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Leaching of cell wall components caused by acid deposition on fir needles and trees

Ado Shigihara[a,*], *Kiyoshi Matsumoto*[a], *Naoki Sakurai*[b], *Manabu Igawa*[a]

[a]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*
[b]*Faculty of Integrated Arts and Science, Hiroshima University, 1-7-1, Kagamiyama, Higashi-Hiroshima, 739-8521, Japan*

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ABSTRACT

Virgin fir forests have been declining since the 1960s at Mt. Oyama, which is located at the eastern edge of the Tanzawa Mountains and adjacent to the Kanto plain in Japan. An acid fog frequently occurs in the mountains. We collected throughfall and stemflow under fir trees and rainfall every week during January–December 2004 at Mt. Oyama to clarify the influence of acid fog on the decline of fir (*Abies firma*) needles. In relation to throughfall and stemflow, D-mannose, D-galactose, and D-glucose are the major neutral sugar components; only D-glucose is a major component of rainfall. The correlation coefficient between the total neutral sugars and uronic acid (as D-galacturonic acid), which is a key component of the cross-linking between pectic polysaccharides, was high except for rainfall. The leached amount of calcium ion, neutral sugars, uronic acid, and boron is related to the nitrate ion concentration in throughfall. Results of a laboratory exposure experiment using artificial fog water simulating the average composition of fog water observed at Mt. Oyama (simulated acid fog: SAF) on the fir seedling needles also shows a large leaching of these components from the cell walls of fir needles. The leaching amount increased concomitantly with decreasing pH of the SAF solution. We also observed that a dimeric rhamnogalacturonan II-borate complex (dRG-II-B) that exists in the cell wall as pectic polysaccharide was converted to monomeric RG-II (mRG-II) by the leaching of calcium ion and boron. Results not only of field observations but also those of laboratory experiments indicate a large effect of acid depositions on fir needles.

1. Introduction

Forest decline, which can be caused by the dry deposition of air pollutants and wet deposition such as acid rain and acid fog on the forest canopy, is a serious environmental problem throughout the world (Ikeda et al., 1995). In addition to acid pollutants entering the forest ecosystem through precipitation and dry deposition, fog has an important impact on forest chemistry because it includes appreciable quantities of air pollutants and has a long residence time in the atmosphere. In Europe and North America, the serious effects of acid fog on forest decline have been underscored because the decline appears widely at high altitudes of mountainous regions (Saxena et al., 1989). Fog water with high acidity has been observed throughout Japan; fog waters with pH values of 2.80 and 2.90 have been reported respectively at Mt. Tsukuba (Ohta, 1981) and at Mt. Akagi (Murano, 1991). Forest decline in Japan has been reported in results of many studies: Siberian silver

* *Corresponding author*. Tel.: +81 45 481 5661; fax: +81 45 491 7915.
E-mail address: r200670202@kanagawa-u.ac.jp (A. Shigihara).

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birch (*Betula platyphylla* var. *japonica*) at Mt. Akagi (Ikeda et al., 1995) and Eastern white pine (*Pinus strobus*) forests at Tomakomai (Yoshitake and Masuda, 1986) are two examples.

The virgin fir (*Abies firma*) forest at Mt. Oyama (1252 m asl, 35°26′N, 139°14′E) has been declining since the 1960s, especially at altitudes of 700 m or more above sea level (Suzuki, 1992). Mt. Oyama is located at the eastern edge of the Tanzawa Mountains, which are adjacent to large source areas of air pollutants such as the Tokyo and Keihin industrial areas. The influence of air pollutants, especially that of SO_2, was pointed out by Suzuki (1992) at a time in the past when the annual mean SO_2 emission was estimated as 4×10^5 tons in Kanagawa prefecture in 1965 (Kanagawa Prefecture, 1994). In addition, beech (*Fagus crenata*) trees at the main peaks of the Tanzawa Mountains have been declining since the 1980s (Maruta and Usui, 1997).

At the midslope (700 m asl) of Mt. Oyama, we have continuously studied fog chemistry since 1988. Fog cover the top at the mountain for 46% of the year, as observed using a night view video camera, and acid fog waters with a pH value of less than 3 frequently occur at the site (Igawa et al., 1998; 2002b). Air pollutants are absorbed efficiently in fog droplets because the fog is suspended in the atmosphere for a long time. It is deposited on plant leaves in wooded regions. Many air pollutants are thereby loaded into plants via fog droplets, which can contribute to forest decline.

To investigate the effects of acid fog on plant growth, we performed a long-term exposure experiment (1992–1995, about 30 months) using simulated acid fog (SAF) of pH 3 on fir seedlings (6–7 years old), which indicated that the shoots of the seedlings died because of the exposure (Igawa et al., 1997). Moreover, the leaching amounts of Mg^{2+} and Ca^{2+} from the needles of the seedlings via ion exchange with H^+ and NH_4^+ in fog water increased with a pH decrease in the SAF. Leaching of the base cations, such as K^+, Mg^{2+}, and Ca^{2+}, from the needles agreed well with those observed in the throughfall in Mt. Oyama, which is an important finding for clarifying the forest decline mechanism by acid fog (Igawa et al., 2002a). In a previous study, we reported that a high content of boron in addition to Ca was observed in the throughfall under the declining fir forest canopy and was also observed from exposure to fog of the needles of fir twigs (Igawa et al., 2002a). Boron is an important trace element for plant growth (Warington, 1923) and cross-links rhamnogalacturonan II (RG-II) with pectic polysaccharide in the cell walls (Matoh et al., 1996). The cell wall pectic polysaccharides are also cross-linked with Ca^{2+}, which binds the carboxyl groups of polygalacturonic acid (Sakurai et al., 1991). To clarify the effects of acid deposition on the fir needles, more detailed information is needed.

The objectives of this study are the following.

(1) We analyze seven neutral sugar components, including L-rhamnose (Rha), L-fucose (Fuc), L-arabinose (Ara), D-xylose (Xyl), D-mannose (Man), D-galactose (Gal) and D-glucose (Glc), and D-galacturonic acid (GalUA) as uronic acid in the throughfall under fir trees. This paper presents the chemical composition of these sugars in the rainfall, throughfall, and stemflow and discusses important factors controlling the leaching process of these sugars. (2) We estimate the leaching of base cations and sugars from fir needles in laboratory exposure experiments using SAF. The leaching of sugars together with boron from the cell walls of needles is reported. In addition, we describe the boron-RG-II (RG-II-B) complex isolated from the cell walls of the fir and discuss the effects of acid fog on the form and molecular weight of RG-II-B.

2. Methods

2.1. Study site

The rainfall, throughfall, stemflow, and fog water samples were collected at the midslope (700 m asl) of Mt. Oyama, Kanagawa prefecture, which is the second most populous prefecture in Japan (Fig. 1). Mt. Oyama is about 50 km distant from the metropolitan area; its distance from Sagami Bay is about 20 km. The base of the mountain is situated along the paths of sea and land breezes between Sagami Bay and the Kanto plain, which is the largest source of air pollution in Japan. Virgin fir trees (about 100 ha) grow at 400–1000 m elevation on Mt. Oyama. However, above 700 m, large numbers of standing dead fir trees have been observed. The annual mean of ambient temperature, relative humidity, and total precipitation amounts at the observation period in Mt. Oyama (700 m asl) were, respectively, 12.1 °C, 73.8%, and 2059 mm. Forest soil types around Mt. Oyama are almost entirely composed of brown forest soils and black soils.

2.2. Sample collection

Field samples were collected during 5 January to 28 December 2004. The sampling interval was about one week. Rainfall samples ($n=27$) and throughfall samples ($n=114$) were collected using five collectors; a collector comprised a funnel, a polycarbonate filter holder (8 cm diameter) with a 1.0 μm pore size mixed-cellulose-ester-type membrane filter (Advantec Toyo Roshi Kaisha, Ltd.) at 1 m above the forest ground level, and a polyethylene sample storage bottle (2 l). Stemflow ($n=53$) samples were collected with double twisted gauze and a polyethylene sample storage bottle (10 l) (Sasa et al., 1990). Throughfall collectors were placed under four fir trees whose heights were 22–28 m. Stemflow samples were collected under two of the four fir trees. An open place with no tree stands was selected for collection of the rainfall sample. After the sample volume was measured using a measuring cylinder, the samples were transported to the laboratory at Kanagawa University, weighed and filtered through a 0.45 μm pore size cellulose type membrane filter (Advantec Toyo Roshi Kaisha, Ltd.). The filtered samples were divided for major ion analysis and for sugar analysis and preserved at 4 °C in a refrigerator until component analysis. To the samples for sugar analysis, trace ethanol was added to prevent degradation. The samples were concentrated to about 2 ml using a rotary evaporator (N-1000V; Tokyo Rikakikai Co. Ltd.) operating in a water bath at 30 °C and then preserved at −20 °C until analysis. Fog water samples were collected at 700 m altitude in Mt. Oyama using an automatic string-type fog water collector (FWG-800; Usui Kogyo Kenkyusho Inc.) with two Teflon string screens (collection efficiency, 0.829; flow rate, 12 m^3 h^{-1}), a refrigerator to store the samples, and a time recorder. After collection, the