

Heterogeneous Atmospheric Nitrogen Deposition Effects Upon the Nitrate Concentration of Stream Waters in a Forested Mountain Area

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Abstract Nitrogen compounds generated by anthropogenic combustion deposits in forest watersheds and induce nitrogen saturation of the area. Because excess nitrogen is derived from atmospheric deposition, this action is expected to uniformly affect a wide area of forest soils. Geographically, heterogeneous nitrate concentration of stream water within a small area has been attributed to the tree type, geological setting and tree cut. In this article, we hypothesized that the effect of the atmospheric nitrogen deposition in the forest watershed may vary within a small area, and that such variation is induced by the degree of air mass containing a high concentration of nitrogen

deposition of combustion origin. We measured major ion concentrations, including nitrate, nitrite oxygen and nitrogen stable isotope of nitrate sampled at 24 water streams in the Chichibu region, which is 50–100 km from the Tokyo metropolitan area. The nitrate concentration showed a wide range (25.6–237 $\mu\text{mol L}^{-1}$) within 300 km^2 , which was explained sufficiently by the air mass advection path and its contact with the mountain's surface. The nitrate concentration showed a significant positive correlation with chloride ($r=0.73$; $p<0.001$). As chloride originates outside of the Chichibu region, the positive correlation between two ions showed that the nitrate concentration of the stream water was affected by the nitrogen compound from the Tokyo Metropolitan area as a form of atmospheric deposition. Between the nitrate concentration and the stable isotope ratio of oxygen of nitrate, there was a positive correlation until nitrate concentration of 100 $\mu\text{mol L}^{-1}$. When the nitrate is over 100 $\mu\text{mol L}^{-1}$, $\delta^{18}\text{O}$ shows a stable value of ca. 5.7‰. This indicates that the nitrification proceeds when the nitrate concentration was low to middle, but the reaction slowed when the nitrate concentration became high. Oxygen stable isotope of nitrate along with a set of nitrate concentrations can be used as a good indicator of nitrogen saturation.

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1 Introduction

The release of oxidized and the reduction of nitrogen compounds from anthropogenic activities, notably agriculture and the burning of fossil fuels, has greatly increased the global cycle of reactive nitrogen. This has a wide-ranging impact on terrestrial and aquatic ecosystems (Gruber and Galloway 2008). In forested areas, excess nitrogen, arising from the burning of fossil fuels, is altering forest ecosystems (Stoddard 1994; Aber et al. 1989; Gundersen et al. 2006).

When nitrogen accumulates in forest ecosystems, the availability of mineral nitrogen exceeds the biological demands of plants and microbes. This process of nitrogen accumulation is termed “nitrogen saturation” (Aber et al. 1998). It is suggested that nitrogen saturation occurs proportional to the amount of nitrogen deposition in the site (Dise and Wright 1995). As nitrogen saturation proceeds, excess mineral nitrogen is released from the forest soil to the stream water as a form of nitrate. This phenomenon is expressed as “nitrogen leaching” (Aber et al. 1998).

According to Stoddard (1994), nitrogen saturation can be evaluated with the concentration of nitrate in stream water. In the nitrogen saturation stages of 0 and 1, nitrate concentration exhibits seasonality. In stage 2, high nitrate concentrations can be detected even in the base-flow of the growing season, and they range from 0.5–1.0 mg N L⁻¹ (35.7–71.4 μmol L⁻¹). In stage 3, the nitrogen saturation is at its peak, and the nitrate concentration is more than 1.0 mg N L⁻¹ (>71.4 μmol L⁻¹).

Nitrogen leaching is detected in many forested areas at high deposition sites (Dise et al. 1998; Gundersen et al. 1998; Dise et al. 2009). High nitrate concentrations of stream water have also been reported in Japan (Ohroi and Mitchell 1997). Elevated nitrate concentrations in the stream water induce the acidification downstream to some other part of Japan (Matsubara et al. 2009).

Because the origin of excess nitrogen is fossil fuel combustion, nitrogen deposition should uniformly affect a wide area of forest soils. Schindler et al. (2006) reviewed nitrogen deposition and the nitrate concentration of rain in eastern North America. The area showed a high, homogenous concentration over a broad area of approximately 3,000 km².

On the other hand, some reports showed a high spatial variability of nitrate concentrations in several

stream waters in small areas according to catchment characteristics. Such high variability was attributed to the variety of tree types, softwood and hardwood; such that softwood forest leaks more nitrogen than hardwood under the same nitrogen deposition conditions (i.e., Magill et al. 2000). Existence of clear-cut patches in the watersheds increases the nitrate concentrations of stream water (Kohlpaintner et al. 2009), while specific geological setting induces nitrate contamination of river water (Holloway et al. 1998).

The distance from the inventory site of nitrogen oxide (NO_x) of combustion origin, however, has not been examined as a cause of the spatial variability of nitrate concentrations in several stream waters in small areas. If the catchment of stream water is close to the inventory site, the mass of air contaminated with NO_x of combustion origin may be transported without dilution and may affect the concentration of stream waters in the limited area that directly receives deposition of such air masses. The different amounts of NO_x deposits may lead to different stages of nitrogen saturation within a small area.

The Chichibu region is 50–100 km from the Tokyo Metropolitan area. The mean nitrate concentration of stream water in the part of Saitama Prefecture containing the Chichibu region is 112.8 μmol L⁻¹, a value 4.4 times larger than that of the mean prefectural concentration of stream water in Japan as a whole (Konohira et al. 2006).

The high nitrate concentration in the Chichibu region is attributed to the atmospheric nitrogen deposition that originates in the Tokyo Metropolitan area (Yoh et al. 2001; Konohira et al. 2006; Shindo et al. 2005). There is a possibility that the amount of NO_x supplied by the Tokyo Metropolitan area to the Chichibu region may not be uniform because the air mass would be transported at a relatively low height and, therefore, experience topographic interference along its passage. This may cause heterogeneous atmospheric nitrogen deposition, affecting the nitrate concentration of stream waters in a relatively small area.

Stable isotope ratios are widely used to trace the inventory of a material along with its chemical reaction history. Morin et al. (2009) reported that the δ¹⁵N of nitrate from anthropogenic NO_x (0±6‰) is significantly higher than that emitted from natural NO_x sources (-4±2‰). Thus, the δ¹⁵N of nitrate in stream water may reflect the contribution of atmospheric

deposition, although it may be altered in some portion during metabolism by microbes in forest soils. If the $\delta^{15}\text{N}$ of nitrate is higher in stream water, the nitrate may have originated from fossil fuel combustion.

Nitrate's $\delta^{18}\text{O}$ is used to reflect reactions in the soil (Durka et al. 1994; Kendall et al. 2007). Durka et al. (1994) investigated the $\delta^{18}\text{O}$ of nitrate in spring water and applied a mixing model of soil water and precipitation to determine each contribution to nitrate. Soil water is known for its low- $\delta^{18}\text{O}$ nitrate and precipitation is known for its high- $\delta^{18}\text{O}$ nitrate (Amberger and Schmidt 1987; Durka et al. 1994). The $\delta^{18}\text{O}$ of spring water nitrate showed that the spring water came mostly from soil water and not from the direct precipitation (Durka et al. 1994). Durka et al. (1994) showed that the $\delta^{18}\text{O}$ of nitrate is a good indicator of the contribution of atmospheric and soil nitrates to spring water nitrate.

Major ions are other keys to determine the nitrate inventory. Honda et al. (2007) sampled stream water near Tokyo and analyzed inorganic ions in stream water. They detected high correlations between chloride and nitrate and sodium and nitrate, which showed that the nitrate of the area was mostly from outside the stream watershed because sodium and chloride are generally introduced to the stream water from outside of the watershed.

In this study, we intensively surveyed the nitrate concentration in streams located in the Chichibu region, which is suggested of being affected by the NO_x from the Tokyo Metropolitan area. The aim of this study is to examine if such variations are caused by the passage of air masses, using the stable isotope ratios of nitrate and major ions of stream water.

2 Methods

2.1 Study Area and Sampling Points

The study area is situated 50–100 km northwest of the Tokyo Metropolitan area (Fig. 1). The annual precipitation in this area is 1262 mm, and its mean temperature is 12.8°C (Japan Meteorological Agency 2009).

Wind passage patterns have been studied around the Tokyo Metropolitan area in connection with the heat land phenomenon (i.e., Kawamura 1982; Fujino et al. 1996). Kawamura (1982) studied wind direction

trends and reported on the typical trends for the warmer season. Fujino et al. (1996) also studied wind direction trends in the area using simulation data. They both showed that strong south east winds that blow from the Tokyo Metropolitan area to the Chichibu region during the afternoons as shown in Fig. 1.

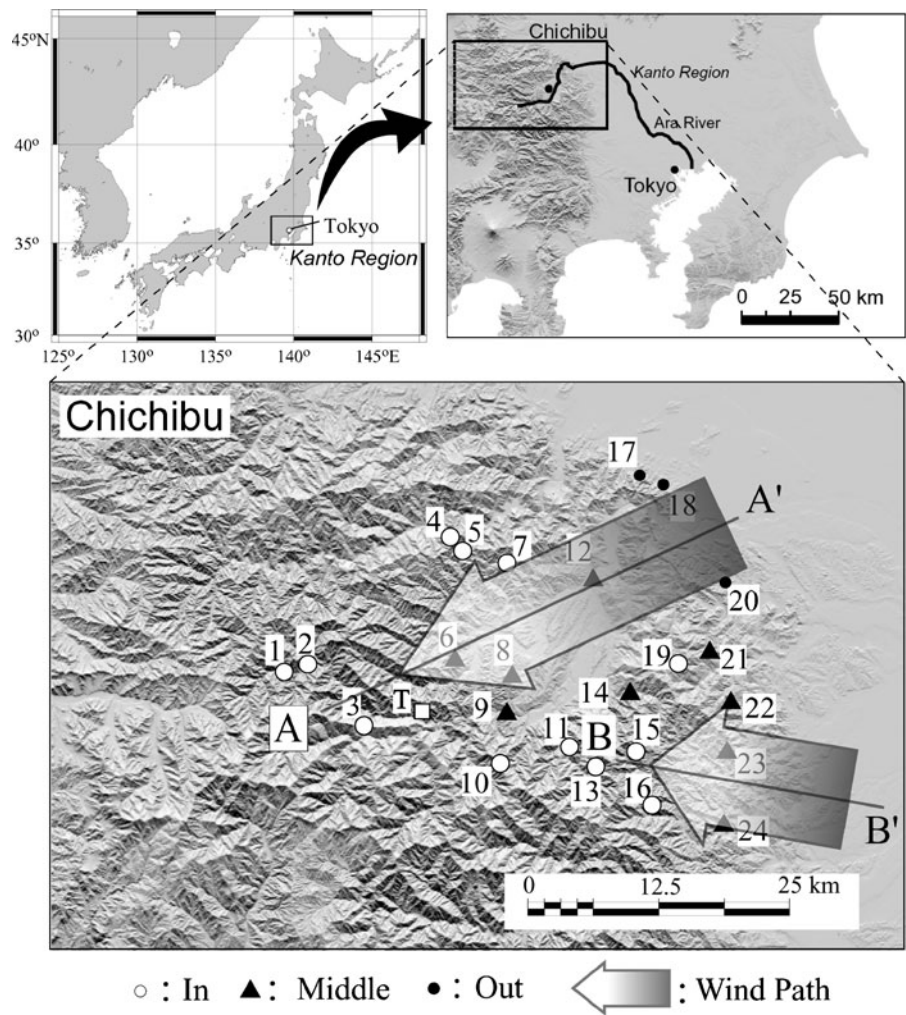
To avoid the other cause of nitrate increase on stream water than the effect of air mass, we selected the streams of the forest watersheds which consist of softwood, more than 60% of the total. Forest type and its area were determined using 1:25,000 geomorphological maps from the Geospatial Information Authority of Japan (Geospatial Information Authority of Japan 2009). The geological setting of the study area was checked with GIS software (MicroImages, TNTmips ver. 6.9), and data from a seamless geological map of Wakita et al. (2009). There was no geological stratum in the study area that contained high nitrogen as suggested by Holloway et al. (1998). No watersheds contained clear-cut areas.

We selected the sampling points so that the sampling points were not nested within one another. This was done so that the water chemistry of the specific points was not affected by other points. Previous studies suggest that the air mass of the Tokyo Metropolitan area induced the nitrogen saturation at the Chichibu region (i.e., Kawamura 1982; Fujino et al. 1996). We hypothesized that the mountain surface which was first hit by the air mass received the biggest amount of nitrogen deposition, and named such area “Out” (Fig. 1). In contrast to this, we classified the “In” area as being located far from the direct hit of the air mass advection. The middle area is conventionally classified as being located between the Out and In areas (Fig. 1).

Konohira et al. (2006) took stream water samples in the Chichibu region at the base-flow condition in summer. We selected some sampling points of Konohira et al. (2006) as our sampling points so that we could see the temporal change of the nitrate concentration. We chose the points so that they cover the wide range of the nitrate concentration. In Table 2, we show the coefficient of variance (CV) for nitrate concentration in stream water in the Chichibu region between our data and that of Konohira's.

As the CV took 3% to 26% between our data and Konohira et al. (2006), we decided that a one-time sampling is enough to represent the stream water nitrate concentration in the region. Because the

Fig. 1 Map of the sampling points. Major Air path (air mass advection direction) is drawn on the Chichibu map with A–A' and B–B' transects, showing a schematic cross section that is drawn in the bottom of the figure. Out points are shown as *solid circles* which are situated on the first air mass advection contacted sites. Middle points are displayed as *solid triangles* which appear on the secondary sites, and In points are shown as *open circles* on the lesser sites. The sub-watersheds of each sampling point are not nested. The letter “T” in the Chichibu map represents the Takizawa dam



number of the points selected from Konohira et al. (2006) were not enough to discuss the effect of the air mass advection, we selected the stream that had only forest area as its watershed based on the geographical and land use map. We tried selecting the same number

of the sampling points for the In, Middle, and Out areas. However, as the Out area was the only restricted area, we could only set three points for Out.

The longitude and latitude of each sampling point was obtained using a GPS system (Magellan, Magellan

Triton 200). The properties of the sampling locations are shown in Table 1. The altitude of the lowest sampling point was 67 m, while that of the highest point was 942 m. The mean altitude was 470 m.

To confirm that our sampling was operated at the base-flow condition, hydrological conditions in the Chichibu region were checked with the monitoring data taken at the stream inflow to the Takizawa Dam (square symbol on Fig. 1) operated by the Japan Water Agency. The water volume flowing in the dam was used to represent the hydrological regime of the study area. This is the only monitored stream that does not experience an artificial intake of water at upstream. The Japan Water Agency records the water level of the stream once a day; and we obtained the records from January to August, 2008. A hydrograph of the stream data was made based on these records. The hydrological status of the study area is shown in

Table 1 Characteristics of each sampling point. Sampling point numbers increase from west to east

#	Site Name	Latitude	Longitude	Altitude [m]
1	Nakatsukyo	35° 59.290'	138° 44.933'	942
2	OukanCamp	35° 59.668'	138° 46.444'	840
3	Yatakezawa	35° 56.531'	138° 50.061'	715
4	Kiri	36° 57.905'	138° 55.525'	526
5	Tsuchisaka	36° 06.230'	138° 55.570'	797
6	Susuki	35° 59.947'	138° 55.808'	801
7	Koumyoji	36° 05.540'	138° 56.340'	408
8	Izusawa	35° 54.591'	138° 58.755'	440
9	Shirahisa	36° 04.894'	138° 59.176'	367
10	Ochigawa	35° 57.179'	138° 59.178'	598
11	Urayama	35° 55.445'	139° 03.197'	546
12	Nomaki	36° 03.961'	139° 04.759'	205
13	Hosokubo	35° 54.422'	139° 04.833'	492
14	Kojimasawa	35° 58.183'	139° 07.132'	377
15	Yamanaka	35° 55.180'	139° 07.460'	690
16	Sakasagawa	36° 09.395'	139° 07.695'	471
17	Negishi	35° 52.410'	139° 08.470'	178
18	Hiroki	36° 08.942'	139° 09.160'	174
19	Sadamine	36° 09.582'	139° 09.778'	645
20	Miyairi	35° 59.676'	139° 10.158'	190
21	Tsudoku	36° 00.272'	139° 12.201'	527
22	Nishikawa	36° 07.132'	139° 13.029'	300
23	Akasawa	35° 51.420'	139° 13.090'	259
24	Mugihara	36° 03.920'	139° 13.137'	555

Fig. 2. Discharges on the 13th, 21st and 22nd of August were 1.41, 1.68 and 1.02 m³ S⁻¹, respectively. The coefficient of variance (CV) for the 3 days was 24.2%. We confirmed that all the samples were taken at base flow and were not affected by storms or rain.

2.2 Ion Concentration and Stable Isotope Ratio of the Stream Water

Stream water was sampled with clean, plastic buckets and immediately filtered using prebaked Whatman GF/F filters (450°C, 2.5 h). The filtrate was stored in 100-ml polyethylene bottles. Water samples were brought to the laboratory at 4°C and frozen within a day. The pH, electrical conductivity (EC) and water temperature were measured with a portable sensor (TOA, WM-22EP) at each sampling point. Packaged colorimetric tests (pack test, Kyoritsu Chemical-Check Lab Co.) were conducted to quantify the nitrate concentrations at each sampling point to check for any contamination during transportation and storage.

Major ions were analyzed with ion chromatography (Shimadzu, Prominence HIC-NS). The ion species that were detected were sodium, magnesium, calcium, chloride, nitrate, and sulfate, with quantification limits of 4.3, 4.1, 2.5, 2.8, 1.6, and 1.0 μmol L⁻¹, respectively. If the value of the concentration was lower than these values, the values were listed as not detected (ND).

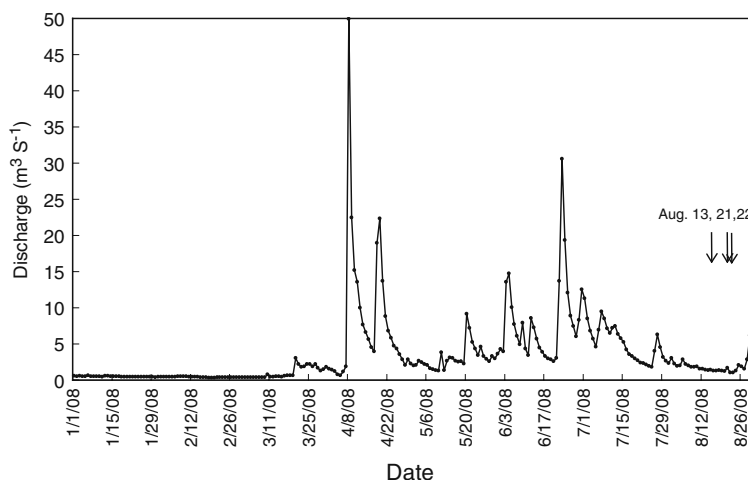
Isotopic measurements of the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios of nitrate were made using the denitrifier method (Sigman et al. (2001) and Casciotti et al. (2002) for nitrogen and oxygen isotope methodologies, respectively).

Standards used for the nitrate stable isotope were atmospheric N₂ for nitrogen and Vienna Standard Mean Ocean Water (VSMOW) for oxygen. Samples were calibrated with international reference standards USGS32, USGS34, USGS35, and IAEA-NO₃. The stable isotope value was expressed as follows:

$$\delta X(\text{‰}) = \left(\frac{R_{\text{unk}}}{R_{\text{std}}} - 1 \right) \times 1000 \quad (1)$$

where R_{unk} is the stable isotope ratio of the sample and R_{std} is the stable isotope ratio of the standard gas. All statistical analyses for the water chemistry were conducted using JMP ver. 6.0 (SAS).

Fig. 2 Hydrograph of the study area. Discharge data were taken at the Takizawa Dam (*T* in Fig. 1), which was not affected by water intake or inflow



3 Results

The electrical conductivity of water from our study area ranged from 65.6 to 220 $\mu\text{S cm}^{-1}$ (Table 2). Most of the area's pH level was neutral, and we could not detect acidification in the stream water. The maximum pH was 8.03 at point 4 and the minimum pH was 6.92 at point 16. For the cation species, sodium ranged from 76.8 to 653 $\mu\text{mol L}^{-1}$, magnesium from 45.4 to 78.3 $\mu\text{mol L}^{-1}$, and calcium from 143.6 to 1086.7 $\mu\text{mol L}^{-1}$. For the anion species, chloride ranged from 19.0 to 199.3 $\mu\text{mol L}^{-1}$, nitrate from 25.6 to 193.7 $\mu\text{mol L}^{-1}$ and sulfate from 57.8 to 439.4 $\mu\text{mol L}^{-1}$.

The concentrations of nitrate gradually decreased as the sampling locations became further west (Fig. 3). Points 17 (471 m), 18 (174 m), and 20 (636 m), in particular, showed high concentrations with values of 194, 237 and 186 $\mu\text{mol L}^{-1}$, respectively. We found that the points along the path of the wind showed high nitrate concentrations. Sampling points were well-categorized by the different geographical categories; Out points showed highest nitrate concentration, Middle showed moderate concentrations, and In showed the lowest concentrations. To check whether these three groups were really in different groups, an analysis of variance (ANOVA) was conducted. After the ANOVA, we tested the nitrate concentration dataset with the Tukey–Kramer test, and the results showed that the three groups are significantly different ($p < 0.001$; Fig. 4).

The $\delta^{15}\text{N}$ increased as the nitrate concentration increased (Fig. 5). There was a gradual increase of $\delta^{15}\text{N}$ from In, to Middle, to Out. The nitrate

concentration also had a relationship with the $\delta^{18}\text{O}$ of nitrate (Fig. 6). Up to a nitrate concentration of 100 $\mu\text{mol L}^{-1}$, the $\delta^{18}\text{O}$ of nitrate increased as the nitrate concentration increased. From more than 100 $\mu\text{mol L}^{-1}$, the $\delta^{18}\text{O}$ of nitrate converged to 6‰.

Correlations among the chemical species were calculated using simple linear regression of each ion (Table 3). Significant correlations of the two ions were detected in regard to nitrate and chloride, chloride and nitrogen, chloride and stable isotope ratio, and sulfate and sodium.

4 Discussion

4.1 The Heterogeneous Effect of Atmospheric Nitrogen Deposition on the Stream Water

Mean nitrate concentration of stream water in the Chichibu region showed 113 $\mu\text{mol L}^{-1}$ (Konohira et al. 2006) which was the highest concentration in Japan. In our study, mean nitrate concentration ranged from 26 to 237 $\mu\text{mol L}^{-1}$ in 24 streams in the Chichibu region (Fig. 3; Table 2). Air mass advection from the Tokyo Metropolitan area is supposed to be the main cause of the high concentration of nitrate in the Chichibu region, although the reason has not fully discussed in the previous studies.

In the present study, we set sampling stations with a watershed that had less of an effect of geological conditions, ratio of softwood and hardwood and clear-cut logging areas. We categorized sampling station as Out, Middle, and In (Fig. 1).

Table 2 Stream water chemistry at each sampling point

#	Site Name	Date	EC ($\mu\text{S cm}^{-1}$)	pH	Na ²⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	$\delta^{15}\text{N}$	$\delta^{18}\text{O}$	CV
1	Nakatsukyo	13-Aug	89.5	7.30	110.2	91.5	303.0	19.0	25.6	65.1	0.8	-6.1	
2	OukanCamp	13-Aug	147.1	7.87	136.6	78.6	655.1	37.8	39.3	88.7	1.2	-5.4	
3	Yatakezawa	22-Aug	124.1	7.23	131.8	56.5	496.7	17.9	33.8	140.6	1.1	-4.0	11
4	Kiri	22-Aug	193.2	8.03	120.2	74.2	912.3	36.6	87.8	81.2	1.6	-1.8	
5	Tsuchisaka	22-Aug	199.3	7.73	111.6	95.1	922.9	61.5	58.8	162.4	1.3	-1.1	
6	Usuki	13-Aug	145.0	7.61	156.1	62.1	607.7	31.6	126.7	117.3	1.2	-0.8	13
7	Koumyoji	13-Aug	189.3	7.66	163.6	95.6	688.5	53.2	84.8	98.2	1.8	-0.3	24
8	Izusawa	13-Aug	167.4	7.58	653.0	141.7	424.6	33.3	75.3	439.4	2.8	-2.7	9
9	Shirahisa	13-Aug	119.0	7.35	146.5	81.6	468.8	31.3	117.0	157.8	1.2	0.5	9
10	Ochigawa	13-Aug	104.3	7.59	103.8	31.2	483.8	19.2	47.4	57.8	0.8	-2.8	5
11	Urayama	21-Aug	65.6	7.40	119.1	31.4	261.7	29.9	52.8	55.4	0.6	-0.7	
12	Nomaki	13-Aug	220.0	7.28	199.0	278.7	605.5	66.6	128.6	253.6	2.9	-1.5	26
13	Hosokubo	21-Aug	74.8	7.53	142.9	45.4	275.7	21.5	64.1	60.0	1.0	-2.4	
14	Kojimasawa	21-Aug	131.6	7.49	220.0	113.0	442.8	46.2	117.4	171.7	1.6	0.8	
15	Yamanaka	21-Aug	91.7	7.66	116.7	80.0	322.3	41.8	91.2	54.6	1.4	0.8	
16	Sakawagawa	21-Aug	52.0	6.92	113.1	46.0	143.6	36.3	70.0	67.6	0.6	3.0	
17	Negishi	22-Aug	116.7	7.05	198.5	115.5	360.8	92.7	193.7	228.7	3.1	4.8	
18	Hiroki	21-Aug	93.9	7.08	194.7	94.7	251.9	98.4	237.1	74.4	2.2	5.7	4
19	Sadamine	22-Aug	84.7	7.36	76.8	171.4	200.0	44.8	73.0	33.9	2.1	0.9	10
20	Miyairi	22-Aug	261.0	7.55	226.8	151.5	1086.7	115.8	186.2	142.0	4.0	5.5	
21	Tsudoku	21-Aug	81.7	7.33	95.1	127.4	257.1	56.8	113.3	18.9	1.9	5.5	
22	Nishikawa	21-Aug	122.0	7.65	170.5	117.8	400.2	74.9	116.9	89.7	-1.0	-8.1	14
23	Akasawa	21-Aug	121.8	7.80	160.0	74.2	458.2	59.0	96.1	84.8	1.9	2.6	6
24	Mugihara	21-Aug	105.6	7.46	171.5	82.8	371.6	52.6	103.6	102.0	1.4	1.8	3

Ion concentration is expressed in $\mu\text{mol L}^{-1}$, and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in ‰. CV in the right edge column is the coefficient of variance (CV) of nitrate for present study and the data taken in Konohira et al. (2006) and the unit for the column is %

Nitrate concentration of stream water increased when we ordered the groups as In, Middle, and Out. In the Chichibu region, air mass is transported from the Tokyo Metropolitan area, and the effect decrease its magnitude as it moves towards deep inside the valley, the western part of the region. As we drew a major wind path in the Chichibu region, Out is located within the first impact point of the air mass; Middle is second, and In is the last. The effect of the nitrogen compound should be the difference between the three groups: Largest in the Out, middle in the Middle and lowest in the In. Thus, the nitrogen compound differences from the Tokyo Metropolitan area cause the difference in the nitrate concentration ($26\text{--}237 \mu\text{mol L}^{-1}$) of stream water.

There is another clue which shows that nitrate is loaded as an atmospheric deposition of nitrogen compound.

Generally, the contribution of the chloride from the base rock minerals is minor, so the origin of the chloride in stream water is usually regarded as an atmospheric deposition (Juang and Johnson 1967; Ratcliffe and Peters 1998). In a volcanic area, chloride could be added to the stream water through sediments and often shows a high concentration of chloride. However, our study area had no volcanic geological layers. A high correlation between nitrate and chloride ($r=0.73$, $p<0.001$; Table 3) shows the source of both chloride and nitrate are atmospheric deposition. The main sources of chloride are sea salt and combustion (Kaneyasu et al. 1999). The same correlation is reported in other streams in the Kanto area (Honda et al. 2007).

An atmospheric chemistry study supports the difference among the nitrogen compound loads in small areas. Wakamatsu et al. (1999) showed typical

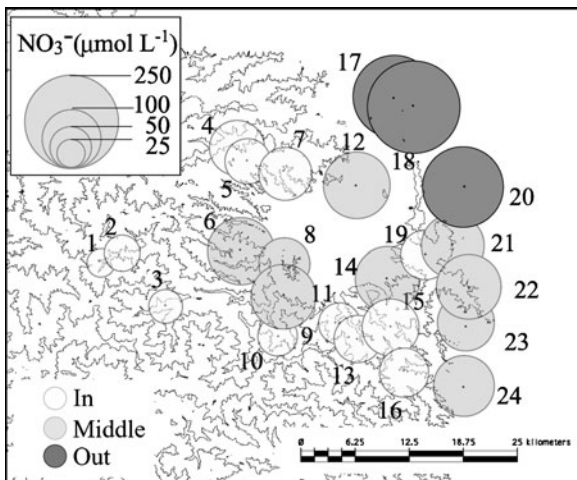


Fig. 3 Nitrate concentration and wind path. Sampling points were classified as In, Middle, and Out, depending on the station's location and the relationship to the wind (Fig. 1). The areas of the circles denote the concentration of nitrate at each sampling point

atmospheric ozone (O_3) and NO_x concentrations in the Kanto region (Tokyo and its surrounding area). The study was conducted for analyzing atmospheric O_3 pollution in the Kanto region. The NO_x is the precursor of O_3 so that both data were shown in the study. Both chemical species showed similar geographical distributions in the Kanto region. According to the study, the air mass often transported from the Tokyo Metropolitan area to the mountain side of the Kanto region has the highest concentration of O_3 at the fringes of the mountain area, including the Chichibu region, and it decreases its concentration by increasing its distance from Tokyo.

In previous studies on atmospheric deposition, constant nitrate concentrations were detected over a

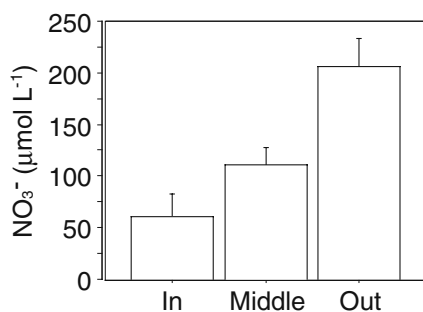


Fig. 4 ANOVA and nitrate concentration of the In, Middle, and Out groups. These three groups are significantly different ($p < 0.0001$) as found by the Tukey–Kramer test

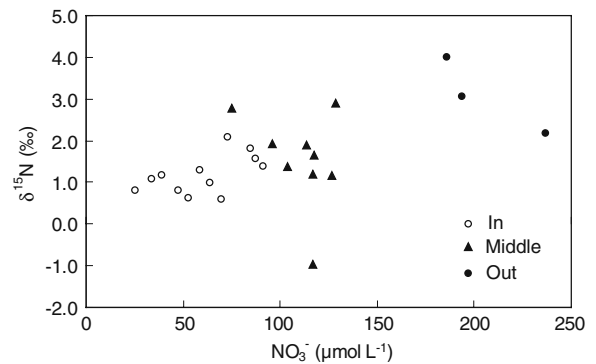


Fig. 5 Scatter plot of nitrate concentrations and $\delta^{15}N$ of nitrate of the points. Points are divided into three classifications, corresponding with Fig. 1

broad area. In the present study, the effect of atmospheric deposition is not homogenous but shows large variations in the small area we studied (ca. 300 km²). The heterogeneous concentrations were explained sufficiently by the position of the study site, geomorphology and wind directions.

4.2 Relationship Between Stages of Nitrate Saturation and $\delta^{18}O$ and $\delta^{15}N$ of Nitrate in the Stream Water

A high nitrogen stable isotope ratio of NO_x generally reflects anthropogenic effects. Kiga et al. (2000) reported a high $\delta^{15}N$ in power plant emissions of NO_x , which ranged from 4.8‰ to 9.6‰. Kendall et al. (2007) reviewed the rather low values of NO_x from natural processes such as lightning or soil emission. In nonpolar areas, Morin et al. (2009) showed that the $\delta^{15}N$ of nitrate, mostly derived

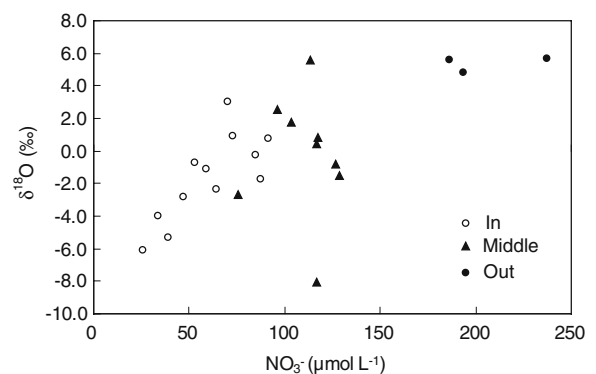


Fig. 6 Scatter plot of nitrate concentrations and $\delta^{18}O$ of nitrate of the points. Points are divided into three classifications, corresponding to Fig. 1

Table 3 Correlation coefficients of simple linear regression between the ions and stable isotopes

	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	δ ¹⁵ N	δ ¹⁸ O
Na ⁺	1.00	0.40	0.12	0.33	0.25	0.84 ^a	0.46	0.04
Mg ²⁺		1.00	0.21	0.61	0.48	0.46	0.57	0.23
Ca ²⁺			1.00	0.28	0.13	0.25	0.28	-0.02
Cl ⁻				1.00	0.73 ^a	0.25	0.83 ^a	0.52
NO ₃ ⁻					1.00	0.18	0.44	0.68
SO ₄ ²⁻						1.00	0.42	0.06
δ ¹⁵ N							1.00	0.42
δ ¹⁸ O								1.00

^aDenotes statistical significance at $p < 0.001$

from anthropogenically emitted NO_x, was significantly different (from 0‰ to 6‰) from nitrate sampled in locations influenced by natural NO_x sources ($-4 \pm 2\%$). Higher nitrate concentrations and elevation of δ¹⁵N can be attributed to deposition of anthropogenically derived atmospheric nitrogen. Highly affected locations had high concentrations of nitrate and high values of δ¹⁵N, and this may be attributed to the effect of fossil fuel combustion.

There was a specific relationship between nitrate and δ¹⁵N, in which the concentration of nitrate increases and the δ¹⁵N value also increases (Fig. 5). The In area showed a low concentration of nitrate with a low δ¹⁵N value that showed a small effect from atmospheric deposition. In the Middle area, the atmospheric effect increased with a rather high nitrate concentration and δ¹⁵N. In the Out area, atmospheric deposition had a strong effect on nitrate concentration and δ¹⁵N; both values were highest in this area. Comparing the differences among In and Middle with Middle and Out, the former showed a greater difference than the latter, which indicated that when nitrogen saturation occurs, at some sampling points, the chemical reactions decreased in speed.

Nitrate concentration has a specific relationship with nitrate δ¹⁸O (Fig. 6). Nitrogen saturation is separated in several stages with the nitrate concentration of stream water (Stoddard 1994). In the nitrogen saturation stages of 0 and 1, nitrate concentration exhibits seasonality. From stage 2, high nitrate concentrations can be detected even in the base-flow of the growing season, and they range from 0.5–1.0 mg N L⁻¹ (35.7–71.4 μmol L⁻¹). In stage 3, the nitrogen saturation is at its peak and the nitrate concentration is

more than 1.0 mg N L⁻¹ (>71.4 μmol L⁻¹). In our study site, there were several nitrogen saturation stages. Applying the definition of nitrogen saturation stages by Stoddard (1994), we could check that most of the In station was in the nitrogen saturation stage of 0 to 2 (Fig. 6) and Middle and Out were in stage 3. Stage 3, with a nitrate concentration of more than 100 μmol L⁻¹, δ¹⁸O showed a constant value (5.7‰). Aber et al. (1998) suggested that nitrification starts in stage 2. We assumed that nitrate of the stream water beyond stage 2 was not directly deposited from rain or atmospheric deposition, but that it came from the nitrification of organic nitrogen. One finding supporting this is that the snow δ¹⁸O of the NO₃ was more than 60‰ (Tabayashi, submitted). If nitrogen deposition directly drains into stream water, the δ¹⁸O of the stream water NO₃ should be larger. Second, the δ¹⁸O of NO₃ generated from nitrification was in the range of -10‰ to +10‰ in the literature (Mayer et al. 2001), and the δ¹⁸O of NO₃ in the present study area, 5.7‰, was within this range. These two reasons suggest that most of the nitrate in the area came from nitrification.

Generally, in nitrification, one third of the oxygen comes from oxygen in the air and two thirds from water (Kendall et al. 2007). Thus, the δ¹⁸O of NO₃ from nitrification closely reflected the values of the δ¹⁸O of water. Because soil water is the source of rainwater over a few months' time, concentrations of dissolved materials and nitrate δ¹⁸O in water should be relatively stable, reflecting the cumulative conditions of a certain period. Spoelstra et al. (2007) reported nitrification in soil water and the δ¹⁸O of NO₃ ranged over 3.1–10.1‰, with a mean value of 5.2‰. Such a range overlaps with our data when nitrate concentrations were higher than 100 μmol L⁻¹ (Fig. 6). When nitrification activates, the δ¹⁸O of NO₃ asymptotically moves close to the value of δ¹⁸O of H₂O, finally showing a stable value. In lower nitrate concentrations, δ¹⁸O increased as the concentration of nitrate increased, but in middle to high concentrations, δ¹⁸O remained at the same value. This trend was the same as that of δ¹⁵N (Fig. 5), but it was much clearer for δ¹⁸O.

Biogeochemical reactions in the soil that increase the δ¹⁸O of nitrate depend on leached nitrate, but they seem to saturate above nitrate concentrations of 100 μmol L⁻¹. This result can be used as a robust tool in determining whether the watershed is in the condition of N saturation and close to leach nitrogen. To determine the mechanism of nitrate reactions using

stable isotope modification, further study including laboratory experiments would be indispensable.

5 Conclusions

In the Chichibu region, 50–100 km from central Tokyo, the nitrate concentration of stream water was high, especially in eastern part of the area. The present study proved these conditions originated from combustion gases. From the wind analysis of the previous study with geomorphological conditions of the study area, high concentrations of NO_x gas should be loaded in the area as a form of air mass advection from the Tokyo Metropolitan area. The stream water nitrate concentration was not so high in the western part of the river because there was less effect on the nitrogen deposition to those tributaries. Nitrogen and oxygen stable isotope ratios were good indicators of the nitrogen saturation stages.

With the economic development in other countries, NO_x emissions will increase as a result of urbanization, and this may increase the mean concentration of stream water nitrate, as shown in this study. If water supply dams are constructed in areas where combustion gases are emitted from nearby urban areas, the water in the dam will have an elevated nitrate concentration. Such an unintended and unplanned effect of urbanization requires further study to prevent deleterious alterations of the aquatic environment. In developing countries in Asia, NO_x emissions are increasing with economic development, and some of these emissions are transported to surrounding countries (Klimont et al. 2001). Japan is situated east of other Asian countries, such that emission gases are transported from these countries to Japan on the westerly jet stream (Uno et al. 2000). Inside Japan itself, NO_x emissions have not decreased sufficiently. For the conserving ecosystems in the forest and water resources, we need further studies to analyze atmospheric loaded nitrogen both from domestic and surrounding countries.

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