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Reconstructing Atmospheric CO_2 Concentration Using Its Relationship with Carbon Isotope Variations in Annual Tree Ring of Red Pine

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Abstract: Carbon isotope ratio ($^{13}C/^{12}C$, expressed as $\delta^{13}C$) of tree ring can be proxy of atmospheric CO_2 concentration ($[CO_2]$) due to the inter-correlation between atmospheric $[CO_2]$, $\delta^{13}C$ of atmospheric CO_2, and $\delta^{13}C$ of plant tissue that assimilates atmospheric CO_2. This study was conducted to investigate if $\delta^{13}C$ of tree ring of *Pinus densiflora* in polluted area may show a lower value than that in unpolluted area and to explore the possibility of reconstructing atmospheric $[CO_2]$ using its relationship with $\delta^{13}C$ of tree ring. During the period between 1999 and 2005, $\delta^{13}C$ of tree annual ring tended to decrease over time, and the $\delta^{13}C$ in polluted area (-27.2‰ in 2009 to -28.3‰ in 2005) was significantly ($P<0.001$) lower than that (-26.0‰ in 1999 to -27.1‰ in 2005) in unpolluted area. This reflects a greater emission of CO_2 depleted in ^{13}C in the polluted area. Atmospheric $[CO_2]$ was significantly ($P<0.01$) correlated with $\delta^{13}C$ of tree ring in a linear fashion. Using the linear regression equation, atmospheric $[CO_2]$ in the polluted area was estimated to range from 392.3 ppm in 1999 to 410.9 ppm in 2005, and these values were consistently higher than the national atmospheric $[CO_2]$ monitored at the Anmyoundo meteorological station (from 370.7 ppm in 1999 to 387.2 ppm in 2005). Our study suggested that it is possible to reconstruct atmospheric $[CO_2]$ in a certain area using the relationship between tree ring $\delta^{13}C$ and atmospheric $[CO_2]$.

Key Words: Air pollution, Carbon isotope ratio, Elevated carbon dioxide, Red pine

Introduction

Increase of atmospheric CO_2 concentration ($[CO_2]$) due to fossil fuel combustion from the industrial period (since 1850) is believed to be a primary reason of global warming (IPCC, 2007). As elevated $[CO_2]$ affects agricultural and natural ecosystem, it is necessary to monitor atmospheric $[CO_2]$ at national scale to understand the increasing pattern of atmospheric $[CO_2]$. In Korea, changes in atmospheric $[CO_2]$ have been monitored at the Anmyoundo meteorological station

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since 1999 (http://www.climate.go.kr). However, atmospheric [CO_2] may show spatial variations; i.e., that in polluted areas (e.g. metropolitan and industrial areas) would be higher than that of unpolluted area (e.g. rural or remote forest area) due to CO_2 emission from traffic and industrial activities (Wagner and Wagner, 2006; Kwak *et al*., 2009a). Such information is important to prepare area-specific agricultural countermeasures against elevating [CO_2].

In this context, annual growth rings of trees may be used to decipher the historical changes in atmospheric [CO_2] in a certain area because tree rings contain valuable information about environmental conditions (e.g. [CO_2]) in the year when the specific growth ring was formed (Choi *et al*., 2005; Bukata and Kyser, 2007, Choi *et al*., 2007; Kwak *et al*., 2009b). A possibility of reconstructing atmospheric [CO_2] is based on the inter-correlation between atmospheric [CO_2], C isotope ratio ($^{13}C/^{12}C$, expressed as $\delta^{13}C$) of atmospheric CO_2, and $\delta^{13}C$ of plant tissue that assimilates atmospheric CO_2 (McCarroll *et al*., 2009). Briefly, it is well understood that tree ring $\delta^{13}C$ exhibits a declining trend with increasing atmospheric [CO_2] since 1850 due to incorporation of CO_2 that is depleted in ^{13}C from fossil fuels at the global scale (Freyer and Belacy, 1983; February and Stock, 1999). Such inter-correlation may result in a negative relationship between atmospheric [CO_2] and tree ring $\delta^{13}C$; i.e., a decrease in $\delta^{13}C$ with increasing atmospheric [CO_2] (Choi *et al*., 2005; Kwak *et al*., 2009b). However, in Korea, such correlation has never been tested due to the lack of atmospheric [CO_2] monitoring data.

The objectives of this study were to investigate the difference in $\delta^{13}C$ of tree ring between unpolluted (rural) and polluted (industrial) areas and to reconstruct atmospheric [CO_2] in the polluted area using the correlation between atmospheric [CO_2] and $\delta^{13}C$ of tree ring in the unpolluted area.

Materials and Methods

Study areas

This study was conducted in conjunction with a series of studies to investigate the different chemistry of *Pinus densiflora* forest samples (soil, foliage, litter, bark, and tree ring) between unpolluted and polluted areas, and some of the results have been reported elsewhere (Kwak *et al*., 2009a; 2009b; 2009c). The descriptions of study areas are provided there in details. Briefly, Mt. Naejang (35° 27′N 126° 51′E) in Jangsung and Mt. Jeongbong (34° 50′N 127° 40′E) in Yeosu were selected as the unpolluted (rural) and polluted (industrial) areas, respectively. Jangsung is a typical rural area with a total area of 520 km^2 with 63% of which is mountainous, and Mt. Jeongbong is located adjacent to the Yeosu industrial complex. Over the past 14 years from 1992 to 2005, the mean annual pH of precipitation ranged from 5.0 to 6.2 in Jangsung and from 5.9 to 4.9 in Yeosu, reflecting atmospheric pollution in the industrial area (Ministry of Environment of Korea, 2007).

Tree disk collection and analysis

In February 2006, three trees were selected at each site and tree stem disk was collected at breast height (1.3 m above ground). The disk was cross-dated using CDendro7 (Cybis Elektronik & Data AB, Saltsjobden, Sweden). The wood disks were oven-dried to constant weight at 60℃. Because annual mean atmospheric [CO_2] data were only available from 1999, annual growth rings formed between 1999 and 2005 were used for the study.

The wood samples were ground with a ball mill (MM200, Retsch GmbH, Haan, Germany) to fine powder and used for $\delta^{13}C$ analysis using a continuous-flow stable isotope ratio mass spectrometer linked with an elemental analyzer (IsoPrime-EA, Micromass, UK). In this study, whole-plant tissue samples instead of a certain component were used for isotope analysis because whole tissue produces the same trend of $\delta^{13}C$ as cellulose (Loader *et al*., 2003; Elhani *et al*., 2005)

The $\delta^{13}C$ was calculated as

$$\delta^{13}C\ (‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where R is the ratio of $^{13}C/^{12}C$, and the standard used was the Vienna Pee Dee Belemnite (VPDB). Precision of the measurements checked (n=10) with an internal reference material, red pine wood sample (-26.3±0.2‰ for $\delta^{13}C$) calibrated against International Atomic Energy Agency carbon isotope standard number 5 (IAEA-C5) (wood, $\delta^{13}C$=-25.5‰) was better than 0.2‰.

Reconstructing atmospheric [CO_2] and statistical analysis

National atmospheric [CO_2] monitored at the Anmyoundo meteorological station was obtained from the Climate Change Information Center of Korea (http://www.climate.go.kr). The $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_{atm}$) from 1999 to 2005 was estimated by the following equation that shows an exponential trend since 1740 (Friedli *et al.*, 1986): $\delta^{13}C_{atm}$ = -6.429 − 0.0060exp[0.0217(year − 1740)].

A linear regression equation between atmospheric [CO_2] (dependent variable) and $\delta^{13}C$ of tree ring (independent variable) from the unpolluted area was developed. Atmospheric [CO_2] of the polluted area was reconstructed by putting $\delta^{13}C$ of tree ring to the equation. All statistical analyses were performed with the SPSS 12.0 package (SPSS, Chicago, Illinois, USA). An α value of 0.05 was chosen to indicate statistical significance.

Results and Discussion

Atmospheric [CO_2] and $\delta^{13}C$

Atmospheric [CO_2] monitored at the Anmyeoundo meteorological station increased linearly from 370.7 ppm to 387.2 ppm between 1999 and 2005; the regression equation was y = 2.7214x+368.4 (r^2=0.99, P<0.001) (Fig. 1). Meanwhile, the $\delta^{13}C$ of atmospheric CO_2 was estimated to decrease from -8.08‰ to -8.32‰ during the same period. These patterns strongly reflect increasing atmospheric [CO_2] due to emission of CO_2 depleted in ^{13}C from fossil fuel combustion (Freyer and Belacy, 1983; February and Stock, 1999).

$\delta^{13}C$ of tree ring

In both unpolluted and polluted areas, $\delta^{13}C$ of tree annual ring tended to decrease (P<0.05) over time between 1999 and 2005 (Fig. 2). In unpolluted area, $\delta^{13}C$ decreased from -26.0‰ in 1999 to -27.1‰ in 2005; meanwhile that decreased from -27.2‰ to -28.3‰ in polluted area during the same period. Although the magnitude of the decrease (1.1‰) in $\delta^{13}C$ over the past 6 years was the same in both areas, the $\delta^{13}C$ in the polluted area was consistently (P<0.001) lower than that in the unpolluted area by 0.9 to 1.4‰, reflecting a greater emission of CO_2 depleted in ^{13}C in polluted area (Kwak *et al.*, 2009a; McCarroll *et al.*, 2009).

Plant $\delta^{13}C$ ($\delta^{13}C_{plant}$) is an integrator of $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_{air}$) and other environmental factors such as water and nutrient availability that affect the ratio of intercellular to atmospheric CO_2 concentration (C_i/C_a) and thus causes carbon isotope discrimination (the preference of $^{12}CO_2$ to $^{13}CO_2$ during the photosynthesis) via influencing either stomatal conductance or carboxylation rate as suggested by Farquhar *et al.* (1989). The effect of $\delta^{13}C_{air}$ and C_i/C_a on $\delta^{13}C_{plant}$ is described by the equation, $\delta^{13}C_{plant} = \delta^{13}C_{air} - a - (b - a)C_i/C_a$, where a and b are discrimination against ^{13}C during CO_2 diffusion through stomata (normally ~4.4‰) and during CO_2 assimilation by RuBP carboxylase (normally ~27‰), respectively. For example, annual changes in $\delta^{13}C$ of tree rings have been shown to be correlated with temperature and precipitation (Edwards *et al.*, 2000), and air pollutants (Heaton and Crossley, 1995; Saurer *et al.*, 1995; Sakata and Suzuki, 2000). In the present study, slight increase in $\delta^{13}C$ of tree at the polluted area in 2001 and 2002 (Fig. 2) could be

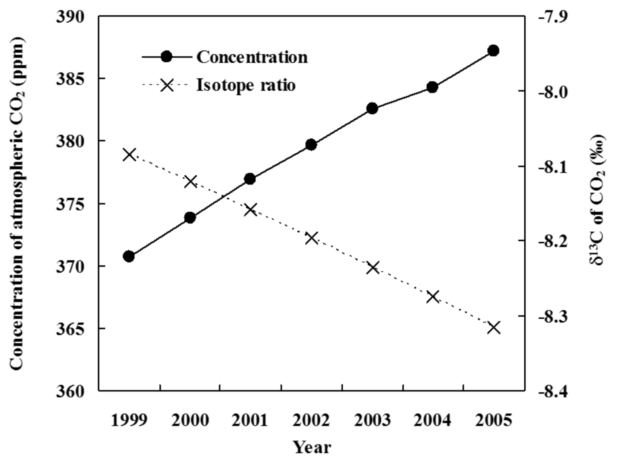

Fig. 1. Changes in annual mean atmospheric CO_2 concentration monitored at Anmyoundo meteorological station and the corresponding $\delta^{13}C$ calculated using the equation of Friedli *et al.* (1986).

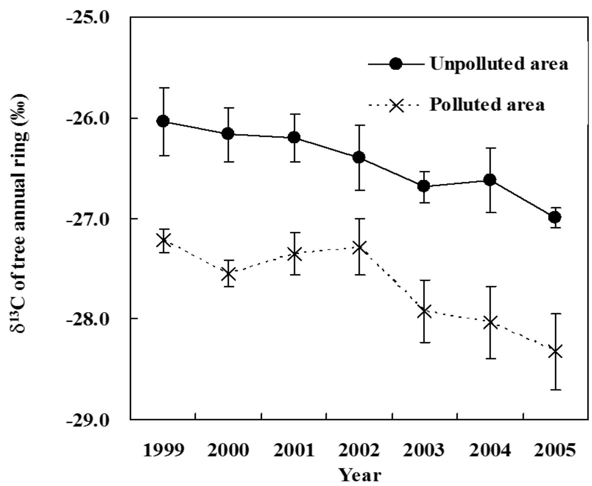

Fig. 2. Changes in $\delta^{13}C$ of tree rings of *P. densiflora* at unpolluted and polluted areas. Vertical bars are standard errors of the means (n = 3).

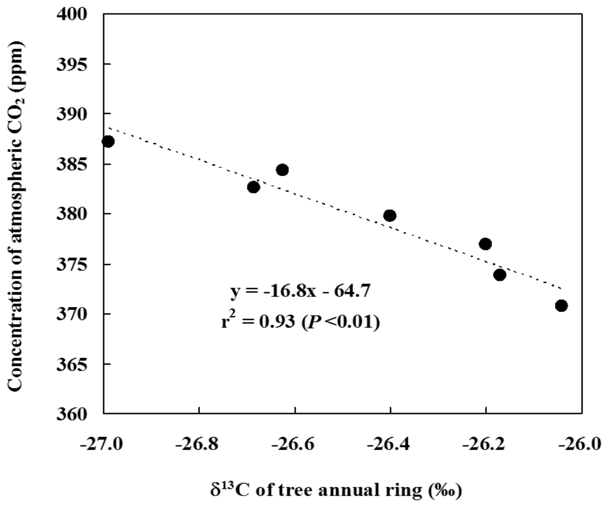

Fig. 3. Correlation between $\delta^{13}C$ of tree ring of unpolluted area and atmospheric CO_2 concentration at the Anmyoundo meteorological station.

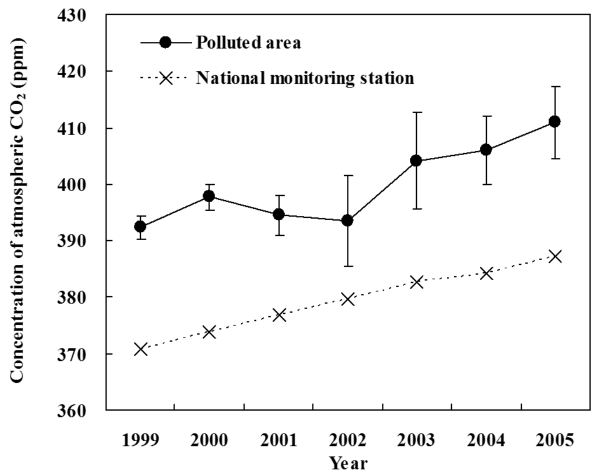

Fig. 4. Changes in atmospheric CO_2 concentration of polluted area estimated by the regression equation shown in Fig. 3. Vertical bars are standard errors of the means (n=3).

attributed to the effect of other environmental conditions on carbon isotope discrimination although the mechanism remains unclear. However, it is believed that $\delta^{13}C$ of atmospheric CO_2 is the strongest factor affecting $\delta^{13}C$ of plant with the progress of global warming primarily due to increased emission of CO_2 from fossil fuel combustion that is depleted in ^{13}C ($\delta^{13}C$ is around -2 5‰) relative to the atmospheric CO_2 ($\delta^{13}C$ is currently around -8‰) (Bert *et al.*, 1997; February and Stock, 1999).

Reconstructing atmospheric [CO_2] in polluted area

Correlation between $\delta^{13}C$ of tree ring from the unpolluted area and national atmospheric [CO_2] was significant, showing an increasing atmospheric [CO_2] (y) with a decrease in $\delta^{13}C$ of tree ring (x); the regression equation was y = -16.8x − 64.7 (r^2=0.93, P<0.01) (Fig. 3). The developed equation was used in reconstructing atmospheric [CO_2] in polluted area. In the polluted area, atmospheric [CO_2] was estimated to be 392.3 ppm in 1999 and tended to increase to 410.9 ppm in 2005 with depression in 2002 and 2003 (Fig. 4). Such depression could be attributed again to other environmental conditions that affect $\delta^{13}C$ of tree and thus the estimated atmospheric [CO_2]. The estimated atmospheric [CO_2] in the polluted area was higher than that in the national monitoring station by 13.7 to 24.0 ppm.

Summary and Conclusions

Our study shows that atmospheric [CO_2] is strongly correlated with $\delta^{13}C$ of *P. densiflora* tree ring due to increase in atmospheric [CO_2] by emission of ^{13}C-depleted CO_2 from fossil fuel combustion. Atmospheric [CO_2] in the polluted area estimated using the correlation between atmospheric [CO_2] and $\delta^{13}C$ of tree ring in the unpolluted area was higher than that in unpolluted area by more than 13.7 ppm. Therefore, it may be possible to reconstruct atmospheric [CO_2] in a certain area using the relationship between tree ring $\delta^{13}C$ and atmospheric [CO_2]. However, as $\delta^{13}C$ of plant is subject to other environmental conditions that affect gas exchange at a leaf level, a further study is necessary to eliminate the noise signal from whole $\delta^{13}C$ and thus to strength the correlation between atmospheric [CO_2] and $\delta^{13}C$ of tree ring.

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