

Measurements of Gaseous Peroxides in the Oceanic Lower Atmosphere

S. Hatakeyama^{1*} and T. Akatsuka²

¹*Institute of Agriculture, Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan*

²*Graduate School of Agriculture, Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan*

*E-mail: hatashir@cc.tuat.ac.jp

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Introduction

Hydrogen peroxide (H_2O_2) is formed by atmospheric photochemical reactions and plays a role of a reservoir for HO_x radicals. It oxidizes sulfur dioxide (SO_2) in air to form an important component of acid rain, sulfate (SO_4^{2-}), which results in the acidification of atmosphere. H_2O_2 is assumed as one of the causative materials for forest decline (Masuch *et al.* 1986). Moreover, when it is adsorbed on aerosol particles and inhaled, it can induce lung epithelial cell damage (Hasson and Paulson 2003).

On the other hand, the East China Sea area is a place where a large amount of air pollutants emitted in the East Asian region are transported to the lower marine boundary layer. Chemical transformation of pollutants during the transport mainly occurs by photochemical reactions taking place in the atmosphere with HO_x radicals. H_2O_2 can act as an indicator of the oxidizing potential of the area. Therefore, measurement of H_2O_2 is important from the point of view of not only the effect on human health, but also the chemical reactions taking place in the target area.

The objectives of this research were to measure H_2O_2 in the marine boundary layer and to analyze its temporal, as well as spatial variations in terms of its transport and various emission sources.

Method

The observations were carried out at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS, $26^\circ 87' \text{ N}$, $128^\circ 26' \text{ E}$, Fig. 2). Okinawa Main Island often receives air masses from China, Korea, and Japan, as well as from the Pacific Ocean. In addition, we can sometimes observe air masses transported from South East Asia. Around the station there is no significant local emission source. The nearest big city is Nago, which is located 50 km southwest with a population of 60,000. The capital of Okinawa prefecture, Naha (population 310,000), is one hundred km southwest of Nago. These cities are far from the station but sometimes we could observe the effects of local emission from these cities, depending on the wind direction.

Intensive measurements were made on Feb. 4–5, 2008 (spring), June 10–14, 2008

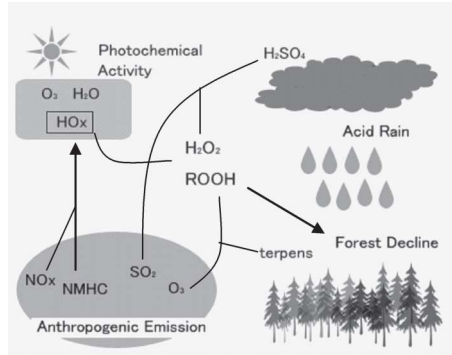


Fig. 1. Dynamics of peroxides in the atmosphere.

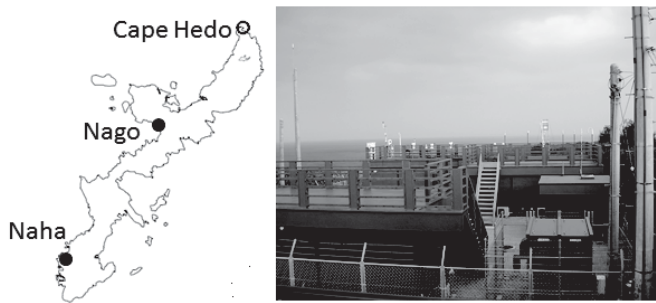


Fig. 2. Location of the station (left) and view of the station (right).

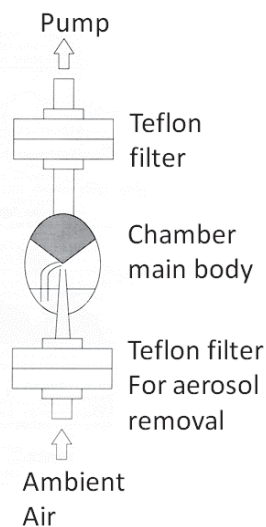


Fig. 3. Image of a mist chamber.

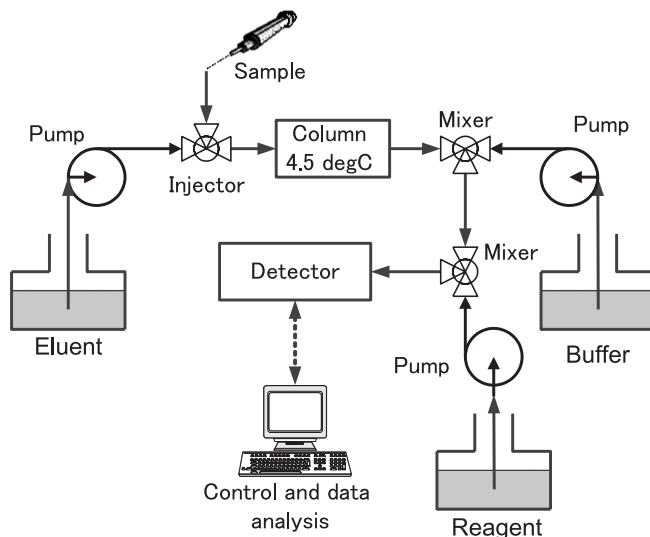


Fig. 4. Schematic diagram of an HPLC system.

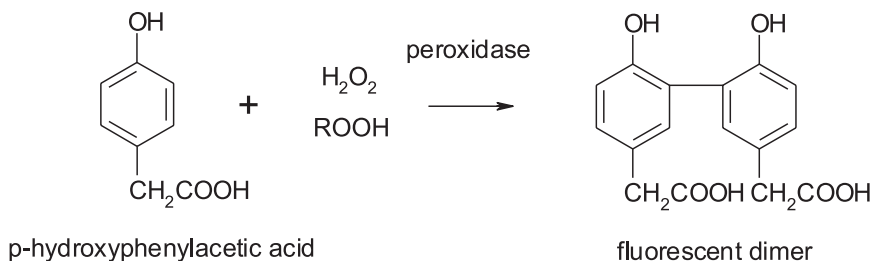


Fig. 5. Reactions to form a fluorescent dimer.

(summer), and Oct. 22–26, 2008 (autumn).

The sampling of peroxides was performed with a glass mist chamber (Fig. 3). Mist chambers have the merit of enabling a large volume of air to be collected in a short period of time, and a collection efficiency of H_2O_2 of almost 100%. During the sampling, the mist chamber was wrapped in aluminum foil to avoid photolysis of the collected H_2O_2 . The sampling time was 25–30 min. The volume of sampling air was measured with a wet flow meter.

Many analysis methods have been utilized for measuring the concentration of

peroxides (Gunz and Hoffmann 1990). In this work, we used a high performance liquid chromatography method for qualitative and quantitative analyses. HPLC analyses were carried out as soon as the samplings were finished. A schematic diagram of the analysis is shown in Fig. 4. By taking into account the facile decomposition of hydroperoxides on a metallic surface, a polymer tubing and column were used. The analytical conditions were as follows.

Eluent: pH 3.5 H_3PO_4 solution flow rate: 0.5 mL/min, Buffer: 0.01M- KH_2PO_4 and NaOH for pH 9.4, flow rate: 0.2 mL/min, Fluorescence Reagent: 0.01M-

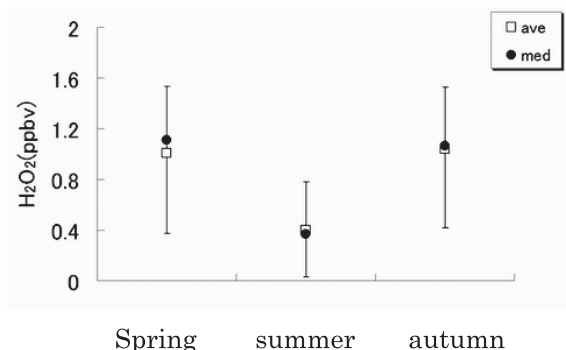


Fig. 6. Seasonal variation of H₂O₂ at CHAAMS.

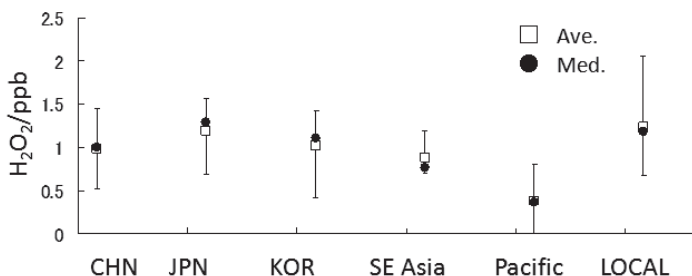


Fig. 7. Concentrations of H₂O₂ from different source regions.

KH₂PO₄ 0.01 mg/mL-p-hydroxyphenylacetic acid 0.02 mg/mL-horseradish peroxidase flow rate: 0.2 mL/min.

For high sensitivity analyses, a post column reaction, i.e., p-hydroxyphenylacetic acid reacts with H₂O₂ to form a fluorescent dimer in the presence of horseradish peroxidase, was utilized (Fig. 5)

Results and Discussion

The presence of atmospheric H₂O₂ is, in general, high in summer and low in winter (Kang *et al.* 2002; Huang *et al.* 2004). These reports were mainly based on data obtained in urban or suburban areas. Ob-

servations made in a background area are very rare. In this work, we compared the data obtained in a background area with previous urban, or suburban, data. As shown in Fig. 6, the concentration of H₂O₂ was higher in spring and autumn than in summer. Average concentrations were 1.01 ppb in spring, 0.40 ppb in summer, and 1.04 ppb in autumn. This seasonal variation is different from the previous results mentioned above. In Okinawa, most air masses come from the Pacific Ocean in summer and the effect of East Asia is small. Clean oceanic air covered the observation area. That is the reason for the low concentration of H₂O₂ in summer in Okinawa.

Average concentrations of H₂O₂ were

also classified based on the back trajectories by source regions as shown in Fig. 7. Air masses transported over China, Korea, and Japan contained a higher concentration of H_2O_2 than that from the Pacific Ocean. Average concentrations of H_2O_2 in the air mass transported from Japan, China, Korea, and the Pacific were 1.19, 0.98, 1.02, and 0.39 ppb, respectively. H_2O_2 in the air mass transported from China was lower than that transported from Japan. That was contrary to our expectation. However, the air mass from China usually contained sulfate, simultaneously. It seems that H_2O_2 was used for the oxidation of SO_2 in the air mass from China.

On the other hand, the average concentration of H_2O_2 in the air mass affected by the local emission in Naha or Nago was 1.23 ppb as is shown as "LOCAL" in Fig. 7, which is the highest concentration

shown.

The concentration of H_2O_2 showed a high correlation with O_3 concentration ($r = 0.71$). A high concentration of H_2O_2 was often observed under conditions of a high concentration of O_3 . Under conditions of strong sunshine in summer the formation of H_2O_2 seemed to be accelerated. A high concentration of aerosol lowered the concentration of H_2O_2 . It can be speculated that H_2O_2 , which has a very high solubility in water, can easily be adsorbed on an aerosol surface.

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