

# Ammonia Emission from a Young Larch Ecosystem Afforested after Clear-Cutting of a Pristine Forest in Northernmost Japan

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**Abstract** The present study aimed to elucidate the atmosphere–forest exchange of ammoniacal nitrogen ( $\text{NH}_x\text{-N}$ ) at a young larch ecosystem.  $\text{NH}_x\text{-N}$  exchanges were measured at a remote site in northernmost Japan where 4-year-old larches were growing after a pristine forest had been clear-cut and subsequent dense dwarf bamboo (*Sasa*) had been strip-cut. The site was a clean area for atmospheric ammonia with mean concentrations of 0.38 and 0.11  $\mu\text{g N m}^{-3}$  in snowless and snow seasons, respectively. However, there was a general net emission of  $\text{NH}_x\text{-N}$ . The annual estimated emission of  $\text{NH}_x\text{-N}$  of 4.8  $\text{kg N ha}^{-1} \text{ year}^{-1}$  exceeded the annual wet deposition of 2.4  $\text{kg N ha}^{-1} \text{ year}^{-1}$ , but the weekly exchange fluxes may have been underestimated by 28–

60%. The main cause of the ammonia loss from the young larch ecosystem was probably enhanced nitrogen supply stimulated by the cutting of the pristine forest and *Sasa*, in particular, the *Sasa*.

**Keywords** Ammoniacal nitrogen · Atmospheric deposition · Emission · Northernmost Japan · Young larch ecosystem

## 1 Introduction

Nitrogen (N) deposition is an important N input to forests from the atmosphere. An increase in the N

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deposition has an accelerative effect on primary production due to the N limitation in general forests. For example, Magnani et al. (2007) pointed out the acceleration of forest growth in the boreal and temperate regions in the northern hemisphere induced by the anthropogenic increase in N deposition since the Industrial Revolution.

On the other hand, there is concern that excess N loads result in possible eutrophication and biodiversity changes due to the disappearance of the oligotrophic species (Stevens et al. 2004). The increased N deposition also has the potential to accelerate global warming through the indirect emission of nitrous oxide (van der Gon and Bleeker 2005) and inhibition of methane oxidation (Saari et al. 1997). Furthermore, the effects of increased N deposition on the perturbation of the N cycle can spread to the carbon cycle (e.g., Oren et al. 2001; Magnani et al. 2007).

It is, therefore, important to monitor the N deposition in forests because of the impacts reported above induced by the increased N deposition. N deposition is divided into wet and dry. Wet deposition can be measured directly by collecting precipitation, whereas dry deposition is difficult to measure directly. Hence, quantitative data of dry deposition are insufficient compared to those of wet deposition.

Ammoniacal nitrogen ( $\text{NH}_x\text{-N}$ ), i.e., ammonia ( $\text{NH}_3$ ) and particulate ammonium ( $\text{NH}_4^+$ ), is the principal reduced N in the atmosphere, and it comprises a large part of the N deposition for both wet and dry deposition (e.g., Hayashi et al. 2007). However, there is less quantitative information of  $\text{NH}_x\text{-N}$  dry deposition in Asia, including Japan. Meanwhile, soil and plants have the potential to emit  $\text{NH}_3$ . Therefore, the atmosphere–forest  $\text{NH}_3$  exchange should be evaluated as a net flux, i.e., the difference between dry deposition and emission.

Furthermore, some  $\text{NH}_3$  in the atmosphere condenses with acid gases to form particulate  $\text{NH}_4^+$ . On the other hand, particulate  $\text{NH}_4^+$  in the atmosphere has the potential to evaporate and release  $\text{NH}_3$ . The equilibrium between these bidirectional reactions depends on their atmospheric concentrations and temperature in addition to the effects of coexisting acid substances. Thus, both the  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  concentrations should be monitored to determine the  $\text{NH}_x\text{-N}$  behavior in the atmosphere.

The objective of the present study was to elucidate the status of the atmosphere–forest  $\text{NH}_x\text{-N}$  exchange

at a young larch ecosystem afforested after clear-cutting in a remote area in northernmost Japan.

## 2 Materials and Methods

### 2.1 Experimental Field and Management

The research site was a 4-year-old plantation (as of 2005) of hybrid larch (*Larix gmelinii* × *L. kaempferi*) with an area of 13.7 ha located on a flat terrace in the Teshio Experimental Forest, Hokkaido University (45°03'N, 142°06'E, 66 m above sea level). Northernmost Hokkaido, where the experimental forest is located, is a clean area regarding anthropogenic air pollution; however, pastures for dairy farming, which is the major industry in the northern part of Hokkaido, Japan, were located at distances of 2–5 km southwest from the research site. Some of the grasslands were fertilized by urea and composted cattle manure mainly in spring.

The soil type of the research site was gleyic Cambisols (FAO-UNESCO-ISRIC 1998). A pristine forest at the research site (Koike et al. 2001), i.e., a conifer-broad leaf mixed forest, was logged from January to March 2003. Subsequently, strip-cutting (4 m width) of the dense undergrowth of dwarf bamboos (*Sasa senanensis*) was conducted for 50% of the research site by crushing and spreading in October 2003 (Fukuzawa et al. 2006). Two-year-old larch saplings were then planted in November 2003 (2,500 saplings  $\text{ha}^{-1}$ ). The saplings were planted in the *Sasa* strip-cut lines. The additional cutting of *Sasa* to maintain the growth of planted larches was conducted for the whole strip-cut lines using power mowers from 20 to 29 June 2005 and from 13 to 20 June 2006; the mown *Sasa* was left there. The height of the larch saplings in 2006 was 1.5 m, which was similar to the seasonal maximum height of *Sasa*. The seasonal maximum leaf area index of the larch saplings and the remaining *Sasa* was 1.4 and 6.4, respectively; thus, *Sasa* dominated the research site.

### 2.2 Meteorological Observation

Micrometeorological observations have been conducted at the research site since 2001 in order to monitor the ecosystem exchanges of carbon dioxide and water vapor (Takagi et al. 2005a, b). The three-

dimensional wind velocity was measured with a frequency of 10 Hz using an ultrasonic anemometer (Kaijo DA600-3TV) installed at a height of 4.6 m, and the signals were recorded to a data logger (CSI CR5000). The air temperature was measured using a temperature–humidity sensor (Vaisala HMP-45) installed at a height of 32 m. The soil temperature was measured at five points using platinum resistance thermometers installed at depths of 1, 5, and 10 cm. The half-hour means of the measured temperatures were recorded to a data logger (CSI CR23X).

### 2.3 Measurement of the Atmospheric Concentration

The annular denuder method (Perrino et al. 1990) was applied to measure the atmospheric concentrations of  $\text{NH}_3$  and particulate  $\text{NH}_4^+$ , in addition to those of other major inorganic gaseous and particulate components in the atmosphere. Handling of the denuders, i.e., preparation, exposure, and extraction, was pursuant to the protocols of U.S. EPA (EPA 1999) and EMEP (EMEP 1996). Figure 1 shows the system used in the present study.  $I_0$  is the impactor (Tokyo Dylec NL-4-10) used to filter out particles larger than  $\text{PM}_{10}$  using a polytetrafluoroethylene (PTFE) doughnut filter (Tokyo Dylec T60A20-20H).  $D_1$ ,  $D_2$ ,  $D_2'$ , and  $D_3$  are the glass denuders (URG 2000-30×150-3CSS) used to collect gaseous components. For this purpose,  $D_1$  was coated with a 1% sodium fluoride + 2% glycerol in a methanol/water (1:4) solution to collect nitric acid ( $\text{HNO}_3$ ),  $D_2$ , and  $D_2'$ , with 1% sodium carbonate + 2% glycerol in methanol/water (1:1) solution to collect sulfur dioxide ( $\text{SO}_2$ ), hydrochloric acid and nitrous acid, and  $D_3$ , with a 1% citric acid + 2% glycerol in methanol solution to collect  $\text{NH}_3$ .  $F_1$ ,  $F_2$ , and  $F_3$  are the filter holders (URG 2000-30FG) used to collect

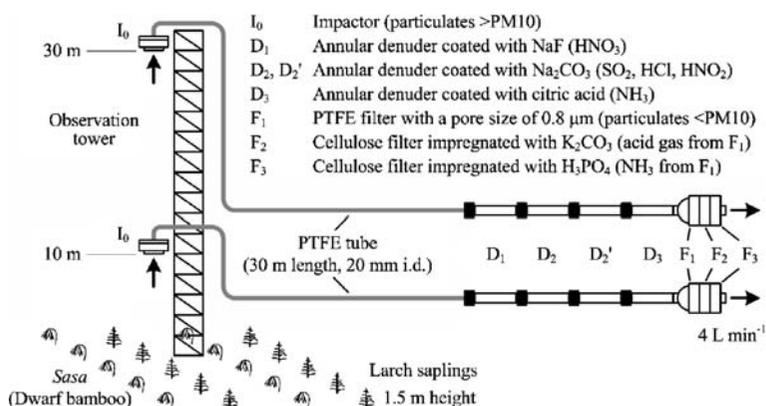
particles smaller than  $\text{PM}_{10}$  and evaporated gases from the collected particles. For this purpose,  $F_1$  contained a PTFE filter (Advantec T080A047A) to collect particles;  $F_2$ , a cellulose filter (Advantec No.51A) impregnated with 6% potassium carbonate + 2% glycerol in water to collect the evaporated acid gases from  $F_1$ ; and  $F_3$ , a cellulose filter (Advantec No.51A) impregnated with 5% phosphoric acid + 2% glycerol in water to collect the evaporated  $\text{NH}_3$  from  $F_1$ .

Weekly sampling with a flow rate of  $4 \text{ L min}^{-1}$  was conducted at heights of 10 and 30 m using an observation tower at the research site.  $I_0$  was set in the inlet at each height with a rain cover. A PTFE tube with the same length (30 m) and inner diameter (20 mm) for each height was used to connect the inlet and the denuder system at the ground. The collected atmospheric components were extracted by deionized water. Ion chromatography (Dionex ICS-1500 and DX-500) was applied to quantify each component. The  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  concentrations were determined from  $D_3$  and the sum of  $F_1$  and  $F_3$ , respectively. Quality assurance and quality control of the data were according to the criteria of the Acid Deposition Monitoring Network in East Asia (EANET) (EANET 2000, 2001); the determination and the detection limit of the air concentration of  $\text{NH}_3$  in the present study were evaluated as 0.0045 and  $0.0015 \mu\text{g N m}^{-3}$ , respectively.

### 2.4 Calculation of the Exchange Flux

The weekly mean exchange flux of  $\text{NH}_x\text{-N}$  was calculated by the gradient method. The flux was calculated by multiplying the difference in concentrations between heights of 10 and 30 m by the diffusion velocity. The diffusion velocity ( $D$ ,  $\text{m s}^{-1}$ )

**Fig. 1** Schematic view of the annular denuder system to monitor the atmospheric concentrations of gaseous and particulate components at heights of 10 and 30 m at the young larch ecosystem



between the two heights above the canopy is expressed by (Harazono and Miyata 1997, Miyata et al. 2000)

$$D = \kappa u_* \left[ \int_{\zeta_{10}}^{\zeta_{30}} \phi_g(\zeta) \zeta^{-1} d\zeta \right]^{-1}, \quad (1)$$

where  $\kappa$ ,  $u_*$ , and  $\phi_g(\zeta)$  are the von Karman's constant (0.4), the friction velocity ( $\text{m s}^{-1}$ ), and the correction factor as a function of the Monin–Obukhov stability parameter ( $\zeta$ ), respectively.  $\zeta$  is defined as  $\zeta = (z-d)L^{-1}$ , where  $z$ ,  $d$ , and  $L$  are the target height (m), the zero-plane displacement (m), and the Monin–Obukhov length (m), respectively. An equation,  $d=0.65h$  (Campbell and Norman 1998), was used to determine  $d$ , where  $h$  denotes the vegetation height. However, the vegetation had a strip-shaped structure due to the strip-cutting (50% area). Therefore, the mean value of  $d$  (= 0.6 m) was derived from each of the  $d$  values for *Sasa* and larches. For the dense *Sasa* vegetation,  $d$  was simply determined as 1.0 m (=0.65×1.5). On the other hand, the larch saplings planted in rows were sparse and wind could blow into the near ground surface at the larch standings. The vegetation height of the sparse larch vegetation to determine  $d$  was, therefore, set to 0.2 m (=0.65×0.3), although the height of larches was similar to that of *Sasa*.

Based on previous field studies over short vegetation,  $\phi_g$  was approximated by the dimensionless gradient of the potential temperature ( $\phi_h$ ) (Denmead 1994). The values of  $u_*$  and  $L$  were determined using an ultrasonic anemometer; and  $\zeta$  and  $\phi_g(\zeta)$  were determined with  $d$ .  $D$  was calculated every 30 min, and weekly mean values were applied to the exchange flux calculation.

## 2.5 Measurement of the Wet Deposition

Weekly sampling of precipitation was conducted using a wet-only sampler (Daisy DCRS-300); however, biweekly sampling using an open-bulk sampler substituted from 10 November 2006 to 10 May 2007 and from 24 May to 7 June 2007 due to a device failure. These samplers were placed at about 10 m north of the observation tower to avoid the leeward of the prevailing wind direction. Ion chromatography (Dionex DX-500) was applied to determine the precipitation concentrations of major ionic species subsequent to the filtration using membrane filters (0.2  $\mu\text{m}$  pore size) (Advantec DISMIC-25CS). Quality assurance and quality control

of the data were conducted on the basis of the criteria of EANET (2000). The wet deposition was calculated by multiplying the determined ionic concentration by the precipitation amount. The observed open-bulk deposition during the device failure of the wet-only sampler was converted into the wet deposition using a linear regression between the wet deposition and the open-bulk deposition as biweekly values from 10 November 2005 to 8 June 2006, i.e.,  $\text{WD} = 0.653 \text{ BD} - 0.676$  ( $R = 0.908$ ,  $n = 9$ ), where WD and BD are the wet deposition ( $\text{mg N m}^{-2}$ ) and the open-bulk deposition ( $\text{mg N m}^{-2}$ ), respectively.

## 2.6 Measurement of the Soil Solution

A soil solution sampling was conducted at four plots at three depths (10, 20, and 40 cm) once or twice a month from June to November 2005 and from May to October 2006 (17 times in all). Tension lysimeters with a ceramic porous cup were used to collect the soil solution. After pH measurement using a glass electrode, soil solution samples were filtered using a glass fiber filter (Whatman GF/F) and kept below 4°C until chemical analysis. Ion chromatography (Dionex DX-500) was used to determine the concentrations of major ionic species subsequent to filtration using membrane filters (0.2  $\mu\text{m}$  pore size) (Advantec DISMIC-25CS).

## 3 Results and Discussion

### 3.1 Atmospheric Concentrations of $\text{NH}_x\text{-N}$

Table 1 summarizes the mean  $\text{NH}_x\text{-N}$  concentrations and their observation ranges throughout the research period and for two seasons, i.e., a snowless season and a snow season. At the research site, the first and second snow seasons were from 17 November 2005 to 5 May 2006 and from 23 November 2006 to 27 April 2007, respectively.

The mean  $\text{NH}_3$  concentration at a height of 10 m in the snowless season was  $0.38 \pm 0.16 \mu\text{g N m}^{-3}$  ( $\pm$ standard deviation) at standard temperature and pressure (0°C and 1,013 hPa) with a range of 0.11–0.75  $\mu\text{g N m}^{-3}$ , and that in the snow season was  $0.11 \pm 0.06 \mu\text{g N m}^{-3}$  with a range of 0.02–0.27  $\mu\text{g N m}^{-3}$  (Table 1). The mean  $\text{NH}_3$  concentration was high in the snowless season ( $p < 0.0001$ ). The range at the research

**Table 1** Mean atmospheric concentrations of ammoniacal nitrogen based on weekly observations with their observation ranges in parentheses

Year	Height	Season	Atmospheric concentration±SD ( $\mu\text{g N m}^{-3}$ at standard temperature and pressure)		$\text{NH}_4^+/\text{NH}_x\text{-N}$ (%)
			$\text{NH}_3$	Particulate $\text{NH}_4^+$	
RY2005–RY2006 <sup>a</sup>	30 m	Snowless season ( $n=58$ )	0.31±0.16 (0.00–0.78)	0.29±0.16 (0.08–0.85)	49±16 (19–100)
		Snow season ( $n=46$ )	0.07±0.04 (0.00–0.17)	0.19±0.09 (0.05–0.44)	73±12 (46–100)
		Whole period ( $n=104$ )	0.20±0.17 (0.00–0.78)	0.25±0.14 (0.05–0.85)	60±19 (19–100)
	10 m	Snowless season ( $n=58$ )	0.38±0.16 (0.11–0.75)	0.31±0.18 (0.11–1.1)	45±13 (19–68)
		Snow season ( $n=46$ )	0.11±0.06 (0.02–0.27)	0.21±0.10 (0.05–0.53)	66±10 (41–85)
		Whole period ( $n=104$ )	0.26±0.18 (0.02–0.75)	0.27±0.16 (0.05–1.1)	54±16 (19–85)

<sup>a</sup> The period was from 9 June 2005 to 7 June 2007.

site in the snowless season ( $0.11\text{--}0.75 \mu\text{g N m}^{-3}$ ) was within the range at a remote hardwood forest in the summer in the USA ( $0.07\text{--}1.2 \mu\text{g N m}^{-3}$ , Langford et al. 1992b). The mean value at the research site throughout the research period ( $0.26 \mu\text{g N m}^{-3}$ ) was comparable but lower than the 3-year mean at a Norway spruce forest in a forested rural area in Saxony, Germany ( $0.44 \mu\text{g N m}^{-3}$ , Zimmermann et al. 2006) and was lower than the 5-year mean at a Norway spruce forest partly surrounded by agricultural lands in western Jutland, Denmark ( $0.66 \mu\text{g N m}^{-3}$ , Andersen et al. 1999). Furthermore, the mean value at the research site in the snowless season ( $0.38 \mu\text{g N m}^{-3}$ ) was lower than the mean values of two field campaigns in spring at a secondary broadleaf forest occasionally affected by animal husbandry activities in Indiana, USA ( $0.54\text{--}0.99 \mu\text{g N m}^{-3}$ , Pryor et al. 2001), and was clearly lower than the mean value in the warm season in a rural area of central Japan ( $2.7 \mu\text{g N m}^{-3}$ , Hayashi et al. 2007). The research site was, thus, a clean area for atmospheric  $\text{NH}_3$  on average.

The mean particulate  $\text{NH}_4^+$  concentration (10 m height) in the snowless season was  $0.31\pm 0.18 \mu\text{g N m}^{-3}$  with a range of  $0.11\text{--}1.1 \mu\text{g N m}^{-3}$ , and that in the snow season was  $0.21\pm 0.10 \mu\text{g N m}^{-3}$  with a range of  $0.05\text{--}0.53 \mu\text{g N m}^{-3}$  (Table 1). The mean particulate  $\text{NH}_4^+$  concentration was high in the snowless season ( $p<0.001$ ). The ratios of particulate  $\text{NH}_4^+$  to  $\text{NH}_x\text{-N}$  (10 m height) in the snowless and snow seasons were  $45\pm 13$  and  $66\pm 10\%$ , respectively (Table 1). The

composition ratio of particulate  $\text{NH}_4^+$  increased in the snow season ( $p<0.001$ ).

To investigate the effect of the PTFE tube (30 m length) of the denuder system on the measured concentrations, biweekly sampling of  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  was conducted from 7 June 2007 to 11 October 2007 using both the denuder system and filter holders (NILU NL-O) set at a height of 30 m. The filter holder, setting a filter for particle collection at the upstream stage, has an artifact to underestimate the particle concentration and overestimate the gas concentration because some particles collected onto the filter have the potential to evaporate (Keck and Wittmaack 2005). Thus, the  $\text{NH}_x\text{-N}$  concentrations were used for comparison. As a result, the  $\text{NH}_x\text{-N}$  concentrations of the denuder system agreed well with those of the filter holder with a 1:1 relationship (slope=0.998,  $R=0.960$ ,  $n=9$ ). Therefore, the delay in the  $\text{NH}_3$  flow within the PTFE tube due to adsorption and desorption and, further, the  $\text{NH}_3$  loss within the PTFE tube were unlikely to have affected the weekly mean concentrations.

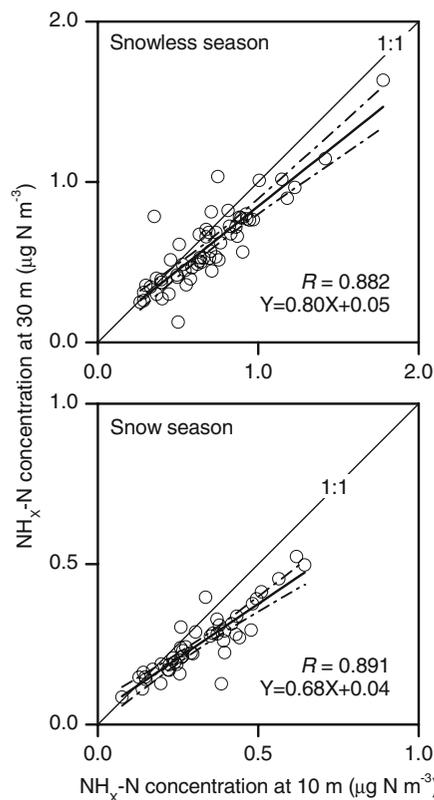
### 3.2 Gaseous and Particulate Exchange of $\text{NH}_x\text{-N}$

The condensation–evaporation reactions of  $\text{NH}_x\text{-N}$  in the atmosphere result in no changes in the  $\text{NH}_x\text{-N}$  concentration itself but cause changes in the  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  concentrations. Therefore, a comparison of the  $\text{NH}_x\text{-N}$  concentrations at two heights

indicates whether the site is a net source or a net sink of  $\text{NH}_x\text{-N}$ . At the research site, the  $\text{NH}_x\text{-N}$  concentrations at a height of 10 m were generally higher than those at a height of 30 m in both the snowless ( $p < 0.0001$ ) and snow seasons ( $p < 0.0001$ ) (Fig. 2), which suggested that the research site was a net source of  $\text{NH}_x\text{-N}$ .

The weekly mean exchange fluxes also showed that the research site was a net source of both  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  in general (Fig. 3); however, the  $\text{NH}_3$  exchange occasionally showed net dry deposition, which was particularly remarkable from 13 to 27 October 2005 (Fig. 3). The causes of the  $\text{NH}_3$  emission in the snowless and the snow seasons will be discussed in Sections 3.5 and 3.6, respectively. The causes of particulate  $\text{NH}_4^+$  emission, although the fluxes were smaller than those of  $\text{NH}_3$  in general (Fig. 3), will be discussed in Section 3.7.

A positive correlation between the weekly appearance rate of unstable conditions derived from the half-hourly



**Fig. 2** Relationships of the weekly mean concentrations of ammoniacal nitrogen ( $\text{NH}_3$  and particulate  $\text{NH}_4^+$ ) between heights of 10 and 30 m at the young larch ecosystem. The dot-dashed curves denote the 95% confidential intervals of the regression lines

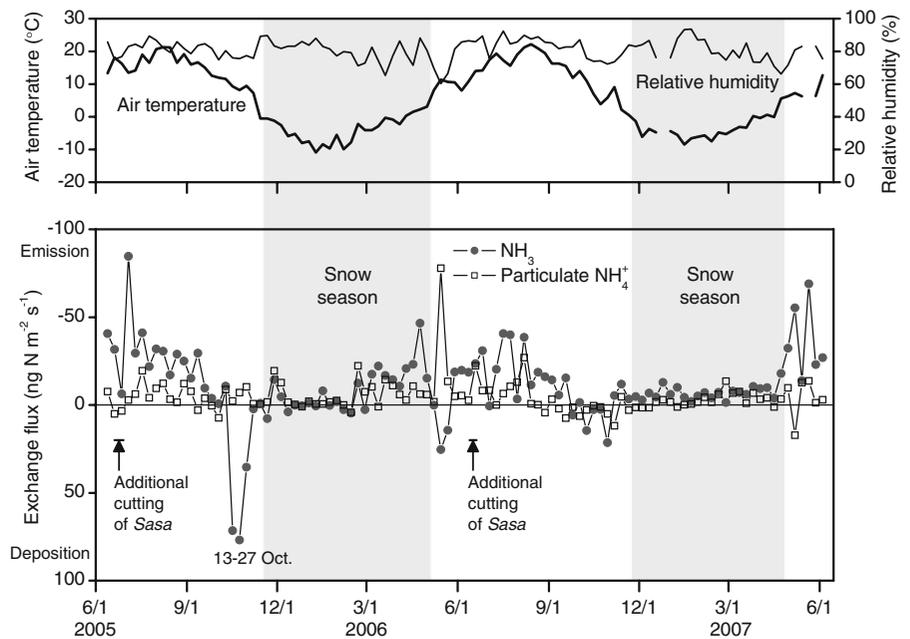
meteorological data and the vertical difference in the weekly mean concentrations was found for  $\text{NH}_3$  in the snowless season ( $p < 0.01$ ) (Fig. 4). Unstable conditions activate convection, which result in enlarging the diffusion velocities. Thus, unstable conditions essentially have an effect of flattening the vertical difference in concentrations. However, the positive correlation of  $\text{NH}_3$  in the snowless season demonstrated that the vertical difference in concentrations rather became large with an increase in the unstable rate (Fig. 4), which resulted in the large exchange fluxes, emission in this case, under the unstable conditions.

There is an error between the weekly mean flux calculated from the weekly mean values and that determined by averaging, e.g., hourly fluxes, which results from the correlation between the concentration and the diffusion velocity. The error can be either an over- or an underestimation (Clarke et al. 1997). Hansen et al. (1998) reported the errors of 10–50% for annual  $\text{NH}_3$  exchange on a heathland in Denmark based on weekly samplings. Furthermore, the exchange fluxes of water vapor at the research site in the snowless season in 2005 showed that the weekly mean fluxes based on the weekly mean values underestimated those averaged from the half-hourly fluxes by 44% (28–60% as the 95% confidential interval,  $n=22$ ). It is possible that the  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  fluxes in the present study also had a similar uncertainty. Although the weekly mean fluxes had large uncertainty, the emission tendency of  $\text{NH}_3$  at the research site was the observed fact.

### 3.3 Wet Deposition of $\text{NH}_x\text{-N}$

The research site had approximately  $1,000 \text{ mm year}^{-1}$  of precipitation. Precipitation peaked in autumn, concentrating in September; however, precipitation occurred year-round. The low air temperature, mostly below freezing, throughout the snow season prevented the snow from melting. As a result, the maximum snow depth at the research site reached 1.3–1.4 m despite the small amount of precipitation during the snow season. The annual wet deposition of  $\text{NH}_4^+$  was  $2.4 \pm 0.6 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Table 2), which corresponded to 65% of the mean annual wet deposition during 1983–2002 at other 23 of the remote sites in Japan ( $3.7 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) (Hayashi et al. 2006).

**Fig. 3** Weekly mean exchange fluxes of ammoniacal nitrogen between the young larch ecosystem and the atmosphere. The weekly mean air temperature and relative humidity are also shown



### 3.4 Atmosphere–Forest Balance of $\text{NH}_x\text{-N}$

Table 2 shows the annual exchange and wet deposition of  $\text{NH}_x\text{-N}$ . A positive or a negative value denotes deposition to or emission from the ecosystem, respectively. The mean value of annual  $\text{NH}_x\text{-N}$  exchange in 2 years, i.e., from 9 June 2005 to 8 June 2006 and from 8 June 2006 to 7 June 2007, was  $-4.8 \pm 0.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Table 2). Although the weekly mean fluxes used to calculate the annual exchange had uncertainty (Section 3.2), the tendency of net emission of  $\text{NH}_x\text{-N}$  from the research site seemed to represent the actual status. The mean value of the  $\text{NH}_x\text{-N}$  balance between the exchange and wet deposition was estimated to be  $-2.5 \pm 0.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Table 2). The young larch ecosystem was a possible source of  $\text{NH}_x\text{-N}$  on an annual basis.

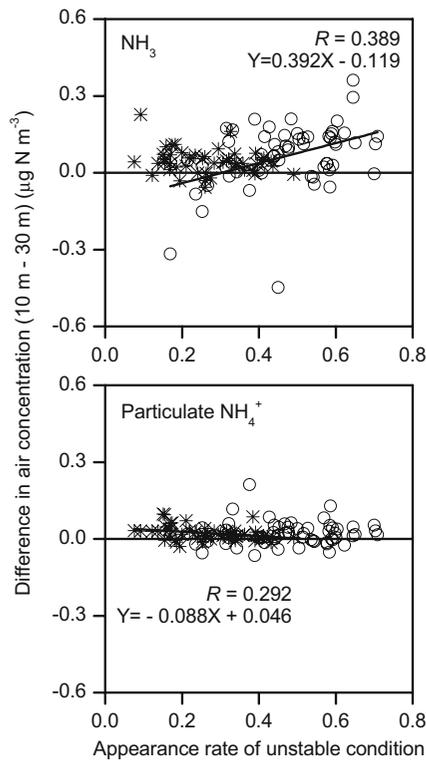
### 3.5 $\text{NH}_3$ Emission in the Snowless Season

No N fertilizer was applied to the research site. On the other hand, the prior cutting of the pristine forest and *Sasa* and the additional cutting of *Sasa* were conducted at the research site (Section 2.1). Soil surface, living plants, and cut plant materials are, therefore, possible emitters of  $\text{NH}_3$ .  $\text{NH}_3$  emission basically occurs as  $\text{NH}_3$  volatilization depending on two equilibriums, i.e., the dissociation of  $\text{NH}_4^+$  in the

liquid phase and the partition of  $\text{NH}_3$  between the liquid and gas phases (Husted and Schjoerring 1996).

For soil at the research site, the mean  $\text{NH}_4^+$  concentration in soil solution at a depth of 10 cm was  $0.1 \text{ mg N L}^{-1}$  ( $n=34$ ). The median value of the soil solution pH was 5.8, with a range of 4.9–6.7 ( $n=28$ ). The mean value of the daily mean soil temperatures (10 cm depth) on the sampling days for soil solution was  $12.4^\circ\text{C}$  with a range of  $6.6\text{--}18.5^\circ\text{C}$  ( $n=17$ ). The gas phase  $\text{NH}_3$  at equilibrium [ $\text{NH}_3(\text{g}) \text{ eq}$ ], corresponding to the soil air  $\text{NH}_3$  concentration at equilibrium, was calculated according to Husted and Schjoerring (1996). In the calculation, the  $\text{NH}_4^+$  concentration and temperature were fixed at their mean values, i.e.,  $0.1 \text{ mg N L}^{-1}$  and  $12.4^\circ\text{C}$ , respectively, and the pH was changed between the maximum and minimum values (4.9–6.7), taking the strongest effect of the pH (Hayashi et al. 2008) into consideration. The derived range of  $\text{NH}_3(\text{g}) \text{ eq}$ ,  $0.001\text{--}0.05 \text{ } \mu\text{g N m}^{-3}$ , was much lower than the range of the atmospheric  $\text{NH}_3$  concentration (10 m height) in the snowless season ( $0.11\text{--}0.75 \text{ } \mu\text{g N m}^{-3}$ ) (Table 1). Consequently, the soil was unlikely to have contributed to the  $\text{NH}_3$  emission in the snowless season.

For living plants, the equilibrium concentration of  $\text{NH}_3$  in the stomatal gas phase is defined as the stomatal compensation point for  $\text{NH}_3$  ( $\chi_s$ ) (Farquhar et al. 1980).  $\text{NH}_3$  emission from the stomata occurs



**Fig. 4** Relationship between the weekly appearance rate of unstable conditions and the difference in air concentrations, subtracting the weekly mean concentrations at a height of 30 m from those at a height of 10 m. *Circles* denote the snowless season; *asterisks*, the snow season. A positive correlation was found for  $\text{NH}_3$  in the snowless season ( $p < 0.01$ ), and a weak negative correlation was found for particulate  $\text{NH}_4^+$  in the snow season ( $p < 0.05$ )

if  $\chi_s$  exceeds the atmospheric  $\text{NH}_3$  concentration. A possible  $\text{NH}_3$  emission from the larches and/or *Sasa* is discussed on the basis of the  $\chi_s$  of other species, since  $\chi_s$  is unknown for both larch and *Sasa*. The following reported values originally at 20°C were converted into those at the mean air temperature at the research site in the snowless season (13.0°C), since  $\chi_s$  is a function of the temperature (Husted and Schjoerring 1996). For trees, the  $\chi_s$  of Norway spruce with an oversaturated N supply was 0.66  $\mu\text{g N m}^{-3}$  (Gessler et al. 2002), and the  $\chi_s$  of a montane mixed forest with a low N supply was 0.21  $\mu\text{g N m}^{-3}$  on average (Langford et al. 1992a). For poaceous species, the  $\chi_s$  of perennial ryegrass was in a range of 0.01–3.7  $\mu\text{g N m}^{-3}$  (Loubet et al. 2002) and 3.3  $\mu\text{g N m}^{-3}$  on average (Kruit et al. 2007). The  $\text{NH}_3$  concentrations (10 m height) in the snowless season at the research site (0.11–0.75  $\mu\text{g N m}^{-3}$ , mean 0.38  $\mu\text{g N m}^{-3}$ , Table 1) were lower or at least in the range of the reported values of  $\chi_s$ , which advocated the possibility of stomatal  $\text{NH}_3$  emission from the larches and *Sasa* at the research site.

For cut plant materials, the additional cutting of *Sasa* at the strip-cut lines (50% area) conducted in late June both in 2005 and 2006 provided fresh leaves and culm of *Sasa*. Milford et al. (2000) reported that the substantial  $\text{NH}_3$  was released from decaying potato leaves. Asman et al. (1998) also gave information of the significant  $\text{NH}_3$  emission from oilseed rape canopies following leaf fall. Fukuzawa (2007) showed that the N contents of the current and biennial

**Table 2** Annual balance of ammoniacal nitrogen between the young larch ecosystem and the atmosphere

			Annual flux ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ )		
			RY2005 <sup>a</sup>	RY2006 <sup>b</sup>	Mean $\pm$ SD
Exchange flux <sup>c</sup>	$\text{NH}_x\text{-N}$ ( $\text{NH}_3$ and particulate $\text{NH}_4^+$ )	Dry deposition	1.7	0.7	1.2 $\pm$ 0.7
		Emission	-6.6	-5.5	-6.0 $\pm$ 0.8
		Total (A)	-4.9	-4.8	-4.8 $\pm$ 0.1
	$\text{NH}_3$	Dry deposition	1.5	0.3	0.9 $\pm$ 0.9
		Emission	-4.4	-4.2	-4.3 $\pm$ 0.2
		Total	-2.9	-3.9	-3.4 $\pm$ 0.7
	Particulate $\text{NH}_4^+$	Dry deposition	0.2	0.4	0.3 $\pm$ 0.2
		Emission	-2.2	-1.3	-1.7 $\pm$ 0.6
		Total	-2.0	-0.9	-1.4 $\pm$ 0.8
	Wet deposition (B)			2.8	2.0
Annual balance of $\text{NH}_x\text{-N}=(\text{A})+(\text{B})$			-2.1	-2.8	-2.5 $\pm$ 0.5

<sup>a</sup> The period was from 9 June 2005 to 8 June 2006.

<sup>b</sup> The period was from 8 June 2006 to 7 June 2007.

<sup>c</sup> Weekly mean exchange fluxes to calculate the annual flux might have several tens percent of uncertainty.

leaves and the current and biennial culm of *Sasa* sampled at the research site were  $2.17 \pm 0.08\%$ ,  $1.62 \pm 0.09\%$ ,  $0.65 \pm 0.09\%$ , and  $0.57 \pm 0.17\%$  dry matter, respectively; thus, the *Sasa* leaves particularly had a high content of N. It is considered that decomposition of the cut *Sasa* materials caused the  $\text{NH}_3$  emission from late June to the subsequent summer to a certain extent.

The N mineralization rate and the inorganic N pool of the surface soils (0–15 cm) were also investigated (Fukuzawa et al. 2006). The soils were collected from the cut *Sasa* plots where both trees and *Sasa* were cut, the uncut *Sasa* plots where *Sasa* remained, and the control plots ( $n=6$ , respectively); the cut *Sasa* and the uncut *Sasa* plots were inside the research site and the control plots were outside. The N mineralization rates at the cut *Sasa*, the uncut *Sasa*, and the control plots in October 2004 after the growing period were  $0.14 \pm 0.13$ ,  $0.03 \pm 0.02$ , and  $0.06 \pm 0.07$  mg N  $\text{kg}^{-1}$  dry soil  $\text{day}^{-1}$ , respectively, and the inorganic N pools at those plots in October 2004 were  $5.5 \pm 3.8$ ,  $3.3 \pm 1.4$ , and  $3.4 \pm 2.4$  mg N  $\text{kg}^{-1}$  dry soil, respectively (Fukuzawa et al. 2006). Although the absolute values were small, both the N mineralization rate and the inorganic N pool in October 2004 tended to increase at the cut *Sasa* plots. Furthermore, in May 2005 before the growing period, the N mineralization rates at the cut *Sasa*, the uncut *Sasa*, and the control plots were  $1.2 \pm 1.5$ ,  $0.17 \pm 0.12$ , and  $0.29 \pm 0.17$  mg N  $\text{kg}^{-1}$  dry soil  $\text{day}^{-1}$ , respectively, and the inorganic N pools at those plots were  $26 \pm 18$ ,  $13 \pm 15$ , and  $10 \pm 6$  mg N  $\text{kg}^{-1}$  dry soil, respectively (unpublished data). Both the N mineralization rate and the inorganic N pool in May 2005 largely increased at the cut *Sasa* plots. Namely, the strip-cutting of *Sasa* (50% area) prior to the planting of larch saplings induced the increases in the N supply, i.e., the N mineralization rate and the inorganic N pool, at the cut *Sasa* area. It is considered that the additional cutting of *Sasa* (50% area) in late June in both 2005 and 2006 also had a similar effect on the N supply.

A higher N supply results in a higher  $\chi_s$  (Gessler et al. 2002). Hence, the increase in the N supply at the research site had the effect of enhancing the stomatal emission. The most possible causes of the  $\text{NH}_3$  emission in the snowless season were, thus, the decomposition of the cut *Sasa* materials and the stomatal emission of the larch saplings and the remaining *Sasa*. It is, however, known that canopy emission of  $\text{NH}_3$  can occur when stomatal emission outweighs cuticular deposition (Neiryneck and Ceulemans 2008). The

observed net emission of  $\text{NH}_3$  at the research site advocated that the total emission often outweighed the total deposition, in which the low atmospheric concentrations of  $\text{NH}_3$  were effective to enhance the  $\text{NH}_3$  emission in relation to the partition equilibrium of  $\text{NH}_3$  between the liquid and gas phases.

### 3.6 $\text{NH}_3$ Emission in the Snow Season

$\text{NH}_3$  emission occurred even in the snow season (Fig. 3). There was no  $\text{NH}_3$  emitter other than the snowpack in the snow season, when the larches shed their leaves and the *Sasa* was snowed under. The air temperatures at the research site in the snow season were generally below freezing (Fig. 3), which was effective to restrict the consolidation of snow. Takagi et al. (2005a) reported that the snow coverage in the same forest in midwinter was highly porous, with bulk snow porosities of 0.73–0.75; the bulk snow porosity remained at 0.56 even in April, when the snow melt started. Takagi et al. (2005a) also reported the carbon dioxide emission from the snowpack in the same forest. The snowpack at the research site, therefore, was unlikely to have inhibited the soil–atmosphere gas exchange completely.

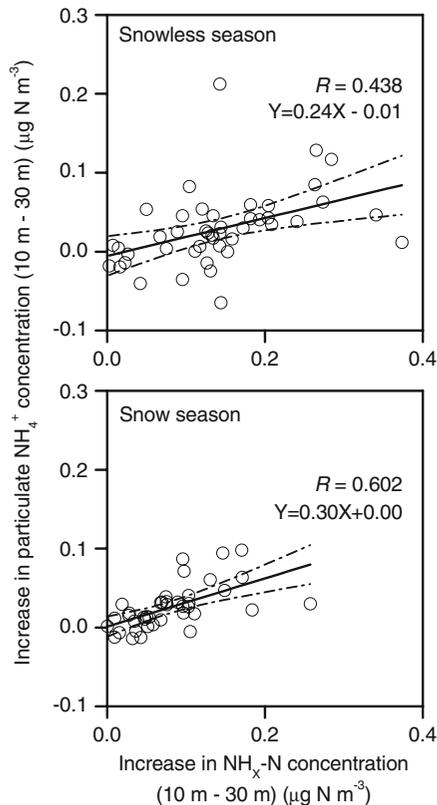
The  $\text{NH}_3$  emission from the snowpack could have originated from the accumulated  $\text{NH}_x\text{-N}$  in the snow cover and/or the produced and accumulated  $\text{NH}_x\text{-N}$  in the soil. For the  $\text{NH}_x\text{-N}$  production in the soil, Kielland et al. (2006) reported on the N mineralization even in the frozen soil in Alaska. At the research site, the snow cover maintained the soil temperatures at 1–2 and 1.5–3°C at depths of 1 and 10 cm, respectively, during the snow season against the minimum air temperature of  $-20^\circ\text{C}$ . Hence, it was highly possible that the soil at the research site maintained the N mineralization in midwinter. Furthermore, the inorganic N pool at the research site increased due to the cutting (Section 3.5), and the decrease in the vertical movement of water in the snow season was effective to accumulate  $\text{NH}_x\text{-N}$  at the surface soil. The relatively low atmospheric concentrations of  $\text{NH}_3$  in the snow season (Table 1) were also an advantageous condition for the  $\text{NH}_3$  emission from the snowpack.

### 3.7 Apparent Emission of Particulate $\text{NH}_4^+$

Similar to  $\text{NH}_3$ , the exchange fluxes of particulate  $\text{NH}_4^+$  showed emission in general (Fig. 3). However,

the main process of particulate  $\text{NH}_4^+$  production is the condensation in the atmosphere, not the direct emission from the ground surface. It is, hence, hypothesized that the condensation of the emitted  $\text{NH}_3$  with acid gases increased the particulate  $\text{NH}_4^+$  concentration, which resulted in an increase in the particulate  $\text{NH}_4^+$  concentration at a lower height and then the apparent emission of particulate  $\text{NH}_4^+$ .

Extracting the data corresponding to the net emission of  $\text{NH}_x\text{-N}$  at which the  $\text{NH}_x\text{-N}$  concentration at a height of 10 m was higher than that at a height of 30 m, the changes in the particulate  $\text{NH}_4^+$  concentrations between the two heights (10 m–30 m) were compared to the increase in the  $\text{NH}_x\text{-N}$  concentrations between the two heights. Although there was a large dispersion, positive correlations were found in both the snowless and snow seasons (Fig. 5). Based on the



**Fig. 5** Relationship between the increase in the  $\text{NH}_x\text{-N}$  concentrations and that in the particulate  $\text{NH}_4^+$  concentrations, subtracting the weekly mean concentrations at a height of 30 m from those at a height of 10 m. The *dot-dashed curves* denote the 95% confidential intervals of the regression lines

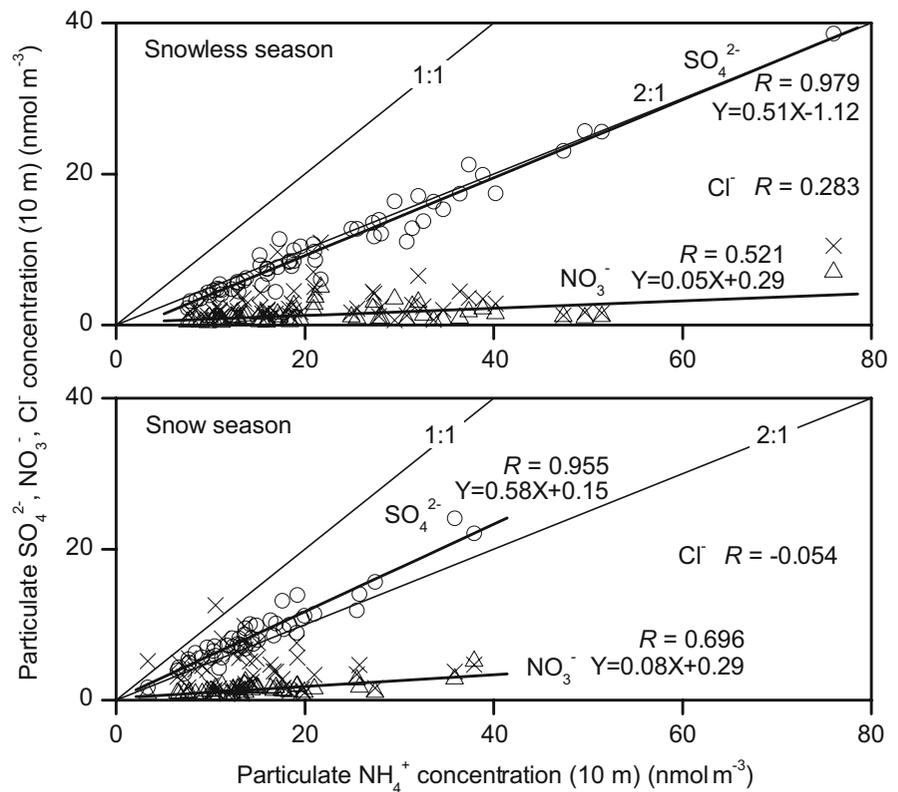
weekly mean values, about 20–30% of the increases in the  $\text{NH}_x\text{-N}$  concentrations according to the slope of regression (Fig. 5) seemed to result in increases in the particulate  $\text{NH}_4^+$  concentrations.

In terms of the counter anion of particulate  $\text{NH}_4^+$ , the particulate  $\text{NH}_4^+$  concentrations (10 m height) showed strongly positive correlations with the particulate sulfate ( $\text{SO}_4^{2-}$ ) concentrations in both the snowless and snow seasons (Fig. 6). The particulate  $\text{NH}_4^+$  concentrations also showed positive correlations with the particulate nitrate ( $\text{NO}_3^-$ ) concentrations; however, the particulate  $\text{NO}_3^-$  concentrations themselves were much lower than the particulate  $\text{SO}_4^{2-}$  concentrations (Fig. 6). The particulate  $\text{NH}_4^+$  concentrations showed no significant correlations with the particulate chloride ( $\text{Cl}^-$ ) concentrations (Fig. 6). The particulate  $\text{SO}_4^{2-}$  accounted for  $81\pm 10\%$  and  $76\pm 13\%$  of the particulate anions on an equivalent basis in the snowless and snow seasons, respectively. Furthermore, Bardouki et al. (2003) reported that particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  showed the same size distribution in the submicron mode. Hence, the most important anion in relation to the particulate  $\text{NH}_4^+$  concentrations at the research site was  $\text{SO}_4^{2-}$  on a weekly mean basis.

The molar ratios of particulate  $\text{NH}_4^+/\text{SO}_4^{2-}$  in the snowless season approximated 2:1 (Fig. 6), considering the relatively low concentrations of particulate  $\text{NO}_3^-$  and  $\text{Cl}^-$  (Fig. 6), which supported the existence of these particles as ammonium sulfate. This result showed that sulfuric acid in the atmosphere was mostly neutralized by  $\text{NH}_3$ . On the other hand, the molar ratios of particulate  $\text{NH}_4^+/\text{SO}_4^{2-}$  in the snow season were between 2:1 and 1:1 (Fig. 6). This result suggested that there was insufficient  $\text{NH}_3$  in the atmosphere to completely neutralize sulfuric acid.

Cape et al. (1998) reported an increase in the codeposition of  $\text{SO}_2$  induced by fumigation with  $\text{NH}_3$  above a forest canopy. Their data were accurately obtained as the additional  $\text{SO}_4^{2-}$  deposition in through-fall. Zimmermann et al. (2006) also reported an increase in the deposition velocity of  $\text{NH}_3$  by codeposition with  $\text{SO}_2$  in a Norway spruce forest. Therefore, the codeposition of the emitted  $\text{NH}_3$  with  $\text{SO}_2$  seemed to increase both the particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations at the research site. As a result of the codeposition, the particulate  $\text{NH}_4^+$  concentrations tended to increase at the lower height and then resulted in the apparent emission of particulate  $\text{NH}_4^+$  at the research site.

**Fig. 6** Relationships between the weekly mean concentrations of particulate  $\text{NH}_4^+$  at a height of 10 m and those of other particles, i.e., particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ . Circles denote particulate  $\text{SO}_4^{2-}$ ; triangles, particulate  $\text{NO}_3^-$ ; and crosses, particulate  $\text{Cl}^-$ . The molar concentration ( $\text{nmol m}^{-3}$ ) was used [e.g.,  $1 \mu\text{g N m}^{-3}$  at standard temperature and pressure (STP)=71.4  $\text{nmol NH}_4^+ \text{m}^{-3}$  at STP]



On the other hand, van Oss et al. (1998) reported that gas-to-particle conversion of ammonium nitrate was possible to result in, inversely, apparent emission of  $\text{NH}_3$  in daytime. Pryor et al. (2001) also pointed out this effect on the observed  $\text{NH}_3$  emission in addition to the canopy emission. However, the composition ratios of particulate  $\text{NO}_3^-$  to the total anion were very low, and the molar ratios of particulate  $\text{NH}_4^+/\text{NO}_3^-$  were far larger than 1:1 at the research site (Fig. 6). It is, therefore, considered that the evaporation of ammonium nitrate had little effect on the apparent  $\text{NH}_3$  emission at the research site.

The effect of the condensation–evaporation reactions on the  $\text{NH}_x\text{-N}$  concentrations was not considered when using the gradient method. Therefore, the calculated fluxes in the present study seem to overestimate the dry deposition and underestimate the emission for  $\text{NH}_3$  and vice versa for particulate  $\text{NH}_4^+$ . There is, however, no error induced by the condensation–evaporation reactions to the fluxes as  $\text{NH}_x\text{-N}$  since the same diffusion velocities were applied to both gases and particles in the gradient method.

#### 4 Conclusion

The research site, a young larch ecosystem composed of larch saplings and *Sasa*, was a clean area for  $\text{NH}_3$  with mean atmospheric concentrations (10 m height) of  $0.38 \pm 0.16$  and  $0.11 \pm 0.06 \mu\text{g N m}^{-3}$  in the snowless and snow seasons, respectively (Table 1).

On the other hand, the young larch ecosystem showed a net emission of  $\text{NH}_3$  in general (Fig. 3, Table 2). In the snowless season, the stomatal emission of the larches and *Sasa* in addition to the decomposition of the cut *Sasa* materials were possible  $\text{NH}_3$  emitters, while the contribution of the soil to the  $\text{NH}_3$  emission seemed negligible (Section 3.5). The cutting of the pristine forest and *Sasa* prior to the planting of larch saplings, particularly, the strip-cutting of *Sasa*, enhanced the N mineralization rate and the inorganic N pool of the young larch ecosystem (Section 3.5), which likely enhanced the stomatal emission of the larches and *Sasa*.

By contrast, the  $\text{NH}_3$  emission in the snow season, when the larches defoliated and the *Sasa* was snowed

under, was ascribed to the emission from the snowpack. The high porosity of the snow, which maintained the gas exchange, and the possibility of  $\text{NH}_4^+$  production and/or accumulation under the snow, where the soil temperature was kept at around  $2^\circ\text{C}$ , seemed to contribute to the snowpack emission (Section 3.6). Furthermore, the low atmospheric concentrations of  $\text{NH}_3$  in the snow season (Table 1) were also advantageous in terms of the  $\text{NH}_3$  emission from the snowpack.

The young larch ecosystem also showed a net emission of particulate  $\text{NH}_4^+$  (Fig. 3, Table 2). However, the particulate  $\text{NH}_4^+$  emission was interpreted as the apparent emission induced by the increase in the atmospheric  $\text{NH}_4^+$  concentrations at a lower height, which resulted from the condensation of the emitted  $\text{NH}_3$  with acid gases. Strongly positive correlations between the particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations were found in both the snowless and snow seasons (Fig. 6), and particulate  $\text{SO}_4^{2-}$  was the dominant anion in relation to the atmospheric concentrations. The codeposition of  $\text{NH}_3$  with  $\text{SO}_2$  seemed to have an important role (Section 3.7). Attention should be given to the effect of the condensation–evaporation reactions on the atmospheric concentrations, as well as on the fluxes calculated by the gradient method.

The young larch ecosystem where the N supply was enhanced by the prior and the additional cutting acted as a source of  $\text{NH}_x\text{-N}$  with annual emission of  $4.8 \pm 0.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ , although the weekly mean fluxes to calculate the annual exchange might have uncertainty (28–60% underestimation) (Section 3.2). The estimated emission exceeded the annual wet deposition of  $\text{NH}_x\text{-N}$  ( $2.4 \pm 0.6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ). In a clean area, forest management, such as the prior and the additional cutting of *Sasa*, has the potential to affect the forest N cycle, including  $\text{NH}_x\text{-N}$  emission from the forest.

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