PHOTOCHEMICAL FORMATION OF OH RADICALS IN DEW FORMED ON THE PINE NEEDLES AT MT. GOKURAKUJI

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Abstract. Photochemical formation rates and sources of the hydroxyl (OH) radical were determined in dew water formed on the surface of Japanese red pine (Pinus densiflora) needles of declining (NO2 polluted area) and healthy pine stands at Mt. Gokurakuji located west of Hiroshima city in western Japan. The measured OH radical photoformation rates in dew water (n=10), which were normalized to the rate at midday on May 1 at 34°N, ranged from 0.67 to 5.18 µM h⁻¹ (1M=1mol L⁻¹). The mean value (2.69 µM h⁻¹) was higher than that in dew water collected on a Teflon board and higher than the mean value in rain water published previously. Of the total OH radical formation rate observed in dew water on the pine needles, 16.4 % was estimated to originate from N (II) (NO2 and HNO2) and 24.6 % was estimated to originate from NOx. There were other sources of OH radical photochemical formation in dew water on the pine needles besides photolysis of NOx and NO2.

Keyword: dew water, hydroxyl radical, NOx, NO2, photochemical formation

1. Introduction

Photochemical formation of oxidants such as hydrogen peroxide and hydroxyl (OH) radical in cloud and fog waters significantly affects atmospheric chemical cycles (Faust and Allen, 1993). Due to their high reactivities, hydrogen peroxide and organic peroxides cause oxidative stresses in plants, and have been suggested to cause forest decline (Moller, 1989; Hewitt et al., 1990). Among all the oxidants, the OH radical is known to be the most reactive one. The OH radical generating solutions reduced the stomatal conductance of the needle of the Japanese red pine (Pinus densiflora) seedlings (Arakaki et al., 2000), although the behaviour of the OH radical in wet depositions on plants are not well known.

As a first step, we have investigated photoformation of the OH radical in rain water (n=69) collected at rain events and in dew water (n=28) collected on a pre-cleaned Teflon board in early morning during June, 1997 to June 1998 in Higashi-
Hiroshima city (Arakaki et al., 1999). Those investigations indicated that OH radical photoformation rates in dew water were higher than in rain water (mean: 1.25 and 0.35 \( \mu \text{M h}^{-1} \) normalized to midday of May 1 at 34° N). Furthermore, they indicated that nitrite ion (NO\(_2^+\)) photolysis accounted for the majority of OH radicals formed in dew water (mean: 106.8% of the total OH radical photoformation rate).

A severe decline of Japanese red pine tree (Pinus densiflora Sieb. et Zucc.) have been observed on the urban-facing area at Mt. Gokurakuji (34°23'N, 132°19'E, and 693m a.s.l. top height) which is located west of Hiroshima City. On this area, high concentrations of NO\(_x\) from heavy traffic could be the main cause of the pine tree decline (Naemura et al. 1997; Kume et al. 2000), and NO\(_x\) accumulated on long-living pine needles (Naemura et al., 2000). We expect that the chemical substances in dew water on pine needles that are sources of the OH radical are different from those on a Teflon board. While there are many reports on the chemical composition of dew water collected on Teflon and polystyrene boards (Mulawa et al., 1986; Foster et al., 1990; Pierson and Brachaczek, 1990; Wagner et al., 1992; Okochi et al., 1996; Takenaka et al., 1999; Ortiz et al., 2000; Takeuchi et al., 2000), there are few reports on the composition of dew water collected on the plant leaves (Brimblecombe and Todd, 1977).

To better understand OH radical photochemical formation on plant leaves, we have collected dew water formed on the surface of Japanese red pine needles in Mt. Gokurakuji, Hiroshima Prefecture, Japan. In the present study, we report (i) the chemical composition, (ii) the photochemical formation rates of the OH radical and (iii) sources of the OH radical in dew formed on the surface of pine needles.

2. Materials and Methods

2.1. Collection of Dew Formed on Pine Needles

Dew water formed on the surface of pine needles were collected from declined pine trees in a declining stand (430m a.s.l.) on the urban-facing side and from healthy pine trees in a healthy stand (130m a.s.l.) on the mountain-facing side of Mt. Gokurakuji from Oct. 18 to Nov. 22 1999. Dew water was collected on the same day at each stand. On the second day following a rain event, between 6:00 and 9:00 in the morning, dew droplets were collected from pine needles at a height of 1-2 m and placed directly in the polyethylene bottles. These collections were made before intense sunlight directly irradiated the dew. Soon after the collection, the dew water was filtered through a 0.45\( \mu \text{m} \) polysulfone membrane filter and stored in the refrigerator at 4°C until chemical analysis.

2.2. Analytical Methods

Within 48 hours of sample collection, OH radical formation rates were determined by