



Tracing atmospheric nitrate in groundwater using triple oxygen isotopes: evaluation based on bottled drinking water

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Abstract. The stable isotopic compositions of nitrate dissolved in 49 brands of bottled drinking water collected worldwide were measured, to trace the fate of atmospheric nitrate ($\text{NO}_{3\text{atm}}^-$) that had been deposited into subaerial ecosystems, using the ^{17}O anomalies ($\Delta^{17}\text{O}$) of nitrate as tracers. The use of bottled water enables collection of groundwater recharged at natural, background watersheds. The nitrate in groundwater had small $\Delta^{17}\text{O}$ values ranging from -0.2‰ to $+4.5\text{‰}$ ($n = 49$). The average $\Delta^{17}\text{O}$ value and average mixing ratio of atmospheric nitrate to total nitrate in the groundwater samples were estimated to be 0.8‰ and 3.1% , respectively. These findings indicated that the majority of atmospheric nitrate had undergone biological processing before being exported from the surface ecosystem to the groundwater. Moreover, the concentrations of atmospheric nitrate were estimated to range from less than $0.1\ \mu\text{molL}^{-1}$ to $8.5\ \mu\text{molL}^{-1}$, with higher $\text{NO}_{3\text{atm}}^-$ concentrations being obtained for those recharged in rocky, arid or elevated areas with little vegetation and lower $\text{NO}_{3\text{atm}}^-$ concentrations being obtained for those recharged in forested areas with high levels of vegetation. Additionally, many of the $\text{NO}_{3\text{atm}}^-$ -depleted samples were characterized by elevated $\delta^{15}\text{N}$ values of more than $+10\text{‰}$. Uptake by plants and/or microbes in forested soils subsequent to deposition and the progress of denitrification within groundwater likely plays a significant role in the removal of $\text{NO}_{3\text{atm}}^-$.

1 Introduction

Anthropogenic activities have increased emissions of fixed nitrogen from land to the atmosphere. Indeed, the amount of these emissions has almost doubled globally, with much greater increases being observed in some regions, and this fixed-nitrogen flux is expected to double again by 2030 (Galloway et al., 2008). Excess fixed-nitrogen input is linked to various environmental problems, including 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).

Previous detailed studies of forested catchments have offered considerable insight into the link between atmospheric nitrate deposition and nitrate discharge to streams (Grennfelt and Hultberg, 1986; Williams et al., 1996; Tietema et al., 1998; Durka et al., 1994). Although water chemistry has been routinely measured through many programs on regional to international scales, our understanding of the mechanisms that regulate the discharge of atmospheric deposition from surface ecosystems is still limited. This is because the fate of atmospheric nitrate deposited onto the subaerial ecosystem is determined through the complicated interplay of several processes that include (1) dilution through nitrification, (2) uptake by plants or microbes, and (3) decomposition through denitrification.

In a previous study, we determined the ^{17}O anomalies of nitrate in groundwater recharged on the island of Rishiri, Japan to trace the fate of atmospheric nitrate ($\text{NO}_{3\text{atm}}^-$) that had been deposited onto and passed through the island

ecosystem. In that study, we estimated the average mixing ratio of atmospheric nitrate to total nitrate in the groundwater to be 7 % (Tsunogai et al., 2010). Based on this mixing ratio, we estimated that direct drainage accounts for 10.5 ± 5.2 % of atmospheric nitrate that has been deposited onto the island, and that the residual portion has undergone biological processing before being exported from the island ecosystem at the groundwater recharge zones.

Anomalies in ^{17}O can be quantified using the $\Delta^{17}\text{O}$ signature, which is defined by the following equation (Miller, 2002; Kaiser et al., 2007):

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

where β is 0.5247 (Miller, 2002; Kaiser et al., 2007), $\delta^{18}\text{O} = R_{\text{sample}}/R_{\text{standard}} - 1$ 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. By using the $\Delta^{17}\text{O}$ values of nitrate, we can distinguish $\text{NO}_3^-_{\text{atm}}$ ($\Delta^{17}\text{O} > 0$) from the remineralized nitrate ($\text{NO}_3^-_{\text{re}}$) ($\Delta^{17}\text{O} = 0$). Additionally, $\Delta^{17}\text{O}$ is stable during usual mass-dependent isotope fractionation processes; therefore, 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 reactions that occur after deposition. Previous studies of the $\Delta^{17}\text{O}$ values of nitrate in freshwater environments demonstrated that $\Delta^{17}\text{O}$ values can serve as robust tracers of the fate of $\text{NO}_3^-_{\text{atm}}$ deposited onto a surface ecosystem without using artificial tracers (Michalski et al., 2004; Tsunogai et al., 2010, 2011; Dejwakh et al., 2012). Measuring the $\Delta^{17}\text{O}$ values of nitrate for water eluted from various watersheds can increase our understanding of fixed-nitrogen processing and fixed-nitrogen retention efficiencies for surface natural ecosystems that are subjected to atmospheric fixed-nitrogen deposition.

In this study, we determined the $\Delta^{17}\text{O}$ values of nitrate in various types of bottled drinking water collected from different markets by applying those representing groundwater recharged at natural watersheds worldwide (Tsunogai and Wakita, 1995, 1996). Using bottled drinking water for the samples reduced the time, labor, and costs relative to those that would be required for direct groundwater sampling. Moreover, the use of bottled water enables collection of groundwater recharged at natural background watersheds where there have been few artificial alterations and little contamination. The use of bottled water also prevents samples of groundwater systems recharged in declining or damaged forested watersheds as well as anoxic nitrate-exhausted groundwater.

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 onto natural subaerial ecosystems. The quantified $\text{NO}_3^-_{\text{atm}}$ output will be useful in future studies as

a basic background data set for evaluation of the amounts of $\text{NO}_3^-_{\text{atm}}$ eluted into groundwater from subaerial ecosystems in general, including the same watersheds under elevated $\text{NO}_3^-_{\text{atm}}$ input in the future.

In addition to clarifying the fate of atmospheric nitrate, this study was also conducted to gain insight into the processes controlling the total nitrate concentrations in groundwater. Because nitrate enrichment of drinking water causes infantile methemoglobinemia, major factors controlling nitrate concentrations must be clarified for each groundwater system. The determination of stable isotopic compositions of nitrate in groundwater will provide insight into the processes controlling the nitrate concentrations in natural groundwater, especially for the contribution of atmospheric nitrate into groundwater.

2 Experimental section

2.1 Sample description

We collected as many bottled drinking water samples as possible from supermarkets in Sapporo and Nagoya, Japan. Because of increasing numbers of people becoming health-conscious in Japan, it is possible to obtain a wide variety of bottled drinking water from supermarkets. In addition to samples collected from Japanese supermarkets, we asked acquaintances abroad to send bottled drinking water to Japan.

We collected a total of 48 brands of bottled drinking water (Nos. 2 to 49 in Table 1) that had been sealed in either polyethylene terephthalate bottles or glass bottles and distributed on the market as drinking water. About 70 % of the samples collected were from abroad (Fig. 1). The longest storage period between bottling and analysis was less than a year. In addition to the water being collected in this study, a brand of bottled drinking water collected and analyzed in Tsunogai et al. (2010) (Rishiri water) has been included in our discussions (No. 1 in Table 1).

The methods of sterilization are presented in the table as well. Because the EU directive for bottled mineral water prohibits sterilization, most of the samples from Europe were non-sterile. Conversely, most samples from Japan were sterilized by either (1) microfiltration (0.2 μm), and/or (2) heating to 130 °C for at least 2 s; therefore, both concentrations and stable isotopic compositions may have been altered from the original to some extent. We previously determined both the concentrations and stable isotopic compositions of nitrate in four sets of the same brand of bottled water (Rishiri water) sold at supermarkets together with those sampled directly at the source well (Meisui factory) (Tsunogai et al., 2010). The differences between the average concentrations, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in the bottled water and those in water from the source well were less than 2 %, 0.2 ‰, 0.2 ‰, and 0.2 ‰, respectively (Tsunogai et al., 2010). Because the Rishiri water had been sterilized by a combination of filtration and heating

Table 1. Sample descriptions.

No.	Name	Location	Bottled date	Sterilization ^a	Note
Japan					
1	Rishiri water ^b	Rishiri, Hokkaido, Japan	18 Mar 2009	F&H	
2	Furano natural water	Furano, Hokkaido, Japan	10 Oct 2008	H	
3	Moiwa natural water	Sapporo, Hokkaido, Japan	28 Jul 2008	F&H	
4	Niseko water	Iwanai, Hokkaido, Japan	3 Mar 2009	H	
5	Sapporo water	Sapporo, Hokkaido, Japan	23 May 2008	H	
6	Yotei Spring	Kyougoku, Hokkaido, Japan	6 Jan 2009	H	
7	Okushiri water	Okushiri, Hokkaido, Japan	11 Dec 2008	H	
8	Yumemizuki	Nanae, Hokkaido, Japan	10 Feb 2008	F	
9	Ryusendo water	Iwaizumi, Iwate, Japan	30 Jul 2008	F	subterranean lake
10	Okushimizu	Kiso, Nagano, Japan	1 Aug 2008	H	
11	Gorogoro water	Tenkawa, Nara, Japan	5 Aug 2008	F	
12	Hou-jun-sui	Nobeoka, Miyazaki, Japan	2 Sep 2008	H	
13	Hotspring 99	Tarumi, Kagoshima, Japan	4 Aug 2008	H	hot spring (47 °C)
14	Joumon water	Yakushima, Kagoshima, Japan	15 Sep 2008	F&H	
15	Higashi-son water	Higashi-son, Okinawa, Japan	28 Nov 2007	F&H	
Asia					
16	Tibetan Magic Water	Gangba County, Tibet, China	26 Sep 2010	F	
17	mim	Kedah Darul Aman, Malaysia	1 Nov 2010	RO	treated tap water
18	Water 0	Kandal, Cambodia	1 Sep 2010	UV	
19	Aura	Chiang Mai, Thailand	21 Dec 2010	NS	
20	Natural Spring	Solan, Himachal Praesh, India	1 Feb 2011	–	
21	Damla	Uludag, Turkey	15 Dec 2010	–	
Africa					
22	Aqualine	Zaghouan, Tunisia	28 Oct 2011	–	
23	diMA	Tajerouine, Tunisia	1 Nov 2011	–	
24	safia	El Ksour, Tunisia	8 Nov 2011	–	
South America					
25	Vital	–, Bolivia	3 Feb 2011	–	
26	cielo	Cielo, Peru	25 Jun 2011	–	
27	san luis	Lima, Peru	18 Jul 2011	–	
28	Vivant	Lima, Peru	26 Jun 2011	–	
29	SOCOSANI	Arequipa, Peru	8 Apr 2011	F&UV	
Europe					
30	Iceland spring	Heidmörk, Reykjavík, Iceland	1 Mar 2008	F	
31	VOSS	Voss, Norway	10 Feb 2011	NS	glass bottle
32	Rosbacher	Bad Vilbel, Germany	27 May 2011	NS	
33	Dobra Voda	Bynov, Czech Republic	24 Jun 2011	–	
34	Bonaqua	Piestany, Slovakia	25 Oct 2010	–	
35	Vittel	Vittel, France	25 Feb 2011	NS	
36	Contrex	Contrexéville, France	11 Feb 2011	NS	
37	Volvic	Auvergne, France	23 May 2010	NS	
38	Perrier	Vergèze, France	3 May 2011	NS	glass bottle
39	PARADISO	Friuli-Venezia Giulia, Italy	31 Jul 2011	NS	
40	ACQUA Filette	Filette, Guarcino, Italy	1 Mar 2008	NS	
41	S. Maria degli Angeli	Rionero in Vulture, Italy	1 Apr 2011	–	
42	Jana	Sveta Jana, Croatia	18 Jun 2011	NS	
43	Studena	Lipik, Croatia	28 Nov 2010	NS	
44	SUZA	Kolasin, Montenegro	19 May 2011	–	
45	UJË I MIRË	Klllokot, Kosovo	28 Mar 2011	–	
46	Jeta	Klllokot, Kosovo	17 Dec 2011	–	
47	GORSKA	Konopishte, Makedonija	30 May 2011	F	
48	Spring Nepravishta	Nepravishta, Albania	17 Apr 2011	–	
49	Loutraki	Loutraki, Greece	13 May 2011	NS	

^a NS: non-sterile water; UV: ultraviolet irradiated; H: heated; F: filtered (0.45 µm or 0.2 µm); RO: filtered through a reverse osmosis membrane; – : treatments not publically available.

^b Data from Tsunogai et al. (2010).

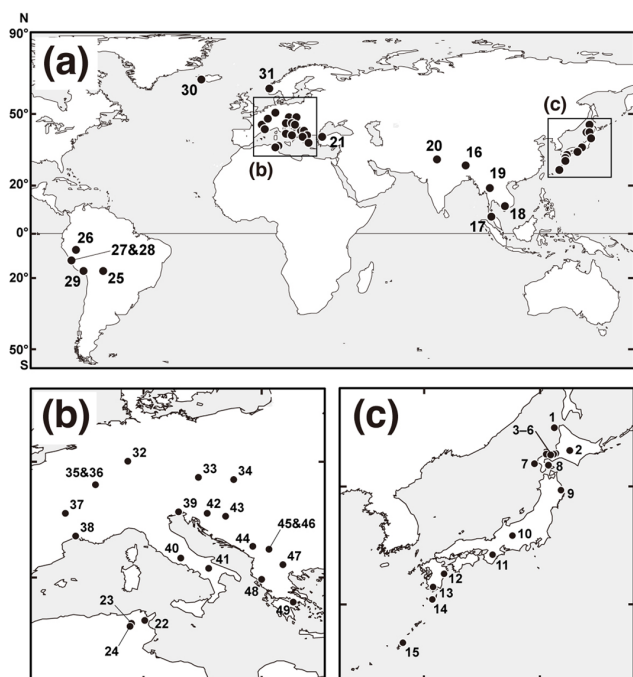


Fig. 1. Maps showing the distribution of the source wells worldwide (a), and regionally (b) and (c).

(Table 1), we concluded that alternations in both concentrations and stable isotopic compositions of nitrate in response to these treatments were small enough to enable bottled water to serve as samples of its source groundwater.

In addition to filtration and heating, some of the samples were sterilized by UV radiation for several seconds (Table 1). UV sterilization could reduce nitrate and increase both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of residual nitrate; however, the extent of any reduction during the short reaction period would be small because the decomposition rates of nitrate estimated for the wastewater treatments were small, especially under neutral conditions (Kosaka et al., 2002). Moreover, the triple oxygen isotopic compositions remained stable during the reduction. Therefore, we used these UV sterilized samples to represent groundwater from each site. However, caution should be taken before applying the values obtained from such samples to detailed discussions, especially those based on the values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

Many of the bottled water samples produced in North America and Asia were sterilized using ozone, which is known to cause large ^{17}O anomalies (Mauersberger et al., 1999). To exclude those with altered triple oxygen isotopic compositions of nitrate, bottled water sterilized using ozone was excluded. As a result, no samples from North America were evaluated (Fig. 1).

2.2 Analysis

The concentration of nitrate together with chloride and other major anions was determined by ion chromatography. The stable isotopic compositions were then determined by converting the nitrate in each sample to N_2O using the chemical method originally developed to determine the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios of seawater and freshwater nitrate (McIlvin and Altabet, 2005), with modifications (Tsunogai et al., 2008, 2010, 2011).

The stable isotopic compositions were determined for N_2O using our Continuous-Flow Isotope Ratio Mass-Spectrometry (CF-IRMS) system (Tsunogai et al., 2008; Hirota et al., 2010), which consists of an original helium purge and trap line, a gas chromatograph (Agilent 6890) and a Finnigan MAT 252 (Thermo Fisher Scientific, Waltham, MA, USA) with a modified Combustion III interface (Tsunogai et al., 2000, 2002, 2005) and a specially designed multi-collector system (Komatsu et al., 2008). An aliquot of N_2O was introduced, purified, and then carried continuously into the mass spectrometer via an open split interface to monitor isotopologues of N_2O^+ at m/z ratios of 44, 45 and 46 to determine δ^{45} and δ^{46} . Each analysis was calibrated using a machine-working reference gas (99.999 % N_2O) that was introduced into the mass spectrometer via an open split interface according to a definite schedule to correct for sub-daily temporal variations in the mass spectrometry. In addition, a working-standard gas mixture containing a known concentration of N_2O (ca. 1000 ppm N_2O in air) that was injected from a sampling loop was analyzed in the same way as the samples at least once a day to correct for daily temporal variations in the mass spectrometry.

After the analyses based on N_2O^+ monitoring, another aliquot of N_2O was introduced to determine the $\Delta^{17}\text{O}$ for N_2O (Komatsu et al., 2008). Using the same procedures as those used in the N_2O^+ monitoring mode, purified N_2O was introduced into our original gold tube unit (Komatsu et al., 2008), which was held at 780°C for the thermal decomposition of N_2O to N_2 and O_2 . The produced O_2 purified from N_2 was subjected to CF-IRMS to determine the δ^{33} and δ^{34} by simultaneous monitoring of O_2^+ isotopologues at m/z ratios of 32, 33 and 34. Each analysis was calibrated with a machine-working reference gas (99.999 % O_2 gas in a cylinder) that was introduced into the mass spectrometer via an open split interface according to a definite schedule to correct for sub-daily temporal variations in the mass spectrometry. In addition, a working-standard gas mixture containing N_2O of known concentration (ca. 1000 ppm N_2O in air) that was injected from a sampling loop was analyzed in the same way as the samples at least once a day to correct for daily temporal variations in the mass spectrometry.

The obtained values of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ for N_2O derived from the nitrate in each sample were compared with those derived from our local laboratory nitrate standards that had been calibrated using the internationally

distributed isotope reference materials (USGS-34 and USGS-35) (Böhlke et al., 2003; Kaiser et al., 2007) to calibrate the δ values of the sample nitrate to an international scale, as well as to correct for both the isotope fractionation during the chemical conversion to N_2O and the progress of oxygen isotope exchange between the nitrate-derived reaction intermediate and water (ca. 20%). All δ values are expressed relative to air (for nitrogen) and VSMOW (for oxygen) in this paper.

In this study, we adopted the internal standard method for accurate calibrations to determine the $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ or $\Delta^{17}\text{O}$ values of N_2O derived from our laboratory nitrate standards. Specifically, we added each of the nitrate standard solutions (containing ca. 10 mmol L^{-1} nitrate with known $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ or $\Delta^{17}\text{O}$ values) to additional aliquots of the samples until the nitrate concentration was 3 to 5 times larger than the original, and then converted it to N_2O and determined the values of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ or $\Delta^{17}\text{O}$ in a similar manner as was used for each pure sample. After correcting the contribution of N_2O from the nitrate in each sample, we could obtain the stable isotopic compositions for N_2O derived from our laboratory nitrate standards. The $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values in the samples were then simply calibrated using calibration curves generated from the N_2O derived from the nitrate standards.

Most samples had nitrate concentrations of more than $1\text{ }\mu\text{mol L}^{-1}$, which corresponds to nitrate quantities of more than 30 nmol in a 30 mL sample and is sufficient to determine $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values with high precision. Indeed, we even attained similar high precision for nitrate-depleted samples showing concentrations of less than $1\text{ }\mu\text{mol L}^{-1}$ through repeated measurements using another aliquot of water. Thus, all isotopic data presented in this study have an error better than $\pm 0.3\text{ ‰}$ for $\delta^{15}\text{N}$, $\pm 0.5\text{ ‰}$ for $\delta^{18}\text{O}$ and $\pm 0.2\text{ ‰}$ for $\Delta^{17}\text{O}$.

Because we used the more precise power law (Eq. 1) to calculate $\Delta^{17}\text{O}$, the estimated $\Delta^{17}\text{O}$ values were somewhat different from those estimated based on traditional linear approximation (Michalski et al., 2002). While the differences were insignificant for groundwater samples newly evaluated in this study (less than 0.05 ‰), the differences would be $0.9 \pm 0.2\text{ ‰}$ for the $\Delta^{17}\text{O}$ values of $\text{NO}_3^-_{\text{atm}}$ (Tsunogai et al., 2010). When using the linearly approximated $\Delta^{17}\text{O}$ values of $\text{NO}_3^-_{\text{atm}}$ available in the literature, we recalculated the $\Delta^{17}\text{O}$ values based on the power law.

Nitrite (NO_2^-) in the samples also interferes with the final N_2O produced (McIlvin and Altabet, 2005) when the chemical conversion method is used to determine the stable isotopic compositions of nitrate (NO_3^-). Therefore, it was necessary to correct for the contribution to accurately determine stable isotopic compositions of the sample nitrate. However, all samples analyzed in this study were originally for drinking water, and were characterized by oxic conditions and little biological activity. As a result, they contained NO_2^- at concentrations less than the detection limit, which corre-

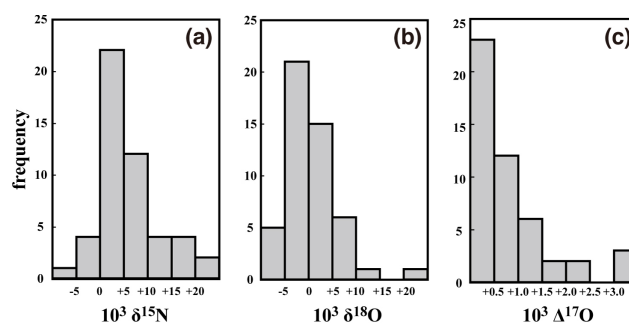


Fig. 2. Histograms of the $\delta^{15}\text{N}$ (a), $\delta^{18}\text{O}$ (b), and $\Delta^{17}\text{O}$ (c) of nitrate in the bottled mineral water samples. Those classified to the outside of each histogram were included in the nearby uppermost/lowermost classes.

sponded to $\text{NO}_2^-/\text{NO}_3^-$ ratios less than 10%. Thus the results were used without any corrections.

The δD and $\delta^{18}\text{O}$ values of H_2O in the samples were also analyzed using Cavity Ring-Down Spectroscopy (Picarro L2120-I with an A0211 vaporizer and autosampler) within an error of $\pm 0.1\text{ ‰}$. Both VSMOW and VSLAP were used to calibrate the values to the international scale.

3 Results and discussion

3.1 Groundwater nitrate: overview

The concentrations and $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of nitrate in the samples are presented in Table 2 with their Cl concentrations and the $\delta^{2}\text{O}$ and $\delta^{18}\text{O}$ values of water. We could not determine the $\Delta^{17}\text{O}$ values of nitrate for one of the water samples (No. 18) that had a nitrate concentration of less than $0.3\text{ }\mu\text{mol L}^{-1}$.

The average and 1σ variation for concentration, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ of nitrate were $84 \pm 197\text{ }\mu\text{mol L}^{-1}$, $+5.8 \pm 6.6\text{ ‰}$, and $+1.2 \pm 7.6\text{ ‰}$, respectively (Table 2, Fig. 2), which are typical values for nitrate in natural groundwater free from artificial pollution (e.g., de Walle and Sevenster, 1998; Hiscock et al., 1991; Kendall, 1998; Moore et al., 2006). A very low $\delta^{15}\text{N}$ value of -11 ‰ was found for No. 13. This is a hot spring water with a temperature of $47\text{ }^\circ\text{C}$ at the source well. Some unusual nitrate production such as microbial nitrification could be responsible for the ^{15}N depletion observed at this site.

The average and maximum $\Delta^{17}\text{O}$ values of nitrate were $+0.8\text{ ‰}$ and $+4.5\text{ ‰}$, respectively (Table 2, Fig. 2). While most of the samples showed positive $\Delta^{17}\text{O}$ values, seven (Nos. 15, 28, 29, 34, 37, 40, and 45) showed negative $\Delta^{17}\text{O}$ values as low as -0.2 ‰ . Because the $\Delta^{17}\text{O}$ value of tropospheric O_2 is around -0.2 ‰ (Luz and Barkan, 2000), the contribution of the oxygen atom derived from tropospheric O_2 during the production of remineralized nitrate from ammonium or organic nitrogen could be partly responsible for

Table 2. Concentration and stable isotopic compositions ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) of nitrate dissolved in the bottled water samples, together with the other parameters.

No.	NO_3^- $\mu\text{mol L}^{-1}$	$\delta^{15}\text{N}$ ‰	$\delta^{18}\text{O}$ ‰	$\Delta^{17}\text{O}$ ‰	$C_{\text{atm}}/C_{\text{total}}$ %	C_{atm} $\mu\text{mol L}^{-1}$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ‰	$\delta\text{D}_{\text{H}_2\text{O}}$ ‰	Cl $\mu\text{mol L}^{-1}$
1	30	-2.3	+3.1	+2.2	8.8 ± 1.7	2.6 ± 0.6	-10.5	-68.7	620
2	11	+1.6	-6.4	+0.6	2.3 ± 1.0	0.3 ± 0.1	-9.8	-76.7	163
3	32	+5.6	-3.4	+0.7	2.6 ± 1.0	0.8 ± 0.3	-9.4	-67.8	196
4	11	+1.7	+0.4	+1.4	5.7 ± 1.3	0.6 ± 0.2	-8.8	-62.3	287
5	27	+5.3	-1.1	+0.6	2.3 ± 1.0	0.6 ± 0.3	-10.1	-70.6	293
6	46	+1.8	-2.6	+1.1	4.4 ± 1.2	2.0 ± 0.6	-8.4	-65.0	156
7	27	+0.1	-2.1	+0.3	1.3 ± 0.9	0.3 ± 0.2	-7.3	-53.0	21
8	6.2	+2.6	-2.7	+1.5	6.1 ± 1.4	0.4 ± 0.1	-7.9	-59.1	352
9	49	+3.7	-5.3	+1.0	4.1 ± 1.2	2.0 ± 0.6	-8.5	-64.2	526
10	9.3	+0.4	+0.3	+2.0	7.9 ± 1.6	0.7 ± 0.2	-12.1	-81.7	157
11	58	-1.4	+2.0	+0.8	3.2 ± 1.1	1.9 ± 0.7	-8.0	-56.4	51
12	26	+5.0	-2.0	+0.3	1.1 ± 0.8	0.3 ± 0.2	-6.1	-47.2	218
13	1.1	-11.0	-1.4	+1.0	4.1 ± 1.2	< 0.1	-5.9	-40.5	134
14	14	+2.6	-0.7	+1.4	5.8 ± 1.3	0.8 ± 0.2	-4.8	-33.5	228
15	4.8	+0.7	+2.5	-0.2	< 0.1	< 0.1	-3.5	-23.3	620
16	9.0	+1.0	+6.2	+4.5	17.9 ± 2.6	1.6 ± 0.3	-18.8	-140.8	9.2
17	1.6	+9.6	-4.7	+0.7	3.4 ± 1.3	< 0.1	-6.6	-43.4	13
18	0.3	+19.2	+44.4	-	-	-	-7.9	-56.6	527
19	77	+7.0	+1.8	+0.5	2.6 ± 1.2	2.0 ± 1.0	-7.3	-50.6	21
20	21	+11.9	-0.2	+0.0	0.0 ± 0.7	< 0.1	-6.2	-41.0	58
21	2.0	-1.2	-1.5	+1.4	5.6 ± 1.3	< 0.1	-10.6	-68.0	21
22	101	+5.7	+3.2	+0.5	2.1 ± 0.9	2.1 ± 1.0	-6.3	-36.9	1819
23	369	+7.6	+3.9	+0.0	0.1 ± 0.7	0.5 ± 2.6	-7.4	-49.9	849
24	231	+7.6	+7.6	+0.1	0.3 ± 0.7	0.6 ± 1.7	-7.5	-48.6	543
25	33	+15.4	-3.4	+0.1	0.5 ± 0.9	0.2 ± 0.3	-15.1	-115.9	83
26	87	+10.7	-2.1	+0.4	2.0 ± 1.1	1.7 ± 1.0	-14.1	-106.9	471
27	28	+8.9	+0.7	+0.4	1.9 ± 1.1	0.5 ± 0.3	-13.6	-102.5	158
28	1271	+8.7	-5.7	-0.0	< 1.1	< 15.1	-13.9	-104.5	2143
29	6.3	+11.6	-6.6	-0.0	< 1.1	< 0.1	-13.7	-100.9	6025
30	3.4	+0.2	+1.0	+2.2	7.4 ± 1.3	0.3 ± 0.1	-5.9	-50.6	282
31	3.0	+3.6	+9.0	+3.9	13.2 ± 1.8	0.4 ± 0.1	-9.1	-63.7	324
32	4.7	+5.8	-5.1	+0.0	0.1 ± 0.6	< 0.1	-8.8	-61.9	1564
33	73	+5.9	-1.9	+0.3	1.1 ± 0.8	0.8 ± 0.6	-11.0	-79.1	16
34	84	+4.9	-0.2	-0.1	< 0.5	< 0.4	-10.4	-72.9	39
35	0.3	+15.5	-4.0	+0.3	1.0 ± 0.8	< 0.1	-8.3	-57.3	98
36	41	+13.3	+1.5	+0.3	1.2 ± 0.8	0.5 ± 0.4	-8.0	-53.9	289
37	123	+4.0	-1.6	-0.2	< 0.1	< 0.2	-9.0	-58.8	394
38	133	+6.7	+3.6	+0.3	1.4 ± 0.9	1.8 ± 1.2	-6.3	-39.4	647
39	332	+3.6	+2.7	+0.6	2.5 ± 1.0	8.5 ± 3.5	-8.0	-53.8	158
40	3.8	+23.0	-3.8	-0.0	< 0.8	< 0.1	-6.2	-42.7	128
41	433	+1.9	-0.8	+0.2	0.9 ± 0.8	4.0 ± 3.5	-8.1	-53.7	185
42	16	+4.4	+9.2	+0.1	0.2 ± 0.7	< 0.2	-10.9	-73.6	24
43	16	+1.6	+6.3	+3.6	14.5 ± 2.3	2.3 ± 0.5	-9.6	-65.9	46
44	8.2	-1.2	-1.1	+0.9	3.7 ± 1.1	0.3 ± 0.1	-9.8	-62.0	15
45	20	+22.4	+6.5	-0.0	< 0.8	< 0.2	-10.6	-72.6	203
46	12	+18.4	+11.6	+0.1	0.4 ± 0.8	< 0.2	-10.5	-72.2	198
47	9.2	+1.4	+1.7	+0.8	3.1 ± 1.0	0.3 ± 0.1	-9.8	-61.5	19
48	96	+4.8	+0.8	+0.5	2.1 ± 0.9	2.0 ± 1.0	-7.1	-43.0	47
49	106	+4.4	-2.4	+0.7	2.7 ± 1.0	2.8 ± 1.1	-6.3	-39.4	470
Avg.	84 ± 197	+5.8 ± 6.6	+1.2 ± 7.6	+0.8 ± 1.0	3.1 ± 3.9	-	-	-	447 ± 927

- : not determined

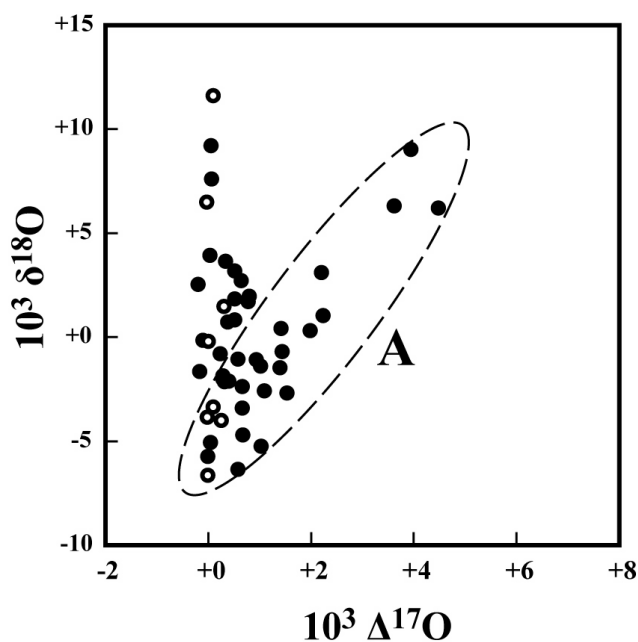


Fig. 3. Relationship between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in NO_3^- from bottled water samples. The open circles denote those showing $\delta^{15}\text{N}$ values of more than +11 ‰.

the observed negative $\Delta^{17}\text{O}$ values less than 0. However, even if the contribution was significant, the possible $\Delta^{17}\text{O}$ value of produced remineralized nitrate would include 0 ‰ within the error of our analytical precision (± 0.2 ‰). Accordingly, 0 ‰ is used for the $\Delta^{17}\text{O}$ value of remineralized nitrate and observed $\Delta^{17}\text{O}$ values less than 0 ‰ are considered to be 0 ‰ for the remainder of this paper. In other words, possible errors in our further discussions derived from the deviations in the $\Delta^{17}\text{O}$ values of remineralized nitrate from 0 ‰ were included within the error of the analyses.

To verify that atmospheric nitrate was responsible for the elevated $\Delta^{17}\text{O}$ values up to 4.5 ‰ in the samples, the $\delta^{18}\text{O}$ values of nitrate in the samples were plotted as a function of $\Delta^{17}\text{O}$ (Fig. 3). Because atmospheric nitrate is also enriched in ^{18}O (Durka et al., 1994; Kendall, 1998), we can anticipate ^{18}O enrichment for those showing elevated $\Delta^{17}\text{O}$ values. As shown in Fig. 3, those showing high $\Delta^{17}\text{O}$ values always accompanied high $\delta^{18}\text{O}$ values; thus, we can find a linear correlation for the samples categorized as Group A in the figure. By extrapolating the linear correlation to the region of $\text{NO}_3^-_{\text{atm}}$ having $\Delta^{17}\text{O} = +20$ to $+30$ ‰, we obtain $\delta^{18}\text{O} = +80 \pm 30$ ‰, which corresponds to the values for $\text{NO}_3^-_{\text{atm}}$ (Durka et al., 1994; Morin et al., 2009; Alexander et al., 2009; Tsunogai et al., 2010). These findings indicate that the $\delta^{18}\text{O}$ values primarily reflect the contribution of $\text{NO}_3^-_{\text{atm}}$ as well as $\Delta^{17}\text{O}$ for the samples in Group A.

Conversely, data plotted outside of Group A (hereafter referred to as Group B) did not present such a linear correlation. While they showed ^{18}O enrichment up to +11.6 ‰

in $\delta^{18}\text{O}$, the $\Delta^{17}\text{O}$ values were always close to 0 ‰. Although the $\Delta^{17}\text{O}$ values of nitrate are stable during the post-depositional isotopic fractionation processes, the $\delta^{18}\text{O}$ values of nitrate can vary. The isotopic fractionations during the partial removal through nitrate uptake or denitrification likely play a significant role in the ^{18}O enrichment because many of the ^{18}O -enriched samples in Group B showed the ^{15}N -enriched $\delta^{15}\text{N}$ values of more than +11 ‰ (Fig. 3).

As shown in Fig. 3, some data in Group B did not show ^{15}N enrichment, despite showing ^{18}O enrichment of up to +9.2 ‰. Without the $\Delta^{17}\text{O}$ data for these samples, such ^{18}O -enrichment would be interpreted as the result of the contribution of atmospheric nitrate (Durka et al., 1994). However, since the $\Delta^{17}\text{O}$ values of these samples were close to zero, we must assume alternative processes for them, such as reducing $\delta^{15}\text{N}$ values through the contribution of some highly ^{15}N -depleted nitrate as well as their partial removal through nitrate uptake or denitrification. The presence of such data implies that interpretation based only on the values of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate is not always straightforward. Accordingly, $\Delta^{17}\text{O}$ data would be essential to quantify the contribution of atmospheric nitrate in the hydrosphere.

3.2 Mixing ratios of atmospheric nitrate within total nitrate in groundwater

The $\Delta^{17}\text{O}$ data of nitrate in each sample can be used to estimate the mixing ratio of $\text{NO}_3^-_{\text{atm}}$ to total NO_3^- (C_{total}) in each groundwater sample by applying Eq. (2):

$$\frac{C_{\text{atm}}}{C_{\text{total}}} = \frac{\Delta^{17}\text{O}}{\Delta^{17}\text{O}_{\text{avg}}}, \quad (2)$$

where $C_{\text{atm}}/C_{\text{total}}$ 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 $\text{NO}_3^-_{\text{atm}}$ (Tsunogai et al., 2010). In a previous $\Delta^{17}\text{O}$ study conducted on Rishiri Island, we used the $\Delta^{17}\text{O}_{\text{avg}}$ value obtained through continuous monitoring on the island. However, in this study, the $\Delta^{17}\text{O}_{\text{avg}}$ value at each recharge area was not available for most samples. Because the $\Delta^{17}\text{O}$ value of atmospheric nitrate varies primarily as a result of the reaction path from NO to nitrate in the atmosphere (Michalski et al., 2003; Morin et al., 2009; Alexander et al., 2009), it is difficult to apply the values obtained from monitoring at distant stations. Therefore, we used the $\Delta^{17}\text{O}_{\text{avg}}$ values of $+20 \pm 3$ ‰, $+25 \pm 3$ ‰, and $+30 \pm 3$ ‰ for samples collected at latitudes of 20°S to 20°N , 20°N to 50°N , and 50°N to 70°N , respectively, based on the global $\Delta^{17}\text{O}$ distribution of atmospheric nitrate estimated by Alexander et al. (2009) as well as those determined in previous investigations of atmospheric nitrate (Michalski et al., 2003; Savarino et al., 2007; Kaiser et al., 2007; Ewing et al., 2007; Kunasek et al., 2008).

Because the $\Delta^{17}\text{O}$ value of $\text{NO}_3^-_{\text{atm}}$ is a function of the reaction path from NO to nitrate in the atmosphere (Michalski et al., 2003; Morin et al., 2009; Alexander et al., 2009),

the $\Delta^{17}\text{O}$ values could be different on days when NO_3^- was deposited in groundwater, especially for that deposited during preindustrial times, when the emission flux of anthropogenic NO_x was substantially smaller than current levels (Duce et al., 2008). This hypothesis was also supported by the global model of $\Delta^{17}\text{O}$ values of NO_3^- , which shows smaller $\Delta^{17}\text{O}$ values in remote regions than in those close to the source regions at the same latitude (Alexander et al., 2009). However, the regional differences in the annual average $\Delta^{17}\text{O}$ values within the same latitude were less than a few ‰ (Alexander et al., 2009), while the highest deposition rate of NO_3^- was more than 10 times that of the lowest. As a result, the historical changes in the $\Delta^{17}\text{O}$ values were included within the error of the $\Delta^{17}\text{O}_{\text{avg}}$ values used in this study. It should be noted that the $\Delta^{17}\text{O}_{\text{avg}}$ values could be revised in the future when a reliable model of the historical changes in the $\Delta^{17}\text{O}$ values is developed. By using the $\Delta^{17}\text{O}_{\text{avg}}$ values, we estimated that, on average, only 3.1 % of the total nitrate in the groundwater samples originates directly from the atmosphere; therefore, the remainder of nitrate is of remineralized origin (NO_3^-) and has been produced through biological processing in soils. The average mixing ratio of NO_3^- within the groundwater nitrate was smaller than that estimated in an oligotrophic lake water column in Japan ($9.7 \pm 0.8\%$) (Tsunogai et al., 2011). A smaller $C_{\text{atm}}/C_{\text{total}}$ ratio corresponds to a larger nitrification rate under the same deposition velocity of atmospheric nitrate (Tsunogai et al., 2011). Accordingly, the results of this study imply rapid turnover, and thus more rapid biological processing of nitrate in forested soils than in the lake water column.

When compared with the average $C_{\text{atm}}/C_{\text{total}}$ ratio ($7.4 \pm 2.6\%$) estimated for nitrate discharged from natural forested watersheds on Rishiri Island, the average $C_{\text{atm}}/C_{\text{total}}$ ratio obtained in this study was much smaller. The value can also be classified to the lower end of those in basic stream flows (3.1 to 7.7 %) and soil extracts (1.9 to 11.4 %) in southern California estimated in a past study (Michalski et al., 2004). The possible reasons for these discrepancies are discussed in Sect. 3.4.

3.3 Concentrations of atmospheric nitrate in groundwater: implications for recharge zones

To investigate the processes regulating the mixing ratios of NO_3^- , the absolute concentration of NO_3^- (C_{atm}) was calculated for each sample using each nitrate concentration (C_{total}) and each $\Delta^{17}\text{O}$ value and employing Eq. (2). The calculated C_{atm} is plotted as a function of C_{total} for the samples in Fig. 4.

While C_{total} varied widely among the samples from 0.3 to $1271 \mu\text{mol L}^{-1}$, C_{atm} was relatively uniform around $1.0 \mu\text{mol L}^{-1}$ on average, ranging from 0 to $8.5 \pm 3.5 \mu\text{mol L}^{-1}$ (sample No. 39). The observed variation in the C_{total} was likely primarily due to different contri-

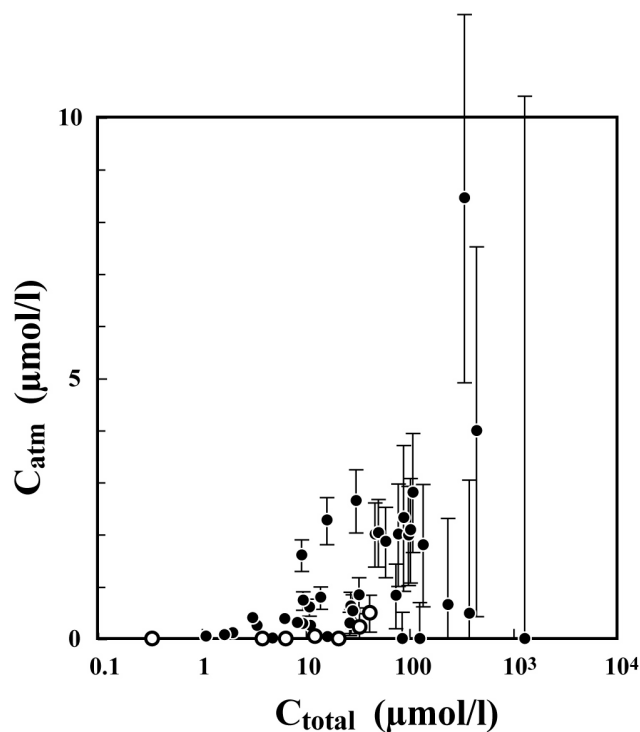


Fig. 4. Calculated concentration of NO_3^- (C_{atm}) in each water sample plotted as a function of the total NO_3^- concentration (C_{total}). Open circles denote those showing $\delta^{15}\text{N}$ values of more than +11 ‰. Error bars smaller than the symbols were deleted.

butions of NO_3^- . Specifically, additional contributions of NO_3^- during groundwater flow through the ground were responsible for the observed differences in C_{total} among groundwater samples.

If nitrate was chemically stable during the processes such as deposition into surface ecosystems and flow through the ground, the C_{atm} in groundwater would be the same or somewhat higher than that in precipitation (wet deposition) due to both evaporative concentration and the addition of NO_3^- through dry deposition. However, the estimated C_{atm} values were substantially lower than those in precipitation (wet deposition) in general (e.g., Stensland et al., 1986; EANET, 2008). Thus a substantial portion of NO_3^- was reduced during the processes of recharge at the source and subsequent flow through the ground. Here, these reduction processes are discussed based on differences in the C_{atm} between samples.

One of the striking features of variations in C_{atm} is that samples with $\delta^{15}\text{N}$ values greater than +11 ‰ always showed low NO_3^- values (Fig. 4). Because partial removal of nitrate increased the $\delta^{15}\text{N}$ values of residual nitrate through kinetic fractionation, uptake by plants or microbes and denitrification are likely both responsible for the NO_3^- depletion. In other words, even if NO_3^- was incorporated into groundwater at its recharge zone to some extent, subsequent nitrate reduction through uptake by plants or microbes

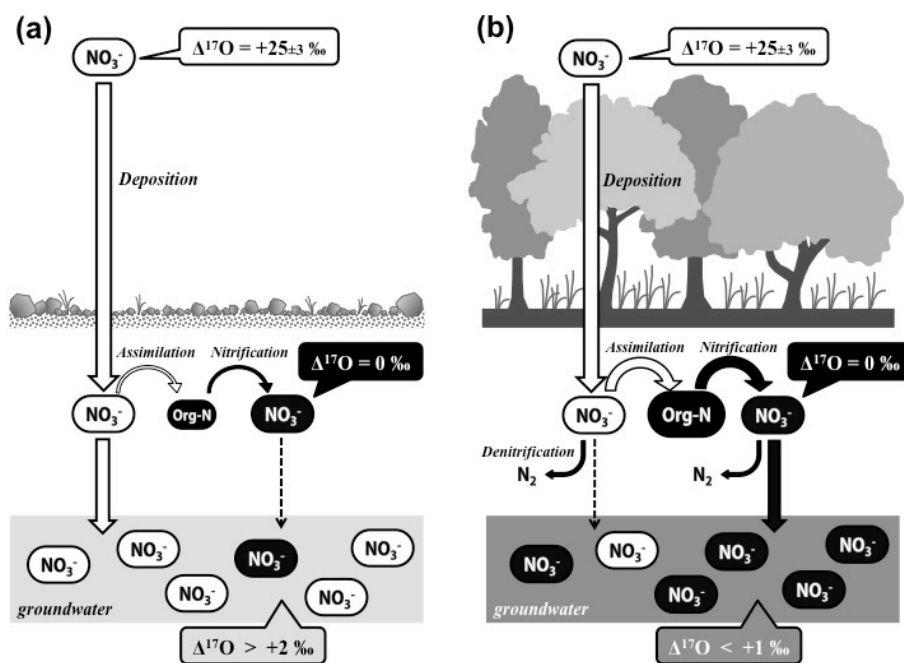


Fig. 5. Schematic diagrams showing the biological processing of atmospheric nitrate in soils covered with little vegetation (a) and high levels of vegetation (b).

and denitrification reduced NO_3^- in the groundwater samples.

In addition to post depositional reduction of NO_3^- within groundwater, vegetation in each recharge area appears to be an important factor influencing C_{atm} in groundwater, especially for samples showing elevated C_{atm} . The most NO_3^- -enriched sample was No. 39 ($8.5 \pm 3.5 \mu\text{molL}^{-1}$). The source spring of No. 39 was Paradiso di Pocenia in northern Italy, at the foot of the Carnic Alps. Thus the mountains in and around the Carnic Alps, which have an elevation of more than 2000 m, are likely the major recharge zone of this groundwater. Accordingly, the rocky surface and low amount of vegetation at the recharge zones are likely responsible for the NO_3^- enrichment owing to the absence of nitrate consumption by soil organisms and trees (Fig. 5). Because NO_3^- enrichment was also found at the drainage from damaged forested watersheds in past studies (Durka et al., 1994), NO_3^- enrichment in the samples implies that vegetation and the related surface ecosystem must be highly responsible for the consumption of NO_3^- (Fig. 5).

In addition to No. 39, Nos. 1 ($2.6 \pm 0.6 \mu\text{molL}^{-1}$), 6 ($2.0 \pm 0.6 \mu\text{molL}^{-1}$), 9 ($2.0 \pm 0.6 \mu\text{molL}^{-1}$), and 11 ($1.9 \pm 0.7 \mu\text{molL}^{-1}$) from Japan, No. 16 ($1.6 \pm 0.3 \mu\text{molL}^{-1}$) from Tibet, China, No. 19 ($2.0 \pm 1.0 \mu\text{molL}^{-1}$) from Thailand, No. 22 ($2.1 \pm 1.0 \mu\text{molL}^{-1}$) from Tunisia, No. 43 ($2.3 \pm 0.5 \mu\text{molL}^{-1}$) from Croatia, and No. 49 ($2.8 \pm 1.1 \mu\text{molL}^{-1}$) from Greece showed C_{atm} values of $\geq 1.0 \mu\text{molL}^{-1}$. The NO_3^- enrichment in Nos. 1, 6, 16, 19, 22, 43, and 49 likely occurred for reasons similar

to that in No. 39, because the sources of these samples are located in high mountains with little vegetation, such as Mt. Rishiri (1721 m) for No. 1, Mt. Yotei (1898 m) for No. 6, the Himalaya Mountains for No. 16, Doi Suthep (1676 m) for No. 19, the Dorsale Mountains (1071 m) for No. 22, Psunj (984 m) for No. 43, and the Gerania Mountains (1369 m at Makryplagi) for No. 49. The absence of rainfall in the source area might also be responsible for the low vegetation and thus less nitrate consumption for water samples produced in arid areas, such as Nos. 16 (Tibet, China) and 22 (Tunisia).

The NO_3^- enrichments in Nos. 9 (Ryusendo water) and 11 (Gorogoro water) were somewhat difficult to explain. Ryusendo is a famous stalactite grotto in Japan located on Mt. Ureira (604 m height), which is covered with dense vegetation, and No. 9 is taken directly from one of the deep subterranean lakes in the stalactite grotto; No. 11 is taken directly from a spring in a stalactite grotto (Goyomatsu stalactite grotto) in Nara Prefecture, Japan. While the source stalactite grotto is located at the middle part of Mt. Inamuragatake (1726 m height) at an altitude of 890 m, the majority of the mountain is covered by dense vegetation.

The common difference between these samples and the other samples is that they were taken from stalactite grottos. Thus, stalactite grottos and other related karst topography might be present in their recharge zones as well. While the reason for the NO_3^- enrichment of these samples is still not clear, unique recharge routes (via holes or cracks on the surface, for instance) that lead to the direct addition of precipitation containing atmospheric nitrate to groundwater may

occur in the recharge zones of the sources of these bottled waters.

Overall, higher NO_3^- concentrations were obtained for samples collected from sources recharged in rocky, arid and/or elevated areas having little vegetation and soils, while lower NO_3^- concentrations were obtained for those recharged in forested areas with high levels of vegetation (Fig. 5).

3.4 Implications for nitrogen cycles through groundwater in general

The water samples analyzed in this study were originally bottled for drinking; thus, most of their recharge zones were natural and remote, and they were not obtained from declining or damaged watersheds. As a result, the estimates of $\Delta^{17}\text{O}$ values, $C_{\text{atm}}/C_{\text{total}}$ ratios, and C_{atm} in groundwater generated in the present study do not reflect global averages of nitrate in groundwater, but rather levels of water from aquifers recharged under healthy conditions.

As shown in Sect. 3.2, we estimated that only 3.1 % of the total nitrate in the groundwater samples originates directly from the atmosphere; therefore, the remainder of nitrate is of remineralized origin. The average mixing ratio of NO_3^- is much smaller than that estimated for Rishiri Island ($7.4 \pm 2.6\%$). Moreover, this value was close to those in basic stream flows (3.1 to 7.7 %) and soil extracts (1.9 to 11.4 %) observed in a semi-arid region in southern California (Michalski et al., 2004). These discrepancies are likely because previously studied fields deviated from the natural, background ecosystem. Because their hinterlands were either elevated mountains (Rishiri) or semi-arid (southern California) areas, the observed enrichment of the mixing ratios of NO_3^- were reasonable, while the present estimations reflect those of nitrate eluted from healthy and slightly declining forested watersheds.

By adding ^{15}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 to European coniferous forest ecosystems, Tietema et al. (1998) found that drainage losses of fixed nitrogen increased as a function of the fixed-nitrogen input. They estimated that drainage accounts for 2 to 35 % of the total fixed-nitrogen input under a fixed-nitrogen input condition of less than $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. The estimated direct drainage of NO_3^- in this study corresponds to the lower region of the variation range estimated using ^{15}N tracer. When using ^{15}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, the value generated in the present study is a more reliable estimate for the direct drainage of NO_3^- under low fixed-nitrogen input conditions of less than $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$.

4 Summary and conclusions

The average mixing ratio of NO_3^- to total nitrate in groundwater recharged in natural, background watersheds was estimated to be 3.1 %. Thus, we concluded that the majority of atmospheric nitrate had undergone biological processing before being exported from the surface ecosystem to the groundwater. Moreover, higher NO_3^- concentrations were obtained for those recharged in rocky, arid or elevated areas with little vegetation, while lower NO_3^- concentrations were obtained for those recharged in forested areas with high levels of vegetation. Uptake by plants and/or microbes in forested soils subsequent to deposition and the progress of denitrification within groundwater likely plays a significant role in the removal of NO_3^- (Fig. 5). The quantified NO_3^- output obtained in this study will be useful in future studies as a basic data set for evaluation of the amounts of NO_3^- eluted into groundwater from subaerial ecosystems in general, including the same watersheds under elevated NO_3^- input in the future.

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