Analysis of Tree-ring Chemistry to Interpret Variations in Tree-ring Growth of Larix leptolepis and Cryptomeria japonica in Relation to Atmospheric Environmental Changes in Southern Korea

Lee, Kye-Han
Department of Forestry, Chonnam National University

Luong, Thi-Hoan
Department of Forestry, Chonnam National University

Jang, Kyoung-Soo
Department of Forestry, Chonnam National University

Choi, Woo-Jung
Department of Rural and Biosystems Engineering, Chonnam National University

他

https://doi.org/10.5109/1526293

出版情報：九州大学大学院農学研究院紀要. 60 (1), pp.33-42, 2015-02-27. 九州大学大学院農学研究院

J. Fac. Agr., Kyushu Univ., **60** (1), 33–42 (2015)

Analysis of Tree–ring Chemistry to Interpret Variations in Tree–ring Growth of *Larix leptolepis* and *Cryptomeria japonica* in Relation to Atmospheric Environmental Changes in Southern Korea

Kye–Han LEE[1], Thi–Hoan LUONG[1], Kyoung–Soo JANG[1], Woo–Jung CHOI[2], Gwan–Soo PARK[3] and Shoji OHGA*

Laboratory of Forest Resources Management, Division of Forest Environmental Sciences,
Department of Agro–Environmental Sciences, Faculty of Agriculture,
Kyushu University, Fukuoka 811–2415, Japan
(*Received October 23, 2014 and accepted November 14, 2014*)

Annual tree rings may have information to help investigate the effects of environmental change caused by temperature, air pollution, and acid rain on tree growth. Annual tree ring growth in relation to environmental changes was studied by analysing the chemistry of tree rings of *Larix leptolepis* (*L. leptolepis*) and *Cryptomeria japonica* (*C. japonica*) in southern Korea. Tree ring growth (diameter, annual increments of ring area) and tree ring chemistry (δ^{13}C, δ^{15}N, N) concentration, and Ca/Al ratios of both species were analysed. Regression analysis was conducted between tree ring data and environmental variables. Annual tree ring growth significantly differed between the two species and increased over time ($p<0.01$). The growth rate of *L. leptolepis* (ring width and ring area) was lower than that of *C. japonica*. Temperature, CO_2, NO_2, and SO_2 affected ($p<0.05$) the tree ring area increment of *C. japonica*, and SO_2 affected ($p<0.05$) the tree ring area increment of *L. leptolepis*. The relationships of temperature, SO_2, and NO_2 concentrations with tree ring δ^{13}C of both species ($p<0.05$) increased C isotope discrimination (Δ) and affected tree ring growth. There was a negative correlation between annual ring area and Δ in tree rings of *L. leptolepis* ($p<0.01$). For *C. japonica*, Δ was positively correlated ($p<0.01$) with annual ring area. The correlation of precipitation pH with tree ring δ^{13}C, δ^{15}N, and N concentration of the two species ($p<0.01$) could provide information on N deposition due to the H^+ input from acid rain. Tree ring δ^{15}N and N concentration may be useful as indicators for precipitation pH. Tree ring growth was influenced by climate change, atmosphere pollutants and precipitation pH. The effects of increased temperature, atmosphere pollutants, and acid precipitation on radial growth may reflect N deposition from fossil fuel combustion. Acid deposition at the study site affected tree ring growth and both species may be at risk from the long–term effects of acid deposition over time.

Key words: acid precipitation, annual tree ring, climate change, δ^{13}C, N deposition, δ^{15}N

INTRODUCTION

Tree growth is affected by various environmental factors associated with climate change, including air temperature, precipitation, and air pollution (Chmura *et al*., 2011). Information on annual tree rings can be used to estimate their environmental history to understand the effects of environmental changes on forests (Choi and Lee, 2012). Environmental change can either constrain or stimulate tree ring growth (Choi *et al*., 2005b). Forest decline in Asia has been linked to acid precipitation (Hirano *et al*., 2007), air pollution and global warming (Kume *et al*., 2000; Woo, 2009).

Impacts of atmospheric NO_2 concentration on forest decline of *Pinus densiflora* in Japan have been reported by Kume *et al*. (2000). A threat to *Cryptomeria japonica* and *Chamaecyparis obtusa* forests in Japan from soil acidification caused by increased nitrogen deposition has also been noted (Ito *et al*., 2011). Effects of precipitation pH on decreased tree–ring growth of *P. densiflora* due to N deposition have been reported by Choi *et al*. (2005b), Kwak *et al*. (2009a; 2009b; 2011), and Lee *et al*. (2011).

Annual tree rings were also used to estimate historical temperature, and the effects of air pollution and precipitation pH (Seftigen *et al*., 2011; Choi *et al*., 2005b; Bukata and Kyser, 2007). The temperature influenced δ^{13}C via the photosynthetic rate due to increased atmospheric CO_2 concentration (Chmura *et al*., 2011; Seftigen *et al*., 2011). The effects of air pollution on δ^{13}C resulted from reduced CO_2 concentration in the intercellular air spaces caused by stomatal closure (Martin and Sutherland, 1990). Precipitation pH and H^+ from acid rain affected δ^{13}C via the carboxylation rate (Shan, 1998; Kwak *et al*., 2009b). Therefore, the relative abundance of δ^{13}C in tree ring tissue can serve as a time integrating indicator of photosynthetic response to environmental conditions and is linked to changes in stomatal conductance and the carboxylation rate (Farquhar *et al*., 1989; Viet *et al*., 2013).

In addition, the correlation between N concentration and δ^{15}N in tree rings with precipitation acidity provides isotopic evidence of the contribution of atmospheric nitrogen deposition (Kwak *et al*., 2009a; 2009b). δ^{15}N of tree rings can be used to estimate historical changes of pre-

[1] Department of Forestry, Chonnam National University, Gwangju 500–757, Korea
[2] Department of Rural and Biosystems Engineering, Chonnam National University, Gwangju 500–757, Korea
[3] Department of Forestry Resources, Chungnam National University, Daejeon 305–764, Korea
* Corresponding Author (E–mail: ohga@forest.kyushu–u.ac.jp)

cipitation pH, while nitrogen concentration in tree rings is not a useful indicator for acid precipitation (Kwak *et al*., 2011). A pattern of increasing N concentration with decreasing δ^{15}N in tree rings has been attributed to increased N deposition (Poulson *et al*., 1995; Bukata and Kyser, 2007; Choi *et al*., 2007; Kwak *et al*., 2011). Although N deposition can improve tree growth in a short term due to the N fertilizer effect, N deposition over decades can lead to nutrient deficiency and imbalance, and tree decline (Shortle *et al*., 1995; Tomlinson, 2003).

Decreased Ca/Al in tree rings associated with a decreasing precipitation pH may reflect reduction in Ca availability due to soil acidification (Kwak *et al*., 2009b; Kwak *et al*., 2011). The ratio of Ca/Al in tree rings of *P. densiflora* was a useful predictor of historical acid precipitation (Kwak *et al*., 2011; Lee *et al*., 2011). Although some studies have reported the effects of environment factors on tree ring chemistry of *P. densiflora* in Korea (Choi *et al*., 2005b; Kwak *et al*., 2009b; Kwak *et al*., 2011), no study has been conducted for Japanese larch (*Larix leptolepis*) and Japanese cedar (*Cryptomeria japonica*), major species planted in Korea.

The aims of this study were to examine the effects of environmental changes on tree ring growth of Japanese larch and cedar forests and to determine the relationships between tree–ring parameters (δ^{13}C, δ^{15}N, N concentration, and Ca/Al in tree rings) and precipitation pH.

MATERIALS AND METHODS

Study area

The study site is located in Jangseong County in South Korea, approximately 35 km north of Gwangju city (Fig. 1). It is in a typical rural area; 63% is mountainous. The research plots were located at 35°22′38″N, 126°44′13″E, 488 m a.s.l with 20o slope for *L. leptolepis* and 35°27′ 19″ N, 126°47′01″E, 218m a.s.l with 15° slope for *C. japonica*. The soils are classified as shallow gravelly silt loam, with a thin brown to dark brown color and a pH range of 4.00 to 4.35. Total N was 3.1 g kg^{-1} for *C. japonica* and 3.7 g kg^{-1} for *L. leptolepis* (Table 1).

All meteorological and environmental monitoring data were obtained at the Gwangju monitoring station, located about 30 km south of the site (Ministry of Environment of Korea, 2010). Climate data were available from 1962 to 2009. The mean annual temperature and precipitation during this period were 13.5˚C and 1,364.7 mm, respectively (Fig. 2a). Mean precipitation pH showed a decrease from 5.5 to 4.9 between 1992 and 2009 (Fig. 2b). Atmospheric pollutants' (NO_2, SO_2, and O_3) concentration data were measured from 1989 to 2009. During this period, SO_2 concentration decreased from 21.0 to 4.0 nL L^{-1}, and mean annual concentrations of O_3 and NO_2 increased from 7.0 to 26.0 nL L^{-1} and from 11.0 to 21.0 nL L^{-1}, respectively (Fig. 2c). Atmospheric CO_2 concentra-

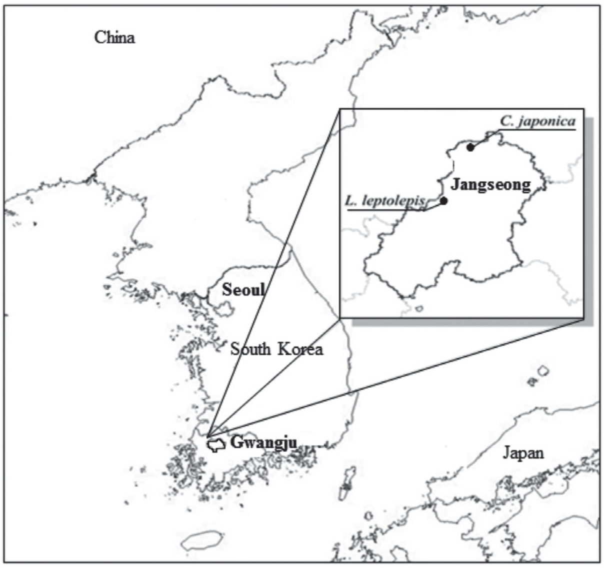

Fig. 1. Geographical locations of the study sites.

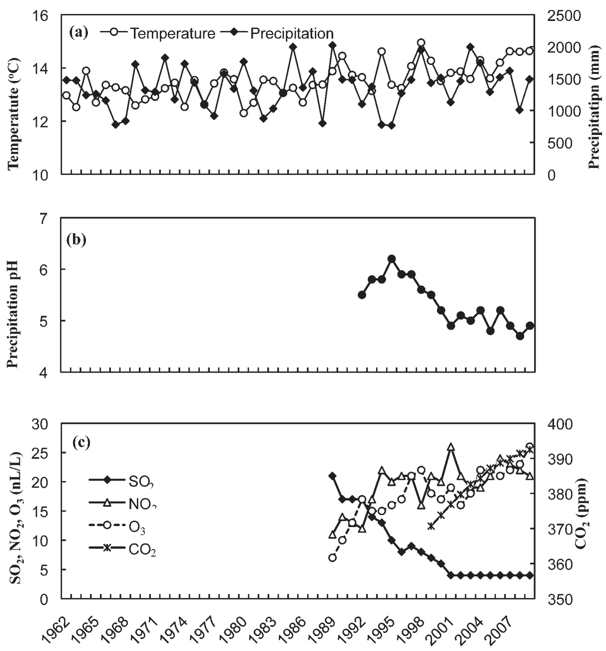

Fig. 2. Changes in mean annual temperature and precipitation (a), mean annual precipitation pH (b), concentration of atmospheric pollutants (SO_2, NO_2, O_3 and CO_2) (c) in the study area. Data were available for those periods.

Table 1. Characteristics of location and soil chemical properties in the study sites

Species	Latitude (N)	Longitude (E)	Altitude (m a.s.l)	Slope	pH	Total N (g kg^{-1})
L. leptolepis	35°22′38″	126°44′13″	488	20˚	4.00±0.01	3.68±0.27
C. japonica	35°27′19″	126°47′01″	218	15˚	4.35±0.03	3.09±0.38

tion increased from 370.7 ppm in 1999 to 389.9 ppm in 2009 (Fig. 2c).

Annual tree–ring analysis

A 20×20 m plot for each species was established at the study site. For each species, three tree–ring disks at breast height were randomly selected from the plots. The ages of these disks ranged from 42 to 46 years old for *L. leptolepis* and from 32 to 34 years old for *C. Japonica* (Table 2).

The disks were sanded and polished. Annual increments of diameter growth were measured on four radii and a mean calculated. The mean annual diameter increment was 0.73 cm yr^{-1} for *C. japonica* and 0.50 cm yr^{-1} for *L. leptolepis*; mean tree–ring width was 3.66 mm for *C. japonica* and 2.47 mm for *L. leptolepis* (Table 2). It was then assumed that tree rings are concentric circles (Choi *et al.*, 2007). The radii were cross–dated to identify the exact year each tree ring was formed. Ring widths were measured to an accuracy of 0.01 mm using CDendro and CooRecorder 7.4 software (Cybis Elektronik and Data AB, Salsjobden, Sweden). Foliage samples were collected from trees sampled for ring disks. The wooden disks and foliar samples were oven–dried at 60°C to constant weight.

Chemical analysis

The wood samples were used for chemical analyses after being ground to fine powder with a centrifugal mill (MM200, Retsch GmbH, Haan, Germany). The $\delta^{13}C$, $\delta^{15}N$, and N concentration were determined using a continuous–flow stable isotope ratio mass spectrometer linked to an elemental analyzer (Iso Prime–EA, Micromass, UK) (Kwak *et al.*, 2009b). In this study, whole–plant tissue samples, instead of cellulose, were used for isotope analysis, because for trees, whole–plant tissue produces the same $\delta^{13}C$, as well as $\delta^{15}N$, as cellulose (Loader *et al.*, 2003). Whole wood samples can be successively used in tree ring isotope studies as in dendrochronology studies, not the exact value of any individual ring (McCarroll and Loader 2004). Carbon and nitrogen isotope composition (δ) were calculated as:

$$\delta\ (‰) = [(R_{sample} / R_{standard}) - 1] \times 1000$$

where, R_{sample} and $R_{standard}$ are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios in a sample and standard, respectively. The standards are the Pee Dee Belemnite (PDB) standard for C and atmospheric N_2 for nitrogen. The analytical error for carbon isotopes was <± 0.1‰ and for nitrogen isotopes less <± 0.2‰.

Carbon isotope discrimination (Δ) was measured using the following equation (Farquhar *et al.*, 1989):

$$\Delta = a + (b-a)C_i/C_a = (\delta^{13}C_{air} - \delta^{13}C_{plant})/(1 + \delta^{13}C_{plant}/1000)$$

Where, Δ is the carbon isotope discrimination; the $\delta^{13}C_{airf}$ or each year (t) was obtained from the regression equation of Feng (1998):

$$\delta^{13}C_{air} = -6.429 - 0.006 \exp[0.0217(t - 1740)]$$

According to this equation, $\delta^{13}C_{air}$ decreased from –7.17‰ in 1962 to –8.40‰ in 2007 for *L. leptolepis* and from –7.48‰ in 1978 to –8.49‰ in 2009 for *C. japonica*. The $\delta^{13}C_{plant}$ is determined by the $\delta^{13}C$ of atmospheric CO_2 and the ratio (C_i/C_a) of intercellular (C_i) to atmospheric (C_a) partial pressure, as described as (Farquhar *et al.*, 1989):

$$\delta^{13}C_{plant} = \delta^{13}C_{air} - a - (b-a)\ C_i/C_a (4)$$

where, a and b are the discrimination against ^{13}C during CO_2 diffusion through stomata (normally ~ 4.4‰) and during CO_2 fixation (normally ~ 27‰), and C_i/C_a is the ratio of intercellular to atmospheric CO_2 concentration.

For tree–ring samples where N concentration was too low to be analyzed for both $\delta^{13}C$ and $\delta^{15}N$ simultaneously using peak jumping, the $\delta^{15}N$ was analyzed again by optimizing the mass spectrometer for $\delta^{15}N$ alone (Kwak *et al.*, 2011; Choi *et al.*, 2007). In this case, up to 10 mg of wood samples were used, depending on the N concentration to meet a minimum N amount to improve the reproducibility of the $\delta^{15}N$ analysis (Choi *et al.*, 2007).

To determine Ca and Al concentration, 0.5 g of wood sample was digested in 10 ml concentrated HNO_3–$HClO_4$–H_2SO_4 mixture (1:8:1) at 200°C for 2 h on a heating block (Kwak *et al.*, 2009a; Kwak *et al.*, 2011). For Ca and Al, concentrations were analyzed using an inductively coupled plasma emission spectrophotometer.

Statistical analysis

Response and correlation function analyses were used to examine relationships between tree ring parameters and climate variables (temperature and precipitation), atmospheric pollutants (SO_2, NO_2, O_3, and CO_2), and precipitation pH. Response function analysis is a form of multiple regression. These relationships were explored by Pearson correlation analysis, because variation in tree–ring growth was likely to be affected by multiple environmental factors.

Table 2. Characteristics of tree ring growth and foliage in the study sites

Species	Tree numbers	Ring numbers (years)	Mean diameter (cm)	Mean annual diameter increment (cm yr^{-1})	Mean annual ring width (mm)	Foliage	
						N(g kg^{-1})	$\delta^{13}C$ (‰)
L. leptolepis	3	42	21.56±3.8	0.50±0.03	2.47±0.13	28.50±0.39	–26.79±0.16
C. japonica	3	32	24.14±3.4	0.73±0.04	3.66 ± 0.16	69.63±0.17	–26.77±0.85

Values are the mean ± SE based on triplicated measurements.

All the response and correlation functions were determined annually for the period 1966–2009, which was common to both tree–ring data and the regional climate records. For relationships of air pollutants with annual ring area and parameters in tree rings ($\delta^{13}C$, $\delta^{15}N$, N concentration and Ca/Al), the response and correlation functions were determined for SO_2, NO_2, and O_3 from 1989, for precipitation pH from 1992, and for CO_2 concentration from1999.

All statistical analyses were performed using the SPSS 11.5 statistical software package (SPSS, Chicago, Illinois, USA). The level of significance for all statistical tests was an α value of 0.05. The significance of annual trends of tree ring parameters was assessed by the analysis of time series using year as an independent variable.

RESULTS

Variation in annual ring growth

Annual radial growth rates were significantly different ($p<0.01$) within a tree species and between the two species. *C. japonica* had higher growth rates of ring width, ring area, and diameter increment than *L. leptolepis* (Fig. 3). Annual growth of ring widths of the two species decreased with time ($p<0.001$) (Fig. 3a). Annual ring area of *L. leptolepis* and *C. japonica* increased until 1989 and 1998, respectively, and then decreased (Fig. 3b).

Temperature was positively ($p<0.01$) correlated with annual ring area of *C. japonica*, but not of *L. leptolepis* (Table 3); no correlations were found between precipitation and annual ring area (Table 3). Annual ring growth of *C. japonica* was positively correlated with NO_2 concentration (p< 0.05) and negatively related with SO_2 and CO_2 concentrations ($p<0.01$). Annual ring growth of *L. leptolepis* was positively correlated with SO_2 concentration ($p<0.05$) (Table 3).

Tree ring $\delta^{13}C$

Tree–ring $\delta^{13}C$ significantly decreased with time ($p<0.001$) from –25‰ to –27.5‰ for *L. leptolepis* and from –22.7‰ to –25.2‰ for *C. japonica* (Fig. 4a). Mean

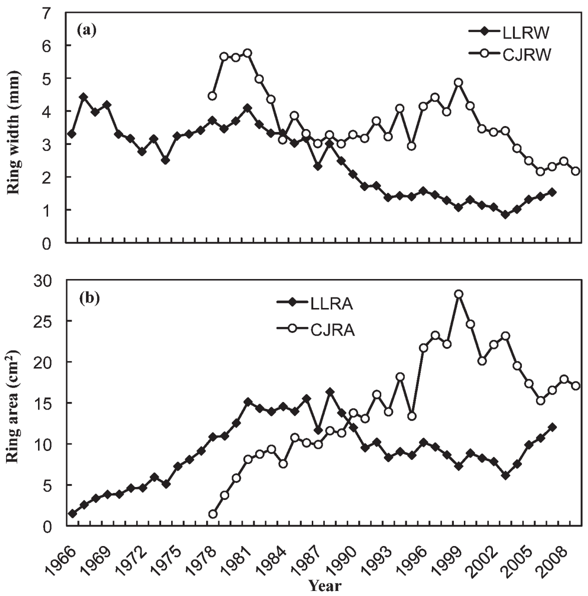

Fig. 3. Annual variation in ring width (a) and tree ring area (b) of two species.

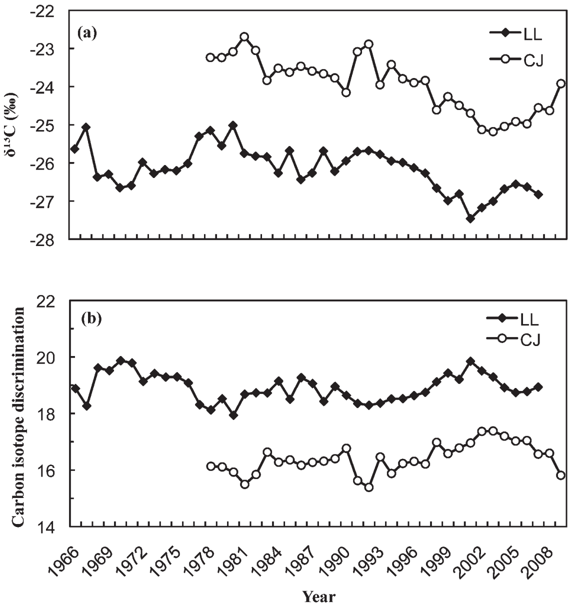

Fig. 4. Annual changes in $\delta^{13}C$ (a), carbon isotope discrimination (b) of two species.

Table 3. Pearson correlation of annual ring area of *L. leptolepis* and *C. japonica* with environmental variables in the study area

Variable	Pearson correlation coefficients	
	L. leptolepis[a]	*C. japonica*[a]
Temperature	0.10[ns](42)	0.49**(32)
Precipitation	0.04[ns](42)	0.10[ns] (32)
Atmospheric CO_2 concentration	0.61[ns](9)	–0.90***(11)
Atmospheric NO_2 concentration	–0.35[ns](19)	0.43*(21)
Atmospheric SO_2 concentration	0.52* (19)	–0.56**(21)
Atmospheric O_3 concentration	–0.41[ns](19)	0.38[ns](21)

Values in the parentheses are the number of data point used for the correlation analysis
[a] The mean values of three trees were used for tree variables in the correlation analysis
[ns] Not significant; ***$p<0.001$; **$p<0.01$; *$p<.05$.

Table 4. Pearson correlation between $\delta^{13}C$ in annual tree ring of two species and environmental variables in the study area

Variable	Pearson correlation coefficients	
	L. leptolepis[a]	*C. japonica*[a]
Temperature	–0.31*(42)	–0.48**(32)
Precipitation	–0.26[ns](42)	–0.27[ns](32)
Atmospheric CO_2 concentration	0.54[ns](9)	0.01[ns](11)
Atmospheric NO_2 concentration	–0.62**(19)	–0.53*(21)
Atmospheric SO_2 concentration	0.80***(19)	0.77***(21)
Atmospheric O_3 concentration	–0.47* (19)	–0.42[ns] (21)

Values in the parentheses are the number of data points used for the correlation analysis.
[a] The mean values of three trees were used for tree variables in the correlation analysis.
[ns] Not significant; ***p<0.001; **p<0.01; *p<0.05

$\delta^{13}C$ was less (–26.2‰) in *L. leptolepis* than *C. japonica* (–23.9‰). The $\delta^{13}C$ of both species was negatively (p<0.05) correlated with temperature and NO_2, and positively (p<0.001) correlated with SO_2 but there was no correlation with precipitation and CO_2 concentration (Table 4). Atmospheric O_3 concentration was correlated (p<0.05) with tree–ring $\delta^{13}C$ of *L. leptolepis* but not of *C. japonica* (Table 4).

The patterns of Δ fluctuated within a narrow range between 17.94 to 19.87 for *L. leptolepis* and 15.39 to 17.38 for *C. japonica* (Fig. 4b) due to the inter–correlation between Δ and C_i/C_a (see equation 2). Better tree growth of *C. japonica* was coupled with lower Δ. The annual pattern of Δ of *C. japonica* was only correlated with SO_2 concentration (p<0.01, data not shown), and of *L. leptolepis* was correlated (p<0.05) with SO_2, NO_2, CO_2 concentration and precipitation pH but not with temperature, precipitation, and O_3 concentration (data not shown). There were linear relationships between annual ring area and Δ for both species across the entire growth period (Fig. 5).

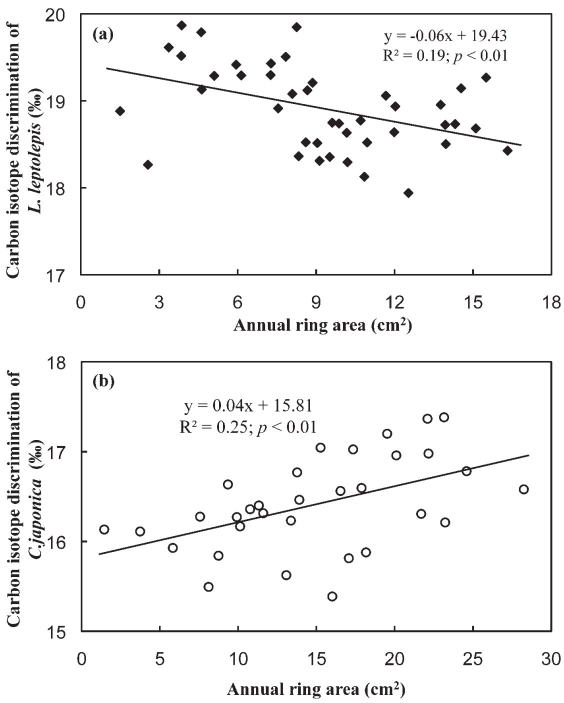

Fig. 5. Regression analysis between tree ring area and carbon isotope discrimination for the entire growth period 1966 to 2007 for *L. leptolepis* (a), 1978 to 2009 for *C. japonica* (b).

Tree ring $\delta^{15}N$, N concentration and Ca : Al ratio

Tree ring $\delta^{15}N$ of *L. leptolepis* decreased significantly with time (p<0.001) and varied between 4.2‰ and –2.9‰; $\delta^{15}N$ of *C. japonica* increased significantly with time (p<0.001) and varied between –8.5‰ and –4.8‰ (Fig. 6a). Total N concentration was significantly greater (p<0.01) in *C. Japonica* than *L. leptolepis* and fluctuated between 1.5 to 2.8 g N kg^{-1} and 0.2 to 1.8 g N kg^{-1}, respectively (Fig. 6b).

Calcium concentrations of *L. leptolepis* increased from 0.1g kg^{-1} to 0.63 g kg^{-1} between 1966 and 2007 (p< 0.001)(Fig. 7a); Al concentration varied between 0.01 g kg^{-1} and 0.04 g kg^{-1} with a significant temporal trend over the study period (p<0.05) (Fig. 7b). Ca/Al fluctuated

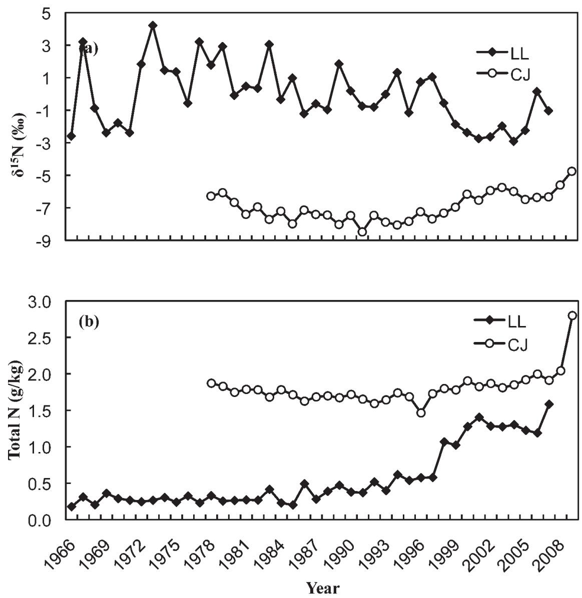

Fig. 6. Annual variations in $\delta^{15}N$ (a) and nitrogen concentration (b) in tree rings of two species.

between 3.6 and 37.9 and did not show a systematic pattern with time (Fig.7c). In *C. japonica*, Ca concentrations decreased from 1.21 g kg^{-1} to 0.54 g kg^{-1}; there was no significant pattern between 1978 and 2009 (Fig. 7a). Al concentration increased from 0.01 g kg^{-1} to 0.18 g kg^{-1}. There was a significant temporal pattern ($p<0.001$) and Ca/Al decreased pattern ($p<0.001$) from 87.4 in 1978 to 24.3 in 2008 (Fig. 7c).

Relation between tree–ring chemistry and precipitation pH

Between 1992 and 2009, precipitation pH was significantly correlated with $\delta^{13}C$, $\delta^{15}N$, and total N concentration in tree rings of both species but not with Ca/Al (Table 5; Fig. 8). The $\delta^{13}C$ of both species increased ($p<0.01$) and N concentration decreased with increasing precipitation pH (Fig. 8a, 8c). The $\delta^{15}N$ in tree rings of *L. leptolepis* increased and of *C. japonica* decreased with increasing precipitation pH (Fig. 8b). Inter–correlations

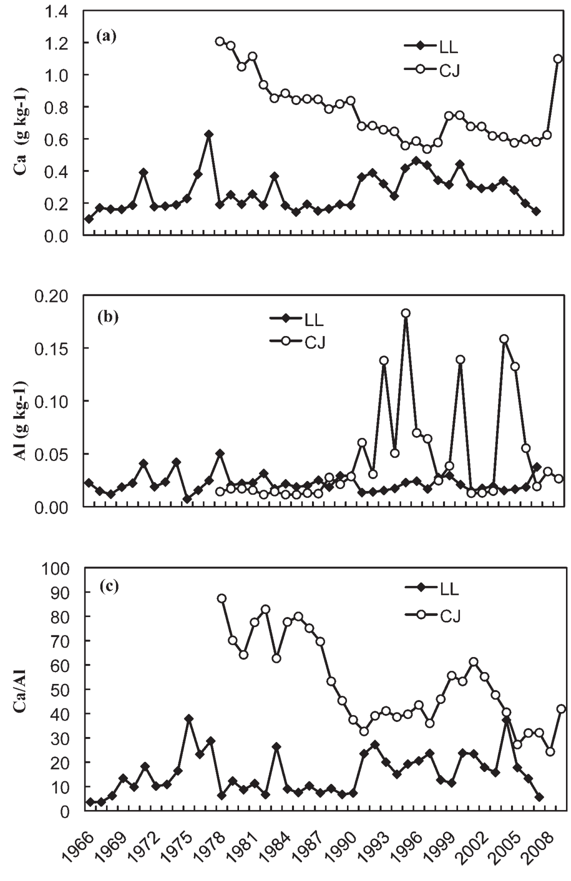

Fig. 7. Annual variations in Ca concentration (a), Al concentration (b), and Ca to Al (c) in tree rings of two species.

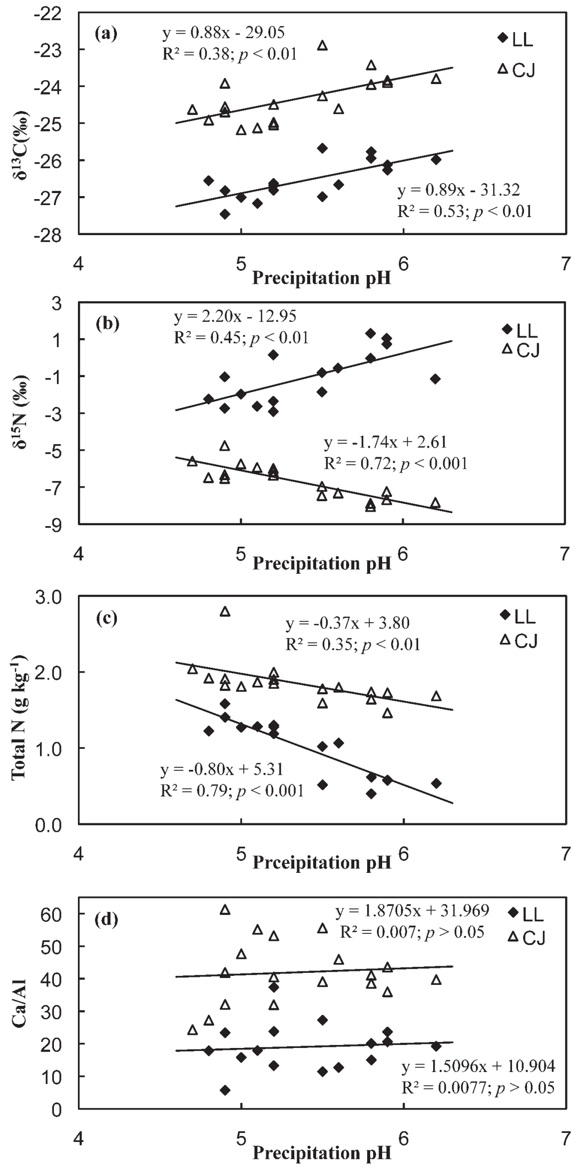

Fig. 8. Regression analysis between precipitation pH and carbon isotope (a), nitrogen isotope (b), nitrogen concentration (c), and Ca/Al (d) of tree rings of two species.

Table 5. The relationship between tree ring chemistry of two species and precipitation pH in the study site

Variable	Pearson correlation coefficients	
	L. leptolepis[a]	*C. japonic*[a]
$\delta^{13}C$ × precipitation pH	0.726**(16)	0.620**(18)
$\delta^{15}N$ × precipitation pH	0.672**(16)	–0.849***(18)
N concentration × precipitation pH	–0.887**(16)	–0.594**(18)
Ca/Al × precipitation pH	0.088[ns] (16)	0.084[ns](18)

Values in the parentheses are the number of data points used for the correlation analysis
[a] The mean values of three trees were used for tree variables in the correlation analysis.
[ns] Not significant; ***$p<0.001$; **$p<0.01$; *$p<0.05$

between species were assessed using linear correlation for multiple regressions. For *L. leptolepis*, a regression model for the estimation of the history of precipitation pH(y) was developed using total N concentrations (y=–0.99N concentration + 6.38, r^2= 0.79, p<0.001). For *C. japonica*, this equation was used to correlate to δ^{15}N(y =–0.41 δ^{15}N + 2.58, r^2=0.72, p<0.001).

DISCUSSION

Annual tree ring growth

Annual ring growth varied markedly between and within species. The tree growth was affected by atmospheric pollutants, temperature, and soil fertility. Variations of annual ring growth of black spruce, tamarack (Choi *et al.*, 2007) and red pine (Kwak *et al.*, 2011) were influenced by changing soil nitrogen dynamics. In our study, the annual ring area increment of *C. japonica* was more sensitive to temperature and atmospheric pollutants in the site. A positive correlation between increased temperature and increased annual ring growth of *C. japonica* (Table 3) suggested that elevated temperature may increase the tree growth. Lebourgeois *et al.* (2005) reported that a positive effect of increased temperature on tree–ring growth may be modified by soil water capacity. Elevated temperature may be directly affecting tree growth and indirectly through interactions with other stressors and disturbances (Chmura *et al.*, 2011). Although temperature between 1962 and 2009 increased from 0.1°C to 1.5°C (Fig 2a) at the study site, temperature has been claimed to be relatively unimportant for tree growth in this site (Luong *et al.*, 2013).

For *C. japonica*, there was a negative correlation between increased CO_2 concentration and annual ring growth, which is possibly linked to stomatal closure (Choi and Lee, 2012). This result is consistent with reductions in tree growth and increased CO_2 concentration (Clark *et al.*, 2003). Elevated atmospheric CO_2 may be responsible for changes in tree growth rings (Luong *et al.*, 2013). A significant correlation between NO_2 concentration and annual ring area of this species (Table 3) may generally form N deposition (Bytnerowicz *et al.*, 2007; Kwak *et al.*, 2011; Luong *et al.*, 2013). N deposition originating from NO_2 is claimed to be the most important factor affecting tree growth (Bytnerowicz *et al.*, 2007; Tomlinson, 2003). The rate of forest decline of *P. densiflora* in Japan has been shown to be negatively correlated with atmospheric NO_2 concentration (Kume *et al.*, 2000). Therefore, increases in annual growth of *C. japonica* at the study site may be cause of interactions among increased availability of CO_2, elevated nitrogen deposition, and increased temperature (Bytnerowicz *et al.*, 2007). The effects of SO_2 concentration on annual ring area of both species (Table 3) could be due to the acid deposition (Kwak *et al.*, 2011).Decreases in atmospheric SO_2 concentration due to national policy were not considered sufficiently high to affect tree growth (Kume *et al.*, 2000). The growth of *L. leptolepis* has been declining since 1989 due to acid deposition from fossil fuel combustion at the site (Tomlinson, 2003; Luong *et al.*, 2013).

δ^{13}C in tree rings

The decreasing pattern of δ^{13}C in tree rings of the two species (Fig 4a) has been ascribed to decreases in δ^{13}C of atmospheric CO_2 due to anthropogenic emissions of CO_2 from fossil fuel combustion (McCarroll and Loader, 2004).However in this study, no significant correlation was noted between δ^{13}C and the atmospheric CO_2 concentrations from 1999 to 2009 (Table 4). The effect of increased atmospheric CO_2 concentration from fossil fuel combustion on decreasing δ^{13}C in tree rings may have been muted to some degree by climate and air pollution. There was a negative correlation between δ^{13}C of both species and temperature; this can be attributed to decreases in δ^{13}C, because of the effect of stomatal conductance (Choi *et al.*, 2005). Increased temperature at the site may increase C isotope discrimination (leading to a more negative δ^{13}C) by increasing stomatal conductance (Warren and Dreyer, 2006).

A significant correlation between atmospheric SO_2 concentration and tree–ring δ^{13}C of both species (Table 4) resulted in impaired photosynthesis and reduced growth because of the history of air pollution (Martin and Sutherland, 1990). A negative correlation between increased atmospheric NO_2 concentrations and decreased δ^{13}C of both species may be related to decreased carboxylation rate and increase C_i/C_a due to the fertilization effect (Livingston *et al.*, 1999; Choi and Lee, 2012). The relationship between O_3 and δ^{13}C of *L. leptolepis* may inhibit photosynthesis by closing stomata and reducing CO_2 diffusion into the leaf (Saurer *et al.*, 1995). Therefore, these relationships showed an increase in carbon isotope discrimination (Fig. 4b) caused by stomatal closure (Farquhar *et al.*, 1982), leading to a negative δ^{13}C under nutrient limited conditions (Livingston *et al.*, 1999); this may affect tree growth.

The regression analysis between annual ring area and Δ (Fig. 5) revealed that the growth of both species was different. For *L. leptolepis*, a negative correlation between annual ring area and Δ (p<0.01) indicated that carboxylation rate played a more important role than stomatal conductance (Fig. 5a) and was the primary mechanism governing photosynthesis (Livingston *et al.*, 1999; Viet *et al.*, 2013). This observation is supported by the lower foliar N concentration of *L. leptolepis* than *C. japonica* (Table 2) because of the effects of atmospheric pollutants on Δ of *L. leptolepis*. Therefore, the decline in growth of *L. leptolepis* was affected more by carboxylation rate than by stomatal limitation (Viet *et al.*, 2013). This may lead to an increase in Δ via maintaining high C_i/C_a due to nutrient limitations, rather than other factors (Farquhar *et al.*, 1982; Choi *et al.*, 2007).

For *C. japonica*, a positive correlation between annual ring area and Δ with time (Fig. 5b) implied that stomatal conductance rather than carboxylation rate was the predominant mechanism influencing photosynthesis and tree growth; i.e. increases in stomatal conductance enhanced photosynthesis by supplying CO_2 (Farquhar *et al.*, 1989; Farquhar *et al.*, 1982). The better growth of *C. japonica* can make it more susceptible to atmospheric pollutants, because of the large leaf surface area for their interception (Viet *et al.*, 2013), and Δ was not affected by environmental variables that maintain lower C_i/C_a, leading to smaller Δ.

These results are evidence that the tree–ring $\delta^{13}C$ of *L. leptolepis* and *C. japonica* in this study was affected more by atmospheric environmental variables than observed for *P. densiflora* (Kwak *et al.*, 2011), Betulapendula (Saurer *et al.*, 1995), and *Pseudotsuga* menziesii (Martin and Sutherland, 1990).

$\delta^{15}N$, N concentration, and Ca/Al in tree rings

The trend of decreasing $\delta^{15}N$ in *L. leptolepis* (Fig. 6a) was consistent with previous studies that indicated increased deposition of N depleted in ^{15}N (Poulson *et al.*, 1995; Choi *et al.*, 2005; Savard *et al.*, 2009). For example, Poulson *et al.* (1995) reported a decreasing pattern over time of $\delta^{15}N$ in tree rings of *Tsuga candensis* and Choi *et al.* (2005) a decrease in *P. densiflora* from +2.0‰ in 1990 to −1.0‰ in 2000. Savard *et al.* (2009) found similar trends with *Fagus grandifolia* and *Pinus strobus*. These patterns reflected the regional N deposition rates. In our study, the decrease in $\delta^{15}N$ in *L. leptolepis* can be seen as a record of long–term anthropogenic impacts of deposition of ^{15}N–depleted N compounds (Bukata and Kyser, 2007; Savard *et al.*, 2009; Kwak *et al.*, 2011).While $\delta^{15}N$ in tree rings of *C. japonica* significantly increased over time, this pattern was consistent with the studies of Bukata and Kyser (2005) and Hietz *et al.* (2010) who reported that increases in tree ring $\delta^{15}N$ values can be related to disturbance by fertilization with N and logging. Increases in $\delta^{15}N$ in tree rings by 1.5–2.5‰ can be related to changes in forest dynamics and production (Hietz *et al.*, 2010) and are consistent with increased $\delta^{15}N$ in tree rings of *C. japonica*. The increase in $\delta^{15}N$ of *C. japonica* could result from the loss of ^{15}N–depleted compounds through denitrification, ammonia volatilization or nitrate leaching (Elhani *et al.*, 2005).

Although the increase of N concentration over time of both species was significant (Fig. 6b), N concentration in tree rings may not be a reliable indicator of time–related information regarding N availability due to the potential movement of N towards the outermost rings (Poulson *et al.*, 1995; Bukata and Kyser, 2005). The trends in tree–ring N and N isotopic composition of both species may be due to changes in tree dynamics via photosynthetic capacity (Choi *et al.*, 2007).

Ca/Al ratios of *L. leptolepis* did not show a significant temporal pattern despite the consistently increasing Ca concentration in tree rings (Fig. 7a, 7c). This was due to low Al concentrations (Fig. 7b) that offset Ca increases in tree rings (DeWalle *et al.*, 1999). Increased Ca concentrations in tree rings may be due to increased numbers of ion exchange sites (Shortle *et al.*, 1995) or indicate a physiological response within the tree rather than an actual change in bioavailability (Read, 2008). In contrast, a significant difference in Ca/Al ratios in *C. japonica* trees was related to a decreasing trend, consistent with decreases in Ca and increases in Al concentrations (Fig. 7). However, both increasing and decreasing Ca concentration may be relative to the binding capacity of acid deposition (Bondietti and Momoshima, 1990; Lee *et al.*, 2011). The radial concentration trends of Ca^{2+}, Al^{3+}, and Ca/Al ratios in *C. japonica* was a higher increase than that of *L. leptolepis*. Bondietti and Momoshima (1990) suggested that the increase in cations present in wood formed is coincident with rapid increases in SO_x and NO_x deposition and with increases in radial growth increment; otherwise, the decrease in cations in wood formed is coincident with a decline in radial growth increment. This is the reason why in our study tree ring growth of *C. japonica* was higher than that of *L. leptolepis*.

Relationship between tree ring chemistry and precipitation pH

Tree ring $\delta^{13}C$, $\delta^{15}N$ and N concentration of both species were significantly ($p<0.01$) correlated with precipitation pH between 1992 and 2009 (Table 5; Fig. 8). The positive correlation between $\delta^{13}C$ and decreased precipitation pH (Fig. 8a) had been shown to be related with the deleterious effects on photosynthesis by the H+ input from acid rain (Shan, 1998) due to the co–emission of NO_2 and SO_2 (Fig. 2c) with ^{13}C–depleted CO_2 from fossil fuel combustion. A simulated acid rainfall (pH 2.3) experiment with *P. densiflora* degraded chlorophyll in the pheophytin and reduced the carboxylation rate (Shan, 1998) in a way that could cause a decrease of $\delta^{13}C$ in plant tissue. In this study, the annual mean precipitation pH was over 5.0 (Fig. 2b). An effect of H^+ in precipitation on $\delta^{13}C$ could also contribute to the positive correlation between precipitation pH and tree ring $\delta^{13}C$. This result contrasts to the tree ring $\delta^{13}C$ of *P. densiflora* of Kwak *et al.* (2009b) who indicated it was negatively correlated with precipitation pH in industrial areas. Therefore, $\delta^{13}C$ in tree rings of *L. leptolepis* and *C. japonica* may be useful as an indicator of precipitation pH.

A negative correlation between increased N concentration in tree rings of both species and precipitation pH (Table 5; Fig. 8c) might provide information on N deposition (Choi *et al.*, 2005), because one of the source compounds of precipitation acidity is fossil fuel combustion emission of, not only CO_2, but also NO_x. This relationship has been observed for various tree species in different regions (Poulson *et al.*, 1995; Bukata and Kyser, 2005; Kwak *et al.*, 2009b) and suggests that total N concentration in tree rings can serve as a semi–quantitative surrogate of soil N availability at the time the tree ring was formed (Kwak *et al.*, 2009b).

Although, the relationship between $\delta^{15}N$ in tree rings and precipitation pH was different between the two species (Fig 8b; Table 5),both negative and positive correlations between $\delta^{15}N$and precipitation pH can be linked to N deposition (Kwak *et al.*, 2009b; Kwak *et al.*, 2011) due to the H^+ input from acid rain (Shan, 1998). N deposition was depleted ^{15}N to the increase in N concentrations of annual growth rings. The nitrogen content from this acid precipitation can be sufficient to stimulate tree growth and can be to override any expected negative effect

(Shan, 1998). Thus tree ring $\delta^{15}N$ and N concentrations of both species can reveal the historical precipitation pH.

The lack of correlation between tree ring Ca/Al ratios and precipitation pH in both species (Table 5) was probably due to the characteristics of the local environment and its pollution history (Read, 2008). Soil pH fluctuated from 4.00 to 4.35 (Table 1) and the soil was acidic (Ito *et al*., 2011) at the site. This suggested that soil acidification had progressed to some degree (Kwak *et al*., 2009a) and is consistent with previous findings for *Q. alba, Q. prunus* (Read, 2008), and *P. densiflora* (Kwak *et al*., 2011).

An equation of precipitation pH was correlated with tree–ring N of *L. leptolepis* and $\delta^{15}N$ of *C. japonica* to estimate precipitation pH using tree–ring chemistry. These correlations reflected the influence of ^{15}N–depleted N compounds deposited via precipitation (Kwak *et al*., 2009b). Decreasing precipitation pH (Fig. 2b) may reflect increased N deposition originating from NO_x emissions that are known to be depleted in ^{15}N relative to the soil mineral N due to soil acidification (Kwak *et al*., 2011) with an average pH of 4.35 (Ito *et al*., 2011). In our study, mean pH ranged from 4.00 to 4.35 (Table 1). Changes in regional H^+ or the soil pH can affect the $\delta^{15}N$ value of nitrogen available to the tree (Bukata and Kyser, 2005) and may be attributed to changes in the nitrogen cycle (Choi *et al*., 2007). This has altered the growth and forest structure and function. However, the applicability of tree–ring N concentration and $\delta^{15}N$ to estimate historical precipitation pH in forest ecology at the study site would be difficult to predict, because multiple stressors were acting in different directions on the $\delta^{15}N$ values of bioavailable nitrogen (Bukata and Kyser, 2005).

CONCLUSION

Tree ring growth of both species was differently correlated with environmental factors. Annual ring growth rate of *C. japonica* was higher than that of *L. leptolepis*, because of species differences in the risk from the long–term effects of acid deposition from fossil fuel combustion. The decline in growth of *L. leptolepis* may be affected more by carboxylation rate rather than by stomatal conductance due to the effects of air pollution on C isotope discrimination that may lead to nutrient limitation. A better growth of *C. japonica* might be the interception of atmospheric pollutants, because increases in stomatal conductance enhanced photosynthesis by supplying CO_2. Decreased $\delta^{13}C$ in tree rings of both species at the site may reflect increased N deposition originating from NOx emission that is typically depleted in ^{15}N due to soil acidification. The increase and decrease in Ca, Al cations and Ca/Al present in tree rings of *C. japonica* and *L. leptolepis* was coincident with increases and decreases in radial increment due to SO_x and NO_x deposition. Therefore, tree ring $\delta^{13}C$, $\delta^{15}N$, and N concentrations may indicators for historical precipitation pH, because air pollutants affected $\delta^{13}C$ and the mobility of N in tree rings provided information on N deposition from acid rain. However, estimation of historical precipitation pH was difficult to apply to tree ring $\delta^{15}N$ of *C. japonica* and N concentration of *L. leptolepis*, because of various impacts on $\delta^{15}N$ values and N availability. The problem of acid deposition may reflect greater risk of decline in *L. leptolepis* forest than for *C. japonica* forest.

ACKNOWLEDGMENTS

This study was supported by a grant (code: NRF–2013R1A1A2064761) from National Research Foundation of Korea.

REFERENCES

Bondietti, E. A. and N. Momoshima 1990 A historical perspective on divalent cation trends in red spruce stemwood and the hypothetical relationship to acidic deposition. *Can. J. For. Res*., **20**: 1850–1858

Bukata, A. and T. K. Kyser 2005 Response of the nitrogen isotopic composition of tree–rings following tree–clearing and land–use change. *Environ. Sci. Technol*., **39**: 7777–7783

Bukata, A. and T. K. Kyser 2007 Carbon and nitrogen isotope variations in tree rings as records of perturbations in regional carbon and nitrogen cycle. *Environ. Sci. Technol*., **41**: 1331–1338

Bytnerowicz, A., K. Omasa and E. Paoletti 2007 Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective. *Environ. Pollut*., **147**: 438–445

Chmura, D. J., P. D. Anderson, G. T. Howe, C. A. Harrington, J. E. Halofsky, D. L. Peterson, D. C. Shaw and J. B. St. Clair 2011 Forest responses to climate change in the north western United States: Ecophysiological foundation for adaptive management. *Forest Ecol. Manag*., **261**: 1121–1142

Choi, W. J., S. X Chang and J. S. Bhatti 2007 Drainage affects tree growth and C and N dynamics in a Minerotropic Peatland. *Ecology*, **2**: 443–453

Choi, W. J. and K. H. Lee 2012 A short overview on linking annual tree ring carbon isotopes to historical changes in atmospheric environment. *Forest Sci. Technol*., **8**: 73–78

Choi, W. J., S. M. Lee, S. X. Chang and H. M. Ro 2005 Variations of $\delta^{13}C$ and $\delta^{15}N$ in *Pinus densiflora* tree rings and their relationship to environmental changes in Eastern Korea. *Water, Air, Soil Pollut*., **164**: 173–187

Clark, D. A., S. C. Piper, C. D. Keeling and D. B. Clark 2003 Tropical rain forest tree growth and atmospheric carbon dynamics linked to interannual temperature variation during 1984–2000. *Proc. Na.t Acad. Sci*., **100**: 5852–5857

DeWalle, D. R., J. S. Tepp, B. R. Swistock, W. E. Sharpe and P. J. Edwards 1999 Tree ring cation response to experimental watershed acidification in West Virginia and Maine. *J. Environ. Qual*., **28**: 299–309

Elhani, S, J. M. Guehl, C. Nys, J. F. Picard and J. L. Dupouey 2005 Impact of fertilization on tree ring $\delta^{15}N$ and $\delta^{13}C$ in beech stands: a retrospective analysis. *Tree Physio.l*., **25**: 1437–1446

Farquhar, G. D., J. R. Ehleringer and K. T. Hubick 1989 Carbon isotope discrimination and photosynthesis. *Ann. Rev. Plant Physiol. Plant Mol. Biol*., **40**: 503–537

Farquhar, G. D., M. H. O'Leary and J. A. Berry 1982 On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Aust. J. Plant Physio*., **l9**: 121–37

Feng, X. 1998 Long–term C_i/C_a responses of trees in western North America to atmospheric CO_2 concentration derived from carbon isotope chronologies. *Oecologia*, **117**: 19–25

Hietz, P., O. Dünisch and W. Wanek 2010 Long term trends in nitrogen isotope composition and nitrogen concentration in Brazilian rainforest trees suggest changes in nitrogen cycle. *Environ. Sci. Technol*., **44**: 1191–1196

Hirano, Y., T. Mizoguchi and I. Brunner 2007 Root parameters of forest tree as sensitive indicators of acidifying pollutants: a review of research of Japanese forest trees. *J. Forest Res.*, **12**: 134–142

Ito, K., Y. Uchiyama, N. Kurokami, K. Sugano and Y. Nakanishi 2011 Soil acidification and decline of trees in forests within the precincts of Shrines in Kyoto (Japan). *Water, Air, Soil Pollut.*, **214**: 197–204

Kume, A., N. Tsuboi, T. Satomura, M. Suzuki, M. Chiwa, K. Nakane, N. Sakurai, T. Horikoshi and H. Sakugawa 2000 Physiological characteristics of Japanese red pine, *Pinus densiflora* Sieb. Et Zucc., in declined forests at Mt. Gokurakuji in Hiroshima Prefecture, Japan. *Trees*, **14**: 305–311

Kwak, J. H., S. S. Lim, S. X. Chang, K. H. Lee and W. J. Choi 2011 Potential use of δ^{13}C, δ^{15}N, N concentration, and Ca/Al of *Pinus densiflora* tree rings in estimating historical precipitation pH. *J. Soil Sediment*, **11**: 709–721

Kwak, J. H., S. S. Lim, H. J. Park, S. I. Lee, K. H. Lee, H. Y. Kim, S. X. Chang, S. M. Lee, H. M. Ro and W. J. Choi 2009 Relating tree ring chemistry of *Pinus densiflora* to precipitation acidity in an industrial area of South Korea. *Water, Air, Soil Pollut.*, **199**: 9–106

Kwak, J. K, W. J. Choi, S. S. Lim and M. A. Arsha 2009 δ^{13}C, δ^{15}N, N concentration, and Ca/Al ratios of forest samples from *Pinus densiflora* stands in rural and industrial areas. *Chem. Geol.*, **264**: 385–393

Lebourgeois F., N. Breda, E. Ulrich and A. Granier 2005 Climate–tree–growth relationships of European beech (*Fagus sylvatica* L.) in the French Permanent Plot Network (RENECOFOR). *Trees*, **19**: 385–401

Lee, K. S., D. V. Hung, J. H. Kwak, S. S. Lim, K. H. Lee and W. J. Choi 2011 Tree ring Ca/Al as an indicator of historical soil acidification of *Pinus densiflora* forest in Southern Korea. *Korean J. Environ. Agric.*, **3**: 229–233

Livingston, N. J., R. D. Guy, Z. J. Dun and G. J Ethier 1999 The effects of nitrogen stress on the stable carbon isotope composition, productivity and water use efficiency of while spruce (*Piceaglauca* (Moench) Voss) seedlings. *Plant, Cell Environ.*, **22**: 281–289

Loader, N. J., I. Robertson and D. McCarroll 2003 Comparison of stable carbon isotope ratios in the whole wood, cellulose and lignin of oak tree–rings. *Palaeogeogr. Palaeoclimato.l Palaeoecol.*, **196**: 395–407

Luong, T. H., K. S. Jang, W. J. Choi and K. H. Lee 2013 Effects of atmospheric environmental changes on annual ring growth of *Cryptomeria japonica* in Southern Korea. *J. Ecol. Environ.*, **36**: 31–38

Martin, B. and E. K. Sutherland 1990 Air pollution in the past recorded in width and stable carbon isotope composition of annual growth rings of Douglas–fir. Plant, *Cell Environ.*, **13**: 839–844

McCarroll, D. and N. J. Loader 2004 Stable isotopes in tree rings. *Quat. Sci. Rev.*, **23**: 771–801

Ministry of Environment of Korea 2010 Annual reports of ambient air quality in Korea. Ministry of Environment, Seoul

Poulson, S. R., C. P. Chamberlain and A. J. Friedland 1995 Nitrogen isotope variation of tree rings as a potential indicator of environmental change. *Chem. Geol.*, **125**: 307–315

Read, Q. D. 2008 Soil and tree ring chemistry changes in an oak forest. Institute for the Environment Highlands Field Site 2008 Internship Research Reports. Highlands Biological Station, North Carolina, pp. 56–65

Roden, J. S., D. R. Bowling, N. G. Mcdowell, B. J. Bond and J. R. Ehleringer 2005 Carbon and oxygen isotope ratios of tree ring cellulose a long a precipitation transect in Oregon, United State. *J. Geophys. Res. Biogeosci.*, **110**: 1–11

Saurer, M., S. Maurer, R. Matyssek, W. Landolt, M. S. Günthardt–Goerg and U. Siegenthaler 1995 The influence of ozone and nutrition on δ^{13}C in *Betulapendula. Oecologia*, **103**: 397–406

Savard, M. M., C. Bégin and A. Smirnoff 2009 Tree ring nitrogen isotopes reflect anthropogenic NOx emissions and climate effects. *Environ. Sci. Technol.*, **43**: 604–609

Shan, Y. 1998 Effects of simulated acid rain on *Pinus densiflora*: inhibition of net photosynthesis by the pheophytization of chlorophyll. *Water, Air, Soil Pollut.*, **103**: 121–127

Shortle, W. C., K. T. Smith, R. Minocha and A. Alexey 1995 Similar patterns of change in stemwood calcium concentration in red spruce and Siberian fir. *J. Biogeogr.*, **22**: 467–473

Tomlinson, G. H. 2003 Acidic deposition, nutrient leaching and forest growth. *Biogeochemistry*, **65**: 51–81

Viet, H. D., J. H. Kwak, K. S. Lee, S. S Lim, M. Matsushima, S. X. Chang, K. H. Lee and W. J. Choi 2013 Foliar chemistry and tree ring δ^{13}C of *Pinus densiflora* in relation to tree growth along a soil pH gradient. *Plant Soil*, **363**: 101–112

Warren, C. R. and E. Dreyer 2006 Temperature response of photosynthesis and internal conductance to CO_2: results from two independent approaches. *J. Exp. Bot.*, **12**: 3057–3067