C-1.2.1 Development of Analysis Systems of High Sensitivity for Oxidative Species and Analysis of Transport and Reactions of Atmospheric Pollutants

Contact Person Shiro Hatakeyama
Senior Research Scientist, Acid Deposition Reseach Team
Global Environment Division, National Institute for Environmental Studies
Environmental Agency
16-2, Onogawa, Tsukuba, Ibaraki 305, Japan
Phone:+81-298-51-6111(Ext. 437) Fax:+81-298-51-4732

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Abstract Aircraft observations of atmospheric pollutants were performed over East China Sea, Yellow Sea, and Sea of Japan in October, 1991 and November, 1992. Ground based observations were also performed at Oki Island and Happo-one. In '91 mission difference between marine atmosphere and continental atmosphere was clearly seen around Japan. In '92 mission distribution of SO_2 showed interesting feature. High concentration of SO_2 up to 10 ppbv was observed over Sea of Japan at 1,500 and 4,500 feet, when wind blew from west or north west.. The concentration decreased when the aircraft approached to Honshu. NOx also showed similar distribution. All the data strongly suggest the transport of pollutants from the Asian continent.

A new analysis system (HPLC with a fluorometric detector) and a new sample collection technique (mist chamber) were introduced. Sensitivity of the analysis of hydroperoxides became more than 10 times higher, and the sample-collection time was reduced to less than 1/3 of former method. The yields of peroxides were obtained and reaction mechanisms were clarified.

Key Words IGAC, Aircraft Observation, High SO_2, Peroxides

1. Introduction

Japan is located in the east of Asian continent and in the north west of Pacific Ocean. Many kinds of substances are transported from both the continent and the ocean, and they are transformed around Japan and deposit there. Such processes of long range transport, chemical transformation, and deposition of atmospheric pollutants are related to not only Japanese local atmospheric pollution problem but also global atmospheric pollution and climate change. Asia is one of the biggest source region of SOx and NOx in the world, and those emissions are anticipated to increase. These pollutants are oxidized in the atmosphere while they are long-range transported. They deposit as SO_4^{2-} or NO_3^- in acid rain, which brings about the death of forests or the acidification of rivers and/or lakes and causes a large effect on the ecosystem. Or they promote atmospheric reactions with anthropogenic and/or natural hydrocarbons, and determine the formation processes of oxidative species such as ozone, PAN, and hydrogen peroxide. The result is in deep relation to the problems of the global environment and climate. Thus, it is very important to elucidate the dynamics of atmospheric trace components by three-dimentional observation of atmospheric pollutants around Japan and over Sea of Japan and East China Sea.

Forest decline is one of the characteristic aspects of acid deposition. Recently, not only acid rain but atmospheric pollutant gases are attributed as causes of forest decline. Hydrogen peroxide and organic peroxides are very toxic to plants and they can oxidize SO_2 in aqueous solution. And those peroxides were reported ,recently, to be produced by the reaction of ozone with natural hydrocarbons emitted by plants themselves. It is important to estimate the yield of peroxides from such reactions and to elucidate the reaction mechanisms.

2. Research Objectives

[1]Aircraft observations and ground-based observations of pollutants in western Pacific region

Objectives for the observations are two fold. They are as follows.

(1) To analyze acidic substances

The most important acidic substances are sulfate (SO_4^{2-}) and nitrate (NO_3^-). Ion compositions of aerosols should be monitored. In addition precursors of acids such as $SO_2$and NOx are also important.

(2)To analyze oxidative substances

Ozone is the most important oxidative compound. Precursors of ozone such as non-methane hydrocarbons and NOx and products of photochemical reactions such as NOy including PAN are also needed to be monitored.

[2]Yields and formation mechanism of hydrogen peroxide and organic peroxides in ozone-natural hydrocarbon reactions

Objectives of this study were to set up a technique highly sensitive to peroxides as well as to develop an efficient technique to collect peroxides in aqueous sollution. By use of those techiniques it was aimed to estimate the yield of peroxides from the reactions of ozone with natural hydrocarbons which are emitted by plants and to elucidsate the reaction mechanisms.

3. Reasearch Methods

[1] Aircraft observations of pollutants were made in 10/5-10/11, 1991 and 11/8-11/12, 1992. Along with those observations ground-based observations were also conducted at Oki (1991, 1992), Happo-one (1991, 1992), Tsusima (1991), and Okinawa (1991). The flight routes for both the observations are depicted in Fig. 1. In 1991, Cessna 404 (Showa Aviation Co.) was used. A rendezvous flight with NASA DC-8 was made on 10/6 on the course from Yoron to Nagasaki. Data capable of inter comparison were obtained. Pollutants observed and methods for observation are listed in Table 1. Flight altitude was mainly 10,000 ft. On the course of the Yoron flights and the Niigata flights the flight altitude was lowered down to 1,500 ft for about 30 min to see the difference of the air mass above and below the marine boundary layer. In 1992, Fairchild Swearingen SA226-T (Showa Aviation Co.) was chartered. Flight courses were between point A and point B over Sea of Japan and between point C and point D over East China Sea. Thirty minutes of level flights were made at each altitude of about 10,000, 7,000, 4,500, and 1,500 feet in one cruise. Pollutants observed and methods for observation are also listed in Table 1.

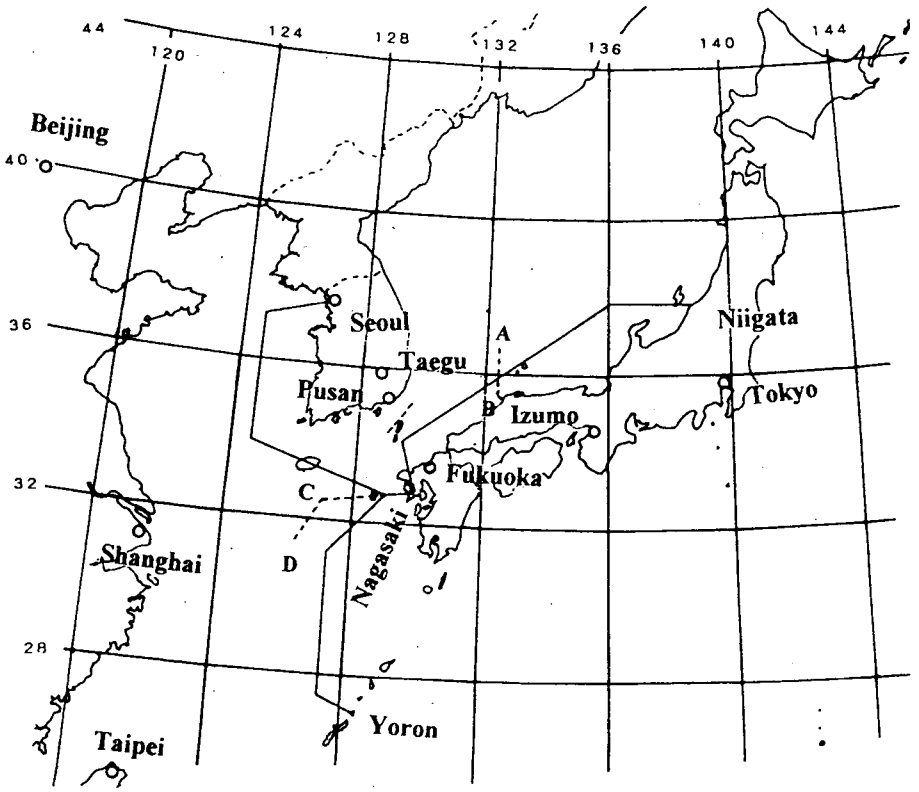

Fig. 1: Flight courses. Solid line: '91 mission, dashed line: '92 mission.

Table 1: Pollutants observed and observation methods.

Pollutants observed	*Methods*	*Year*
SO_2	pulse fluorescence	'92
SO_2	impregnated filters	'91
ozone	UV absorption	'91, '92
NOx	ozone chemiluminescence	'91, '92
PAN	low temp. collection	'92
HNO_3, HCl, NH_3	diffusion scrubber	'92
HCl, NH_3	impregnated filters	'91
aldehydes	impregnated cartridges	'91
non-methane hydrocarbons	grab sampling	'91
CO	grab sampling	'91
inorganic aerosols	high volume sampler	'91, '92
aerosols (Al, Si, Fe)	low volume sampler	'91
aerosol features	impacter-EM	'91, '92
aerosol number concentration	particle counter	'92

[2] A mist chamber (Fig. 2) was introduced to collect gaseous peroxides efficiently in water. A high performance liquid chromatograph with fluorescence detector was used to analyze peroxides. To eliminate decomposition of peroxides during analysis a separation column and tubing made of PEEK polymer were used and the column was set in a low temperature (~ 1 ° C) cabinet. A large volume (~ $4m^3$) photochemical reaction chamber was used as a reactor. As for reactants isoprene (~ 4 ppm), 1-methylcyclohexene (~ 2 ppm), or methylenecyclohexane (~ 2 ppm) were chosen. One of those hydrocarbons and a half amount of ozone were introduced in the chamber. Produced peroxides were collected with the mist chamber and analyzed by means of above HPLC-FD system.

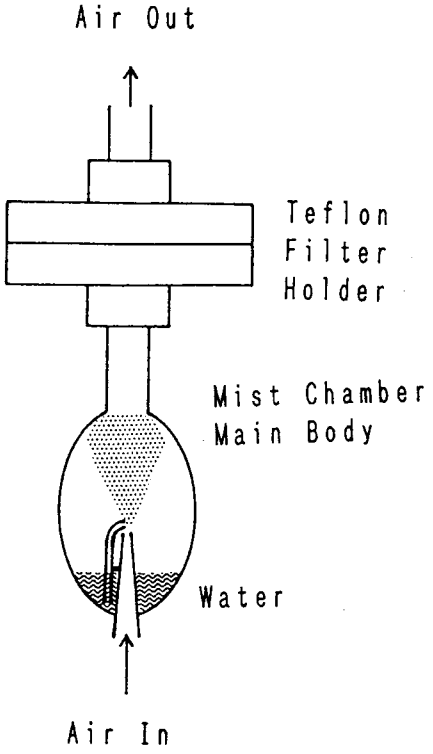

Fig. 2: Outline of a mist chamber.

4. Results and Discussion

[1] (1)Results of '91 mission

Figures 3 and 4 are variation of ozone and NOx observed on 10/5 and 10/10. The data of 10/5 shows that the air mass before 12:30 and after 13:30 are different. Around 13:00 we went across a stationary front. The air mass we met earlier contained high concentration of ozone. Relative humidity of this air mass was quite low. Thus, it can be concluded that this air mass suffered strong influence from stratospheric atmosphere. On the other hand later air mass contains much NOx. It implies that this air mass was not aged very long. Cool and aged continental air

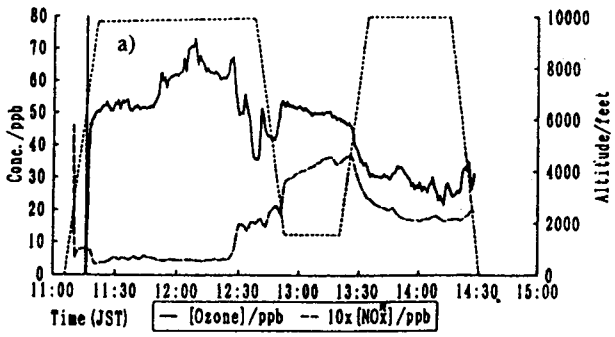

Fig. 3: NOx and O_3 on Oct. 5, 1991

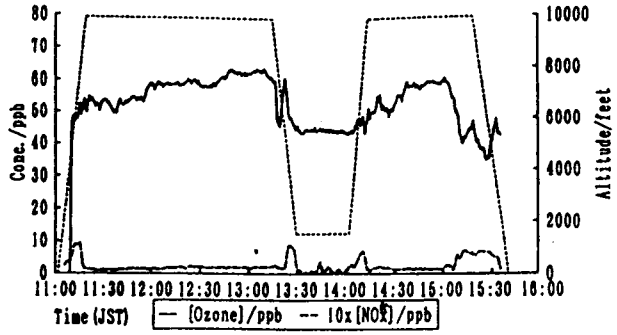

Fig. 4: NOx and O_3 on Oct. 10, 1991

mass containing much ozone seems to have lifted up the warm and less aged marine air mass,

since the concentration of ozone at low altitude was higher than that at high altitude. The data of 10/10 shows that the air mass staying for long time above Sea of Japan was caught in this cruise, since the concentration of NOx was quite low throughout the flight. Back trajectory calculation supported this contention.

(2) Results of '92 mission

Figures 5 and 6 are variation of ozone, NOx, and SO_2. On 11/11 south wind blew. High concentration of SO_2 was observed near Honshu rather sharply. In contrast, on 11/12, very high concentration of SO_2 was monitored above Sea of Japan. On this day wind blew from west or north-west. The concentration of SO_2 came down when the airplane approached to Honshu. Distribution of NOx was similar to SO_2. It indicates that there is a very strong influence of continental air mass to Japan when wind blows from west or north-west.

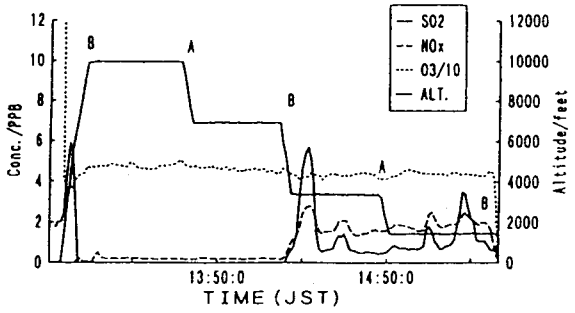

Fig. 5: SO_2, NOx, and O_3 on Nov. 11, 1992

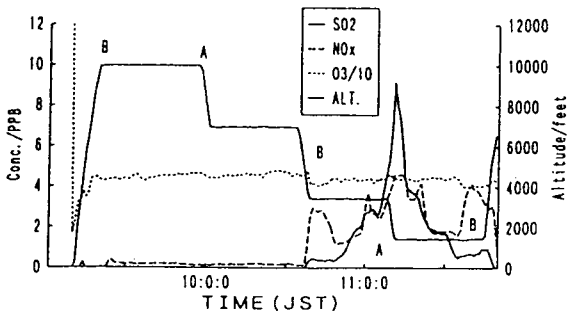

Fig. 6: SO_2, NOx, and O_3 on Nov. 12, 1992

[2]Figure 7 is a chromatogram of the products of an ozone-isoprene reaction. Peaks 1-3 were identified as hydrogen peroxide, hydroxymethylhydroperoxide ($HOCH_2OOH$), and methylhydroperoxide (CH_3OOH), respectively. Average yields were 0.8, 2.3, and 1.8 %, respectively. Reaction mechanisms were elucidated as follows.

$$RCH{=}CH_2 + O_3 \rightarrow CH_2OO + \text{Aldehydes}$$
$$CH_2OO + H_2O \rightarrow HOCH_2OOH^{\ddagger}$$
$$HOCH_2OOH^{\ddagger} \rightarrow HCOOH + H_2O$$
$$HOCH_2OOH^{\ddagger} \rightarrow HOCH_2OOH$$
$$HOCH_2OOH^{\ddagger} \rightarrow H_2O_2 + HCHO$$
$$CH_3OO + HO_2 \rightarrow CH_3OH + O_2$$

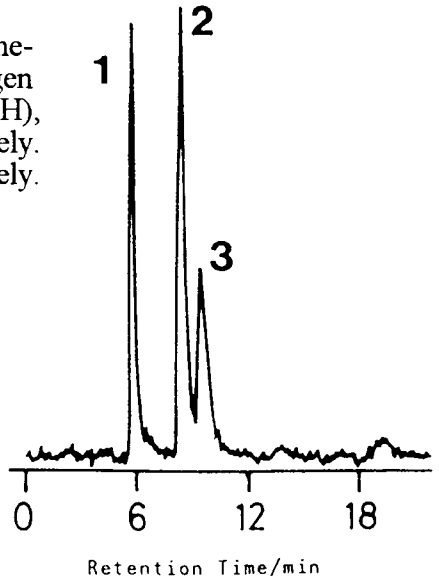

Fig. 7: A chromatogram of products of ozone-isoprene reaction

Publication

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