Variations in Ambient Nitrogen Concentrations between an Inland Area of Tree Decline and a Coastal Area in Northern Japan

TAKASHI YAMAGUCHI* AND IZUMI NOGUCHI

Department: Environmental and Geological Research Department, Institute of Environmental Sciences, Hokkaido Research Organization, Kita 19 Nishi 12-1-6, Kitaku, Sapporo 060-0819, Japan

** Corresponding author: Takashi Yamaguchi, +81-11-747-3550; Email: t-yamaguchi@hro.or.jp*

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Abstract

Tree decline has recently been reported around the somma of Lake Mashu, Hokkaido, northeastern Japan, although its cause is uncertain. We have evaluated the concentrations of ambient reactive nitrogen compounds such as gaseous ammonia (NH_3), ammonium particles (NH_4^+), and nitrate particles (NO_3^-) both at Lake Mashu, located inland, and at Ochiishi, located on the Japanese coast. These gas and particles were measured at both sites by a multiple filter-pack method. The concentrations of NH_3 and NH_4^+ were greater during the warm season—from May to Sep.—at Lake Mashu (40.8 nmol m^{-3} and 25.3 nmol m^{-3}, respectively) than at Ochiishi, (20.1 nmol m^{-3} and 16.6 nmol m^{-3}, respectively), whereas the concentration of NO_3^- at Lake Mashu (1.0 nmol m^{-3}) was lower than at Ochiishi (7.7 nmol m^{-3}). The emission of NH_3 and NH_4^+ via agricultural activity in the area is thought to have contributed to their ambient concentrations at Lake Mashu; however, NO_3^- particles are thought to have been removed by gravitational settling during transport. Compared to other areas in Japan and Asia, the concentrations measured in this study were relatively low; however, the amount of nitrogen deposited in mountainous areas was heterogeneous and incorporated a contribution from fog. Further comprehensive investigation is thus required in order to gain a complete understanding of the influence that nitrogen compounds have on various ecological systems.

Key words: ammonia emission, fog chemistry, reactive nitrogen.

Introduction

Lake Mashu – a mountain caldera lake located in eastern Hokkaido, Japan (Figures 1(a) and (b)) – is frequently covered with fog that flows inland from the Pacific Ocean during the warm season each year (mainly May to Sep.; Hori 1953). A decline in the abundance of the Japanese mountain birch (*Betula ermanii*) around the lake's somma has recently been reported by various authors (Yamaguchi et al. 2012, Hoshika et al. 2013, Sakuma et al. 2014). These areas of tree decline are thought to be distributed mainly on the southern and western flanks of the somma (Figure 1(c)), although the reasons for this deterioration are uncertain. This decline is not thought to be related to anthropic influence, given that new infrastructure developments (e.g. road construction) in the region are restricted to the western mountain slope only. Field investigation has revealed that Sika deer (*Cervus nippon yesoensis*) overbrowsing on woody species in eastern Hokkaido – including in the Lake Mashu region – can seriously damage vegetation, although the interpreted impact on Japanese mountain birch is relatively small (Maeda Ippoen Foundation 1994). There are numerous other natural processes that can contribute to tree decline, such as typhoons and diseases; however, no such events have been recorded in the area over the last fifty years. The average temperature in eastern Hokkaido has been rising in recent years due to the effects of global warming, although the magnitude of change is no larger than that recorded elsewhere in Hokkaido, therefore, is unlikely to be a contributing factor. Furthermore, there are no significant spatial trends in precipitation across the region (Sapporo Regional Headquarters of Japan Meteorological Agency 2010), which may otherwise affect growth characteristics.

Acid fog has often been observed in Japanese mountainous areas (Igawa et al. 2002, Ikeda et al. 1995) and some previous studies have suggested that the decline of beech (*Fagus crenata*) could be caused by acid fog, alongside the deposition of other air pollutants (Igawa and Okochi 2009, Nara et al. 2001, Shigihara et al. 2008). Acid fog also has been reported over the northwestern Pacific Ocean and along the coastal

areas of eastern Hokkaido (Sasakawa and Uematsu 2005, Yoshida et al. 2007, Nishio et al. 1995) (Table 1). Previous studies have shown that fog at Lake Mashu is only slightly acidic (pH of 4.6–5.1), which is not a cause for concern (Yamaguchi et al. 2015, Yamaguchi et al. 2013); however, the NH_4^+ concentration and NH_4^+/nss-SO_4^{2-} ratio in fog water at Lake Mashu are three- to five-times higher than those in the North Pacific Ocean (Table 1), and the amount of nitrogen deposition via fogwater deposition is typically comparable with that of rainfall (Yamaguchi et al. 2015). Gaseous ammonia (NH_3) emissions from agricultural activity might, therefore, play a role in neutralizing the fog's pH and act as a source of nitrogen around Lake Mashu.

Nitrogen is an essential nutrient for plant and tree growth, although excess amounts can have significant detrimental effects on vegetation (Bobbink et al. 2010). In addition, NH_3 and ammonium particles (NH_4^+), emitted mainly from agricultural activity, and nitrogen oxides (NOx), derived mainly from combustion, also have substantial impacts on the ecosystem (Asman and van Jaarsveld 1992, Bouwman et al. 1997, Fowler et al. 2013, Galloway et al. 2013). For example, changes in nitrogen load can affect the compositions of plant species (Duprè et al. 2010), their physiologies, sensitivities to other stresses such as drought and frost (Bobbink et al. 2010), and the response of birch to ground-level ozone (Pääkkönen and Holopainen 1995). Changing ozone levels has also been suggested by Feng et al. (2005) to have caused a recent decline of *Betula ermanii* trees in Japan.

Figure 1(b) shows that large areas of land around Lake Mashu and southeastern Hokkaido are used for agriculture, with NH_3 being a common byproduct of such activity (e.g. used as fertilizer and produced by livestock; Kannari et al. 2007). Large-scale development of dairy farms was carried out in this region in the 1950s. The rate and magnitude of NH_3 and NH_4^+ emissions would therefore have increased dramatically since that time, and it is thought that an increased nitrogen load to the somma of Lake Mashu may have altered the nutrient imbalance of trees growing there, owing to the presence of an extremely nutrient-poor soil caused by volcanic eruptions of Mt. Mashu (Sakuma et al. 2014). It is clear, therefore, that evaluating the origin of atmospheric nitrogen at the somma of Lake Mashu (hereafter, Lake Mashu) is important to understanding how different nitrogen species interact and influence various ecosystems. In this study, we (i) evaluated the concentrations of – and seasonal changes in – gaseous NH_3, and NH_4^+ and NO_3^- particles at both Lake Mashu and the coastal station of Ochiishi, and (ii) determined the amount of nitrogen in both regions that was sourced from agricultural activity.

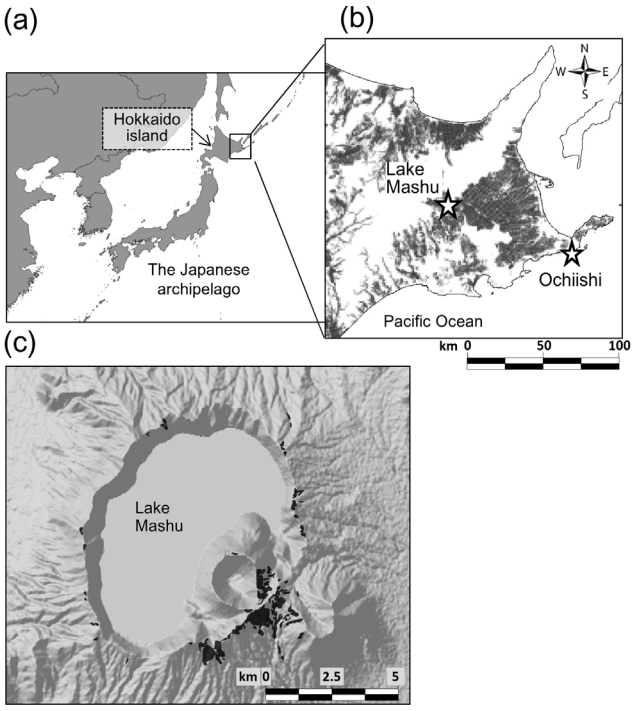

Figure 1. Map showing the locations of sites studied in this work (a). Lake Mashu is located inland in eastern Hokkaido, and Ochiishi station is located on the Pacific coast. The main land use in both areas is agriculture, as shown by gray shaded areas in (b). Lake Mashu is a mountain caldera lake and surrounded by steep slopes on all sides (c). Areas, where tree decline may have occurred, were identified by comparing aerial photographs taken in 1977 and 2008, and are shown in (c) as black domains

Methods

Site description

Figure 1 (c) shows the area of tree decline investigated herein, which was estimated using a supervised classification of aerial photographs taken in 1977 and 2008. This result has not been verified across the entire area due to limited access within the Akan National Park, although tree decline has been confirmed by field reconnaissance on the southern slope.

The sampling site at Lake Mashu was an observatory located on the edge of the caldera (43.5°N, 144.5°E, 542 m above sea level). The dominant tree species in the area is Japanese mountain birch (*Betula ermanii*) and its growing season is almost the same as the foggy season, from late May to Sep. The forest floor is densely covered by dwarf bamboo (*Sasa senanensis*) (Igarashi 1986). Agriculture is the main land use within a 50-km radius of Lake Mashu (Figure 1 (b)), especially, to the south. Meteorological data for the region were obtained from the closest weather

station operated by the Japan Meteorological Agency. Annual mean rainfall and temperature in the last 30 years were 1,068 mm and 4.9 °C, respectively, and were 578.7 mm and 13.7 °C, respectively, between May and Sep. (the warm season).

Ochiishi station is located at Cape Ochiishi (43.2°N, 145.5°E, 50 m above sea level), is surrounded mostly by marshland, faces the Pacific Ocean, and is 20 km away from the nearest city. The Acid Deposition Monitoring Network in East Asia (EANET) has carried out wet and dry deposition monitoring in the area. Annual mean rainfall and temperature measured at the closest weather station were 929 mm and 6.3 °C, respectively, and were 542 mm and 13.0 °C, respectively, in the warm season (Network Center for EANET 2014).

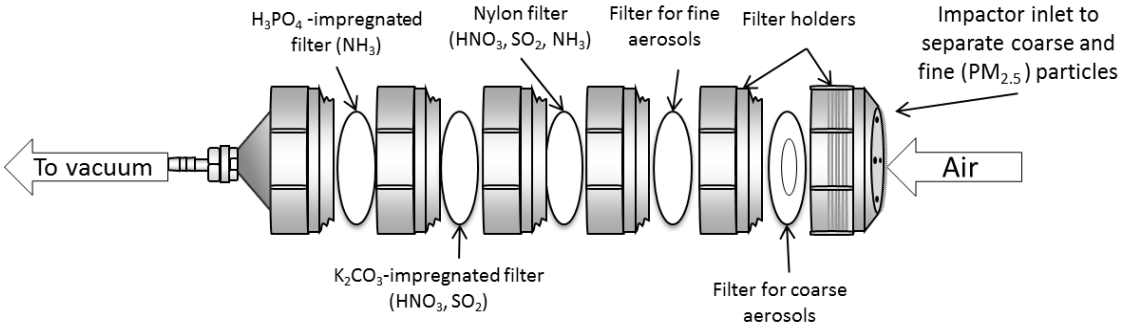

Figure 2. Schematic diagram of a filter pack used in this study

Aerosol and gas sampling, and their analyses

At Lake Mashu, a multiple filter-pack method was used to measure ambient gas/particle concentrations, based on procedures outlined in the *EMEP manual for sampling and chemical analysis* (Norwegian Institute for Air Research 2001). The filter packs utilized consisted of five filter holders (Figure 2) and the flow rate was 4.0 L min^{-1}. NH_3 was collected on nylon and phosphoric acid-impregnated filters, whereas aerosols were collected on Teflon filters. Filter-pack measurements began in May 2010; however, since May 2011, particles have been collected with a $PM_{2.5}$ impactor in order to separate aerosols into fine and coarse particles. In this study, we used both fine and coarse particles to calculate NH_4^+ and NO_3^- concentrations. Samples were collected weekly from Apr. to Oct., and biweekly from Nov. to Mar. Detection limits for gases and ions were: $NH_3 = 1.0 \times 10^{-3}$ nmol m^{-3}, $NH_4^+ = 0.6 \times 10^{-3}$ nmol m^{-3}, and $NO_3^- = 0.2 \times 10^{-3}$ nmol m^{-3}.

Data published by the EANET was used to represent conditions at Ochiishi (Network Center for EANET 2014), which were collected using the same multiple filter-pack method described above. A detailed methodology can be found in the *Technical Manual for Air Concentration Monitoring in East Asia* (Network Center for EANET 2013). The value under-reporting limit was calculated as zero, and the reporting limit of nitric acid (HNO_3) was set to 0.1 ppb (4.1 nmol m^{-3}). Many HNO_3 concentrations at Ochiishi were below the detection limit, and so we did not include nitric acid in this study. Non-sea-salt sulfate (nss-SO_4^{2-}) is mainly converted from sulfur dioxide (SO_2) emitted from anthropogenic combustion and volcanic eruption. The concentration of nss-SO_4^{2-} was calculated in our work via the following equation, which eliminated the contribution of sulfate contained in sea-salt aerosols:

$$[\text{nss-}SO_4^{2-}]\ (\mu\text{mol L}^{-1}) = [SO_4^{2-}] - 0.06028\ [Na^+].$$

The significance of the differences in concentrations were calculated by a *t-test* at the $p = 0.05$ level.

Results

Ammonia gas (NH_3)

Ammonia gas concentrations exhibited a clear seasonal variation at both sites (Figures 3 and 4). At Lake Mashu, measured concentrations were in the range of 30–50 nmol m^{-3} during the warm season, and decreased to less than 10 nmol m^{-3} in the cold season. At Ochiishi, the measured concentrations showed a similar seasonal change; however, a maximum of 30 nmol m^{-3} was recorded during the warm season, which was lower than at Lake Mashu. The mean NH_3 concentrations during the warm season at Lake Mashu and Ochiishi were 40.8 nmol m^{-3} and 20.1 nmol m^{-3}, respectively (Table 2). The difference in NH_3 warm-season monthly mean concentrations between these sites was statistically significant.

Ammonium particle (NH_4^+)

Measured concentrations of NH_4^+ at Lake Mashu and Ochiishi were 20–40 nmol m^{-3} and 10–30 nmol m^{-3},

respectively (Figures 3 and 4). The mean concentration in the warm season at Lake Mashu (25.3 nmol m^{-3}) was higher than at Ochiishi (15.6 nmol m^{-3}). As for NH_3, the difference of NH_4^+ warm-season mean concentrations was also statistically significant. The concentrations of NH_4^+ also showed a seasonal variation: at Ochiishi, measured values were high from winter to spring (Feb.–Mar.), though decreased during the warm season. In contrast, the NH_4^+ concentration at Lake Mashu was the highest during the warm season.

nss-SO_4^{2-}

The monthly mean concentrations of nss-SO_4^{2-} at Lake Mashu and Ochiishi were similar (10–30 nmol m^{-3}; Figure 3), with neither exhibiting a clear seasonal trend (Figure 4). The warm-season mean concentration of nss-SO_4^{2-} at both localities was 15.9 nmol m^{-3} and 19.4 nmol m^{-3}, respectively (Table 2), again with no significant differences between localities recorded. These concentrations are comparable with those reported from within the marine area in previous studies (Table 1). As such, the warm-season nss-SO_4^{2-} concentration in eastern Hokkaido is considered to be controlled by the background concentration in the marine area, as the concentration level does not differ between coastal and inland areas. In addition, the observed nss-SO_4^{2-} monthly-mean concentration variations were similar to those recorded for NH_4^+ (Figure 3), indicating that NH_4^+ was the dominant sulfate counter ion.

NH_4^+/nss-SO_4^{2-} ratio

The NH_4^+/nss-SO_4^{2-} ratio (equivalent) showed clear seasonal changes at Ochiishi, with high values (0.7–1.0) in winter and spring, and low values (0.2–0.6) in the warm season (Figure 3). The lowest ratio (0.2) is similar to that reported by previous studies (Sasakawa and Uematsu 2002, Jung et al. 2013) (Table 1). The mean ratio in the warm season from 2011 to 2013 was 0.42, indicating that $(NH_4)HSO_4$ was the dominant component of the sulfate. By contrast, the ratio at Lake Mashu was greater than 0.8 in the warm season, but was notably lower in the cold season (Figure 4). The mean ratio across all 2011–2013 warm seasons was 0.8.

Nitrate particle

The concentration of NO_3^- at Ochiishi was high in March–April (10.0–12.5 nmol m^{-3}) and low in the warm season (7.2–8.9 nmol m^{-3}) (Table 2). It subsequently rose to 10.0 nmol m^{-3} during Oct. and then decreased during the winter. The seasonal increases and decreases at Lake Mashu, were similar to those at Ochiishi; however, the concentration was notably lower during April (4.5 nmol m^{-3}) and the warm season (0.4–1.5 nmol m^{-3}) (Table 2).

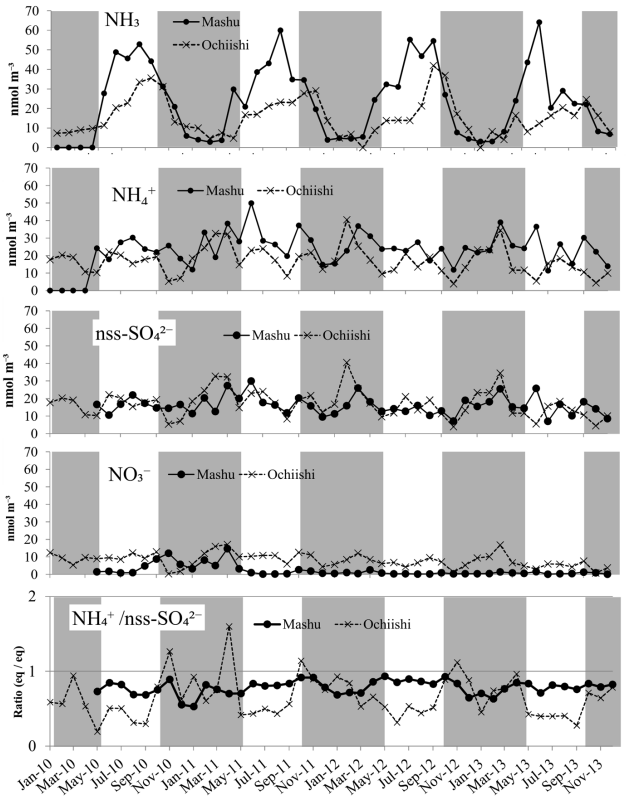

Figure 3. Monthly variations in concentrations of gaseous NH_3, and NH_4^+, nss-SO_4^{2-}, and NO_3^- particles from 2010 to 2013. The NH_4^+/nss-SO_4^{2-} ratio over the same time period is also shown. White and gray areas denote warm and cold seasons, respectively

The NO_3^-/nss-SO_4^{2-} ratio at Ochiishi exhibited a clear seasonal trend that was similar to that of NH_4^+/nss-SO_4^{2-}, whereby it was low in the warm season (0.18–0.22), and high beforehand and afterwards (>0.5) (Figure 4 and Table 2). By contrast, the NO_3^-/ nss-SO_4^{2-} ratio throughout the year at Lake Mashu was lower than that at Ochiishi, and exhibited a trend similar to the NO_3^- concentration due to the nss-SO_4^{2-} concentration having remained stable over time.

Discussion

Ammonia

The concentration of NH_3 recorded at Lake Mashu was higher than at Ochiishi; in particular, the mean concentration at Lake Mashu (40.8 nmol m^{-3}) was twice as high as that at Ochiishi (20.1 nmol m^{-3}) during the warm season.

As NH_3 has a high deposition velocity (Asman and van Jaarsveld 1992), any emissions will readily accumulate in the local area. Abundant agricultural activity close to Lake Mashu may therefore have

Table 1. Gas and particle concentrations in ambient air and fog, water chemistry in the North Pacific Ocean, the coastal area of Hokkaido, and at Lake Mashu

	Gas/Aerosol				Fog			
	NH_3	NH_4^+	nss-SO_4^{2-}	NH_4^+/nss-SO_4^{2-}	pH	NH_4^+	nss-SO_4^{2-}	NH_4^+/nss-SO_4^{2-}
	(nmol m^{-3})			(eq/eq)		(μmol L^{-1})		(eq/eq)
North Pacific Ocean								
Tsunogai (1971) (Nov.–Mar.)	2.9	1.6						
Quinn (1988) (May)	1.3	5.9	5.1	0.58				
Sasakawa et al. (2002) (Jul.)		11	19	0.29	4.2	25	41	0.30
Sasakawa et al. (2005) (Jul.–Aug.)					3.7–4.2	25–99	41–115	0.30–0.45
Yoshida et al. (2007) (Jul.–Aug.)					3.9	52	84	0.31
Jung et al. (2013) (Jul.–Aug.)		5.6	18	0.16	4.2	22	36	0.31
Coastal area								
Nishio (1995) (Jun.–Sep.)					3.48–4.79 (4.07)*			
Ochiishi								
This study (May–Sep.)	20.1	16.6	19.4	0.43				
Lake Mashu								
Yamaguchi et al. (2013) (Jun.–Oct.)					5.08	166	59	1.40
Yamaguchi et al. (2015) (Jun.–Oct.)					4.61	175	69	1.27
This study (May–Sep.)	40.8	25.3	15.9	0.80				

* mean pH

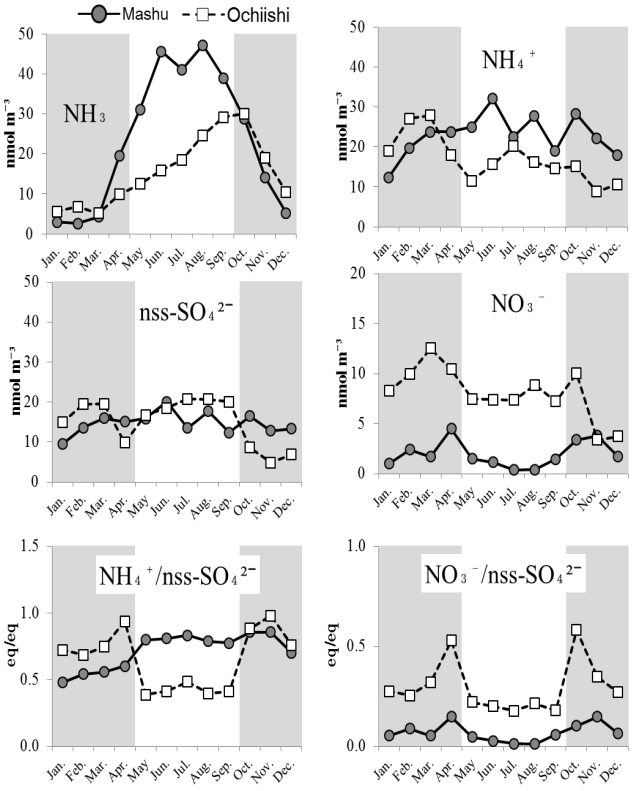

Figure 4. Averages of monthly mean concentrations, and ratios of aerosols and gases at Lake Mashu and Ochiishi from 2010 to 2013. White areas indicate the warm season (May–September) and gray areas indicate the cold season (October–April)

caused the relatively higher concentrations of NH_3 observed herein.

The dominant wind at Ochiishi during the summer is southerly and comes from over the Pacific Ocean. The concentration of NH_3 measured in this marine air during cold season was close to the levels recorded in this study (Tsunogai 1971) (Table 1); however, the monthly mean NH_3 concentration in May measured in this work (12.5 nmol m^{-3}) was considerably higher than that measured in May 1987 (1.3 nmol m^{-3}) by Quinn et al. (1988). Therefore, even in coastal regions (e.g. Ochiishi), we suggest that the NH_3 concentration was affected by agricultural NH_3 emissions during the warm season. The low concentration recorded during winter may be attributed to low NH_3 emissions, low temperatures, and snow cover.

The NH_4^+/nss-SO_4^{2-} ratio

NH_4^+ and SO_4^{2-} are the main components of fine particulate matter and can be transported over long distances. The NH_4^+/nss-SO_4^{2-} ratio at Ochiishi showed a clear seasonal change, having been low in the warm season (around 0.2) and high in the cold season. The low warm-season NH_4^+/nss-SO_4^{2-} ratio at Ochiishi indicates that the main components of sulfate particles were ammonium hydrogen sulfate ($(NH_4)HSO_4$) and sulfuric acid (H_2SO_4) mist, whereas the high ratio at Lake Mashu (0.8) indicates that the dominant NH_4^+ particle was ammonium sulfate ($(NH_4)_2SO_4$). These re-

Table 2. Averages of monthly mean concentrations, and ratios of gaseous and aerosol components at Lake Mashu and Ochiishi from 2010 to 2013

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Mean (May–Sep.)	Annual mean
Lake Mashu														
Concentration (nmol m^{-3})														
NH_3	3.0	2.6	4.3	19.5	31.1	45.6	41.1	47.2	39.0	28.7	14.1	5.3	40.8	23.5
NH_4^+	12.3	19.7	23.7	23.8	25.0	32.1	22.5	27.7	19.0	28.3	22.2	17.9	25.3	22.9
NO_3^-	1.0	2.4	1.7	4.5	1.5	1.1	0.4	0.4	1.5	3.4	3.8	1.7	1.0	2.0
nss-SO_4^{2-}	9.5	13.6	16.0	15.1	15.9	20.1	13.5	17.7	12.4	16.5	12.8	13.4	15.9	14.7
Ratio (eq/eq)														
NH_4^+/ nss-SO_4^{2-}	0.48	0.54	0.56	0.60	0.80	0.81	0.83	0.79	0.78	0.86	0.86	0.70	0.80	0.72
NO_3^-/nss-SO_4^{2-}	0.05	0.09	0.05	0.15	0.05	0.03	0.01	0.01	0.06	0.10	0.15	0.06	0.12	0.07
Ochiishi														
Concentration (nmol m^{-3})														
NH_3	5.6	6.8	5.2	9.9	12.5	15.9	18.5	24.6	29.2	30.1	18.9	10.5	20.1	15.6
NH_4^+	19.1	27.1	27.9	18.0	11.6	15.6	20.2	16.1	14.7	15.1	8.8	10.6	15.6	17.1
NO_3^-	8.3	10.0	12.5	10.4	7.5	7.4	7.4	8.9	7.2	10.0	3.4	3.8	7.7	8.1
nss-SO_4^{2-}	15.0	19.5	19.6	9.9	16.8	18.5	20.8	20.7	20.1	8.6	4.9	6.9	19.4	15.1
Ratio (eq/eq)														
NH_4^+/nss-SO_4^{2-}	0.72	0.69	0.75	0.94	0.39	0.41	0.48	0.40	0.41	0.88	0.98	0.76	0.42	0.65
NO_3^-/nss-SO_4^{2-}	0.28	0.26	0.32	0.53	0.22	0.20	0.18	0.21	0.18	0.58	0.35	0.27	0.85	0.30

Table 3. Mean concentrations of ammonia gas and ammonium particles from May to September, 2013, in rural and remote sites in Asia. With the exception of Lake Mashu and Moshiri, concentrations were calculated from a report from the Network Center for EANET (2014)

			Concentration (nmol m^{-3})	
Characteristic	Country	Site name	NH_3	NH_4^+
Rural				
	Russia	Primorskaya	49.1	37.2
	Japan	Lake Mashu	35.9	22.8
		Moshiri* (Hokkaido)	34.8	33.8
		Ijira	84.2	60.2
	Korea	Kanghwa	364.0	184.3
		Imsil	164.4	134.6
	Indonesia	Serpong	587.3	26.6
	Thailand	Chiang mai	118.6	3.6
		Nakhon Ratchasima	134.1	32.4
	Vietnam	Hoa Binh	64.6	24.9
Remote				
	Japan	Ochiishi	14.7	12.9
		Rishiri (Hokkaido)	27.6	27.4
		Sado-seki	38.4	52.7
		Happo	21.3	57.9
		Oki	32.7	63.8
		Ogasawara	27.0	12.3
	Korea	Cheju	205.3	99.0
	Malaysia	Tanah Rata	59.7	24.2
		Danum Valley	185.1	7.5
	Philippines	Mt. Sto. Tomas	36.0	11.2

*The concentrations at Moshiri were calculated from a report produced by the Environmental Laboratories Association (2015). Elsewhere, they were calculated from a report produced by the Network Center for EANET (2014)

sults imply that NH_3 gas converted the sulfate particles to ammonium sulfate during its inland transportation from the coast. Consequently, we suggest that extensive agricultural activity in eastern Hokkaido may have been the main source of ammonium particles that neutralized acidic particles during the warm season.

The NH_4^+/nss-SO_4^{2-} ratio recorded during the cold season at Ochiishi was high, and the absolute concentration of NH_4^+ was also high in February and March, which may have been due to atmospheric aerosols transported from Asia to Hokkaido (Akiyama et al. 2007). The ratio in the cold season at Lake Mashu tended to be lower than that at Ochiishi, which we attribute to anthropogenic nss-SO_4^{2-} emissions around Lake Mashu. Human activities such as power generation via the combustion of fossil fuels may be the cause.

Nitrate particles

The measured NO_3^- concentration at Lake Mashu in the warm season was significantly lower (1.0 nmol m^{-3}) than at Ochiishi (7.7 nmol m^{-3}) (Table 2); however, the NO_3^-/ nss-SO_4^{2-} ratio was also low at Ochiishi at this time (Figure 4). As NO_3^- is mainly contained in coarse particles and rapidly removed by gravitational deposition (Yoshida et al. 2007), settling during transportation inland–coupled with the higher elevation than at the coast – would lower the concentration of NO_3^- at Lake Mashu.

The higher concentration of NO_3^- in spring and autumn further indicates the influence of anthropogenic pollution transported from the Asian continent to Hokkaido (Akiyama et al. 2007).

From these results, we conclude that the concentrations of NH_3 gas and NH_4^+ particles in Hokkaido's rural areas have increased due to increased NH_3 emissions

caused by nearby agricultural activities, although NO_3^- concentrations were lower inland than along the coast.

Comparison with other areas

We compared the mean concentrations of NH_3 and NH_4^+ measured from May to Sep. in 2013 to those reported from other rural and remote areas in Hokkaido, and other regions in Asia (Environmental Laboratories Association 2015, Network Center for EANET 2014). Concentrations of both species reported from Moshiri and Rishiri (central and north Hokkaido) were similar to those from Lake Mashu and Ochiishi, with those from other sites being even larger. The island of Hokkaido has a subarctic, humid climate, and eastern Hokkaido is frequently covered by a dense fog in summer. This fog reduces temperatures and so summer NH_3 emissions in the region would be relatively low. The concentrations of NH_3 and NH_4^+ in tropical regions such as Indonesia and Vietnam and in temperate region such as Korea were significantly higher than those reported herein by a factor of 5–10. It has been previously pointed out by Vet et al. (2014) that eastern Asia has the highest NH_3 emissions and total nitrogen deposition in the world.

The dry deposition of nitrogen at Ochiishi during the warm season (here, considered as the sum of NH_3, NH_4^+ and NO_3^-) was reported by the Network Center for EANET (2014) to be 1.8 mmol m^{-2} (0.25 kg N ha^{-1}). We could not evaluate the dry deposition at Lake Mashu in this study because of its complex terrain and insufficient meteorological measurements. However, for reference, the annual dry deposition of nitrogen in Hokkaido in 2013 reported by the Environmental Laboratories Association (2015) was 5.5 mmol m^{-2} (0.8 kg N ha^{-1}) at Moshiri (a rural site) and 7.6 mmol m^{-2} (1.1 kg N ha^{-1}) at Rishiri (a remote site). It is therefore likely that the dry deposition of nitrogen at Lake Mashu would be ~1.0 kg N ha^{-1}.

A critical threshold, at which nitrogen deposition would affect sensitive species in boreal forests, has been suggested to be 5–10 kg N ha^{-1} $year^{-1}$ (Bobbink et al. 2010), which is lower than that for temperate and tropical forests. Yamaguchi et al. (2015) showed that nitrogen deposited via fog at Lake Mashu was approximately 3.6–4.2 kg N ha^{-1} in the warm season, showing that increases in NH_3 and NH_4^+ concentrations (and their dry deposition amounts) are not negligible. Moreover, forest edges would act as "effective concentrators" (Weathers et al. 2001), with the amounts of air pollution deposited over the forest being heterogeneously distributed (Weathers et al. 2006). Nitrogen concentrations and spatio-temporal variations in depositional amounts should therefore be carefully evaluated, especially in mountainous areas in Asia.

Conclusions

Measured concentrations of NH_3 gas and NH_4^+ particulate matter at Lake Mashu were higher in the warm season than the cold season, which is concluded to have been due to increased NH_3 emissions related to agricultural activities in eastern Hokkaido. Agricultural development in recent decades is likely to have increased the amount of nitrogen deposition in this area. Although these measured concentrations of NH_3 and NH_4^+ imply that the amount of nitrogen in dry deposition at Lake Mashu may be small, a comprehensive estimation of total nitrogen input (including that from rain and fog) is necessary to evaluate its effect on the local ecosystem. Nitrogen concentrations reported from other regions in Japan and Asia are higher than those measured in our work. Air pollution has a wide range of impacts on the biodiversity and function of natural ecosystems. As such, further observation-based investigations into nitrogen deposition in mountainous areas are needed to fully understand its role in the biosphere, allowing the effects of air pollution to be considered in long-term conservation strategies.

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