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$\delta^{13}C$, $\delta^{15}N$, N concentration, C/N, and Ca/Al of *Pinus densiflora* foliage in Korean cities of different precipitation pH and atmospheric NO_2 and SO_2 levels

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ABSTRACT

Forest decline due to atmospheric pollution is a consequence of long-term chronic exposure, and thus chemical proxies that are sensitive to the pollution are helpful in estimating the impact of atmospheric pollution on forest health. In this study, we explored changes in the isotopic and elemental compositions of needles of red pine (*Pinus densiflora*) with varying precipitation pH and concentrations of NO_2 and SO_2 across 18 cities to identify isotopic and chemical signatures that are sensitive to acid deposition. The cities had different intensity of traffic and industrial activities, and thus were expected to have varying levels of atmospheric pollution. The pine needles were analyzed for carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios, N concentrations, C-to-N ratio (C/N), and calcium-to-aluminum ratio (Ca/Al). Analysis of variance, simple linear correlation, and redundancy analysis were used to investigate the variations in foliar chemistry with atmospheric variables. Neither NO_2 nor SO_2 concentration was correlated with foliar $\delta^{13}C$, $\delta^{15}N$, N concentration, and C/N; whereas precipitation pH was correlated with the foliar parameters, suggesting that foliar chemistry is more sensitive to total acidifying materials than to individual pollutant. The foliar $\delta^{13}C$ decreased with lowered precipitation pH, reflecting the increased ^{13}C-depleted CO_2 that was co-emitted with acidifying materials from fossil fuel combustion. Foliar $\delta^{15}N$ decreased and foliar N concentration increased with lowered precipitation pH, indicating tree uptake of ^{15}N-depleted N from acid deposition. Accordingly, the C/N ratio also decreased with lowered precipitation pH. However, there was no relationship between foliar Ca/Al and precipitation pH; rather. Our result suggests that $\delta^{13}C$, $\delta^{15}N$, N concentration, and C/N of pine needle samples are associated with the level of precipitation pH and thus pine needles could be used as bio-indicators of the impacts of total acidifying pollutants on forest.

1. Introduction

Emission of acidifying pollutants such as NO_x and SO_2 from fossil fuel combustion has been frequently identified as a principal cause of forest decline in industrialized East Asian countries including China (Li et al., 2014), Japan (Hirano et al., 2007), and Korea (Kwak et al., 2009). Acid deposition impacts forests slowly through a long-term chronic influence, and thus the effects of atmospheric pollution on forests are unlikely to be detected before visible symptoms appear (de Vries et al., 2014). In this context, chemical signatures that are sensitive to acid deposition may be helpful in identifying forests that are susceptible to acid deposition.

The carbon ($^{13}C/^{12}C$, expressed as $\delta^{13}C$) and nitrogen ($^{15}N/^{14}N$, expressed as $\delta^{15}N$) isotope ratios, N concentration, C-to-N ratio (C/N), and the ratio of base cations to aluminum (Al) of tree tissue samples including tree ring, bark, foliage and litter have been analyzed for the development of such chemical proxies (de Vries et al., 2014; Kwak et al., 2009; Proemse et al., 2016). The $\delta^{13}C$ of plant samples is affected not only by the $\delta^{13}C$ of atmospheric CO_2 but also by several environmental factors that alter C isotope discrimination through influences on stomatal conductance and/or carboxylation rate (Farquhar et al., 1982). For example, the $\delta^{13}C$ of tree samples in polluted areas may

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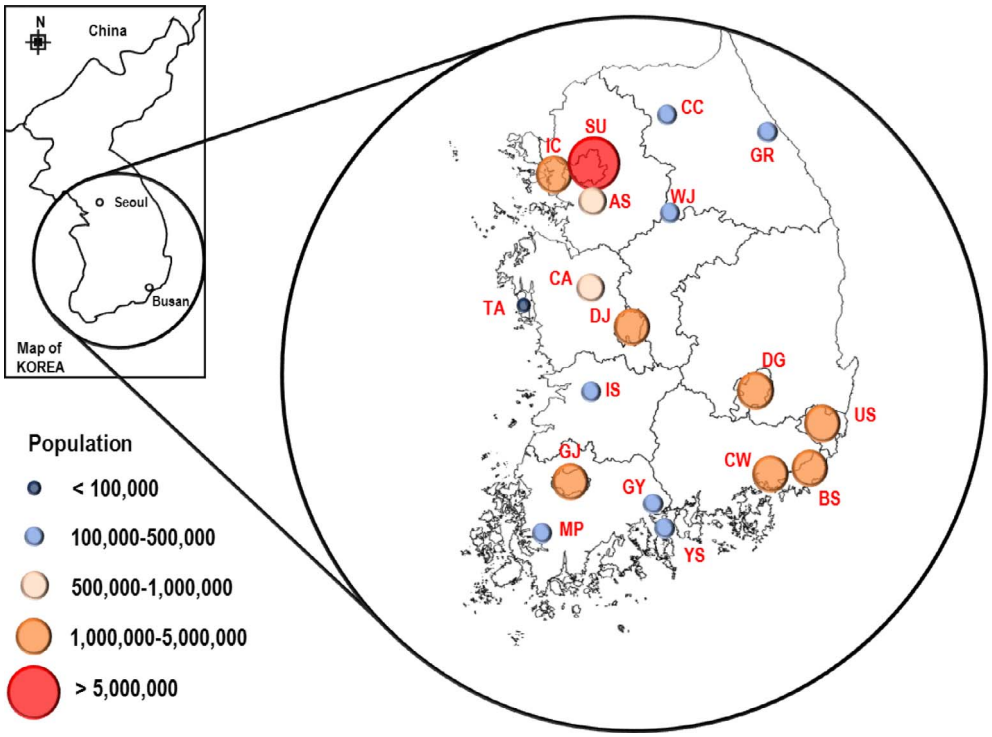

Fig. 1. Locations of cities where *P. densiflora* needles were sampled. City codes: AS, Ansan; BS, Busan; CA, Cheonan; CC, Chuncheon; CW, Changwon; DG, Daegu; DJ, Daejeon; GJ, Gwangju; GR, Gangreung; GY, Gwangyang; IC, Incheon; IS, Iksan; MP, Mokpo; SU, Seoul; TA, Taean; US, Ulsan; WJ, Wonju; YS, Yeosu.

show more negative $\delta^{13}C$ due to emission of CO_2 from fossil fuel ($\delta^{13}C$ is around −25‰) combustion that is depleted in ^{13}C relative to atmospheric CO_2 of which $\delta^{13}C$ is currently estimated to be around −9‰ (February and Stock, 1999; Feng, 1998). For this reason, the tree $\delta^{13}C$ may decrease with the progress of atmospheric pollution as ^{13}C-depleted CO_2 is co-emitted with NO_x and SO_2 from fossil fuel combustion, resulting in a positive correlation between foliar $\delta^{13}C$ and precipitation pH (Sensula, 2015). At the same time, increased NO_x and SO_2 may also affect the $\delta^{13}C$; increased NO_x is known to increase carboxylation rate due to N fertilization effect (Ammann et al., 1999) and increased SO_2 induces stomatal closure (Rinne et al., 2010), both leading to decreased C isotope discrimination and thus the less negative $\delta^{13}C$ (Kwak et al., 2016).

The $\delta^{15}N$ and N concentration of forest samples can also be correlated with precipitation pH since increased deposition of ^{15}N-depleted N compounds originating from fossil fuel combustion is likely to increase N concentration while decreasing the $\delta^{15}N$ of vegetation (Bukata and Kyser, 2007; Emmett et al., 1998; Stewart et al., 2002). When foliar N concentration increases, the C/N of forest sample decreases accordingly (Kwak et al., 2009). The ratio of base cations to Al of plant samples may also respond to changes in precipitation pH as acid precipitation increases Al ion activity with subsequent leaching of base cations, leading to a decreased ratio of base cations to Al in foliage samples (de Vries et al., 2014). For this reason, the ratio of calcium (Ca) to Al (Ca/Al) is frequently used as a proxy of changed soil solution chemistry by acid deposition (Barton et al., 2002; Reuss, 1983; Wolt, 1990).

Most existing studies that attempted to use such isotopic and chemical variables as proxies of the long-term impact of atmospheric pollution on forest health are largely limited to tree ring samples (e.g., Kwak et al., 2011; Savard, 2010); whereas the isotopic and chemical compositions of foliage samples have rarely been considered. A few studies have investigated changes in multiple isotopic and elemental compositions of foliage samples with varying distance from point sources of pollution such as mining operation sites and power plants (Proemse et al., 2016; Sensula, 2015). However, no attempt has been made to investigate the changes in the isotopic and elemental compositions of foliage samples of trees exposed to diffuse pollution sources across a wide geographical area.

To fill the research gap, in this study, we investigated the relationship between atmospheric pollution parameters (e.g., precipitation pH and atmospheric NO_2 and SO_2 concentrations) and foliar chemistry across forest sites in 18 cities that have different atmospheric pollution levels. We considered precipitation pH as a key parameter as it is an index of the total acidifying materials. In this study, red pine (*Pinus densiflora* Sieb. Et Zucc.) was selected since this is an important timber species in East Asia including China, Japan, and Korea (Lee et al., 2004) and is known to be sensitive to air pollution (Kwak et al., 2016; Lee et al., 1999). Based on the current understanding of the potential impact of acid deposition on the isotopic and chemical compositions of tree samples, we hypothesized that 1) foliar $\delta^{13}C$ may be either negatively or positively correlated with precipitation pH depending on the relative contribution of increases in ^{13}C-depleted CO_2 concentration (CO_2 source effect) and increases in NO_x and SO_2 concentrations (C isotope discrimination effect) to variations in foliar $\delta^{13}C$, 2) $\delta^{15}N$ may be positively correlated with precipitation pH due to assimilation of ^{15}N-depleted N by trees, 3) N concentration may be negatively correlated with precipitation pH due to N fertilization effect and thus C/N may be positively correlated with precipitation pH, and 4) Ca/Al may be positively correlated with precipitation pH as soil acidification decreases Ca availability while increasing Al solubility.

2. Materials and methods

2.1. Atmospheric pollution status of South Korea and sampling site description

In South Korea, the national NO_x and SO_2 emission data are available from 2005 (Ministry of Environment of Korea, 2013). Emission of NO_x decreased from 1306 thousand tons in 2005 to 1075 thousand tons in 2012, and SO_2 emission fluctuated between 388 and 447 thousand tons during the same period. National atmospheric CO_2 concentration in South Korea has been monitored at the Climate Change Information Centre in Anmyoundo from 1999 (Kwak et al., 2016). According to the Climate Information Portal of Korea Global Atmosphere Watch Centre (www.climate.go.kr), the national atmospheric CO_2 concentration