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Cation Leaching from Leaves Sprayed with Simulated Sulphuric Acid Rain

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人工 酸性 빗물로 인한 잎으로부터의 陽이온 洗脫

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ABSTRACT

After spraying simulated sulphuric acid rain (SSAR) to the leaves of *Glycine max, Quercus aliena* var. *pellucida* and *Pinus rigida*, the leachates were consecutively collected and quantitatively determined for the concentration of K and Ca. The amount of the leached ion decreased with subsequent acid treatment for all plants. But as the pH of SSAR decreased, the amount of the leached ion increased. The cumulative quantities of K leached from each species were 1.04 to 1.46 times higher at pH 4.0, 1.09 to 1.58 times higher at pH 3.5 and 1.24 to 2.03 times higher at pH 3.0 compared with pH 5. 6 treatments. The cumulative quantities of Ca leached from each species were 1.23 to 1.47 times higher at pH 4.0, 1.50 to 1.92 times higher at pH 3.5, and 2.45 to 3.30 times higher at pH 3.0 compared with pH 5.6 treatments. The Ca/K ratio in 1000 ml leachate was 1.10 to 2.91 for *Q. aliena* var. *pellucida* and 1.68 to 2.98 for *P. rigida*, but 0.66 to 0.91 for *G. max*. The Ca/K ratio in 1000 ml leachate increased for all three species, as the pH of SSAR decreased. Foliage analysis after acid rain treatment showed leaching effect at pH 3.0.

Key words: Simulated sulphuric acid rain, Foliar cation leaching, Ca/K ratio

INTRODUCTION

Air pollution leads to a significant acid deposition problem in industrial complex, in urban area and on high elevation mountains. Forest decline syndrome in central Europe has been known to occur in the forests wetted frequently by acid rain (Zoettle and Huettle 1986). The droplets of rain and fog are acidified by reaction with strong acid gases (HNO_3 and SO_2), acid aerosols (H_2SO_4 and NH_4HSO_4), and by the *in situ* oxidation of S in aqueous phase (Waldmann and Hoffmann 1988). In precipitation chemistry it is known that small particles of fog can concentrate more ions than large rain droplets do. In fact, ionconcentrations in fog are 10 to 100 folds higher than those in acid rain (Paoletti *et al.* 1989b).

The deposition of acid rain is of considerable interest in light of observations that foliar leaching of cations is markedly intensified as H^+ concentration increases. It is supposed that cations on exchange sites of the cuticle of leaves are exchanged by H^+ ions from acid rain. Recently, considerable enhancement of concentration of K^+, Ca^{2+}, and Mg^{2+} has been observed in fog droplets collected from pine foliage by Waldmann and Hoffmann (1988). Magnesium deficiency and low Ca concentration in foliage have accompanied decline symptoms in Norway spruce at high elevation forests across central Europe. German scientists have hypothesized that foliar leaching of Ca^{2+} and Mg^{2+} caused by acid deposition is one of several primary factors in this 'high altitude Norway spruce disease' (Zoettle and Huettle 1986).

Most work in acid deposition affecting foliar nutrient fluxes has involved analysis of throughfall without looking at the resultant foliar chemistry. Therefore the purpose of this study is to examine the effects of simulated sulphuric acid rain on foliar leaching of K^+ and Ca^{2+} from leaves of *Glycine max, Quercus aliena* var. *pellucida* and *Pinus rigida* during a short period not long enough to translocate the ions from root to leaves.

METHODS

Preparation of simulated sulphuric acid rain (SSAR)

The pHs of simulated sulphuric acid rain (SSAR) with pH 4.0, 3.5 and 3.0 were adjusted by diluted H_2SO_4. The pH of control rain was adjusted by dissolving CO_2 gas in deionized water.

Culture of material plants

Glycine max, Quercus aliena var. *pellucida* and *Pinus rigida* were selected for experiments. Seeds of *G. max* were germinated in sandy soil in early May, 1989. Seedlings were transplanted to pots having 3.3 kg soil mixed with compost and then cultured in greenhouse. Seeds of *Q. aliena* var. *pellucida* were germinated in April, 1988 and cultured in greenhouse under the same soil condition for *G. max*. Eight year-old *P. rigida* plants growing at Mt. Kwanak were selected for this study. Only the experiment for *P. rigida* was carried out *in situ*. All plants were sufficiently supplied with Hoagland solution at every other day for 3 weeks before the experiment. Experiment was carried out in August and September, 1989.

Spraying of SSAR and collecting of leachate

Lateral branches of *G. max* and *Q. aliena* var. *pellucida* were bound to the stake set up at the center of pots. Round plastic tray with 34 cm diameter and 1 cm high rim was used as leachate collector. Until 100 ml of leachate from leaves was collected, the plants were sprayed with SSAR with hand sprayer, and generally it took an hour to spray about 200~250 ml of SSAR. These procedures were repeated consecutively 10 times for 10 hours. In the case of *P. rigida*, terminal shoot was towed, bent and fixed to soil surface with a string. The rectangle plastic collector with 50cm×60cm lay under croocked shoot, and SSAR was sprayed and leachate was collected as for other plants. Replication was carried out 3~5 times per treatment for each species.

Chemical analysis for plant and leachate

As soon as the plants were sprayed, leaves were separated. The fresh leaves were copied on the paper with a xerox machine except *P. rigida*. The outline of leaves copied was cut by a pair of scissors. Leaf area was calculated from the ratio of weight to area of the paper. All the leaves were weighed after drying at 80℃ for 48 hrs, and ground for chemical analysis. The 0.2 g of samples was shaken with 50 ml of 0.2 N HCl and filtered with Whatman No. 44 filter paper. K^+ and Ca^{2+} in leachate and extracted solution were determined by using an atomic absorption spectrophotometer (GBS 903). pH of leachate was measured with a pH meter (Fisher 230).

RESULTS AND DISCUSSION

Change in pH of leachate

After spraying with control rain, pH of leachates from *Pinus rigida* gradually decreased (Fig. 1). But in the case of spraying with SSAR of pH 4.0, 3,5 and 3.0, the pH values of initial leachate were higher than the values of original pHs of SSAR and then came back gradually to the values of original pH of SSAR.

High pH values of initial leachates were shown also in the experiments with *G. max* and *Q. alliena* var. *pellucida*. Such neutralization of acidic rain might be due to solubilization of basic dusts and exudates from the leaf surface and ion exchange removal of H^+ by the leaves (Hutchinson 1986, Gaber and Hutchinson 1987).

Changes of K and Ca in leachate

K contents in the first 100 ml leachate of *G. max* after spraying did not differ among treatments of different pHs (Fig. 2). From the second spraying treatment, however, the amount of K were higher in leachate by SSAR of pH 3. 0 than by SSAR of other pHs. In *Quercus aliēna* var. *pellucida*, K contents in the leachates increasd with acidity of SSAR, but amount of K leached did not change with time. In *Pinus rigida*, K contents in the leachates increasd with acidity of SSAR. The total amount of K leached after spraying with SSAR of pH 4.0, 3.5 and 3.0 were 1.46, 1.09 and 2.03 times higher in *G. max*, 1.04, 1.12 and 1. 23 times higher in *Q. aliena* var. *pellucida*, and 1.33, 1.58 and 1.68 times higher in *P. rigida* compared with spraying with SSAR of pH 5.6 (Table 1).

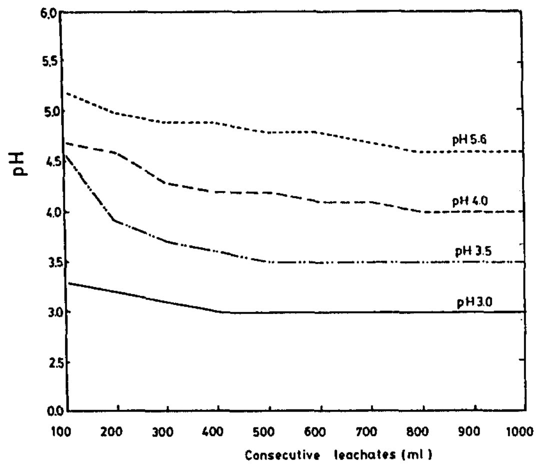

Fig. 1. Changes of pH of leachates from *Pinus rigida* leaves after consecutive spraying with simulated sulphuric acid rain.

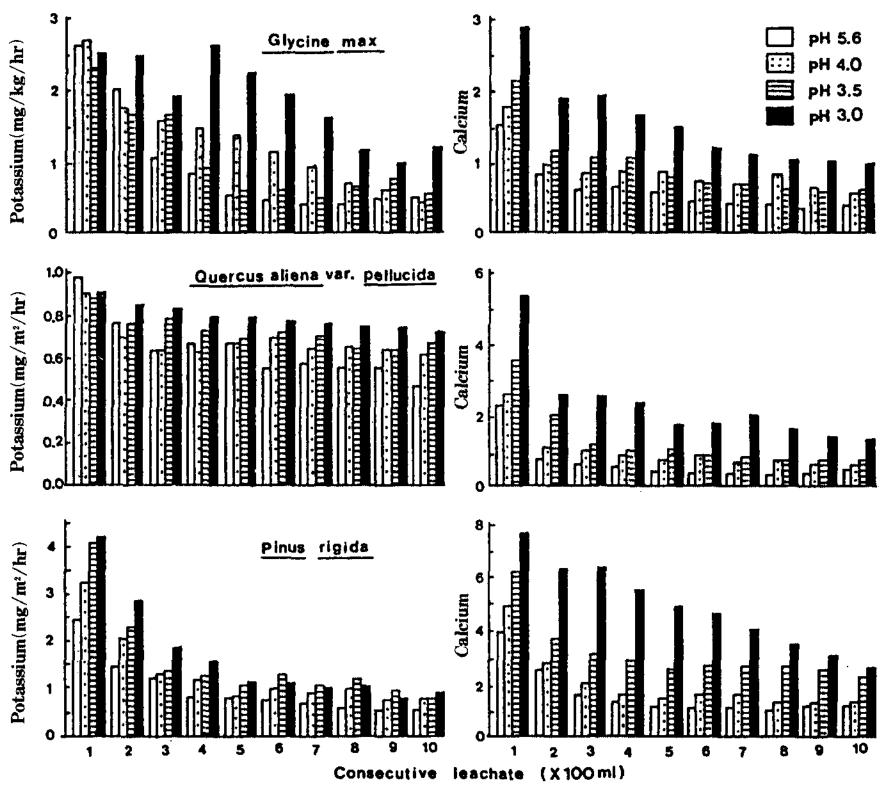

Fig. 2. Changes of potassium (left) and calcium (right) content in leachates from leaves of *Glycine max* (above), *Quercus aliena* var. *pellucida* (middle) and *Pinus rigida* (below) after consecutive spraying with simulated sulphuric acid rain.

Table 1. Total amount of nutrients in 1,000 ml leachate leached from leaves after spraying with simulated sulphuric acid rain of 1,000 ml. Numerals are mean and a standard deviation. Numerals in parentheses indicate the ratio of treatment to control rain.

Species	pH of treatment	Total amount of ions in 1000ml leachate			
		K ($mg/m^2/10hr$)		Ca ($mg/m^2/10hr$)	
Glycine max	5.6	9.2±3.4	(1.00)	6.1±1.2	(1.00)
	4.0	13.5±2.1	(1.46)	8.6±2.1	(1.40)
	3.5	10.1±2.2	(1.09)	9.2±2.4	(1.50)
	3.0	18.7±6.1	(2.03)	15.0±2.8	(2.45)
Quercus aliena var. *pellucida*	5.6	6.3±1.2	(1.00)	6.9±1.5	(1.00)
	4.0	6.6±1.3	(1.04)	10.2±4.2	(1.47)
	3.5	7.1±1.5	(1.12)	13.0±2.3	(1.88)
	3.0	7.8±1.5	(1.23)	22.8±9.5	(3.30)
		K (mg/kg/10hr)		Ca (mg/kg/10hr)	
Pinus rigida	5.6	9.6±1.9	(1.00)	16.2±3.1	(1.00)
	4.0	12.8±7.0	(1.33)	20.0±3.7	(1.23)
	3.5	15.2±3.8	(1.58)	31.2±7.7	(1.92)
	3.0	16.2±7.0	(1.68)	48.2±7.6	(2.97)

Amount of Ca leached from all three species increased with acidity of SSAR. Especially foliar Ca leaching was greatly increased by pH 3.0 of SSAR. The amount of Ca leached from all species decreased with time (Fig. 2). The total amount of Ca leached after treatment of pH 4.0, 3.5 and 3.0 were 1.40, 1.50, and 2.45 times higher in *G. max*, 1.47, 1.88 and 3.30 times higher in *Q. aliena* var. *pellucida* and 1.23, 1.92 and 2.97 times higher in *P. rigida* compared with treatment of pH 5.6 (Table 1).

The trend of foliar ion leachings decreased with subsequent acid fog spraying (Paoletti *et al.* 1989b); ions are often leached most quickly from leaves by initial spraying. Such initial leaching is thought to partly represent washoff of previous dry deposition and plant exudates. After this initial decrease, diminishing loss of cations with time is due to depletion of readily available internal pools (Hutchinson *et al.* 1986, Muir 1990).

In this study the cumulative amount of K leached from each species was 1.04 to 1.46 times higher at pH 4.0, 1.09 to 1.58 times higher at pH 3.5, and 1.23 to 2.03 times higher at pH 3.0 than those in the pH 5.6 spraying. Paoletti *et al.* (1989a), have not observed significant variation of K leaching among treatments of the different pH in *Phaseolus vulgaris* and *Quercus ilex*. They also observed that content of T-N, Ca, Mg and P were low, but content of K in *P. vulgaris* were not low under the condition of exposing to simulated acidic fog once a week for 6 weeks. Therefore it was thought that K was the least sensitive element to change in acid treatment. Efflux rates of K are often relatively unaffected by duration or acidity of rain, perhaps because K is more mobile within plant tissues than Ca or Mg and exists in large internal pools that furnish a ready resupply despite slow translocation through the root system (Muir 1990). Haines *et al.* (1985), however, reported that K leachability increased by acidity.

In this study the cumulative amount of Ca leached from each species was 1.23 to 1.47 times higher at pH 4.0, 1.50 to 1.92 times higher at pH 3.5, and 2.45 to 3.30 times higher at pH 3.0 than those in the pH 5.6 spraying. Amount of Ca leached from all species increased with acidity of SSAR. In leachates from the leaves of *P. vulgaris, Eucca japonicus, Quercus ilex*, and *Fagus sylvatica*, after spraying with acid fog, the cumulative amount of Ca leached was 5 to 7 times higher at pH 2.5, and 1.5 to 3.0 times higher at pH 3.0 than that at pH 5.6 sprayings (Paoletti *et al.* 1989a). In addition, leaching of Ca, Mg, K, and Na from foliage of *Quercus ilex* increased 3.8, 2.4, 3.7, and 1.4 folds, respectively, in sixteen sprayings for 6-hr exposure with acid fog of pH 2.5 compared with pH 5.6 treatment (Paoletti *et al.* 1989b). The leachings of Ca, Mg and K from foliage of young Norway spruce were 4.0 to 6.5 times higher, 4.5 to 6.0 times higher, and 2.0 to 3.0 times higher at pH 2.7 treatment, respectively, compared with pH 5.2 treatment (Joslin *et al.* 1988). Scherbatskoy and Klein (1983) found that Ca leached from *Picea glauca* seedlings was enhanced almost 6 times as pH of mist reduced from pH 4.3 to pH 2.8 but that of K was enhanced 40% only.

Ratio of K to Ca in leachates

To compare Ca or K leaching sensitivities from leaves to acidity of simulated rain, Ca/K ratio in leachate after different pH treatment was calculated. Ca/K ratio in 1000 ml leachate was bigger than 1 for *Q. aliena* var. *pellucida* (1.10~2.91) and *P. rigida* (1.68~2.98), but was smaller than 1 for *G. max* (0.66~0.91)(Table 2). K in leaves of *G. max* was more leachable than Ca by acid rain, but K in leaves of *Q. aliena* var. *pellucida* and *P. rigida* was leached less than Ca by acid rain. Ca/K ratio in foliar leaching increased with an increase of the acidity of SSAR for all three species.

Of the major base cations, Muir (1990) showed that Ca exhibits the most consistant increasing of efflux rates with increasing acidity of the leaching solution for a variety of plant species (e. g. spruce, birch, maple, pinto bean, tulip poplar, white oak, and virginia pine). If cation efflux is caused partially by ion exchange involving H^+ in rain or fog, efflux of K and Na might be expected to be less tightly coupled to mist pH than Ca and Mg, as K and Na are held less tightly on exchange surfaces than Ca and Mg.

Remaining content of K and Ca in leaves after spraying with SSAR

K and Ca contents of *G. max, Q. aliena* var. *pellucida* and *P. rigida* after spraying with

Table 2. The Ca/K ratio in total leachate from the leaves after treatment of simulated sulphuric acid rain

Species	pH	Ca/K	Species	pH	Ca/K	Species	pH	Ca/K
Glycine max	5.6	0.66	*Quercus aliena*	5.6	1.10	*Pinus rigida*	5.6	1.68
	4.0	0.63	var. *pellucida*	4.0	1.53		4.0	1.56
	3.5	0.91		3.5	1.82		3.5	2.05
	3.0	0.80		3.0	1.80		3.0	2.96

Table 3. K and Ca content in leaves after treatment of simulated sulphuric acid rain of 1,000ml. Numerals in parentheses indicate standard deviation

Species	pH of treatment	Leaves K (mg/g)	Leaves Ca (mg/g)
Glycine max	5.6	16.6(0.12)	17.3(0.83)
	4.0	16.5(1.40)	17.2(1.19)
	3.5	15.8(0.44)	16.5(1.23)
	3.0	13.4(1.35)**	14.2(1.34)**
Quercus aliena var. *pellucida*	5.6	10.2(1.06)	11.7(0.47)
	4.0	10.1(0.56)	10.8(1.24)
	3.5	10.1(1.14)	10.7(1.02)
	3.0	9.8(0.69)	10.2(0.92)*
Pinus rigida	5.6	5.7(0.73)	3.2(0.37)
	4.0	5.6(1.72)	3.2(0.44)
	3.5	5.2(0.89)	3.1(0.16)
	3.0	4.9(0.78)*	2.9(0.17)*

* : $p < 0.05$, ** : $p < 0.01$

1000 ml SSAR were significantly affected only when the pH of SSAR was 3.0.(Table 3). K and Ca contents in the leaves of three species seemed to be affected by SSAR of pH 3.5 except K of *Q. aliena* var. *pellucida* and Ca of *P. rigida*. But SSAR of pH higher than pH 4.0 did not affect foliar ion leaching.

Several authors showed that foliar applications of acidic solutions did not alter foliar nutrient status (Kelly and Strickland 1986, Paoletti *et al.* 1989a). Muir (1990) also showed that foliar Ca content after spraying with mist of pH 2.5 was either higher or not different compared with less acidic mist. Because their experiments, however, were carried out for longer period, leached ions from leaves thought to be compensated from the stem or the root. In contrast as our leaching experiment was carried out with the large amount of rain during a short period, deficient ions within leaves by ion leaching did not have enough time to be compensated from root or stem (Jacobson *et al.* 1990). Muir (1990) and Turner and Tingey (1990) indicated that losses of foliar cations were sometimes small compared with total foliar pool sizes, and suggested that the losses were not important, at least on fertile soils. But accelerated foliar leaching of trees only resulted in foliar deficiencies of Ca and Mg when trees were growing on soils especially poor in these nutrients. Therefore, the low or deficient foliar concentrations of cations were the results of the combination of soils low in cations and sufficient acid deposition to amplify foliar cation losses.

적 요

인공산성빗물을 대두(*Glycine max*), 청갈참(*Quercus aliena* var. *pellucida*) 및 리기다소나무 (*Pinus rigida*)에 살포한 후 연속적으로 일정량을 받아서 이온량을 정량하였다. 모든 잎에서 세

탈된 이온의 양은 초기에 많았으나 시간이 지날수록 감소하였으며, 세탈되는 이온량은 빗물의 pH가 낮을수록 세탈되는 이온량은 많았다. 총 세탈된 K의 양은 정상빗물 (pH 5.6)보다 pH 4.0의 빗물에서 1.04~1.46배, pH 3.5의 빗물에서 1.09~1.58배, 그리고 pH 3.0의 빗물에서 1.24~2.03배 만큼 많았다. 총 세탈된 Ca량은 정상빗물보다 pH 4.0의 빗물에서 1.23~1.47배, pH 3.5 빗물에서 1.50~1.92배, 그리고 pH 3.0의 빗물에서 2.45~3.30배 만큼 많았다. 총 세탈액 속의 Ca/K의 비는 청갈참에서 1.10~2.91, 리기다소나무에서 1.68~2.98, 그리고 대두에서 0.66~0.91이었다. 조사된 모든 식물에서 빗물의 pH가 낮아질수록 Ca/K 비율이 커졌다. 산성빗물 처리 후의 식물체를 분석한 결과 이온세탈 효과는 pH 3.0 처리구에서만 유일하게 나타났다.

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