

### C-1.3.3 Studies on the Formation Process of Acidic and Oxidative Substances in Air

**Contact Person** Shiro Hatakeyama

Senior Research Scientist,

Global Environment Division, National Institute for Environmental Studies,  
Environment Agency

16-2, Onogawa, Tsukuba, Ibaraki 305, Japan

Phone +81-298-50-2502, Fax +81-298-56-7170

E-mail: hatashir@nies.go.jp

**Total Budget for FY1994 - FY1995** 14,275,000 Yen (FY1995; 6,190,000 Yen)

**Abstract** Formation mechanism of organic peroxides in ozone-olefin reactions was studied. Main organic peroxides studied were methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ , MHP), hydroxymethyl hydroperoxide ( $\text{HOCH}_2\text{OOH}$ , HMHP), and 2-hydroxyethyl hydroperoxide ( $\text{HOCH}_2\text{CH}_2\text{OOH}$ , 2-HEHP). A large volume photochemical reaction chamber was employed for experiments. The mist chamber technique was introduced to collect hydroperoxides in air. It was found that the Criegee intermediate ( $\text{CH}_2\text{OO}$ ), which is the primary product of ozone-olefin reactions, reacts with water vapor to give HMHP. 2-HEHP was only found in ozone-ethylene reactions. This compound was identified as MHP in previous studies. We found a small difference in HPLC retention time between MHP and the product of ozone-ethylene reactions. It was speculated that the compound must be 2-HEHP formed by a side reaction, *i.e.*, an OH-ethylene reaction.

High concentration of ozone was observed at Mt. Maeshirane, where serious forest decline is visible. A battery driven ozone sensor and a small data logger were used with batteries and solar panels. More than 100 ppb of ozone was observed when wind blew from south east, which indicates the impact of a large amount of emission of atmospheric pollutants in Tokyo metropolitan area.

Analysis techniques for atmospheric peroxides were developed and applied for field measurements.

The reactions of  $\text{SO}_2$  on the surface of Kosa particles were also investigated employing a cylindrical reaction vessel. Collected Kosa particles and desert soil particles collected in China were submitted for experiments.

**Key Words** Organic Peroxides, Hydrogen Peroxide, Kosa Particles, OH Radicals

#### 1. Introduction

Acid deposition is an expression of the acidification of the tropospheric atmosphere. In order to understand this phenomenon it is necessary to deepen our understanding of the processes of emission, transport, transformation, and deposition of atmospheric pollutants in the troposphere. Particularly, it is required to make a model more precise and reliable when we estimate the future state of the environment. To improve the reliability of models it is important to develop a new technique to analyze acidic and/or oxidative substances which were not paid attention to so far, and also to investigate the formation/transformation mechanisms of those substances.

In this project three studies were done. [1]The clarification of the formation mechanisms of organic hydroperoxides in air. This type of compounds are thought to be very toxic to plants. They are also thought to take part in the oxidation of  $\text{SO}_2$  in aqueous solution. [2]The development of the technique to analyze peroxidic compounds and the application of the

technique for field measurements. [3]The experiments of the oxidation of SO<sub>2</sub> on the surface of Kosa or soil particles. Kosa particles are transported from Asian continent in every spring. They neutralize the acidic substances with contained calcium carbonate on the one hand, they promote the oxidation of SO<sub>2</sub> on their surfaces on the other hand.

## 2. Research Method, Results, and Discussion

### [1] Formation mechanisms of organic peroxides that can take part in the forest damage and the observation of high concentration of ozone in mountainous region around Kanto Plain

These days serious forest damage is seen in mountainous area around Kanto Plain. The cause for the damage is not specified by now. NAPAP<sup>1)</sup> pointed out that ozone can be the largest contributor to such forest damage. Takahashi *et al.*<sup>2)</sup> reported that the area of seriously damaged forests in Kanto Plain overlaps very well with the area of high concentration of photochemical oxidant. Organic peroxide is another candidate for the cause of forest decline because it is reported to be formed in the reactions of ozone with natural hydrocarbons emitted by plants. Hewitt and Terry<sup>3)</sup> pointed out that organic peroxides are more toxic to plants than ozone itself. Therefore, it is important to clarify the formation mechanism of organic peroxides in air. And it is necessary to confirm that high concentration of ozone reaches those area where serious forest decline is observed.

#### (1) Experiments

A 4 m<sup>3</sup> photochemical reaction chamber was employed to make the experiments of the reactions to form organic peroxides. Reactants studied were isoprene, α-pinene, β-pinene, 1-methylcyclohexene, methylenecyclohexane, ethylene, propene, and 2-butene. One of these hydrocarbons was reacted with less than half initial concentration of ozone.

Products were collected in distilled water with a mist chamber (Fig. 1)<sup>4)</sup> and analyzed with a high performance liquid chromatography (HPLC) equipped with a fluorescence detector. In order to improve the separation and to avoid decomposition of peroxides inside, the separation column was kept cooled at around 1 °C. For ethylene-OH reactions photo-decomposition of hydrogen peroxide was used as a source of OH radicals. Gaseous mixture of ethylene and hydrogen peroxide was irradiated with xenon arc lamps with quartz windows.

Ozone was monitored with a conventional UV-absorption ozone monitor. Hydrocarbons were monitored intermittently with an FID-gas chromatograph.

Concentration of ozone was measured from August 19 to 20, 1995 near the summit of Mt. Maeshirane (2,377 m) at the altitude of about 2,320 m. An electro-chemical ozone sensor working on batteries and solar panels was used with a small data logger (Fig. 2).

#### (2) Results and Discussion

##### i) Formation mechanisms of organic peroxides in ozone-olefin reactions<sup>5)</sup>

Figures 3a, b, and c are chromatograms of the products formed by the reaction of ozone with isoprene, 1-methylcyclohexene, and methylenecyclohexane, respectively. As shown in Fig.

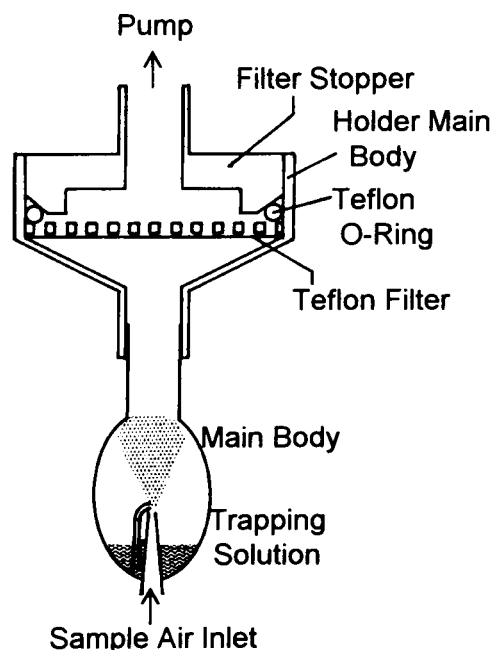


Fig. 1: Outline of a mist chamber

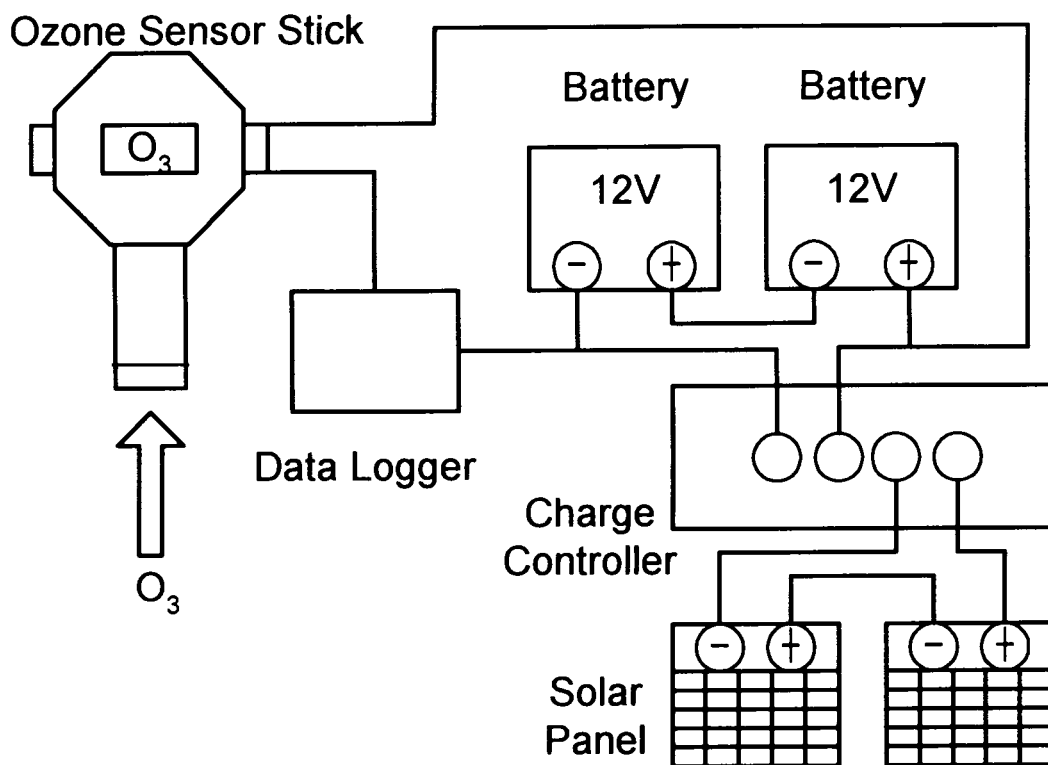


Fig. 2: Ozone-sensor, small data logger, batteries, and solar panels

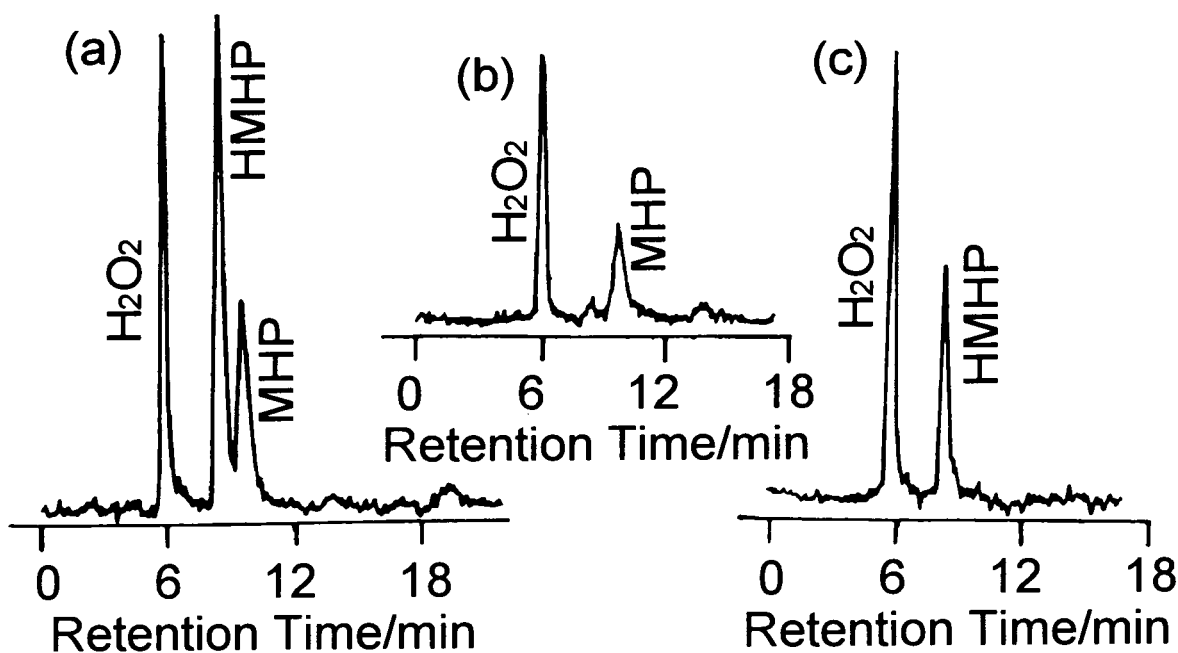
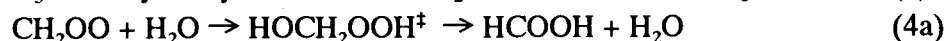
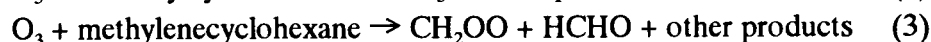
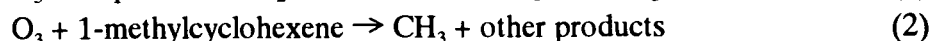
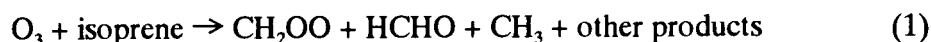


Fig. 3: Chromatograms of the products of the reactions of ozone with isoprene (a), 1-methylcyclohexene (b), and methylenecyclohexane (c).

3a, isoprene yielded  $H_2O_2$ , HMHP, and MHP as major peroxidic products. Some unidentified peaks in the chromatogram were observed. 1-Methylcyclohexene gave  $H_2O_2$  (molar yield: 1.2-1.6 %) and MHP (1.6-1.7 %), mainly, with a very small amount of HMHP (<0.02 %). From methylenecyclohexane  $H_2O_2$  (0.5-1.3 %) and HMHP (0.4-3.0 %) were produced. Formation of the above products can be explained as follows. The reaction of  $CH_2OO$  with water gives

HMHP. We have reported that the Criegee intermediate can react with water to give formic acid *via* hot HMHP (Reaction 4a).<sup>6,7</sup> The result of this study shows that the hot HMHP thus formed is stabilized (Reaction 4b) to some extent. MHP is formed by the reaction of CH<sub>3</sub>OO radical with HO<sub>2</sub> radical (Reaction 5-6).



Since methylenecyclohexane has no methyl group, no MHP was formed. 1-Methylcyclohexene does not have a terminal methylene group, it cannot form CH<sub>2</sub>OO directly. Thus, the yield of HMHP from 1-methylcyclohexene was quite low. Since isoprene has not only a methyl group but also terminal methylene groups, both HMHP and MHP were formed.

ii) Formation mechanisms of 2-HEHP in ethylene-OH reactions<sup>9)</sup>

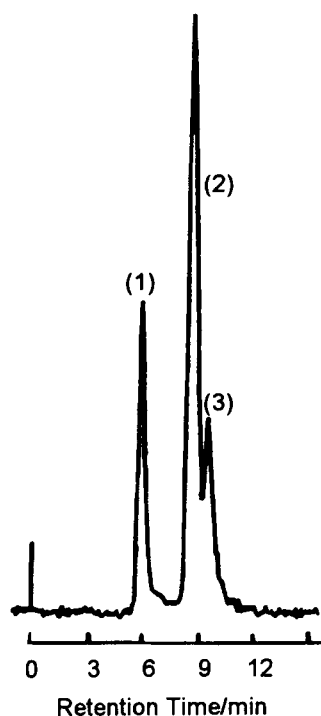
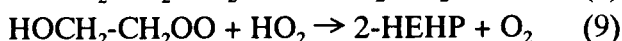


Fig. 4: Chromatogram of the products of the ozone-ethylene reaction. (1): H<sub>2</sub>O<sub>2</sub>, (2): HMHP, (3): 2-HEHP

The reaction of ozone with ethylene gave three distinct peroxide products. The liquid chromatograph peaks No. 1 and No. 2 shown in Fig. 4 correspond to H<sub>2</sub>O<sub>2</sub> and HMHP, respectively. The molar yields of H<sub>2</sub>O<sub>2</sub> and HMHP in dry air were 1.1 % and 2.8 %, respectively. Peak No. 3 appeared very soon after that of MHP. The yield of this compound was estimated to be ~2 %. This peak was assigned to MHP in previous studies. However, the retention time of peak No. 3 (9.4 ± 0.06 min) was slightly shorter than that of MHP (9.6 ± 0.06 min). Reactions of ozone with each of the alkenes which have a methyl group attached to the double bond gave a product peak at 9.6 min. For example, propene, 2-butene, isoprene, 1-methyl cyclohexene, and α-pinene gave peaks identical to that of MHP standard. Thus, we concluded that peak No. 3 in the chromatogram shown in Fig. 4 is not MHP, but 2-HEHP (HOCH<sub>2</sub>CH<sub>2</sub>OOH). Formation of 2-HEHP can be easily explained by OH reactions with ethylene (Reactions 7-9), if we take into account the generation of OH in ozone-olefin reactions.



In order to check the possibility of OH reactions, OH-ethylene reactions were examined. OH reactions of ethylene in air in the absence of NO produced a compound which showed an HPLC peak at a retention time of 9.4 min. The 9.4 min peak was formed even in the initial stage of the reaction. The yield of this compound was nearly constant during the reaction. Thus, we conclude that this is a direct product of the OH-

ethylene reaction, and it must be 2-HEHP.

iii) High concentration of ozone at high elevation mountainous area<sup>9)</sup>

Concentration of ozone was measured from August 19 to 20, 1995 near the summit of Mt. Maeshirane (2,377 m) at the altitude of about 2,320 m. An electro-chemical ozone sensor working on batteries and solar panels was used with a small data logger. High concentration of ozone up to 109 ppb was observed (Fig. 5, solid line). Ozone concentration was high when wind blew from south east. The concentration of ozone was much lower (Fig. 5, broken line) at a nearby field station (near Yumihari Pass, altitude ~1,450 m) around which forest decline is not observed. It indicates that ozone is one of the most important causes of forest damage observed around Mt. Shirane.

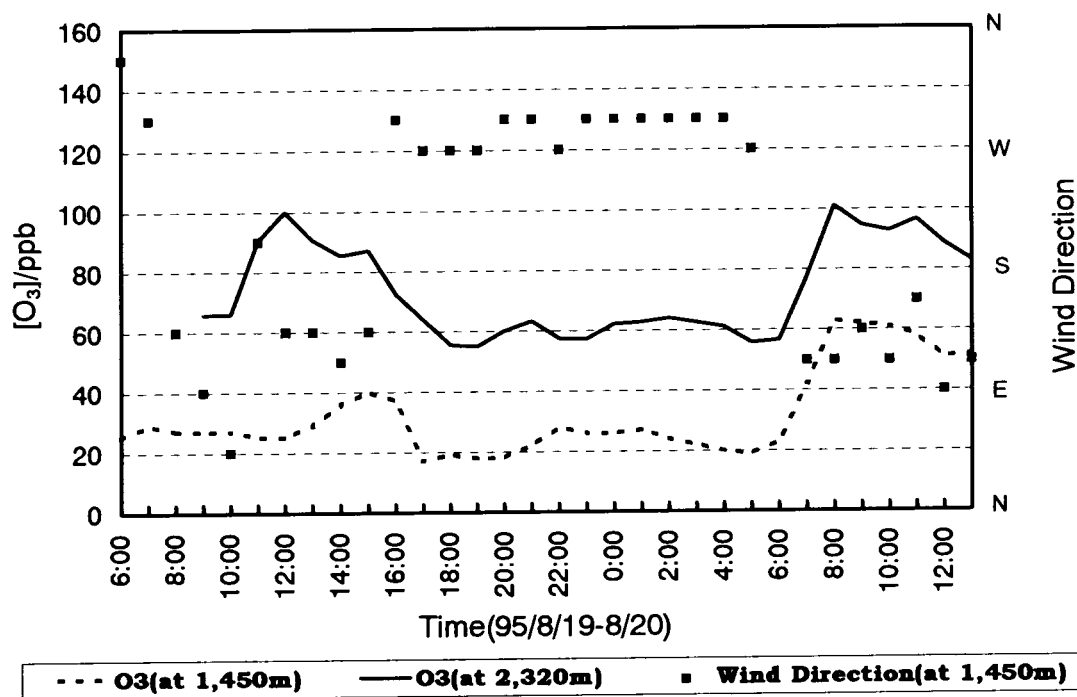


Fig. 5: Ozone measured at Mt. Maeshirane (2,320 m) and at the field station (1,450 m) as well as wind direction at the field station

[2] Measurements of peroxides in the atmosphere

Aqueous oxidation of SO<sub>2</sub> is one of the major sources of atmospheric sulfuric acid. H<sub>2</sub>O<sub>2</sub> is the main oxidizing agent in liquid phase oxidation of SO<sub>2</sub>. Organic peroxides are also important as oxidizing agents. In this study a technique to measure H<sub>2</sub>O<sub>2</sub> as well as total organic peroxides was developed and applied to field measurements.

(1) Experiments

H<sub>2</sub>O<sub>2</sub> and organic peroxides were measured with flow injection method that utilizes the formation of fluorescent dimers of *p*-hydroxyphenylacetic acid in the presence of peroxidase. Since H<sub>2</sub>O<sub>2</sub> can be decomposed by catalase very easily, the difference in the concentrations of peroxidic substances between the sample with 500 units/mL of catalase and that without catalase was taken as the concentration of H<sub>2</sub>O<sub>2</sub>. Similarly, the difference in the concentrations of peroxidic substances between the sample with 5000 units/mL of catalase (all peroxides were assumed to be decomposed) and that with 500 units/mL of catalase was taken as the concentration of total organic peroxides.

(2) Results and Discussion

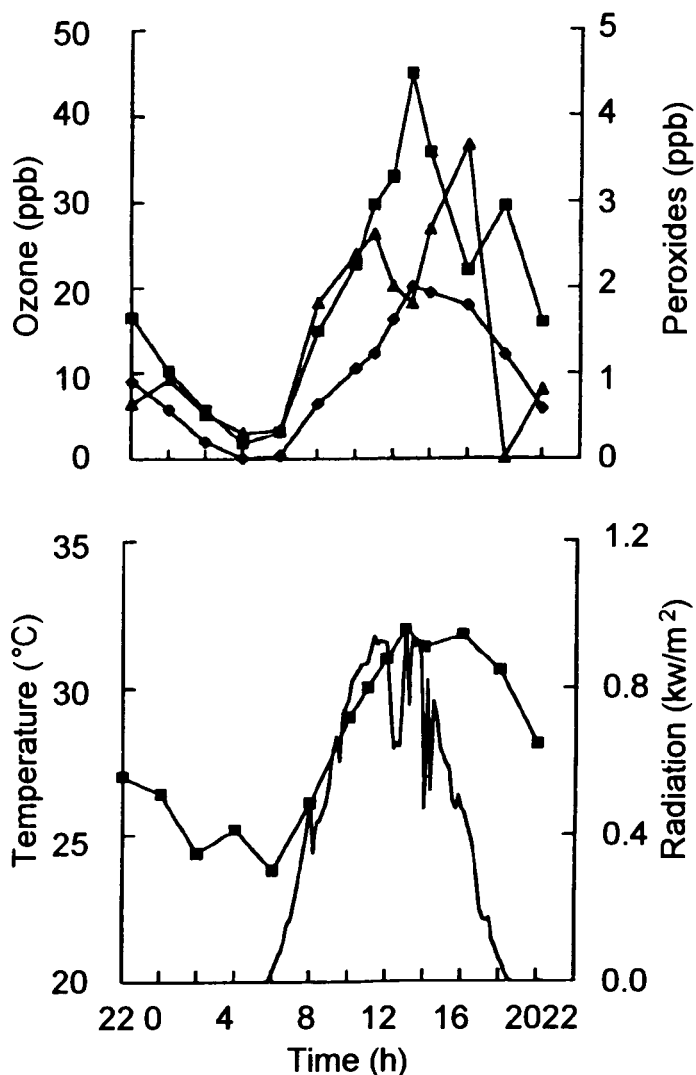


Fig. 6: Time variation of ozone, H<sub>2</sub>O<sub>2</sub>, organic peroxides, temperature, and radiation

reactor.

### (1) Experiments

Figure 7 shows the reactor. It is a dual glass cylinder and the inner cylinder is divided into ten sectors. The outer surface of the inner cylinder was coated with powdered Kosa particles. Reactant air containing 400 ppb of SO<sub>2</sub> was flown through the cylinder for 15 h or 20 h at 25 ± 1 °C. Concentration of SO<sub>2</sub> was monitored at the entrance and the exit of the reactor with an SO<sub>2</sub> monitor (Kimoto Model-317).

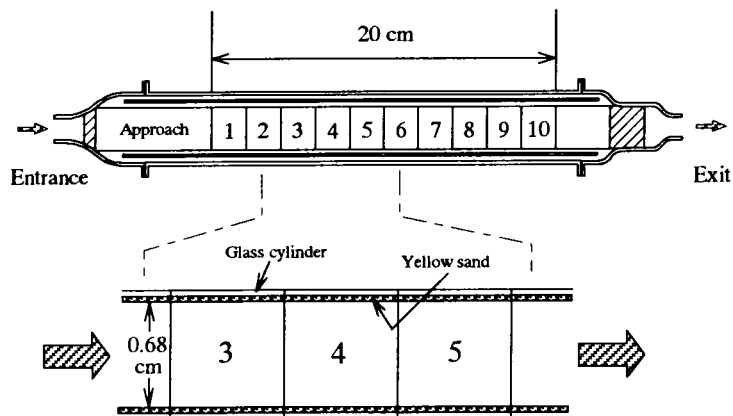


Fig. 7: Outline of a flowreactor

Typical concentration changes of ozone, H<sub>2</sub>O<sub>2</sub>, and total organic peroxides measured on August 5, 1995 are shown in Fig. 6 with the variation of temperature and radiation intensity. Ozone and H<sub>2</sub>O<sub>2</sub> followed the variation of radiation well. Under the conditions of very weak radiation, however, the change of the concentration was very complicated. In August the maximum concentrations of H<sub>2</sub>O<sub>2</sub> and organic peroxides reached 5 ppb and 4ppb, respectively, but in April daily maximum concentration was 1 ppb.

### [3] Oxidation of SO<sub>2</sub> on Kosa particles

Kosa (yellow sand) is originated in the deserts in China and transported with the north west monsoon to Japan. In some cases sulfate and fluoride are enriched in Kosa particles compared to the original desert soil, which indicates that SO<sub>2</sub> and HF are adsorbed during the transport of Kosa. Kosa particles are mainly composed of basic soil and it can neutralize atmosphere and soil after deposition. In this study a cylindrical flow reactor was used to allow the reaction of SO<sub>2</sub> with the soil particles coated on the surface of the

After the experiments the sectors of odd number were submitted for analysis of deposited components and the sectors of even number were submitted for the analysis of carbonated contained in Kosa particles.

Anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$ ) and cations ( $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) in water soluble components in Kosa particles were analyzed with an ion chromatograph and an atomic flame-emission/atomic absorption spectrometer, respectively. The analysis of carbonate was done as

follows. First the carbonates contained in Kosa particles were converted to  $CO_2$  with dilute phosphoric acid. Then the amount of  $CO_2$  was measured with NDIR.

## (2) Results and Discussion

Concentrations of  $SO_2$  at the exit of the flow reactor are plotted in Fig. 8. In the experiments employing the carbonate-poor soil sampled at Wuchuan the exit concentration of  $SO_2$  got back quickly. On the other hand, the exit concentration of  $SO_2$  did not get back even after long-term exposure in the experiments employing carbonate-rich soil of Yinchuan and Cele. No desorption of  $SO_2$  from the coated Kosa particles was observed by flowing pure air over them after 20 h exposure of reactant gas. Thus, it can be concluded that  $SO_2$  is chemically absorbed on Kosa particles.

Deposited amount of  $SO_2$  and decreased amount of carbonates are plotted in Fig. 9. In the carbonate-rich sample of Huoyanshan the amount of deposited  $SO_2$  and that of decreased carbonate is larger at around entrance of the reactor, which is in marked contrast to the result in carbonate-poor soil of Wuchuan.

Those results clearly shows that the deposited  $SO_2$  reacted with carbonates contained in Kosa particles.

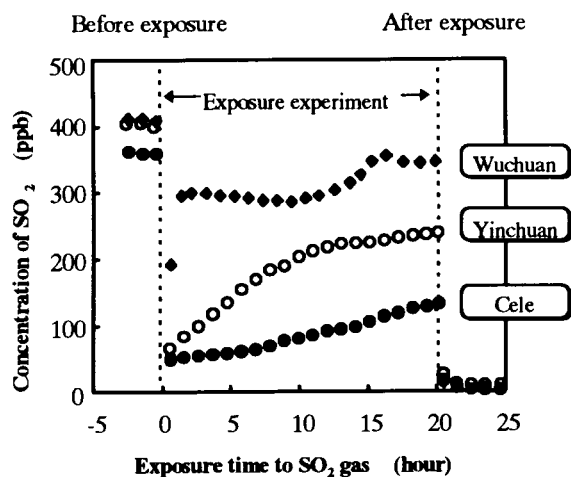


Fig. 8: Change of the exit concentration of  $SO_2$  after exposure of sample air to Kosa particles

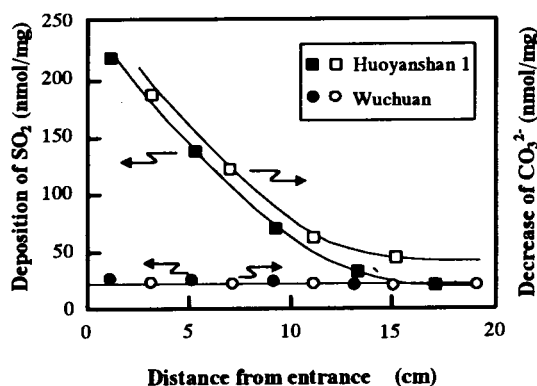


Fig. 9: Relation between deposited  $SO_2$  and decreased  $CO_3^{2-}$

## Reference

- 1) NAPAP, "1992 Report to Congress", NAPAP Office of the Director, Washington, DC, pp130, 1992.
- 2) K. Takahashi *et al.*, 98th *Nichirinron*, 177 (1987).
- 3) N. Hewitt and G. Terry, Understanding ozone plant chemistry, *Environ. Sci. Technol.*, **26**, 1891 (1992).
- 4) S. Hatakeyama *et al.*, Collection of gaseous hydroperoxides with a mist chamber, *J. Chem. Soc. Jpn.*, **1993**, 998 (1993).
- 5) S. Hatakeyama *et al.*, Production of hydrogen peroxide and organic hydroperoxides in the reactions of ozone with natural hydrocarbons in air, *Chem. Lett.*, **1993**, 1287 (1993).
- 6) S. Hatakeyama *et al.*, Reactions of  $CH_2OO$  and  $CH_2(^1A_1)$  with  $H_2O$  in the gas phase, *J. Phys. Chem.*, **85**, 2249 (1981).

- 7) S. Hatakeyama and H. Akimoto, Reactions of Criegee intermediates in the gas phase, *Res. Chem. Intermed.*, **20**, 503 (1994).
- 8) S. Hatakeyama *et al.*, Formation of 2-hydroxyethyl hydroperoxide in an OH-initiated reaction of ethylene in air in the absence of NO, *Environ. Sci. Technol.*, **29**, 833 (1995).
- 9) S. Hatakeyama *et al.*, High concentration of ozone observed in Mt. Maeshirane in Oku-Nikko, *J. Jpn. Soc. Atmos. Environ.*, **31**, 106 (1996).