

C-3.2.4 Studies on the Impacts of Controlling Techniques for the Emission of Acid-Precursors on the Formation Processes of Acidic and/or Oxidative Substances

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Abstract Although there are many factors affecting the forest trees, acid deposition and oxidative air pollutants are most important from a point of view of atmospheric chemistry. In this study following three researches were carried out. (1) Back trajectories of air mass which reached the top of Mt. Daisen every day in 1992 were calculated and classified. The contribution of air masses passing over northern or central China was found more than 60 % in winter. (2) Gaseous hydrogen peroxide, which is suspected being one of causes for forest decline, was measured in National Institute for Environmental Studies. Impacts of meteorological factors and air pollutants on the variation of concentration were analyzed. (3) Ozone reactions with natural hydrocarbons were examined in a large-volume (6 m³) smog chamber in order to elucidate the reaction mechanisms to produce gaseous hydroperoxides.

Key Words Forest Damage, Peroxides, Ozone, Natural hydrocarbons, Acid deposition

1. Introduction

Impacts of acid rain and/or regional scale air pollution become visible these days. Acidic substances mainly transported from East Asia are thought to affect the ecosystems in Japan. Serious forest decline in Tohoku, Hokuriku, and San'in area is reported, and impacts of the deposition of acidic substances transported from East Asia are suspected. On the other hand, serious forest decline is also found in the mountains around the Kanto Plain. Effects of photochemical air pollutants transported from urban area are pointed out.

In East Asia the emission of NO_x is growing very rapidly. Accordingly, it is pointed out that the continental background ozone in East Asia is now approaching the level of being harmful to plants.¹⁾ Ozone concentration is usually higher than 40 ppb in winter when northwestern monsoon prevails.²⁾ We have already reported that ozone can react with natural hydrocarbons such as terpenes to produce peroxides, which are very toxic to plants.³⁾

It is very interesting to know what will happen if emission control technology develops and amount of emission decreases. In Europe and North America, fuel switching from coal to oil or natural gas caused significant reduction of sulfur oxides from exhaust gases, whereas coal will be kept using for a long time in Asia. Nevertheless, the emission of NO_x will increase in Asia, and increase of ozone and peroxides is anticipated. To cope with such situation it is necessary to clarify the chemical processes in the atmosphere, the concentrations of ozone and peroxides in/around forests, and the factors controlling the concentration of peroxides there.

2. Research Objectives

The objectives of this study are 1) to investigate what kind of chemical substances or

chemical phenomena damage plants; 2) to evaluate the effect of the reduction of emission brought about by the spread of the emission control technology studied in sub-theme 1 of this project ("Studies on techniques to control emission of acid-precursors in East Asia and evaluation of impact of their application on the environment").

In the first year the purpose of this study was to clarify the chemical or geophysical situation around forests; to get insight into the processes which can cause damage to plants. Namely, (1) Mt. Daisen, where many yew trees were reported to die back in 1996, was chosen as a sample field of typical forest decline. (2) Meteorological and atmospheric-chemical factors controlling the concentration of peroxide were investigated using air samples collected in National Institute for Environmental Studies (NIES).

In the second and third year this study was focused on the clarification of reaction pathways to form peroxides from ozone and natural hydrocarbons. Ozone is anticipated to increase when the emission of NO_x increases. Thus, (3) laboratory studies using a large smog chamber were carried out to elucidate the reaction mechanisms. (4) Field observation of peroxides was carried out in Oku-nikko, where forest decline is visible. Factors controlling the concentration of peroxides were analyzed.

3. Methods

(1) Back trajectory analysis of air masses reaching the top of Mt. Daisen.

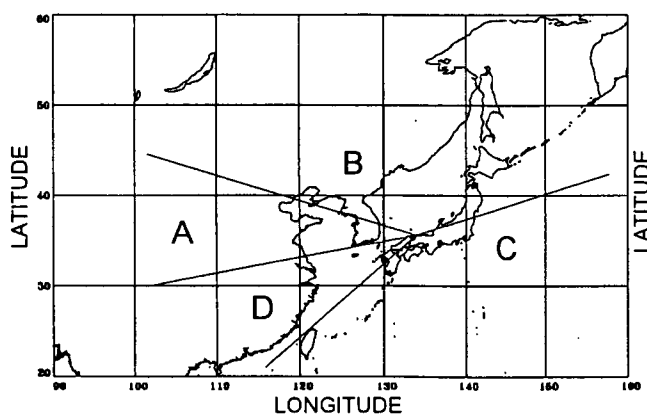


Fig. 1: Classification of the origin of the air masses arriving at the top of Mt. Daisen.

In order to clarify the relation between forest decline observed at the top of Mt. Daisen and acidic air pollutants transported from East Asia, back trajectory analyses of air masses reaching the top of Mt. Daisen were made by use of 1 year (1992) data of ECMWF. As shown in Fig. 1 the area where trajectories pass over was divided into 4 parts: (A) central China and Korea, (B) north Asia, northern Japan, and northwestern Pacific, (C) Pacific Ocean, (D) southern China and northern

Kyushu. Three days backward trajectories were calculated and the percentage of each part was evaluated. (2) and (4) *Field measurements of gaseous H₂O₂ and factors controlling*

their concentration.

Water-soluble components in air were collected by use of a mist-chamber and analyzed with high-performance liquid chromatograph equipped with a fluorescence detector. The concentrations of H₂O₂ were mainly measured and factors controlling them such as temperature, humidity, solar radiation, wind direction, wind velocity, ozone, and NO_x were investigated.

(3) Laboratory experiments to clarify the formation process of gaseous peroxides.

Purified air up to 1 atm, ozone up to 2.5 ppm, and one of hydrocarbons up to 5 ppm were introduced into a large photochemical reaction chamber in this order. After all the ozone was consumed, products and remaining reactants were analyzed. Reactant hydrocarbon and product formic acid were analyzed with a long-path FTIR. Product peroxides were analyzed by use of a mist chamber for sample-collection and a liquid chromatograph for analysis.

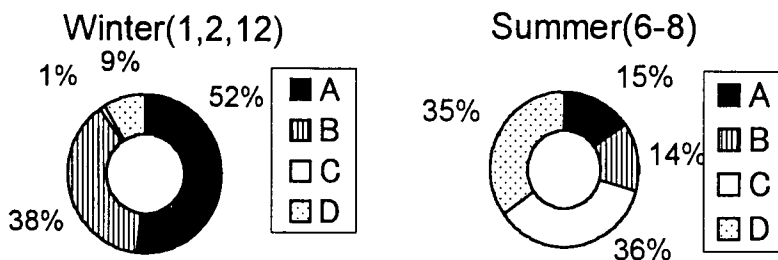


Fig. 2: Contribution of the origin of air mass

4. Results and Discussion

(1) Back trajectory analysis of air masses reaching the top of Mt. Daisen.

Three days back trajectory of air mass arriving at the top of Mt. Daisen at 9 a.m. for everyday of 1992. We observed high

concentration of SO_2 (~10 ppb) in 1992 above the Sea of Japan near Oki Islands.⁴⁾ One year's data were classified in 4 parts (A-D). It became clear that more than 50 % of air masses passed over China (A and D) throughout the year. In winter, particularly, more than 60 % of air masses passed over that area. As described above, high concentration of SO_2 was observed above the sea near Mt. Daisen in that year. Therefore, it can be thought that a large amount of acid or acid-precursors was transported to the top of Mt. Daisen at a high probability. On Mt. Daisen many yew trees died back in 1996. Serious forest decline is observed not only on Mt. Daisen but also in wide area along the coast of the Sea of Japan. The effect of acid rain/snow cannot be denied. It is necessary to take enough care of these areas not to deteriorate the forestal environment.

(2) and (4) Field measurements of gaseous H_2O_2 and factors controlling their concentration.

Photochemical air pollution is suspicious of one of the causes of forest decline observed around metropolitan area like Oku-Nikko. Among those pollutants gaseous H_2O_2 is very important since it is very toxic to plants. We analyzed the relation between concentrations of gaseous H_2O_2 measured in NIES and meteorological or atmospheric-chemical factors. It became clear that H_2O_2 concentration showed a good correlation with solar radiation as depicted in Figure 3. The formation process of H_2O_2 is basically controlled by solar radiation. H_2O_2 in the atmosphere is mainly formed by the

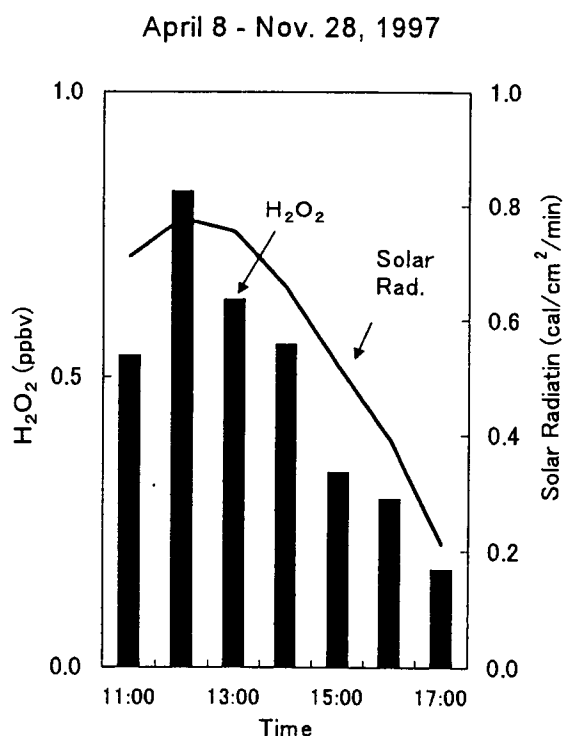
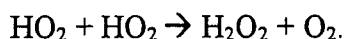


Fig. 3: Variation of H_2O_2 and solar radiation

following reaction



Since the HO_2 concentration depends on solar radiation, such result could be obtained.

On the other hand, it is very interesting to see how the concentrations of peroxides are controlled in the area of declined forest. Oku-Nikko is one of such places; high concentration of ozone has been measured on the mountains.⁵⁾ Oku-Nikko locates among the mountains surrounding Tokyo metropolitan area. Many declined forests are seen in this area in Mt. Oku-Shirane, Mt. Nantai, and so on. However, it is very difficult to carry out experiments in those mountains because there is no electric power supply. Thus, measurements of atmospheric peroxides were made in Oku-Nikko Environment Observation Station of NIES (1,450 m asl). This station locates halfway up the Mt. Mae-Shirane, where serious forest decline is observed. There is a 30 m tower in the station and the top of the tower projects out the forest canopy. Air samples were collected both on the top of the tower and on the ground.

Observations were carried out in summer 1998 and 1999. Peroxides showed diurnal variation; peak in the daytime and low concentration at night. H_2O_2 could be transported from outside of the forest, because peak in the daytime appeared later than the peak of solar radiation. In 1999 the peaks of H_2O_2 appeared 4-5h later (data not shown). Sometimes peaks at midnight were seen. Either upper air coming down or polluted air transported from urban area can cause those midnight peaks. Because slight increase of ozone and temperature as well as a peak of NO_x were observed simultaneously, these peaks should be caused by polluted air transported. In 1999 H_2O_2 showed high correlation only with ozone ($r=0.76$), temperature ($r=0.51$) and NO_x ($r=0.52$). Since the concentration of NO was low, good correlation between H_2O_2 and NO_x was seen. NO scavenges HO_2 and RO_2 which are precursors of peroxides.

At Oku-Nikko site O_3 -terpene reactions should not be the main way of forming ROOH . Peroxides are strongly controlled by air mass transported from urban area.

(3) *Laboratory experiments to clarify the formation process of gaseous peroxides.*

Table 1: Yields of peroxides and formic acid from reactions of ozone with methyl substituted cyclohexenes

Hydrocarbon	No. of runs	[HC] ₀ ppm	[O ₃] ₀ ppm	Yield / %				
				H ₂ O ₂	MHP	HMHP	PAA	HCOOH
1-Methyl-cyclohexene	3	4.7-4.9	2.0-2.4	0.87	1.06	5.0E-03	0.19	5.6
				0.73	0.95	9.0E-03	0.19	6.0
α-Pinene	3	1.3-1.8	0.9-1.2	0.71	0.65	7.3E-02	0.33	15
				0.74	0.71	8.9E-02	0.39	15
3-Methyl-cyclohexene	4	4.7-4.8	1.7-2.4	0.50	0.03	1.3E-02	0	34
				0.43	0.03	7.0E-03	0	35
4-Methyl-cyclohexene	4	4.7-4.9	2.1-2.3	0.65	0.04	1.3E-02	0	19
				0.57	0.04	1.4E-02	0	20

2-methyl-2-butene and 2,3-dimethyl-2-butene with ozone were tested. In both the reactions H₂O₂, MHP, and PAA were identified. Thus, it can be said that the (CH₃)CROO type Criegee biradical can form peroxyacetic acid in the presence of ozone. Since 3- and 4-methylcyclohexene gave high yield of formic acid, it can be assumed that only hydrogen-substituted Criegee intermediate ([B] in Fig. 4) should be able to produce formic acid.

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Peroxidic products observed in the reaction of ozone with 1-methylcyclohexene were H_2O_2 , CH_3OOH (MHP), peracetic acid (PAA) and HOCH_2OOH (HMHP). Yields of the products are listed in Table 1. In the table, upper two reactants and lower two reactants show

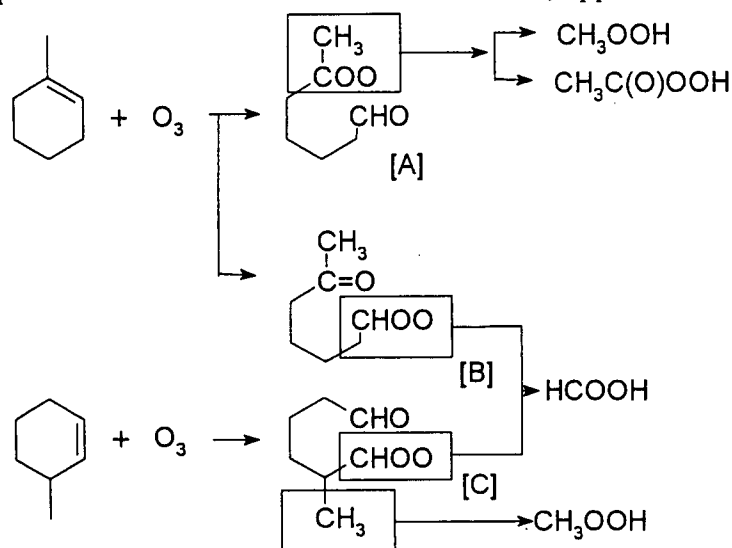


Fig. 4: The first step of the ozone reaction with cyclic olefins and subsequent reactions to form peroxides or formic acid.

very interesting contrast. Upper two olefins yielded formic acid at relatively low yield, and MHP and PAA at relatively high yields. In contrast, lower two olefins yielded formic acid at high yield, no PAA, and MHP at low yield. Initial Criegee cleavage at the double bond of 1-methylcyclohexene as well as 3-methylcyclohexene, and subsequent formation of peroxides and formic acid from substituted Criegee intermediates ($\text{RR}'\text{COO}$ type biradical; R and R' are alkyl group or H atom) must take place (Figure 4). On account of the difference in the structure of the intermediates, it can be assumed that the Criegee intermediate having no H atom as [A] can form peroxyacetic acid (PAA). The Criegee intermediate having H atom can form formic acid. If we apply the lower yield of CH_3CHOO (in the ozone reaction with 2-methyl-2-butene the ratio of the yield of $(\text{CH}_3)_2\text{COO}$ to CH_3CHOO is 7:3) from the reaction of ozone with 2-methyl-2-butene to 1-methylcyclohexene, the low yield of formic acid from 1-methyl compounds can be easily recognized.

Yields of PAA are the most interesting. It is clear from the Table 1 that the methyl group at 3- or 4- position of cyclohexene cannot promote PAA formation. It suggests that only the Criegee intermediate that has methyl group at the radical carbon can form PAA. Figure 5 shows the reaction mechanism of the formation of olefinic hydroperoxide. Ozone attack on the double bond can form PAA. Previously, it was believed that such an olefinic hydroperoxide is unstable. However, the production of PAA suggests that the olefinic hydroperoxide has a lifetime long enough to react with ozone under the atmospheric conditions, if this reaction mechanism is correct. In order to get more supportive evidence for the reaction mechanisms, reactions of

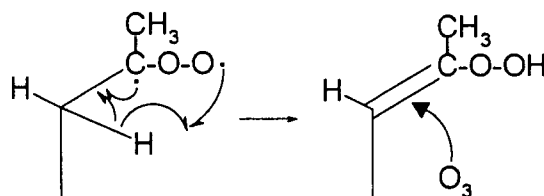


Fig. 5: Formation of olefinic hydroperoxide and subsequent reaction with ozone.