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Tree Ring Ca/Al as an Indicator of Historical Soil Acidification of *Pinus Densiflora* Forest in Southern Korea

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Abstract

BACKGROUND: Soil acidification, which is known to be one of the reasons of forest decline, is associated with decreases in exchangeable Ca and increases in Al concentration, leading to low Ca/Al ratio in soil solution. As tree rings are datable archives of environmental changes, Ca/Al ratios of annual growth ring may show decreasing pattern in accordance with the progress of soil acidification. This study was conducted to investigate Ca/Al pattern of *Pinus densiflora* tree ring in an attempt to test its usefulness as an indicator of historical soil acidification.

METHODS AND RESULTS: Three *P. densiflora* tree disks were collected from *P. densiflora* forests in Jeonnam province, and soil samples (0-10, 10-20, and 20-30 cm in depth) were also collected from the tree locations. Soils were analyzed for pH and exchangeable Ca and Al concentrations, and Ca/Al was calculated. Annual growth rings formed between 1969 and 2007 were separated and analyzed for Ca/Al. Soil Ca/Al was positively ($P<0.01$) correlated with soil pH, suggesting that soil acidification decreased Ca while increasing Al availability, lowering Ca/Al in soil solution. The Ca/Al of tree rings also showed a decreasing pattern from 18.2 to 5.5 during the period, and this seemed to reflect historical acidification of the soils.

CONCLUSION(s): The relationship between soil pH and Ca/Al and the decreasing pattern of Ca/Al of tree ring suggest that Ca/Al of tree ring needs to be considered as a proxy of the progress of soil acidification in *P. densiflora* forest in southern Korea.

Key Words: Acidification, Annual growth ring, Ca-to-Al ratio, Red pine, Soil pH

Introduction

Decline of red pine (*Pinus densiflora* Sieb. et Zucc.), which is one of the most important timber species in East Asia, caused by acid precipitation has been reported (Kume *et al.*, 2000). Acid precipitation may inhibit tree growth via either disruption of leaf chlorophyll induced by high H^+ concentration or changes in soil chemistry (specifically Al toxicity) coupled with pH changes (Shan *et al.*, 1997; Shan, 1998). As H^+-induced degradation of chlorophyll into pheophytin occurs when pH of precipitation is extremely low<3.0 (Shan, 1998), however, it is hardly to be detected under natural environmental conditions with precipitation pH at least over 4.0 (Kwak *et al.*, 2009a; 2009b).

Meanwhile, chronic exposure to moderate acid precipitation (pH 4.0 to 5.6) may change soil solution chemistry, particularly exchangeable cations composition, as soil acidification induced by acid precipitation may increase solubility of Al that takes the exchangeable sites occupied by Ca^{2+}, leading to leaching of Ca^{2+} (Sakata *et al.*, 2001; Barton *et al.*, 2002). Therefore, it is

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expected that Ca availability decreases with increasing Al species ($Al(OH)_2^+$, $AlOH^{2+}$, and Al^{3+}, especially Al^{3+} when soil pHs are between 4.0 and 5.5) due to the progress of soil acidification (Brady and Weil, 2002). Such changes in soil chemistry may be recorded in plant tissue; i.e. decreasing Ca-to-Al ratio (Ca/Al) in plant tissue with progress of soil acidification (Kwak *et al.*, 2009b). In this context, change in Ca/Al of annual ring of tree can serve as a datable archive of soil acidification history since tree rings form annually and they contain information on environmental conditions when the specific ring formed (Choi *et al.*, 2005; 2007).

Because forest decline caused by acid precipitation is the consequence of long-term chronic exposure, understanding the history of soil acidification is crucial to evaluate the impact of acid precipitation on the forest ecosystem concerned (Kwak *et al.*, 2011). There are a few studies that correlates tree ring Ca/Al pattern with precipitation pH (Kwak *et al.*, 2009; 2011). For example, with *P. densiflora* in an industrial area (Yeosu), Kwak *et al.* (2009) showed that a decreasing pattern of Ca/Al in tree ring was linearly correlated with precipitation pH; meanwhile, in a non-polluted area (Jangsung), Kwak *et al.* (2011) also found similar correlation between precipitation pH and tree ring Ca/Al although decreasing pattern of Ca/Al was not apparent. However, as changed exchangeable Ca/Al ratio in soil solution coupled with soil pH was not directly investigated in the previous studies, it is still doubt that decreasing pattern of Ca/Al in tree ring reflects changed soil solution chemistry by soil acidification. Therefore, further study is necessary to explore the potential use of tree ring Ca/Al in investigating soil acidification history. The objectives of this study were to investigate the relationship between pH and Ca/Al in soil solution and to test if Ca/Al of tree annual rings shows a decreasing pattern that may be an indicative of historical soil acidification.

Materials and Methods

Soil and tree disk sampling

Soil and tree disk samples were collected from mountainous areas of three sites in Jeonnam province (see Table 1 for the detailed locations). All the soils were Inceptisol according to the Soil Taxonomy (Rural Development Administration of Korea, 2000). At each site, one *P. densiflora* tree that represents average growth status (diameter and height) was selected and felled down to collect disks at breast height (1.3 m) in October 2007. The disk was cross-dated using CDendro7 (Cybis Elektronik & Data AB, Saltsjobden, Sweden). From the three trees disks, wood samples of annual growth rings formed between 1969 and 2007 were separated and combined into one sample for each year in order to produce enough amounts (>0.5 g) for the chemical analysis. The samples were dried at 60℃ to a constant weight and ground with a ball mill (MM200, Retsch GmbH, Haan, Germany) to fine powder.

Soil samples were collected from three depths to 30 cm at 10 cm interval around the tree stump to investigate vertical variation of the pH, exchangeable Ca and Al, and Ca/Al. The collected soils were air-dried, passed through a 2-mm sieve, and used for chemical analyses.

Table 1. Location and soil classification of the study sites

Administrative district	GPS data	Soil classification in the Soil Taxonomy
Jangsung	35° 26' 20"N 126° 45' 59"E	Coarse loamy, mesic family of Typic Dystrudepts
Youngkwang	35° 17' 30"N 126° 35' 46"E	Coarse loamy, mesic family of Typic Dystrudepts
Hampyung	35° 06' 22"N 126° 33' 25"E	Fine loamy, mesic family of Lithic Dystrudepts

Chemical analysis

Soil texture was determined in USDA classification after particle size analysis by the pipette method (Gee and Bauder, 1986), pH was measured at a 1-to-5 ratio of soil-to-water, and exchangeable Ca and Al concentration was determined with an inductively coupled plasma (ICP) emission spectrometer (IRIS-AP, Thermo Jarrell Ash Corp., Franklin, MA, USA) after extraction with ammonium acetate (Sumner and Miller, 1996).

To determine Ca and Al concentration in tree ring samples, 0.5 g of wood sample was placed into a digesting tube and digested with 10 mL of a concentrated HNO_3-$HClO_4$-H_2SO_4 (1:8:1) on a heating block (Kwak *et al.*, 2011). The concentrations of Ca and Al in the digested solution were analyzed with the ICP.

Statistical analysis

All statistical analyses were conducted using the SPSS 12.0 software package (SPSS, Chicago, IL, USA). An α value of 0.05 was selected to indicate statistical significance. Relationship between soil pH and exchangeable Ca and Al, and their ratio (Ca/Al) was assessed by simple regression analysis using all the soil data pooled regardless of sites and soil depth. The significance of annual trends of Ca, Al, and Ca/Al of tree rings was explored by autoregressive error model of time series analysis using the year as an independent variable as the Durbin-Watson test statistics *d* for the variables were lower than 1.5, indicating there were negative serial correlation (Ott and Longnecker, 2001).

Results and Discussion

Soil pH and exchangeable Ca and Al concentration

Across the three sites, pH ranged from 4.32 to 4.63, and exchangeable Ca and Al concentrations were between 0.13 and 0.83 cmol$_c$ kg^{-1} and between 0.01 and 0.13 cmol$_c$ kg^{-1}, respectively (Table 2). For Jangsung and Hampyung sites, the pHs and Ca/Al ratios of surface soil (0 to 10 cm) were relatively lower than those of deeper soil; meanwhile, such pattern was not observed for Youngkwang site. The pHs in the present study was slightly higher than those (4.07 to 4.10) for other *P. densiflora* forest soils reported by Kwak *et al.* (2009a). Similar to the pH pattern, the Ca/Al ratio (from 2.6 to 11.2, Table 2) was higher than those (0.20 to 0.72) in Kwak *et al.* (2009a), suggesting that soil acidification of the present study sites has progressed to less degree compared to the sites of Kwak *et al.* (2009b) assuming that the effects of other factors including parent materials are negligible.

The patterns of exchangeable Al and Ca/Al ratio but Ca concentration show the effect of soil acidification

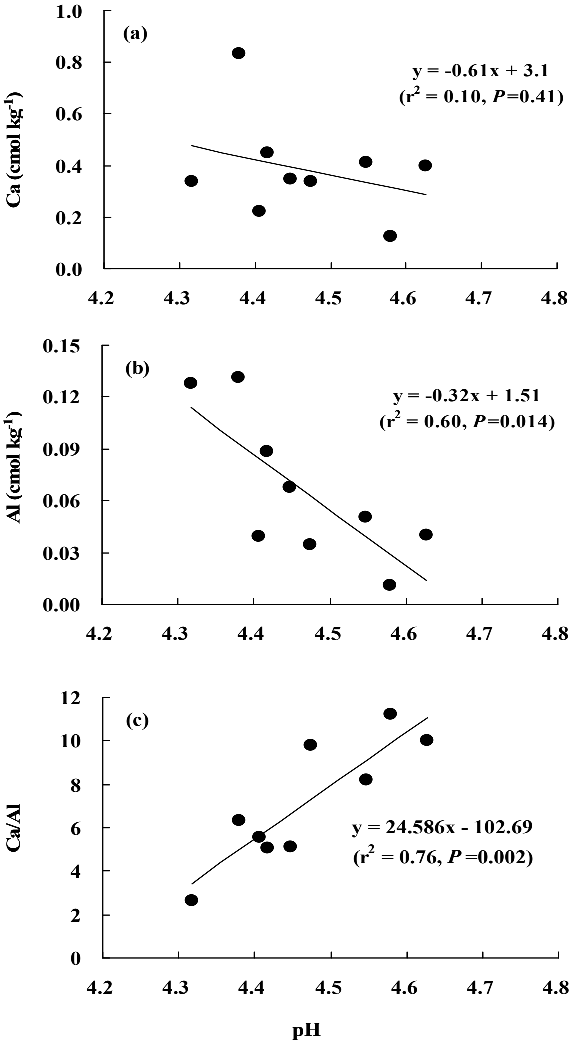

Fig. 1. Relationship of (a) exchangeable Ca concentration, (b) exchangeable Al concentration, and (c) Ca/Al ratio of soils with soil pH. The regression analysis was conducted with all the soil data regardless of soil depth. Very small error bars of triplicated measurements are not depicted.

Table 2. pH and exchangeable Ca and Al concentration of the soils used

Administrative district	Soil depth (cm)	Texture	pH$_{water\ (1:5)}$	Exchangeable cations		
				Ca (cmol$_c$ kg^{-1})	Al (cmol$_c$ kg^{-1})	Ca/Al
Jangsung	0-10	Loam	4.42 (0.05)	0.45 (0.13)	0.09 (0.02)	5.1 (0.9)
	10-20	Loam	4.45 (0.09)	0.35 (0.02)	0.07 (0.01)	5.1 (2.2)
	20-30	Loam	4.47 (0.05)	0.34 0.06)	0.03 (0.01)	9.8 (1.7)
Youngkwang	0-10	Sandy loam	4.38 (0.04)	0.83 (0.17)	0.13 (0.02)	6.3 (2.4)
	10-20	Silt loam	4.32 (0.06)	0.34 (0.08)	0.13 (0.04)	2.6 (1.1)
	20-30	Loam	4.41 (0.08)	0.22 (0.07)	0.04 (0.01)	5.6 (2.1)
Hampyung	0-10	Silt loam	4.55 (0.12)	0.41 (0.19)	0.05 (0.01)	8.2 (2.8)
	10-20	Loam	4.63 (0.06)	0.40 (0.12)	0.04 (0.01)	10.0 (3.1)
	20-30	Clay loam	4.58 (0.09)	0.13 (0.02)	0.01 (0.01)	11.2 (3.7)

of soil solution chemistry (Fig. 1). Reductions in the Ca/Al ratios of soil solution resulting from changes in Ca and Al concentration caused by long-term chronic acid deposition have been observed in Europe (e.g. Alewell *et al.*, 2000), Asia (Dawei *et al.*, 2001), and America (Barton *et al.*, 2002; Yanai *et al.*, 2005). However, direct correlation between pH and Ca/Al in forest soils has rarely been reported. It is well documented that as soil pH decreases from 5.5 to 4.0, Al ions (especially Al^{3+}) take the exchange sites in soil colloids, resulting in a low Ca/Al (Brady and Weil, 2002). Therefore, the positive correlation (P<0.01) between soil pH and Ca/Al observed in the present study can be regarded as an evidence of changes in Ca/Al in soil solution by soil acidification resulting from acid deposition. Decomposition of Ca-poor litter of coniferous tree (red pine in the present study) should have also contributed to the soil acidification (van Breemen and Finzi, 1998).

Ca, Al, and Ca/Al in annual tree rings

In tree rings, Ca concentration decreased from 3.6 cmol kg^{-1} in 1969 to 1.7 cmol kg^{-1} in 2007 (Fig. 2a); meanwhile Al concentration showed increasing pattern during the same period (Fig. 2b). Such reciprocal pattern of Ca and Al resulted in annual decrease of Ca/Al (Fig. 2c). All the temporal patterns assessed by autoregressive error model of time series analysis were significant at α=0.001.

Decrease in Ca concentration in tree rings from the innermost to the outermost growth rings has widely been reported (e.g. Sakata *et al.*, 2001; Kwak *et al.*, 2009a; 2011). Although Sakata *et al.* (2001) suggested that decreasing pattern of Ca concentration may indicate soil acidification history, such pattern can be a natural process due to reduced cation binding capacity of trees towards the cambium (Bondietti *et al.*, 1990; Momoshima and Bondietti, 1990). In this regard, it is suggested that Ca/Al rather than Ca or Al alone could be a better proxy of soil acidification as the ratio of Ca to Al can overcome the physiological pattern of single cation in tree rings (DeWalle *et al.*, 1990; Kwak *et al.*, 2009a). Therefore, the pattern of Ca/Al in tree rings in combination with the relationship between pH and Ca/Al of soil observed in the present study is believed to reflect historical progress of soil acidification.

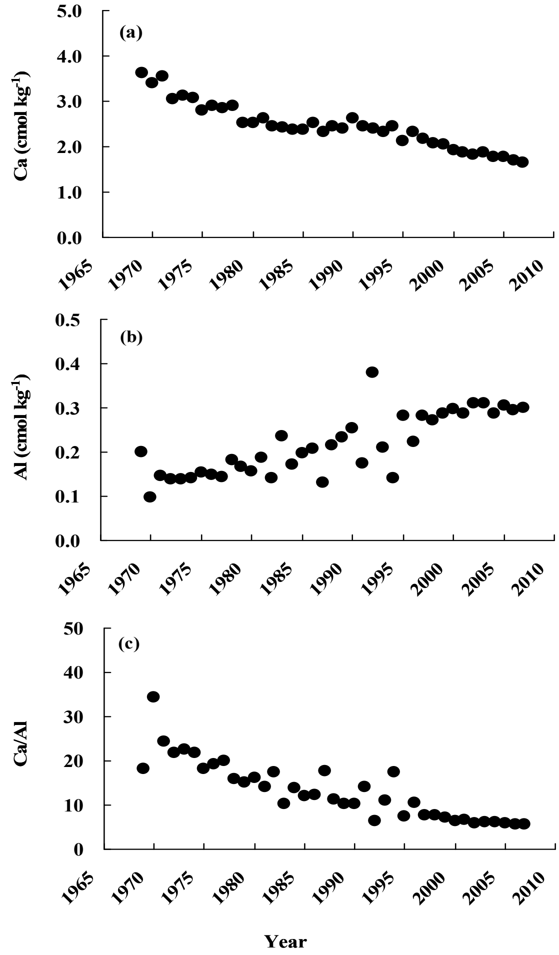

Fig. 2. Annual changes in (a) Ca concentration, (b) Al concentration, and (c) Ca/Al ratio in the tree rings. Very small error bars of triplicated measurements are not depicted.

Conclusion

In this study, we found that the ratio of exchangeable Ca to Al ratio of forest soils was significantly (P<0.01) correlated with soil pH, suggesting that progress of soil acidification increased exchangeable Al concentration while inducing leaching of Ca. Therefore, the decreasing pattern of Ca/Al in tree annual growth rings is believed to reflect historical Ca/Al changes of the soils by soil acidification. The results of this study suggest that Ca/Al in tree rings could serve as a proxy of the history of soil acidification in forest dominated by *P. densiflora*.

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