JARQ 26, 171-177 (1992)

Acid Precipitation in Japan and Its Impact on Plants

1. Acid precipitation and foliar injury

Isamu NOUCHI

Department of Natural Resources, National Institute of Agro-Environmental Sciences
(Tsukuba, Ibaraki, 305 Japan)

Abstract
Acid precipitation is presently a major environmental issue worldwide and a great deal of information concerning the effects of acid precipitation on terrestrial ecosystems is becoming available. This review describes the status of acid precipitation in Japan and the impact of acid precipitation on the growth of agricultural crops and forest trees. Annual mean pH value of precipitation in Japan which was about 4.7 did not change significantly in the past decade. The acidity of rainwater which was caused by H_2SO_4 and HNO_3 mainly was neutralized by alkaline species such as NH3 and Ca^{2+} in urban areas. In simulated acid rain experiments, visible foliar injury of most of the crop species and some sensitive tree species occurred at pH values below 3.5 and pH 3.0, respectively. It has been suggested that the decrease in intercellular pH levels is one of the possible mechanisms of occurrence of foliar injury. Acid rain droplets on leaves accelerate the leaching of cellular materials such as minerals, amino acids, proteins and carbohydrates, which may neutralize acidic rain droplets on the leaf surfaces. Since these materials which contribute to the buffering system of plants were leached by acid rain, residual H^+ ions may penetrate into the leaf tissues across the cuticular layer, and lead to the increase of the acidity in leaf tissues and development of foliar injury symptoms.

Discipline: Agricultural environment
Additional key words: crop, epicuticular wax, leaching, pH, acid rain

Introduction

Recently there has been a growing concern about global changes, namely planetary warming due to the increase of the concentration of greenhouse gases such as carbon dioxide, methane, nitric oxide and chlorofluorocarbons in the atmosphere, increase of ultraviolet-B radiation on the earth's surface caused by stratospheric ozone depletion, rapid depletion of tropical forest land by human activities associated with various land-uses or over-logging and expansion of desert areas due to over-grazing of livestock. On the other hand, it has been recognized for a long time that the emissions of sulfur and nitrogen oxides to the atmosphere from metal refineries, electric power plants and auto-exhaust gases caused local air-pollution problems. However, it is now being realized that the increase of these emissions could affect areas over distances a few thousand kilometers apart from the main emission source, resulting in the acidification of the atmosphere and adverse ecological effects in many regions of the world. Therefore, acid deposition (including both wet and dry deposition) has recently become a subject of widespread concern, in relation to global changes. This deposition occurs mostly in highly industrialized regions, mainly Europe and the eastern part of North America, as evidenced by the reports on the alteration of the chemistry and biology of lakes and marshes in the 1970s and terrestrial ecosystems in the 1980s[3].

Sulfur dioxide and nitrogen oxides emitted into the atmosphere may be transformed into particulates which can be transported over long distances. Particulate sulfur and nitrous compounds and sulfur dioxide or nitrogen oxides may be incorporated into precipitation by conversion to H_2SO_4 or HNO_3 associated with various chemical reactions and resulting in the decrease of the pH of precipitation. Under non-polluted conditions, natural acidity in precipitation may occur at around pH 5.6, a value which is in equilibrium with gas–liquid phase reactions between the atmospheric CO_2 concentration (about 350 ppm) and cloud water. Therefore, acid precipitation may be defined as rain, snow, fog, or other forms of precipitation with pH values less than 5.6 and a hydrogen ion concentration above 2.5×10^{-6} mol/*l*.

Both wet deposition such as rain, mist and snow and dry deposition such as acidic gases and aerosols may affect directly or indirectly plants in various aspects. The direct effects consist of foliar injury, leaching of cellular components from plant leaves and alteration of physiological and biological metabolism when the acid precipitation occurs on the surface of aerial parts of plants. The indirect ones appear when the wet and dry deposition of air pollutants enhances the acidity of soils, which induces the increase of solubility of phytotoxic aluminum ion in the soils, the acceleration of leaching of essential elemental magnesium and calcium for plant from soils, inhibition of activity or destruction of mycorrhizae, and increase of the susceptibility of plants to other stress factors such as drought, nutrient deficiency, and biotic pathogens.

Acid precipitation in Japan and its impact on plants were reviewed in a series of two papers. The first paper presents the current status of ambient precipitation in Japan and foliar injury due to acid precipitation. The second paper will analyse the possible impact of acidity in precipitation on growth or yield of agricultural crops and forest decline phenomenon.

Current status of acid precipitation in Japan

1) Background of acid precipitation studies

Studies on precipitation chemistry in Japan were initiated at the end of the 19th century. However, the significance of acid precipitation was not recognized in Japan until about 30,000 people suffered from eye and skin irritation arising from contaminated drizzle droplets, particularly in June and July of 1973 to 1974 in the Kanto District (Metropolitan Tokyo and its surrounding prefectures)[20]. Since then many studies on acid precipitation chemistry in Japan have been conducted by collecting data on pH and related chemical parameters in a number of prefectural institutes, national institutes and universities.

2) Sampler for precipitation

There are two types of samplers for precipitation: filtering bulk samplers and wet only samplers. Since the filtering bulk sampler is not fitted with a lid on the collecting funnel, it is exposed to the atmosphere all the time. On the other hand, the wet only sampler is covered during the periods without precipitation by a lid which automatically opens when it rains due to the presence of a rain sensor and a mortar. The filtering bulk samplers are currently being utilized in almost all the research institutes in Japan, while the wet only samplers have not yet been disseminated. A schematic illustration of the filtering bulk sampler is shown in Fig. 1. The rain collector of the filtering bulk sampler consists essentially of three parts: a collection funnel, a storage bottle and a membrane filter at the interface between the other two parts. The membrane filter fulfills three functions: separation of the soluble fraction of collected

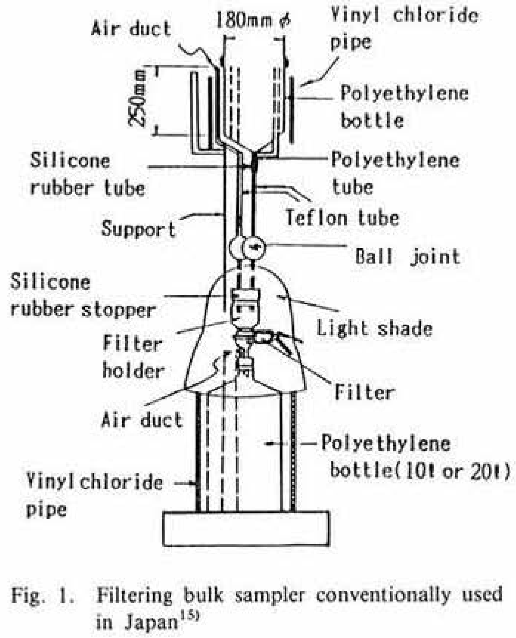

Fig. 1. Filtering bulk sampler conventionally used in Japan[15]

precipitation from insoluble substances, prevention of bacteria-induced chemical transformations of the filtrates, and reduction of the vaporization of rainwater in the storage bottle. The pH value determined by using the bulk sampler is somewhat higher, by 0.1 pH unit on the average, than that determined by using the wet only sampler[11], the difference being due to the dissolution of deposits of alkaline gases and particles during the periods without rain into rainwater[11].

3) *Annual mean pH of precipitation*

Hara[12] and Tamaki et al.[25] summarized the results of the phase 1 survey on acid precipitation carried out by the Japan Environment Agency (JEA) at 29 monitoring stations from April 1986 until March 1988. Fig. 2 shows the annual average pH (volume weighted) using bulk samplers for weelky collections[12]. The annual average pH at each station ranged from 4.5 to 5.2 with a mean value of 4.7 in Japan. This annual mean of pH 4.7 in Japan was similar to that recorded in the U.S.A. (regional annual average of 1980), Europe (EMEP network) and China (data from several sites during the period 1980–1984)[11].

4) *Ionic concentrations*

Mean ionic composition of precipitation over Japan is shown in Fig. 3[15]. It is considered that approximately 60% of the ionic components had originated from seasalt, since most of the monitoring stations were located in coastal areas. The sum of the equivalent concentrations of H^+, NH^{4+} and non-seasalt-Ca^{2+} (nss-Ca^{2+}) corresponded well with that of nss-SO_4^{2-} and NO_3^- reflecting the original acidity, the equivalent sum of H_2SO_4 and HNO_3, and the fact that the components were neutralized by ammonia and calcium species. The concentrations of nss-SO_4^{2-} and Ca^{2+} were estimated under the assumption that all the Na^+ was derived from seawater and that the ratios of Na^+ to seasalt-SO_4^{2-} and to Ca^{2+} were identical with those of seawater. Hara et al.[11] pointed out that if these alkaline species were not present in the precipitation, the resulting pH would have been 4.3, a decrease of 0.4 pH unit. The annual pH value did not change significantly in the past decade[24].

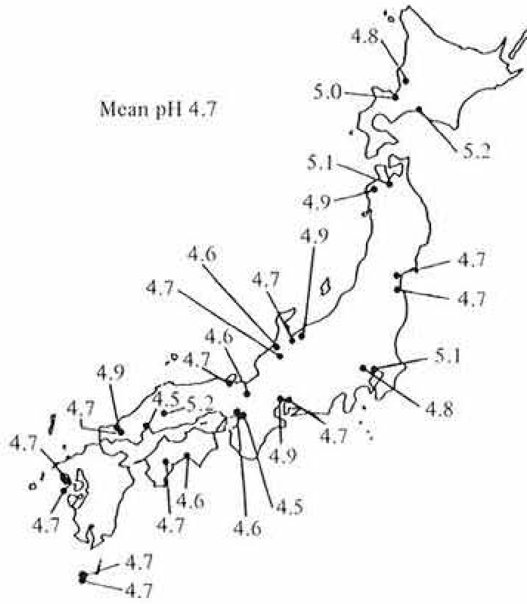

Fig. 2. Annual mean pH values of precipitation in Japan[12]
This illustration is cited from phase 1 survey on acid precipitation carried out by the Japan Environment Agency at 29 sampling stations from April 1968 to March 1988.

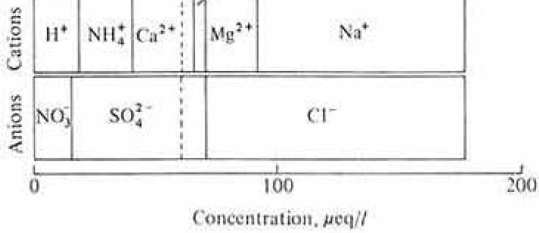

Fig. 3. Mean ion composition of precipitation[15]
This illustration is cited from phase 1 survey on acid precipitation carried out by the Japan Environment Agency at 29 sampling stations from April 1986 to March 1988. Annual mean ion composition of several major ions is as follows: H^+, 20; NH_4^+, 22; Ca^{2+}, 26; K^+, 4.6; Mg^{2+}, 21; Na^+, 86; NO_3^-, 16; SO_4^{2-}, 55; Cl^-, 108 $\mu eq/l$. The broken lines in the SO_4^{2-} and Ca^{2+} boxes indicate the partition of total ion amount into non-seasalt (left part) and seasalt origin (right part).

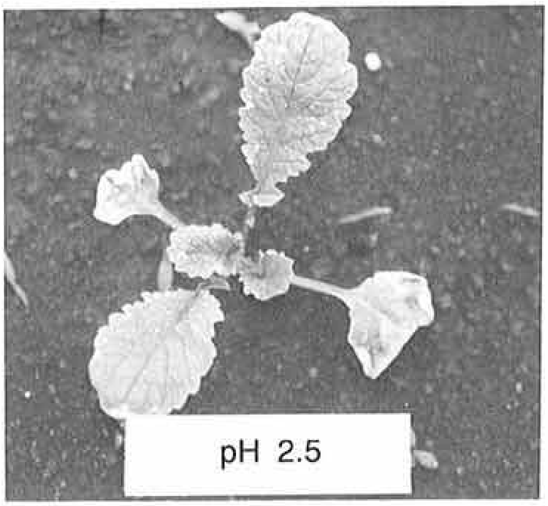

Plate 1. Bleached lesions on upper surface of radish leaves caused by simulated acid rain with pH 2.5

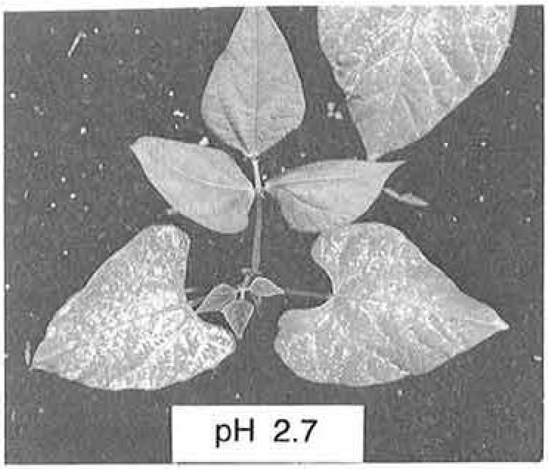

Plate 2. Relatively large brown necrosis on upper surface of primary leaves of bush bean after simulated acid rain precipitation occurred twice

5) Acid deposition

Deposition, defined as the product of concentration and rainfall amount, is another major parameter in the analysis of the acid deposition phenomenon. Annual mean deposition of several major ions is as follows: nss-SO_4^{2-}, 4.63; NO_3^-, 1.68; NH_4^+, 0.68; Ca^{2+}, 0.90 g/m^2/yr[12]. Deposition levels of nss-SO_4^{2-} and NO_3^- in Japan are comparable to or relatively larger than those in North America. It should be noted that Japan has a larger amount of rainfall, the average precipitation amounting to about 1800 mm/yr while 760 mm/yr in the U.S.A.

Foliar injury symptoms due to acid precipitation

Acid rain or mist induces bleaching or brown necrotic lesions on the upper surface of leaves and bleaching spots on petals (Plates 1 & 2). In simulated acid rain experiments, visible foliar injury of most herbaceous plants and some sensitive woody plants occurred at pH values below 3.5 and 3.0, respectively[14,16,21]. On the other hand, damage to petals of sensitive horticultural species like morning glory had been observed when the petals were exposed to natural and simulated acid rain at pH 4.3 or lower[19]. The degree of injury of leaves or petals by simulated acid rain depends upon the effective dosage which is a function of both hydrogen ion concentration and the period of exposure. The degree of injury increases with the increase in the hydrogen ion concentration (lowering pH) and the increase in the period of contact of acid droplets or films on the leaf or petal surface[9]. For example, small necrotic lesions on wormwood leaves appeared at a pH value of about 3.0, while larger areas of bifacial necrosis occurred at pH 2.5 or lower[2].

Foliar injury symptoms due to acid rain are attributed to the following processes[2]. As droplets or films of acid rain slowly evaporate, the concentration of ions (including protons) increases, and may result in the increase of local acidity, which leads initially to the collapse of a few epidermal cells, followed by progressive injury of the underlying mesophyll tissues (palisade and spongy parenchyma). The number of collapsed cells increases and the cells coalesce at a lower pH after repeated exposure to acid rain, resulting in the formation of necrotic lesions. Foliar lesions due to acid rain tend to occur where droplets normally accumulate along the side of a leaf vein or margins[2,7,8,22]. In addition, Evans[9] demonstrated in a variety of plant species that following the exposure to simulated acid rain about 95% of all the lesions occurred near the base of trichomes, the guard and subsidiary cells of stomata and along veins.

The susceptibility of crops to visible foliar injury was in the order of root, leafy, cole, legume, grain, and leaf and seed forage crops, respectively[17)].

Mechanisms of foliar injury by acid rain

1) Cuticle

Plant cuticle is composed of epicuticular wax, wax layer, cutin layer and pectin layer and covers the surface of leaves. The cuticle fulfills numerous functions and adaptive roles including the prevention of water evaporation from leaves and protection of leaf cells against physical and chemical injury. Therefore, the cuticle is the first target of acid rain and acts as the main barrier to acid rain. The crystalline epicuticular wax, on the surface of the cuticle, not only prevents the contact between droplets of precipitation and the leaf surface and decreases wettability, but also reduces water and ion movements into leaves[9,18,21)]. It is considered that the micropores in the cuticle act as the main route for the penetration of chemicals into the intracellular structures of leaves, as well as for cation exchange[4)]. The large number of cuticular micropores in specialized areas such as the base of trichomes, hydathodes, and glandular hairs may account for the fact that injury from acidic precipitation occurs more frequently at the base of trichomes and hydathodes[10)].

2) Erosion of cuticular wax

The decrease of the pH of droplets or films of acid rain which is accelerated by concentration processes involving evaporation leads to the erosion or degradation of cuticular wax. Strong acids are able to oxidize and hydrolyse the wax esters and to release some of the long fatty acid chains from the wax matrix. According to a review on the reaction of epicuticular wax of conifer needles to air pollutants (including acid rain) by Turunen and Huttunen[27)], the degradation of cuticular wax, which appears as a fusion of wax tubes in epistomatal chambers and eventually results in the amorphous appearance of wax, is the most common micromorphological type of injury observed in studies on fir, larch, spruce and pine trees. They concluded that the erosion of epicuticular wax is a significant factor for the multiple forest decline syndrome. On the other hand, Paparozzi et al.[22)] who used scanning and transmission electron microscopy did not observe any erosion of epicuticular or cuticular wax in either yellow birch or kidney bean after exposure to simulated rainfall with pH values as low as 2.8. Berg[4)] suggested that the disruption of the cuticle was a secondary effect associated with the loss of support from injured underlying cells.

Acid rain can erode wax as well as alter its biosynthesis, which may reduce the concentration of wax or modify the composition of wax[21)]. Thus the erosion and inhibition of biosynthesis of cuticular wax due to acid rain may drain cuticular wax and lead to the acceleration of cuticular transpiration and leaching of cellular components from leaves. The eroded and damaged epicuticular wax with cracks and rupture is more easily infiltrated or infected by fungal pathogens or insects than intact wax structures[27)], which may adversely affect the growth of agricultural crops or forest trees.

3) Buffering capacity to acid rain

Some plants appear to develop limited or do not experience foliar injury from acidic precipitation. It is possible that the plant tissues may effectively buffer the acid before the occurrence of any significant physical or physiological injury and this ability may differ among species[6)]. Adams and Hutchinson[1)] demonstrated that the leaves of wormwood, spinach and wax bean exhibited different buffering capacities. The initial pH values of simulated rain droplets (50 μl) which were 5.6, 3.5 and 3.0 usually increased after contact with leaves in certain plant species. However, when the initial pH was 2.5, the pH always decreased with time. The pH of the Parafilm surface (control) was always lower than the pH of any of the leaf surfaces, suggesting that the leaves produced substances that neutralized the acidity. The neutralization of acidic droplets was higher in wormwood plants, which showed the lowest sensitivity to foliar injury from simulated acid rain. Spinach leaves were the least able to neutralize acid droplets and also were most sensitive to foliar injury damage. Then Adams and Hutchinson[1)] concluded that the ability to neutralize acidic droplets on the leaf surface may be an effective mechanism for alleviating the damage caused by acid rain.

4) Foliar leaching

Although some foliar leaching normally occurs, the application of simulated acidic rain droplets on leaves of trees such as maple and spruce or crops such as bean accelerated the leaching of potassium, magnesium, calcium, amino acids, proteins and carbohydrorates from the leaves[23,28]. Wood and Bormann[28] demonstrated that K^+, Ca^{2+} and Mg^{2+} were leached from pinto bean leaves more rapidly at pH levels of 3.0 and 3.3 than at pH levels of 4.0 and 5.0. Leaching of cations involves exchange reactions on the leaf surface, in which cations on the exchange sites of the cuticle and cell walls are exchanged for H^+ from the leaching solutions[1]. Although these processes may partially neutralize acidic droplets on the leaf surface, prolonged exposure to acid rain droplets results in the exudation of salts from leaves, leading to increased damage due to the loss of the buffering capacity[13].

Foliar buffering and acceleration of leaching due to acidity may be related processes. As cellular materials which contribute to the buffering system of the plants were leached by acid rain, residual H^+ ions may penetrate into the leaf tissues across the cuticular layer, and lead to the increase of the acidity in leaf tissues and development of foliar injury symptoms[5].

References

1) Adams, C. M. & Hutchinson, T. C. (1984): A comparison of the ability of leaf surfaces of three species to neutralize acidic rain drops. *New Phytol.*, **97**, 463–478.
2) Adams, C. M., Dengler, N. G. & Hutchinson T. C. (1984): Acid rain effects on foliar histology of *Artemisia tilesii*. *Can. J. Bot.*, **62**, 463–474.
3) Adriano, D. C. & Jonhson, A. H. (ed.) (1989): Acidic precipitation (vol. 2) — Biological and ecological effects. Springer-Verlag, New York.
4) Berg, V. S. (1987): Plant cuticle as a barrier to acid rain penetration. *In* Effects of atmospheric pollutants on forests, wetlands and agricultural ecosystems. eds. Hutchinson, T. C. & Meema, K. M., Springer-Verlag, Berlin, 145–154.
5) Bytnerowicz, A., Temple, P. J. & Taylor, O. C. (1986): Effects of simulated acidic fog on leaf acidification and injury development of pinto bean. *Can. J. Bot.*, **64**, 918–922.
6) Craker, L. E. & Bernstein, D. (1984): Buffering of acid rain by leaf tissue of selected crop plants. *Environ. Pollut.* (Ser. A)., **36**, 375–381.
7) Evans, L. S., Gmur, N. F. & DaCosta. F. (1977): Leaf surface and histological perturbations of leaves of *Phaseolus vulgaris* and *Helianthus annus* after exposure to simulated acid rain. *Amer. J. Bot.*, **64**, 903–913.
8) Evans, L. S. & Curry, T. M. (1979): Differential responses of plant foliage to simulated acid rain. *Amer. J. Bot.*, **66**, 953–962.
9) Evans, L. S. (1982): Biological effects of acidity in precipitation on vegetation; A review. *Environ. Exp. Bot.*, **22**, 155–169.
10) Evans, L. S. (1984): Botanical aspects of acidic precipitation. *Bot. Rev.*, **50**, 449–490.
11) Hara, H. et al. (1990): Analysis of two-year results of acid precipitation survey within Japan. *Bull. Chem. Soc. Jpn.*, **63**, 2691–2697.
12) Hara, H. (1991): Acid precipitation chemistry of Japan. *Jpn. J. Limnol.*, **52**, 125–126.
13) Hutchinson, T. C. & Adams, C. M. (1987): Comparative ability of leaf surfaces to neutralize acidic raindrops. I. The influence of calcium nutrition and charcoal-filtered air. *New Phytol.*, **106**, 169–183.
14) Jacobson, J. S. & Van Leuken, P. (1977): Effects of acid precipitation on vegetation. *In* Proc. 4th Int. Clean Air Congress, 124–127.
15) Japan Environmental Agency (1990): Acid precipitation in Japan: The report of phase 1 survey.
16) Lee, J. J. et al. (1981): Effect of simulated sulfuric acid rain on yield, growth and foliar injury of several cops. *Environ. Exp. Bot.*, **21**, 171–185.
17) Legge, A. H. & Crowther, R. A. (1987): Acidic deposition and the environment: Overview, acid deposition research program. Calgary.
18) Martin, J. T. & Juniper, B. E. (1970): The cuticle of plants. St. Martin's Press, New York.
19) Nouchi, I. (1990): Effects of acid precipitation on agricultural crops and forest trees. *Taiki Osen Gakkaishi* (*J. Jpn. Soc. Air Pollut.*), **25**, 295–312 [In Japanese with English summary].
20) Ohta, S., Okita, T. & Kato, C. (1981): A numerical model of acidification on cloud water. *J. Met. Soc. Jpn.*, **59**, 892–901.
21) Percy, K. E. & Baker, E. A. (1987): Effects of simulated acid rain on production, morphology and composition of epicuticular wax and on cuticular membrane development. *New Phytol.*, **107**, 577–589.
22) Poparozzi, E. T. & Tukey, H. B., Jr. (1983): Developmental and anatomical changes in leaves of yellow birch and red kidney bean exposed to simulated acid precipitation. *J. Amer. Soc. Hort. Sci.*, **108**, 890–898.
23) Scherbatskoy, T. & Klein, R. M. (1983): Response of spruce and birch foliage to leaching by acidic mists. *J. Environ. Qual.*, **12**, 189–195.
24) Tamaki, M. & Koyama, I. (1991): The acid rain observed on ground level in Japan: A review of major recent issues and problems. *Taiki Osen Gakkaishi* (*J. Jpn. Soc. Air Pollut.*), **26**, 1–22 [In Japanese with English summary].
25) Tamaki, M. et al. (1991): Acid precipitation over Japan. *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*), 667–674 [In Japanese with English summary].

26) Tukey, H. B., Jr. (1970): The leaching of substances from plants. *Ann. Rev. Plant Physiol.*, **21**, 305-324.
27) Turunen, M. & Huttunen, S. (1990): A review of the response of epicuticle wax of conifer needles to air pollution. *J. Environ. Qual.*, **19**, 35-45.
28) Wood, T. & Bormann F. H. (1975): Increases in foliar leaching caused by acidificication of an artificial mist. *AMBIO*, **4**, 169-171.

(Received for publication, Dec. 18, 1991)