1 **Triple oxygen isotopes indicate urbanization affects sources of**

2 **nitrate in wet and dry atmospheric deposition**

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24   **Abstract**

25   Atmospheric nitrate deposition resulting from anthropogenic activities negatively affects human and

26   environmental health. Identifying deposited nitrate that is produced locally vs. that originating from long-distance

27   transport would help inform efforts to mitigate such impacts. However, distinguishing the relative transport

28   distances of atmospheric nitrate in urban areas remains a major challenge since it may be produced locally and/or

29   come from upwind regions. To address this uncertainty we assessed spatiotemporal variation in monthly

30   weighted-average $\Delta^{17}O$ and $\delta^{15}N$ values of wet and dry nitrate deposition during one year at urban and rural sites

31   along the western coast of the northern Japanese island of Hokkaido, downwind of the East Asian continent. $\Delta^{17}O$

32   values of nitrate in wet deposition at the urban site mirrored those of wet and dry deposition at the rural site, ranging

33   between ~ +23 and +31 ‰ with higher values during winter and lower values in summer, which suggests greater

34   relative importance of oxidation of NO_2 by O_3 during winter and OH during summer. In contrast, $\Delta^{17}O$ values of

35   nitrate in dry deposition at the urban site were lower (+19 - +25 ‰) and displayed less distinct seasonal variation.

36   Furthermore, the difference between $\delta^{15}N$ values of nitrate in wet and dry nitrate deposition was, on average, 3 ‰

37   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

38   sites with the exception of dry deposition at the urban site. These results suggest that, relative to nitrate in wet and

39   dry deposition in rural environments and wet deposition in urban environments, nitrate in dry deposition in urban

40   environments forms from relatively greater oxidation of NO by peroxy radicals and/or oxidation of NO_2 by OH.

41   Given greater concentrations of peroxy radicals and OH in cities, these results imply that dry nitrate deposition

42   results from local NO_x emissions more so than wet deposition, which is transported longer distances. These results

43   illustrate the value of stable isotope data for distinguishing the transport distances and reaction pathways of

44   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 (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, 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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69   unique alternative that has recently emerged is the triple oxygen isotope (Δ^{17}O) value of nitrate[1], which reflects (as

70   the result of mass-independent isotopic fractionation during the formation of O_3) the number of oxygen atoms

71   derived from O_3 that are involved in the oxidation of NO_x (Alexander et al., 2009; Morin et al., 2008; Michalski et

72   al., 2003; Tsunogai et al., 2010; Tsunogai et al., 2016) since direct emissions of nitrate during combustion are

73   relatively small (Fraser et al., 1998). An advantage of Δ^{17}O relative to δ^{18}O of nitrate is that Δ^{17}O values are

74   primarily a function of the chemical pathways of nitrate formation, whereas δ^{18}O values are also influenced by δ^{18}O

75   of atmospheric water and temperature (Michalski et al., 2011). The fraction of NO oxidized to NO_2 by O_3 relative to

76   peroxy radicals (HO_2 + RO_2) determines two-thirds of the Δ^{17}O value of nitrate. The remaining fraction results from

77   the extent to which O_3 vs. OH molecules oxidize NO_2 (Geng et al., 2017). Δ^{17}O values of atmospheric nitrate

78   deposition are often highest in winter and lowest in summer (Michalski et al., 2003; Savarino et al., 2007; Tsunogai

79   et al., 2010; Tsunogai et al., 2016), because greater darkness and lower temperatures favor the oxidation of NO_x by

80   O_3, as well as N_2O_5 hydrolysis reactions, whereas oxidation of NO_2 by OH is more important when daylight is

81   longer and temperatures higher (Figure 1). Peroxy radicals, which form from oxidation of carbon monoxide, reactive

82   hydrocarbons, and volatile organic compounds (Saito et al., 2002), are thought to compete with O_3 to oxidize NO in

83   polluted settings and thus depress Δ^{17}O values of nitrate (Guha et al., 2017; Fang et al., 2011). Decreasing

84   nitrate-Δ^{17}O values during the past ~150 years in West Antarctica suggest that anthropogenic activities have

85   increased the relative importance of peroxy radicals in NO_x cycling globally (Sofen et al., 2014). However, reactive

86   hydrocarbons and aerosols can also facilitate the formation of nitrate directly or through N_2O_5, respectively, which

87   elevates Δ^{17}O values of nitrate (Michalski et al., 2011). Although wet (aqueous nitrate) and dry (gaseous HNO_3 or

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

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

88   particulate nitrate) deposited nitrate are often presumed to have similar $\Delta^{17}O$ values (Guerrieri et al., 2015), dry

89   deposition may be less prone to long-distance transport (Celle-Jeanton et al., 2009; Dasch and Cadle, 1985;

90   Balestrini et al., 2000). Shorter transport distances could lead to distinct oxidation pathways and thus different $\Delta^{17}O$

91   values of nitrate between these forms of deposition in urban environments where concentrations of atmospheric

92   pollutants are typically elevated. Yet, this hypothesis cannot be evaluated using existing data, as prior studies

93   typically analyzed $\Delta^{17}O$ values of only wet or dry nitrate deposition at single sites (Guha et al., 2017; Tsunogai et al.,

94   2010).

95   Here we assess the effect of urbanization on the oxidation chemistry of NO_x and the sources of nitrate in

96   wet and dry atmospheric deposition using measurements of the $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$ values of nitrate. Our two study

97   sites (Figure 2) are located at a similar longitude, are separated by only ~2° of latitude, and have comparable

98   synoptic climatologies, but there is a major difference in the degree of urbanization between them (see below).

99   These sites were chosen to be downwind of several megacities on the East Asian continent, a region where NO_x

100   emissions have increased approximately four-fold during the past forty years (Akimoto, 2003; Uno et al., 2007).

101   This arrangement of sites provides an ideal setting to investigate potential differences in the oxidation pathways and

102   sources of nitrate pollution in urban and rural environments against high background levels of atmospheric nitrate

103   deposition.

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105   **2 Material and Methods**

106   **2.1 Study sites**

107   Rishiri is a remote (population size: ~5,000; density: ~28 people/km^2) and small island in the Sea of Japan

108   off the coast of the island of Hokkaido in northern Japan. Samples of wet and dry atmospheric deposition were

109   collected at the Rishiri National Acid Rain Monitoring station (Figure 2; 45° 07' 11" N, 141° 12' 33" E; 40 m a.s.l.),

110   which is part of the Acid Deposition Monitoring Network in East Asia (EANET), between January and December in

111   2009. The mean annual precipitation is ~920 mm and mean annual temperature is ~7.1°C

112   (http://www.jma.go.jp/jma/indexe.html). Precipitation amounts are the highest in the late summer through winter,

113   with lower amounts in the spring and early summer. The main land cover within a ~10 km radius of the monitoring

114   station is forest and shrub land.

115   Sapporo is a city of ~1.9 million people (density: ~1,710 people/km^2) that is ~200 km south of Rishiri.

116   Samples of wet and dry atmospheric deposition were obtained from the roof of the Institute of Environmental

117   Sciences in Sapporo (Figure 2; 43° 04' 55" N, 141° 20' 00" E; ~26 m a.s.l.) between January and December in 2009.

118   The sampling site in Sapporo is not part of EANET. The mean annual precipitation is ~1,100 mm and mean annual

119   temperature is ~8.9°C (http://www.jma.go.jp/jma/indexe.html). Rishiri and Sapporo are both located on the Sea of

120   Japan side of Hokkaido prefecture and thus they have similar seasonal precipitation patterns and air-mass

121   back-trajectories on daily and longer time scales. Sapporo is bordered by the Sea of Japan to the north and by

122   mountains to the west, south, and east. The major sources of local NO_x emissions are automobile exhaust and boilers

123   used for domestic heating. There are no major factories or combustion-based electricity generation facilities in

124   Sapporo (Kaneyasu et al., 1995). The prevailing winds in Hokkaido typically originate from the northwest in winter

125   and southeast in summer (Kaneyasu et al., 1995).

126   **2.2 Sample collection**

127   Samples were collected using the standard operating methods of EANET

128   (http://www.eanet.asia/product/manual/techacm.pdf). Composite samples of wet deposition falling on a daily and

129   weekly basis were collected at Rishiri (n= 62) and Sapporo (n = 41), respectively, using auto samplers (DKK

130   DRS-200(S), DKK and US-420, Ogasawara Keiki Corp, respectively). The wet deposition samples were filtered

131   through a 0.45 μm filter and stored at 4°C until measurement of nitrate and nitrite (NO_2^-) concentrations and

132   isotopes.

133   Samples of dry deposition were obtained using the filter-pack method, which has been widely used in dry

134   deposition monitoring programs throughout the world (Aikawa et al., 2010; Endo et al., 2011; Mehlmann and

135   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

136   to collect gaseous HNO_3 and particulate nitrate. Composite samples collected using this approach (which we refer to

137   as dry deposition) were obtained on a monthly basis at Rishiri (n = 12). Sampling of dry deposition at Sapporo

138   occurred approximately bi-weekly (n = 24); sampling occurred bi-weekly rather than monthly (as at Rishiri) because

139   we anticipated higher nitrate concentrations in dry deposition at Sapporo than Rishiri. However, only 15 of the 24

140   dry deposition samples from Sapporo were available for analysis in the present study. The first stage of the filter

141   pack is a multi-nozzle cascade impactor (NL-4-10P, Tokyo Dylec. Corp.) and Teflon binder filter (T60A20-20H,

142   Tokyo Dylec. Corp.) that collects coarse particles >10 μm in diameter. The second stage is a Teflon filter

143   (ADVANTEC T080A047A) that collects fine particles <10 μm in diameter that passed through the first filter. The

144   third stage is a 0.45 μm nylon filter (PALL ULTIPOR N66-NX047100) that collects HNO_3 gas and some SO_2, HCl,

145   HONO, NH_3, and NO_2. The 4th and 5th stage filters (ADVANTEC No. 51A, alkaline impregnated filter) are used to

146   collect the remaining SO_2, HCl, and HONO. The last filter (ADVANTEC No. 51A, acid impregnated filter) is used

147   to collect the remaining NH_3. The nitrate and nitrite on the first, second, and third filters were extracted using

148   ultrapure water, passed through a 0.45 μm filter, and stored at 4°C until measurement of nitrate and nitrite

149   concentrations and isotopes.

150   The maximum filter blank was 0.2 μg (=3 nmol) for nitrate, which corresponds to 0.16 μmol/L nitrate

151   when 20 mL of milli-Q water is used to extract nitrate from each filter based on the EANET procedure. The

152   minimum nitrate concentrations in the solutions extracted from the filters and measured for isotopic values were

153   30.7 μmol/L, 1.5 μmol/L, and 22.4 μmol/L in the portions of coarse particles, fine particles, and gas, respectively,

154   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,

155   respectively, for Sapporo. Thus, we concluded that the blanks had little influence on the isotopic values of dry

156   deposition. This is true even for fine particle samples with nitrate concentrations <5 μmol/L, because the deposition

157   rates of these nitrate-depleted samples were low. We did not directly assess filter breakthrough limits, but prior

158   results based on changes in the duration of sampling at our sites suggest that such limits are much higher than the

159   amount of nitrate present in our samples (Noguchi et al., 2009).

160   **2.3 Analysis**

161   Within a few months of collection, nitrate and nitrite in the filtered samples of wet and dry deposition

162   were quantified using ion chromatography (Dionex DX-500, ICS-1500 and ICS-2000, Nippon Dionex Co., Ltd.,

163   Osaka, Japan). Based on replicate analyses of samples, the precision of these concentration measurements was 1.6 %.

164   The detection limit was 0.03 µmol/L. Nitrite concentrations were < 1.0 % of the sum of nitrite and nitrate

165   concentrations in all samples of wet deposition, and they were $\leq$ 5.0 % in 72 % and 87 % of samples of dry

166   deposition at Rishiri and Sapporo, respectively. The pH values of the wet deposition samples ranged between 4.51

167   and 5.02 at Rishiri and between 4.65 and 5.29 at Sapporo.

168   Isotopic analysis was performed in 2013 for samples from Rishiri and in 2011 for samples from Sapporo.

169   Prior to isotopic analysis we reanalyzed nitrate and nitrate concentrations in the samples and found that differences

170   between these and the original concentration measurements were <10 %. For isotopic analysis, nitrite and nitrate in

171   each filtrate sample was converted to N_2O using chemical conversion (McIlvin and Altabet, 2005) with slight

172   modification (Tsunogai et al., 2016; Tsunogai et al., 2008). Isotopic analysis of nitrite alone was also performed on

173   samples with nitrite concentrations > 5.0 % of the total nitrite plus nitrate concentrations (McIlvin and Altabet,

174   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

175   mass spectrometry system (Komatsu et al., 2008; Hirota et al., 2010). The obtained $\delta^{18}O$ values were normalized to

176   VSMOW using local laboratory nitrate standards calibrated against USGS 34 ($\delta^{18}O$ = -27.9 ‰, $\Delta^{17}O$ = 0.04 ‰, and

177    $\delta^{15}N$ = -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). $\Delta^{17}O$

178   values were measured directly from the δ^{33} and δ^{34} of O_2 data. The obtained $\delta^{15}N$ values were normalized to Air

179   using local laboratory nitrate standards calibrated against USGS 32 ($\delta^{18}O$ = +25.7 ‰ and $\delta^{15}N$ = +180 ‰) and

180   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

181   and 11.8 ‰, respectively. The $\Delta^{17}O$ values of the local standards are ~0 ‰. Analytical precision (1σ) was $\pm$ 0.3 ‰

182   for $\delta^{15}N$, $\pm$ 0.5 ‰ for $\delta^{18}O$, and $\pm$ 0.2 ‰ for $\Delta^{17}O$ based on repeated measurements of the local nitrate standards

183   (Tsunogai et al., 2010). Besides using the local nitrate standards for routine calibration and as checks of isotopic

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

185   instrument linearity.

186   For samples with nitrite concentrations $\geq$ 5 % of the total nitrite plus nitrate concentrations the δ^{15}N and

187   δ^{18}O values of nitrate were calculated by mass balance (e.g. $\delta^{15}N_{NO3^-} = (\delta^{15}N_{NO2^-+NO3}^- * [NO_2^- + NO_3^-] - \delta^{15}N_{NO2}^- *$

188    $[NO_2^-])/[NO_3^-])$. The measured Δ^{17}O value of nitrite for samples on which this analysis was performed was 0 ‰.

189   Therefore, we presumed that the Δ^{17}O value of nitrite is 0 ‰ because of rapid oxygen change between NO_2 and

190   water at near-neutral pH condition (Casciotti et al., 2007), and we corrected the Δ^{17}O values of nitrate as $\Delta^{17}O_{NO3^-} =$

191    $\Delta^{17}O_{NO2^-+NO3}^- * [NO_2^- + NO_3^-]/[NO_3^-]$. For all samples (at both sites), the maximum nitrite/nitrate ratios in the

192   samples were 28.6, 13.3, and 7.4 % for coarse particles, fine particles, and gas, respectively. Therefore, the

193   maximum extent of δ^{15}N corrections for the limited number of dry deposition samples with nitrite concentrations > 5

194   % of the total nitrite plus nitrate concentrations were 1.1, 0.9 and <0.1 ‰, respectively, the maximum extent of δ^{18}O

195   corrections were 15.0, 11.2, and<0.1 ‰, respectively, and the maximum extent of Δ^{17}O corrections were 5.7, 3.1,

196   and 0.4 ‰, respectively. From these results we conclude that the potential bias in the isotopic values of dry

197   deposition associated with nitrite was much smaller than the errors assumed in the final total isotopic values of dry

198   deposition (around ±2.5 ‰ for δ^{15}N, ±8.0 ‰ for δ^{18}O, and ±3 ‰ for Δ^{17}O).

199   To quantify the Δ^{17}O, δ^{18}O, and δ^{15}N values of nitrate in dry deposition, we calculated monthly

200   weighted-average (weighted based on mass) Δ^{17}O, δ^{18}O, and δ^{15}N values of nitrate (e.g. $\Delta^{17}O_{dry}$ and $\delta^{15}N_{dry}$,

201   respectively) among coarse and fine particles and gas phases using each isotopic value and concentration. For

202   Sapporo, isotopic values for samples of dry deposition collected during the same month were averaged as monthly

203   weighted-average values. To compare isotopic values of wet and dry deposition within and between sites, we

204   calculated monthly weighted-average Δ^{17}O, δ^{18}O and δ^{15}N values of nitrate for wet deposition (e.g. $\Delta^{17}O_{wet}$ and

205    $\delta^{15}N_{wet}$). 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

206    $\delta^{15}N_{wet}$ and $\delta^{15}N_{dry}$, within sites. Paired t-tests were also used to compare monthly weighted-average $\Delta^{17}O_{coarse}$ and

207    $\Delta^{17}O_{fine}$, $\delta^{18}O_{coarse}$ 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

208 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

209 Rishiri with $\delta^{15}N_{wet}$ at Sapporo. Statistical analyses were performed in PAST version 3.01 (Hammer et al., 2001).

210 Volatilization of particulate to gaseous nitrate that occurs using the filter-pack method (e.g. Noguchi et al., 2009)

211 may bias assessment of the isotopic values of gaseous and particulate nitrate. Therefore, we do not compare the

212 concentrations and isotopic values of particulate and gaseous nitrate at our sites.

213   Wet deposition flux was calculated using precipitation amount and nitrate concentration data obtained for

214 each site from the National Institute for Environmental Studies, Japan (http://www.nies.go.jp/index-e.html). The

215 monthly flux is the sum of precipitation amount multiplied by nitrate concentration for all samples in each month.

216 Dry deposition flux was estimated following the inferential method (Hicks, 1986), where

217 $F_{dry} = V_d \times C$

218 and F_{dry} represents the dry deposition flux, V_d the deposition velocity, and C the nitrate concentration in air

219 (calculated from measured nitrate concentrations in the sample extracts and pumped air volume). Calculation of V_d

220 by the inferential method requires meteorological and land use data. Meteorological data were obtained from the

221 Japan Meteorological Agency (http://www.jma.go.jp/jma/indexe.html). Landuse was presumed to be forest at

222 Rishiri and city at Sapporo. The height of the forest canopy at Rishiri was presumed to be 10 m, and seasonal

223 canopy resistance was determined from NDVI values (Noguchi et al., 2006). Deposition velocity was calculated

224 using the inferential method version 4.2 (Noguchi et al., 2011; Wesely, 1989; Walcek et al., 1986; Erisman et al.,

225 1997; Zhang et al., 2003) (the program file is available at

226 http://www.hro.or.jp/list/environmental/research/ies/katsudo/acid_rain/kanseichinchaku/dry_deposition.html).

227 Deposition velocities of gaseous and particulate materials are estimated separately, although these results should be

228 interpreted with caution because of the potential for bias from volatilization of particulate nitrate. Fluxes of coarse

229 and fine particles were not differentiated.

230

231 **3 Results**

232   At the rural site, Rishiri, there was no difference between monthly weighted-average $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$,

233   which ranged between +22.3 and +30.1 ‰ and between +22.7 and +30.3 ‰, respectively (Figure 3; p = 0.57, n =

234   12). Monthly weighted-average $\delta^{18}O_{dry}$ was overall slightly less than $\delta^{18}O_{wet}$, with ranges between +66.9 and

235   +94.4 ‰ and +71.2 and +90.9 ‰, respectively (Figure 3; p = 0.005, n = 12). Both forms of deposition exhibited

236   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

237   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

238    $\delta^{18}O_{fine}$ (p = 0.01, n = 12; Figure S1). Monthly weighted-average $\delta^{15}N_{dry}$ at Rishiri varied between -4.8 and +7.5 ‰

239   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).

240    $\delta^{15}N_{coarse}$ was slightly lower than $\delta^{15}N_{fine}$ at Rishiri (p = 0.06, n = 10).

241   At the urban site, Sapporo, monthly weighted-average $\Delta^{17}O_{wet}$ ranged between +23.0 and +30.8 ‰ and was

242   higher than $\Delta^{17}O_{dry}$, which ranged between +18.8 and +25.0 ‰ (p < 0.001, n = 12; Figure 3). Monthly

243   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 ‰,

244   respectively (Figure 3; p < 0.0001, n = 12). $\Delta^{17}O_{dry}$ and $\delta^{18}O_{dry}$ at Sapporo displayed less pronounced seasonal

245   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

246    $\Delta^{17}O_{fine}$ (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 =

247   12, respectively) at Sapporo (Figure S1). Monthly weighted-average $\delta^{15}N_{dry}$ at Sapporo varied between +0.5 and

248   +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,

249   n = 12). $\delta^{15}N_{coarse}$ was on average 3.4 % less than $\delta^{15}N_{fine}$ at Sapporo (p = 0.04, n = 12).

250    $\Delta^{17}O_{wet}$ at Sapporo exhibited similar values and seasonal patterns as $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri (p = 0.97,

251   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

252   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

253   =12) and $\delta^{15}N_{dry}$ (p = 0.46, n =12) at Rishiri (Figures 3 and 4). There were positive correlations between the $\delta^{15}N$

254   and $\Delta^{17}O$ values of wet and dry deposition at both sites, with the exception of dry deposition at Sapporo (Figure 5).

255   Fluxes of nitrate in dry particulate deposition and gaseous dry deposition were generally greater at Sapporo than

256   Rishiri (Figure S1) because the dry deposition velocity dominates the flux value of dry deposition and it is greater

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

258

4 Discussion

260   The similar values and seasonal trends of $\Delta^{17}O_{dry}$ and $\Delta^{17}O_{wet}$ at Rishiri imply that both forms of

261   deposition experienced similar seasonal variation in photochemical reactions during their production from NO_x. The

262   values and trends are consistent with prior empirical studies of $\Delta^{17}O_{wet}$ at Rishiri between 2006 and 2007 (Tsunogai

263   et al., 2010) and elsewhere in Japan (Tsunogai et al., 2016). These results also coincide well with model predictions

264   (Alexander et al., 2009), which suggest that they indicate seasonal variation in the relative importance of oxidation

265   of NO_2 by O_3 vs. OH in background, free tropospheric air. During summer when solar radiation is high, the relative

266   importance of oxidation of NO_2 by OH is likely greatest, thus decreasing nitrate $\Delta^{17}O$ values. In contrast, solar

267   radiation is low in winter, which likely causes pathways involving oxidation of NO_2 by O_3 to be relatively more

268   important, thus increasing nitrate $\Delta^{17}O$ values. Values of $\Delta^{17}O_{wet}$ at Sapporo were indistinct from those of $\Delta^{17}O_{dry}$

269   and $\Delta^{17}O_{wet}$ at Rishiri, and the most straightforward interpretation of these results is that wet deposition at Sapporo

270   underwent similar photochemical formation processes as both forms of deposition at Rishiri.

271   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

272   lower and displayed less seasonal variation. These results suggest unique oxidation processes that display little

273   seasonal variation and are associated with dry deposition at this site. One potential explanation for the relatively low

274    $\Delta^{17}O_{dry}$ values at Sapporo relates to OH. Concentrations of OH are typically higher in urban than rural areas as the

275   result of the formation of OH from Criegee intermediates during alkene oxidation and/or photolysis of nitrous acid

276   or formaldehyde in more polluted urban settings (Monks, 2005). OH competes with O_3 to oxidize NO_2, and thus

277   greater oxidation of NO_2 by OH in dry deposition would drive down $\Delta^{17}O_{dry}$ values (Morin et al., 2011). Another

278   potential explanation for the relatively low $\Delta^{17}O_{dry}$ at Sapporo relates to peroxy radicals potentially being of greater

279   importance in the oxidation of NO to NO_2 in dry deposition at this site. Peroxy radicals typically form via

280   photochemical oxidation of non-methane hydrocarbons that originate from anthropogenic sources, such as vehicle

281   exhaust, and their concentrations are usually higher in urban than rural environments (Saito et al., 2002; Carslaw et

282   al., 2002). These radicals rapidly compete with O_3 to oxidize NO to NO_2 (Monks, 2005), which results in lower

283    $\Delta^{17}O_{dry}$ values (Morin et al., 2011). A recent study also suggested that formation of NO_2 by reaction of peroxy

284   radicals with NO in polluted air caused short-term shifts toward lower $\Delta^{17}O_{dry}$ in Taiwan (Guha et al., 2017).

285   Atmospheric inversions are common in Sapporo (Uno et al., 1988) and other Japanese cities (Saito et al., 2002; Uno

286   et al., 1996), particularly during winter, and such conditions may trap pollutants and alter the NO_x to nitrate

287   photo-oxidation pathway thereby helping facilitate reaction of OH with NO_2 and/or NO with peroxy radicals.

288   Regardless of the precise mechanism driving down $\Delta^{17}O_{dry}$ at Sapporo, such low values suggest two

289   distinct sources of nitrate in wet and dry deposition in our study region. The first is likely transported relatively long

290   distances to both Rishiri and Sapporo in wet deposition and to Rishiri in dry deposition. Below-cloud scavenging of

291   local/regional particulate nitrate and gaseous HNO_3 undoubtedly occurs at the beginning of precipitation events, but

292   the similar absolute values and temporal variations of $\Delta^{17}O_{wet}$ at both sites suggest that the majority of nitrate in wet

293   deposition at Sapporo (as well as Rishiri) originates from afar and is transported to Japan in cloud water. The second

294   source is likely local anthropogenic NO_x emissions that are deposited in dry deposition near their point of production

295   at the urban site, Sapporo, as concentrations of OH and peroxy radicals are typically elevated in more polluted urban

296   environments (Monks, 2005). Similarly, the more positive values of $\Delta^{17}O_{coarse}$ than $\Delta^{17}O_{fine}$ at both sites suggest that

297   nitrate in coarse particles is subject to greater supply through long-range transport (produced in free troposphere)

298   than is nitrate in fine particles, which are more influenced by local sources (produced within the boundary layer of

299   the urban area).

300   To aid our interpretations based on $\Delta^{17}O$ we evaluated $\delta^{15}N$ values of nitrate, which we interpret as

301   primarily indicating variation in NO_x oxidation efficiency (e.g. Walters and Michalski, 2015, 2016; Walters et al.,

302   2016). We recognize that nitrate $\delta^{15}N$ values are influenced by factors that are difficult to constrain in our study,

303   including the $\delta^{15}N$ values of NO_x from the East Asian continent, the removal rate of NO_x (or production rate of

13

304   nitrate) during transport, isotopic fractionation between NO_x and nitrate during in-cloud and below-cloud

305   scavenging processes during transport, the $\delta^{15}N$ values of locally produced NO_x, and the relative amount of NO_x

306   derived locally vs. that from the East Asian continent. Nevertheless, the last factor likely differs the most between

307   our sites since there is more locally produced NO_x in the urban environment at Sapporo. During long-distance

308   transport of NO_x there is greater ^{15}N-enrichment in NO_2 than NO (Freyer, 1991), which causes the residual NO_x to

309   become depleted in ^{15}N during partial removal of NO_x as nitrate in the troposphere. Therefore, nitrate derived from

310   long-distance transport from the East Asian continent is likely to have lower $\delta^{15}N$ values than nitrate from more

311   local sources. The relatively high $\delta^{15}N_{dry}$ values at Sapporo are consistent with this interpretation and with the

312    $\Delta^{17}O$-based inference that nitrate in dry deposition at Sapporo originates from more local sources than does that in

313   wet deposition at Sapporo and both forms of deposition at Rishiri.

314   The correlations between $\Delta^{17}O$ and $\delta^{15}N$ for both forms of deposition at both sites, with the exception of

315   dry deposition at Sapporo, suggest a relationship between oxidation pathways (recorded by $\Delta^{17}O$) and NO_x oxidation

316   efficiency (recorded by $\delta^{15}N$). Both NO_x oxidation pathways and efficiencies are primarily controlled by the rate of

317   the NO_2 + OH reaction, which suggests that this reaction drives these correlations. The lack of correlation between

318    $\Delta^{17}O_{dry}$ and $\delta^{15}N_{dry}$ at Sapporo likely reflects the unique oxidation pathways (and thus $\Delta^{17}O$ values) associated with

319   locally produced NO_x in the urban environment.

320   At both sites, wet and dry deposition exhibited generally larger $\delta^{15}N$ values in the winter than summer

321   months. This result probably occurs because of seasonal changes in temperature on isotopic fractionation of nitrogen

322   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

323   undergoing long-distance transport and/or production during the summer is likely to have experienced higher NO_x

324   oxidation efficiency than that produced locally and/or during the winter. $\delta^{15}N$ values of nitrate likely only reflect

325   those of the source NO_x for nitrate produced locally during the winter. Indeed, the relatively high $\delta^{15}N_{dry}$ values

326   during the winter at Sapporo are consistent with those expected for sources such as nearby combustion of fossil fuels

327   (Redling et al., 2013; Walters et al., 2015).

14

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

329   emissions will be most effective to the extent that dry deposition is the dominant form of atmospheric deposition.

330   Local efforts may be less effective in places and times where atmospheric deposition arrives as wet deposition, since

331   wet deposition seems more likely to originate from long distances. Thus, regional, national and global efforts will

332   likely be required to reduce the effects of atmospheric nitrate in wet deposition that is transported long distances in

333   air masses. Additional datasets with paired measurements of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ would be valuable to evaluate our

334   interpretation of the oxidation pathways and sources and transport distances of nitrate deposited in urban

335   environments.

336   The $\Delta^{17}O$ values of nitrate are increasingly used in watershed studies to determine the relative abundance of

337   unprocessed atmospheric nitrate in environmental waters, such as rivers and lakes (Sabo et al., 2016; Riha et al.,

338   2015; Tsunogai et al., 2016; Tsunogai et al., 2010; Michalski et al., 2004). Such studies often use $\Delta^{17}O_{wet}$ or $\Delta^{17}O_{dry}$

339   as an end-member for calculating the amount of unprocessed atmospheric nitrate in a sample. Although they should

340   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

341   similar in rural settings, since the annual weighted-average $\Delta^{17}O$ values of wet and dry were nearly identical (+27.2

342   and +27.1 ‰, respectively) at Rishiri. However, in urban settings or settings downstream of urban environments the

343   potential differences between $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ may need to be considered to avoid over- or under-estimating the

344   amount of unprocessed atmospheric nitrate when using $\Delta^{17}O$ values of nitrate as a tracer of atmospheric nitrate. For

345   example, consider a simple mixing model such as % atmospheric nitrate = $100 \times [(\Delta^{17}O_{measured}$ -

346    $\Delta^{17}O_{terrestrial})/(\Delta^{17}O_{atmospheric} - \Delta^{17}O_{terrestrial})]$

347   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

348   no atmospheric nitrate (i.e., 0 ‰), and $\Delta^{17}O_{atmospheric}$ is the $\Delta^{17}O$ value of atmospheric nitrate (either +27.6 or

349   +21.8 ‰, representing the average weighted-average annual values of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ measured at Sapporo in

350   the present study). The difference in % atmospheric nitrate when +27.6 vs. +21.8 ‰ are used as end-members for

351    $\Delta^{17}O_{atmospheric}$ is small when $\Delta^{17}O_{measured}$ is small (e.g. ~1 % when $\Delta^{17}O_{measured}$ is ~1 ‰), but increases when

352     $\Delta^{17}O_{measured}$ is large (e.g. ~19 % when $\Delta^{17}O_{measured}$ is 20 ‰). Thus, our results suggest a weighted average of $\Delta^{17}O_{wet}$

353   and $\Delta^{17}O_{dry}$ should be used when $\Delta^{17}O$ values of nitrate are used to quantify the amount of unprocessed atmospheric

354   nitrate exported from urban watersheds. At Sapporo, the weighted average of $\Delta^{17}O_{wet}$ and $\Delta^{17}O_{dry}$ is +25.7 ‰, which

355   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

356   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

357   sites, such as semi-closed and/or highly polluted urban areas, where the majority of deposition comes from local

358   sources.

359

360   **5 Conclusions**

361   Our isotopic data suggest differences in the oxidation chemistry and transport distances of wet and dry

362   deposition in urban settings: wet deposition tends to originate from afar, whereas dry deposition is produced largely

363   from local sources as the result of unique NO_x oxidation pathways that occur in polluted urban settings. These

364   results imply that reductions in local NO_x emissions will be most effective when and where dry deposition is the

365   dominant form of atmospheric deposition, which has implications for efforts to reduce nitrate deposition and its

366   negative environmental impacts in cities and downwind areas. The approach used herein of comparing isotopic

367   values of wet and dry deposition in different environmental settings is likely to provide continued insight into the

368   transport distances and reaction pathways of atmospheric nitrate pollution.

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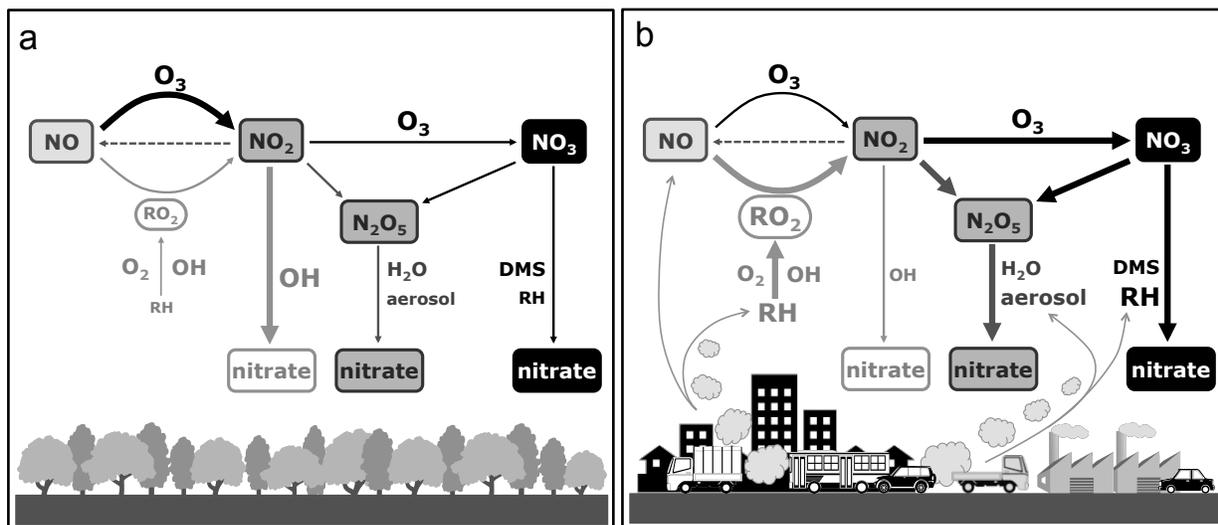
Figure 1. Conceptual diagrams of pathways for conversion of NO_x ($NO + NO_2$) to nitrate (NO_3^-) in a) background

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

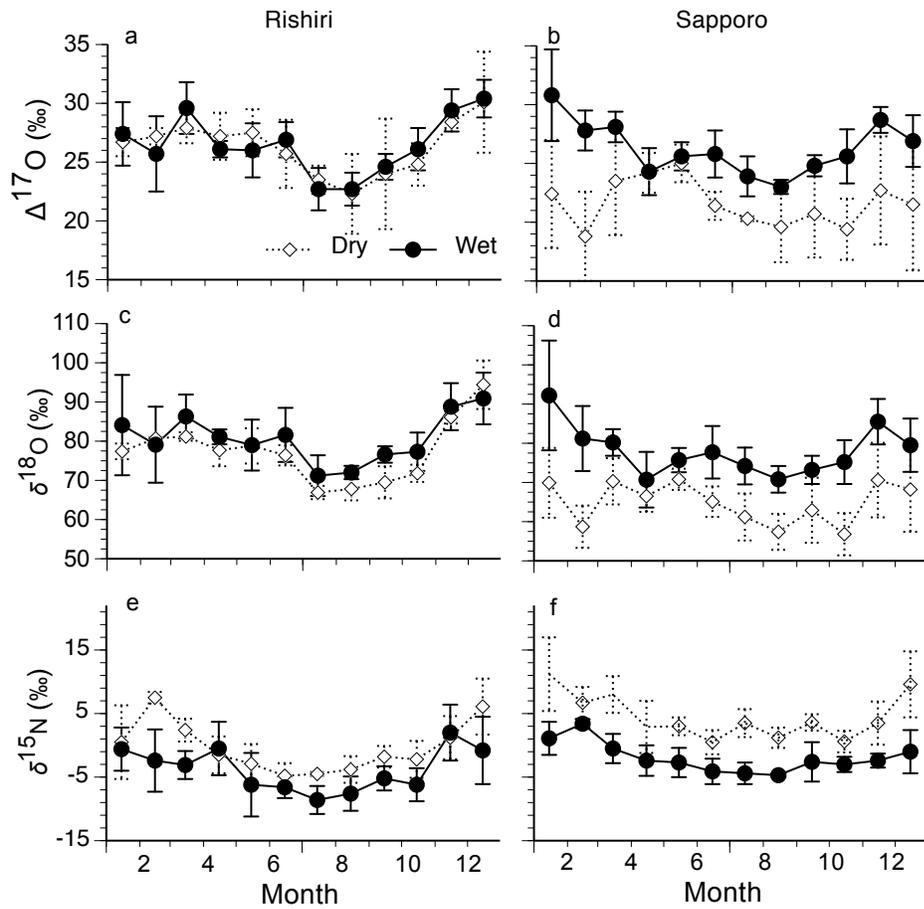more important in urban environments during the summer than winter.

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604 **Figure 2.** Location of study sites, Rishiri and Sapporo, in northern Japan. The base layer of the map was obtained

605 from **https://www.amcharts.com/svg-maps/**.

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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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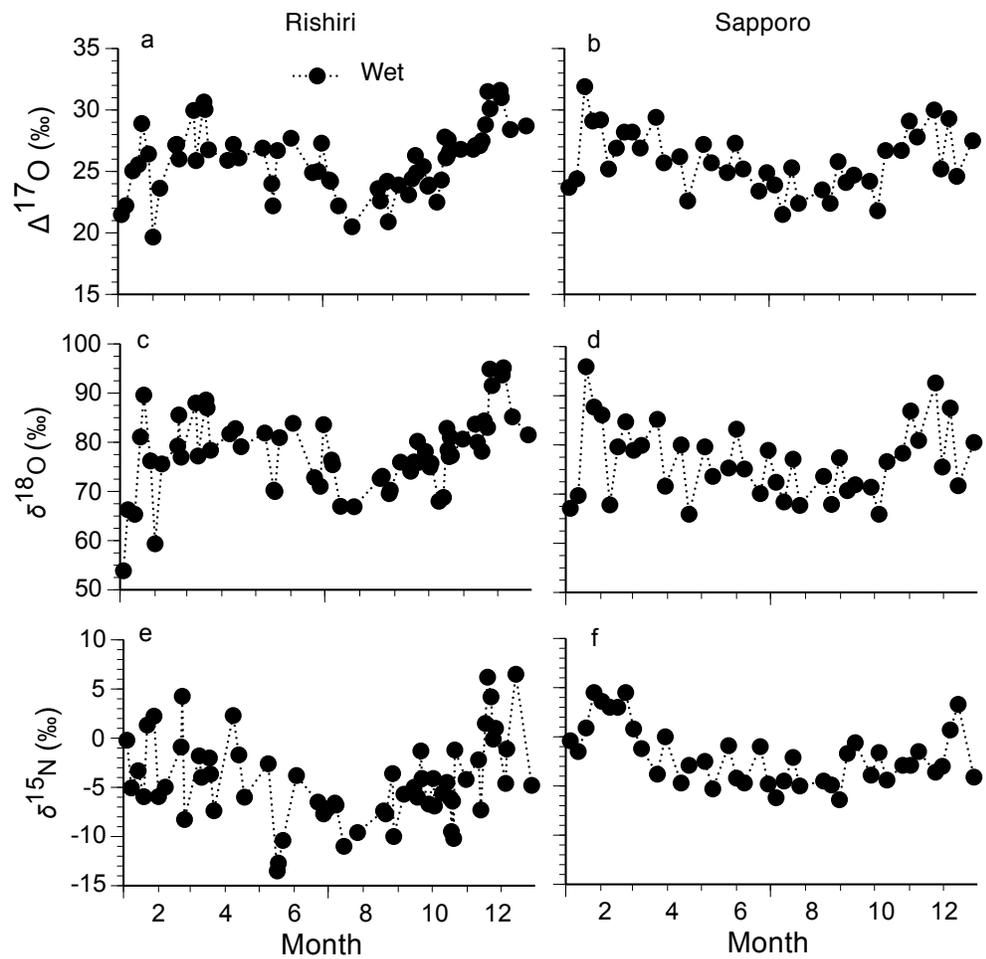
Figure 4. Time series of a, b) $\Delta^{17}O$ values of nitrate in wet deposition, c, d) $\delta^{18}O$ values of nitrate in wet deposition, and e, f) $\delta^{15}N$ values of nitrate in wet deposition. Data from Rishiri (rural) are in left column and data from Sapporo (urban) are in right column.
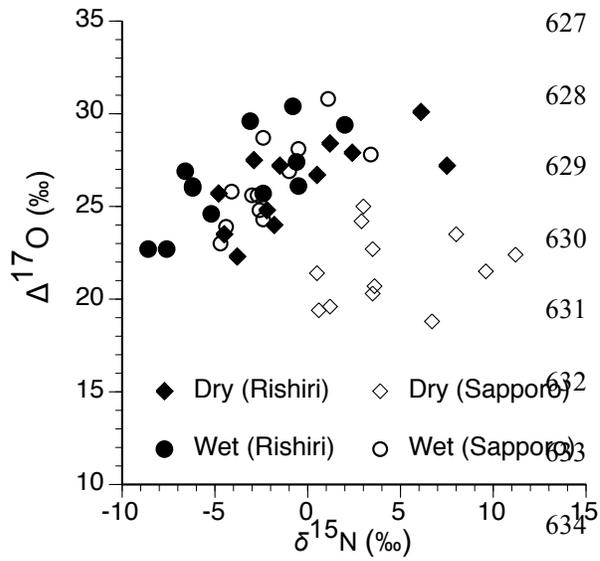
Figure 5. Correlation of $\delta^{15}N$ and $\Delta^{17}O$ values of nitrate in wet and dry deposition at Rishiri and Sapporo. Dry

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.