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Foliar Nutrients Status of *Pinus thunbergii* Influenced by Chronic Air Pollution in Yochon Industrial Complex in Korea[1]

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麗川産業團地의 慢性 大氣汚染에 의한 海松 葉中 無機養料의 變化[1]

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ABSTRACT

To investigate the effect of sulfate deposition on forest tree nutrition, 15 forest stands of *Pinus thunbergii* were selected throughout Yochon industrial complex, in which is influenced by chronic air pollution. Concentrations of sulfate sulfur, nitrogen, phosphorus, potassium, calcium, and magnesium were analysed for current and 1-year-old needles of *Pinus thunbergii* trees. The results obtained were as follows ;

1. Significant higher accumulation of sulfate S, compared with that of unpolluted needles, was observed at all sites, ranging from 0.11% to 0.35% in current needles, and from 0.13% to 0.32% in 1-year-old needles.
2. Ranging from 0.60% to 1.42% in current needles, and from 0.58% to 0.88% in 1-year-old needles, respectively, nitrogen concentrations were significantly lower at 7 sites for current needles, and at all sites for 1-year-old needles than at unpolluted site.
3. Phosphorus and potassium levels were significantly lower at very few sites, compared with unpolluted site.
4. Calcium concentrations were significantly lower at 8 sites and 9 sites for current and 1-year old needles than at unpolluted site, ranging from 0.123% to 0.352% and from 0.201% to 0.371% in 1-year old needles, respectively.
5. Ranging from 0.077% to 0.152% in current needles, and from 0.056% to 0.105% in 1-year-old needles, magnesium concentrations were lower at only 2 sites for current needles but at 12 sites for 1-year-old needles.
6. There were significant declines of concentrations of calcium and magnesium in current needles as sulfate accumulation increased. For 1-year-old needles, there were significant negative correlationships between sulfate and nitrogen, potassium, calcium, and magnesium concentration. It is concluded that deposition of sulfuric air pollutant deteriorated nutrients status, resulting in tree decline, in *Pinus thunbergii* forest in Yochon industrial complex.

Key words : *Air Pollution, Nutrients Deficiency, Sulfate Accumulation,* Pinus thunbergii.

요 약

만성적인 대기오염의 영향을 받고 있는 여천산업단지 지역에서 15개 해송임분을 선정하여 당년생 엽과, 1년생 엽중 수용성 유황의 축적과 질소, 인, 칼륨, 칼슘, 마그네슘 등 무기양료의 함량변화를 파악하였다. 수용성 유황 함량은 당년생 엽이 0.11% - 0.35%, 1년생 엽이 0.13% - 0.32%로서 전 지역

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에서 대조지역보다 높았다. 질소의 경우 당년생 엽은 0.60% - 1.42%로써 7개 지점에서, 1년생 엽은 0.58% - 0.88%로써 전 지역에서 대조구에 비해 그 함량이 낮아 1년생 엽에서의 질소 결핍이 뚜렷하였다. 인과 칼륨의 경우에는 일부 지역에서 대조구에 비하여 함량이 낮은 수준을 보였다. 칼슘은 당년생 엽에서는 0.12% - 0.35%로 8개 지역에서, 1년생 엽에서는 0.20% - 0.37%로써 9개 지역에서 대조구보다 낮았다. 마그네슘은 당년생 엽에서 0.08% - 0.15%로 2개 지역에서, 1년생 엽에서는 0.06% - 1.11%로써 12개 지역에서 결핍증세를 보였다.

대조구를 제외한 15개 지점에 대해서 각 분석 항목들의 상관관계를 살펴본 결과 당년생 엽의 경우에 칼슘과 마그네슘은 유황이 축적될수록 유의적으로 감소하였다. 1년생 엽의 경우에는 질소, 칼륨, 칼슘, 마그네슘의 함량이 수용성 유황함량과 유의적인 부의 상관을 나타내 여천산업단지에서 배출되는 황화합물의 퇴적이 해송의 양료상태를 교란시켜 해송림의 쇠퇴에 영향을 미치는 것으로 파악되었다.

INTRODUCTION

Exposure of foliage to gaseous air pollutants such as SOx results in increase of sulfur concentration in the plant. Sulfur dioxide is known to be absorbed into tree leaves via stomata and rapidly oxidized to sulfate in mesophyll cells in dry condition. But when leaf surfaces are wet, sulfur dioxide is absorbed to leaf surfaces because of its high solubility in water. Once absorbed, it could have effects on numerous reactions of metabolism. Small amount of atmospheric sulfur can be nutritional to trees in a short term. But if more amount of sulfur is accumulated in the leaf tissues, the foliar sulfur accumulation can reach toxic levels and adversely affect plant growth (Linzon, 1978). Therefore, the atmospheric sulfur deposition may have a contributing role in the tree declines observed in the forests of central Europe and eastern North America(McLaughlin, 1985).

Long term exposure to air pollutants may cause adverse impacts on forest nutrients cycling by increasing leaching losses, decreasing decomposition rates, increasing toxic ion availability, and decreasing nutrient uptake rates(Zinke, 1980). Thus, the alteration of foliar mineral nutrients of trees exposed to chronic air pollution may be a good indicator and significant factor to forest nutrients cycles. SO_2 exposure may predispose foliage to vegetative leaching loss by epicuticular erosion, membrane dysfunction or metabolic abnormality. Nutritional problems associated with foliar discoloration and crown transparency, which appeared to have arisen as a result of nutritional imbalance by air pollution, have been reported (Innes, 1995 ; Cape *et al.*, 1990).

Since a number of industrial complexes were constructed in Ulsan, Onsan, Yochon etc., accumulation of phytotoxic substances has caused subtle or serious changes in the structure and function of forest ecosystems near the complexes. There are lots of studies on forest decline symptoms and changes in community structure of forest in Yochon(Kim and Kim, 1986), Ulsan (Kim *et. al.*, 1982) and Onsan(Kim, 1992). Impaired mineral nutrition was reported on *Pinus thunbergii* influenced by chronic combined air pollution such as sulfur dioxide and hydrogen fluoride in Yochon(Kim, 1992) and Sasang(Kim and Lee, 1994). But it was not sufficient to understand the single effect of sulfuric gas emissions on tree nutrition in Yochon industrial complex in which sulfur dioxide and hydrogen fluoride were major air pollutants.

This study aimed to determine if chronic long term exposure of single sulfur gas emissions had adverse effects on mineral nutrients status of *Pinus thunbergii* needles in Yochon industrial complex.

MATERIALS AND METHODS

1. Site Description

The study was carried out at the black pine (*Pinus thunbergii*) forests around Yochon industrial complex(YIC), Chonnam Province, Korea. The complex consists of a great number of petrochemical plants and a phosphatic fertilizer manufacturing factory. The air quality in YIC has been rapidly worse with emission of SO_2 and HF(about 10,000t and 200t, respectively, per year) since it was established. Black pine, decline of which was observed in late 1970s, is a dominant tree species in most area around YIC. The forest soils were acidified to pH 4.5 as acidic substances accumulated(Lee and Min, 1989).

2. Sampling

To avoid synergism of SO_2 and HF, sampling sites were randomly chosen in the northwestern area of the complex. It was because that HF pollution is apparent near Namhae Chemical Co., which is located in southeastern area of the complex(Kim, 1985).

Fifteen sampling sites were chosen along SO_2 affected black pine forests on September, 1994. Three black pine, dbh of which is around 15㎝, were selected randomly in canopy layer. About 500 grams of current and 1-year-old needle was collected from the upper crown and transported to the laboratory. Needles were washed in tap water to remove surfacial materials, dried at 65℃ for 48 hours to remove any moisture, and ground to particle sizes of 40 mesh or below with using a wiley mill. As a control site, air pollution-free black pine forest was selected in experimental forest of Sunchon National University.

3. Plant tissue analysis

Five grams of ground material was burned at 550℃ for 12 hrs, and washed with deionized water. Nitrogen was determined by micro-kjeldahl method, and phosphorus by colorimetry measuring absorbance at 420*nm* after vanado-molybdate treatment. Potassium, calcium, and magnesium were determined by atomic absorption spectrophotometry. Water soluble sulfur(sulfate-S) was analyzed by gravimetric(Kim, 1985). Correlation analysis between sulfate and inorganic nutrients were undertaken using SAS.

RESULTS

The concentrations of sulfate-S and nutrients in needles of black pine are presented in Fig. 1. As expected, it is clear that sulfate accumulation in current two years of growth of black pine needle has been substantially increased throughout the YIC. Sulfate concentrations ranged from 0.11% to 0.35% in current year needles and 0.13% to 0.32% in 1-year-old needles, respectively, which were significantly higher at all the sites compared with pollution-free site by LSD.

Generally, N, P and K tend to be decreased, but Ca and Mg increased at pollution-free site as needle aged. The concentration of elements in black pine needles, however, tended to vary as sulfate had accumulated in needle tissues. N concentration ranged from 0.60% to 1.42% for current needles, and from 0.58% to 0.88% for 1-year-old needles, respectively. N concentration was significantly lower at 7 sites for current needles, but quite lower for 1-year-old needles at all the polluted sites than at unpolluted site. Thus, nitrogen deficiency is likely to be widespread in 1-year-old needles as affected by chronic air pollution exposures.

P and K levels were significantly low at very few sites compared with unpolluted site. P levels declined at 2 sites for current needle and 6 sites for 1-year-old needle, ranging from 0.076% to 0.134% in current needles and from 0.046% to 0.083% in 1-year-old needles, respectively. K levels were significantly low at 4 sites for current needles and 3 sites for 1-year old needles, which ranged from 0.331% to 0.473% in current needles and 0.255% to 0.391% in 1-year-old needles.

In contrast, calcium deficiency was likely to be widespread. Among 15 sites, Ca concentrations were significantly lower at 8 sites and 9 sites for current and 1-year old needles than at unpolluted site, respectively. Ca concentrations ranged from 0.123% to 0.352% in current needles and 0.201% to 0.371% in 1-year old needles.

Mg concentrations ranged from 0.077% to 0.152% in current needles, and from 0.056% to 0.105% in 1-year-old needles. Comparing the Mg levels of 0.123% for current year and 0.127% for 1-year-old needles at unpolluted site, Mg concentration were lower at only 2 sites for current needles but 12 sites for 1-year-old needles. It

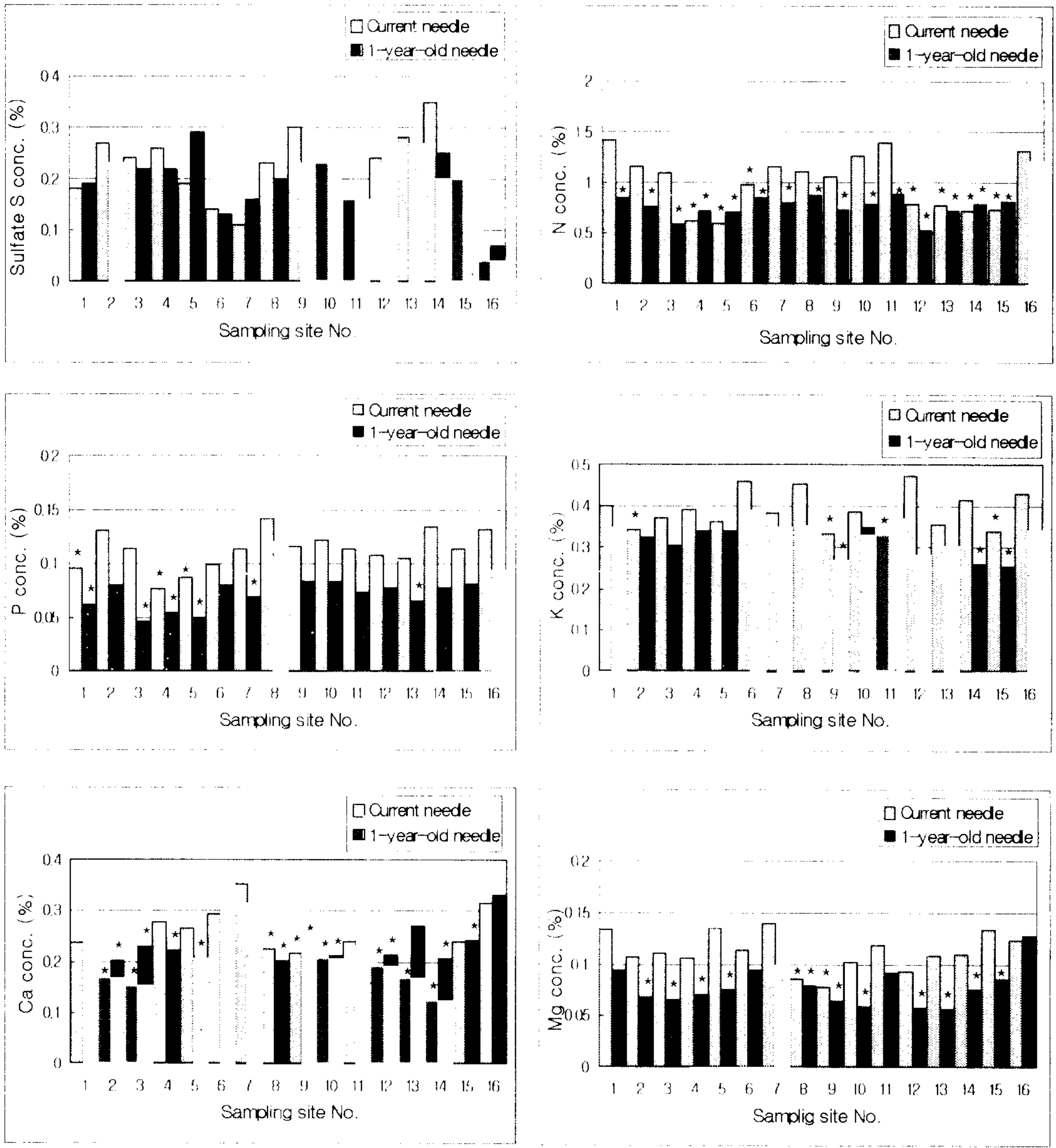

Fig. 1. Concenmtration of sulfate-S, N, P, K, Ca, and Mg in current and 1-year-old needles of Pinus thunbergii in Yochon industrial compelx.
(*'s indicate significance at the 5% level compared with control site)

seemed that Mg deficiency was apparent for 1-year-old needles with decreasing significantly at 10 sites, not for current year needle.

The data indicated that nutrients status of black pine needles exposed to chronic atmospheric sulfur pollution was disturbed by accumulation of sulfate sulfur. The correlations between sulfate-S and the nutrients were investigated for both needle age classes. There were significant declines in concentrations of Ca(r=0.804) and Mg(r=0.621) of current needles as sulfate accumulation increased (Fig. 2). N, P and K in current needles showed no correlationship with sulfate. For 1-year-old needles, there were significant negative correlationship between sulfate and N(r=0.686), P(r=0.673), Ca(r=0.746), and Mg(r=0.736)(Fig. 3).

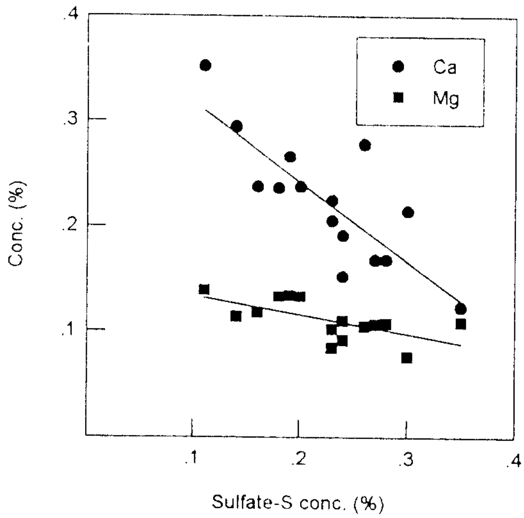

Fig. 2. Correlationships between sulfate-S and Ca and Mg in current-year needles of *Pinus thunbergii*.
(r=0.804 for Ca and, 0.621 for Mg)

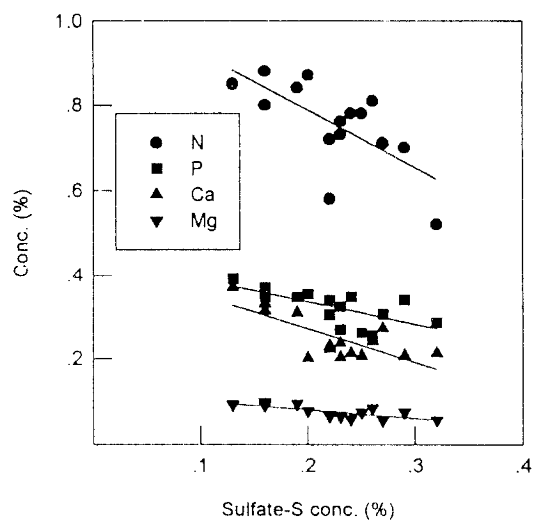

Fig. 3. Correlationships between sulfate-S and N, P, Ca and Mg in 1-year-old needles of *Pinus thunbergii*.
(r=0.686 for N, 0.673 for P, 0.746 for Ca, and 0.736 for Mg)

DISCUSSION

Acidic deposition could directly injure foliage, reduce effective light-capturing leaf area or damage water regulation. Furthermore, acidic air pollutants could increase the leaching of cations from plant leaves, causing foliar nutrients imbalances. Alteration in assimilation rate may occur as a result from lowered nutrients status caused by cuticle damage or cation loss from either leaves or soils. It is, however, difficult to estimate the metabolic responses of plant to acidic deposition and soil acidity, respectively.

Sulfur dioxide can be removed from the atmosphere by dry deposition(uptake by vegetation and adsorption on plant) and by wet deposition (scavenging by precipitation). Analyses of needle sulfate-S concentrations showed that sulfate-S had been accumulated significantly more within needle tissue of black pines at YIC sites than at pollution-free site. As sulfur content in black pine needles can be used as an indicator for sulfur dioxide pollution(Kim *et al.* 1993), these elevated concentrations of sulfate-S in needles indicated that a vast amount of sulfuric gas from the sources had been deposited at the investigated sites, affecting sulfur cycling and availability of other essential nutrients within black pine forest ecosystem. As salts of the SO_4- deposited with H^+ in the foliage via wet and dry deposition, equivalent amount of basic cations, calcium, magnesium and potassium is leached from the leaves. Detailed analyses of foliar mineral nutrients concentration of trees influenced by acidic deposition have been described by other authors. Amundson *et. al.*(1990) analysed foliar sulfur and mineral nutrients of lodgepole pine x jack pine and found that nearer the pollution source, foliar sulfur increased but foliar P tended to be lower. Cape *et. al.*(1990) measured the major nutrients such as N, K, Ca, Mg and S for Norway spruce needles in Europe and found that element ratios involving sulfur(S/Ca, S/Mg, S/N) reflected the underlying nutrient stresses caused by sulfate deposition.

The nutrients analyses in this study showed that nutrients status were likely to be altered by acidic deposition in black pine forest ecosystem in and around YIC. Macro-nutrients such as N, P, K, Ca, and Mg were more declined in 1-year old needles than in current needles. Negative correlations were observed for Ca and Mg but not for N, P, and K with sulfate-S concentration in current needles. For 1-year old needles, however, N, K, Ca, Mg except P were significantly decreased with sulfate-S accumulation. This indicated that older leaves were more susceptible to acidic deposition, resulting in nutrients deficiency of whole trees. Negative correlationship between sulfur and Ca was ever observed for black pine needles in Sasang industrial complex by Kim and Lee(1994).

It is generally assumed that nutrients deficiency of trees due to acidic deposition was attributable to both foliar leaching and soil acidification. Foliar leaching by acid deposition is well described by Tomlinson and Tomlinson(1990). Increased canopy losses of cations in forest have been reported in polluted regions(Wood and Bormann, 1975). Fritsche(1991) noted that, for spruce needles and beach leaves, leaching from old needles exceeded leaching from young needles to greatly and the leaching kinetics seemed to be more influenced by the structure of the plant surface than by the percentage of the stored material. Air pollutant exposure may predispose tree foliage to leaching loss by cuticular erosion, membrane dysfunction, or metabolic abnormality. Keller (1986) found that water stress and sulfur dioxide treatment increased leaching loss in Norway spruce foliage. For black pine needles influenced by chronic air pollution in Yochon, the altered surface structure such as eroded cuticular wax, which increased the gas permeability and thus foliar leaching, was found(Kim *et. al.*, 1993).

Recent result in Ulsan Industrial Estate revealed that contents of Ca and Mg in foliage of *Alnus hirsuta, Quercus acutissima, Pinus rigida*, and *P. thunbergii* were greater in unpolluted area than in industrial area, which seemed to be due to altered soil acidity by acidic deposition(Lee and Lee, 1995). The soils in coniferous forest around YIC were found to have been acidified, resulting in lowered base saturation and increased aluminium content in soils(Lee and Min, 1989). Nyborg *et. al.*(1977) quantified S deposited by wet and dry deposition at different distances from a large emitter(135t SO_2-S day^{-1}) and found an increase in SO_2 at ground level and a subsequent decrease in soil pH. It is well known that acidic soils generally have low levels of essential major nutrients and high levels of polyvalent catincluding elements required by plants in trace amount. Accelerated leaching of base cations and increased mobilization of aluminum and other metals are regarded to lead nutrients deficiency or imbalance of forest trees(Lucier and Haines, 1990).

It is certain that the lowered concentration of Ca and Mg in this study seemed to be due to leaching from needles and soil acidification with increased sulfate accumulation in forest ecosystem. But it is not clear whether the foliar nutrients deficiency resulted from excessive foliar leaching, from insufficient supply in the soil, or from impaired root uptake caused by air pollutant input. The increased foliar leaching of mobile elements caused by exogenous factors can be compensated by increased nutrients uptake from the soil, if the supply in the rooting horizons is sufficient. However, if the soils are acidified by acidic deposition, supply of nutrients may be limited, resulting in accelerated foliar nutrients deficiency or imbalance(Zottl and Huttl, 1986). Mg deficiency in 1-year-old needles in this study is due to the mobility of Mg in the trees' system. When the supply is insufficient, Mg in older needles or other tissues moves to more recently formed new tissues. This Mg deficiency in older needles resulted in chlorosis or yellowing of needles, subsequently dropping off in 2 or 3 years, as reported by Kim(1985). Dead leaves of trees provide the source for the breakdown of organic matter by the decomposers. The decomposing organic matter gradually release the mineral nutrients which promote successive forest growth through nutrient recycling. It has been found that acid deposition in black pine forest resulted in nutritional imbalance of needles, which might cause altered nutrients cycling within the forest ecosystem in and around Yochon industrial complex.

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