the clean 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-NO3 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, as we now state on lines 166-167 of the clean 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.*

# Triple oxygen isotopes indicate urbanization affects sources of nitrate in wet and dry atmospheric deposition

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**Abstract**

Atmospheric nitrate deposition resulting from anthropogenic activities negatively affects human and environmental health. Identifying deposited nitrate that is produced locally vs. that originating from long-distance transport would help inform efforts to mitigate such impacts. However, distinguishing the relative transport distances of atmospheric nitrate in urban areas remains a major challenge since it may be produced locally and/or come from upwind regions. To address this uncertainty we assessed spatiotemporal variation in monthly weighted-average $\Delta^{17}O$ and $\delta^{15}N$ values of wet and dry nitrate deposition during one year at urban and rural sites along the western coast of the northern Japanese island of Hokkaido, downwind of the East Asian continent. $\Delta^{17}O$ values of nitrate in wet deposition at the urban site mirrored those of wet and dry deposition at the rural site, ranging between ~ +22 and +30 ‰ with higher values during winter and lower values in summer, which suggests greater relative importance of oxidation of $NO_2$ by $O_3$ during winter and OH during summer. In contrast, $\Delta^{17}O$ values of nitrate in dry deposition at the urban site were lower (+19 - +25 ‰) and displayed less distinct seasonal variation. Furthermore, the difference between $\delta^{15}N$ values of nitrate in wet and dry nitrate deposition was, on average, 3 ‰ greater at the urban than rural site, and $\Delta^{17}O$ and $\delta^{15}N$ values were correlated for both forms of deposition at both sites with the exception of dry deposition at the urban site. These results suggest that, relative to nitrate in wet and dry deposition in rural environments and wet deposition in urban environments, nitrate in dry deposition in urban environments forms from relatively greater oxidation of NO by peroxy radicals and/or oxidation of $NO_2$ by OH. Given greater concentrations of peroxy radicals and OH in cities, these results imply that dry nitrate deposition results from local $NO_x$ emissions more so than wet deposition, which is transported longer distances. These results illustrate the value of stable isotope data for distinguishing the transport distances and reaction pathways of atmospheric nitrate pollution.

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## 1 Introduction

The world's urban population has rapidly grown in recent decades, and this trend is expected to continue for at least a generation (Nations, 2014). Besides socioeconomic transformation, urbanization also has environmental consequences, such as air pollution (Bloom et al., 2008; Cumming et al., 2014; Akimoto, 2003; Gurjar et al., 2016; von Glasow et al., 2013). For example, fossil fuel combustion from mobile and stationary sources produces nitrogen oxides ($NO_x = NO + NO_2$), which mediate atmospheric ozone ($O_3$) and fine-particle production, thus affecting human health. Furthermore, oxidation of $NO_x$ leads to the formation of nitrate ($NO_3^-$), which when deposited on Earth's surface contributes to the acidification and eutrophication of ecosystems (Galloway et al., 2004; Brown et al., 2006; Crutzen, 1979). Efforts to reduce $NO_x$ emissions can mitigate nitrate deposition (Liu et al., 2016; Zhao et al., 2015), but $NO_x$ and atmospheric nitrate are also transported long distances and thus can affect areas far downwind of production hotspots (Holtgrieve et al., 2011; Akimoto, 2003; Lin et al., 2017). The pathways that transform $NO_x$ to nitrate (Figure 1), as well as the spatiotemporal patterns of atmospheric nitrate deposition, are relatively well understood (Ban et al., 2016; Li et al., 2016). However, it remains challenging to identify the sources of many pollutants, including nitrate produced locally vs. originating from long-distance transport, which impedes efforts to improve air quality and environmental conditions (Wagstrom and Pandis, 2011; Skyllakou et al., 2014).

The stable nitrogen and oxygen isotope compositions of nitrate have been suggested as potential tracers of the sources and fate of $NO_x$ in the environment (Elliott et al., 2009; Kendall et al., 2007; Freyer et al., 1993). Nitrogen isotopes ($\delta^{15}N$) of nitrate can potentially reflect those of $NO_x$, but mass-dependent isotopic fractionations during the oxidation of $NO_x$ to nitrate can also alter the original $\delta^{15}N$ value of $NO_x$, thus complicating efforts to use $\delta^{15}N$ values of nitrate for source partitioning (e.g. Walters and Michalski, 2015, 2016; Walters et al., 2016). A

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unique alternative that has recently emerged is the triple oxygen isotope ($\Delta^{17}O$) value of nitrate[1], which reflects (as the result of mass-independent fractionation during the formation of $O_3$) the number of oxygen atoms derived from $O_3$ that are involved in the oxidation of $NO_x$ (Alexander et al., 2009; Morin et al., 2008; Michalski et al., 2003; Tsunogai et al., 2010; Tsunogai et al., 2016) since direct emissions of nitrate during combustion are relatively small (Fraser et al., 1998). An advantage of $\Delta^{17}O$ relative to $\delta^{18}O$ of nitrate is that $\Delta^{17}O$ values are primarily a function of the chemical pathways of nitrate formation, whereas $\delta^{18}O$ values are also a function of $\delta^{18}O$ of atmospheric water and temperature (Michalski et al., 2011). The fraction of NO oxidized to $NO_2$ by $O_3$ relative to peroxy radicals ($HO_2$ + $RO_2$) determines two-thirds of the $\Delta^{17}O$ value of nitrate. The remaining fraction results from the extent to which $O_3$ vs. OH molecules oxidize $NO_2$ (Geng et al., 2017). $\Delta^{17}O$ values of atmospheric nitrate deposition are often highest in winter and lowest in summer (Michalski et al., 2003; Savarino et al., 2007; Tsunogai et al., 2010; Tsunogai et al., 2016), because greater darkness and lower temperatures favor the oxidation of $NO_x$ by $O_3$, as well as $N_2O_5$ hydrolysis reactions, whereas oxidation of $NO_2$ by OH is more important when daylight is longer and temperatures higher (Figure 1). Peroxy radicals, which form from oxidation of carbon monoxide, reactive hydrocarbons, and volatile organic compounds (Saito et al., 2002), are thought to compete with $O_3$ to oxidize NO in polluted settings and thus depress $\Delta^{17}O$ values of nitrate (Guha et al., 2017; Fang et al., 2011). Decreasing nitrate-$\Delta^{17}O$ values during the past ~150 years in West Antarctica suggest that anthropogenic activities have increased the relative importance of peroxy radicals in $NO_x$ cycling globally (Sofen et al., 2014). However, reactive hydrocarbons and aerosols can also facilitate the formation of nitrate directly or through $N_2O_5$, respectively, which elevates $\Delta^{17}O$ values of nitrate (Michalski et al., 2011). Although wet (aqueous nitrate) and dry (gaseous $HNO_3$ or

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[1] $\Delta^{17}O$ values are defined as: $$\Delta^{17}O_{nitrate} = \frac{1+\delta^{17}O_{nitrate}}{\left(1+\delta^{18}O_{nitrate}\right)^{\beta}} - 1$$

where $\beta = 0.5279^{18}$, $\delta = [R_{sample}/R_{standard}] - 1$, and R represents the elemental ratios (i.e., $^{17}O/^{16}O$ and $^{18}O/^{16}O$) between a sample and standard.

particulate nitrate) deposited nitrate are often presumed to have similar $\Delta^{17}O$ values (Guerrieri et al., 2015), dry deposition may be less prone to long-distance transport (Celle-Jeanton et al., 2009; Dasch and Cadle, 1985; Balestrini et al., 2000). Shorter transport distances could lead to distinct oxidation pathways and thus different $\Delta^{17}O$ values of nitrate between these forms of deposition in urban environments where concentrations of atmospheric pollutants are typically elevated. Yet, this hypothesis cannot be evaluated using existing data, as prior studies typically analyzed $\Delta^{17}O$ values of only wet or dry nitrate deposition at single sites (Guha et al., 2017; Tsunogai et al., 2010).

Here we assess the effect of urbanization on the oxidation chemistry of $NO_x$ and the sources of nitrate in wet and dry deposition using measurements of the $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$ values of atmospheric nitrate. Our two study sites (Figure 2) are located at a similar longitude, are separated by only ~2° of latitude, and have comparable synoptic climatologies, but there is a major difference in the degree of urbanization between them (see below). These sites were chosen to be downwind of several megacities on the East Asian continent, a region where $NO_x$ emissions have increased approximately four-fold during the past forty years (Akimoto, 2003; Uno et al., 2007). This arrangement of sites provides an ideal setting to investigate potential differences in the oxidation pathways and sources of atmospheric nitrate pollution in urban and rural environments against high background levels of atmospheric nitrate deposition.

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## 2 Material and Methods

### 2.1 Study sites

Rishiri is a remote (population size: ~5,000; density: ~28 people/km$^2$) and small island in the Sea of Japan off the coast of the island of Hokkaido in northern Japan. Samples of wet and dry atmospheric deposition were collected at the Rishiri National Acid Rain Monitoring station (Figure 2; 45° 07' 11" N, 141° 12' 33" E; 40 m a.s.l.), which is part of the Acid Deposition Monitoring Network in East Asia (EANET), between January and December in 2009. The mean annual precipitation is ~920 mm and mean annual temperature is ~7.1°C (http://www.jma.go.jp/jma/indexe.html). Precipitation amounts are the highest in the late summer through winter, with lower amounts in the spring and early summer. The main land cover within a ~10 km radius of the monitoring station is forest and shrub land.

Sapporo is a city of ~1.9 million people (density: ~1,710 people/km$^2$) that is ~200 km south of Rishiri. Samples of wet and dry atmospheric deposition were obtained from the roof of the Institute of Environmental Sciences in Sapporo (Figure 2; 43° 04' 55" N, 141° 20' 00" E; ~26 m a.s.l.) between January and December in 2009. The sampling site in Sapporo is not part of EANET. The mean annual precipitation is ~1,100 mm and mean annual temperature is ~8.9°C (http://www.jma.go.jp/jma/indexe.html). Rishiri and Sapporo are both located on the Sea of Japan side of Hokkaido prefecture and thus they have similar seasonal precipitation patterns and air-mass back-trajectories on daily and longer time scales. Sapporo is bordered by the Sea of Japan to the north and by mountains to the west, south, and east. The major sources of local $NO_x$ emissions are automobile exhaust and boilers used for domestic heating. There are no major factories or combustion-based electricity generation facilities in Sapporo (Kaneyasu et al., 1995). The prevailing winds in Hokkaido typically originate from the northwest in winter and southeast in summer (Kaneyasu et al., 1995).

**2.2 Sample collection**

Samples were collected using the standard operating methods of EANET (http://www.eanet.asia/product/manual/techacm.pdf). Composite samples of wet deposition falling on a daily and weekly basis were collected at Rishiri (n= 62) and Sapporo (n = 41), respectively, using auto samplers (DKK DRS-200(S), DKK and US-420, Ogasawara Keiki Corp, respectively). The wet deposition samples were filtered through a 0.45 µm filter and stored at 4°C until measurement of nitrate and nitrite ($NO_2^-$) concentrations and isotopes.

Samples of dry deposition were obtained using the filter-pack method, which has been widely used in dry deposition monitoring programs throughout the world (Aikawa et al., 2010; Endo et al., 2011; Mehlmann and Warneck, 1995; Tørseth et al., 1999). At each site, air was drawn through a four-stage filter pack at a rate of 4 L/min

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to collect gaseous $HNO_3$ and particulate nitrate. Composite samples collected using this approach (which we refer to as dry deposition) were obtained on a monthly basis at Rishiri (n = 12). Sampling of dry deposition at Sapporo occurred approximately bi-weekly (n = 24); sampling occurred bi-weekly rather than monthly (as at Rishiri) because we anticipated higher nitrate concentrations in dry deposition at Sapporo than Rishiri. However, only 15 of the 24 dry deposition samples from Sapporo were available for analysis in the present study. The first stage is a multi-nozzle cascade impactor (NL-4-10P, Tokyo Dylec. Corp.) and Teflon binder filter (T60A20-20H, Tokyo Dylec. Corp.) that collects coarse particles >10 µm in diameter. The second stage is a Teflon filter (ADVANTEC T080A047A) that collects fine particles <10 µm in diameter that passed through the first filter. The third stage is a 0.45 µm nylon filter (PALL ULTIPOR N66-NX047100) that collects $HNO_3$ gas and some $SO_2$, HCl, HONO, $NH_3$, and $NO_2$. The 4th and 5th stage filters (ADVANTEC No. 51A, alkaline impregnated filter) are used to collect the remaining $SO_2$, HCl, and HONO. The last filter (ADVANTEC No. 51A, acid impregnated filter) is used to collect the remaining $NH_3$. The nitrate and nitrite on the first, second, and third filters were extracted using ultrapure water, passed through a 0.45 µm filter, and stored at 4°C until measurement of nitrate and nitrite concentrations and isotopes.

The maximum filter blank was 0.2 µg (=3 nmol) for nitrate, which corresponds to 0.16 µmol/L nitrate when 20 mL of milli-Q water is used to extract nitrate from each filter based on the EANET procedure. The minimum nitrate concentrations in the solutions extracted from the filters and measured for isotopic values were 30.7 µmol/L, 1.5 µmol/L, and 22.4 µmol/L in the portions of coarse particles, fine particles, and gas, respectively, for Rishiri, and 26.1 µmol/L, 3.5 µmol/L, and 10.2 µmol/L in the portions of coarse particles, fine particles, and gas, respectively, for Sapporo. Thus, we concluded that the blanks had little influence on the isotopic values of dry deposition. This is true even for fine particle samples with nitrate concentrations <5 µmol/L, because the deposition rates of these nitrate-depleted samples were low. We did not directly assess filter breakthrough limits, but prior results based on changes in the duration of sampling at our sites suggest that such limits are much higher than the amount of nitrate present in our samples (Noguchi et al., 2009).

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## 2.3 Analysis

Within a few months of collection, nitrate and nitrite in the filtered samples of wet and dry deposition were quantified using ion chromatography (Dionex DX-500, ICS-1500 and ICS-2000, Nippon Dionex Co., Ltd., Osaka, Japan). Based on replicate analyses of samples, the precision of these concentration measurements was 1.6%. The detection limit was 0.03 µmol/L. Nitrite concentrations were < 1.0 % of the sum of nitrite and nitrate concentrations in all samples of wet deposition, and they were ≤ 5.0 % in 72 % and 87 % of samples of dry deposition at Rishiri and Sapporo, respectively. The pH values of the wet deposition samples ranged between 4.51 and 5.02 at Rishiri and between 4.65 and 5.29 at Sapporo.

Isotopic analysis was performed in 2013 for samples from Rishiri and in 2011 for samples from Sapporo. Prior to isotopic analysis we reanalyzed nitrate and nitrate concentrations in the samples and found that differences between these and the original concentration measurements were <10%. For isotopic analysis, nitrite and nitrate in each filtrate sample was converted to $N_2O$ using chemical conversion (McIlvin and Altabet, 2005) with slight modification (Tsunogai et al., 2016; Tsunogai et al., 2008). Isotopic analysis of nitrite alone was also performed on samples with nitrite concentrations > 5.0 % of the total nitrite plus nitrate concentrations (McIlvin and Altabet, 2005). The $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$ values of $N_2O$ in each vial were determined using a continuous-flow isotope ratio mass spectrometry system (Komatsu et al., 2008; Hirota et al., 2010). The obtained $\delta^{18}O$ values were normalized to VSMOW using local laboratory nitrate standards calibrated against USGS 34 ($\delta^{18}O$ = -27.9 ‰, $\Delta^{17}O$ = 0.04 ‰, and $\delta^{15}N$ = -1.8 ‰) and USGS 35 ($\delta^{18}O$ = +57.5 ‰, $\Delta^{17}O$ = +20.88 ‰, and $\delta^{15}N$ = +2.7 ‰) (Kaiser et al., 2007). $\Delta^{17}O$ values were measured directly from the $\delta^{33}$ and $\delta^{33}$ of $O_2$ data. The obtained $\delta^{15}N$ values were normalized to Air using local laboratory nitrate standards calibrated against USGS 32 ($\delta^{18}O$ = +25.7 ‰ and $\delta^{15}N$ = +180 ‰) and USGS 34. The $\delta^{18}O$ and $\delta^{15}N$ values of the three local standards range between 1.1 and 22.4 ‰ and between -2.1 and 11.8 ‰, respectively. The $\Delta^{17}O$ values of the local standards are ~0 ‰. Analytical precision (1σ) was ± 0.3 ‰ for $\delta^{15}N$, ± 0.5 ‰ for $\delta^{18}O$, and ± 0.2 ‰ for $\Delta^{17}O$ based on repeated measurements of the local nitrate standards (Tsunogai et al., 2010). Besides using the local nitrate standards for routine calibration and as checks of

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fractionation and oxygen isotope exchanges, we also analyzed USGS34 and USGS 35 at least monthly to assess instrument linearity.

For samples with nitrite concentrations $\geq$ 5 % of the total nitrite plus nitrate concentrations the $\delta^{15}N$ values of nitrate were calculated by mass balance: $\delta^{15}N_{NO3^-} = (\delta^{15}N_{NO2^- + NO3^-} * [NO_2^- + NO_3^-] - \delta^{15}N_{NO2^-} * [NO_2^-])/[NO_3^-]$. The measured $\Delta^{17}O$ values of nitrite for samples on which this analysis was performed was 0 ‰. Therefore, we presumed that the $\Delta^{17}O$ value of nitrite is 0 ‰ because of rapid oxygen change between $NO_2$ and water at near-neutral pH condition (Casciotti et al., 2007), and we corrected the $\Delta^{17}O$ values of nitrate as $\Delta^{17}O_{NO3^-} = \Delta^{17}O_{NO2^- + NO3^-} * [NO_2^- + NO_3^-]/[NO_3^-]$. 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 extent of $\delta^{15}N$ 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 extent of $\Delta^{17}O$ corrections were 5.7, 3.1, and 0.4‰, respectively. From these results we conclude that the potential bias in the isotopic values of dry deposition associated with nitrite was much smaller than the errors assumed in the final total isotopic values of dry deposition (around ±2.5 ‰ for $\delta^{15}N$ and ±3‰ for $\Delta^{17}O$).

To quantify the $\Delta^{17}O$ and $\delta^{15}N$ values of nitrate in dry deposition, we calculated monthly weighted-average (weighted based on mass) $\Delta^{17}O$ and $\delta^{15}N$ values of nitrate ($\Delta^{17}O_{dry}$ and $\delta^{15}N_{dry}$, respectively) among coarse and fine particles and gas phases using each isotopic value and concentration. For Sapporo, isotopic values for samples of dry deposition collected during the same month were averaged as monthly weighted-average values. To compare isotopic values of wet and dry deposition within and between sites, we calculated monthly weighted-average $\Delta^{17}O$ and $\delta^{15}N$ values of nitrate for wet deposition ($\Delta^{17}O_{wet}$ and $\delta^{15}N_{wet}$). Paired t-tests were used to compare monthly weighted-average $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$, $\delta^{18}O_{wet}$ and $\delta^{18}O_{dry}$, and $\delta^{15}N_{wet}$ and $\delta^{15}N_{dry}$, within sites. Paired t-tests were also used to compare monthly weighted-average $\Delta^{17}O_{coarse}$ and $\Delta^{17}O_{fine}$, $\delta^{18}O_{coarse}$ and $\delta^{18}O_{fine}$, and $\delta^{15}N_{coarse}$ and $\delta^{15}N_{fine}$ at each site. A one-way ANOVA was used to compare monthly weighted-average $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ at Rishiri with $\Delta^{17}O_{wet}$ at Sapporo, as well as $\delta^{15}N_{wet}$ and $\delta^{15}N_{dry}$ at Rishiri with $\delta^{15}N_{wet}$ at Sapporo.

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Statistical analyses were performed in PAST version 3.01 (Hammer et al., 2001). Volatilization of particulate to gaseous nitrate that occurs using the filter-pack method (e.g. Noguchi et al., 2009) may bias assessment of the isotopic values of gaseous and particulate nitrate. Therefore, we do not compare the concentrations and isotopic values of particulate and gaseous nitrate at our sites.

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Wet deposition flux was calculated using precipitation amount and nitrate concentration data obtained for each site from the National Institute for Environmental Studies, Japan (http://www.nies.go.jp/index-e.html). The monthly flux is the sum of precipitation amount multiplied by nitrate concentration for all samples in each month. Dry deposition flux was estimated following the inferential method (Hicks, 1986), where

$F_{dry} = V_d \times C$

and $F_{dry}$ represents the dry deposition flux, $V_d$ the deposition velocity, and $C$ the nitrate concentration in air (calculated from measured nitrate concentrations in the sample extracts and pumped air volume). Calculation of $V_d$ by the inferential method requires meteorological and land use data. Meteorological data were obtained from the Japan Meteorological Agency (http://www.jma.go.jp/jma/indexe.html). Landuse was presumed to be forest at Rishiri and city at Sapporo. The height of the forest canopy at Rishiri was presumed to be 10 m, and seasonal canopy resistance was determined from NDVI values (Noguchi et al., 2006). Deposition velocity was calculated using the inferential method version 4.2 (Noguchi et al., 2011; Wesely, 1989; Walcek et al., 1986; Erisman et al., 1997; Zhang et al., 2003) (the program file is available at http://www.hro.or.jp/list/environmental/research/ies/katsudo/acid_rain/kanseichinchaku/dry_deposition.html). Deposition velocities of gaseous and particulate materials are estimated separately, although these results should be interpreted with caution because of the potential for bias from volatilization of particulate nitrate. Fluxes of coarse and fine particles were not differentiated.

## 3 Results

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At the rural site, Rishiri, there was no difference between monthly weighted-average $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$, which ranged between +22.3 and +30.1 ‰ and between +22.7 and +30.3 ‰, respectively (Figure 3; $p = 0.57$, $n = 12$). Monthly weighted-average $\delta^{18}O_{dry}$ was overall slightly less than $\delta^{18}O_{wet}$, with ranges between +66.9 and +94.4 ‰ and +71.2 and +90.9 ‰, respectively (Figure 3; $p = 0.005$, $n = 12$). Both forms of deposition exhibited generally larger $\Delta^{17}O$ and $\delta^{18}O$ values in the winter than summer (Figures 3 and 4). $\Delta^{17}O_{coarse}$ was more positive (by 4.2 ‰, on average) than $\Delta^{17}O_{fine}$ ($p = 0.002$, $n = 10$) and $\delta^{18}O_{coarse}$ was more positive (by 4.6 ‰, on average) than $\delta^{18}O_{fine}$ ($p = 0.01$, $n = 12$; Figure S1). Monthly weighted-average $\delta^{15}N_{dry}$ at Rishiri varied between -4.8 and +7.5 ‰ and was on average 3.5 ‰ larger than $\delta^{15}N_{wet}$, which varied between -8.6 and +2.0 ‰ (Figure 3; $p = 0.02$, $n = 12$). $\delta^{15}N_{coarse}$ was slightly lower than $\delta^{15}N_{fine}$ at Rishiri ($p = 0.06$, $n = 10$).

At the urban site, Sapporo, monthly weighted-average $\Delta^{17}O_{wet}$ ranged between +23.0 and +30.8 ‰ and was higher than $\Delta^{17}O_{dry}$, which ranged between +18.8 and +25.0 ‰ ($p < 0.001$, $n = 12$; Figure 3). Monthly weighted-average $\delta^{18}O_{wet}$ was higher than $\delta^{18}O_{dry}$, with ranges between +70.7 and +92.2 ‰ and +56.8 and +70.8 ‰, respectively (Figure 3; $p < 0.0001$, $n = 12$). $\Delta^{17}O_{dry}$ and $\delta^{18}O_{dry}$ at Sapporo displayed less pronounced seasonal variation than $\Delta^{17}O_{wet}$ and $\delta^{18}O_{wet}$ (Figures 3 and 4). $\Delta^{17}O_{coarse}$ was more positive (by 3.9 ‰, on average) than $\Delta^{17}O_{fine}$ ($p < 0.001$, $n = 12$) and $\delta^{18}O_{coarse}$ was more positive (by 7.3 ‰, on average) than $\delta^{18}O_{fine}$ (and $p = 0.004$, $n = 12$, respectively) at Sapporo (Figure S1). Monthly weighted-average $\delta^{15}N_{dry}$ at Sapporo varied between +0.5 and +11.2 ‰ and was on average 6.5 % larger than $\delta^{15}N_{wet}$, which varied between -4.7 and +3.4 ‰ (Figure 3; $p < 0.001$, $n = 12$). $\delta^{15}N_{coarse}$ was on average 3.4 % less than $\delta^{15}N_{fine}$ at Sapporo ($p = 0.04$, $n = 12$).

$\Delta^{17}O_{wet}$ at Sapporo exhibited similar values and seasonal patterns as $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri ($p = 0.97$, $n = 12$). The difference between $\delta^{15}N_{dry}$ and $\delta^{15}N_{wet}$ was greater at Sapporo than Rishiri, and thus $\delta^{15}N_{dry}$ was greater at Sapporo than Rishiri despite $\delta^{15}N_{wet}$ at Sapporo having similar values and seasonal patterns as $\delta^{15}N_{wet}$ ($p = 0.36$, $n = 12$) and $\delta^{15}N_{dry}$ ($p = 0.46$, $n = 12$) at Rishiri (Figure 4). There were positive correlations between the $\delta^{15}N$ and $\Delta^{17}O$ values of wet and dry deposition at both sites, with the exception of dry deposition at Sapporo (Figure 5). Fluxes of nitrate in dry particulate deposition and gaseous dry deposition were generally greater at Sapporo than Rishiri (Figure S1) because the dry deposition velocity dominates the flux value of dry deposition and it is greater for

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Rishiri (assumed to be forest) than Sapporo (assumed to be urban).

## 4 Discussion

The similar values and seasonal trends of $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri imply that both forms of deposition experienced similar seasonal variation in photochemical reactions during their production from $NO_x$. The values and trends are consistent with prior empirical studies of $\Delta^{17}O_{wet}$ at Rishiri between 2006 and 2007 (Tsunogai et al., 2010) and elsewhere in Japan (Tsunogai et al., 2016). These results also coincide well with model predictions (Alexander et al., 2009), which suggest that they indicate seasonal variation in the relative importance of oxidation of $NO_2$ by $O_3$ vs. OH in background, free tropospheric air. During summer when solar radiation is high, the relative importance of oxidation of $NO_2$ by OH is likely greatest, thus decreasing nitrate $\Delta^{17}O$ values. In contrast, solar radiation is low in winter, which likely causes pathways involving oxidation of $NO_2$ by $O_3$ to be relatively more important, thus increasing nitrate $\Delta^{17}O$ values. Values of $\Delta^{17}O_{wet}$ at Sapporo were indistinct from those of $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri, and the most straightforward interpretation of these results is that wet deposition at Sapporo underwent similar photochemical formation processes as both forms of deposition at Rishiri.

In contrast to $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri and $\Delta^{17}O_{wet}$ at Sapporo, values of $\Delta^{17}O_{dry}$ at Sapporo were lower and displayed less seasonal variation. These results suggest unique oxidation processes that display little seasonal variation and are associated with dry deposition at this site. One potential explanation for the relatively low $\Delta^{17}O_{dry}$ values at Sapporo relates to OH. Concentrations of OH are typically higher in urban than rural areas as the result of the formation of OH from Criegee intermediates during alkene oxidation and/or photolysis of nitrous acid or formaldehyde in more polluted urban settings (Monks, 2005). OH competes with $O_3$ to oxidize $NO_2$, and thus greater oxidation of $NO_2$ by OH in dry deposition would drive down $\Delta^{17}O_{dry}$ values (Morin et al., 2011). Another potential explanation for the relatively low $\Delta^{17}O_{dry}$ at Sapporo relates to peroxy radicals potentially being of greater importance in the oxidation of NO to $NO_2$ in dry deposition at this site. Peroxy radicals typically form via photochemical oxidation of non-methane hydrocarbons that originate from anthropogenic sources, such as vehicle

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exhaust, and their concentrations are usually higher in urban than rural environments (Saito et al., 2002; Carslaw et al., 2002). These radicals rapidly compete with $O_3$ to oxidize NO to $NO_2$ (Monks, 2005), which results in lower $\Delta^{17}O_{dry}$ values (Morin et al., 2011). A recent study also suggested that formation of $NO_2$ by reaction of peroxy radicals with NO in polluted air caused short-term shifts toward lower $\Delta^{17}O_{dry}$ in Taiwan (Guha et al., 2017). Atmospheric inversions are common in Sapporo (Uno et al., 1988) and other Japanese cities (Saito et al., 2002; Uno et al., 1996), particularly during winter, and such conditions may trap pollutants and alter the $NO_x$ to nitrate photo-oxidation pathway thereby helping facilitate reaction of OH with $NO_2$ and/or NO with peroxy radicals.

Regardless of the precise mechanism driving down $\Delta^{17}O_{dry}$ at Sapporo, such low values suggest two distinct sources of nitrate in wet and dry deposition in our study region. The first is likely transported relatively long distances to both Rishiri and Sapporo in wet deposition and to Rishiri in dry deposition. Below-cloud scavenging of local/regional particulate nitrate and gaseous $HNO_3$ undoubtedly occurs at the beginning of precipitation events, but the similar absolute values and temporal variations of $\Delta^{17}O_{wet}$ at both sites suggest that the majority of nitrate in wet deposition at Sapporo (as well as Rishiri) originates from afar and is transported to Japan in cloud water. The second source is likely local anthropogenic $NO_x$ emissions that are deposited in dry deposition near their point of production at the urban site, Sapporo, as concentrations of OH and peroxy radicals are typically elevated in more polluted urban environments (Monks, 2005). Similarly, the more positive values of $\Delta^{17}O_{coarse}$ than $\Delta^{17}O_{fine}$ at both sites suggest that nitrate in coarse particles is subject to greater supply through long-range transport (produced in free troposphere) than is nitrate in fine particles, which are more influenced by local sources (produced within the boundary layer of the urban area).

To aid our interpretations based on $\Delta^{17}O$ we evaluated $\delta^{15}N$ values of nitrate, which we interpret as primarily indicating variation in $NO_x$ oxidation efficiency (e.g. Walters and Michalski, 2015, 2016; Walters et al., 2016). We recognize that nitrate $\delta^{15}N$ values are influenced by factors that are difficult to constrain in our study, including the $\delta^{15}N$ values of $NO_x$ from the East Asian continent, the removal rate of $NO_x$ (or production rate of nitrate) during transport, isotopic fractionation between $NO_x$ and nitrate during in-cloud and below-cloud

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scavenging processes during transport, the $\delta^{15}N$ values of locally produced $NO_x$, and the relative amount of proportion of $NO_x$ derived locally vs. that from the East Asian continent. Nevertheless, the last factor likely differs the most between our sites since there is more locally produced $NO_x$ in the urban environment at Sapporo. During long-distance transport of $NO_x$ there is greater $^{15}N$-enrichment in $NO_2$ than NO (Freyer, 1991), which causes the residual $NO_x$ to become depleted in $^{15}N$ during partial removal of $NO_x$ as nitrate in the troposphere. Therefore, nitrate derived from long-distance transport from the East Asian continent is likely to have lower $\delta^{15}N$ values than nitrate from more local sources. The relatively high $\delta^{15}N_{dry}$ values at Sapporo are consistent with this interpretation and with the $\Delta^{17}O$-based inference that nitrate in dry deposition at Sapporo originates from more local sources than does that in wet deposition at Sapporo and both forms of deposition at Rishiri.

The correlations between $\Delta^{17}O$ and $\delta^{15}N$ for both forms of deposition at both sites, with the exception of dry deposition at Sapporo, suggest a relationship between oxidation pathways ($\Delta^{17}O$) and $NO_x$ oxidation efficiency ($\delta^{15}N$). Both $NO_x$ oxidation pathways and efficiencies are primarily controlled by the rate of the $NO_2$ + OH reaction, which suggests that this reaction drives these correlations. The lack of correlation between $\delta^{15}N_{dry}$ and $\Delta^{17}O_{dry}$ at Sapporo thus also likely reflects the unique oxidation pathways (and thus $\Delta^{17}O$ values) associated with locally produced $NO_x$ in the urban environment.

At both sites wet and dry deposition exhibited generally larger $\delta^{15}N$ values in the winter than summer months. This result probably occurs because of seasonal changes in temperature on isotopic fractionation of nitrogen isotopes and/or in the proportion of $NO_2$ in $NO_x$ (Walters et al., 2016). Overall, our $\delta^{15}N$ data suggest that nitrate undergoing long-distance transport and/or production during the summer is likely to have experienced higher $NO_x$ oxidation efficiency than that produced locally and/or during the winter. $\delta^{15}N$ values of nitrate likely only reflect those of the source $NO_x$ for nitrate produced locally during the winter. Indeed, the relatively high $\delta^{15}N_{dry}$ values during the winter at Sapporo are consistent with those expected for sources such as nearby combustion of fossil fuels (Redling et al., 2013; Walters et al., 2015).

Overall, our results imply that local-scale efforts to reduce nitrate deposition resulting from local $NO_x$

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emissions will be most effective to the extent that dry deposition is the dominant form of atmospheric deposition. Local efforts may be less effective in places and times where atmospheric deposition arrives as wet deposition, since wet deposition seems more likely to originate from long distances. Thus, regional, national and global efforts will likely be required to reduce the effects of atmospheric nitrate in wet deposition that is transported long distances in air masses. Additional datasets with paired measurements of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ would be valuable to evaluate our interpretation of the oxidation pathways and sources and transport distances of nitrate deposited in urban environments.

$\Delta^{17}O$ values of nitrate are increasingly used in watershed studies to determine the relative abundance of unprocessed atmospheric nitrate in environmental waters, such as rivers and lakes (Sabo et al., 2016; Riha et al., 2015; Tsunogai et al., 2016; Tsunogai et al., 2010; Michalski et al., 2004). Such studies often use $\Delta^{17}O_{wet}$ or $\Delta^{17}O_{dry}$ as an end-member for calculating the amount of unprocessed atmospheric nitrate in a sample. Although they should be validated at other sites, our results suggest that it may be reasonable to assume that $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ are similar in rural settings, since the annual weighted-average $\Delta^{17}O$ values of wet and dry were nearly identical (+27.2 and +27.1 ‰, respectively) at Rishiri. However, in urban settings or settings downstream of urban environments the potential differences between $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ may need to be considered to avoid over- or under-estimating the amount of unprocessed atmospheric nitrate when using $\Delta^{17}O$ values of nitrate as a tracer of atmospheric nitrate. For example, consider a simple mixing model such as % atmospheric nitrate = 100 × [($\Delta^{17}O_{measured}$ - $\Delta^{17}O_{terrestrial}$)/( $\Delta^{17}O_{atmospheric}$ - $\Delta^{17}O_{terrestrial}$)]

where $\Delta^{17}O_{measured}$ is the $\Delta^{17}O$ value of nitrate in a stream sample, $\Delta^{17}O_{terrestrial}$ is the $\Delta^{17}O$ value of nitrate containing no atmospheric nitrate (i.e., 0 ‰), and $\Delta^{17}O_{atmospheric}$ is the $\Delta^{17}O$ value of atmospheric nitrate (either +27.6 or +21.8 ‰, representing the average weighted-average annual values of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ measured at Sapporo in the present study). The difference in % atmospheric nitrate when +27.6 vs. +21.8 ‰ are used as end-members for $\Delta^{17}O_{atmospheric}$ is small when $\Delta^{17}O_{measured}$ is small (e.g., ~1 % when $\Delta^{17}O_{measured}$ is ~1 ‰), but increases when $\Delta^{17}O_{measured}$ is large (e.g., ~19 % when $\Delta^{17}O_{measured}$ is 20 ‰). Thus, our results suggest a weighted average of $\Delta^{17}O_{wet}$

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**Deleted:** are required to more definitively assess the influence of urban pollution on oxidation chemistry. Samples of wet and dry nitrate deposition are collected by ongoing air-quality monitoring efforts throughout the world, and stable isotope measurements from such samples could

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and $\Delta^{17}O_{dry}$ should be used when $\Delta^{17}O$ values of nitrate are used to quantify the amount of unprocessed atmospheric nitrate exported from urban watersheds. At Sapporo, the weighted average of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ is +25.7 ‰, which is more similar to $\Delta^{17}O_{wet}$ than $\Delta^{17}O_{dry}$ at this site since wet deposition comprised the majority of the total deposition at this site. However, $\Delta^{17}O_{wet}$ may not as closely approximate the weighted average of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ at some sites, such as semi-closed and/or highly polluted urban areas, where the majority of deposition comes from local sources.

## 5 Conclusions

Our isotopic data suggest differences in the oxidation chemistry and transport distances of wet and dry deposition in urban settings: wet deposition tends to originate from afar, whereas dry deposition is produced largely from local sources as the result of unique $NO_x$ oxidation pathways that occur in polluted urban settings. These results imply that reductions in local $NO_x$ emissions will be most effective when and where dry deposition is the dominant form of atmospheric deposition, which has implications for efforts to reduce nitrate deposition and its negative environmental impacts in cities and downwind areas. The approach used herein of comparing isotopic values of wet and dry deposition in different environmental settings is likely to provide continued insight into the transport distances and reaction pathways of atmospheric nitrate pollution.

*Data availability.* All data are available upon request from the corresponding author. *Author contributions***.** UT, TO, and FN designed the study. UT, TO, DD, FN, IN, TY carried out the research. DMN and DD performed data analysis. DMN and TO wrote the manuscript with contributions from all authors. All authors have given approval to the final version of the manuscript.

*Competing interests.* The authors declare that they have no conflict of interest.

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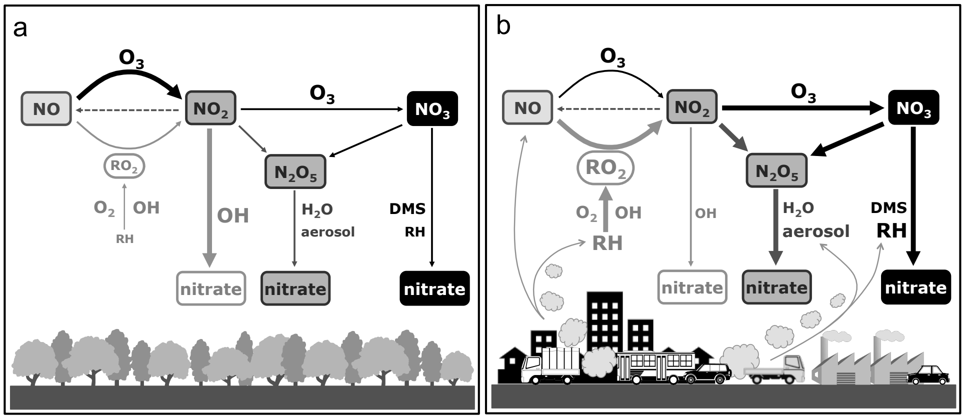


**Figure 1**. Conceptual diagrams of pathways for conversion of $NO_x$ (NO + $NO_2$) to nitrate ($NO_3^-$) in a) background atmosphere and b) urban atmosphere. The first step in the process is the conversion of NO to $NO_2$, which is accomplished primarily by $O_3$ or peroxy radicals ($HO_2$ + $RO_2$). The second step is the oxidation of $NO_2$. In daylight OH oxidizes $NO_2$ to nitrate and at night $O_3$ oxidizes $NO_2$ to nitrate. Reactions with dimethylsulfide (DMS) or reactive hydrocarbons (RH) or $NO_2$ (to form $N_2O_5$, followed by hydrolysis on aerosol surfaces) provide a pathway for nitrate deposition. Thicker arrows and larger fonts suggest greater relative importance of different pathways between panels on an annual basis. These diagrams are oversimplifications and the arrow and font sizes are qualitative. Furthermore, these diagrams ignore potential seasonal variation, such as the $N_2O_5$ pathway being relatively more important in rural environments during the winter than summer and the OH pathway being relatively more important in urban environments during the summer than winter.

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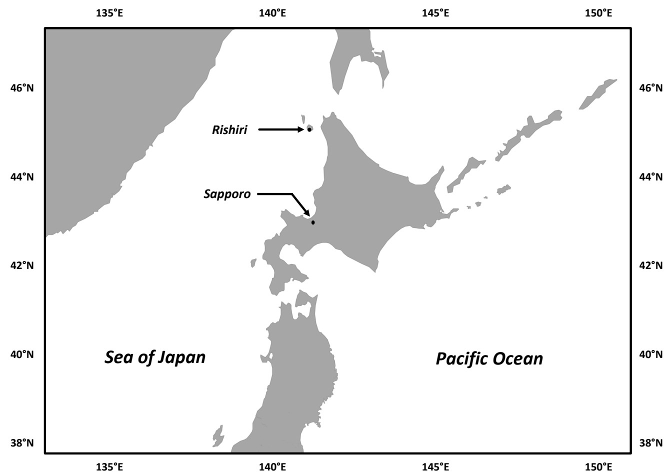


**Figure 2.** Location of study sites, Rishiri and Sapporo, in northern Japan. The base layer of the map was obtained from **https://www.amcharts.com/svg-maps/**.

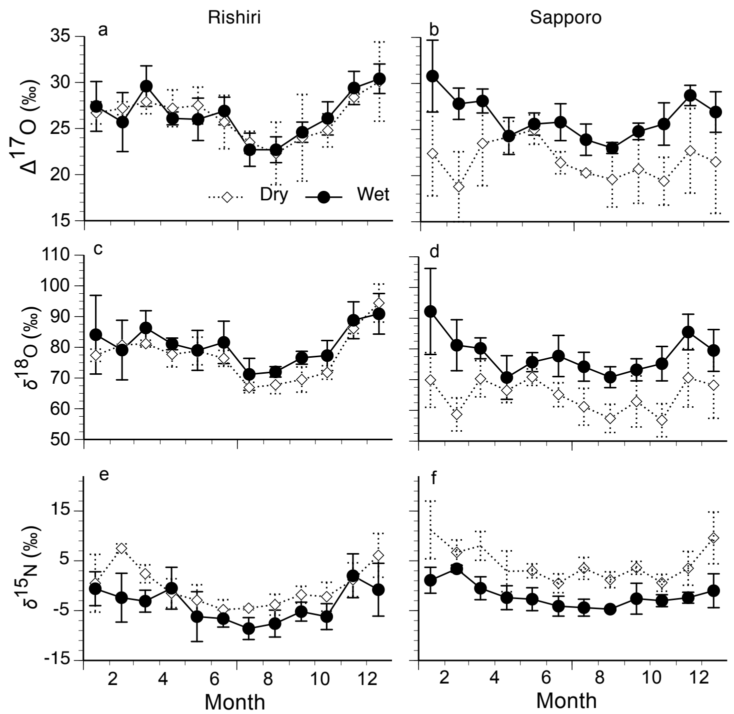


**Figure 3.** Time series of monthly weighted-average a, b) $\Delta^{17}O$ values of nitrate in dry and wet deposition c, d) $\delta^{18}O$ values of nitrate in dry and wet deposition, and e, f) $\delta^{15}N$ values of nitrate in wet deposition. Data from Rishiri (rural) are in left column and data from Sapporo (urban) are in right column. Error bars on isotopic values of nitrate in dry deposition represent one standard deviation of isotopic values of nitrate in coarse and fine particles and in gaseous form, whereas errors bars on isotopic values of nitrate in wet deposition represent one standard deviation of all isotopic values of nitrate in wet deposition made during the sampling period.

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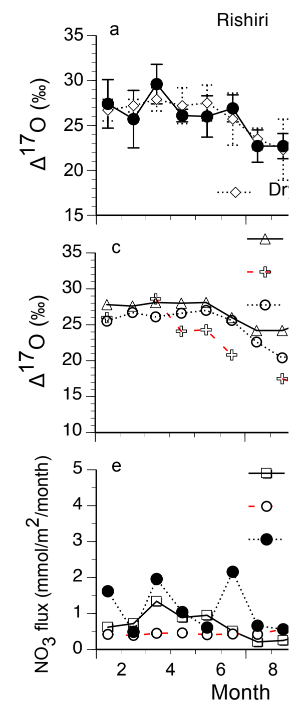


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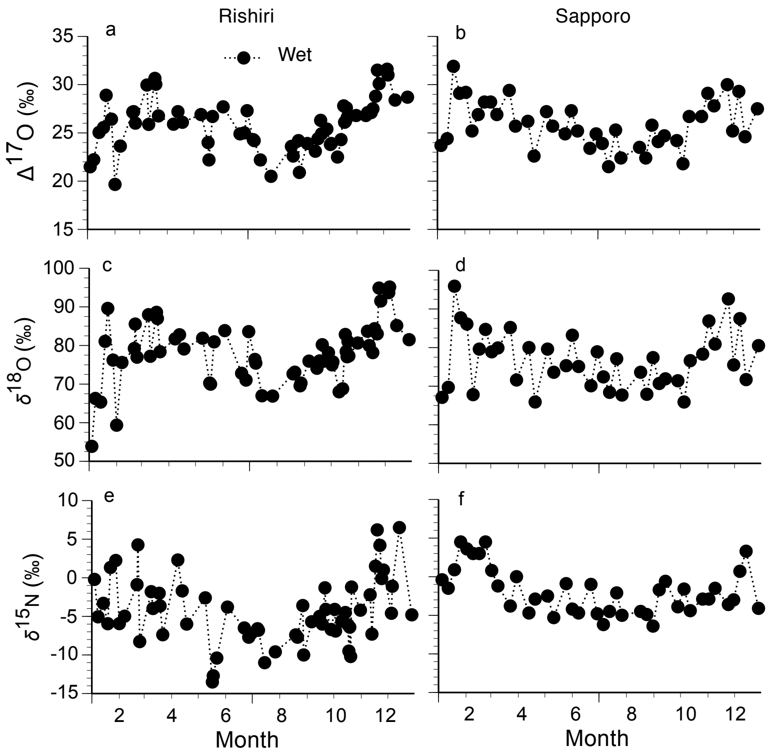


**Figure 4.** Time series of a, b) $\Delta^{17}O$ values of nitrate in wet deposition, c, d) $\delta^{18}O$ values of nitrate in wet deposition, and e, f) $\delta^{15}N$ values of nitrate in wet deposition. Data from Rishiri (rural) are in left column and data from Sapporo (urban) are in right column.

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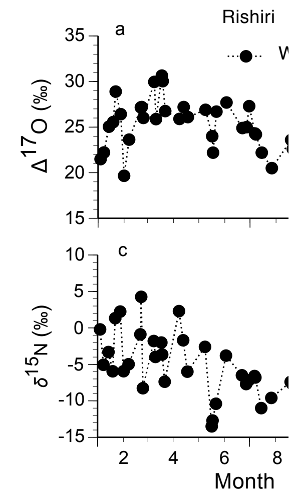


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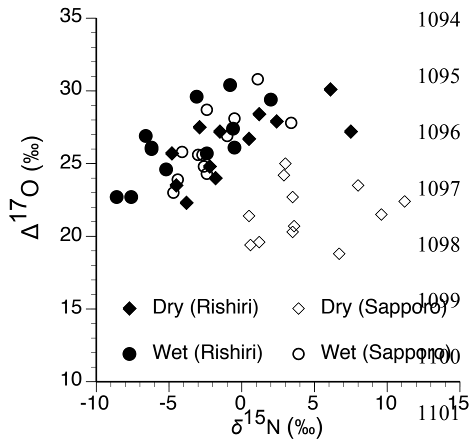


**Figure 5.** Correlation of $\delta^{15}N$ and $\Delta^{17}O$ values of nitrate in wet and dry deposition at Rishiri and Sapporo. Dry deposition at Rishiri: slope = 0.57 (95% confidence interval = 0.15 – 0.79), r = 0.70, p = 0.01, n = 12; Wet deposition at Rishiri: slope = 0.74 (95% confidence interval = 0.43 – 0.97), r = 0.73, p = 0.007, n = 12; Dry deposition at Sapporo: r = 0.17, p = 0.59, n = 12; Wet deposition at Sapporo: slope = 0.95 (95% confidence interval = 0.33 – 1.35), r = 0.73, p = 0.007, n = 12.