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Seasonal Variations of Nitrogen Isotopic Ratios of Ammonium and Nitrate in Precipitations Collected in the Yahiko–Kakuda Mountains Area in Niigata Prefecture, Japan

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Abstract Precipitation was collected from May 15, 2001 to November 18, 2002, at the mountain top (620 m a.s.l.) and mountain foot (47 m a.s.l.) of the Yahiko–Kakuda Mountains area, which is located in the western part of the Niigata Plain in central Japan. Major ion constituents and nitrogen isotopic ratios of ammonium (δ^{15}N-NH_4^+) and nitrate (δ^{15}N-NO_3^-) were measured in order to investigate the sources and behavior of NH_4^+ and NO_3^- in precipitations. The concentrations of sea salt constituents considerably increased in the cold season from November to March, and for the majority of the ion species, the concentrations at the mountain foot were higher than those at the mountain top. The precipitation weighed monthly and seasonal means of δ^{15}N-NH_4^+ values in the warm season were lower than those in the cold season at both the mountain top and mountain foot. The δ^{15}N-NH_4^+ values at the mountain foot were lower than those of mountain top in both seasons. This seasonal variation of ^{15}N-NH_4^+ could be caused by the incorporation of ammonia gas (NH_3) with lower δ^{15}N values, emitted from agricultural activities. On the other hand, the monthly and seasonal means of δ^{15}N-NO_3^- values showed noticeable seasonal difference with higher in the cold season at both the mountain top and mountain foot; however, the elevation difference was not observed either in the warm or cold season. The obtained δ^{15}N-NH_4^+ and δ^{15}N-NO_3^- values were regarded as intermediate in comparison with the reported values. No significant correlations were observed either between NH_4^+ concentrations and δ^{15}N-$NH4^+$ values or between NO_3^- concentrations and δ^{15}N-NO_3^- values. These results suggest that different factors may affect the nitrogen isotopic variations and concentration variations of NH_4^+ and NO_3^- in precipitations collected at the two sites.

Keywords Nitrogen isotope ratio · Ammonium · Nitrate · Precipitation · Seasonal variation

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1 Introduction

In East Asia, the emission of ammonia gas (NH_3) and nitrogen oxides (NO_x) to the atmosphere is increasing owing to the rapid economy development and the wet deposition amounts of ammonium ions (NH_4^+) and nitrate ions (NO_3^-) are both in upward trend in Japan (Fujita 2002). The main natural sources of NH_3 to the atmosphere are emissions from soils, emissions from the oceans, and animal excreta. Anthropogenic sources include domestic animal excreta, fertilizers, and biomass burning (Prospero et al. 1996; Russell et al. 1998). Reported inventories have shown that 14% and 23% of global emission of NH_3 is derived from global application of synthetic nitrogen fertilizers and animal manure, respectively (Bouman et al. 2002). The emission of NH_3 from applied fertilizers varies considerably, depending on soil properties, fertilizer types, and atmospheric conditions (Sommer et al. 2004). On the other hand, major sources of NO_x to the atmosphere are biological fixation, fossil-fuel combustion by power plants and automobiles, and biomass burning (Russell et al. 1998; Xiao and Liu 2002). Ammonium and nitrate in precipitation may cause not only acidification of environment but also eutrophication of closed waters. So, it is very important to clarify the sources and behavior of these ion species in the atmospheric environment so that the counter-measures against acid deposition and eutrophication can be devised in future (Xiao and Liu 2002).

Nitrogen isotopic studies have been applied to the investigation of the sources and behavior of NH_4^+ and NO_3^- in the environment (Heaton 1986). Nitrogen (N) has two naturally occurring stable isotopes—one with an atomic mass of 14 and the other of 15 (referred to as ^{14}N and ^{15}N, respectively). The most common, ^{14}N, has an abundance in N_2 gas of 99.63% and ^{15}N with 0.37% and is considered to be globally uniform (Heaton 1986; Yeatman et al. 1987). The nitrogen isotopic composition of a sample is reported by its deviation from atmospheric N_2, the standard nitrogen isotopic reference material. The ^{15}N deviation is reported as "$\delta^{15}N$" which is defined as:

$$\delta^{15}\mathrm{N}\left(‰\right)=\left\{\left[\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)_{\mathrm{sample}}\Big/\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)_{\mathrm{reference}}\right]-1\right\}\times 1,000. \tag{1}$$

A $\delta^{15}N$ value is expressed as "per mil" (‰) and the $\delta^{15}N$ value of N2 in the atmosphere is 0‰ (Russell et al. 1998; Heaton 1986; Moore 1977) by definition.

This paper gives $\delta^{15}N$ values of NH_4^+ ($\delta^{15}N$-NH_4^+) and NO_3^- ($\delta^{15}N$-NO_3^-) coupled with the concentrations of major ion species in the precipitations collected at the mountain top and mountain foot of the Yahiko–Kakuda Mountains area which is located in the western part of Niigata Plain in central Japan.

2 Methods

The location of the sampling sites of precipitations is shown in Fig. 1. Samples were collected at the Mt. Yahiko Environmental Observatory Site of Niigata University (herein after "mountain top", 37°43′ N, 138°49′ E, 620 m a.s.l.) near the top of Mt. Yahiko (638 m a.s.l.) and National Acid Deposition Monitoring Station (herein after "mountain foot", 37°48′ N, 138°51′ E, 47 m a.s.l.) in the mountain foot of the Mt. Kakuda (482 m, a.s.l.) which is located about 9 km northeast of Mt. Yahiko. The Yahiko–Kakuda Mountains are separated mountains in the western part of the Niigata Plain which is located in central Japan.

During May 15, 2001 to November 18, 2002, the precipitation samples were collected on a weekly basis using wet-only sampler (Ogasawara Co. US-330H, attached by a refrigerator, diameter 200 mm). Electric conductivity, pH, and major cation and anion species were measured according to the Technical Manual for Acid Deposition Monitoring in East Asia (EANET 2000). The concentrations of non sea salt sulfate and calcium ions were calculated on the basis of sodium concentrations in sea salt.

For the determination of $\delta^{15}N$-NH_4^+ and $\delta^{15}N$-NO_3^- in precipitation samples, the simple and rapid method developed by Sakata (Sakata 2001) was used. This method is based on an on-line isotope analysis using an elemental analyzer coupled to an isotope ratio mass spectrometer system (THERMO QUEST Co. DELTA^{plus}). NH_4^+ and NO_3^- in precipitation samples are separated as NH_4^+ into diluted H_2SO_4 from each other by sequential distillation techniques. Then, the NH_4^+ in the distillate is precipitated directly as insoluble salt of $(C_6H_5)_4BNH_4$, which is subsequently combusted in an elemental analyzer for $\delta^{15}N$ determination. As reference materials for the $\delta^{15}N$ calibration, $(NH_4)_2SO_4$ and KNO_3 prepared by US Geological Survey and International

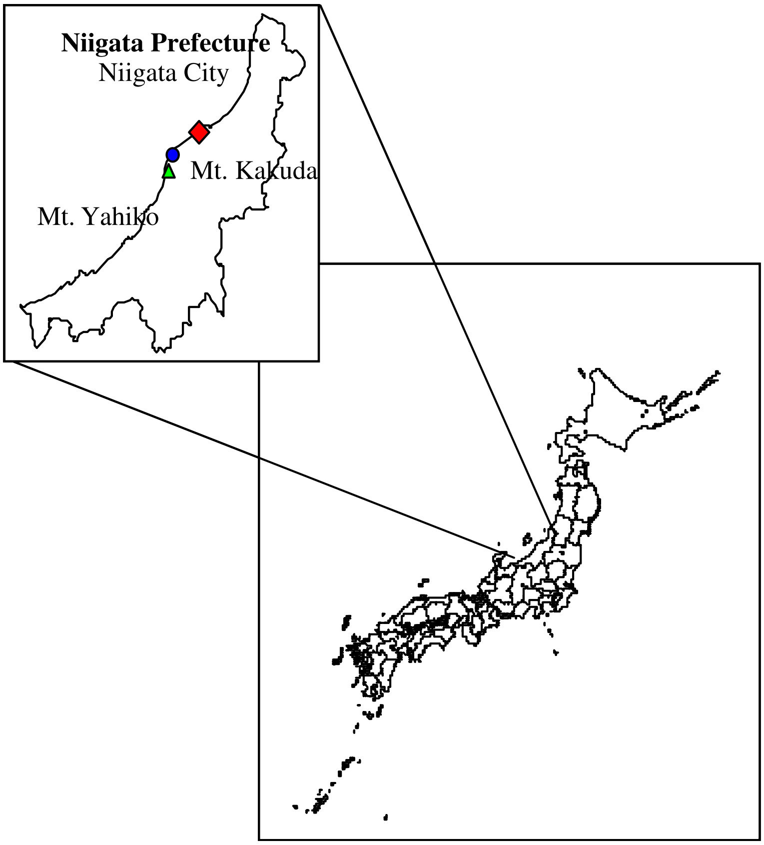

Fig. 1 Location of the Yahiko–Kakuda Mountains area

Atomic Energy Agency (δ^{15}N −30.4‰, +0.40‰, +53.7‰, +180‰) were used. Coefficient of variation obtained in the sequential repetition measurements of the $(NH_4)_2SO_4$ was 0.7% (n=10) as a maximum and 1.2% (n=6) on the different days. For monthly and seasonal comparisons of the data, the precipitation weighed monthly, and seasonal means of warm (April to October) and cold (November to March) were calculated.

3 Results and Discussion

3.1 Seasonal and Altitude Differences in Major Ion Concentrations and δ^{15}N Values

The precipitation weighted mean concentrations of major ion species, δ^{15}N-NH_4^+ and δ^{15}N-NO_3^- at the mountain top and mountain foot for the warm and cold seasons, together with the precipitation depths are shown in Table 1. The precipitation depths at the mountain top and mountain foot in the warm season were 2,171 and 1,918 mm, respectively, and in the cold season, 1,086 and 1,097 mm, respectively. Concerning the concentrations of major ion species, the majority species' concentrations at the mountain foot are higher than those at the mountain top, excluding K^+ in warm season, nss-SO_4^{2-}, nss-Ca^{2+}, and NH_4^+ in the cold season. The concentrations of sea salt components, such as Na^+, Cl^-, Mg^{2+} are especially higher in the cold season, and the concentration ratios of cold to warm season at the mountain top and mountain foot are about 6 and 5, respectively.

Regarding the seasonal difference, the precipitation weighed mean δ^{15}N-NH_4^+ values in the warm season were lower than those of the cold season both at the mountain top and mountain foot. Namely, the ratios of cold to warm season at the mountain top and mountain foot were 0.82 and 0.81, respectively. On the other hand, from the altitude point of view, the δ^{15}N-NH_4^+ values obtained at the mountain foot were lower than those of the mountain top both in the warm and cold seasons. The ratios of mountain top to mountain foot for the warm and cold season were

Table 1 Precipitation depth, precipitation weighed mean concentrations of major ion species, and $\delta^{15}N$ values in warm and cold seasons, in precipitations collected at mountain top and mountain foot of the Yahiko–Kakuda Mountains area

		Concentrations				Ratios			
		Mountain top		Mountain foot		Mountain top	Mountain foot	Warm season	Cold season
Species	Unit	Warm	Cold	Warm	Cold	Cold/warm	Cold/warm	Top/foot	Top/foot
Precipitation	mm	2,171	1,086	1,918	1,097	0.50	0.57	1.13	0.99
$\delta^{15}N\text{-}NH_4^+$	‰	−3.4	−2.8	−4.5	−3.7	0.82	0.81	0.76	0.77
$\delta^{15}N\text{-}NO_3^-$	‰	−5.5	−1.7	−5.3	−2.1	0.31	0.40	1.04	0.79
H^+	μeq/L	22.9	27.0	25.4	28.1	1.18	1.11	0.90	0.96
SO_4^{2-}	μeq/L	31.6	72.8	36.9	77.8	2.31	2.11	0.86	0.94
nss-SO_4^{2-}	μeq/L	26.7	43.0	29.5	38.9	1.61	1.32	0.91	1.11
NO_3^-	μeq/L	13.6	18.5	15.5	19.6	1.36	1.26	0.87	0.95
Cl^-	μeq/L	47.4	283.9	71.5	369.5	5.98	5.17	0.66	0.77
Na^+	μeq/L	40.4	246.8	61.1	323.3	6.12	5.29	0.66	0.76
K^+	μeq/L	2.4	7.2	2.2	8.3	2.98	3.74	1.10	0.88
Ca^{2+}	μeq/L	5.4	25.7	7.4	28.3	4.80	3.82	0.73	0.91
nss-Ca^{2+}	μeq/L	3.6	15.0	4.8	14.3	4.16	3.00	0.76	1.05
Mg^{2+}	μeq/L	9.5	58.2	14.4	74.6	6.13	5.18	0.66	0.78
NH_4^+	μeq/L	12.7	17.2	15.1	17.0	1.35	1.13	0.84	1.01

0.76 and 0.77, respectively. These phenomena were considered to be the influence of the incorporation of ^{14}N-enriched NH_3 gas emitted from the ground surface by kinetic isotope fractionation. Comparing with the reported $\delta^{15}N\text{-}NH_4^+$ values (Table 2; −12.2‰ to −0.5‰), the obtained isotopic values in this work were intermediate ones.

There are noticeable differences in the $\delta^{15}N\text{-}NO_3^-$ values between the warm and cold seasons both at the mountain top and mountain foot. The ratios of cold to warm season at the mountain top and mountain foot were 0.31 and 0.40, respectively. However, not so much difference was found between the mountain top and mountain foot in the warm season. The ratios of mountain top to mountain foot for the warm and cold season were 1.04 and 0.81, respectively. It is considered that the incorporation of precursors of nitrate to precipitations, through the altitude difference of about 600 m from the mountain top to mountain foot, do not causes the change in $\delta^{15}N\text{-}NO_3^-$ values. The obtained $\delta^{15}N\text{-}NO_3^-$ values in this work (see Table 2; −6.6‰ to 4.1‰) can be regarded as medium values among the reported values.

3.2 Monthly Variations in $\delta^{15}N\text{-}NH_4^+$ and $\delta^{15}N\text{-}NO_3^-$

The precipitation weighed monthly variations in $\delta^{15}N\text{-}NH_4^+$ values are shown in Fig. 2. Somewhat large differences were detected in $\delta^{15}N\text{-}NH_4^+$ values between the mountain top and mountain foot. The $\delta^{15}N\text{-}NH_4^+$ values of mountain foot fell in May to June in comparison with the mountain top. In the other seasons, the differences in $\delta^{15}N\text{-}NH_4^+$ values between the sites were reduced. Theses monthly fluctuations may come from the incorporation of NH_3 with lower $\delta^{15}N\text{-}NH_4^+$ values emitted from the ground by agriculture activities, which is increased during spring to summer seasons (Russell et al. 1998; Yeatman et al. 2001).

The monthly variations of $\delta^{15}N\text{-}NO_3^-$ values are shown in Fig. 3. The variations of $\delta^{15}N\text{-}NO_3^-$ values both at the mountain top and mountain foot shows a good coincidence, excluding relatively small differences in August and September in 2001, and shows higher in January and February in 2002. Freyer (1978, 1991) reported almost same seasonal variations of the $\delta^{15}N\text{-}NO_3^-$ in precipitations and aerosols as our

Table 2 Reported δ^{15}N-$NH_4{}^{+}$ and δ^{15}N-$NO_3{}^{-}$ values in precipitation

Sampling sites	δ^{15}N-NH4^{+} (‰; mean)	δ^{15}N-NO3^{-} (‰; mean)
Colorado, USA (Moore 1977)	−1.4	−6.6
Julich, Germany (Freyer 1978)	−12.1	−3.1
Pretoria, South Africa (Heaton 1987)	−3.8	−3.5
Germany and France (Freyer 1991)		
Summer	–	−5
Winter	–	0
Tennessee and Virginia, USA (Garten 1992)	−3.4	2.3
Lews, Delaware, USA (Russell et al. 1998)	−0.5	−1.1
Yorkshire, England (Heaton et al. 1997)	−7.3	0.1
Gyiyang, China (Xiao and Liu 2002)		
Light rainfall[a]	−12.2	2.0
Heavy rainfall[b]	–	4.1
Across midwestern and northeastern USA (Elliott et al. 2007)	–	−1.5
This work; Yahiko–Kakuda Mountains area, Japan		
Top	−3.4[c], −2.8[d]	−5.5[c], −1.7[d]
Foot	−4.5[c], −3.7[d]	−5.3[c], −2.1[d]

[a] Light rain means that precipitation is <5 mm and duration is 4 h

[b] Heavy rain means that precipitation is >100 mm and duration is <24 h

[c] Warm season: April–October

[d] Cold season: November–March

results with higher in winter than in summer. There may be several factors which could contribute to the observed seasonal variation in δ^{15}N-$NO_3{}^{-}$ with higher in winter precipitations (Heaton 1987; Freyer 1991; Elliott et al. 2007): (1) anthropogenic NO_x sources including coal-fired power plants and vehicles have relatively higher δ^{15}N-$NO_3{}^{-}$ values with about 0‰ to +13‰ than natural sources including biogenic NO_x emissions with about less than 0‰ and natural NO_x is emitted during spring and summer; (2) temperature-dependent isotope exchange equilibrium between atmospheric oxinitrogen species, gaseous NO and NO_2, and $NO_3{}^{-}$ in aqueous solution, exist with enrichment of the heavier nitrogen isotope in the more oxidized form in lower temperature; and (3) incorporation of particulate nitrate with higher δ^{15}N

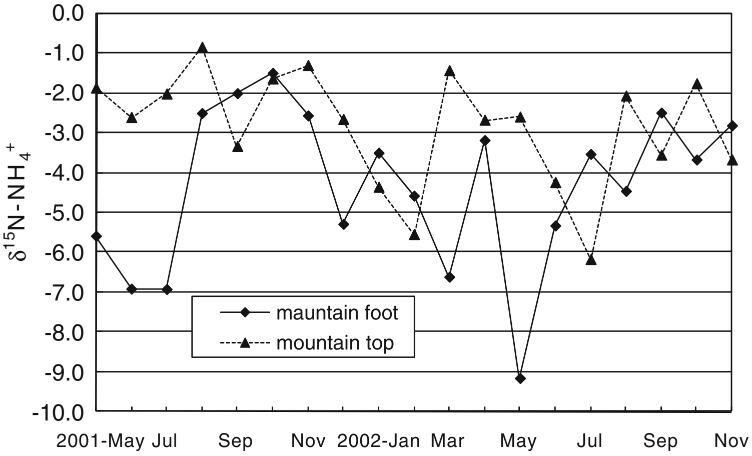

Fig. 2 Monthly variations of δ^{15}N-$NH_4{}^{+}$

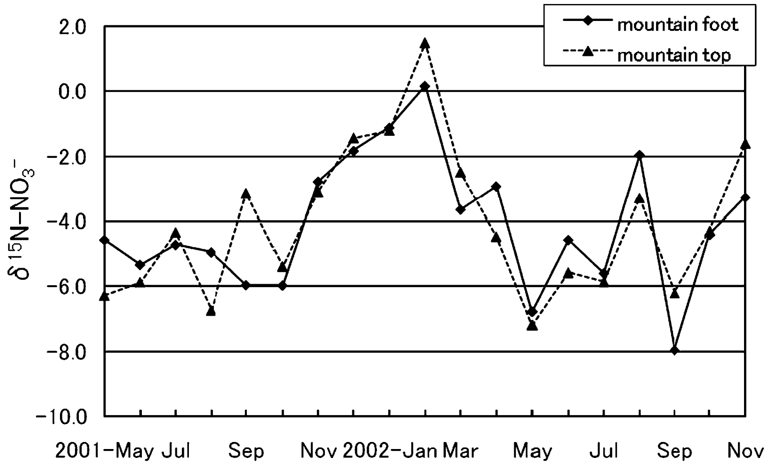

Fig. 3 Monthly variations of δ^{15}N-NO_3^-

due to formation mechanisms for particulate nitrate associate with temperature dependent isotope exchange equilibrium and seasonal variations in the molar NO_3^-/HNO_3 ratio. However, the weight of these effects has to be evaluated by further measurements.

3.3 Correlations Between Concentration Variations and Nitrogen Isotopic Ratios

Correlation coefficients between NH_4^+ concentrations and δ^{15}N-NH_4^+ values for the same data sets at the mountaintop and mountain foot were calculated separately, together with those between NO_3^- concentrations and δ^{15}N-NO_3^- values. No significant correlations between NH_4^+ and NO_3^- concentrations and nitrogen isotopic ratios at either site were observed. These results suggest different factors may affect the nitrogen isotopic variations and concentration variations of NH_4^+ and NO_3^- in precipitations collected at the two sites. Concentrations of NH_4^+ and NO_3^- in precipitations may strongly depend upon precipitation characteristics such as precipitation depth and intensity, cloud types, and also atmospheric concentrations of aerosols and gasses. On the other hand, the isotopic ratios of those ions in precipitation probably result from combinations of isotopic ratios of incorporated gases and aerosols in the atmosphere and of isotopic compositions of their sources. The δ^{15}N values of NH_3 and of NH_4^+ in aerosols measured at the mountain foot ranged, from −14.5 to −1.0 with a mean −8.3‰ and from 12.2 to 39.6 with a mean 22.1‰, respectively (Hayasaka et al. 2004). Thus, there was a large difference in δ^{15}N values in NH_3 and NH_4^+ probably by the equilibrium isotopic fractionation effect between gas and aerosol. Particulate nitrate also has higher δ^{15}N than HNO_3 due to formation mechanisms for particulate (Heaton 1987; Freyer 1991) as mentioned before. Additional δ^{15}N measurements associated with various sources of NH_3 and NO_x to the atmosphere and with seasonal variations in gases (NH_3 and HNO_3) and aerosols (NH_4^+ and NO_3^-) are needed to elucidate the relationships between observed variations of δ^{15}N values and concentrations in precipitations.

4 Conclusion

Precipitation samples were collected at the mountain top and mountain foot of the Yahiko–Kakuda Mountains area, which is located in the western part of the Niigata Plain in central Japan. Concentrations of the major ion species and nitrogen isotopic ratios of ammonium (δ^{15}N-NH_4^+) and nitrate ions (δ^{15}N-NO_3^-) in the precipitations were measured.

1. The concentrations of sea salt components were increased considerably in the cold season from November to March, and the majority of major ion species' concentrations in the precipitations at the mountain foot were higher than those at mountain top excluding K^+ in the warm season and nss-SO_4^{2-}, nss-Ca^{2+}, and NH_4^+ in the cold season.
2. The precipitation weighed monthly and seasonal means of δ^{15}N-NH_4^+ values of the warm season were lower than those of the cold season both at the mountain top and mountain foot, and the δ^{15}N-NH_4^+ at the mountain foot were lower than

those of mountain top both in the two seasons. This may be caused by the incorporation of ammonia gas (NH_3) with lower $\delta^{15}N$ values during warm season, emitted from the ground by agricultural activities.

3. The noticeable differences with higher in the cold season were observed in the precipitation weighed monthly and seasonal means of $\delta^{15}N\text{-}NO_3^-$ values both at the mountain top and mountain foot. However, not so large difference was observed between the two sites, especially in the warm season. Some effects can be considered for the cause of this seasonal difference.
4. The $\delta^{15}N\text{-}NH_4^+$ and $\delta^{15}N\text{-}NO_3^-$ values in this studies are regarded as intermediate ones in comparison with reported values from other studies.
5. No significant correlations between NH_4^+ and NO_3^- concentrations and nitrogen isotopic ratios were observed.

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