Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1071
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 2 January 2018

Atmospheric Chemistry and Physics
Discussions
Open Access

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 deposition in urban environments and wet and dry deposition in rural 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.

1 Introduction

The percentage of the world's population living in cities has rapidly grown in recent decades, and this trend is expected to continue for at least a generation (United 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 when nitrate production rates are high, 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 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). 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 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 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 $\Delta^{17}O$

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

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

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 Δ^{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 Δ^{17}O and δ^{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 in East Asia, 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.

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 ~400 km south of Rishiri.

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Manuscript under review for journal Atmos. Chem. Phys.
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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). Seasonal precipitation patterns in Sapporo are similar to those in Rishiri. Sapporo is bordered by the Sea of Japan to the north and by mountains to the west and south. 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

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 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 of the 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 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. Although HNO_3 volatilization from the filter may occur during the monthly (Rishiri) and bi-weekly (Sapporo) sampling periods, volatilization results in mass-dependent isotopic fractionation and therefore should not affect the $\Delta^{17}O$ values of nitrate remaining on the filter. 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.

2.3 Analysis

Nitrite and nitrate 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). 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.

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 and USGS 35 (Tsunogai et al., 2014; Nakagawa et al., 2013). The obtained $\delta^{15}N$ values were normalized to Air using local laboratory nitrate standards calibrated against USGS 32 and USGS 34. The $\delta^{18}O$ values of the three local standards range between 1.1 and 22.4 ‰, and the $\delta^{15}N$ values of the three local standards range between -2.1 and 11.8 ‰. Analytical precision (1σ) was $\pm$ 0.3 ‰ for $\delta^{15}N$, $\pm$ 0.5 ‰ for $\delta^{18}O$, and $\pm$ 0.2 ‰ for

Δ^{17}O based on repeated measurements of the local nitrate standards (Tsunogai et al., 2010). For samples with nitrite concentrations $\geq$ 5 % of the total nitrite plus nitrate concentrations the δ^{15}N values of nitrate were calculated by mass balance: $\delta^{15}N_{NO_3^-} = (\delta^{15}N_{NO_2^- + NO_3^-} * [NO_2^- + NO_3^-] - \delta^{15}N_{NO_2^-} * [NO_2^-])/[NO_3^-]$. The measured Δ^{17}O values of nitrite for samples on which this analysis was performed was 0 ‰. Therefore, we presumed that the Δ^{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 Δ^{17}O values of nitrate as $\Delta^{17}O_{NO_3^-} = \Delta^{17}O_{NO_2^- + NO_3^-} * [NO_2^- + NO_3^-]/[NO_3^-]$.

To quantify the Δ^{17}O and δ^{15}N values of nitrate in dry deposition, we calculated monthly weighted-average (weighted based on mass) Δ^{17}O and δ^{15}N values of nitrate ($\Delta^{17}O_{dry}$ and $\delta^{15}N_{dry}$, respectively) among coarse ($\Delta^{17}O_{coarse}$ and $\delta^{15}N_{coarse}$, respectively) and fine ($\Delta^{17}O_{fine}$ and $\delta^{15}N_{fine}$, respectively) particles and gas ($\Delta^{17}O_{gas}$ and $\delta^{15}N_{gas}$, respectively) 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 Δ^{17}O and δ^{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 $\Delta^{17}O_{dry}$, as well as $\delta^{15}N_{wet}$ and $\delta^{15}N_{dry}$, within sites. A one-way ANOVA, followed by a Tukey's pairwise comparison when appropriate, was used to compare monthly weighted-average $\Delta^{17}O_{coarse}$, $\Delta^{17}O_{fine}$, and $\Delta^{17}O_{gas}$, as well as $\delta^{15}N_{coarse}$, $\delta^{15}N_{fine}$, and $\delta^{15}N_{gas}$ at each site. A one-way ANOVA was also 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. Statistical analyses were performed in PAST version 3.01 (Hammer et al., 2001).

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. Fluxes of coarse and fine particles were not differentiated.

3 Results and discussion

3.1 Oxidation pathways of NO_x inferred from triple oxygen isotopes

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; $p = 0.57$, $n = 12$). Both forms of deposition exhibited generally larger $\Delta^{17}O$ values in the winter than summer (Figures 3 and 4). $\Delta^{17}O_{coarse}$ was on average 4.0 ‰ more positive than $\Delta^{17}O_{fine}$ ($p = 0.01$, $n = 10$), an offset similar to that observed in prior studies (Morin et al., 2009; Patris et al., 2007), although the difference was overall greater during the summer months.

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. The values and trends are consistent with prior studies in East Asia (Tsunogai et al., 2010; Tsunogai et al., 2016) and elsewhere (Michalski et al., 2011; Michalski et al., 2003), which suggest that they indicate seasonal variation in the relative importance of oxidation of NO_2 by O_3 vs. OH. 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.

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). $\Delta^{17}O_{dry}$ at Sapporo displayed less pronounced seasonal variation than $\Delta^{17}O_{wet}$ (Figures 3 and 4). $\Delta^{17}O_{wet}$ 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 most straightforward interpretation of these results is that wet deposition at Sapporo underwent similar photochemical formation processes as both forms of deposition at Rishiri. Like Rishiri, $\Delta^{17}O_{coarse}$ was more positive (by 3.9 ‰, on average) than $\Delta^{17}O_{fine}$ ($p = 0.005$, $n = 12$), as well as 5.4 ‰ more positive on average than $\Delta^{17}O_{gas}$ ($p < 0.001$, $n = 12$). The fluxes of nitrate in dry particulate deposition and gaseous dry deposition were generally greater at Sapporo than Rishiri (Figure 3) because the dry deposition velocity dominates the flux value of dry deposition and it is greater for Rishiri (assumed to be forest) than Sapporo (assumed to be urban).

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 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. 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 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. 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 help facilitate reaction of OH with NO_2 and/or NO with peroxy radicals.

3.2 Nitrogen isotopes of nitrate

To aid our interpretations we evaluated $\delta^{15}N$ values of nitrate, recognizing that such values may not conservatively trace the $\delta^{15}N$ values of the source NO_x (e.g. Walters and Michalski, 2015, 2016; Walters et al., 2016). Furthermore, we realize that $\delta^{15}N$ values of nitrate are influenced by several factors that are difficult to constrain, including the $\delta^{15}N$ values of NO_x from East Asia, the removal rate of NO_x (or production rate of nitrate) during transport from East Asia, isotopic fractionation between NO_x and nitrate during in-cloud and below-cloud scavenging processes during transport from East Asia, the $\delta^{15}N$ values of locally produced NO_x, and the relative amount of proportion of NO_x derived locally vs. that from East Asia. The former three factors are likely similar between our sites, whereas the latter two factors likely vary between sites with more locally produced NO_x at Sapporo than Rishiri.

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 5; $p = 0.02$, $n = 12$). At Sapporo monthly weighted-average $\delta^{15}N_{dry}$ 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 5; $p < 0.001$, $n = 12$). Generally larger values of $\delta^{15}N_{dry}$ than $\delta^{15}N_{wet}$ has been observed in prior studies and suggest differential partitioning of isotopes between dry and wet deposition (Elliott et al., 2009; Freyer, 1991; Garten, 1996). Furthermore, the fact that both forms of deposition exhibited generally larger $\delta^{15}N$ values in the winter than summer months at both sites (Figures 4 and 5) may reflect the effect 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).

In contrast to these similarities between sites, 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 5). Furthermore, 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 6). Presuming that the $\delta^{15}N$ values from NO_x emissions sources in Sapporo are not much less than those from East Asia (which seems reasonable given that local emissions from East Asia and Sapporo are dominated by anthropogenic sources), we interpret the relatively high $\delta^{15}N_{dry}$ values and lack of correlation between $\delta^{15}N_{dry}$ and $\Delta^{17}O_{dry}$ at Sapporo to result from relatively high locally-produced NO_x concentrations and low conversion rates of NO_x to nitrate in Sapporo.

3.3 Inference of transport distances of wet and dry deposition in urban settings

Regardless of the precise mechanism driving down $\Delta^{17}O_{dry}$ at Sapporo, such values, greater $\delta^{15}N_{dry}$ at Sapporo than Rishiri, and the lack of correlation of $\Delta^{17}O_{dry}$ and $\delta^{15}N_{dry}$ at Sapporo 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).

Our results illustrate that isotopic data are useful for investigating the sources and relative transport distances of atmospheric nitrate pollution in wet and dry deposition. Furthermore, these results imply that local-scale efforts to reduce nitrate deposition resulting from local NO_x 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.

3.4 Implications for oxidation chemistry and watershed studies

Our results have implications for understanding oxidation chemistry in different forms of deposition in urban and polluted settings. For example, they suggest that urban pollution alters the NO_x to nitrate photo-oxidation pathway in dry deposition by enhancing the importance of either OH in NO_2 oxidation and/or the peroxy radical in NO oxidation relative to background atmospheric reactions of NO_x. 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, particularly during summer and autumn (Guha et al., 2017). In contrast to our $\Delta^{17}O_{dry}$ data, our $\Delta^{17}O_{wet}$ data do not suggest an overall shift to increased importance of OH in NO_2 oxidation or peroxy radicals in NO oxidation in wet deposition in urban (or rural) environments. A previous study at Rishiri found a short-term increase in $\Delta^{17}O_{wet}$ (up to values of ~ +34.5 ‰) during February 2007, likely because of increased relative importance of reaction of NO_2 with reactive hydrocarbons and aerosols in polluted air that promoted the formation of nitrate deposition directly or through N_2O_5 (Tsunogai et al., 2010). We observed short-term peaks in $\Delta^{17}O_{wet}$ values at our sites (to a maximum of 31.9 ‰ at Sapporo and 31.6 ‰ at Rishiri), which could also suggest increased importance of such pathways in production of nitrate in wet deposition (Figure 4). Thus, our results in combination with prior studies, suggest that urban pollution may be more prone to alter oxidation reactions of NO associated with dry deposition and oxidation reactions of NO_2 associated with wet deposition. However, additional datasets with paired measurements of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ 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 be used 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 also 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. 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 = $100 \times [(\Delta^{17}O_{measured} - \Delta^{17}O_{terrestrial})/(\Delta^{17}O_{atmospheric} - \Delta^{17}O_{terrestrial})]$ 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 $\Delta^{17}O_{wet}$ 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.

4 Conclusions

Our results 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* ***c****ontributions***.** 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.

Acknowledgements. We thank the Ministry of the Environment, Japan, for providing the monitoring data of the acid deposition survey and Joel Bostic for providing feedback on an earlier version of the manuscript. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan under grants 26241006 and 17H00780 (to UT and FN), 15H02804 and 15K12187 (to FN), as well as a visiting research fellowship from Nagoya University and short-term invitation fellowship (grant S17093) from Japan Society for Promotion of Science (to DMN).

References

Aikawa, M., Ohara, T., Hiraki, T., Oishi, O., Tsuji, A., Yamagami, M., Murano, K., and Mukai, H.: Significant geographic gradients in particulate sulfate over Japan determined from multiple-site measurements and a chemical transport model: Impacts of transboundary pollution from the Asian continent, Atmos Environ, 44, 381-391, 10.1016/j.atmosenv.2009.10.025, 2010.

Akimoto, H.: Global air quality and pollution, Science, 302, 1716-1719, DOI 10.1126/science.1092666, 2003.

Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}O$) of atmospheric nitrate, Atmos Chem Phys, 9, 5043-5056, 2009.

Balestrini, R., Galli, L., and Tartari, G.: Wet and dry atmospheric deposition at prealpine and alpine sites in northern Italy, Atmos Environ, 34, 1455-1470, Doi 10.1016/S1352-2310(99)00404-5, 2000.

Ban, S., Matsuda, K., Sato, K., and Ohizumi, T.: Long-term assessment of nitrogen deposition at remote EANET sites in Japan, Atmos Environ, 146, 70-78, 10.1016/j.atmosenv.2016.04.015, 2016.

Bloom, D. E., Canning, D., and Fink, G.: Urbanization and the wealth of nations, Science, 319, 772-775, 10.1126/science.1153057, 2008.

Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dube, W. P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-70, 10.1126/science.1120120, 2006.

Carslaw, N., Creasey, D. J., Heard, D. E., Jacobs, P. J., Lee, J. D., Lewis, A. C., McQuaid, J. B., Pilling, M. J., Bauguitte, S., Penkett, S. A., Monks, P. S., and Salisbury, G.: Eastern Atlantic Spring Experiment 1997 (EASE97) - 2. Comparisons of model concentrations of OH, HO_2, and RO_2 with measurements, J Geophys Res-Atmos, 107,

Artn 4190

10.1029/2001jd001568, 2002.

Casciotti, K. L., Bohlke, J. K., McIlvin, M. R., Mroczkowski, S. J., and Hannon, J. E.: Oxygen isotopes in nitrite: Analysis, calibration, and equilibration, Anal Chem, 79, 2427-2436, 10.1021/ac061598h, 2007.

Celle-Jeanton, H., Travi, Y., Loye-Pilot, M. D., Huneau, F., and Bertrand, G.: Rainwater chemistry at a Mediterranean inland station (Avignon, France): Local contribution versus long-range supply, Atmos Res, 91, 118-126, 10.1016/j.atmosres.2008.06.003, 2009.

Crutzen, P. J.: Role of NO and NO_2 in the chemistry of the troposphere and stratosphere, Annu Rev Earth Pl Sc, 7, 443-472, DOI 10.1146/annurev.ea.07.050179.002303, 1979.

Cumming, G. S., Buerkert, A., Hoffmann, E. M., Schlecht, E., von Cramon-Taubadel, S., and Tscharntke, T.: Implications of agricultural transitions and urbanization for ecosystem services, Nature, 515, 50-57, 10.1038/nature13945, 2014.

Dasch, J. M., and Cadle, S. H.: Wet and dry deposition monitoring in southeastern Michigan, Atmos Environ, 19, 789-796, Doi 10.1016/0004-6981(85)90067-8, 1985.

Elliott, E. M., Kendall, C., Boyer, E. W., Burns, D. A., Lear, G. G., Golden, H. E., Harlin, K., Bytnerowicz, A., Butler, T. J., and Glatz, R.: Dual nitrate isotopes in dry deposition: Utility for partitioning NO_x source contributions to landscape nitrogen deposition, J Geophys Res-Biogeo, 114, -, 2009.

Endo, T., Yagoh, H., Sato, K., Matsuda, K., Hayashi, K., Noguchi, I., and Sawada, K.: Regional characteristics of dry deposition of sulfur and nitrogen compounds at EANET sites in Japan from 2003 to 2008, Atmos Environ, 45, 1259-1267, 10.1016/j.atmosenv.2010.12.003, 2011.

Erisman, J. W., Draaijers, G., Duyzer, J., Hofschreuder, P., VanLeeuwen, N., Romer, F., Ruijgrok, W., Wyers, P., and Gallagher, M.: Particle deposition to forests - Summary of results and application, Atmos Environ, 31, 321-332, Doi 10.1016/S1352-2310(96)00223-3, 1997.

Fang, Y. T., Koba, K., Wang, X. M., Wen, D. Z., Li, J., Takebayashi, Y., Liu, X. Y., and Yoh, M.: Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China, Atmos Chem Phys, 11, 1313-1325, 10.5194/acp-11-1313-2011, 2011.

Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel, Environ Sci Technol, 32, 2051-2060, DOI 10.1021/es970916e, 1998.

Freyer, H. D.: Seasonal variation of $^{15}N/^{14}N$ ratios in atmospheric nitrate species, Tellus B, 43, 30-44, DOI 10.1034/j.1600-0889.1991.00003.x, 1991.

Freyer, H. D., Kley, D., Volzthomas, A., and Kobel, K.: On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen, J Geophys Res-Atmos, 98, 14791-14796, Doi

10.1029/93jd00874, 1993.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vorosmarty, C. J.: Nitrogen cycles: past, present, and future, Biogeochemistry, 70, 153-226, 2004.

Garten, C. T.: Stable nitrogen isotope ratios in wet and dry nitrate deposition collected with an artificial tree, Tellus B, 48, 60-64, DOI 10.1034/j.1600-0889.1996.00006.x, 1996.

Geng, L., Murray, L. T., Mickley, L. J., Lin, P., Fu, Q., Schauer, A. J., and Alexander, B.: Isotopic evidence of multiple controls on atmospheric oxidants over climate transitions, Nature, 546, 133-+, 10.1038/nature22340, 2017.

Guerrieri, R., Vanguelova, E. I., Michalski, G., Heaton, T. H. E., and Mencuccini, M.: Isotopic evidence for the occurrence of biological nitrification and nitrogen deposition processing in forest canopies, Glob Change Biol, 21, 4613-4626, 10.1111/gcb.13018, 2015.

Guha, T., Lin, C. T., Bhattacharya, S. K., Mahajan, A. S., Ou-Yang, C.-F., Lan, Y.-P., Hsu, S. C., and Liang, M.-C.: Isotopic ratios of nitrate in aerosol samples from Mt. Lulin, a high-altitude station in Central Taiwan, Atmos Environ, 154, 53-69, 2017.

Gurjar, B. R., Ravindra, K., and Nagpure, A. S.: Air pollution trends over Indian megacities and their local-to-global implications, Atmos Environ, 142, 475-495, 10.1016/j.atmosenv.2016.06.030, 2016.

Hammer, Ø., Harper, D. A. T., and Ryan, P. D.: PAST: Paleontological statistics software package for education and data analysis, Palaeontologia Electronica, 4, 9, 2001.

Hicks, B. B.: Measuring dry deposition: A reassessment of the state-of-the-art, Water Air Soil Poll, 30, 75-90, Doi 10.1007/Bf00305177, 1986.

Hirota, A., Tsunogai, U., Komatsu, D. D., and Nakagawa, F.: Simultaneous determination of δ^{15}N and δ^{18}O of N_2O and δ^{13}C of CH_4 in nanomolar quantities from a single water sample, Rapid Commun Mass Sp, 24, 1085-1092, 10.1002/rcm.4483, 2010.

Holtgrieve, G. W., Schindler, D. E., Hobbs, W. O., Leavitt, P. R., Ward, E. J., Bunting, L., Chen, G. J., Finney, B. P., Gregory-Eaves, I., Holmgren, S., Lisac, M. J., Lisi, P. J., Nydick, K., Rogers, L. A., Saros, J. E., Selbie, D. T., Shapley, M. D., Walsh, P. B., and Wolfe, A. P.: A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the Northern hemisphere, Science, 334, 1545-1548, 2011.

Kaneyasu, N., Ohta, S., and Murao, N.: Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan, Atmos Environ, 29, 1559-1568, Doi 10.1016/1352-2310(94)00356-P, 1995.

Kendall, C., Elliott, E. M., and Wankel, S. D.: Tracing anthropogenic input of nitrogen to ecosytems, in: Stable Isotopes in Ecology and Environmental Science, edited by: Michener, R. H., and Lajtha, L. J., Blackwell, Oxford, 2007.

Komatsu, D. D., Ishimura, T., Nakagawa, F., and Tsunogai, U.: Determination of the $^{15}N/^{14}N$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ ratios of nitrous oxide by using continuous-flow isotope-ratio mass spectrometry, Rapid Commun Mass Sp, 22, 1587-1596, 2008.

Li, Y., Schichtel, B. A., Walker, J. T., Schwede, D. B., Chen, X., Lehmann, C. M. B., Puchalski, M. A., Gay, D. A., and Collett, J. L.: Increasing importance of deposition of reduced nitrogen in the United States, P Natl Acad Sci USA, 113, 5874-5879, 10.1073/pnas.1525736113, 2016.

Lin, M. Y., Horowitz, L. W., Payton, R., Fiore, A. M., and Tonnesen, G.: US surface ozone trends and extremes from 1980 to 2014: Quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate, Atmos Chem Phys, 17, 2943-2970, 10.5194/acp-17-2943-2017, 2017.

Liu, F., Zhang, Q., Ronald, J. V., Zheng, B., Tong, D., Yan, L., Zheng, Y. X., and He, K. B.: Recent reduction in NOx emissions over China: synthesis of satellite observations and emission inventories, Environ Res Lett, 11, Artn 114002
10.1088/1748-9326/11/11/114002, 2016.

McIlvin, M. R., and Altabet, M. A.: Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater, Anal Chem, 77, 5589-5595, 10.1021/ac050528s, 2005.

Mehlmann, A., and Warneck, P.: Atmospheric gaseous HNO_3 particulate nitrate, and aerosol-size distributions of major ionic species at a rural site in western Germany, Atmos Environ, 29, 2359-2373, Doi 10.1016/1352-2310(95)00056-5, 1995.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate, Geophys Res Lett, 30, 2003.

Michalski, G., Meixner, T., Fenn, M., Hernandez, L., Sirulnik, A., Allen, E., and Thiemens, M.: Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using $\Delta^{17}O$, Environ Sci Technol, 38, 2175-2181, 2004.

Michalski, G., Bhattacharya, S. K., and Mase, D. F.: Oxygen Isotope Dynamics of Atmospheric Nitrate and Its Precursor Molecules, in: Handbook of Environmental Isotope Geochemistry, Advances in Isotope Geochemistry, edited by: Baskaran, M., Springer Verlag, Berlin, 613-635, 2011.

Monks, P. S.: Gas-phase radical chemistry in the troposphere, Chem Soc Rev, 34, 376-395, 10.1039/b307982c, 2005.

Morin, S., Savarino, J., Frey, M. M., Yan, N., Bekki, S., Bottenheim, J. W., and Martins, J. M. F.: Tracing the origin and fate of NO_x in the Arctic atmosphere using stable isotopes in nitrate, Science, 322, 730-732, 10.1126/science.1161910, 2008.

Morin, S., Savarino, J., Frey, M. M., Domine, F., Jacobi, H. W., Kaleschke, L., and Martins, J. M. F.: Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65 degrees S to 79 degrees N, J Geophys Res-Atmos, 114, Artn D05303 10.1029/2008jd010696, 2009.

Nakagawa, F., Suzuki, A., Daita, S., Ohyama, T., Komatsu, D. D., and Tsunogai, U.: Tracing atmospheric nitrate in groundwater using triple oxygen isotopes: evaluation based on bottled drinking water, Biogeosciences, 10, 3547-3558, 10.5194/bg-10-3547-2013, 2013.

Noguchi, I., Aosier, B., Takada, M., Hamahara, K., Takahashi, H., and Tamada, K.: Developing NDVI Estimation Model of Forest Area in Japan, using Temperature data, Report of Institute of Environmental Sciences, 43-56, 2006.

Noguchi, I., Yamaguchi, T., Kawamura, M., Matsumoto, R., and Matsuda, K.: Updated program file for dry deposition velocity, Report of Institute of Environmental Sciences, 21-31, 2011.

Patris, N., Cliff, S. S., Quinn, P. K., Kasem, M., and Thiemens, M. H.: Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size, J Geophys Res-Atmos, 112, Artn D23301
10.1029/2005jd006214, 2007.

Riha, K. M., Michalski, G., Gallo, E. L., Lohse, K. A., Brooks, P. D., and Meixner, T.: High atmospheric nitrate inputs and nitrogen turnover in semi-arid urban catchments, Ecosystems, 17, 1309–1325, 2015.

Sabo, R. D., Nelson, D. M., and Eshleman, K. N.: Episodic, seasonal, and annual export of atmospheric and microbial nitrate from a temperate forest, Geophys Res Lett, 43, 683-691, 10.1002/2015gl066758, 2016.

Saito, S., Nagao, I., and Tanaka, H.: Relationship of NO_x and NMHC to photochemical O_3 production in a coastal and metropolitan areas of Japan, Atmos Environ, 36, 1277-1286, Pii S1352-2310(01)00557-X
Doi 10.1016/S1352-2310(01)00557-X, 2002.

Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, Atmos Chem Phys, 7, 1925-1945, 2007.

Skyllakou, K., Murphy, B. N., Megaritis, A. G., Fountoukis, C., and Pandis, S. N.: Contributions of local and regional sources to fine PM in the megacity of Paris, Atmos Chem Phys, 14, 2343-2352, 10.5194/acp-14-2343-2014, 2014.

Sofen, E. D., Alexander, B., Steig, E. J., Thiemens, M. H., Kunasek, S. A., Amos, H. M., Schauer, A. J., Hastings, M. G., Bautista, J., Jackson, T. L., Vogel, L. E., McConnell, J. R., Pasteris, D. R., and Saltzman, E. S.: WAIS Divide ice core suggests sustained changes in the atmospheric formation pathways of sulfate and nitrate since the 19th century in the extratropical Southern Hemisphere, Atmos Chem Phys, 14, 5749-5769, 10.5194/acp-14-5749-2014, 2014.

Tørseth, K., Hanssen, J. E., and Semb, A.: Temporal and spatial variations of airborne Mg, Cl, Na, Ca and K in rural areas of Norway, Sci Total Environ, 234, 75-85, Doi 10.1016/S0048-9697(99)00261-2, 1999.

Tsunogai, U., Kido, T., Hirota, A., Ohkubo, S. B., Komatsu, D. D., and Nakagawa, F.: Sensitive determinations of stable nitrogen isotopic composition of organic nitrogen through chemical conversion into N_2O, Rapid Commun Mass Sp, 22, 345-354, 10.1002/rcm.3368, 2008.

Tsunogai, U., Komatsu, D. D., Daita, S., Kazemi, G. A., Nakagawa, F., Noguchi, I., and Zhang, J.: Tracing the fate of atmospheric nitrate deposited onto a forest ecosystem in Eastern Asia using $\Delta^{17}O$, Atmos Chem Phys, 10, 1809-1820, 2010.

Tsunogai, U., Komatsu, D. D., Ohyama, T., Suzuki, A., Nakagawa, F., Noguchi, I., Takagi, K., Nomura, M., Fukuzawa, K., and Shibata, H.: Quantifying the effects of clear-cutting and strip-cutting on nitrate dynamics in a forested watershed using triple oxygen isotopes as tracers, Biogeosciences, 11, 5411-5424, 10.5194/bg-11-5411-2014, 2014.

Tsunogai, U., Miyauchi, T., Ohyama, T., Komatsu, D. D., Nakagawa, F., Obata, Y., Sato, K., and Ohizumi, T.: Accurate and precise quantification of atmospheric nitrate in streams draining land of various uses by using triple oxygen isotopes as tracers, Biogeosciences, 13, 3441-3459, 10.5194/bg-13-3441-2016, 2016.

United Nations.: World Urbanization Prospects, the 2014 Revision, United Nations, Population Division, Department of Economic and Social Affairs, New York, 2014.

Uno, I., Wakamatsu, S., and Ueda, H.: Behavior of nocturnal urban boundary layer and air pollutants, Journal of Japan Society of Air Pollution, 23, 102-114, 1988.

Uno, I., Ohara, T., and Wakamatsu, S.: Analysis of wintertime NO_2 pollution in the Tokyo Metropolitan area, Atmos Environ, 30, 703-713, Doi 10.1016/1352-2310(95)00177-8, 1996.

Uno, I., Uematsu, M., Hara, Y., He, Y. J., Ohara, T., Mori, A., Kamaya, T., Murano, K., Sadanaga, Y., and Bandow, H.: Numerical study of the atmospheric input of anthropogenic total nitrate to the marginal seas in the western North Pacific region, Geophys Res Lett, 34, Artn L17817
10.1029/2007gl030338, 2007.

von Glasow, R., Jickells, T. D., Baklanov, A., Carmichael, G. R., Church, T. M., Gallardo, L., Hughes, C., Kanakidou, M., Liss, P. S., Mee, L., Raine, R., Ramachandran, P., Ramesh, R., Sundseth, K., Tsunogai, U., Uematsu, M., and Zhu, T.: Megacities and large urban agglomerations in the coastal zone: Interactions between atmosphere, land, and marine ecosystems, Ambio, 42, 13-28, 10.1007/s13280-012-0343-9, 2013.

Wagstrom, K. M., and Pandis, S. N.: Contribution of long range transport to local fine particulate matter concerns, Atmos Environ, 45, 2730-2735, 10.1016/j.atmosenv.2011.02.040, 2011.

Walcek, C. J., Brost, R. A., Chang, J. S., and Wesely, M. L.: SO_2, sulfate and HNO_3 deposition velocities computed using regional landuse and meteorological data, Atmos Environ, 20, 949-964, Doi 10.1016/0004-6981(86)90279-9, 1986.

Walters, W. W., and Michalski, G.: Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules, Geochim Cosmochim Ac, 164, 284-297, 10.1016/j.gca.2015.05.029, 2015.

Walters, W. W., and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NO_y molecules, OH, and H_2O and its implications for isotope variations in atmospheric nitrate, Geochim Cosmochim Ac, 191, 89-101, 10.1016/j.gca.2016.06.039, 2016.

Walters, W. W., Simonini, D. S., and Michalski, G.: Nitrogen isotope exchange between NO and NO_2 and its implications for $\delta^{15}N$ variations in tropospheric NO_x and atmospheric nitrate, Geophys Res Lett, 43, 440-448, 10.1002/2015gl066438, 2016.

Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos Environ, 23, 1293-1304, Doi 10.1016/0004-6981(89)90153-4, 1989.

Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, Atmos Chem Phys, 3, 2067-2082, 2003.

Zhao, Y., Qiu, L. P., Xu, R. Y., Xie, F. J., Zhang, Q., Yu, Y. Y., Nielsen, C. P., Qin, H. X., Wang, H. K., Wu, X. C., Li, W. Q., and Zhang, J.: Advantages of a city-scale emission inventory for urban air quality research and policy: The case of Nanjing, a typical industrial city in the Yangtze River Delta, China, Atmos Chem Phys, 15, 12623-12644, 10.5194/acp-15-12623-2015, 2015.

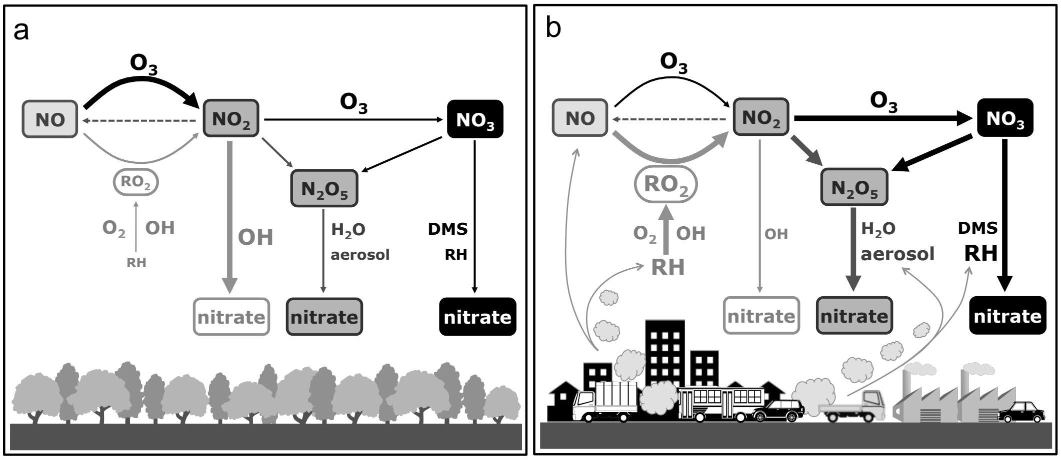

Figure 1. Conceptual diagram of pathways for conversion of NO$_x$ (NO + NO$_2$) to nitrate (NO$_3^-$) in a) background atmosphere and b) urban atmosphere. The first step in the process is the conversion of NO to NO$_2$, which is accomplished primarily by O$_3$ or peroxy radicals (HO$_2$ + RO$_2$). The 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$_2$O$_5$, 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; for example, they ignore potential seasonal variation, such as the N$_2$O$_5$ 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.

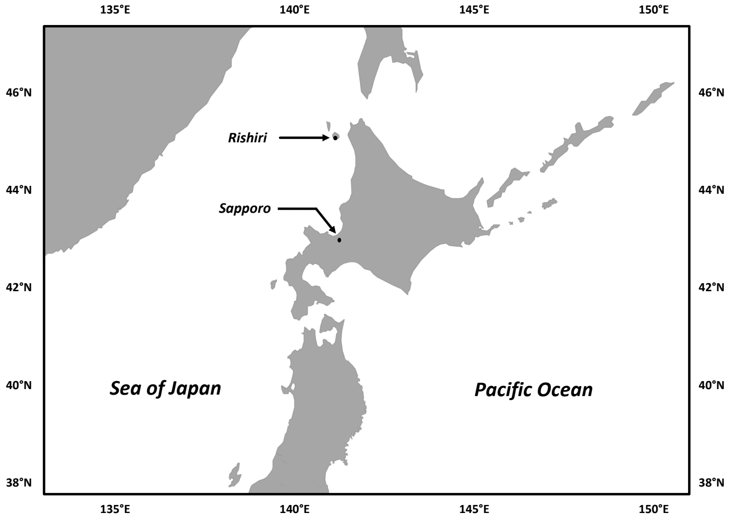

Figure 2. Location of study sites, Rishiri and Sapporo, in northern Japan. The base layer of the map was obtained from **https://www.amcharts.com/svg-maps/**.

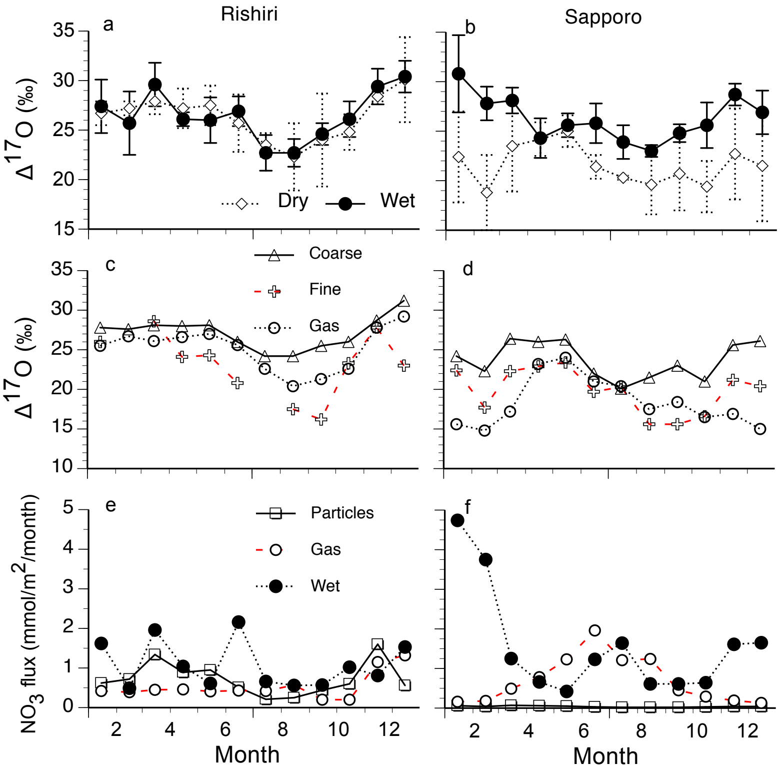

Figure 3. Time series of monthly weighted-average a, b) $\Delta^{17}O$ values of nitrate in dry and wet deposition c, d) $\Delta^{17}O$ values of nitrate in coarse and fine particles and in gaseous form, and e, f) fluxes of particulate nitrate, gaseous nitrate, and wet nitrate. Data from Rishiri (rural)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

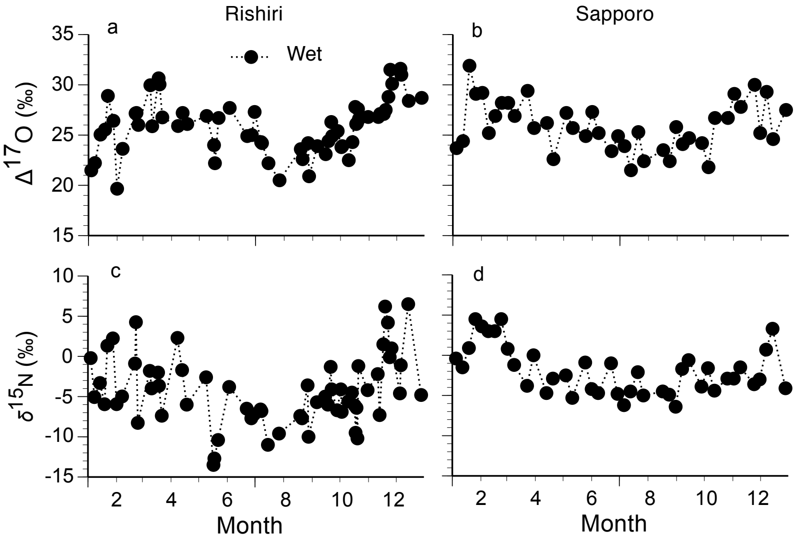

Figure 4. Time series of a, b) Δ^{17}O values of nitrate in wet deposition and c, d) δ^{15}N values of nitrate in wet deposition. Data from Rishiri (rural) are in left column and data from Sapporo (urban) are in right column.

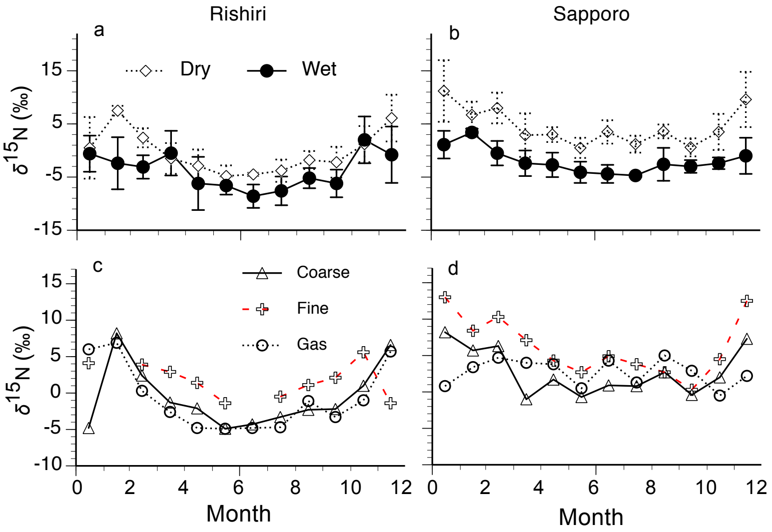

Figure 5. Time series of monthly weighted-average a, b) δ^{15}N values of nitrate in dry and wet deposition, and c, d) δ^{15}N values of nitrate in coarse and fine particles and gaseous form. Data from Rishiri (rural) are in left column and data from Sapporo (urban) are in right column. Error bars were calculated as described in the legend of Figure 3. Please note that the values on the y axes in panels a and b are different from those in panels c and d. Overall, there was no difference among $\delta^{15}N_{coarse}$, $\delta^{15}N_{fine}$, and $\delta^{15}N_{gas}$ ($p = 0.28$, $n = 10$) at Rishiri, whereas $\delta^{15}N_{fine}$ was on average 3.4 ‰ larger than $\delta^{15}N_{coarse}$ ($p = 0.04$, $n = 12$) and 3.5 ‰ larger than $\delta^{15}N_{gas}$ ($p = 0.03$, $n = 12$) at Sapporo.

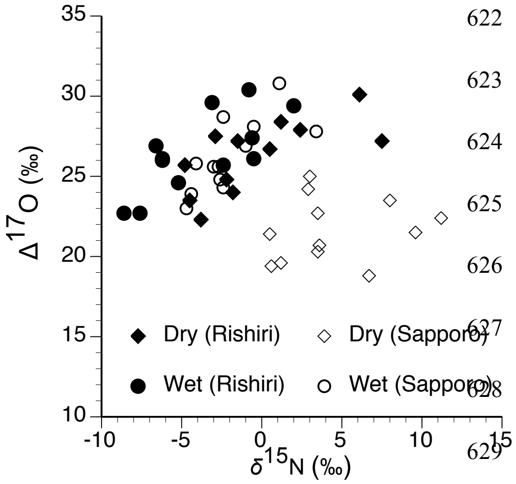

Figure 6. Correlation of $\delta^{15}N$ and $\Delta^{17}O$ values of nitrate in wet and dry deposition at Rishiri and Sapporo. Dry deposition at Rishiri: slope = 0.57 (95% confidence interval = 0.15 – 0.79), r = 0.70, p = 0.01, n = 12; Wet deposition at Rishiri: slope = 0.74 (95% confidence interval = 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.