

# Isotope Ratio of Mineral N in *Pinus Densiflora* Forest Soils in Rural and Industrial Areas: Potential Indicator of Atmospheric N Deposition and Soil N Loss

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Deposition of atmospheric N that is depleted in <sup>15</sup>N has shown to decrease N isotope ratio (<sup>15</sup>N/<sup>14</sup>N, expressed as δ<sup>15</sup>N) of forest samples such as tree rings, foliage, and total soil-N. However, its effect on δ<sup>15</sup>N of mineral soil-N which is biologically active N pool has never been tested. In this study, δ<sup>15</sup>N of mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) in forest soils from organic and two depths of mineral soil layers (0 to 20 cm and 20 to 40 cm depth) of *Pinus densiflora* stands located at two distinct areas (rural and industrial areas) in southern Korea was analyzed to investigate if there is any difference in δ<sup>15</sup>N of mineral N between these areas. We also evaluated potential N loss of the study sites using δ<sup>15</sup>N of mineral N. Across the soil layers, the δ<sup>15</sup>N of NH<sub>4</sub><sup>+</sup> ranged from +8.9 to +24.8‰ in the rural area and from +4.4 to +13.8‰ in the industrial area. Soils from organic layer (+4.4‰) and mineral layer between 0 and 20 cm (+13.8‰) of industrial area showed significantly lower δ<sup>15</sup>N of NH<sub>4</sub><sup>+</sup> than those of rural area (+8.9 and +24.3‰, respectively), probably indicating the greater contribution of <sup>15</sup>N-depleted NH<sub>4</sub><sup>+</sup> from atmospheric deposition to forest in the industrial area than in the rural area. Meanwhile, δ<sup>15</sup>N of NO<sub>3</sub><sup>-</sup> was not different between the rural and industrial areas, probably because δ<sup>15</sup>N of NO<sub>3</sub><sup>-</sup> is more likely to be altered by the N loss that causes <sup>15</sup>N enrichment of the remaining soil N pool. Compared with the δ<sup>15</sup>N of soil mineral N reported by other studies (from -10.9 to +15.6‰ for NH<sub>4</sub><sup>+</sup> and -14.8 to +5.6‰ for NO<sub>3</sub><sup>-</sup>), the δ<sup>15</sup>N observed in our study was substantially high, suggesting that the study sites are more subject to the N loss. It was concluded that NH<sub>4</sub><sup>+</sup> rather than NO<sub>3</sub><sup>-</sup> can conserve the δ<sup>15</sup>N signature of atmospheric N deposition in forest ecosystems.

**Key words:** Acid rain, Forest soil, N deposition, N isotopic fractionation, Red pine, Tree ring age

## Introduction

Deposition of nitrogen (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) via acid precipitation is considered as an important N source for forest ecosystems where artificial fertilization is very rare (Norby, 1998; Nadelhoffer et al., 1999). For example, using mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) concentration in precipitation and precipitation amount in 2006 (Ministry of Environment, 2007), the annual N deposition rate in Korea is estimated to be 28.5 kg N ha<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> and 13.3 kg N ha<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>. However, mineral N concentration

alone can not be used as an indicator of the magnitude of atmospheric N deposition in the ecosystems, since mineral N concentration is subject to change as affected by the various factors, that influence N mineralization, such as temperature, moisture, and organic matter accumulation (Choi et al., 2007). Nitrogen isotope ratio (<sup>15</sup>N/<sup>14</sup>N, expressed as δ<sup>15</sup>N) of precipitation is distinctively lower than forest soil; δ<sup>15</sup>N is typically +2 to +10‰ for soil N and less than 0‰ for precipitation N (Heaton, 1986; Xiao and Liu, 2002; Bedard-Haughn et al., 2003). Particularly, δ<sup>15</sup>N of atmospheric NH<sub>4</sub><sup>+</sup> (between -12.2 and -0.5‰) and NO<sub>3</sub><sup>-</sup> (between -6.6 and +4.1‰ for NO<sub>3</sub><sup>-</sup>) originated from NH<sub>3</sub> volatilization and

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NO<sub>x</sub> emission from the fossil fuel combustion or agricultural activities are typically depleted in <sup>15</sup>N (Xiao and Liu, 2002). In this context,  $\delta^{15}\text{N}$  of mineral N could serve as a potential indicator of atmospheric N deposition.

Using such a distinctive  $\delta^{15}\text{N}$  between the forest soil N and precipitation N, several study suggested that forest samples including soil, foliage, and tree ring disks could be used as an indicator of historical and spatial variations in N deposition in Korea (Choi et al., 2005b), United States (Poulson et al., 1995), Canada (Bukata and Kyser, 2007), and Europe (Jung et al., 1997; Emmett et al., 1998). According to these studies, the mineral N of forest soils from industrial areas where N deposition is greater than rural areas could show a lower  $\delta^{15}\text{N}$  due to the lower  $\delta^{15}\text{N}$  of precipitation N when other conditions are the same. However, up to now, there is very few study on  $\delta^{15}\text{N}$  of mineral N of forest soils despite that mineral N is directly available for tree uptake and thus it may affect  $\delta^{15}\text{N}$  of tree tissues substantially (Emmett et al., 1998; Koba et al., 1998; Chang and Handley, 2000; Choi et al., 2007). Therefore, comparison of  $\delta^{15}\text{N}$  of mineral N in forest soils between industrial and rural areas may enlarge our understanding of the effect of N deposition on  $\delta^{15}\text{N}$  of forest samples such as tree rings, foliage, and total soil-N.

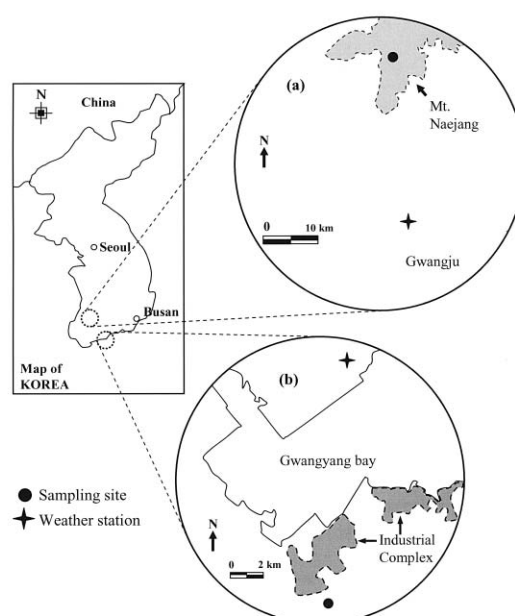
Because the mineral N is very active pool and thus is susceptible to N processes accompanied with N isotopic fractionation (Choi et al., 2003),  $\delta^{15}\text{N}$  of mineral N may reflect not only  $\delta^{15}\text{N}$  of N source such as N deposition via acid precipitation but also N isotopic fractionation (faster reaction of <sup>14</sup>N-bearing molecules than <sup>15</sup>N) associated with N transformations and subsequent losses. Among the various N processes, the mineralization of organic N can decrease  $\delta^{15}\text{N}$  of NH<sub>4</sub><sup>+</sup> pool, while the nitrification of NH<sub>4</sub><sup>+</sup> can increase  $\delta^{15}\text{N}$  of the NH<sub>4</sub><sup>+</sup> pool due to the N isotopic fractionation associated with N transformations and losses (Högberg, 1997). It has been also shown that the denitrification and leaching of <sup>15</sup>N-depleted NO<sub>3</sub><sup>-</sup> produced from incomplete nitrification is the most important process of N loss causing enrichment of <sup>15</sup>N in the remaining N in forest soils (Vervaet et al., 2002). Therefore,  $\delta^{15}\text{N}$  of mineral N can also serve as an indicator of N loss potential of forest soils.

In this study, we analyzed  $\delta^{15}\text{N}$  of mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) in soils of *Pinus densiflora* stands located in rural and industrial areas in southern Korea to test if  $\delta^{15}\text{N}$  of mineral N in the soils shows distinct signatures between the areas and to evaluate the potential use of  $\delta^{15}\text{N}$  of

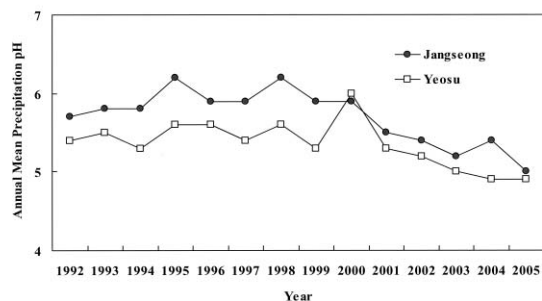
mineral N in estimating forest soil N dynamics in both terms of N sources (atmospheric N deposition) and N loss potential.

## Materials and Methods

**Study Area** This study was conducted with soils from *P. densiflora* stands located at two distinct areas, rural and industrial areas in southern Korea (Jeonnam province). *Pinus densiflora* stands in Mt. Naejang (35°27' N 126°51' E) in Jangseong and Mt. Jeonbong (34°50' N 127°40' E) in Yeosu were selected (Fig. 1). Jangseong is a typical rural area of which total area is 520 km<sup>2</sup> with 63% mountainous area. Mt. Jeonbong is 1 km from the Yeosu industrial complex where about 130 manufacturing plants are in operation (Korea Industrial Complex Corp., 2006). Therefore, it could be assumed that the *P. densiflora* stands in Yeosu might have received N deposition more than that in Jangseong. The annual mean pH of precipitation that is available from 1992 was lower in the Yeosu (mean pH: 5.4±0.1) than in the Jangseong site (mean pH: 5.7±0.1) except in 2000 (Ministry of Environment, 2007), indicating a higher potential of N deposition in Yeosu than in Jangseong via acid precipitation (Fig. 2), because NO<sub>3</sub><sup>-</sup> in precipitation is one of the ion species acidifying precipitation. Because the pH data of precipitation were not available at the study sites, the pH data from Gwangju meteorological station that is 20 km south of the Jangseong site and Gwangyang



**Fig. 1.** Location of the study site: (a) Jangseong (rural area) and (b) Yeosu (industrial area).



**Fig. 2. Changes in annual mean precipitation pH in Janseong (rural area) and Yeosu (industrial area) between 1992 and 2005.**

meteorological station that is 8 km north of the Yeosu site were used. During the past 45 years, the annual mean precipitation was 1366 mm and the annual mean temperature was 13.4°C for Jangseong and was 1417 mm and 14.1°C for Yeosu, respectively (Ministry of Environment, 2007).

The age of the forest stands was determined by tree ring counting. In 2006, three trees of *P. densiflora* were cut at breast height (around 1.3 m) for each site and rings were counted. Tree ages ranged from 42 to 46 years old for Jangseong and from 19 to 24 years old for Yeosu, suggesting that *P. densiflora* stand in Jangseong is maturer than in Yeosu.

**Soil Sampling** The soil in the rural area is classified as a fine loamy mesic family of Lithic Dystrudepts and has a shallow with thin brown to dark brown gravelly silt loam of A horizon (Rural Development Administration, 2000). The soil in the industrial area is classified as a loamy skeletal mesic family of Lithic Udorthents according to Soil Taxonomy and has an A horizon of brown color and very gravelly loam and silt loam over hard rhyolite or tuff materials (Rural Development Administration, 2000). Three sampling points (n=3) were selected at each study site. In each point, the soil samples were collected from the organic layer (around 7.5 cm thick for rural and 4.3 cm thick for industrial areas) and two depths of mineral soil layers (0 to 20 cm and 20 to 40 cm depth). The samples were air-dried, passed through a 2-mm sieve, and used for analysis of concentration and  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Some of the properties of the mineral soils have been reported by Choi et al. (2007) and Kwak et al. (2009). Briefly,  $\text{pH}_{\text{water}}$  was 4.07 and 4.10 and  $\text{pH}_{\text{KCl}}$  was 3.61 and 3.70 in the industrial and rural areas, respectively. Total C and N concentrations were 13.1 g C  $\text{kg}^{-1}$  and 0.55 g N  $\text{kg}^{-1}$  in the industrial area and

31.5 g C  $\text{kg}^{-1}$  and 1.28 g N  $\text{kg}^{-1}$  in the rural area, respectively.

**Chemical Analyses** The concentration of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were analyzed by steam distillation using MgO and Devarda's alloy sequentially after 2 M KCl extraction. During the distillation, the liberated  $\text{NH}_3$  was collected in 0.005 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solutions (Keeney and Nelson, 1982). To prevent isotopic cross-contamination between samples, 25 mL reagent-grade ethanol was added to distillation flasks and steam-distilled for 3 min between each sample distillation (Hauck, 1982). Nitrogen concentrations were determined by titration with 0.01 mol  $\text{L}^{-1}$  NaOH potentiometrically with the aid of a pH meter. The  $\text{H}_2\text{SO}_4$  solution containing  $\text{NH}_4^+$  was evaporated to dryness at 65°C in an oven after adjusted to pH 3 using 0.05 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  (Feast and Dennis 1996) and analyzed for  $\delta^{15}\text{N}$  using a continuous-flow stable isotope ratio mass spectrometer (IsoPrime-EA, Micromass, Manchester, UK) linked to a CN analyzer (NA Series 2, CE Instruments, Italy). The accuracy and reproducibility of the analytical procedure checked with reference materials, IAEA-N2 (ammonium sulfate, +20.3‰), IAEA-N3 (potassium nitrate, +4.6‰), and an internal reference soil material (+3.4‰) were better than 0.2 and 0.1‰, respectively. The concentration and isotope ratios of each soil sample were measured in triplicate and the mean values with standard error were reported.

Nitrogen isotope compositions were calculated as

$$\delta^{15}\text{N} (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (1)$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are the ratio of  $^{15}\text{N}/^{14}\text{N}$  for sample and standard (atmospheric  $\text{N}_2$ ), respectively.

The  $\delta^{15}\text{N}$  of mineral N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) was calculated using the following isotope mass balance equation (Karamanos and Rennie, 1981):

$$\delta^{15}\text{N}_{\text{in mineral N}} = (\delta^{15}\text{N}_{\text{NH}_4} \times C_{\text{NH}_4} + \delta^{15}\text{N}_{\text{NO}_3} \times C_{\text{NO}_3}) / (C_{\text{NH}_4} + C_{\text{NO}_3}) \quad (2)$$

where  $\delta^{15}\text{N}_{\text{NH}_4}$  and  $\delta^{15}\text{N}_{\text{NO}_3}$  are  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively; and  $C_{\text{NH}_4}$  and  $C_{\text{NO}_3}$  are their concentrations, respectively.

**Statistical Analyses** The *t*-test for two independent samples was performed using SPSS 12.0 package (SPSS, Chicago, Illinois, USA) to assess the significance of the difference in concentration and  $\delta^{15}\text{N}$  of mineral N

between the rural and industrial areas.

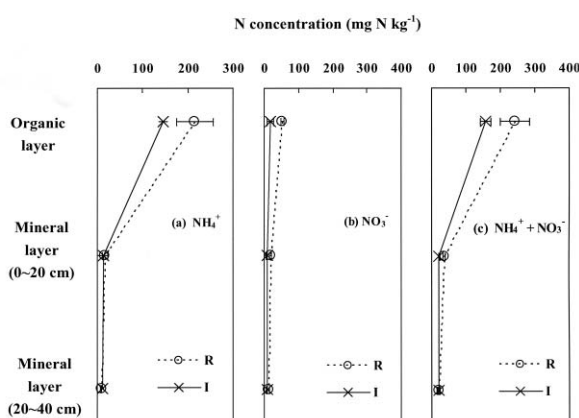
## Results and Discussion

**Soil mineral N concentration** In both study sites (rural and industrial areas), soil mineral N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) concentrations showed a pattern of decrease with soil depth (Fig. 3). For example, total mineral N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) concentration decreased from 241.7 and 156.7  $\text{mg N kg}^{-1}$  for organic layer to 19.8 and 19.9  $\text{mg N kg}^{-1}$  for the mineral layer between 20 and 40 cm depth in the rural and industrial areas, respectively. Such a higher mineral N concentration in organic layer than that in mineral layer by more than 10-folds suggests that organic layer is the principal reservoir of nutrients in forest (Van Cleve et al., 1983). Comparing between the rural and industrial areas, soil mineral N concentration in the organic layer of rural area was much higher than that of industrial area by 48.4% for  $\text{NH}_4^+$ , 184.7% for  $\text{NO}_3^-$ , and 54.3% for  $\text{NH}_4^+ + \text{NO}_3^-$ . Even though forest in the industrial area might have been exposed to atmospheric N deposition via precipitation more severely than that in the rural area as inferred from the precipitation pH (Fig. 2), soil mineral N concentration in organic layer seemed not to reflect N deposition history. Rather than, the higher mineral N concentration in the organic layer of the rural area than that of the industrial area could be attributed to the older age of *P. densiflora* stands in the former (42~46 years old) than in the latter (19~24 years old) as identified by tree rings counting. The older forest stands could provide soils with mineral N more than the younger as mineralization of N accompanying decomposition of organic matter is time-dependent (Lee

et al., 2002; Choi et al., 2006). These explanations are also supported by the thicker organic layer in the rural (7.5 cm) area than that in the industrial (4.5 cm).

In the mineral layer between 0 and 20 cm, concentrations of  $\text{NO}_3^-$  and total mineral N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) but not  $\text{NH}_4^+$  were still higher in the rural than in the industrial areas (Fig. 3) probably due to a higher leaching of  $\text{NO}_3^-$  from the upper organic layer (Vervaet et al., 2002). Meanwhile, for the mineral soil between 20 and 40 cm depth, there was no significant difference in the mineral N concentrations between rural and industrial areas. These results suggest that a single measurement of mineral N concentrations without data on N balance during a certain period do not provide any information on the N deposition and loss because N concentration is largely affected by other factors such as the age of tree stands that controls the amount of potentially mineralizable N.

**$\delta^{15}\text{N}$  of soil mineral N** In our study, the  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  ranged from +8.9 to +24.8‰ in the rural area and from +4.4 to +13.8‰ in the industrial area (Fig. 4a). Meanwhile,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  were between +18.6 and +21.9‰ and between +15.1 and +27.7‰ in the rural and industrial areas, respectively (Fig. 4b). The *t*-test revealed that  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in the organic layer (+4.4‰) and mineral layer of the soils between 0 and 20 cm (+13.8‰) at industrial area were significantly lower than those (+8.9 and +24.3‰, respectively) at rural area (Table 1). Such a difference could be attributed primarily to the greater contribution of  $^{15}\text{N}$ -depleted  $\text{NH}_4^+$  from the atmospheric deposition to the forest in industrial than that in rural area. In our study,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  was not significantly different in any soil depth between the rural and industrial areas (Table 1), suggesting that  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  is more subject to change than  $\text{NH}_4^+$  as affected by the N transformations including leaching of  $\text{NO}_3^-$  produced from incomplete nitrification and denitrification, and thus the  $\delta^{15}\text{N}$  signal of N source is likely to be masked by the N isotopic fractionation (Vervaet et al., 2002). The higher deposition rate of  $\text{NH}_4^+$  (28.5  $\text{kg N ha}^{-1}$ ) than  $\text{NO}_3^-$  (13.3  $\text{kg N ha}^{-1}$ ) in Korea (Ministry of Environment, 2007) could also allow  $\text{NH}_4^+$  preserving the  $\delta^{15}\text{N}$  signal of atmospheric N deposition better than  $\text{NO}_3^-$ . Therefore, our study suggests that not only  $\delta^{15}\text{N}$  of plant and total soil-N, but also  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  can be used in identifying the forest ecosystems that are more susceptible to atmospheric N deposition (Poulson et



**Fig. 3.** Changes in concentrations of (a)  $\text{NH}_4^+$ , (b)  $\text{NO}_3^-$ , and (c) total mineral N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) with soil depth of *P. densiflora* forest soils in rural (R) and industrial (I) areas. Horizontal bars indicate standard error of the means ( $n=3$ ).

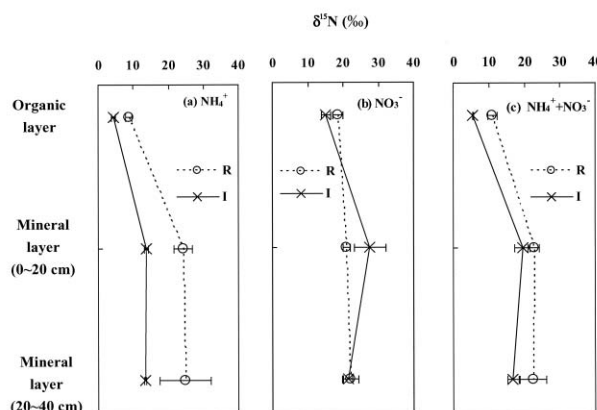
**Table 1.** The t-test for two independent samples to assess the significance of the difference in concentration and  $\delta^{15}\text{N}$  of mineral N between the rural and industrial areas.

Soil layer	Variables	<i>t</i>	Probability
Organic layer	$[\text{NH}_4^+]$	-7.986	<b>0.007**</b>
	$[\text{NO}_3^-]$	-3.154	<b>0.049*</b>
	$[\text{NH}_4^+ + \text{NO}_3^-]$	-9.718	<b>0.002**</b>
	$\delta^{15}\text{N}$ of $\text{NH}_4^+$	-3.972	<b>0.020*</b>
	$\delta^{15}\text{N}$ of $\text{NO}_3^-$	-1.750	0.156
	$\delta^{15}\text{N}$ of $(\text{NH}_4^+ + \text{NO}_3^-)$	-4.558	<b>0.041*</b>
Mineral layer (0~20 cm)	$[\text{NH}_4^+]$	-0.406	0.717
	$[\text{NO}_3^-]$	-7.714	<b>0.002**</b>
	$[\text{NH}_4^+ + \text{NO}_3^-]$	-3.882	<b>0.031*</b>
	$\delta^{15}\text{N}$ of $\text{NH}_4^+$	-3.945	<b>0.029*</b>
	$\delta^{15}\text{N}$ of $\text{NO}_3^-$	1.465	0.270
	$\delta^{15}\text{N}$ of $(\text{NH}_4^+ + \text{NO}_3^-)$	-1.159	0.318
Mineral layer (0~40 cm)	$[\text{NH}_4^+]$	1.759	0.213
	$[\text{NO}_3^-]$	-0.655	0.557
	$[\text{NH}_4^+ + \text{NO}_3^-]$	0.016	0.989
	$\delta^{15}\text{N}$ of $\text{NH}_4^+$	-1.533	0.265
	$\delta^{15}\text{N}$ of $\text{NO}_3^-$	-0.229	0.832
	$\delta^{15}\text{N}$ of $(\text{NH}_4^+ + \text{NO}_3^-)$	-1.369	0.276

\* Soil layer indicates that the means between the rural and industrial areas are significantly different at  $\alpha = 0.05$ .

al., 1995; Jung et al., 1997; Emmett et al., 1998; Choi et al., 2005b; Bukata and Kyser, 2007).

There are very few studies on  $\delta^{15}\text{N}$  of mineral N of forest soils as most of studies investigated  $\delta^{15}\text{N}$  of total soil-N. Emmett (1998) reported that  $\delta^{15}\text{N}$  of mineral N in four European forest soils were between -10.9 and +8.0 ‰ for  $\text{NH}_4^+$  and between -12.0 and +2.4 ‰ for  $\text{NO}_3^-$ . Koba et al. (1998) found that  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ranged from +2.5 to +15.6 ‰ and from -14.8 to +5.6 ‰, respectively, in a Japanese red cedar forest. In a minerotrophic peatland of Canada,  $\delta^{15}\text{N}$  were between +0.6 and +7.0 ‰ for  $\text{NH}_4^+$  and between -3.4 and +2.7 ‰ for  $\text{NO}_3^-$  (Choi et al., 2007). Much lower  $\delta^{15}\text{N}$  of mineral N was observed in a loblolly pine stand in USA; the values ranged from -4.6 to +5.2 ‰ for  $\text{NH}_4^+$  and from -8.6 to -5.8 ‰ for  $\text{NO}_3^-$  (Choi et al., 2005a). These published  $\delta^{15}\text{N}$  of mineral N are lower than the  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  (+4.4 to +13.8 ‰ in the industrial and +8.9 to +24.8 ‰ in the rural areas) and  $\text{NO}_3^-$  (+15.1 to +27.7 ‰ and +18.6 and +21.9 ‰, respectively) observed in our study. Since N loss through volatilization, leaching, and denitrification substantially increase  $\delta^{15}\text{N}$  of the remaining soil N pool, such a high  $\delta^{15}\text{N}$  of mineral N suggests that *P. densiflora* stands investigated in our study is more susceptible to N loss than other forest



**Fig. 4.** Changes in  $\delta^{15}\text{N}$  of (a)  $\text{NH}_4^+$ , (b)  $\text{NO}_3^-$ , and (c) total mineral N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) with soil depth of of *P. densiflora* forest soils in rural (R) and industrial (I) areas. Horizontal bars indicate standard error of the means (n=3).

stands found in the publications (Högberg, 1990; Högberg and Johannisson, 1993; Choi et al., 2007). In our study,  $\delta^{15}\text{N}$  of mineral N tended to be higher in the mineral layer than in the organic layer (Fig. 4), suggesting that the magnitude of N loss is higher in the mineral than in the organic layer. As nitrification which is the predominant N process causing N loss through leaching and denitrification is hardly measurable in the mineral layer (Laverman et al., 2000), it could be hypothesized that loss of  $\text{NO}_3^-$  derived from the upper organic layer occurred in the mineral layer. Because N loss potential of forest soils is proportional to mineral N concentration, the higher  $\delta^{15}\text{N}$  of mineral N in our study could be attributed primarily to the relatively higher concentration of mineral N (Högberg, 1990; Högberg and Johannisson, 1993; Emmett et al., 1998). For example, Choi et al. (2005a) reported much lower mineral N concentration (below  $3.0 \text{ mg N kg}^{-1}$ ) in a loblolly pine stand in USA.

In conclusion, our study showed that  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  of forest soils in industrial areas was lower than that in rural areas, probably reflecting a higher deposition of atmospheric N which is depleted in  $^{15}\text{N}$ . Therefore, it is suggested that  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  is worth being analyzed along with plant and total soil samples to investigate the effect of atmospheric N deposition on N cycling in forest soils. However, a further study is needed to confirm our findings; particularly under controlled environment using the same soils and ages of trees to minimize the effect of site history.

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## 질소공급, 고추의 생육 및 수량에 대한 녹비작물 환원 효과

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질소동위원소비( $\delta^{15}\text{N}$ )가 낮은 대기질소 강하물의 유입에 의해 산림 생태계 내 다양한 시료(나이테, 엽, 토양)의  $\delta^{15}\text{N}$  값이 낮아지는 것으로 보고되고 있다. 하지만, 토양 미생물과 식물이 쉽게 이용할 수 있는 토양 무기태 질소의  $\delta^{15}\text{N}$ 에 대한 연구는 진행된 바 없다. 본 연구는 대기질소 강하물이 상대적으로 적은 농촌지역과 많은 공업지역에 위치한 적송 산림지역의 유기토양층과 무기토양층(0~20 cm와 20~40 cm) 중  $\text{NH}_4^+$ 과  $\text{NO}_3^-$ 의  $\delta^{15}\text{N}$  값을 분석하여 두 지역간의 차이를 조사하였으며, 이들  $\delta^{15}\text{N}$  값을 근거로 조사 지역의 질소손실 민감성을 평가하였다. 농촌지역과 공업지역에서  $\text{NH}_4^+$ 의  $\delta^{15}\text{N}$  값은 각각 +8.9 ~ +24.8%과 +4.4 ~ +13.8%로 분포하였다. 유기토양층과 무기토양층(0~20 cm)에서 두 지역간  $\text{NH}_4^+$ 의  $\delta^{15}\text{N}$  값 차이가 나타났는데, 공업지역에서 각각 +4.4%과 +13.8%이었고, 농촌지역에서는 각각 +8.9%과 +24.3%로 공업지역에서 더 낮은  $\delta^{15}\text{N}$  값이 나타났다. 이는 공업지역에서  $\delta^{15}\text{N}$  값이 낮은 대기 유래  $\text{NH}_4^+$  유입량이 더 많았음을 의미한다. 한편,  $\text{NO}_3^-$ 의  $\delta^{15}\text{N}$  값은 지역간 차이가 없었는데, 이는  $\text{NO}_3^-$ 가 용탈과 탈질 등에 의해 쉽게 손실되는 과정에서 수반되는 질소동위원소 분할 효과에 의해 강하물에서 유래된  $\text{NO}_3^-$ 의  $\delta^{15}\text{N}$  기여도가 낮아지기 때문으로 판단된다. 본 연구에서 관측된 무기태 질소의  $\delta^{15}\text{N}$  값은 다른 지역에서 조사된  $\text{NH}_4^+$ (-10.9 ~ +15.6%)과  $\text{NO}_3^-$ (-14.8 ~ +5.6%)의  $\delta^{15}\text{N}$  값보다 매우 높는데, 이는 본 연구지역에서 토양 질소 손실 가능성이 높음을 보여준다. 이상의 연구 결과에 의하면 산림토양의 무기태 질소 중  $\text{NO}_3^-$ 보다  $\text{NH}_4^+$ 이 질소공급원(대기 질소 강하)에 대한  $\delta^{15}\text{N}$  정보를 보다 잘 반영하는 것으로 판단된다.