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**Tracing the fate of  
atmospheric nitrate  
deposited onto  
a forest ecosystem**

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# Tracing the fate of atmospheric nitrate deposited onto a forest ecosystem in eastern Asia using $\Delta^{17}\text{O}$

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## Abstract

The stable isotopic compositions of nitrate in precipitation (wet deposition) and ground-water (spring, lake, and stream water) were determined for the island of Rishiri, Japan, so as to use the  $^{17}\text{O}$  anomalies ( $\Delta^{17}\text{O}$ ) to trace the fate of atmospheric nitrate that had deposited onto the island ecosystem, which is a representative background forest ecosystem for eastern Asia. The deposited nitrate had large  $^{17}\text{O}$  anomalies with  $\Delta^{17}\text{O}$  values ranging from +20.8‰ to +34.5‰ ( $n=32$ ) with +26.2‰ being the annual average. The maximum  $\Delta^{17}\text{O}$  value of +34.5‰, obtained for precipitation on 23 to 24 February 2007, was an extraordinarily large value among values for all samples of precipitation. Most nitrate in the sample might have been produced through the heterogeneous reaction of  $\text{NO}_3$  radical with hydrocarbons in a highly polluted air mass that had been supplied from megacities on the eastern coast of the Asian continent. On the other hand, nitrate in groundwater had small  $\Delta^{17}\text{O}$  values ranging from +0.9‰ to 3.2‰ ( $n=19$ ), which corresponds to an average mixing ratio of atmospheric nitrate to total nitrate of 7%. Comparing the inflow and outflow of atmospheric nitrate in groundwater within the island, we estimated that the direct drainage accounts for  $10.5 \pm 5.2\%$  of atmospheric nitrate that has deposited on the island and that the residual portion has undergone biological processing before being exported from the forest ecosystem.

## 1 Introduction

Anthropogenic activities have increased emissions of fixed nitrogen from land to the atmosphere. The amount has almost doubled globally, with much greater increases in some regions, and this fixed-nitrogen flux is expected to again double by 2030 (Galloway et al., 2008). In particular, the increase in  $\text{NO}_x$  emissions in eastern Asia have been dramatic over the last decade (Akimoto, 2003; Zhang et al., 2007; Uno et al., 2007) owing to rapid growth in both industry and the number of automobiles. Most of the  $\text{NO}_x$  is transported eastward by the Asian monsoon and is deposited in the area

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of the western north Pacific, which includes Japan, as atmospheric nitrate ( $\text{NO}_3^-$ ) (Akimoto, 2003; Uno et al., 2007).

Excess fixed-nitrogen input is linked to various environmental problems such as forest decline (e.g. Fenn et al., 1998), degradation of groundwater quality (e.g. Murdoch and Stoddard, 1992; Williams et al., 1996), eutrophication of the hydrosphere (e.g. Paerl, 1997; Duce et al., 2008), and shifts in biodiversity (e.g. Tilman et al., 1996). Past detailed studies on forested catchments offered considerable insight into the link between the atmospheric deposition and the transport of nitrate to streams (Grennfelt and Hultberg, 1986; Williams et al., 1996; Tietema et al., 1998). Although water chemistry has been routinely measured through many programs on a regional to national scale, our understanding of the mechanisms that regulate the transport of atmospheric deposition to streams in forested ecosystems is still limited because the fate of atmospheric nitrate deposited onto a forest is complicated; the fate is determined through an interplay of several processes such as (1) dilution through nitrification, (2) uptake by plants or microbes, and (3) decomposition through denitrification.

The natural stable isotopic compositions of nitrate have been used to determine the sources of nitrate in natural stream/spring water systems (Burns and Kendall, 2002; Campbell et al., 2002; Durka et al., 1994; Ohte et al., 2004; Williard et al., 2001). In particular, the oxygen isotopic compositions of nitrate can be a useful tracer of  $\text{NO}_3^-$  because  $\text{NO}_3^-$  has distinctly larger  $\delta^{18}\text{O}$  values than does nitrate originating from microbial processing (i.e., nitrification) in forest soils (Durka et al., 1994), where  $\delta^{18}\text{O} = R_{\text{sample}}/R_{\text{standard}} - 1$  and  $R$  is the  $^{18}\text{O}/^{16}\text{O}$  ratio (or the  $^{17}\text{O}/^{16}\text{O}$  ratio in the case of  $\delta^{17}\text{O}$  or the  $^{15}\text{N}/^{14}\text{N}$  ratio in the case of  $\delta^{15}\text{N}$ ) of the sample and each international standard. However, it is not always straightforward to quantify  $\text{NO}_3^-$  in total nitrate pool applying the isotopic mass balance model for the  $\delta^{18}\text{O}$  or  $\delta^{15}\text{N}$  tracer, especially for those having mixing ratios of  $\text{NO}_3^-$  to total nitrate of less than 20%, because of the wide range of variation in  $\delta^{18}\text{O}$  (or  $\delta^{15}\text{N}$ ) values even within the representative sources of  $\text{NO}_3^-$  (e.g. Michalski et al., 2004). In addition, subsequent isotopic

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fractionation processes in soils, such as denitrification and/or uptake by plants or microbes, could alter  $\delta^{18}\text{O}$  values of nitrate, complicating their interpretation beyond that of the simple isotope mass balance approach.

To overcome the limitation in using the  $\delta^{18}\text{O}$  tracer, Michalski et al. (2004) applied  $\delta^{17}\text{O}$  of nitrate as an additional tracer of  $\text{NO}_3^-_{\text{atm}}$  in stream water in a complex semiarid ecosystem in southern California (USA).  $\delta^{17}\text{O}$  was used because remineralized nitrate ( $\text{NO}_3^-_{\text{re}}$ ), the oxygen atoms of which are derived from either terrestrial  $\text{O}_2$  or  $\text{H}_2\text{O}$  through nitrification, shows mass-dependent relative variations between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ , whereas  $\text{NO}_3^-_{\text{atm}}$  displays an anomalous enrichment in  $^{17}\text{O}$  reflecting oxygen atom transfers from ozone during the conversion of  $\text{NO}_x$  to  $\text{NO}_3^-_{\text{atm}}$  (Michalski et al., 2003). Using the  $\Delta^{17}\text{O}$  signature defined by the following equation (Miller, 2002; Kaiser et al., 2007), we can distinguish  $\text{NO}_3^-_{\text{atm}}$  ( $\Delta^{17}\text{O} > 0$ ) from the other nitrate ( $\text{NO}_3^-_{\text{re}}$ ) ( $\Delta^{17}\text{O} = 0$ ).

$$\Delta^{17}\text{O}_{\text{REF}}^{\text{X}} = \frac{1 + \delta^{17}\text{O}_{\text{REF}}^{\text{X}}}{\left(1 + \delta^{18}\text{O}_{\text{REF}}^{\text{X}}\right)^{\beta}} - 1, \quad (1)$$

where the constant  $\beta$  is 0.5247 (Miller, 2002; Kaiser et al., 2007). In addition,  $\Delta^{17}\text{O}$  is stable in mass-dependent isotope fractionation processes and so we can use  $\Delta^{17}\text{O}$  as a conserved tracer of  $\text{NO}_3^-_{\text{atm}}$  and trace  $\text{NO}_3^-_{\text{atm}}$  irrespective of partial removal through denitrification and/or uptake reaction subsequent to deposition.

In this study, we determined  $\Delta^{17}\text{O}$  values of nitrate in spring, lake, and stream water on the island of Rishiri (Japan) as those representing groundwater charged by natural forested watersheds on the surface, where atmospheric fixed-nitrogen input has been low; less than  $5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . Besides  $\Delta^{17}\text{O}$  values for groundwater, we determined values for precipitation (wet deposition) on the island for comparison. Using the  $\Delta^{17}\text{O}$  tracer, we quantified the fraction of  $\text{NO}_3^-_{\text{atm}}$  within the total nitrate output in groundwater to gain insight into the processes controlling the fate and transport of  $\text{NO}_3^-_{\text{atm}}$  deposited

on the forested watershed with small anthropogenic fixed-nitrogen input. The quantified  $\text{NO}_{3\text{atm}}^-$  output will be useful in future studies to evaluate the amounts of  $\text{NO}_{3\text{atm}}^-$  eluted from the region with different  $\text{NO}_{3\text{atm}}^-$  inputs, including the amount eluted by the same forested watershed in the case of probable elevated  $\text{NO}_{3\text{atm}}^-$  input in the future.

## 2 Experimental section

### 2.1 Site description

Rishiri (182.1 km<sup>2</sup>) is a circular island located in the north of the Japan islands (Fig. 1). A large part of the island is occupied by the lofty volcanic Mt. Rishiri (1721 m), which has a conical shape with gentle slopes and the most recent eruptions of which occurred at least several thousand years ago. Little volcanic activity, including fumaroles, can be observed at present.

One of the features of this island is that perennial streams are scarce on the surface. Instead, rain and snow-melt on the mountain, that have passed through the surface forest ecosystem without evaporation, penetrate into the rocky underground, travel downward along a horizontal slope of the subsurface hydraulic gradient as groundwater, and emerge around the shore area of the island as either terrestrial springs or submarine discharges, having a constant temperature of  $7 \pm 1^\circ\text{C}$  all year round (Yamaguchi, 1975; Yamaguchi and Ohara, 1971; Marui et al., 1999; Hayashi et al., 1999; Marui, 2003). The terrestrial springs also produce lakes and small streams around the shore area of the island. Using geochemical tracers such as tritium, chlorofluorocarbons, and  $\text{SF}_6$ , the mean residence time of the groundwater in the island is estimated to be 5 to 40 years (Asai et al., 2008).

Most of the island is designated as a national park of Japan (Rishiri-Rebun-Sarobetsu National Park), so local human activities have little impact on either the hydrology or vegetation of the island. Thus, we can evaluate the background fraction of  $\text{NO}_{3\text{atm}}^-$  within the total  $\text{NO}_3^-$  eluted from the normally forested watersheds

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from the groundwater of the island, which finally appears on the surface as spring, lake and/or stream water in shore areas. In addition, a monitoring observatory of the Acid Deposition Monitoring Network in East Asia (EANET) was established on the island in 2000 to quantify the acid deposition rate in background areas of eastern Asia (EANET, 2008; Noguchi et al., 2007). The monitoring has shown that the island received  $12.7 \text{ mmol NO}_3^- \text{ m}^{-2} \text{ yr}^{-1}$  and  $19.3 \text{ mmol NH}_4^+ \text{ m}^{-2} \text{ yr}^{-1}$  on average from 2000 to 2007 (EANET, 2008), which corresponds to a small total fixed-nitrogen deposition rate of  $4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ .

In addition, the vegetation on the island had been well recorded through extensive ecological studies performed in 1977, 1979 and 2003 (Haruki et al., 2004). The forest on the island comprises *Picea glehnii*, *P. jezoensis*, *Abies sachalinensis*, *Betula ermanii*, *Alnus maximowiczii* and *Pinus pumila*.

## 2.2 Sampling

Water samples were gathered from most of the major natural springs, lakes, and streams on the island (Table 1 and Fig. 1). After measuring both pH and conductivity, the samples were collected in clean polyethylene bottles in the field, rinsed at least twice with the sample itself, and then filtered through a pre-combusted Whatman GF/F filter ( $0.7 \mu\text{m}$  pore size) within two days of collection. In addition, commercial mineral drinking water taken from a well at a Meisui factory (site number 10 in Fig. 1), filtered through a  $0.2 \mu\text{m}$  filter, and bottled in polyethylene terephthalate (PET) bottles on different days from July 2007 to March 2009 were collected from markets in Sapporo (sample numbers 5–8; Table 1) and used as spring water samples on days when actual spring samples were not taken (Tsunogai and Wakita, 1995).

Samples of wet deposition were taken at the Rishiri National Acid Rain Monitoring Station (RIO; Tanimoto et al., 2000) located in the south of the island ( $45^\circ 7' 11'' \text{ N}$ ,  $141^\circ 12' 33'' \text{ E}$ ; Fig. 1) at 40 m above sea level using standard methods for evaluating acid deposition in Japan. An automatic wet deposition sampler (DRS-200, DKK) with a funnel (200 mm diameter) and a heater for melting snow deposition was used in

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the collection. All samples deposited on the funnel were introduced and stored within a polyethylene bottle (1 L) under refrigeration until daily recovery. After measuring both the conductivity and pH, the recovered samples were filtered through a 0.2  $\mu\text{m}$  pore-size membrane filter (Dismic-25CS, ADVANTEC) and stored in a refrigerator until analysis.

### 2.3 Analysis

The concentration of nitrate was determined by traditional ion chromatography (EANET, 2008). To determine the stable isotopic compositions, the sample  $\text{NO}_3^-$  was chemically converted to  $\text{N}_2\text{O}$  using a method originally developed for  $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$  isotope ratios of seawater and freshwater nitrate (McIlvin and Altabet, 2005) with slight modification (Tsunogai et al., 2008). In brief, the procedures are as follows.

15 mL sample solutions were pipetted into 20 mL clean screw-cap vials with butyl rubber septum caps. Then, 0.7 g of spongy cadmium was added, followed by 150  $\mu\text{L}$  of a 1 M  $\text{NaHCO}_3$  solution with a resultant pH of approximately 8.5. The samples were then shaken for 20–30 h on a horizontal shaker at a rate of 2 cycles/s. 10 mL quantities of the samples were then decanted into other clean 20 mL vials and capped tightly with Teflon-lined septum caps. After the evacuation of air in the head space and in the sample solution for 20 min via a needle, 0.4 mL of the azide/acetic acid buffer was added to each 20 mL vial via the needle and the mixture was shaken vigorously. Owing to the volatility and toxicity of  $\text{HN}_3$ , all the reactions were performed on an original automatic reaction line. In addition, all exhaust was vented via a fume hood. After 30 min, the solution was made basic by adding 0.2 mL of 6 M  $\text{NaOH}$  with a syringe and shaken to prevent residual  $\text{HN}_3$  escaping into the laboratory during subsequent isotope analysis.

The stable isotopic compositions of  $\text{N}_2\text{O}$  were determined using our Continuous-Flow Isotope Ratio Mass-Spectrometry (CF-IRMS) system (Tsunogai et al., 2008), which consists of an original helium purge and a trap line and a Finnigan MAT 252

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(Thermo Fisher Scientific, Waltham, MA, USA) with a modified Combustion III interface and Agilent 6890 gas chromatograph (Tsunogai et al., 2002, 2005). First, about 0.1 to 5 mL of head space gas in each vial was sampled in a gas-tight syringe and injected to a helium sparging line via an injection port (Ijiri et al., 2003), sent through a purification port packed with Ascarite II and magnesium percholate to remove both the CO<sub>2</sub> and residual H<sub>2</sub>O, and then gathered to a final stainless steel trap immersed in liquid nitrogen. After changing the flow path, the liquid nitrogen bath was then removed to introduce the sample into a PoraPLOT-Q analytical capillary column (0.32 mm i.d. ×50m) at a column oven temperature of +30°C, where the N<sub>2</sub>O was separated from any remaining CO<sub>2</sub>. The eluted N<sub>2</sub>O was carried continuously into a Finnigan MAT 252 isotope-ratio-monitoring mass spectrometer with a specially designed multi-collector system via an open split interface to monitor isotopologues of N<sub>2</sub>O<sup>+</sup> at *m/z* ratios of 44, 45, and 46 to determine δ<sup>45</sup> and δ<sup>46</sup>. Each analysis was calibrated with a machine-working reference gas (99.999% N<sub>2</sub>O gas in a cylinder) introduced to the mass spectrometer via an open split interface according to a defined schedule to correct for subdaily temporal variations in the mass spectrometry. In addition, a working-standard gas mixture containing N<sub>2</sub>O of known concentration (ca. 1000 ppm N<sub>2</sub>O in air), injected from a sampling loop attached to the sparging unit, was analyzed in the same way as for the samples at least once a day to correct for daily temporal variations in the mass spectrometry.

After the analyses based on the N<sub>2</sub>O<sup>+</sup> monitoring, another aliquot of head space was introduced in the same purge and trap line to determine Δ<sup>17</sup>O for N<sub>2</sub>O (Komatsu et al., 2008). Using the same procedures as those used in the N<sub>2</sub>O<sup>+</sup> monitoring mode, purified N<sub>2</sub>O, eluted from the PoraPLOT-Q analytical capillary column, was introduced into our original gold tube unit (Komatsu et al., 2008) held at 780°C for the thermal decomposition of N<sub>2</sub>O to N<sub>2</sub> and O<sub>2</sub>. The produced O<sub>2</sub>, purified from N<sub>2</sub> through separation using a MolSieve 5A PLOT column, was subjected to CF-IRMS to determine δ<sup>33</sup> and δ<sup>34</sup> by simultaneous monitoring of O<sub>2</sub><sup>+</sup> isotopologues at *m/z* ratios of 32, 33, and 34. Each analysis was calibrated with a machine-working reference gas (99.999%



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O<sub>2</sub> gas in a cylinder) introduced to the mass spectrometer via an open split interface according to a defined schedule to correct for subdaily temporal variations in the mass spectrometry. In addition, a working-standard gas mixture containing N<sub>2</sub>O of known concentration (ca. 1000 ppm N<sub>2</sub>O in air), injected from a sampling loop attached to the sparging unit, was analyzed in the same way as for the samples at least once a day to correct for daily temporal variations in the mass spectrometry.

To calibrate the  $\delta$  values of the sample NO<sub>3</sub><sup>-</sup> on an international scale, as well as to correct for both the isotope fractionation during the chemical conversion to N<sub>2</sub>O and the progress of the oxygen isotope exchange between the sample NO<sub>3</sub><sup>-</sup> and water (ca. 20%), the obtained values of the sample-derived N<sub>2</sub>O were compared with those of international standards. We used both USGS-34 ( $\delta^{15}\text{N} = -1.8\text{‰}_{\text{air}}$ ,  $\delta^{18}\text{O} = -27.93\text{‰}_{\text{VSMOW}}$ ,  $\Delta^{17}\text{O} = +0.04\text{‰}_{\text{VSMOW}}$ ) and USGS-35 ( $\delta^{15}\text{N} = +2.7\text{‰}_{\text{air}}$ ,  $\delta^{18}\text{O} = +57.5\text{‰}_{\text{VSMOW}}$ ,  $\Delta^{17}\text{O} = +20.88\text{‰}_{\text{VSMOW}}$ ), the internationally distributed isotope reference materials for NO<sub>3</sub><sup>-</sup>, for the primary isotopic scale normalization. In addition, three local laboratory standards that had been calibrated using the internationally distributed isotope reference materials, HDLW-00 ( $\delta^{15}\text{N} = -1.2\text{‰}_{\text{air}}$ ,  $\delta^{18}\text{O} = +22.4\text{‰}_{\text{VSMOW}}$ ), HDLW-02 (mixture KNO<sub>3</sub> of reagent grade KNO<sub>3</sub> and <sup>15</sup>N-enriched KNO<sub>3</sub>;  $\delta^{15}\text{N} = +11.8\text{‰}_{\text{air}}$ ,  $\delta^{18}\text{O} = +22.2\text{‰}_{\text{VSMOW}}$ ) and HDLW-01 ( $\delta^{15}\text{N} = -2.1\text{‰}_{\text{air}}$ ,  $\delta^{18}\text{O} = +1.1\text{‰}_{\text{VSMOW}}$ ), were also used for routine calibration purposes by measuring them in the same manner in which we measured the samples.

In calculating  $\delta^{15}\text{N}$  or  $\Delta^{17}\text{O}$ , the values were simply calibrated using calibration lines obtained from the measurements of N<sub>2</sub>O derived from the NO<sub>3</sub><sup>-</sup> standards. In the case of calculating  $\delta^{18}\text{O}$  for NO<sub>3</sub><sup>-</sup>, we additionally corrected for the oxygen exchange between the  $\delta^{18}\text{O}$  of NO<sub>3</sub><sup>-</sup> and water to consider the cases in which the  $\delta^{18}\text{O}$  of the water that dissolved the standards differed from the  $\delta^{18}\text{O}$  of the sample water. Thus, we used the following formula to correct for  $\delta^{18}\text{O}$ .

$$\delta^{18}\text{O}_{\text{nitrate}} = \frac{(\delta^{18}\text{O}_{\text{N}_2\text{O}} - b) - (1 - m) \times \Delta^{18}\text{O}_{\text{water}}}{m}, \quad (2)$$

where  $b$  is the intercept of the standards and  $m$  is the slope obtained using the standards and  $\Delta^{18}\text{O}_{\text{water}}$  is the  $\delta^{18}\text{O}$  difference between the sample water and standard water. All oxygen isotopic data are presented relative to VSMOW and have an error of  $\pm 0.5\%$  for  $\delta^{18}\text{O}$  and  $\pm 0.2\%$  for  $\Delta^{17}\text{O}$ . All nitrogen isotopic data are presented relative to air  $\text{N}_2$  and have an error of  $\pm 0.3\%$  for  $\delta^{15}\text{N}$ .

### 3 Results and discussion

#### 3.1 Atmospheric nitrate

The triple oxygen isotopic compositions ( $\Delta^{17}\text{O}$ ) of atmospheric nitrate ( $\text{NO}_3^-$ ) are plotted as a function of the sampling day (local time, +9:00 UT) in Fig. 2c, together with  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  in Fig. 2a and b. The figures shows large  $^{17}\text{O}$  anomalies with  $\Delta^{17}\text{O}$  values from +20.8‰ to +31.5‰, except for a sample taken from 23 to 24 February, 2007, which has an extraordinary large  $\Delta^{17}\text{O}$  value of +34.5‰ (shown by arrows in Fig. 2).

The observed  $\Delta^{17}\text{O}$  values of  $\text{NO}_3^-$  can be understood in terms of the transfer of the isotope anomaly from  $\text{O}_3$  to  $\text{NO}_3^-$  (Michalski et al., 2003). In addition, the observed temporal variations in the  $\Delta^{17}\text{O}$  values reflect variations in the atmospheric formation channels of  $\text{NO}_3^-$  from  $\text{NO}$  (Michalski et al., 2003; Morin et al., 2008). Regardless of the  $\text{NO}_x$  source,  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  is a direct function of the isotope anomaly of  $\text{O}_3$  having large  $\Delta^{17}\text{O}$  due to rapid photochemical recycling to  $\text{NO}$  (Michalski et al., 2003; Morin et al., 2008). During the  $\text{NO}_2$  oxidation to  $\text{NO}_3^-$ , an additional oxygen atom is incorporated from various source molecules depending on the  $\text{NO}_2$  oxidation channel (Michalski et al., 2003; Morin et al., 2008), which results in a characteristic  $\Delta^{17}\text{O}$  value of  $\text{NO}_3^-$ . Within the  $\text{NO}_2$  oxidation channels, the reaction with  $\text{OH}$  produces  $\text{NO}_3^-$  with  $\Delta^{17}\text{O}$  values around +17‰ at mid-latitude (Michalski et al., 2003; Morin et al., 2008, 2009). On the other hand, the reaction of  $\text{NO}_2$  with  $\text{O}_3$  produces

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$\text{NO}_{3\text{atm}}^-$  with larger  $\Delta^{17}\text{O}$  values (Michalski et al., 2003; Morin et al., 2008, 2009) by once yielding the  $\text{NO}_3$  radical at night, which then reacts with hydrocarbons to give  $\text{NO}_{3\text{atm}}^-$  with  $\Delta^{17}\text{O}$  around +35‰ at mid-latitude (Morin et al., 2009) or with  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$ , the hydrolysis of which forms  $\text{NO}_{3\text{atm}}^-$  with  $\Delta^{17}\text{O}$  around +29‰ at mid-latitude (Morin et al., 2009).

On the basis of both the temporal variation in the depositional flux of  $\text{NO}_{3\text{atm}}^-$  and the  $\Delta^{17}\text{O}$  value, we estimated the annually averaged  $\Delta^{17}\text{O}$  of  $\text{NO}_{3\text{atm}}^-$  ( $\Delta^{17}\text{O}_{\text{avg}}$ ) deposited on the island as +26.2‰ using

$$\Delta^{17}\text{O}_{\text{avg}} = \frac{\sum_i (C_i \times V_i \times \Delta^{17}\text{O}_i)}{\sum_i (C_i \times V_i)}, \quad (3)$$

where  $C_i$  denotes the concentration of nitrate in each wet deposition sample and  $V_i$  denotes the total water volume of each wet deposition sample. Substituting  $\Delta^{17}\text{O}$  with  $\delta^{15}\text{N}$  (or  $\delta^{18}\text{O}$ ) in the Eq. (3), we estimated  $\delta^{15}\text{N}_{\text{avg}}$  as  $-1.1\text{‰}_{\text{air}}$  and  $\delta^{18}\text{O}_{\text{avg}}$  as  $+87.1\text{‰}_{\text{VSMOW}}$ .

The annual average  $\Delta^{17}\text{O}$  coincided well with annual average  $\Delta^{17}\text{O}$  values of  $\text{NO}_{3\text{atm}}^-$  reported for mid-latitudes, such as at La Jolla (33° N; Michalski et al., 2003) and Princeton (40° N; Kaiser et al., 2007). In addition, the annual average  $\delta^{18}\text{O}$  values of  $\text{NO}_{3\text{atm}}^-$  were in reasonable agreement with those reported recently for nitrate in deposition (+60 to +95‰ by Michalski et al., 2004; +60 to +90‰ by Morin et al., 2009). Furthermore, the seasonal variations in  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  coincided well with those reported. In summer, the reaction between OH and  $\text{NO}_2$  is the main  $\text{NO}_x$  oxidation channel. In contrast, the reaction of  $\text{NO}_2$  with  $\text{O}_3$  becomes relatively important for the production of  $\text{NO}_{3\text{atm}}^-$  in winter. While past reports on  $\Delta^{17}\text{O}$  of  $\text{NO}_{3\text{atm}}^-$  have been limited to the United States (Michalski et al., 2003, 2004), Europe (Kaiser et al., 2007), and the Atlantic Ocean (Morin et al., 2009) at mid-latitudes, the correspondence further supports that  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_{3\text{atm}}^-$  are determined by  $\text{NO}_x$  oxidation channels that

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shift depending on the season and oxidant species; for example, shifts in oxidation chemistry (an increased importance of  $\text{N}_2\text{O}_5$  hydrolysis in winter) that vary with sunlight, temperature, and oxidant levels but not with  $\text{NO}_x$  sources. The average  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  is substantially higher than values resulting from the reaction between OH and  $\text{NO}_2$  (+17‰; Morin et al., 2009). Therefore, the reaction between OH and  $\text{NO}_2$  cannot be the only channel from  $\text{NO}_2$  to  $\text{NO}_3^-$ , including that deposited in eastern Asia.

Among the  $\Delta^{17}\text{O}$  data of nitrate in wet deposition, an extraordinarily large  $\Delta^{17}\text{O}$  value was obtained from 23 to 24 February 2007 (LT), as indicated by arrows in Fig. 2. It is difficult to produce  $\text{NO}_3^-$  with such a  $\Delta^{17}\text{O}$  value (+34.5‰) through usual  $\text{NO}_2$  oxidation reaction channels such as the reaction between OH and  $\text{NO}_2$  or  $\text{N}_2\text{O}_5$  hydrolysis. Rather, the elevated  $\Delta^{17}\text{O}$  value implies that the  $\text{NO}_3^-$  is primarily produced directly from  $\text{NO}_3$  radical without dilution in the  $\text{O}_3$ -derived oxygen atoms, through the H abstraction from hydrocarbons by the  $\text{NO}_3$  radical.

To test this hypothesis, we compared the  $\Delta^{17}\text{O}$  results with the other components monitored successively at the Rishiri National Acid Rain Monitoring Station and found an episodic contribution of highly polluted air-mass from 22 to 23 February until the beginning of the precipitation in which the extraordinarily large  $\Delta^{17}\text{O}$  value was detected (Fig. 3). The polluted air was characterized by significant enrichments in  $\text{SO}_2$  (6 ppbv),  $\text{NO}_2$  (6 ppbv),  $\text{O}_3$  (65 ppbv), and  $\text{PM}_{10}$  ( $100 \mu\text{g}/\text{m}^3$ ) while concentrations in background air were 1 ppbv, 1 ppbv, 40 ppbv, and  $15 \mu\text{g}/\text{m}^3$ , respectively in the observatory (Fig. 3). The backward trajectory analyses of air parcels (Fig. 4; Zeng et al., 2003) suggest that the polluted air was derived from the megacities on the eastern coast of Asia at latitudes of 35 to 40° N (Fig. 4), where air pollution is significant (e.g. Guttikunda et al., 2005). The observed large  $\Delta^{17}\text{O}$  values of  $\text{NO}_3^-$  suggest an elevated role for the reaction of  $\text{NO}_3$  radical with hydrocarbons in the polluted air mass to produce  $\text{NO}_3^-$ , possibly owing to the large surface area of aerosols within the polluted air mass. The  $\text{NO}_3^-$  production channel involving the H abstraction from hydrocarbons by the  $\text{NO}_3$  radical is not a significant source of  $\text{NO}_3^-$  in the troposphere

(e.g. Michalski et al., 2003; Alexander et al., 2009). The present result implies that a future increase in air pollution could increase the importance of the heterogeneous reaction of  $\text{NO}_3$  with hydrocarbons to produce  $\text{NO}_3^-_{\text{atm}}$ .

### 3.2 Groundwater nitrate

The concentrations and  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  values of nitrate in the samples of spring, lake, and stream water are presented in Table 1, together with their temperature, pH and conductivity. We could not determine  $\Delta^{17}\text{O}$  values of nitrate for two of the three lake water samples (Nos. 17 and 18) owing to nitrate depletion in the samples, probably due to nitrate uptake (assimilation) by phytoplankton in the lakes during stasis of seeping water in the lake. In addition, we could not determine  $\Delta^{17}\text{O}$  of nitrate for a spring water sample (No. 11) owing to nitrate depletion in the samples, probably due to denitrification in and/or around the well. The rest of the samples had nitrate concentrations of more than  $5\ \mu\text{M}$ , and the temperature and conductivity were similar to values of representative groundwater within the island ( $7 \pm 1^\circ\text{C}$  and  $100 \pm 20\ \mu\text{S}/\text{cm}$ ) (Yamaguchi and Ohara, 1971; Hayashi et al., 1999). In further discussions to evaluate the interaction of  $\text{NO}_3^-_{\text{atm}}$  with the forest ecosystem on the island based on nitrate in groundwater, we use the data for the spring, lake, and stream water samples except for Nos. 11, 17, and 18 to represent the groundwater of the island.

The  $\Delta^{17}\text{O}$  data of samples taken at the same site (sample numbers 1 and 2, and from 4 to 8) on different days coincided well, within the analytical precision. We concluded that the hydrological system including the nitrogen cycle was stable on the island under a steady state condition and that the data obtained represented long-range mean values (at least of annual range) for groundwater within the island. The fairly long residence times of 5 to 40 years for the groundwater within the island (Asai et al., 2008) also supports this conclusion.

All the groundwater samples in this study had small but positive  $\Delta^{17}\text{O}$  values ranging from +0.9 to +3.2‰. The groundwater within the island contained  $\text{NO}_3^-_{\text{atm}}$  to some

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extent. Using the  $\Delta^{17}\text{O}$  data of nitrate in each sample, we estimated the mixing ratio of  $\text{NO}_{3\text{atm}}^-$  to total  $\text{NO}_3^-$  ( $\text{NO}_{3\text{total}}^-$ ) in the groundwater to be 7% on average, with a range from 3.4 to 12.2%, applying the equation

$$\frac{[\text{NO}_{3\text{atm}}^-]}{[\text{NO}_{3\text{total}}^-]} = \frac{\Delta^{17}\text{O}}{\Delta^{17}\text{O}_{\text{avg}}}, \quad (4)$$

5 where  $[\text{NO}_{3\text{atm}}^-]/[\text{NO}_{3\text{total}}^-]$  is the mixing ratio of  $\text{NO}_{3\text{atm}}^-$  to  $\text{NO}_{3\text{total}}^-$  and  $\Delta^{17}\text{O}_{\text{avg}}$  denotes the average  $\Delta^{17}\text{O}$  value of  $\text{NO}_{3\text{atm}}^-$  estimated in the previous section (+26.2‰).

We conclude that only 7% of the total nitrate in groundwater originates directly from the atmosphere on average, and so the substantial remainder of nitrate is of rem-

10 mineralized origin ( $\text{NO}_{3\text{re}}^-$ ) and has been produced through biological processing in soil. The mixing ratios estimated from  $\text{NO}_{3\text{atm}}^-$  in the groundwater coincide well with those estimated from basic stream flows (3.1 to 7.7%) and soil extracts (1.9 to 11.4%) in southern California using  $\Delta^{17}\text{O}$  in a past study (Michalski et al., 2004), except during storms. We conclude that the mixing ratios can be considered as representative mixing ratios of  $\text{NO}_{3\text{atm}}^-$  in natural  $\text{NO}_3^-$  eluted from usual forest ecosystems.

15 To discuss the processes regulating the mixing ratios of  $\text{NO}_{3\text{atm}}^-$ , the absolute concentration of  $\text{NO}_{3\text{atm}}^-$  in each sample ( $[\text{NO}_{3\text{atm}}^-]$ ) was calculated using each nitrate concentration ( $[\text{NO}_{3\text{total}}^-]$ ) and each  $\Delta^{17}\text{O}$  value and employing Eq. (4). The calculated  $[\text{NO}_{3\text{atm}}^-]$  is plotted as a function of  $[\text{NO}_{3\text{total}}^-]$  for the samples in Fig. 5.

20 While  $[\text{NO}_{3\text{total}}^-]$  varied widely from 7.6 to 35.5  $\mu\text{M}$ ,  $[\text{NO}_{3\text{atm}}^-]$  was almost uniform for the samples around 1.4  $\mu\text{M}$  on average, ranging from 0.7 to 2.9  $\mu\text{M}$ . We conclude that  $\text{NO}_{3\text{atm}}^-$  concentrations were almost uniform within the groundwater of the island while the observed variation in the total  $\text{NO}_3^-$  concentration is primarily due to different contributions of  $\text{NO}_{3\text{re}}^-$ . That is, additional contributions of  $\text{NO}_{3\text{re}}^-$  during groundwater flow through the ground were responsible for the observed differences in total  $\text{NO}_3^-$

25 among the surface water samples. In addition, the present results suggest that all

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spring water samples contained almost the same level of  $\text{NO}_3^-$  irrespective of the recharge area on the island. The  $\text{NO}_3^-$  concentration might represent the lowest limit for the forest ecosystem to uptake atmospheric nitrate.

### 3.3 Post-depositional processes

While the  $\Delta^{17}\text{O}$  values of nitrate are not affected by post-depositional processes such as partial removal through nitrate uptake or denitrification, the  $\delta^{18}\text{O}$  values of nitrate vary through isotopic fractionation during post-depositional processes within the forest ecosystem. To evaluate the extent of fractionation, the  $\delta^{18}\text{O}$  of groundwater is plotted as a function of  $\Delta^{17}\text{O}$  (Fig. 6). There is a linear correlation with  $r^2=0.63$ . By extrapolating the least-square-fitted line to the region of  $\text{NO}_3^-$  having  $\Delta^{17}\text{O}=+26.2\text{‰}$ , we obtain  $\delta^{18}\text{O}=+80\pm 26\text{‰}$ , which corresponds to values for  $\text{NO}_3^-$  (+87.1‰), in the island. We conclude the  $\delta^{18}\text{O}$  values primarily reflect the contribution of  $\text{NO}_3^-$  as well. While the  $\delta^{18}\text{O}$  values vary through isotopic fractionation during post-depositional processing such as partial removal through assimilation or denitrification, the range of variation was small on the island. The result is somewhat different from that obtained in a previous study conducted in southern California, where there was no clear linear correlation between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for stream nitrate (Michalski et al., 2004). Each forest ecosystem has its different characteristics for post-depositional processes and we can evaluate the extent from the dispersion in the  $\Delta^{17}\text{O}-\delta^{18}\text{O}$  plot.

On the other hand, we can obtain the  $\delta^{18}\text{O}$  value of  $-4.2\pm 2.4\text{‰}_{\text{VSMOW}}$  as the intercept ( $\Delta^{17}\text{O}=0$ ) of the plot in Fig. 6. The value corresponds to the average  $\delta^{18}\text{O}$  value of remineralized nitrate produced through nitrification in the forest ecosystem. The remineralized nitrate in the marine environment has  $\delta^{18}\text{O}$  values similar to that of ambient water (sea water) of close to  $0\text{‰}_{\text{VSMOW}}$  owing to the exchange of oxygen atoms between nitrification intermediates and the ambient water during nitrification (Casciotti et al., 2002). On the contrary, the present results suggest that the remineralized nitrate have  $\delta^{18}\text{O}$  values substantially larger than those of the groundwater

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( $\delta^{18}\text{O} = -13 \pm 1\text{‰}_{\text{VSMOW}}$ ) within the island, probably owing to the contribution of oxygen atoms from oxygen molecules ( $\text{O}_2$ ) having  $\delta^{18}\text{O}$  values of  $+23.5\text{‰}_{\text{VSMOW}}$  or more during nitrification in the forest soil. The exchange of oxygen atoms between nitrification intermediates and the ambient water is limited by some environmental conditions (Kool et al., 2007).

### 3.4 Removal flux of atmospheric nitrate through the forest ecosystem

Yamaguchi et al. (1975) estimated that  $1.68 \times 10^8 \text{ m}^3$  of groundwater emerges around the shore area of the island as either terrestrial springs or submarine discharges on the basis of an extensive hydrological survey on the water cycle of the island. Our present  $\Delta^{17}\text{O}$  results show that the spring water on Rishiri contains  $1.4 \pm 0.7 \mu\text{M}$  of  $\text{NO}_3^-$  on average (Fig. 5 and Table 1). Assuming the same average  $\text{NO}_3^-$  content for all the springs on the island irrespective of whether they are terrestrial or submarine, we can estimate the direct drainage flux of  $\text{NO}_3^-$  through the forest ecosystem on Rishiri to be  $2.4 \pm 1.2 \times 10^5 \text{ molyr}^{-1}$ .

On the other hand, the Rishiri National Acid Rain Monitoring Station quantified the annual deposition rate of  $\text{NO}_3^-$  as  $12.7 \text{ mmolm}^{-2}\text{yr}^{-1}$  (average total deposition rate from 2000 to 2007), which corresponds to a total deposition rate of  $\text{NO}_3^-$  of  $2.3 \times 10^6 \text{ molyr}^{-1}$  on the island (EANET, 2008). Thus, the direct drainage of  $\text{NO}_3^-$  through the forest ecosystem on Rishiri corresponds to  $10.5 \pm 5.2\%$  ( $1.3 \pm 0.7 \text{ mmolm}^{-2}\text{yr}^{-1}$ ) of the total  $\text{NO}_3^-$  that deposited onto the island, and the residual nitrate (ca. 90% or ca.  $11 \text{ mmolm}^{-2}\text{yr}^{-1}$ ) was removed by plants or microbes before being exported from the forest ecosystem into the groundwater.

The present estimation did not include the increasing depositional flux of  $\text{NO}_3^-$  in eastern Asia. Because the residence times were from 5 to 40 years for the groundwater within the island, the direct drainage ratio could be the minimum value since the deposition rate could be less on days when  $\text{NO}_3^-$  in spring water was deposited

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(Akimoto, 2003). The depositional flux of fixed nitrogen on Rishiri ( $4.5 \text{ kgNha}^{-1} \text{ yr}^{-1}$ ), however, is still one of the lowermost depositional fluxes in the area around the Japan islands (EANET, 2008). In addition, the Rishiri National Acid Rain Monitoring Station found little evidence for an increasing trend in the nitrate deposition rate from 2000 to 2007. Thus, we considered that the discrepancy is small, less than 20% difference from the depositional flux used in our estimation, and thus omitted the variation in the depositional flux in our estimation.

By adding  $^{15}\text{N}$ -labeled nitrogen ( $^{15}\text{NH}_4^{15}\text{NO}_3$  or  $\text{Na}^{15}\text{NO}_3$ ) for a duration of 9 to 12 months in European coniferous forest ecosystems, Tietema et al. (1998) found drainage losses of fixed nitrogen increased as a function of the fixed-nitrogen input. They estimated the drainage accounts for 2 to 35% of the total fixed-nitrogen input under a fixed-nitrogen input condition of less than  $30 \text{ kgNha}^{-1} \text{ yr}^{-1}$ . The estimated direct drainage of  $\text{NO}_3^-$  through the forest ecosystem on Rishiri corresponds to the lower region of the variation range estimated using  $^{15}\text{N}$  tracer. When using  $^{15}\text{N}$  tracer, direct drainage could be overestimated for the portion of secondary elution of  $^{15}\text{NO}_3^-$  that was once assimilated to organic nitrogen. Thus, we believe that our present value is a more reliable estimate for the direct drainage of  $\text{NO}_3^-$  under a low fixed-nitrogen input condition of less than  $5 \text{ kgNha}^{-1} \text{ yr}^{-1}$ .

#### 4 Conclusions

Nitrate in groundwater of Rishiri had the  $\Delta^{17}\text{O}$  values ranging from +0.9‰ to 3.2‰ ( $n=19$ ), which corresponds to an average mixing ratio of atmospheric nitrate to total nitrate of 7%. Comparing the inflow and outflow of atmospheric nitrate in groundwater within the island, we estimated that the direct drainage accounts for  $10.5 \pm 5.2\%$  of atmospheric nitrate that has deposited on the island and that the residual portion has undergone biological processing before being exported from the forest ecosystem. The present estimation is a more reliable estimate for the direct drainage of  $\text{NO}_3^-$  under

a low fixed-nitrogen input condition of less than  $5 \text{ kgNha}^{-1} \text{ yr}^{-1}$ .

This study clearly demonstrates that  $\Delta^{17}\text{O}$  can be a powerful tracer of the fate of  $\text{NO}_3^-$  deposited onto a forest ecosystem including those having small fixed-nitrogen input. By measuring  $\Delta^{17}\text{O}$  data of nitrate for water eluted from various forested watersheds, we can increase our understanding of fixed-nitrogen processing and fixed-nitrogen retention efficiencies for forested ecosystems that are subjected to atmospheric fixed-nitrogen deposition.

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**Table 1.** Concentration and stable isotopic compositions ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$ ) of nitrate dissolved in water samples taken at springs, lakes, and streams on Rishiri, together with related parameters.

Spl. No.	Site name	Site No. <sup>a</sup>	Date	Temp °C	pH	EC $\mu\text{S}/\text{cm}$	$\text{NO}_3^- \mu\text{M}$	$\delta^{15}\text{N} \text{‰}$	$\delta^{18}\text{O} \text{‰}$	$\Delta^{17}\text{O} \text{‰}$
spring										
1	Reihou sp.	20	27 Sep 07	6.7	6.5	123	20.4	-3.8	+1.0	+1.0
2	ibid.	20	28 Sep 07	-	-	-	19.6	-	-	<sup>c</sup> +0.9
3	Kiyokawa PS	17	28 Sep 07	6.0	7	81	17.9	-1.4	+0.4	+1.8
4	Meisui factory	10	28 Sep 07	6.8	7.1	77	29.8	-1.9	+3.6	+2.6
5 <sup>b</sup>	ibid.	10	Jul 07	-	-	-	28.7	-1.3	+4.2	+2.3
6 <sup>b</sup>	ibid.	10	Oct 08	-	-	-	28.2	-3.0	+3.7	+2.7
7 <sup>b</sup>	ibid.	10	Jan 09	-	-	-	30.7	-1.6	+2.7	+2.5
8 <sup>b</sup>	ibid.	10	Mar 09	-	-	-	30.1	-2.3	+3.1	+2.2
9	Sagidomari PS	8	28 Sep 07	5.7	7.1	73	35.5	-0.7	+1.3	+1.4
10	Kanro sp.	1	28 Sep 07	6.4	6.9	97	9.7	+0.5	+5.2	+2.0
11	Choujyu sp.	2	28 Sep 07	8.0	7.2	345	0.1	+9.3	+17.6	-
12	Himenuma sp.	6	28 Sep 07	7.0	6.8	116	9.1	+0.8	+7.2	+3.2
13	Ochiushinai	11	29 Sep 07	6.2	6.7	88	17.6	-1.7	+5.2	+3.2
14	Nishindomari sp.	13	30 Sep 07	6.5	7.0	89	7.6	+0.4	+5.0	+3.0
15	Fuyobashi-jo sp.	7	30 Sep 07	6.7	6.9	102	16.9	+0.4	+2.8	+2.1
lake										
16	Kiyokawa PS	17	28 Sep 07	-	-	-	23.2	-1.7	+1.6	+1.9
17	lake Himenuma	6	28 Sep 07	12.0	7.4	76	0.1	+0.8	+18.8	-
18	lake Otadomari	19	29 Sep 07	13.9	5.8	112	0.2	+4.5	+45.0	-
stream										
19	Kokusei br.	14	30 Sep 07	8.1	7.0	83	21.4	+1.1	+2.0	+2.3
20	Yusui river	15	30 Sep 07	7.9	7.2	86	14.3	-2.6	+1.6	+2.3
21	Yamunai river	18	30 Sep 07	7.7	6.9	103	17.3	-4.0	-0.2	+2.1
22	Osatsunai river	16	30 Sep 07	8.0	6.2	101	18.4	+4.6	-0.7	+1.3
23	Minamisawa	12	30 Sep 07	9.1	6.5	90	9.8	+3.7	+0.2	+1.3
24	Ichinosawa br.	5	30 Sep 07	7.6	7.1	118	9.1	-1.1	+0.4	+1.4
25	Notsuka br.	9	30 Sep 07	8.5	7.2	97	14.8	-1.6	+0.3	+1.6
26	Aioi br.	3	30 Sep 07	10.0	7.1	87	9.8	+0.2	+2.8	+1.4
25	Yunagi br.	4	30 Sep 07	7.7	7.1	91	12.7	-1.7	-1.6	+1.4

- : not determined. <sup>a</sup> location of each site is presented in Fig. 1. <sup>b</sup> bottled mineral water (drinking water) manufactured at the factory. <sup>c</sup> calculated assuming the same  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values as for sample No. 1. EC: conductivity

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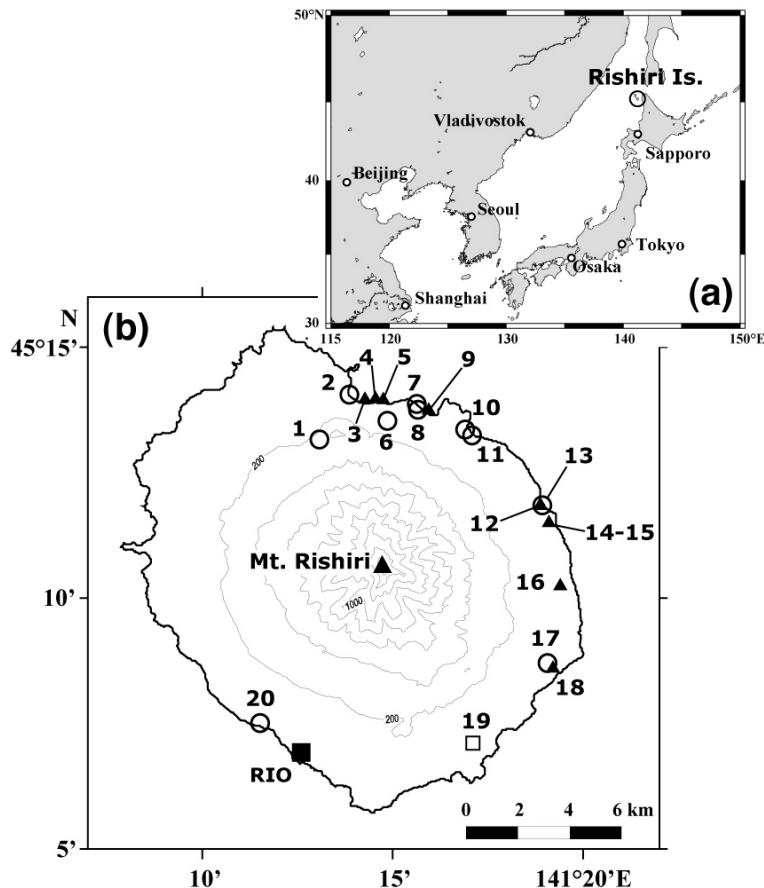
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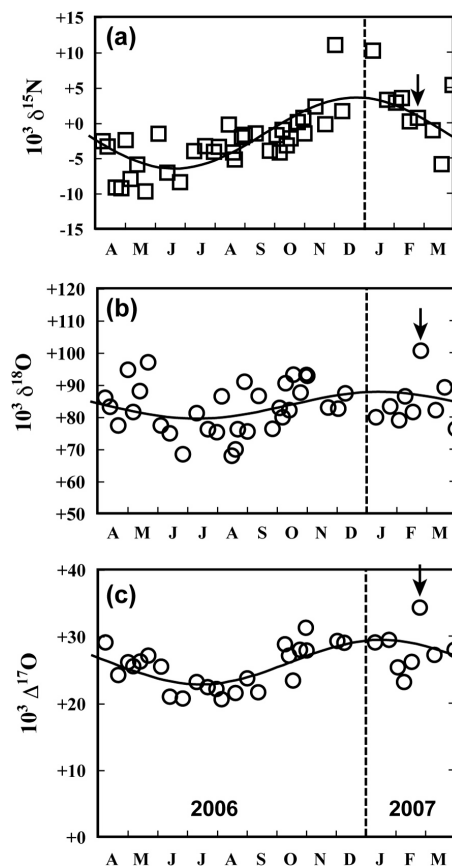
**Fig. 1.** Maps showing the island of Rishiri in eastern Asia (a) and the sampling stations of spring water (white circles), lake water (white square), and stream water (black triangles) on the island, together with the Rishiri National Acid Rain Monitoring Station (RIO; black square) (b). The numbers in the figure correspond to the site numbers in Table 1.

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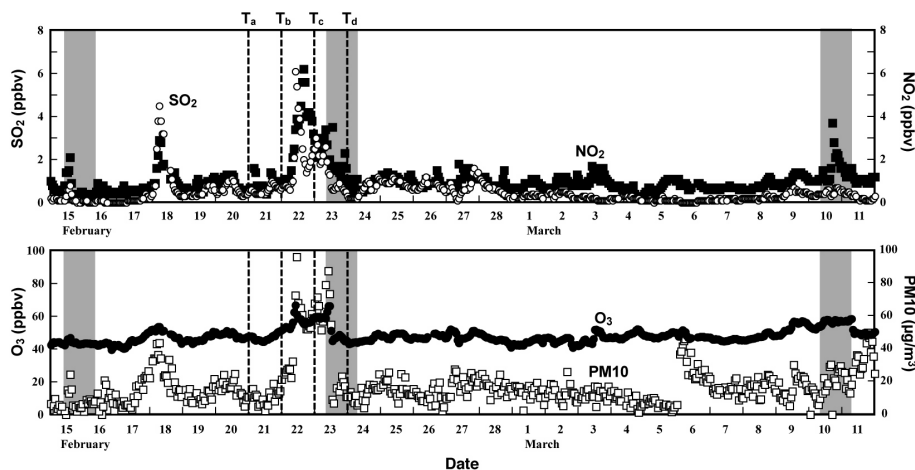


**Fig. 2.** Temporal variations in the values of  $\delta^{15}\text{N}$  (a),  $\delta^{18}\text{O}$  (b), and  $\Delta^{17}\text{O}$  (c) of nitrate in wet deposition recorded at the Rishiri National Acid Rain Monitoring Station. The curved lines are sinusoidal curves fitting the data assuming annual periodicity (determined using unweighted least squares). The arrows indicate sampling from 23 to 24 February 2007 (LT).

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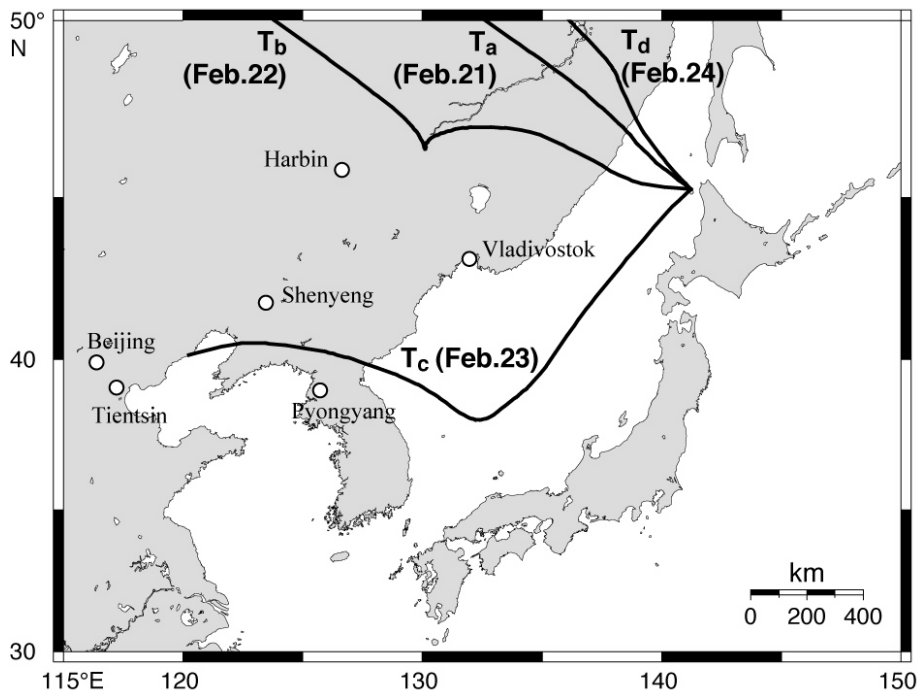


**Fig. 3.** Temporal variations in the atmospheric components monitored at the Rishiri National Acid Rain Monitoring Station ( $\text{SO}_2$ : white circles,  $\text{NO}_2$ : black squares, ozone: black circles,  $\text{PM}_{10}$ : white squares), together with the sampling durations of wet deposition analyzed in this study (grey zones). The dotted lines ( $T_a$ ,  $T_b$ ,  $T_c$ , and  $T_d$ ) denote the initial points of backward trajectory calculated in this study (Fig. 4).

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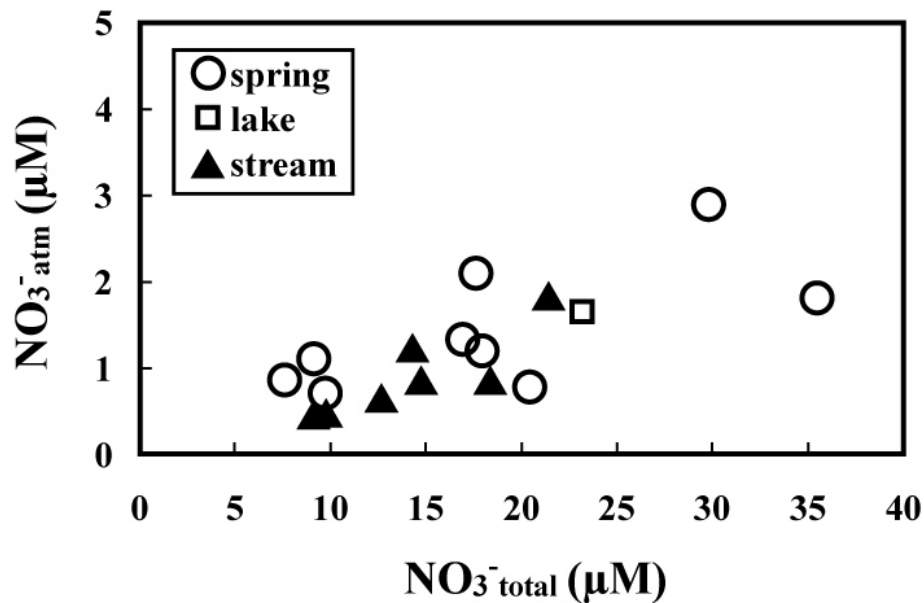


**Fig. 4.** The backward trajectory (3 days) of the air parcel reaching Rishiri at 00:00 a.m. on 23 February 2007 LT (UT+09:00), together with those reaching Rishiri on 21, 22, and 24 February 2007, calculated using METEX software (<http://db.cger.nies.go.jp/metex/index.html>) and NCEP datasets.

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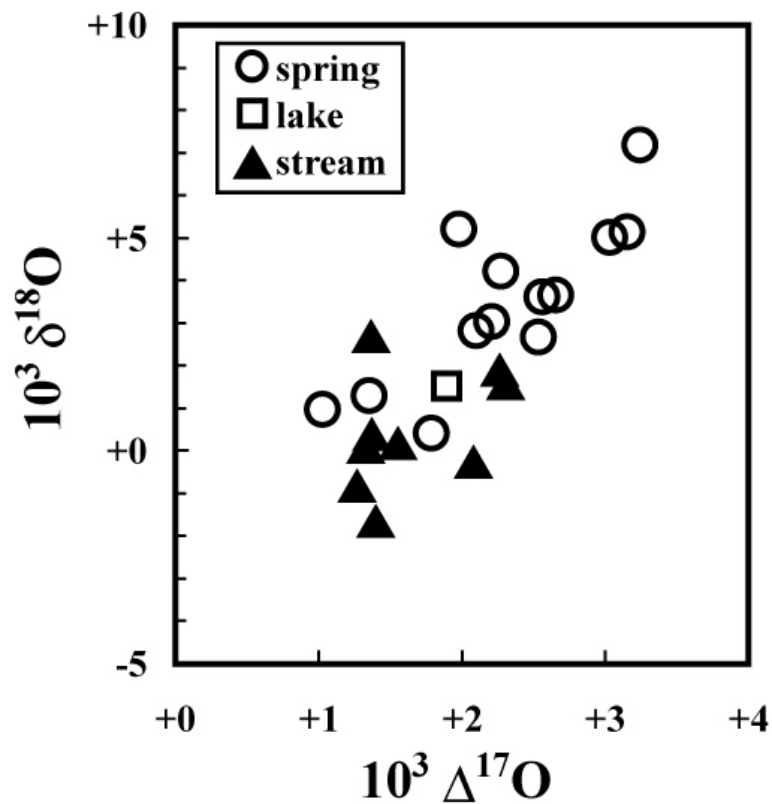


**Fig. 5.** Calculated concentration of atmospheric  $\text{NO}_3^-$  ( $\text{NO}_3^-_{\text{atm}}$ ) in each sample of spring (white circles), lake (white square), and stream (black triangles) water plotted as a function of the total  $\text{NO}_3^-$  concentration ( $\text{NO}_3^-_{\text{total}}$ ).

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**Fig. 6.** Relation between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$  from spring (white circles), lake (white square), and stream (black triangles) water. The symbols are the same as those in Fig. 5.

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