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A Study on the Behavior of Monoterpenes in the Atmosphere

大気中モノテルペンの挙動に関する研究

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THE NATIONAL INSTITUTE FOR ENVIRONMENTAL STUDIES

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Preface

The project of "Studies on the behavior of monoterpens in the atmosphere" was carried out as one of the general research projects at the air quality measurement section of chemistry and physics division.

It has been known that some compounds of terpenes are excreted from trees and that they make the main cause of so-called "blue haze" of forests as well as forest's smell. The purpose of the project is to identify the materials and to trace their fates in relation with other parameters of the atmosphere, so that one can estimate the rate of contribution by the natural hydrocarbons to the background level of atmospheric hydrocarbons.

The results shown in this report have given answers to these points and clearly established a base for the further studies in the field of ecosystem of the forest.

Mrs.Y.Yokouchi is the main investigator of the project, together with the section chief Dr.Y.Ambe, and the content consists the major part of the doctoral thesis of Mrs.Y.Yokouchi.

K.FUWA
Chief. Chemistry and Physics Div.

January 1985

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Abstract

Terpenes are emitted into the atmosphere by many species of plants in the world. Their behavior in the atmosphere, however, has been almost unknown. The present investigation was carried out to establish the behavior of monoterpenes in a variety of atmospheric processes.

The mechanism of monoterpene emission was studied using an environmentally controlled gas cabinet. It was found that monoterpene emission rate increased exponentially with temperature and was also influenced by light. These observations were explained reasonably by the model that monoterpene emission rate depends on the monoterpene amount in the leaf oil and its saturated vapor pressure.

A technique to observe terpene emission rate in a forest without disturbing plant environment, was developed, and seasonal variation of monoterpene emission rate from a branch in a pine forest was observed. In this temperate conifer forest, monoterpene emission rate was approximately 400 $\mu g/(m^2 \cdot h)$ (at 30°C) and was lower by a factor of ten than the previous worker's observation, which was considered to suffer from the error resulting from the unsatisfactory sampling technique.

Trace analysis of monoterpenes in the atmosphere by GC-MS was developed. Seasonal and diurnal variations of atmospheric monoterpenes in a pine forest were measured using this method. The analysis of their variations showed that atmospheric concentration of monoterpenes is clearly correlated with ambient temperature and ozone concentration in the air, and most of plant-emitted monoterpenes disappear through their reaction with ozone in a forest.

As for their reaction products, the chamber experiments were conducted for the ozonolysis of the major atmospheric monoterpenes; α-pinene, β-pinene and limonene. It was found that α-piene-O_3 reaction produced mainly 2', 2'-dimethyl-3'-acetyl cyclobutyl ethanal (pinon aldehyde) and β-pinene-O_3 reaction produced mainly 6,6-dimethyl-bicyclo [3.1.1] hept-2-one. As for limonene-O_3 reaction, several unidentified products were observed. These reaction products were searched for in forest aerosols, and pinon aldehyde was detected for the first time, confirming that some of terpene-origin products are likely to exist as aerosols.

CHAPTER
1

General Introduction

It is well known that many species of plants emit terpenes and their derivatives into the atmosphere. They are potentially important participants in the chemistry of the background air. The involvement of biogenic terpenes in urban and rural oxidant formation has received considerable attention recently. It has been suspected that terpenes contribute largely to the total nonmethane hydrocarbons (TNMHC) in several rural areas.

Their worldwide emission rate has been estimated to be $1.75 \times 10^8 \sim 8.3 \times 10^8$ t/y (Went, 1960; Rasmussen & Went, 1965; Robinson and Robbins, 1968; Zimmerman, 1979), exceeding the emission rate of hydrocarbons from man-made sources, $6.5 \times 10_7$ t/y (Duce, 1978). Their estimations, however, could be in error resulting from the unsatisfactory way to measure *in situ* terpene emission, and from extrapolation of the local emission rates to different places and times.

In the atmosphere, isoprene and monoterpenes including α-pinene, β-pinene, myrcene, limonene and 3-carene (Fig. 1.1) have been detected and identified by gas chromatography or gas chromatographic mass spectrometry (Rasmussen and Went, 1965; Whitby and Coffey, 1977; Holdren *et al.*, 1979). Their worldwide concentrations, however, are not known sufficiently either in quality or in quantity.

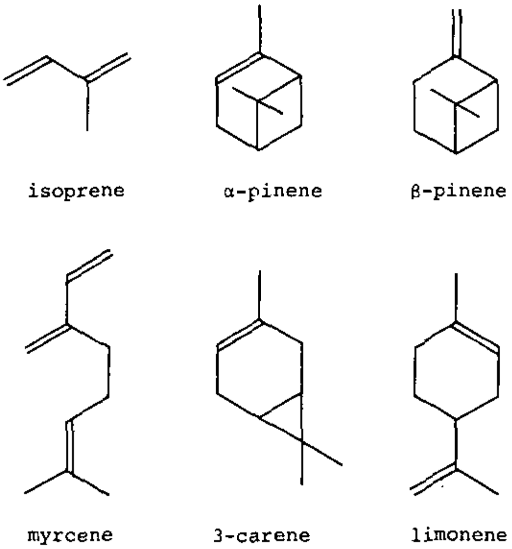


Fig. 1.1 Structures of atmospheric terpenes.

Terpenes are olefinic compounds that have high reactivity in the atmosphere, and are supposed to polymerize into aerosols through chemical reactions in a manner similar to that of man-made olefins converted into city smog. Went (1960) speculated that these aerosols resulted in a "blue haze" surrounding forest, although this has not been cofirmed. Laboratory studies have shown that monoterpenes are capable of reacting with oxides of nitrogen (NO_x) in the presence of sunlight to produce ozone and other oxidants (Westberg & Rasmussen, 1972). Since then, it has been discussed whether terpenes can be significant sources of ozone (Rasmussen, 1972; Gay & Arnts, 1977; Graedel, 1979; Holdren *et al.*, 1979; Budiansky, 1980; Dimitriades, 1981). The possibility of the destruction of ozone in the lower atmosphere by plant-origin terpenes is another interesting issue, because terpenes, as well as most olefins, play the dual role of ozone production and ozone destruction. Although laboratory studies have shown that terpenes can produce aerosols when undergoing ozonolysis or photooxidation in the presence of NO_x (Went, 1960; Stephens and Scott, 1962; Wilson *et al.*, 1972), there have been few studies to determine the aerosol materials resulting from the reaction and to detect them in the atmosphere.

Fig. 1.2 shows the possible atmospheric cycle of terpenes. It can be said that uncertainties in defining the atmospheric cycle of terpenes and in assessing their importance in atmospheric processes result from sparse information concerning the behavior of terpenes in the real atmosphere. To understand the behavior of terpenes in the air and to estimate their impact on the atmospheric chemistry, the following researches are indispensable : (1) to know the variation of terpene emission rate under various environmental conditions, (2) to investigate the variation of atmospheric concentration of terpenes and to analyze the factors affecting their behavior, and (3) to identify the atmospheric reaction products of terpenes and to detect them in the ambient air.

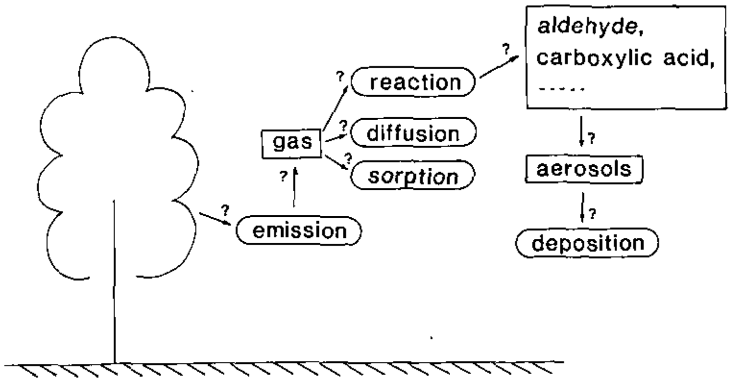


Fig. 1.2 A possible terpene cycle in the atmosphere.

From these points of view, the following studies were conducted.

a) A gas chromatographic-mass spectrometric technique was developed for the analysis of trace concentration (sub-ppb) of monoterpenes in the air. To know typical monoterpene concentration and composition in Japanese forest air, atmospheric monoterpenes were analyzed in several kinds of forests. (Chapter 2)

b) The relationship of monoterpene emission rate and environmental conditions was studied through the experiment using a dynamic mass balance gas chamber and the examination of the difference between monoterpene compositions of the leaf oil and the emitted gas. In the chamber experiment, the timelag effects on terpene emission rate after changing environmental conditions were carefully observed. (Chapter 3)

c) The variation of atmospheric concentration of monoterpenes was measured in a pine forest over a period of one year. The relationship between various environmental factors and terpene concentration was analyzed. Seasonal variation of monoterpene emission rate from a branch in the forest was also measured using an improved method. (Chapter 4)

d) The main products of monoterpene-ozone reaction in a chamber were determined by GC-MS. Aerosols collected in a forested area were subjected to capillary GC-MS analysis to detect terpene-origin compounds. (Chapter 5)

The present study revealed that (i) plant-origin terpenes play an ozone-destruction role rather than an ozone-producing role, (ii) their atmospheric concentration is dependent mainly on temperature and ozone concentration in the air, (iii) their worldwide annual emission rate should be reestimated based on the variation of their biosynthetic rate and temperature and (iv) terpene-origin aerosols exist commonly in forest air.

CHAPTER
2

GC-MS Analysis of Monoterpenes in the Atmosphere

2.1 INTRODUCTION

The data of terpene concentrations in the air have been incomplete both qualitatively and quantitatively to permit reliable estimation of the geochemical cycle of terpenes. Rasmussen and Went (1965) identified α-pinene, β-pinene, myrcene and isoprene in the countryside air using gas chromatography (GC). Whitby and Coffey(1977) obtained the total terpene concentration typically observed during the summer in the Adirondack Mountain region. But in these GC methods, it is difficult to determine terpene compounds exactly only from comparisons of retention times because the peaks of many terpenes and non-terpene hydrocarbon derivatives may overlap on the chromatogram. Recently, Holdren *et al.*(1979) detected α-pinene (at a level between 10 and 730 ppt), β-pinene, 3-carene and limonene in the Moscow Mountain region with capillary gas chromatography-mass spectrometry (GC-MS).

In the present study, a sensitive and more convenient GC-MS procedure for the analysis of monoterpenes in the atmosphere was developed based upon trapping of the compounds on Tenax GC adsorbent and selected ion monitoring (SIM) detection. Using the trapping method, monoterpenes in the atmosphere could be preconcentrated during sampling, and their samples were handy to carry. SIM offered a sensitive and selective detection of monoterpenes in combination with an adequate GC condition. The technique was used to measure monoterpene concentrations and compositions in different kinds of forests in Tsukuba district and other regions in Japan.

2.2 ANALYTICAL METHOD

Apparatus

A microprocessor-controlled Hewlett-Packard 5992A GC-MS instrument equipped with a SIM function was used to perform analyses. The system (Fig. 2.1) contains a two-way valve to switchover the carrier gas, and a block heater (FLS-3 flush sampler ; Shimadzu, Kyoto, Japan) for desorption of the sample from the sampling tube.

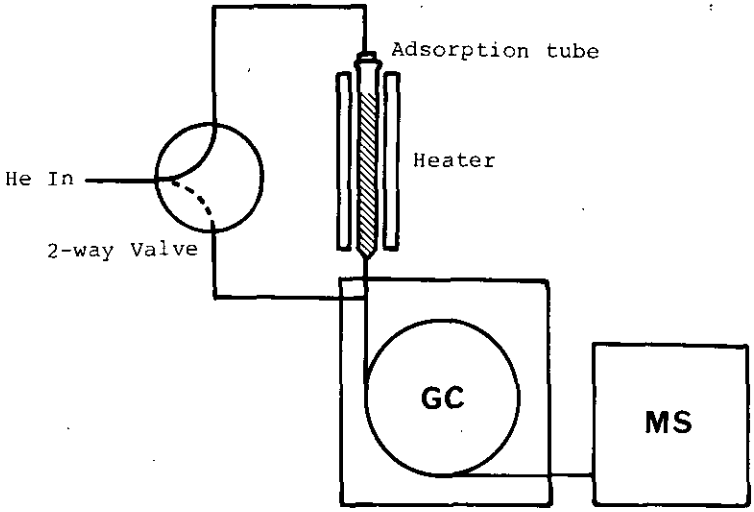


Fig. 2.1 Experimental GC-MS system

Sampling tube

Sampling tubes filled with Tenax GC adsorbent were employed for collecting samples, as shown in Fig. 2.2. A 0.3g amount of Tenax GC (80-100 mesh) was packed into a Pyrex tube (15cm× 4.5mm i.d.)(A type) or into a stainless-steel tube coated with glass inside (B type) to from a bed ca.10cm long, and was secured at both ends with glass-wool plugs. The adsorption tube of B type was used for the sampling at remote areas to avoid contamination during several days' storage before analysis. The tube was connected to the analytical column by inserting the needle end into the injection of the gas chromatograph. Prior to use, the tubes were conditioned overnight at 280°C with passage of nitrogen gas at a flow-rate of 30 ml/min.

Procedure

One litre volume of air was drawn through an adsorption tube by a portable

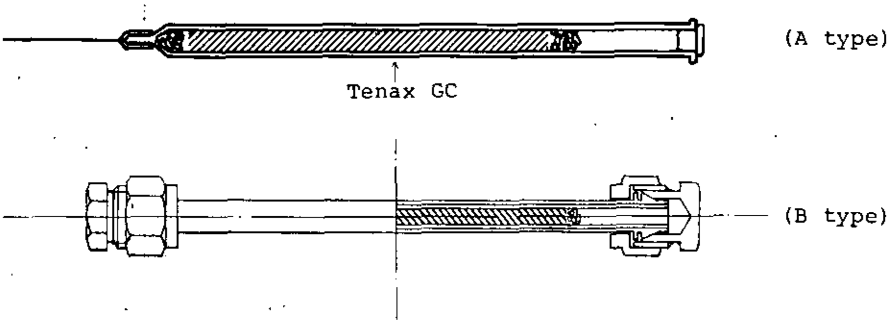


Fig. 2.2 Adsorption tube

pump (Charles Austen Pumps) with a needle-valve or by a portable flow control system using thermal mass flow meter (Tylan). The sampling flow-rate was controlled at the rate of 100 ml/min in both cases. The adsorption tubes (A type) were sealed with silicone rubber and GC-MS analysis was performed as soon as possible after sampling. B-type tubes were sealed tightly with nuts. Chromatographic separations were accomplished on 5% Silicone DC-200 + 5% Bentone 34 on Chromosorb W AW DMCS (60-80 mesh) packed in a glass column (8 ft.×2 mm i.d.). Desorption of the sample from the adsorbent was carried out at 200°C with the carrier gas (high-purity helium) flowing at a rate of 16 ml/min for 2 min. The monoterpenes transferred onto the analytical column were temporarily trapped at the top of it for 2 min at a temperature of 0°C and the carrier flow was then switched from the bypass to the GC. The SIM chromatograms of the ions having m/z 93, 136, 68, 41, 78 and 91 were obtained by temperature programming at 16°/min to 100°C. Positive identifications of monoterpenes were made on the basis of a combination of retention times and the ratio of peak heights at m/z 93, 136, 68 and 41 which are the main peaks in the mass spectra of many monoterpenes. The concentrations of monoterpenes in the samples were usually determined from the peak heights of the SIM chromatogram at m/z 93 using a calibration curve prepared from the standard solutions. The ions at m/z 41, 78 and 91 were monitored to determine other aliphatic and aromatic hydrocarbons for reference.

2.3 RESULTS AND DISCUSSION

2.3.1 Trace analysis of monoterpenes using a sampling tube

Breakthrough volumes for α-pinene, β-pinene and limonene were determined using two adsorption tubes connected in series. Standard gases of each compound at 100 ppb were passed through the tubes at 100 ml/min. After a known volume of air had passed through the adsorption tubes at ambient temperature, the second tube was analyzed to determine whether the compound had eluted from the first tube, indicating breakthrough. The sampling tube containing 0.3 g Tenax GC adsorbent had breakthrough volumes of more than 4 l for these three compounds. As α-pinene is one of the most volatile monoterpenes, it is reasonable to assume that all monoterpenes are trapped in the sampling tube without any loss when the sampling volume is less than 3 l.

A study was made to determine the desorption efficiency of the sampling tube. One ng each of α-pinene, β-pinene and limonene in 1μl hexane was injected directly onto the analytical column and analyzed using SIM. These results were compared to those obtained when the test mixture was injected into the sampling tube and then analyzed using the technique described above. A quantitative result was achieved for three runs : the recoveries of α-pinene, β-pinene and limonene were 96 ± 3%, 94 ± 1% and 96 ± 2% respectively.

The total recovery efficiency was measured using the standard gas in the ppb range, which was prepared with a dynamic gas calibration system based on the diffusion cell method and the secondary dilution. The recovery of α-pinene for three runs was 91 ± 5%.

The detection limit of this analytical method for α-pinene was 0.1 ng at a signal-to-noise (S/N) ratio of >3.

2.3.2 Measurements of monoterpenes in forested areas

Monoterpenes in different kinds of forests in the Tsukuba district

Atmospheric monoterpene concentrations were measured at several forests during the late autumn, spring and summer months of 1979-1980. The forests are situated in the Tsukuba district and prompt analysis after sampling was possible. Primary objective of this field-sampling program was to provide both qualitative and quantitative information concerning monoterpenes in the forests of pine *(Pinus densiflora)*, hinoki *(Chamaecyparis obtusa)* and sugi *(Cryptomeria japonica)* which are the predominant species in japanese mountain areas.

Fig. 2.3 shows the SIM chromatogram at m/z 93 of a 1 l sample collected in a pine forest. Monoterpenes identified in the atmosphere of coniferous forests are listed with their retention times in Table 2.1.

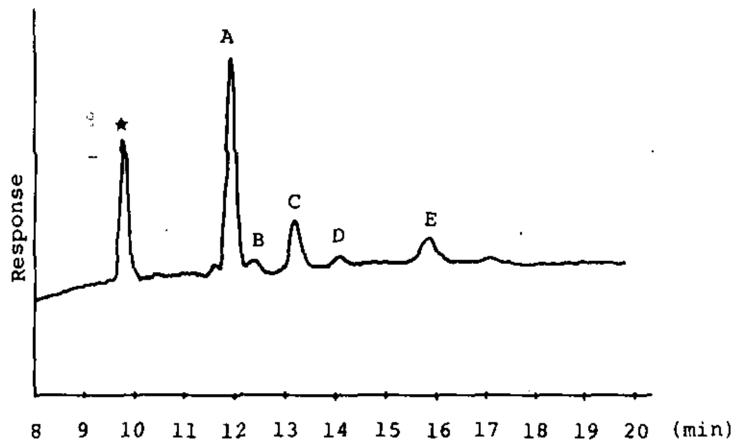


Fig. 2.3 Selected ion chromatogram (m/z 93) of an air sample collected in a pine forest. Peaks: A = α-pinene, B = camphene, C = β-pinene, D = myrcene, E = β-phellandrene, the asterisk indicates an isotope of the molecular ion of toluene.

Table 2.1 Retention Times of Monoterpenes Identified in the Atmosphere of Conifer Forests

Compound	Retention time (min)
α-Pinene	12.0
Camphene	12.4
β-Pinene	13.2
Myrcene	14.1
3-Carene	14.5
Limonene	15.6
β-Phellandrene	15.9

Terpene concentrations measured in the several kinds of forests in the Tsukuba district are presented in Table 2.2. All the samples were collected under the forest canopy at a level of 1.5 m above the ground. The most noticeable feature of Table 2.2 is that the ambient terpene concentrations vary greatly from day to day. This suggests that there may be a close relationship between the monoterpene concentration in the air and climate. Concerning the monoterpene compositions, characteristic patterns for particular classes of forests were found. In the case of pine forests, α-pinene was dominant, and β-pinene, β-phellandrene and myrcene were detected. In hinoki and sugi forests, α-pinene and β-pinene prevailed, and limonene and 3-carene were also detected, but β-phellandrene was not observed. The differences in monoterpene composition depending on forest type suggest that the composition of the leaf oil is responsible for the atmospheric concentrations.

Table 2.2 Terpene Concentrations (ppb) in Several Kinds of Forests in Tsukuba District. (n.d.=Not detected)

Date	Location	Type of forest	α-Pinene	Camphene*	β-Pinene	Myrcene	3-Carene	Limonene	β-Phellandrene*	Weather
Nov.14, 1979	1	Pine	0.10	+	0.03	n.d.	n.d.	n.d.	+	Fine
Nov.16, 1979	2	Pine	0.18	+	0.05	0.02	n.d.	n.d.	+	Fine
	3	Hinoki	0.19	+	0.14	0.03	0.02	0.07	n.d.	Fine
	4	Sugi	0.10	n.d.	0.07	0.02	0.02	0.27	n.d.	Fine
Nov.22, 1979	2	Pine	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	+	Rain
	3	Hinoki	0.06	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	Rain
	5	Sugi	0.06	+	0.03	n.d.	n.d.	0.09	n.d.	Rain
Nov.29,1979	1	Pine	1.30	+	0.54	0.12	0.04	0.09	+	Cloudy
Mar.24, 1980	4	Sugi	0.13	+	0.08	0.02	0.01	0.03	n.d.	Fine
	3	Hinoki	0.07	+	0.09	0.03	0.02	0.06	n.d.	Fine
May.15, 1980	1	Pine	0.20	+	0.03	0.01	0.01	n.d.	+	Cloudy
June.13, 1980	1	Pine	0.20	+	0.07	0.01	n.d.	n.d.	+	Cloudy
July.19, 1980	1	Pine	0.35	+	0.12	0.04	n.d.	n.d.	+	Fine
Aug.21, 1980	4	Sugi	0.22	+	0.10	n.d.	n.d.	0.09	n.d.	Cloudy
	6	Pine	0.38	+	0.13	n.d.	n.d.	n.d.	+	Cloudy
	7	Hinoki	0.05	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	Cloudy

*Camphene and β-phellandrene were not quantified and only their existence (+) is noted.

Monoterpenes in forest air in various districts of Japan

The monoterpene concentrations were measured at Lake Mashu (the northern part of Japan), Yaku Island (the southern part of Japan) and Kurobe (the central part of Japan) in the summer of 1981. This study was conducted to get a rough estimate of atmospheric monoterpenes in Japanese forests. α-Pinene was dominant in all the samples and its concentrations at the three districts are shown in Table 2.3 with climatical conditions. From Tables 2.2 and 2.3, it was found that the seasonal or daily variation of atmospheric monoterpene concentration at Tsukuba district exceeded its variation in different localities in the summer.

Table 2.3 α-Pinene Concentrations in Forest Air in Various Districts of Japan

Location	Date	Time	Weather	α-Pinene (ppb)
Mashu				
St.1	Jun.27	15 : 55	Fine	0.02
St.2	Jun.28	14 : 26	Cloudy	0.06
St.3	Jun.28	16 : 50	Rain	0.09
Yaku Island				
St.1	Jul.29	10 : 35	Cloudy	0.12
St.2	Jul.29	14 : 05	Cloudy	0.09
St.3	Jul.30	13 : 22	Rain	0.05
Kurobe				
St.1	Aug.18	21 : 00	Cloudy	0.06
St.1	Aug.19	15 : 04	Fine	0.04
St.2	Aug.19	11 : 30	Cloudy	0.08

CHAPTER
3

Factors Affecting the Emission of Monoterpenes from Pine Needles

3.1 INTRODUCTION

The estimations of terpene emission rate could be subject to the error resulting from extrapolation of local emission rates to different places and times. It would be necessary for reliable estimation to establish a clear relationship between monoterpene emission rates and environmental conditions. Only limited data have been available concerning the mechanism of terpene emission or the influence of environmental factors on terpene emission. Kamiyama *et al.* (1978) measured terpene emission from a potted pine during three days, and found its high correlation with air temperature and light intensity. For the environmentally controlled chamber experiment, Dement *et al.* (1975) examined the mechanism of terpene emission in *Salvia mellifera* and concluded that emission was dependent on the vapor pressure of the terpenes, the humidity of the air surrounding the leaf and the surface area of essential oil present on the leaf. Tingey *et al.* (1980) examined the influence of light and temperature on monoterpene emission rates from slash pine under controlled enviromental conditions and found that the monoterpene emission rates did not depend on light and depended on temperature in a log-linear manner. In these chamber studies, however, the influence of these environmental parameters on monoterpene emission was observed for only a short-time (30～60min) after each change of environmental conditions, and effects requiring a longer time scale for development might not have been found.

In this study, the long-term effects of light, temperature and humidity on monoterpene emission from pine trees were investigated in order to establish a more reliable relationship between monoterpene emission rates and those environmental factors (Section 3.2). This experiment was conducted usining a dynamic mass balance gas cabinet under natural solar radiation.

It was suggested in Chapter 2, that the composition of terpenes in the leaf oil of trees in forests is responsible for the monoterpene composition in the atmosphere. Relationship between the monoterpene compositions of the leaf oil and the emitted gas was also studied to examine the mechanism of terpene emission from plants (Section 3.3).

3.2 INFLUENCE OF LIGHT, TEMPERATURE AND HUMIDITY ON MONOTERPENE EMISSION RATES FROM *Pinus densiflora*

3.2.1 Experimental

Plant material

Eight seedlings of Japanese red pine *(Pinus densiflora)*used for the experiment were supplied from the Biology Division of the National Institute for Environmental Studies. The seedlings were 50~70cm in height and were planted in 16cm ϕ pots. These plants were cultured in a greenhouse for approximately 2 years at a temperature of 25°C and at a relative humidity of 70% and were watered once a week. The plants had mature needles and there were no significant bark lacerations or gum exudations. The trees were transferred a week before the measurement for monoterpene emissions into a gas cabinet controlled at a similar environmental condition to that in the greenhouse. No significant growth of the plants was observed during the experiment.

Gas cabinet

A dynamic mass balance gas cabinet (2,000W × 2,000D × 1,800H mm)(Fig. 3. 1) was used to determine monoterpene emission. The gas cabinet was surrounded by window glass and was housed in a controlled environment chamber. The temperature and humidity of the air coming into the cabinet were regulated to within ±1°C and within ±5% respectively. Light was supplied by natural sunlight at an intensity which was reduced to approximately one-fourth of that of the radiation outside due to passage through glass. Ambient air was pumped into the cabinet after passing through charcoal to remove pollutants such as sulfur oxides and nitrogen oxides. Air flow was controlled at $15m^3/h$, resulting in residence time of 30 min in the cabinet, and was introduced into the cabinet uniformly through small holes scattered on the whole surface of the floor. Leaf temperature was measured with a thermography apparatus. Radiation intensity at canopy height was measured with a photometer.

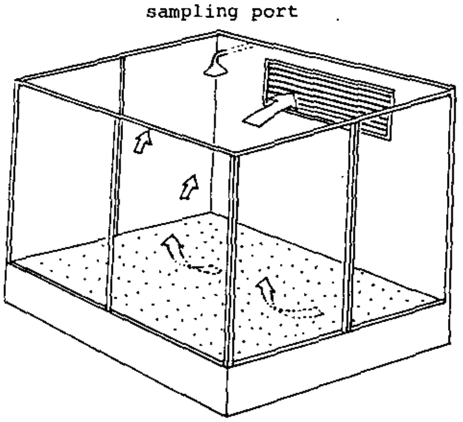


Fig. 3.1 A dynamic mass balance gas cabinet.

Experimental procedure

The influence of temperature on monoterpene emissions at various light levels was examined at 15°C, 20°C and 25°C. To study the effect of humidity on monoterpene emissions, the experiments were conducted at 70% and 90% relative humidity at 20°C. After each change of experimental conditions, air samples for monoterpene analysis were collected a few times (usually at 10:00, 13:00, 16:00) in the daytime for the following several days. To evaluate the effect of light intensity on monoterpene emissions, diurnal variation of monoterpene emission was observed.

Sampling and analysis of monoterpenes in the gas cabinet were conducted with the same way as in Section 2.2. For each analysis, dual 1 l air samples were collected from the sample port of the gas cabinet (Fig. 3.1).

The monoterpene emission rate was calculated from the mean concentration of monoterpenes in the gas cabinet by the following equation.

$$E = CF/W$$

where, E : monoterpene emission rate, μg [g dry wt]$^{-1}$ h^{-1}
C : monoterpene concentration in the cabinet, μg m^{-3}
F : air volume exchanged per unit time, m^3 h^{-1}
W : dry weight of pine needles, g dry wt.

3.2.2 Results and discussion

The major monoterpenes emitted from the pine trees were α-pinene, β-pinene, myrcene, limonene and β-phellandrene. Their emission rates and the solar radiation measurements at the roof top are shown in Fig. 3.2. A significant diurnal change of monoterpene emission rates with a maximum around noon was observed with the exception of cloudy or rainy days (degrees of cloudiness can be found from the data of solar radiation in Fig. 3.2). This conflicts with the previous studies (Dement *et al.*, 1975; Tingey *et al.*, 1980) reporting that monoterpene emissions were independent of light intensity. It was observed that the emission rates of four monoterpenes varied in a similar fashion. Correlation coefficients were calculated to analyze their relationship mathematically (Table 3.1). It was found that β-pinene has rather small correlation with the other three monoterpenes. This difference of β-pinene is remarkable in the data immediately after a change of environmental conditions (*e.g.* Feb.1 16:00, Feb.5 16:00, Mar.4 16:00 in Fig. 3.2). This might be relevant to the observation by Renwick and Potter (1981) that the effect of SO_2 fumigation on β-pinene emission was signficant compared to the effect on other monoterpene emission.

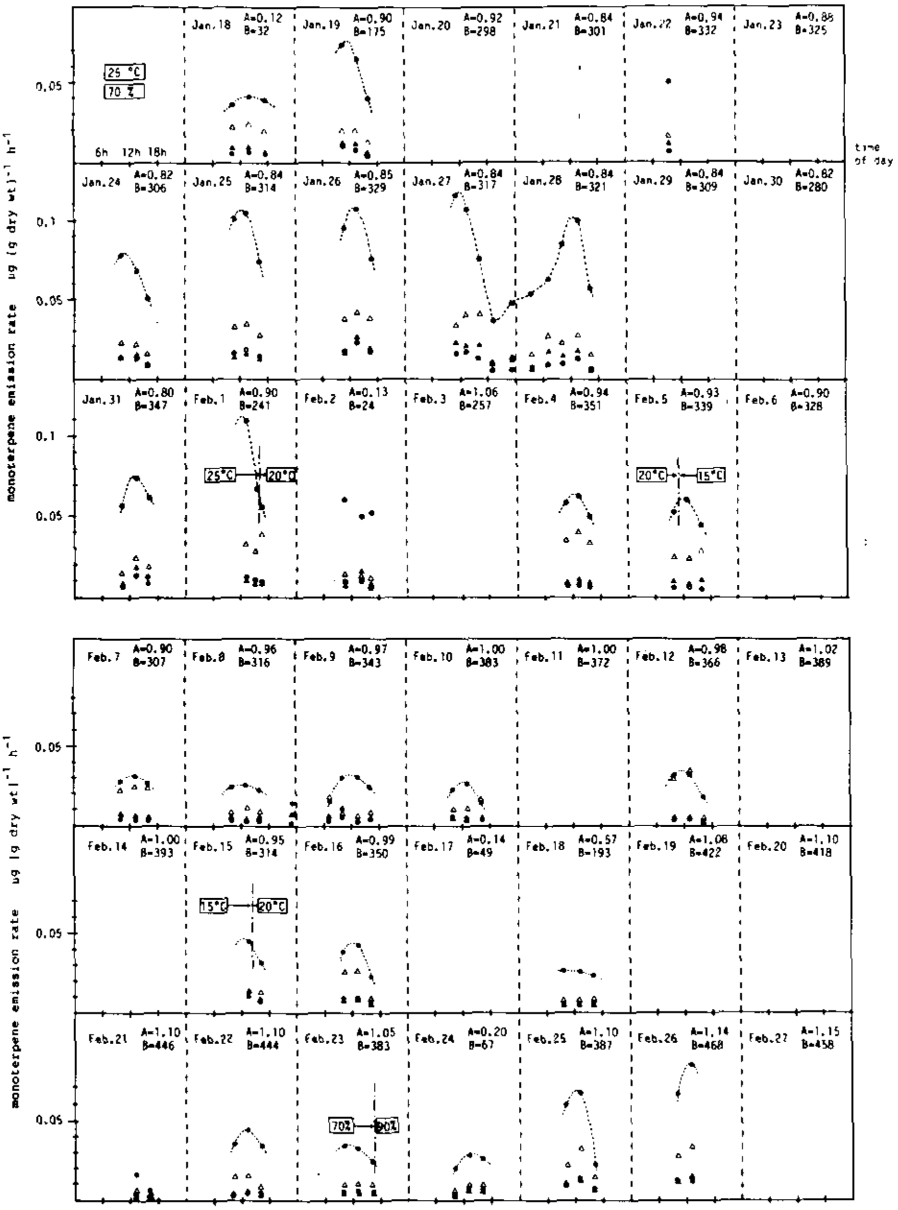


Fig. 3.2 Variation of monoterpene emission rate from *Pinus densiflora*

●: α-pinene, △ : β-pinene, ○ : myrcene, ▲ : β-phellandrene

A : solar radiation at noon (cal/cm^2 • min)

B : integrated radiation over the daytime (cal/cm^2)

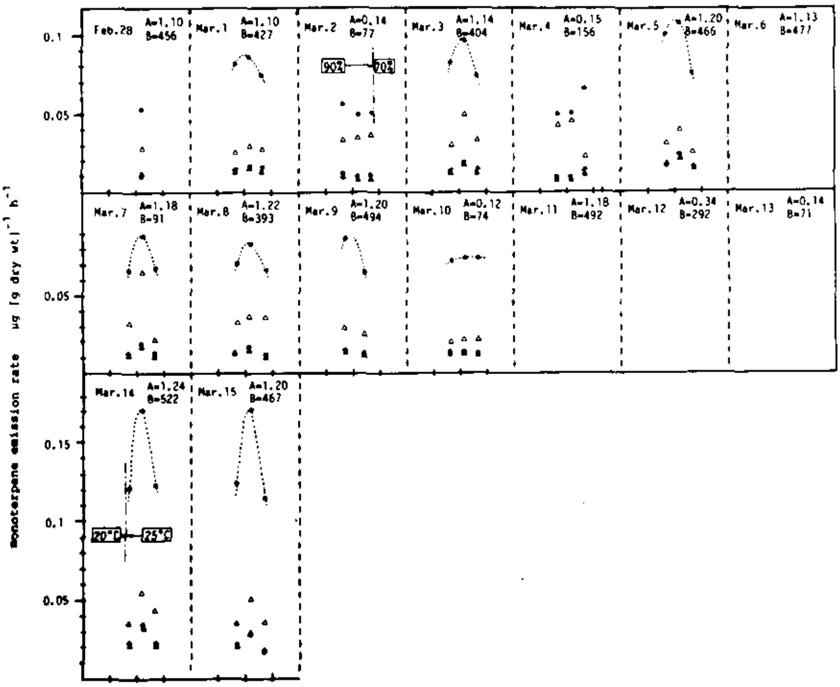


Fig. 3.2 Continued

Table 3.1 Correlation coefficients among the emission rates of four monoterpenes from *Pinus densiflora*

	α-pinene	β-pinene	myrcene	β-phellandrene
α-pinene	1	0.73	0.92	0.87
β-pinene		1	0.66	0.63
myrcene			1	0.91
β-phellandrene				1

To determine the influence of temperature, all the data on α-pinene emission rates interpolated to noon (Fig.3.2) were grouped according to the intensities of the solar radiation at noon (0.8~1.0, 1.0~1.2, >1.2cal/cm^3 min) and they were plotted against temperature (Fig. 3.3a.). The emission rate of α-pinene was log-linearly related to temperature at each range of solar radiation. A single regression line (—) for the logarithm of α-pinene emission rate versus temperature was fitted to the most abundant data with a solar radiation 0.8~1.0cal/cm^2 min. The broken line (---) connecting the data from the two nights with different temperature has the same slope as this regression line. This log-linear relationship indicates that emissions increased exponentially with temperature. Comparing this relationship between α-pinene emission rate and temperature with the results for slash pine studied by Tingey *et al.* (1980) (Fig. 3.3b), it is found that the slope is higher in the former. The significant effect of temperature on monoterpene emission observed in the present study was considered to be the result of measuring the effect of changing conditions over a longer period of time

As for humidity, there was no difference between the monoterpene emission rates at 70% r.h. and at 90% r.h. (Fig. 3.3a). This suggests that humidity of this range does not significantly influence terpene emission rate.

The influence of light intensity on monoterpene emission rate is apparent in diurnal variation in Fig. 3.2. In Fig. 3.3a, it is also found that, at the same ambient tempereture, α-pinene emission rate tends to be higher under intensive solar radiation. A part of the effect of light on terpene emission could be explained by the variation of leaf temperature as a result of exposure to radiation. At midday, the leaf temperature of some leaves exposed to the sun was often as much as 5~6 degrees higher than the air temperature, while that of shaded leaves was nearly equal to the air temperature. In Fig.3.3a, a five-degree increase of temperature corresponds to a 70% increase of α-pinene emission rate. However, the increase of monoterpene emission due to the average increase of leaf temperature is considered to be much less than that, because some leaves are shaded by other leaves. Therefore, the large difference of monoterpene emission rate due to radiation, twice higher in the daytime than at night (Fig. 3.2), cannot be explained completely by the increase of leaf temperature. This means that "light" does influence terpene emission rate, although Dement *et al.* (1975) and Tingey *et al.* (1980) reported its independence of light.

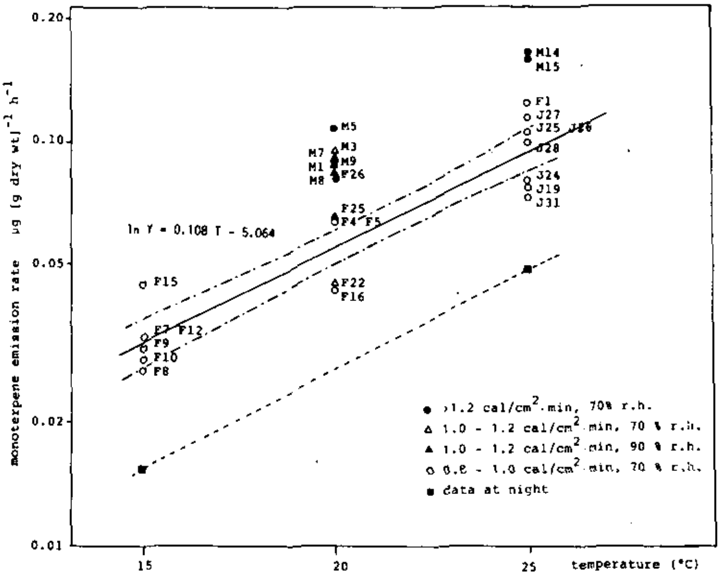


Fig. 3.3 (a) Temperature curve for α-pinene emission rate by red pine

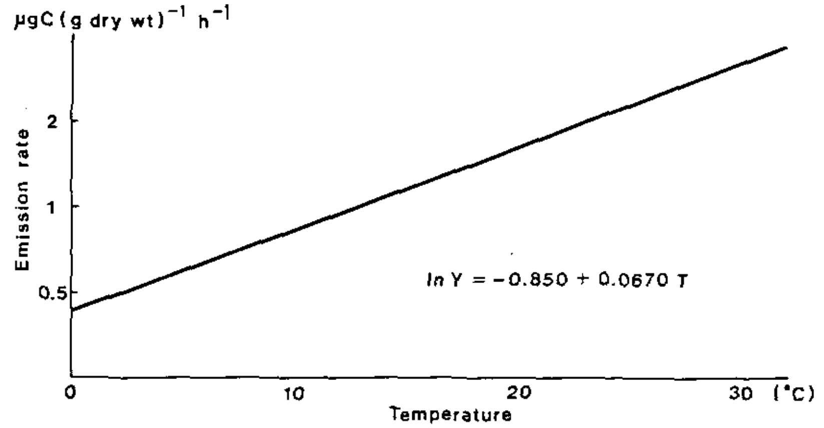


Fig. 3.3 (b) Temperature curve for α-pinene emission rate by slash pine (Tingey *et al.*, 1978).

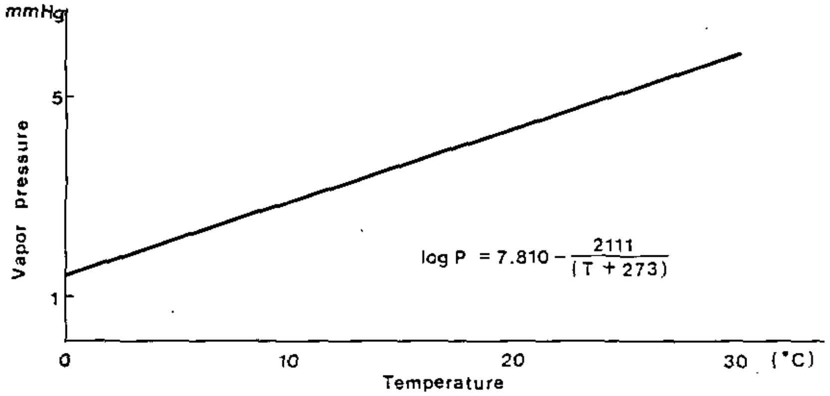


Fig. 3.3 (c) Temperature curve for α-pinene vapor pressure (Jordan, 1954)

The relationship of α-pinene emission rate and temperature observed by Tingey *et al.* (1980) (Fig. 3.3c), is similar to that of its vapor pressure and temperature (Fig. 3.3c), suggesting that the monoterpene emission from leaves is controlled primarily by vapor pressure in a short term. The more significant dependence of monoterpene emission on temperature and its dependence on light found in the present study are considered to be correlated with the variation of the monoterpene amount in the leaves. That is, monoterpene amount in leaves is influenced by temperature and light, and affects its emission rate together with its vapor pressure. This is a reasonable interpretation, considering that monoterpenes are products of synthetic process in plant originated from photosynthesis, and that photosynthesis is dependent on light and temperature (Kramer & Kozolowski, 1979). These influences on monoterpene emission rate through the variation of monoterpene amount are rather indirect and may require some time-lag before they are evident.

From the above considerations, it can be concluded that the variation of monoterpene emission rate depends on the monoterpene amount, affected both by light and by temperature, and on its vapor pressure, controlled only by temperature. This means that for the reliable estimation of the seasonal variation of monoterpenes emission rates, knowledge of their biosynthetic rates is essential in addition to that of temperature.

3.3 THE RELATIONSHIP BETWEEN THE MONOTERPENE COMPOSITIONS OF THE FOLIAR EMISSION GAS AND THE LEAF OIL OF *Pinus densiflora*

3.3.1 Experimental

The monoterpene compositions in the leaf oil and the foliar emission gas of *Pinus densiflora* were analyzed and compared for the study of the mechanism of monoterpene emission. Samples of pine needles were collected in a pine forest at Tsukuba district and the analytical experiments were started within 1 hr. after sampling.

Needle oil sample : The freshly gathered pine needles (200g) were steam distillated for 1.5 hrs. in an all-glass apparatus. The steam distillate was extracted with hexane and was concentrated *in vacuo* at 35°C.

Foliar emission gas sample : The freshly gathered pine needles (100g) with their ends wrapped with polyethylene film were placed in a gas exchange flask where high purity air was flowing at the rate of 100ml/min at room temperature. After 10 min equilibration time, the volatile constituents in the air flowing out of the flask were sampled by adsorption onto a Tenax GC adsorbent packed in a tube.

Analytical runs were performed on a Hewlett-Packard 5992A GC-MS equipped with a selected ion monitoring (SIM) function. The chromatographic conditions were : GC analytical column, 5% Silicone DC-200 + 5% Bentone 34 on Chromosorb W AW DMCS (60-80mesh) ; temperature program, 0°C (2min)→100°C (at 16°/min) ; carrier gas, helium at 20ml/min. The monoterpenes contained in the needle oil sample and the foliar emission gas sample were identified by their retention times and mass spectra. The SIM chromatograms of m/z 93 ion were also obtained for quantitative comparison.

3.3.2 Results and discussion

The components of the needle oil were α-pinene, camphene, β-pinene, myrcene, limonene, β-phellandrene and terpinolene. Fig. 3-4 shows the m/z 93 ion chromatograms of a) the needle oil and b) the foliar emission gas. The chromatographic patterns of a) and b) are considerably different from each other and this difference might be of value in indicating the mechanism of terpene volatilization from the leaves. In Fig. 3.4, it was found that monoterpenes with high volatility such as α-pinene are more dominant in the emission gas than in the leaf oil. This suggests that the difference of those monoterpene compositions is correlated with the vapor pressure of each monoterpene. If monoterpene emission rates were controlled by vapor pressure, the emission rate of each monoterpene is supposed to be proportional to the product of its amount in the leaf oil and its vapor pressure. In that case, the chromatographic pattern for the emission gas can be predicted from the peak height in the chromatogram of the leaf oil (Fig. 3.4a) multiplied by the vapor pressure of the corresponding monoterpene. Table 3.2 shows the vapor pressures of the major monoterpenes and the data of their peak heights. The predicted peak heights normalized to α-pinene are plotted in Fig. 3-4b as the ★ marks, and fairly coincide with those of the observed ones.

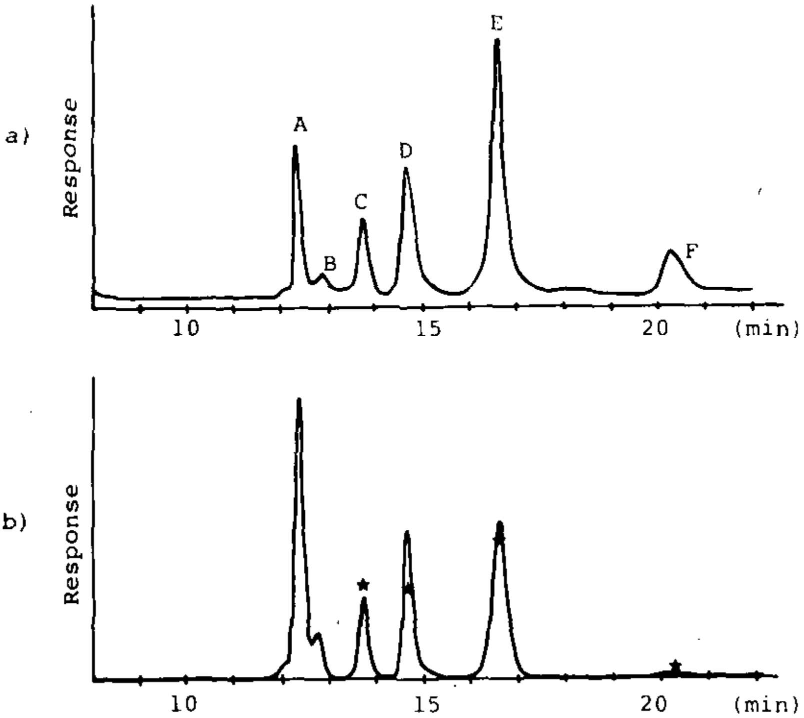


Fig. 3.4 M/z 93 ion chromatograms of a) the pine needle oil and b) the foliar emission gas.
A : α-pinene, B : camphene, C : β-pinene, D : myrcene, E : β-phellandrene, F : terpinolene

Table 3.2 Major monoterpenes in the Needle Oil and the Foliar Emission Gas of *Pinus densiflora*

Compound	Vapor Pressure[a] (mmHg) at 30°C (VP)	Peak height[b] in the needle oil (H_o)	Peak height[b] in the emission gas (H_g)	Predicted peak height[b] in the emission gas ($VP \times H_o$)
α-pinene	7.0	100	100	100
β-pinene	5.0	48	29	34
myrcene	2.6	90	54	33
β-phellandrene	2.0	174	55	50
terpinolene	0.8	25	2	3

a: Vapor pressure were based on the data of Jordan (1954). Because of the similarities in boiling point and molecular structures, the vapor pressure of β-phellandrese was assumed to be equal to that of α-phellandrehe.

b: Peak heights were normalized to that of α-pinene(100).

It is concluded that the difference between the monoterpene composition of the leaf oil and that of the emission gas from pine leaves depends mainly on the vapor pressure of monoterpene component, that is, vapor pressure is an important factor involved in the emission of monoterpene.

3.4 THE MECHANISMS OF MONOTERPENE EMISSION FROM PLANTS

The model of monoterpene emission from plants which accounts for the above experimental results was investigated.

Although normal gas exchange occurs via stomatal opening, the emission of terpenes log-linearly related to temperature is considered to be independent of stomatal opening. Dement *et al.* (1975), who studied monoterpene volatilization in *Salvia mellifera,* also reported that volatilization of camphor is independent of stomatal opening. Therefore, the pathway through stoma on leaves was omitted in the model. Fig. 3.5 shows the possible pathway for monoterpene emission through cuticles. Monoterpenes contained in oil cells exude as vapor into surrounding epithelial cells or intercellular space, and emanate into the atmosphere through mesophyll cells, epidermal cells and cuticles. The relationship of vapor pressure (P_i) of each monoterpene which exudes from oil cells and its molar fraction (x_i) in an oil cell is given by the following equation ;

$$P_i = K_i x_i \qquad (1)$$

where, K_i = constant = P_{is}/x_{is}

P_{is} = saturated vapor pressure of monoterpene(i)

x_{is} = saturated mole fraction of monoterpene(i)

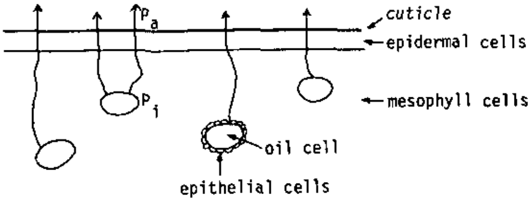


Fig. 3.5 Possible mechanism of monoterpene emission from leaves.

When monoterpene around oil cells emanates into the atmosphere through mesophyll cells, epidermal cells and cuticles, its flux(F) is given by eq. (2).

$$F_i=((P_i-P_a)/(r_{1i}+r_{2i}+r_{3i}))\cdot A \tag{2}$$

where, P_a = vapor pressure of monoterpene in air near leaf surface, $<<P_i$
r_{1i} = mesophyll cell resistance
r_{2i} = epidermal cell resistance
r_{3i} = cuticular resistance
A = surface area of oil bodies

As P_a is negligible compared with P_i, eq.(2) becomes,

$$\begin{aligned} F_i &= ((P_i/(r_{1i}+r_{2i}+r_{3i}))\cdot A \\ &= ((P_{is}x_i/x_{is}(r_{1i}+r_{2i}+r_{3i}))\cdot A \end{aligned} \tag{3}$$

In Section 3.3 the emission rate of each monoterpene was found to be proportional to the product of its concentration in the leaf oil and its saturated vapor pressure. This can be explained by eq.(3) under the assumption that the saturated molar fraction and resistances are similar for all monoterpenes. In eq.(3), P_{is} is greatly influenced by temperature and results in log-linear relationship of temperature and monoterpene flux which was experimentally observed in Section 3.2. The surface area of oil bodies, A in eq. (3), is considered to depend on temperature and light through the variation of oil amount, the products of secondary metabolism following photosynthesis. This effect on monoterpene emission rate was also observed in Section 3.2.

Although this model is only hypothetical one, it accounts for the experimental results roughly. For validation of this model, further investigations are necessary.

CHAPTER
4

Variation of Monoterpene Concentration and Emission Rate in a Pine Forset

4.1 INTRODUCTION

As for seasonal variation in ambient terpene concentration, there has been only one paper by Rasmussen and Went (1965). These authors analyzed air samples for a few months from several vegetated areas with GC-FID (the identification of terpenes was based only on a comparison of gas chromatogram retention times), and reported 10ppb (v/v) organic volatiles during summer and 2ppb during winter. They also reported that high concentrations were observed at the time of the dying of leaves and the mowing of meadows. In their study, environmental factors such as temperature and wind velocity were not sufficiently taken into consideration, besides the times and the periods for the measurements were not enough.

More systematic measurements of terpene concentration and emission rates (variation with time of day, season and location) are necessary to establish their role and fate in the atmosphere. The purposes of this Chapter are (1) to present in detail the variation in atmospheric monoterpene concentration measured with GC-MS in a forest over a period of one year and to discuss the relationship between various environmental factors and terpene concentration, and (2) to present seasonal variation of monoterpene emission rate from a branch in the forest and to evaluate the worldwide emission estimate using these emission data and the information obtained in Chapter3.

4.2 SEASONAL AND DIURNAL VARIATIONS OF MONOTERPENES IN THE ATMOSPHERE IN A PINE FOREST

4.2.1 Experimental

The analytical technique for measuring sub-ppb monoterpenes in the atmosphere has been described in Chapter 2.

A forest at Tsukuba was selected for this study. In the forest, pine *(Pinus densiflora)* trees are planted with a spacing of 2～3m in an area of 20,000m^2 extending from east to west. The trees were twenty-five years old, each averaging approximately 8m in height. In order to study seasonal variation, the atmospheric monoterpene concentration was measured at 11:00 a.m. almost every day during one year period (May 14, 1980～May 20, 1981 : 248 data points). The diurnal variation was measured on June 5 - June 6, 1980. Dual samples were collected at the same time.

All samples were collected 1.5m above the ground at the center of the forest. The horizontal and vertical distributions of monoterpenes in the forest were also studied.

Environmental factors (atmospheric temperature, humidity, wind direction wind velocity, UV radiation and atmospheric concentration of nitrogen oxides and ozone) were monitored at the edge of the forest, 20m apart from the sampling point. The concentration of nitrogen oxides (NO and NO_2) was determined by the Saltzman method (GRH-74, Denki-kagaku-keiki Co.) and that of ozone was measured by the chemiluminescence method (Ozone meter 806, Kimoto Electronic Co.).

4.2.2 Results and discussion

(1) Seasonal variation

The detected monoterpenes in the pine forest were α-pinene camphene, β-pinene, myrcene, limonene and β-phellandrene. α-Pinene was always dominant among them throughout the 12-month study period.

The concentraion of monoterpenes varied greatly from day to day, and from season to season. Fig. 4.1(a) shows the variation in α-pinene concentration each day at 11:00 a.m. during the one year period (from May in 1980 to May in 1981). The values ranged from n.d. (less than 0.02ppb) to 0.65ppb and their average was 0.13ppb. The concentration during January to March was relatively low with little variation. In contrast to the winter data, those in summer and autumn showed high and irregular values.

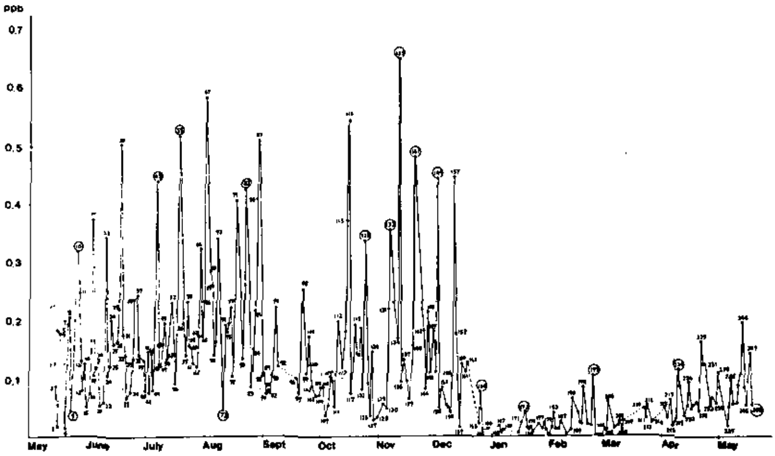


Fig. 4.1 (a) Seasonal variation in the concentration of α-pinene in the pine forest at Tsukuba at 11:00 a.m. (14 May 1980$\sim$19 May 1981)

These variations are considered to reflect the change in emission rate of α-pinene and its rate of disappearance. The emission rate of monoterpenes is known to depend on temperature and the amount of essential oil present on leaf surfaces as discussed in Chapter 3. As for the rate of disappearance, photochemical reactions and ozonolysis are considered to play important roles. Physical dilution due to wind is another important factor. Fig. 4.1(b) and (c)show variations in temperature and ozone concentration during the same period as in Fig. 4.1(a). In Table 4.1, the correlation coefficients between α-pinene concentration and various environmental factors are summarized. Any of these correlation coefficients is not definitive, but α-pinene concentration seems to be somewhat correlated positively to temperature and relative humidity, and negatively to ozone concentration.

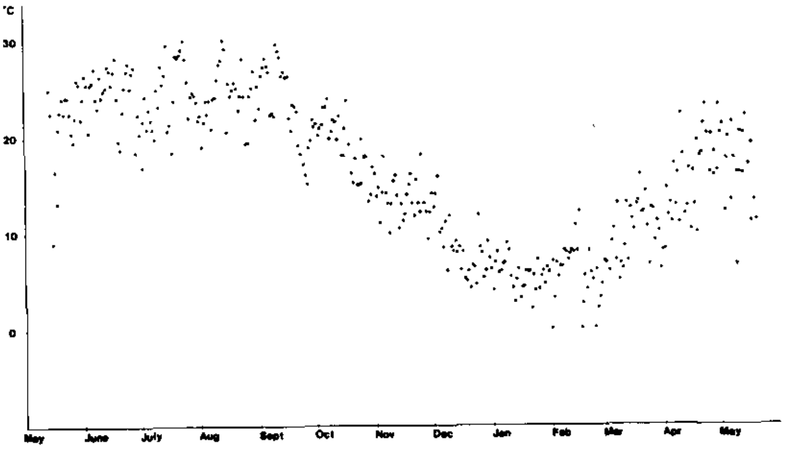


Fig. 4.1 (b) Seasonal variation in ambient temperature in the pine forest at Tsukuba at 11:00 a.m. (14 May 1980~19 May 1981)

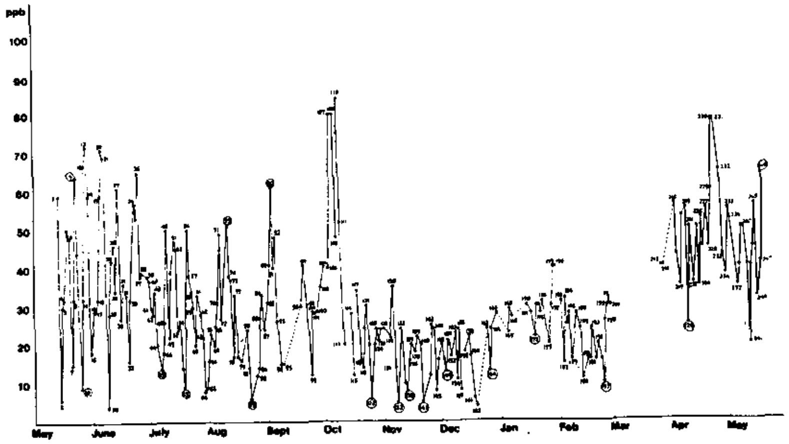


Fig. 4.1 (c) Seasonal variation in ozone concentration in the air in the pine forest at Tsukuba at 11:00 a.m. (14 May 1980~19 May 1981)

Table 4.1 Correlation Matrix (226 data)

	α-pinene	temprature	relative humidity	UV radiation	Wind velocity	Wind direction*	O_3	NO_x
α-pinene	1.00							
temperature*	0.41	1.00						
relative humidity*	0.51	0.38	1.00					
UV radiation*	−0.13	0.39	−0.41	1.00				
wind velocity*	−0.21	−0.05	−0.13	0.06	1.00			
wind direction*,**	0.08	−0.28	−0.16	−0.11	−0.06	1.00		
O_3*	−0.28	0.36	−0.36	0.66	0.07	−0.27	1.00	
NO_x*	0.16	−0.21	0.14	−0.29	−0.19	−0.07	−0.34	1.00

* These factors were measured at the edge of the forest, 20 m apart from the sampling point.

** Since the forest extended from east to west, the wind direction was designated by "1" for east and west winds and by "0" for north and south winds.

In order to find the factors related to α-pinene concentration and evaluate them in the order of importance, a multiple regression analysis was carried out with the "MAP" program (Okuno *et al.*, 1976). Two hundred and twenty-six days' complete sets of data were employed for this regression analysis. Table 4.2 shows the results calculated by a stepwise backward regression method. Judging from the standard partial regression coefficient values, it can be said that a high concentration of α-pinene is present under conditions of high temperature, and low ozone concentrations. NO_x and wind do not seem to have any distinct effects. From Fig. 4.1(a), (b) and (c), it can be seen that (1) the rough seasonal variation of α-pinene may possibly be explained on the basis of temperature difference, and (2) changes from day to day may be correlated with ozone concentration. The latter correlation is particularly apparent in the data shown by encircled numbers in Fig. 4.1(a) and (c). This is consistent with the fact that temperature influences the emission rate of monoterpene and ozone contributes to the breakdown of these compounds in the air. The positive correlation between α-pinene concentration and relative humidity in Table 4.2 is presumed to stem from their correlation with other environmental factors. For instance, both are positively correlated to temperature and negatively correlated to ozone concentration.

Table 4.2 Multiple Regression Output

Sample Size 226

Selected independent variable

1/TEMP	: reciprocal of absolute temperature
HUM	: relative humidity
LOGO 3	: logarithm of ozone concentration*
LOGNOX	: logarithm of NO_X cocentration*
UV	: UV radiation
WIND V	: wind velocity
WIND D	: wind direction

Selected dependent variable

LOGP : logarithm of α-pinene concentration*

Multiple correlation R=0.81

variable	standard partial regression coefficient
1/TEMP	−0.66
HUM	0.18
LOGO 3	−0.30
LOGNOX	0.14
WIND V	−0.13
WIND D	0.11

* To obtain a nearly normal distribution, a small fixed value (2 ppb for $[O_3]$, $[NO_x]$, 0.1ppb for [α-pinene]) was added to each data set.

(2) The relationship of [α-pinene], $[O_3]$ and temperature

Here, the effect of environmental factors on α-pinene concentration will be discussed in more detail. Supposing that the reaction with ozone is the only one mechanism for the removal of emitted terpenes (the effect on the removal of terpenes by hydroxyl radicals will be discussed later), the following equation holds for the emission rate and the concentration of α-pinene in the air in a steady state.

$$E_{\alpha\text{-pinene}} = k_{O_3} \times [\alpha\text{-pinene}] \times [O_3] \quad (1)$$

where, $E_{\alpha\text{-pinene}}$	: α-pinene emission rate from leaves
[α-pinene]	: α-pinene concentration in the atmosphere
$[O_3]$	: ozone concentration in the atmosphere
k_{O_3}	: second-order ozone-α-pinene rate constant

The product of [α-pinene] and $[O_3]$ was calculated for each set of the data and its variation is shown in Fig. 4.2. Although the graph exhibits a high degree of variability, the rough seasonal variation is closer to the temperature pattern, compared with the α-pinene concentration pattern. The correlation coefficient of log ([α-pinene] × $[O_3]$) and temperature was 0.78 (cf. the correlation coefficient of log [α-pinene] and temperature was 0.60). Since [α-pinene] × [O_3], which is considered here to be proportional to the α-pinene emission rate, was not of a significant amount around November, the high α-pinene concentrations in that season are considered to have resulted from the lower ozone levels. This is in contrast with Rasmussen's concept that high concentration of terpenes in late autumn may be attributable to the increase in terpene emission at the time of the dying of leaves. Multiple regression showed that wind does not greatly influence α-pinene concentration in the air (Table 4.2). For the 170 data with a wind velocity of 1, 2 or $3m \cdot s^{-1}$, the data of [α-pinene] × [O_3] were grouped by wind velocity and temperature (at intervals of two degrees) and the average of each group was calculated. The results are shown in Fig. 4.3. If wind plays an important role in the dispersion of α-pinene, k_{O_3} × [α-pinene] × [O_3] should be less than $E_{\alpha-pinene}$, since [α-pinene] × [O_3] becomes smaller at higher wind velocity. Indeed, the data with high wind velocity (7-9m s^{-1}) indicated much smaller values. In the range of wind velocity 1-3 m s^{-1}, however, no remarkable difference among the data was observed as shown in Fig. 4.3. This means that a wind velocity less than 3m s^{-1} does not greatly affect the disappearance of α-pinene in the forest.

This relationship of [α-pinene] × [O_3] and temperature was compared with that of α-pinene emission rate from pine seedlings in a chamber and terpemature (Fig.3.3a). They are similar to each other when the temperature is in the range of 10-25°C, as shown with a dotted line. This is expected to be, when eq. (1) holds for $E_{\alpha\text{-pinene}}$, [α-pinene] and [O_3]. In Fig.4.3, the data below about 10°C and above 25°C are smaller than the extrapolated values (broken line) from those in the range of 10-25°C. Possible explanations for this are as follows. (1) As monoterpene emission rate is influenced by temperature and light (Section 3.2), in winter, the rate would be smaller than the predicted value based only on the variation of temperature. (2) In mid-summer, the concentration of hydroxyl radicals in the atmosphere is highest, resulting in the increase of the removal of α-pinene due to its reaction with OH radicals. In this case, the product k_{O_3} × [α-pinene] × [O_3] is smaller than the emission rate.

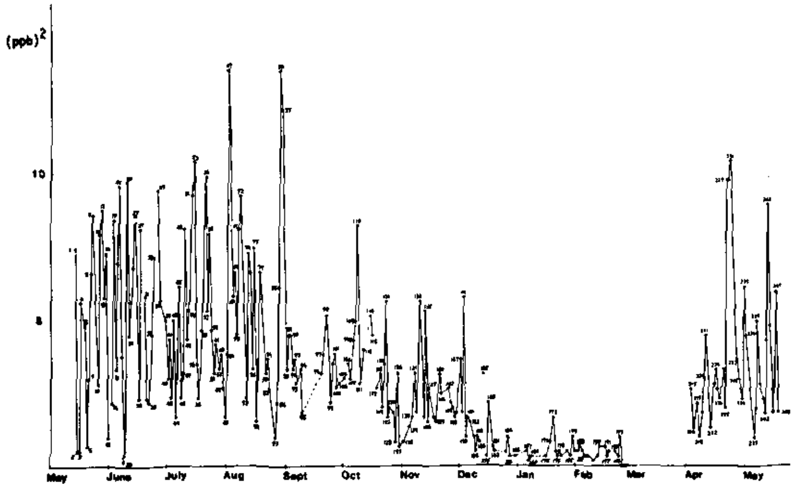


Fig. 4.2 Seasonal variation in the product of the α-pinene concentration and ozone concentration

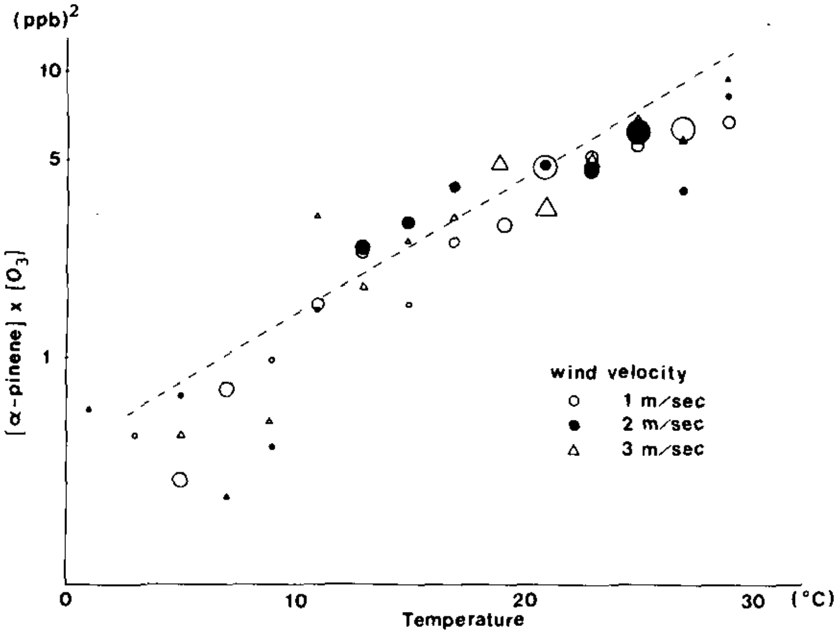


Fig. 4.3 The product of the concentration of α-pinene and ozone vs. temperature
The size of the mark is proportional to the number of data in each division.

(3) Consideration on the reaction with OH radicals

Taking the reacion with OH and other effects into consideration, eq.(1) may be rewritten as follows,

$$E_{\alpha\text{-pinene}} = k_{O_3} \times [\alpha\text{-pinene}] \times [O_3] + k_{OH} \times [\alpha\text{-pinene}] \times [OH] + k_X \times [\alpha\text{-pinene}] \quad (2)$$

where, $E_{\alpha\text{-pinene}}$: α-pinene emission rate from leaves
[α-pinene] : α-pinene concentration in the atmosphere
$[O_3]$: ozone concentration in the atmosphere
k_{O_3} : second-order ozone-α-pinene rate constant
k_{OH} : second-order OH-α-pinene rate constant
k_X : total rate constant of diffusion, adsorption etc.

If the OH concentration in the forest were available, an easier and more precise interpretation would be possible. But, the information on the atmospheric OH is quite scarce. Only a few direct measurements of OH concentration in the atmosphere have been made (Wang *et al.*, 1975; Davis *et al.*, 1976: Perner *et al.*, 1976: Campbell *et al.*, 1979). Considering that the emission rate of α-pinene depends on temperature as shown in Section 3.2, the emission rate at T°C ($E^T_{\alpha\text{-pinene}}$) is expressed with the emission rate at 30°C ($E^{30}_{\alpha\text{-pinene}}$), using the relationship of the emission rate and temperature in Fig. 3.3a :

$$E^T_{\alpha\text{-pinene}} = E^{30}_{\alpha\text{-pinene}} \times \exp(0.11T - 3.3)$$

Transforming eq.(2) with the above relationship, we obtain

$$\frac{\exp(0.11T-3.3)}{[\alpha\text{-pinene}]\cdot[O_3]}=\frac{k_{O_3}}{E^{30}_{\alpha\text{-pinene}}}+\left(\frac{k_{OH}\cdot[OH]+k_X}{E^{30}_{\alpha\text{-pinene}}}\right)\cdot\frac{1}{[O_3]} \qquad (3)$$

If there is no strong correlation between $[O_3]$ and $[OH]$, the intercept of the graph of the regression equation of $\frac{\exp(0.11T-3.3)}{[\alpha\text{-pinene}]\cdot[O_3]}$ vs. $\frac{1}{[O_3]}$ corresponds to $\frac{k_{O_3}}{E^{30}_{\alpha\text{-pinene}}}$. If k_X is negligible in comparison to $k_{OH}\times[OH]$, its slope should be treated as the mean of $\frac{k_{OH}\times[OH]}{E^{30}_{\alpha\text{-pinene}}}$. For regression, 156 sets of data were selected with the following conditions : (1) a wind velocity less than 4m s^{-1} so as to make negligible the wind dispersion effect, and (2) use of data obtained during April-November, omitting the data during winter when photosynthesis is decreased. From the results of the regression, the following values were obtained (1) the emission rate of α-pinene at 30°C ($E^{30}_{\alpha\text{-pinene}}$) : 1.92$\mu$g m^{-3} h^{-1}, and (2) the mean of OH concentration : 1.5×10^{-5}ppb or 4×10^{5} molecules cm^{-3} using the laboratory data of k_{O_3} (8.9×10^{-3} ppm^{-1} s^{-1}, Japar *et al.*(1974)) and k_{OH} ($1.6\times10^{3}$$ppm^{-1}$ s^{-1},Winer *et al.*(1976)). The concentration of OH, 4×10^{5} molecules cm^{-3}, agrees with the average $[OH]$, 0.3 - 2×10^{6} molecules cm^{-3}, in the northern hemisphere (Levy, 1974; Wofsy, 1976; Crutzen & Fishman, 1977). However, there is often some positive correlation between $[O_3]$ and $[OH]$ in the actual atmosphere, and in such cases, the values of $E^{30}_{\alpha\text{-pinene}}$ and $[OH]$ might be somewhat larger than those calculated above (cf. eq. (3)). Judging from the reaction rates and the average concentrations described above, it may be considered that the reaction of α-pinene with OH contributes to the breakdown of α-pinene to a somewhat lesser extent than the reaction with O_3.

(4) Diurnal variation

The diurnal variation should be commented upon. Fig. 4.4 shows the diurnal variation in α-pinene on June 5 - 6 in 1980 plotted with variation in temperature, $[O_3]$ and $[\alpha\text{-pinene}]\times[O_3]$. During the sampling time, the weather was good with little wind, and washout and wind effects did not require consideration. The concentration of α-pinene in the daytime was low, but quite high at night when photochemical reactions and ozonolysis were negligible. The product of $[\alpha\text{-pinene}]$ and $[O_3]$ showed a variation pattern similar to that of temperature except for the data at night when there was an inversion layer at a height of 150m. The increase in the product at the appearance of this inversion layer suggests that the mixing height had a considerable influence on the estimation of emission rate values of monoterpene based on atmospheric concentration.

Because of little variation in α-pinene concentration during the daytime, our particular sampling time (11:00 a.m.), however, did not seem to cause any serious problem in studying seasonal variation in atmospheric monoterpenes in the daytime.

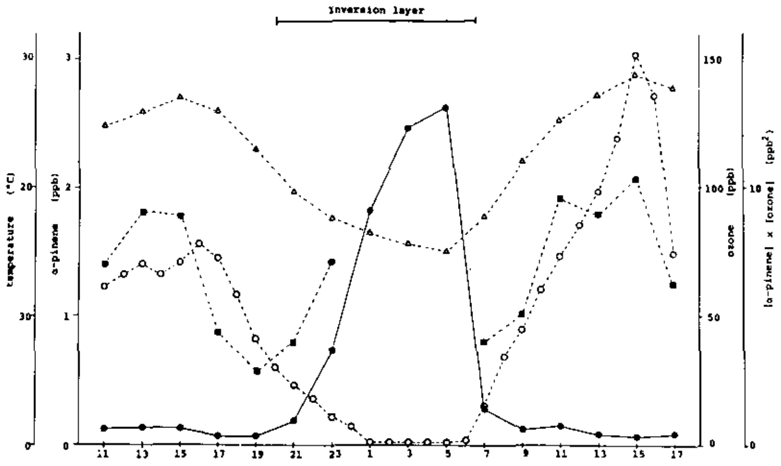


Fig. 4.4 Diurnal variation in the concentration of α-pinene in the air of a pine forest (5-6 June 1980)

● : α-pinene concentration, △ : temperature, ○ : ozone concentration, ■ : the product of the concentration of α-pinene and ozone.

(5) Horizontal and vertical distributions of α-pinene

The vertical distribution of α-pinene was measured in the center of the forest on May 28, 1981. It was cloudy and windless. The results are shown in Table 4.3. It was found that α-pinene concentrations are uniform under the forest canopy and decrease slowly with height above the canopy, on windless days.

Fig. 4.5 shows the horizontal distribution of the α-pinene concentration at several points in and around the forest on May 29 in 1981. There was a small wind from the south-west. Here, we can see that the α-pinene concentration was uniform within the forest and decreased sharply outside the forest.

Table 4.3 Vertical Distribution of α-Pinene Concentration in the Forest (May 28, 1981)

height (m)	α-pinene concentration (ppb)
1.5	0.12±0.02
5	0.12
10	0.13
15	0.11
20	0.10

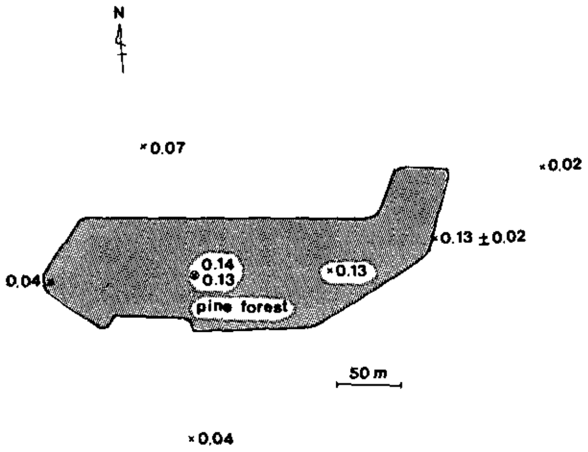


Fig. 4.5 Horizontal distribution of α-pinene concentration (ppb)
⊗ : sampling point for the study of the seasonal variation in monoterpenes.

4.3 SEASONAL VARIATION OF MONOTERPENE EMISSION RATE IN A PINE FOREST AND EVALUATION OF PREVIOUS WORLDWIDE EMISSION ESTIMATE

4.3.1 Measurements of monoterpene emission rate in a pine forest

To assess the contributions of plant-emitted terpenes to the overall hydrocarbon budgets, a valid estimate of terpene emission is essential. Zimmerman developed a simple, practical method for collecting samples to complete the field sampling program. His system involves (1) enclosing a portion of vegetation in a Teflon bag, (2) collecting a background sample of the enclosed air in the bag, (3) filling the bag with hydrocarbon-free air, (4) leaving it over the vegetation for about ten minutes and (5) collecting a sample of the bag air for GC analysis. The emission rate is equal to the total number of microgram of hydrocarbons released per gram of vegetation sampled per unit time. This bag-enclosure method, however may not be a satisfactory way to measure emission for two reasons. Firstly, the leaves may be damaged by touching the enclosing bag, when the air in the bag is being collected. In our preliminary experiment, it was observed that the terpene emission from the leaves damaged by rubbing was significantly higher than from the normal leaves. Secondly, the use of the zero gas in this technique brings about an abrupt change in the environment around the vegetation ; namely the sudden changes in the concentrations of carbon dioxide and water vapor may affect the terpene emission rates from the plants. These could cause some changes in the terpene emission rates from plants.

Improving Zimmerman's method, a more reliable method for measuring the monoterpene emission rates from a branch was developed. The system developed is shown in Fig. 4.6. Basically the method involves (1) collecting a 1 l background air sample in a box for GC-MS analysis, (2) enclosing a branch by the box made of teflon-coated methacrylic resins with one side open, (3) putting the cover leaving a small hole for the branch, (4) enclosing a crevice left between the branch and the edge of the hole with teflon sheet, (5) leaving it over the vegetation for about ten minutes and (6) collecting only 1 l sample of the air in the box for GC-MS analysis. The emission rate (E) can be calculated by the following equation ;

$$E = (C - C_0) \times V/t$$

where, C_o : background concentration of monoterpene
C : sample concentration of monoterpene in the box
V : volume of the box = 297 l
t : the elapsed time after enclosing the vegetation until sampling (intermediate of collection start and end)

This method is free from any touching of the leaves and a drastic change of environment surrounding the vegetation.

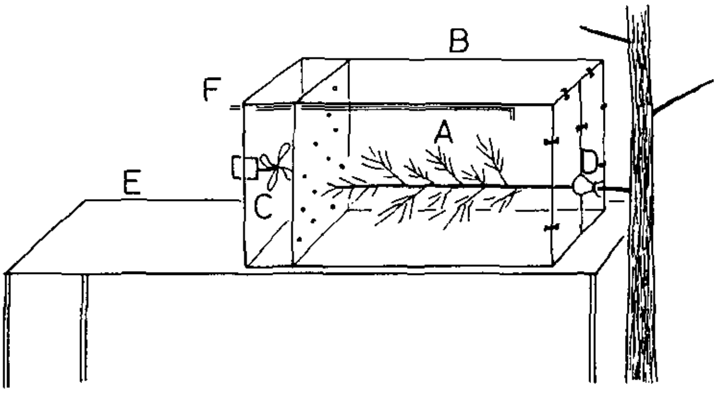


Fig. 4.6 An apparatus for the measurement of monoterpene emission rate from a branch

A : a branch of a pine tree, B : box made of methacrylic resins (inside teflon-coated), C : fan, D : teflon sheet, E : stand, F : sampling port,

Fig. 4.7 shows the increase of α-pinene concentration in the box after enclosing a branch of pine. The liner increase of the concentration suggests that the α-pinene emission rate is almost constant at least for half an hour after enclosure.

The seasonal variation (May, July, Sept., Nov. in 1982, Jan., Mar. in 1983) of α-pinene emission rate from a branch was measured in the pine forest, where seasonal variation of atmospheric monoterpenes were also investigated. Through the experimental period, the number of needles were almost the same (2624 on Aug. 24 and 2492 on Dec. 6). The results are listed in Table 4.4. The relationship between the α-pinene emission rate and the temperature is shown in Fig. 4.8. This relationship was very similar to that obtained for the emission rate predicted from the product of [α-pinene] and [O_3] in the previous section (Fig. 4.3). The approximate emission rate per gram of vegetation per unit time was calculated from the emission rate from the branch, and an average weight of needles (31mg [wet wt] or 10mg [[dry wt])multiplid by the number of needles(2500). The emission rate from pine needles on summer days (at 11:00 a.m., extrapolated to 30°C) was found to be approximately 0.05μg/g [wet wt] h or 0.15μg/g [dry wt] h.

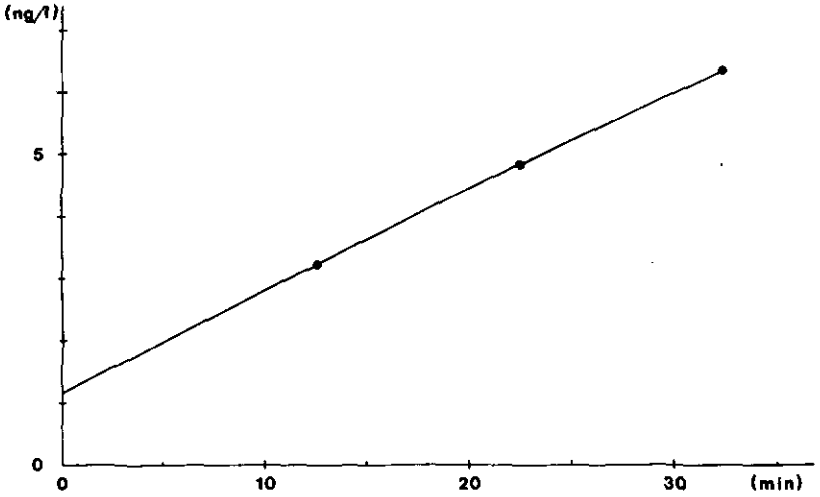


Fig. 4.7 Increase of α-pinene concentration in the box after enclosing a branch of pine (July 9, 1982)

Table 4.4 Seasonal Variation of α-Pinene Emission Rate from a Branch of Pine (at 11:00 a.m.)

date	temperature (°C)	α-pinene emission rate (μg [g dry wt]$^{-1}$h^{-1})
May 7	18	0.048
Jul.9	27	0.110
Sept.17	22	0.076
Nov.2	15	0.024
Jan.12	8.5	0.007
Mar.12	9.8	0.009

4.3.2 Evaluation of the previous estimate for worldwide terpene emission

Houly α-pinene emission rate for the pine forest could be calculated to be 150μg m^{-2} h^{-1} from the emission rate of 0.15μg [g dry wt]$^{-1}$h^{-1} and approximate leaf biomass density factors for conifers in temperate zone, 990g/cm^2(Zimmerman, 1979). In Section 4.2.2(3), α-pinene emission rate in the forest was estimated to be 2μg m^{-3} h^{-1} based on the variation of atmospheric concentration of α-pinene and

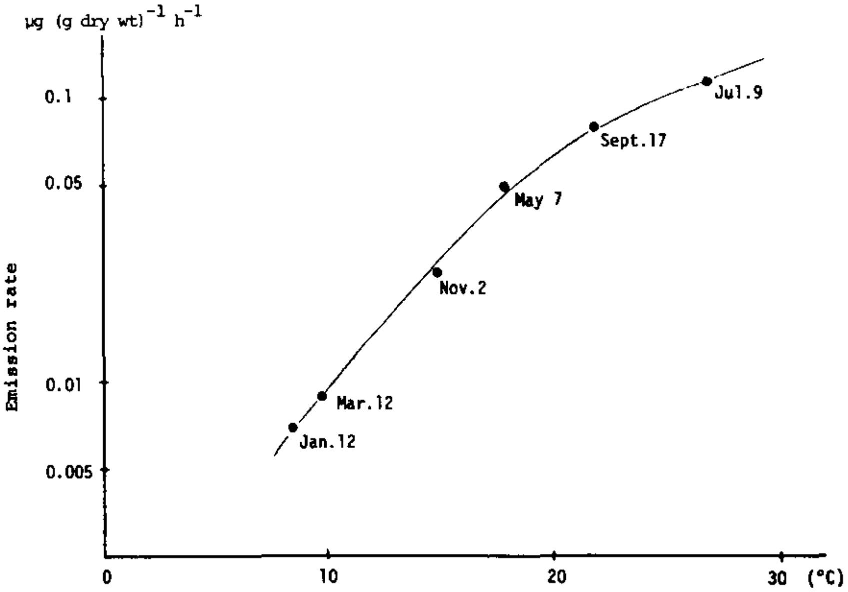


Fig. 4.8 The relationship of α-pinene emission rate from a branch of pine and ambient temperature

ozone. Assuming the mixing height in the forest to be about 50m, the emission rate in the pine forest was calculated to be 100μg m^{-2} h^{-1}, which does not conflict with estimation from the measurement of the emission rate from a branch. This supports that most of atmospheric monoterpenes emitted from plants disapper by their reactions with ozone and hydroxyl radicals in forests.

As α-pinene represented 30-50% (av. 40%)of monoterpenes emitted from the pine trees, the monoterpene emission rate was calculated to be about 400μg m^{-2} h^{-1} in the forest. This is one-order less than the estimated rate 4975μg m^{-2} h^{-1} for coniferous forest at 30°C) by Zimmerman (1979). This difference is considered to result from the overestimation of the latter using bag-enclosure method with some measurement errors as suggested in the previous section.

As for seasonal variation of monoterpene emission rate, it was found that Tingey's algorithm (Fig. 3.3b) for terpene emission rate used by Zimmerman to correct the emission factors from 30°C to average monthly temperature could not account for the variation in the field (Fig. 4.8), and the emission rate was much lower at winter when photosynthetic rate was greatly reduced. Zimmerman's estimation would also suffer from some errors resulting from the neglect of light influence on monoterpene emission rate

As mentioned above, Zimmerman's estimation, the most extensive work for the estimation of terpene emission rate, was found to be probably in error both in measurement and extrapolation. Annual global terpene emission rate is probably necessary to be decreased by one-order. In this case, however, nealy 1 × 10^8 t/y of terpenes are still emitted into the atmosphere, and their role as ozone consumer or aerosol producer in the atmosphere remains important.

CHAPTER
5

Aerosol Particles Formed from the Products of Chemical Reaction of Terpenes with Ozone

5.1 INTRODUCTION

In Chapter 4, it has been shown that monoterpenes emitted from plants into the atmosphere react with ozone rapidly and most of them seem to disappear before they diffuse out of forests. A large fraction of the terpene products is expected to be in the aerosol phase, since the oxygenated products through reactions with O_3 and OH should have a lower vapor pressure than the parent compound (the monoterpenes have boiling points higher than 150°C). Aerosol or particulate matter in the atmosphere is a major source of contamination, having an impact upon visibility, health, and even weather and climate as a result of light scattering. Went (1960) first observed a blue haze by placing O_3 and pine needles in a bell jar, and further laboratory studies demonstrated that atmospheric monoterpenes are very reactive and their products result in aerosols.

Haze formation was studied by Wilson *et al.* (1972). They synthesized aerosol products in an environmental smog chamber, and collected the aerosols produced from the photooxidation of α-pinene by extraction and derivation technique. Gas chromatogram and mass spectra of the extracted compounds indicated the presence of pinonic acid and nor-pinonic acid. In a later study on haze formation also involving photooxidation of α-pinene in a smog chamber, Schwarz (1974)was able to identify an additional product, pinononic aldehyde, in the neutral fraction. Another work on the aerosol products formed from limonene and terpinolene has also been carried out (Schuetzle & Rasmussen, 1978). However, their identification of the products, based only on the high resolution mass spectrometry of the mixture, is not considered to be confirmative. As for field study, the aerosols collected at the Blue Ridge Mountains contained pinonic acid (Wilson *et al.*, 1972). However, there have been few other observations of terpene-origin aerosols even in and around forests. This might be due to the fact that little data are available for compounds which would be present in the terpene-origin aerosols. In the above chamber studies by Wilson *et al.* (1972) and Schwarz (1974), only photochemical products of α-pinene were studied and ozonolysis products of monoterpenes were not investigated, while the olefin-ozone reaction is considered to be the most important of the atmospheric reactions of olefins including terpenes (O'Neal *et al.*, 1973).

Therefore, ozone reaction products of α-pinene, β-pinene and limonene, which are common monoterpenes in forest air, were investigated using chamber experiment in order to obtain information useful for identifying terpene-ozone reaction products in the ambient atmosphere (Section 5.2). The products were analyzed by capillary GC-MS, since the packed column which was used for GC analyses by preceding workers is unsatisfactory for resolving complicated and unknown mixtures. Field studies to characterize the aerosols in a forested area were conducted in a cedar forest at Kiyosumi in Chiba Prefecture and in a pine forest at Tsukuba in the summer of 1982, and it was found that pinon aldehyde, which has not been reported as terpene-reaction product, is common in forest air (Section 5.3).

5.2 ANALIYSIS OF PRODUCTS FROM THE OZONOLYSIS OF α-PINENE, β-PINENE AND LIMONENE BY *GC-MS*

5.2.1 Experimental

Monoterpene - ozone reaction

Monoterpene-ozone reaction was conducted with the apparatus shown in Fig. 5.1 at room temperature. Ozonized air and monoterpene-containing air were mixed flowing through a 3 l glass bulb (J) (50 cm long) which served as a flow reactor. Individual flow rate was controlled at 1.0 l min^{-1} with flow meters. The concentration of ozone was calibrated iodometrically. The monoterpenes used (α-pinene, β-pinene and d-limonene) were of the highest grade available and their gas chromatograms are shown in Fig, 5.2. The concentration of monoterpene, which was diffusing constantly into the flowing air from the liquid sample with a constantly maintained level (H), was determined from its loss in quantity through the reaction experiment. Experimental conditions for the ozonolysis of three monoterpenes are listed in the left column of Table 5.1. For each monoterpene, two experiments were conducted with ozone concentration in excess of (No.1, 3, 5) and nearly equal (No.2, 4, 6) to monoterpene. Under these conditions, formation of smog-like aerosols was observed in the reactor. The products were collected in a cold trap (K) cooled to -70°C. For the analysis of low-molecule carbonyls, 1 ml of the gas coming out of the reactor was sampled with a gas-tight syringe just before the trap, and immediately submitted to GC-MS analyses. After the reaction for several hours, the gas supplies were turned off, and the trap was allowed to warm to ambient temperature. The remaining light-yellow, odorous, viscous liquid was dissolved in acetone and analyzed with GC and GC-MS.

Analytical procedure

(1) Low-molecule carbonyl products

One ml of the product gas was analyzed with GC-MS (Hewlett-Packard 5992A). Chromatographic separations were accomplished on Porapak N (80/100) packed in a glass column (6 ft. × 2 mm ID). The oven temperature was maintained at 120°C and the carrier gas (He) was let flow at a rate of 20 ml/min. The selected ion monitoring (SIM) detection with high sensitivity was used for determination. The ions having m/z 29, 30, 43, 44 and 58 were monitored for the identification and quantification of formaldehyde, acetaldehyde and acetone.

(2) Viscous liquid products

The solution of the viscous liquid products was submitted to GC and GC-MS analyses. Fractionation into acid and neutral components was also performed. Prior to fractionation, the solvent was evaporated and the residue was redissolved with methylene chloride. The acid fraction was isolated by extraction of the

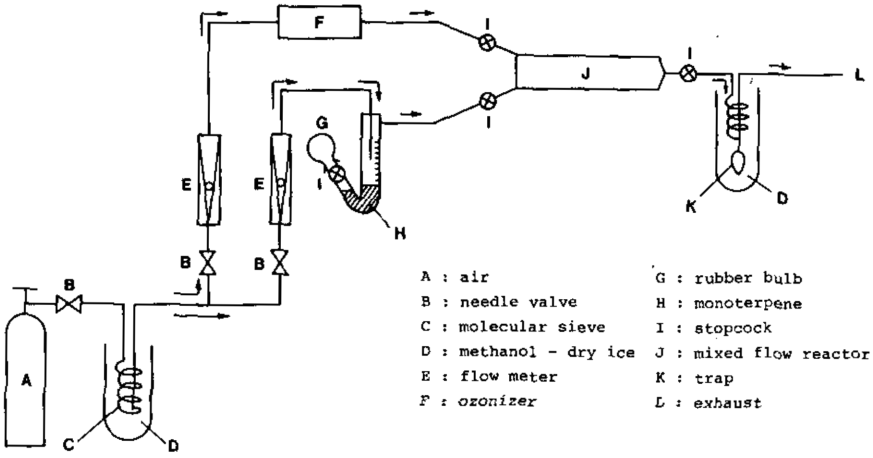


Fig. 5.1 Apparatus for the reaction of monoterpenes with ozone

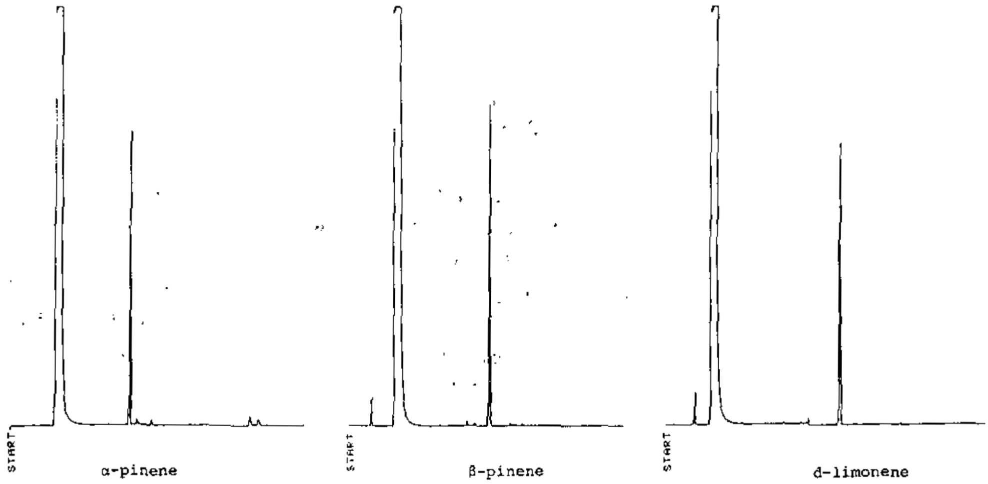


Fig. 5.2 Gas chromatograms of the monoterpenes used for the reaction experiment

methylene chloride solution with 2 N NaOH. The basic aquatic extract was then reacidified to pH ~ 1 with HCl and extracted with methylene chloride. Each methylene chloride solution containing neutral and acid components was dried over anhydrous Na_2SO_4, and was concentrated into several ml. The acid fraction was treated with diazomethane to form methyl esters. Each fraction was submitted to GC and GC-MS analyses.

Analytical gas chromatography was performed on a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector (FID) and fitted with a glass capillary column (0.2 mm ID × 25 m) coated with methyl silicone (like OV-1). The carrier gas was He at 1.2 ml/min and the oven was programmed from 30°C

Table 5.1 Concentration of Reactants and Low-Molecule Carbonyl Products of Monoterpene-Ozone Raction

No.	reactants (ppm)		low-molecule carbonyl products (ppm)		
	α-pinene	O_3	HCHO	CH_3CHO	CH_3COCH_3
1	380	650	39	3.0	39
2	380	340	19	1.2	15
	β-pinene	O_3			
3	217	650	107	6.2	20
4	215	340	100	1.9	20
	d-limonene	O_3			
5	115	650	25	1.0	1.4
6	105	65	12	1.0	1.4

(2 min) to 260°C at 4°/min. Samples were injected into the GC at a split ratio of 1/20. Computerized GC-MS analyses were carried out on a JMS DX-300 with a Hewlett-Packard 5710A gas chromatograph. The GC conditions were identical with those in the above GC analytical runs. Most of the analyses were performed in the electron impact ionization (EI) mode. In some cases, a chemical ionization (CI) mode using isobutane as reagent gas was adopted to obtain information concerning molecular ions. The mass spectral data were processed using a JMA-3000/3500 MS Data Analysis System. The components of the reaction products were characterized by their EI and CI mass spectra, and chemical class.

5.2.2 Results and discussion

Low-molecule carbonyl products

Formaldehyde, acetaldahyde and acetone were observed in all the experiments of the monoterpene-ozone reaction. Their concentrations contained in each reaction product gas are listed in Table 5.1. Although there were some differences in the concentrations of reactant monoterpenes, it seemed that β-pinene-O_3 reaction yieldeded more formaldehyde than the reactions of the other two monoterpenes, and that d-limonene produced less acetone than α-pinene and β-pinene. Comparing the structure of β-pinene with that of α-pinene (Fig. 1.1), the former has one methylene group ($CH_2=$) outside the ring. This structural feature accounts for the observation that β-pinene produced more formaldehyde when its double bond was attacked and split by ozone.

Collection of non-volatile products

As noted previously, collections were made using cold trap which was later warmed to ambient temperature. The yields ranged 70~110 wt. % of the monoterpene as precursor. The collected light-yellow viscous liquid was not completely dissolved with either methylene chloride or ethyl ether, and was dissolved completely only with acetone, indicating that the product contains highly polar organics.

GC analyses of the non - volatile products

Figs. 5.3, 5.4 and 5 5 show the gas chromatograms of the crude samples of the non-volatile products from the experiments No. 1, 3 and 5 in Table 5.1. The gas chromatographic patterns of the samples from the experiments No. 2, 4 and 6 (lower ozone concentration) were not so different from the above ones except that peaks resulting from unreacted monoterpenes were found on the former chromatograms. The chemical class of each component on the chroratograms was identified on the basis of GC analyses of the fractionated samples; (n) for neutral and (a) for acid in Fig. 5.3, 5.4 and 5.5.

(i) α-pinene-O_3 reaction products

The gas chromatogram (Fig. 5.3) of α-pinene-O_3 products showed a prominent peak at 27.6 min which amounted to 50% of total peak area in the chromatogram. Besides, about ten relatively prominent peaks were found.

(ii) β-pinene-O_3 reaction products

The gas chromatogram (Fig. 5.4) of β-pinene-O_3 products was very simple. The component appearing at 22.8 min on the chromatogram amounted to more than 70 % of all the non-volatile products.

(iii) d-limonene-O_3 reaction products

As shown in Fig. 5.5, six major peaks were found on the gas chromatogram of d-limonene-O_3 products. All their retention times were in the range of 28-32 min, suggesting that the correnponding compounds have similar molecular weights and chemical structures. Besides, these peaks had no remakable difference in magnitude, in contrast to those from ozonolysis of α-pinene and β-pinene, each of which produced one prominent compound. This can be accounted for by considering that the two double bonds of limonene (Fig. 1.1) participate in its ozonolysis, and make the reaction products diversify.

GC-MS analyses of the non-volatile products

The crude samples of the non-volatile products and their neutral and esterified acid fractions were analyzed by GC-MS (EI mode for all samples, and CI mode only for the crude samples).

(i) α-pinene-O_3 reaction products

The EI mass spectra of the components corresponding to the numbered gas chromatographic peaks (Fig. 5.3) are shown in Fig.5.6 (a)~(j). The molecular ions suggested from CI mass spectra are shown as M^+ in the figures. The most prominent component, chomatographic peak No.9, has been tentatively identified as pinon aldehyde (2', 2'-dimethyl 3'-acetyl-cyclobutyl-ethanal) on the basis of the mass spectrum. Chromatographic peak No.12, main acid component, has been identified as pinonic acid (2', 2'-dimethyl-3'-acetyl-cyclobutyl acetic acid) in a similar way. The mass spectral fragmentation patterns for these compounds were rationalized in Figs. 5.7 and 5.8. The mass spectral fragmentations for the other components were also studied, and some of them were tentatively identified (Fig. 5.6). Peak No.1 was assigned to formic acid and peak No.2 was assigned to acetic acid from the comparison with their standard mass spectra.

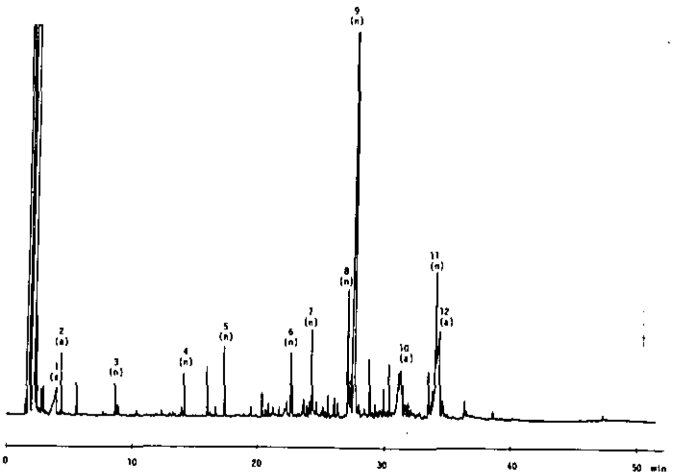


Fig. 5.3 Gas chromatogram of α-pinene-O_3 reaction products

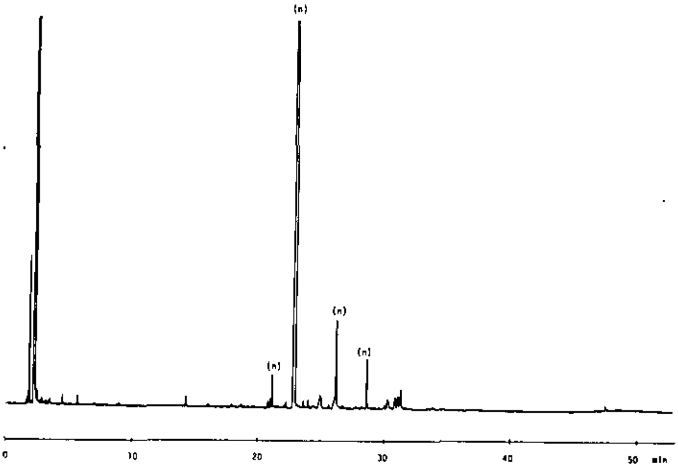


Fig. 5.4 Gas chromatogram of β-pinene-O_3 reaction products

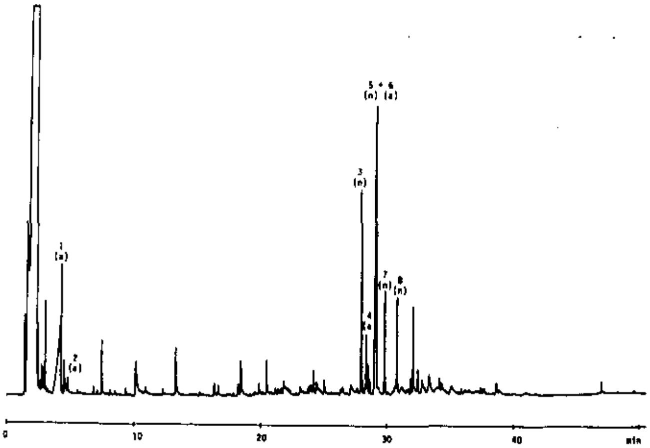


Fig. 5.5 Gas chromatogram of d-limonene-O_3 reaction products

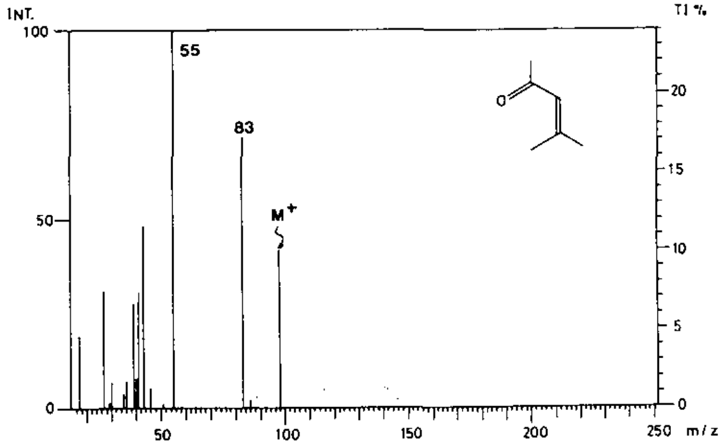


Fig. 5.6 (a) Mass spectrum and proposed structure of chromatographic peak 3 of α-pinene-O_3 reaction products

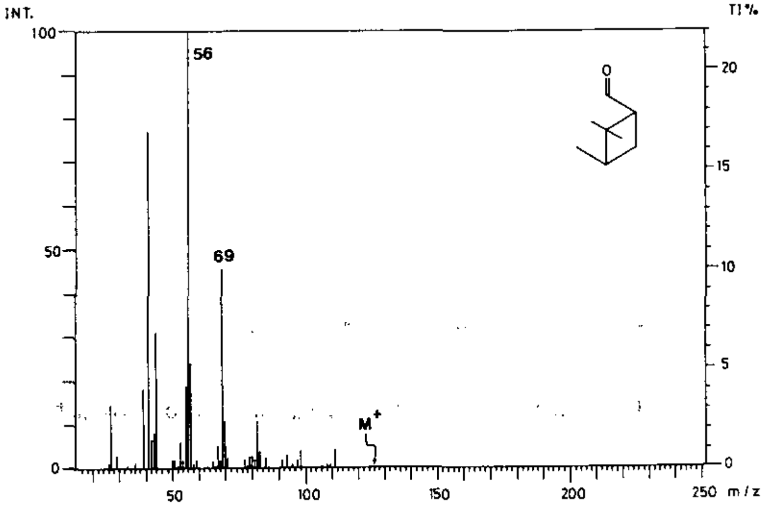


Fig. 5.6 (b) Mass spectrum and proposed structure of chromatographic peak 4 of α-pinene-O_3 reaction products

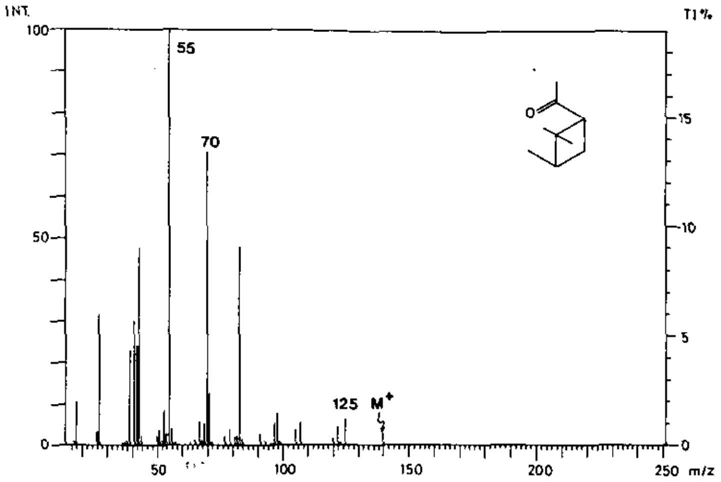


Fig. 5.6 (c) Mass spectrum and proposed structure of chromatographic peak 5 of α-pinene-O_3 reaction products

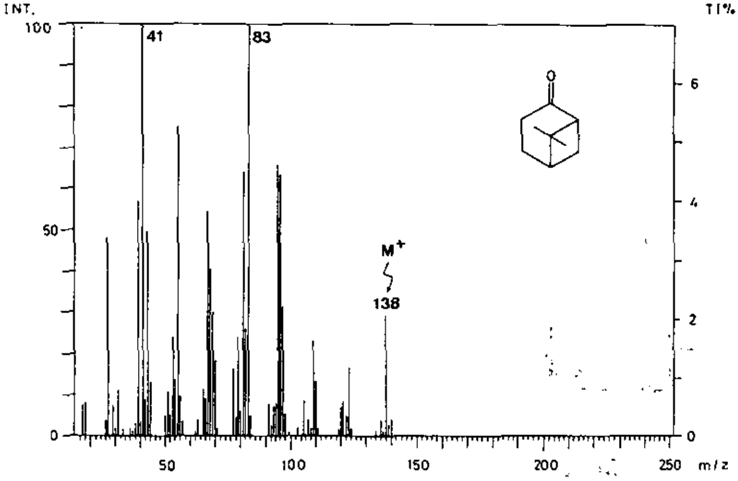


Fig. 5.6 (d) Mass spectrum and proposed structure of chromatographic peak 6 of α-pinene-O_3 reaction products

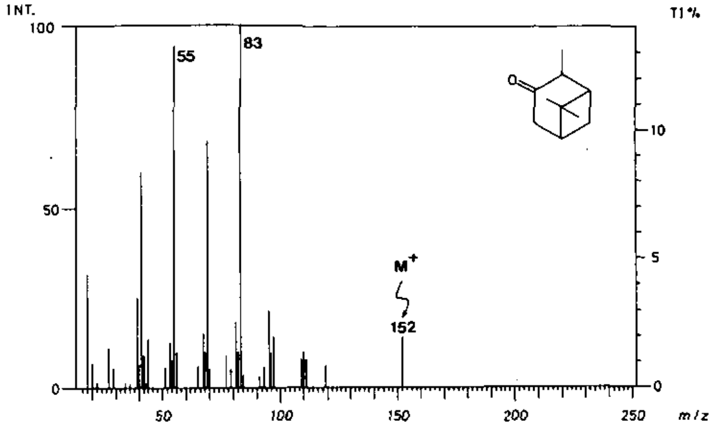


Fig. 5.6 (e) Mass spectrum and proposed structure of chrmatographic peak 7 of α-pinene-O_3 reaction products

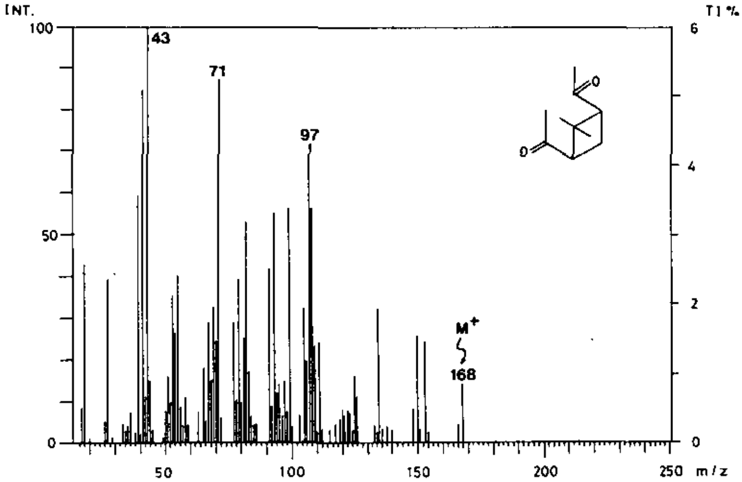


Fig. 5.6 (f) Mass spectrum and proposed structure of chromatographic peak 8 of α-pinene-O_3 reaction products

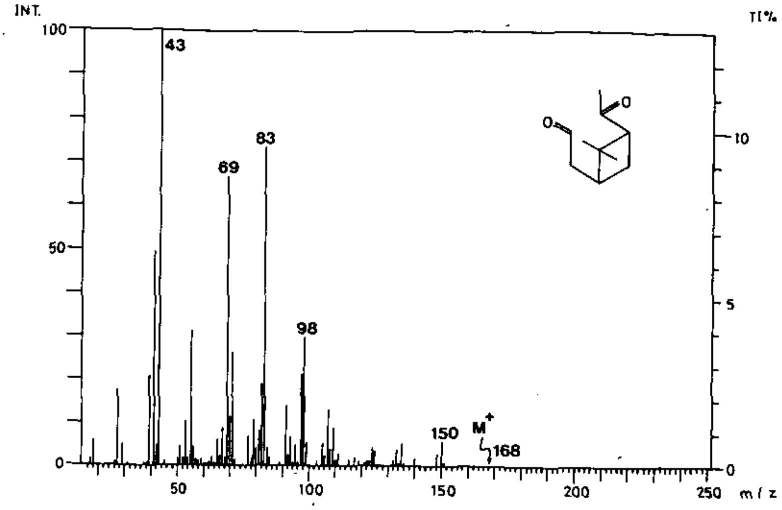


Fig. 5.6 (g) Mass spectrum and proposed structure of chromatographic peak 9 of α-pinene-O_3 reaction products

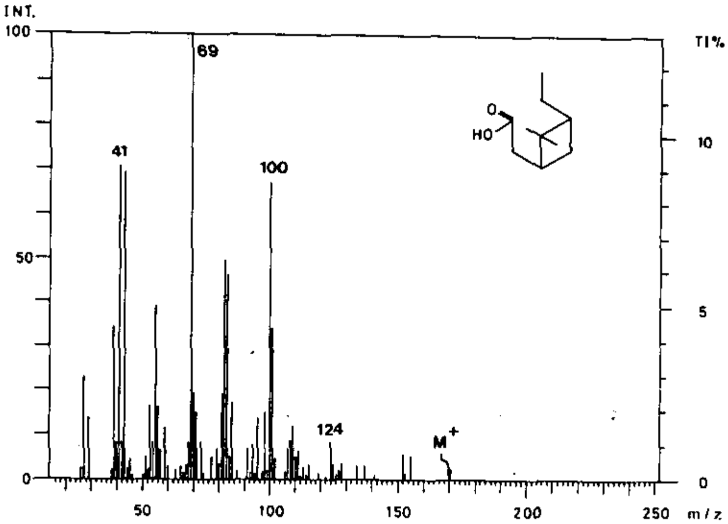


Fig. 5.6 (h) Mass spectrum and proposed structure of chromatographic peak 10 of α-pinene-O_3 reaction products

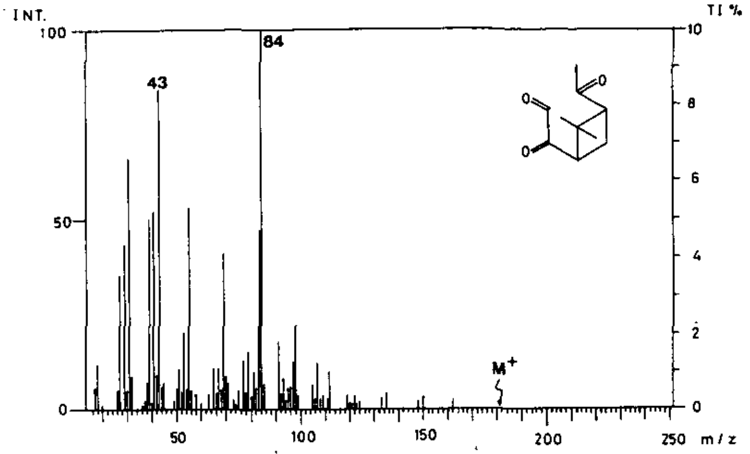


Fig. 5.6 (i) Mass spectrum and proposed structure of chromatographic peak 11 of α-pinene-O_3 reaction products

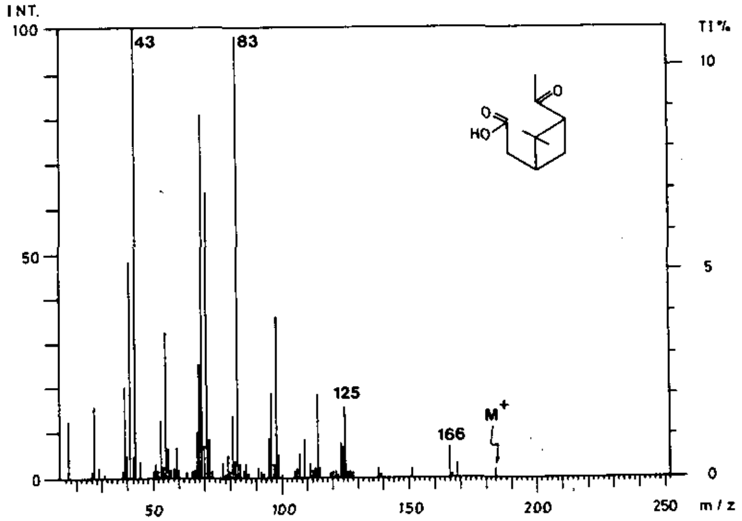


Fig. 5.6 (j) Mass spectrum and Proposed structure of chromatographic peak 12 of α-pinene-O_3 reaction products

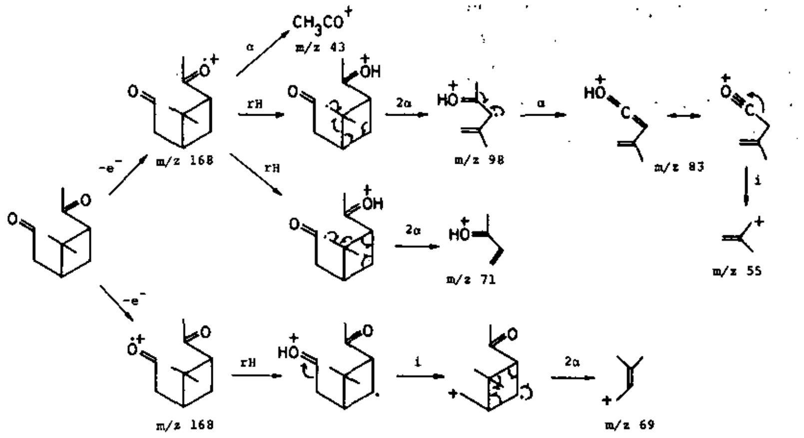


Fig. 5.7 Rationalized fragmentation of pinon aldehyde

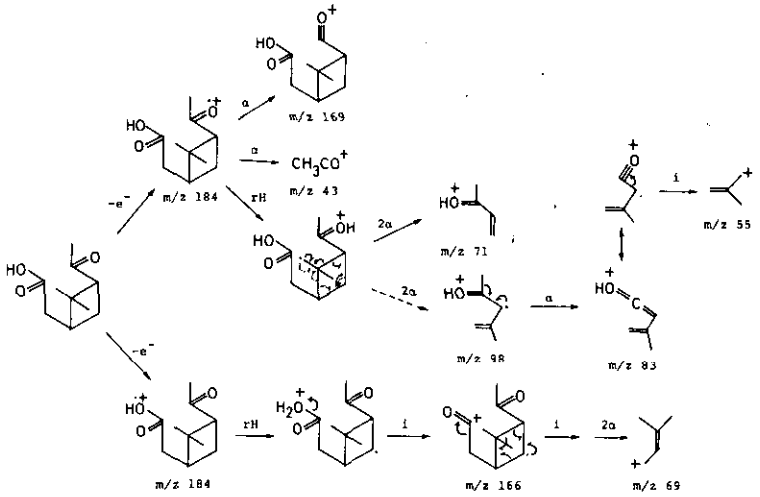


Fig. 5.8 Rationalized fragmentation of pinonic acid

(ii) β-pinene-O_3 products

Fig. 5.9 shows the mass spectrum of the main component of β-pinene-O_3 product. The molecular ion was suggested to be m/z 138 from its CI mass spectrum. The chemical structure was identified as 6, 6-dimethyl-bicyclo [3.1.1] hept-2-one and the mass spectral fragmentation pattern was rationalized as shown in Fig. 5.10.

(iii) d-limonene-O_3 products

The EI mass spectra of the main components of d-limonene-O_3 products are shown in Fig. 5.11 (a)~(f). All these mass spectra have base peaks of m/z 43, and few other fragment ions useful for the study of fragmentation patterns were observed. Limonene has two double-bonds (Fig. 1.1), and each of them can

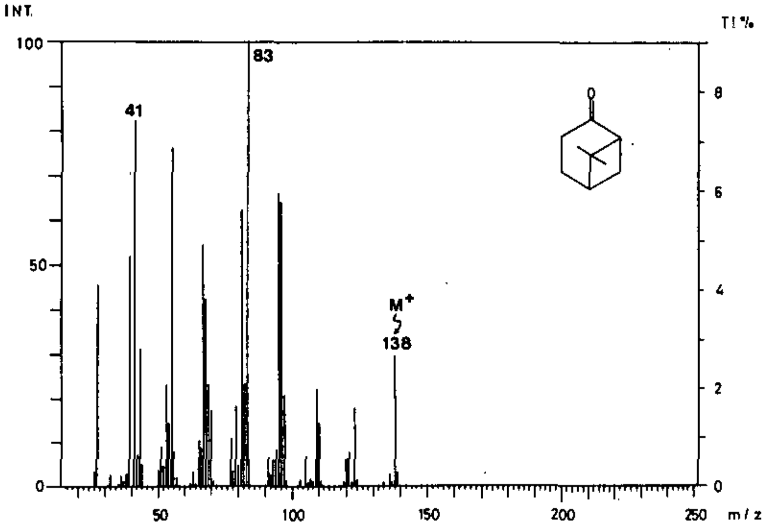


Fig. 5.9 Mass spectrum and proposed structure of the main peak at 22.6 min on the chromatogram of β-pinene-O_3 reaction products

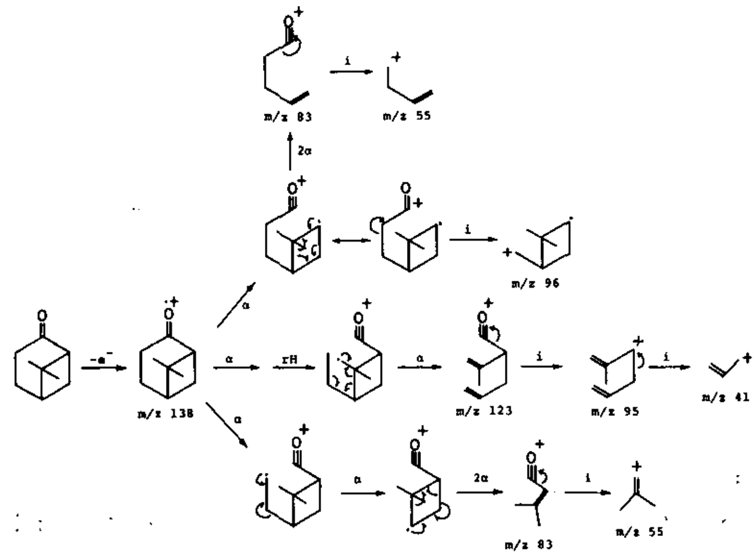


Fig. 5.10 Rationalized fragmentation of 6,6-dimethyl-bicyclo [3.1.1] hept-2-one

participate in ozonolysis. Besides, when one double-bond is attacked by ozone, the other double-bond remains in the molecule. This means that rearrangement of the remaining double bond in the molecule might occur during mass fragmentation. These features of limonene make it quite difficult to identify the products of its reaction with O_3 only from the mass spectra.

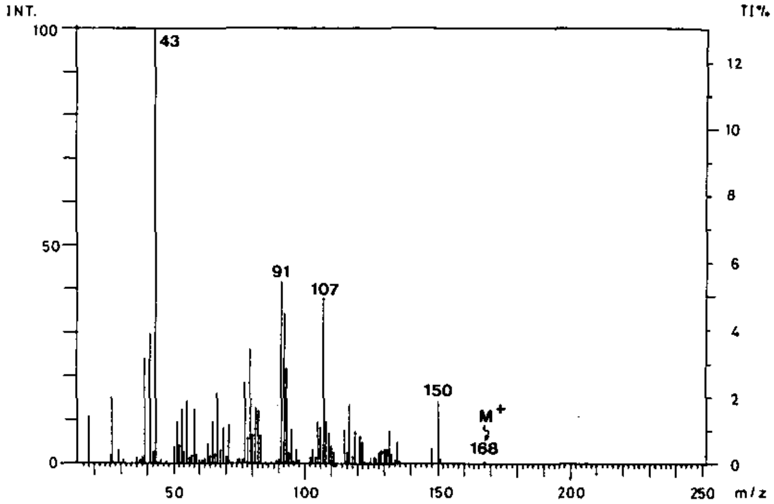


Fig. 5.11 (a) Mass spectrum of chromatographic peak 3 of d-limonene-O_3 reaction products

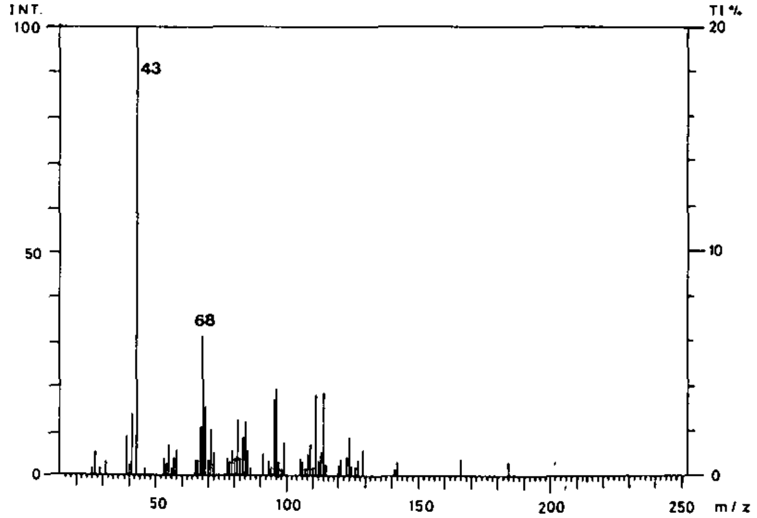


Fig.5.11 (b) Mass spectrum of chromatographic peak 4 of d-limonene-O_3 reaction products

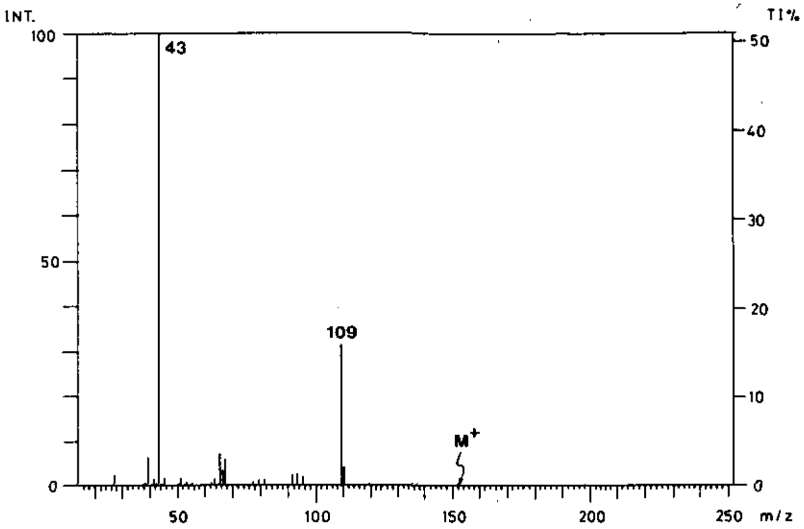


Fig.5.11 (c) Mass spectrum of chromatographic peak 5 of d-limonene-O_3 reaction products

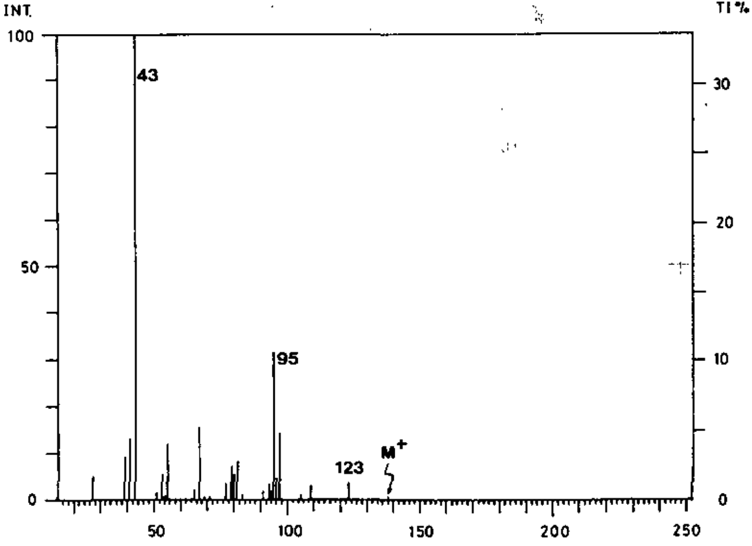


Fig.5.11 (d) Mass spectrum of chromatographic peak 6 of d-limonene-O_3 reaction products

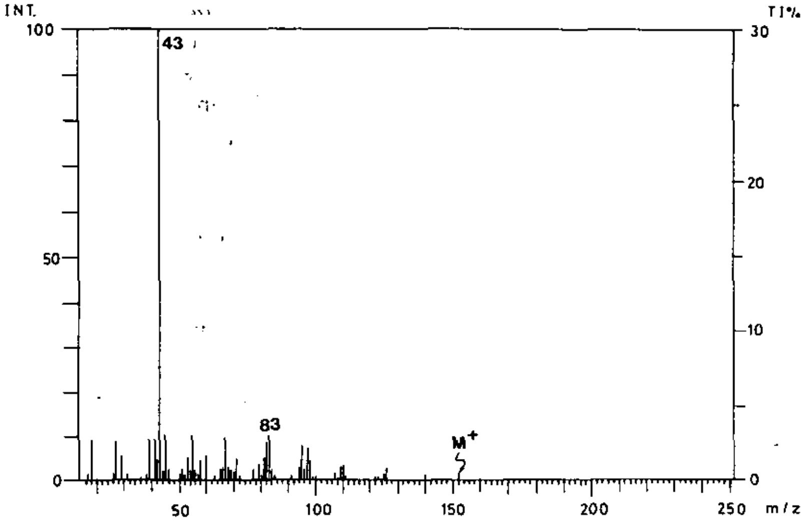


Fig.5.11 (e) Mass spectrum of chromatographic peak 7 of d-limonene-O_3 reaction products

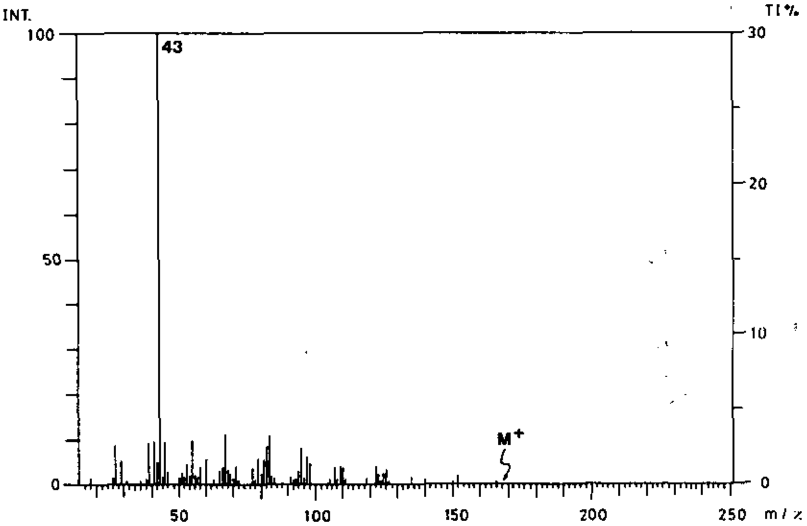


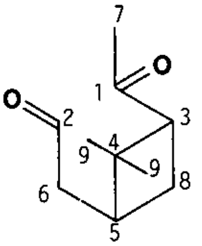
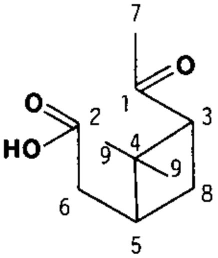
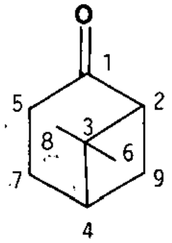
Fig.5.11 (f) Mass spectrum of chromatographic peak 8 of d-limonene-O_3 reaction products

Although the chemical structures of non-volatile products of limonene-O_3 reaction could not be identified as described, these data of mass spectra and GC retention times are useful in identifying the limonene-origin components in the atmospheric aerosols.

NMR studies of major products of the ozonolysis of α-pinene and β-pinene

To confirm tentative identification of major products of α-pinene and β-pinene ozonolysis based on the mass spectra, ^{13}C-NMR studies were conducted. Samples were the neutral fractions of α-pinene-O_3 and β-pinene-O_3 reaction products, and the acid fraction of α-pinene-O_3 products, each dissolved in $CDCl_3$. Table 5.2 shows the chemical shifts of major signals on the NMR charts, and their spin-spin coupling multiplicity found from off-resonance decoupling. They were reasonably assigned to the major components of each fraction.

Table 5.2 Assignment of major signals of ^{13}C-NMR of monoterpene-O_3 reaction products

	No.	chemical shift (ppm)	multiplicity
	1	207.5	s
	2	201.9	d
	3	54.3	d
	4	43.3	s
	5	37.9	d
	6	34.6	t
	7	30.3	q
	8	23.1	t
	9	17.4	q
	1	208.4	s
	2	178.5	s
	3	54.3	d
	4	43.4	s
	5	37.8	d
	6	34.9	t
	7	30.2	q
	8	23.1	t
	9	17.3	q
	1	214.9	s
	2	58.1	d
	3	41.3	s
	4	40.5	d
	5	32.9	t
	6	26.0	q
	7	25.4	t
	8	22.2	q
	9	21.5	t

Reaction mechanisms

The reaction mechanisms of the ozonolysis of α-pinene and β-pinene were considered, based on the chemical structures of the products identified above.

For the olefin-ozone reactions in solution, Criegee mechanism (Criegee, 1957), shown in Fig. 5.12, has been confirmed by numerous studies. The mechanism is accounted for by the initial reactions (I , II), Criegee splits (III) and subsequent zwitterion reactions(V) including various rearrangements, additions and dimerizations. However, the gas-phase reactions are more complex and produce a variety of products (O'Neal *et al.*, 1973; Walter *et al.*, 1977). The reaction pathway for simple olefin-ozone reactions in the atmosphere has been explained by ring opening to a biradical of the first adduct (molozonid) and subsequent various reactions including Criegee split and different types of intramolecular H-abstraction. For the case of complicated olefins like monoterpenes, the reactions would be more complex.

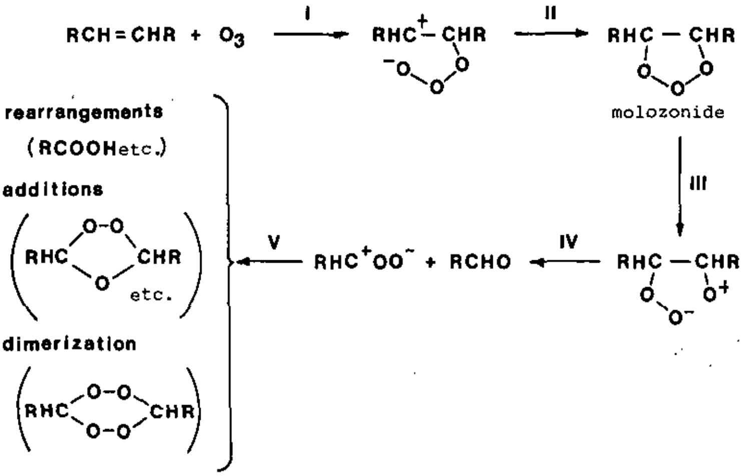


Fig. 5.12 Criegee reaction mechanism for solution

The reaction pathway for the two main products of α-pinene-O_3 reaction shown in Fig. 5.13 were proposed based on the chemical structures of the reaction products and the mechanistic consideration. The other products might be produced by differnt pathways including H-abstraction or subsequent oxidative degradation of the above two compounds.

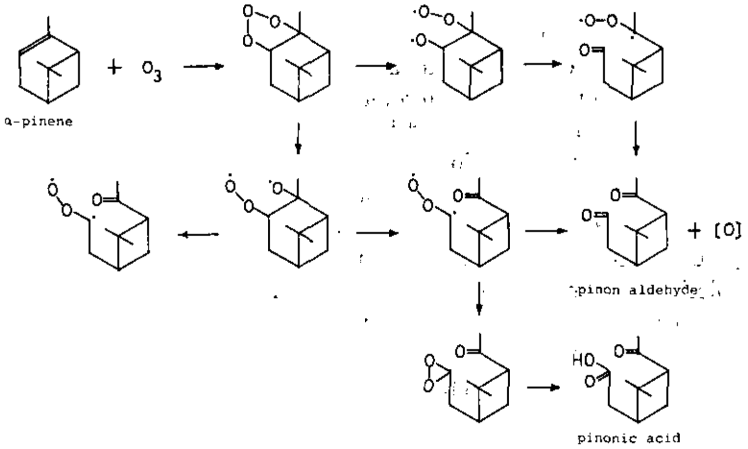


Fig. 5.13 Reaction pathways in α-pinene-O_3 gas phase reaction

The main product of β-pinene-O_3 reaction, 6,6-dimethyl-bicyclo [3.1.1] hept-2-one might be produced by the pathway (A and/or B) as shown in Fig. 5.14. Process B is consistent with the observation that relatively significant amount of formaldehyde was produced by this reaction.

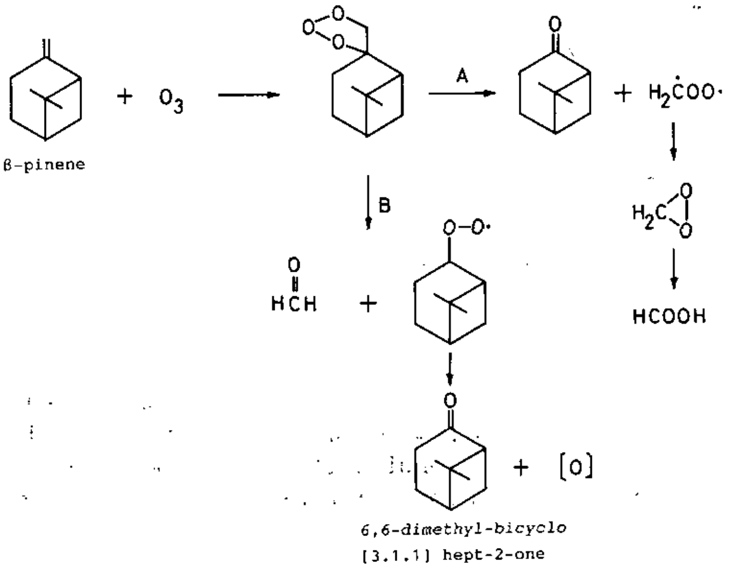


Fig. 5.14 Reaction pathways in β-pinene-O_3 gas phase reaction

5.2.3 Conclusion

In this section, research has been concentrated on the identification of the monoterpene-O_3 reaction products. In addition to pinon aldehyde and pinonic acid, eight main compounds in the non-volatile products of α-pinene-O_3 reaction were tentatively identified on the basis of mass spectra. It was proved that β-pinene-O_3 reaction yielded 6,6-dimethyl-bicyclo [3.1.1] hept-2-one as its non-volatile product almost exclusively. As for limonene-O_3 reaction, it seemed impossible to identify the products only on the basis of mass spectra.

5.3 GC-MS ANALYSIS OF AEROSOL PARTICLES SAMPLED IN A RURAL FOREST

5.3.1 Experimental

Sampling

Samplings were made in forests at Kiyosumi and Tsukuba in the summer of 1982. Kiyosumi is 50 km south of Chiba City and represents a rural environment. Samplings at Kiyosumi were made in a cedar forest in the center of an area of mountains and forests covering 2200 ha. Automobiles are usually prohibited from entering this area. The sampling site at Tsukuba was the same forest as that where the studies of Chapter 4 were conducted.

Aerosol samples were collected by filtering air through a Pallflex 8" × 10" quartz fiber filter using a Kimoto Model 120A high-volume sampler pump with a capacity of 1 m^3/min. The filters had been in advance heated at 250°C in vacuum. Table 5.3 presents a summary of aerosol sampling conditions performed. At Kiyosumi, to obtain daytime and nighttime aerosols, filters were replaced in the morning and in the evening. All samples were stored at ambient temperature until analyses were started.

Table 5.3 Summary of aerosol sampling conditions

location	date, time	sampling volume (m^3)	sample weight (mg)
Kiyosumi(D)	8/4 15:15 - 8/4 17:26 8/5 6:00 - 8/5 17:37 8/6 6:02 - 8/6 15:51	997.4	30.91
Kiyosumi(N)	8/4 17:26 - 8/5 6:00 8/5 17:42 - 8/6 5:58	1,373.8	50.15
Tsukuba	7/5 9:00 - 7/6 8:55	1,408.1	72.94

Extraction of the filters

Preparation of an analytical sample involved soxhlet extraction of the filter in an all-glass apparatus with 100 ml of high purity methylene chloride for 4 h and subsequently with 100 ml of high purity methanol for 4 h. These extracts were concentrated to a trace quantity under vacuum on a rotary evaporator. They were fractionized into neutral and acid fractions in the same way as in the preceding section.

GC and GC-MS analysis

All separations were performed by a glass capillary gas chromatograph, coated with methyl silicone (0.2 mm ID × 25 m). Temperature was programmed from 30°C to 250°C at 8 °/min and then remained isothermal. Cyclic scans of the mass spectrometer from mass 15 up to mass 500 were repeated every 2 sec. The data obtained were stored on a disc. Identifications were made based on the mass spectra. As for terpene-origin compounds, mass spectra of the reaction products of monoterpenes and ozone mentioned in the previous section were used as a library for identification.

5.3.2 Results and discussion

Aerosols sampled at Kiyosumi

Gas chromatograms were obtained for the methylene choride extract and the methanol extract of the aerosols sampled at Kiyosumi in the daytime and in the nighttime. The total area response of the chromatogram was calculated excluding the solvent peak. This response was converted to the weight of organics using a response factor calculated from the response of n-alkanes (C_{10}-C_{20}). Table 5.4 shows the weight of organics appearing on the chromatogram, its concentration in the aerosol sample and its concentration in the atmosphere. It was found that (1) the concentrations of particulate organics in the atmosphere which could be analyzed with GC were higher in the daytime than at night although the weight concentration of aerosols was higher at night, and (2) the chromatographic patterns of the aerosols sampled in the daytime and at night were similar for most of the main peaks.

Table 5.4 Concentrations of solvent extracts appearing on the gas chromatogram

aerosol sample	solvent	weight(μg)	concentration	
			(mg/g aerosol)	(μg/m^3 air)
Kiyosumi(D) (sampled in the daytime)	CH_2Cl_2 CH_3OH	201 250	6.5 8.1	0.20 0.25
Kiyosumi(N) (sampled in the night)	CH_2Cl_2 CH_3OH	129 113	2.6 2.3	0.09 0.08

Fig. 5.15 shows the total ion monitoring (TIM) chromatogram of the CH_2Cl_2 extract of the sample from Kiyosumi (D). A list of the compounds identified is presented in Table 5.5 ; the numbers correspond to the numbers on the chromatogram. Peaks marked with one asterisk in Table 5.5 were only tentatively identified. A double asterisk indicates that the MS pattern was clearly correlated with the proposed structure according to MS theory. A triple asterisk indicates that the mass spectra corresponded fully with published reference spectra. The mass spectrum of Peak No.3 of Fig. 5.15 is shown in Fig. 5.16 and it was for the first time identified as pinon aldehyde by comparison with the mass spectra of the α-pinene-O_3 products in the previous section. Quantification was conducted using the area responese of the corresponding peak on the gas chromatogram. The concentration of pinon aldehyde was 2.0 ng/m^3(w/v) in the air, 65 ppm (w/w) in the aerosol sampled and ca. 0.5% of particulate organics. The spectrum corresponding to Peak No.1 (Fig. 5.17) was similar to that of the β-pinene-O_3 reaction product observed in the chamber experiment (Fig. 5.9) except for the lack of an m/z 83 base peak, and was considered to be that of the reaction product from a monoterpene, having the chemical formula of $C_9H_{14}O$. The gas chromatographic peaks corresponding to these two compounds (pinon aldehyde and $C_9H_{14}O$) have more discrepancy in magnitude between the samples taken during daytime and at night than the other major peaks. This is in accordance with the fact that more terpenes are emitted from plants in the daytime and therefore more terpene-origin products are expected to exist in the atmosphere. Peak No.6 was considered to have the chemical formula $C_{15}H_{24}O_2$, which may be a sesquiterpene originating from plants. It might have been introduced into the atmospheric aerosols by the blowing-up of humus soil containing sesquiterpenes.

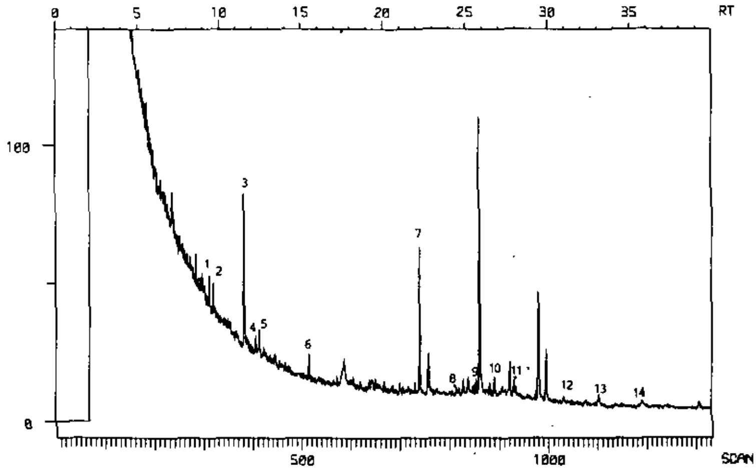


Fig. 5.15 TIM chromatogram of the CH_2Cl_2 extract of the aerosols sampled at Kiyosumi in the daytime

Table 5.5 Compounds Found in the CH_2Cl_2 Extract of the Aerosol Collected in a Rural Forest at Kiyosumi

Peak No.	Compound		
1*		$C_9H_{14}O$	(138)
2***	2-ethyl hexanoic acid	$C_8H_{16}O_2$	(144)
3**	pinon aldehyde	$C_{10}H_{16}O_2$	(168)
4***	phthalic anhydride	$C_8H_4O_3$	(148)
5***	nonanoic acid+?	$C_9H_{18}O_2$	(158)
6*		$C_{15}H_{24}O_2$	(236)
7***	dibutyl phthalate	$C_{16}H_{22}O_4$	(278)
8***	heneicosane	$C_{21}H_{44}$	(296)
9***	docosane	$C_{22}H_{46}$	(310)
10***	tricosane	$C_{23}H_{48}$	(324)
11***	tetracosane	$C_{24}H_{50}$	(338)
12***	hexacosane	$C_{26}H_{54}$	(366)
13***	heptacosane	$C_{27}H_{56}$	(380)
14***	octacosane	$C_{28}H_{58}$	(394)

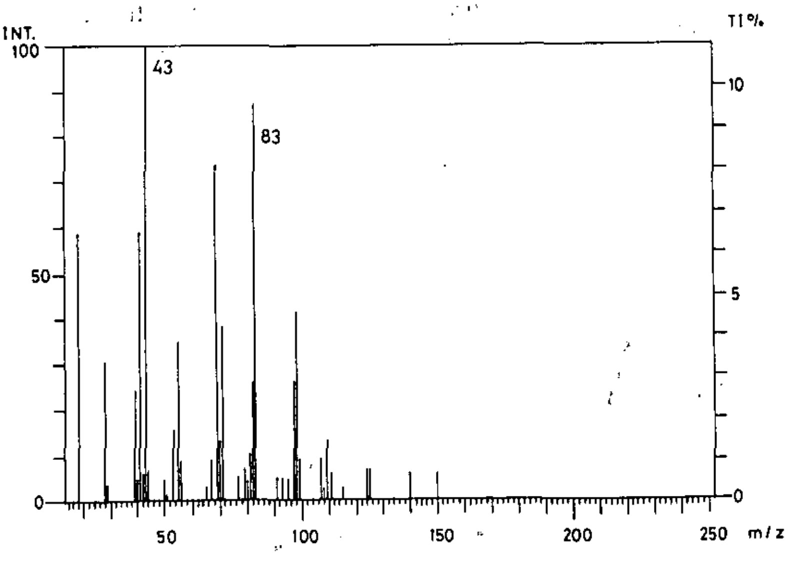


Fig. 5.16 Mass spectrum of peak No.3 on the TIM chromatogram of the CH_2Cl_2 extract of the aerosols collected at Kiyosumi

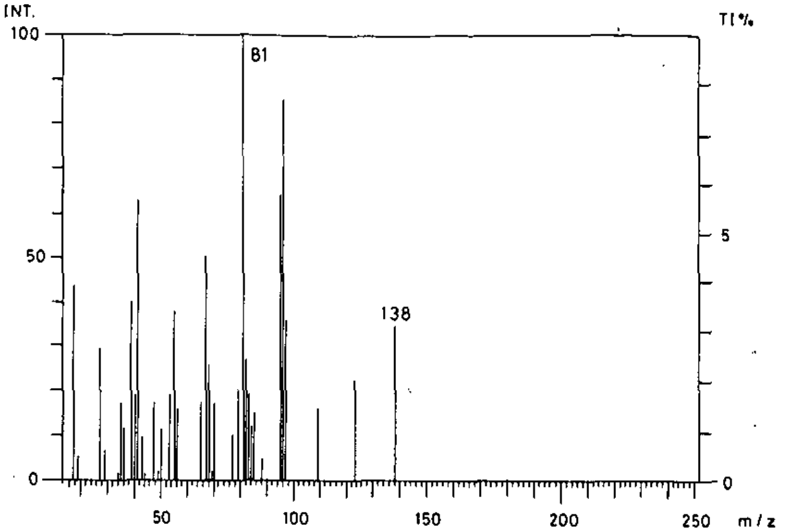


Fig. 5.17 Mass spectrum of peak No.1 on the TIM chromatogram of the CH_2Cl_2 extract of the aerosols collected at Kiyosumi

Methanol extracts contained methyl esters resulting from carboxylic acid. Its TIM chromatogram is shown in Fig. 5.18 and a list of the compounds identified is presented in Table 5.6. The three most significant peaks (9, 11, 12) corresponded to palmitic acid, oleaic acid and stearic acid which are typical carboxylic acids produced by biota. The presence of little carboxylic acids other than the three acids suggests that this sampling point is rather free from anthropogenic pollution as urban aerosols usually contain more kinds of carboxylic acids.

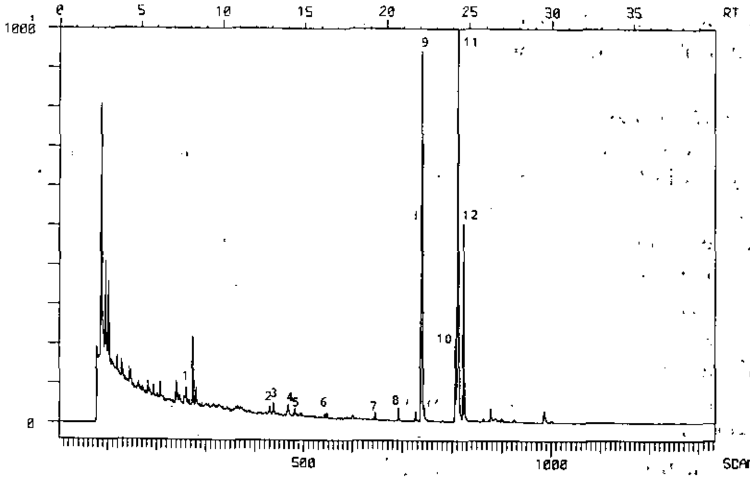


Fig. 5.18 TIM chromatogram of the CH_3OH extract of the aerosols sampled at Kiyosumi in the daytime

Table 5.6 Compounds Found in the CH_3OH Extract of the Aerosol Collected in a Rural Forest at Kiyosumi

Peak No.	Compound		
1***	3,4-dimethyl-2-butenoic acid gamma lactone	$C_6H_8O_2$	(112)
2***	phthalide	$C_8H_6O_2$	(134)
3***	nicotine	$C_{10}H_{14}N_2$	(162)
4***	methyl decanoate	$C_{11}H_{22}O_3$	(202)
5***	methyl undecanoate	$C_{12}H_{24}O_3$	(216)
6***	methyl dodecanoate	$C_{13}H_{26}O_3$	(230)
7***	methyl myristate	$C_{15}H_{30}O_3$	(258)
8***	methyl pentadecanoate	$C_{16}H_{32}O_3$	(272)
9***	methyl palmitate	$C_{17}H_{34}O_3$	(286)
10***	methyl linoleate	$C_{19}H_{34}O_3$	(310)
11***	methyl oleate	$C_{19}H_{36}O_3$	(312)
12***	methyl stearate	$C_{19}H_{38}O_3$	(314)

Aerosols sampled at Tsukuba

The aerosol sample collected in a pine forest at Tsukuba was analyzed in the same way as that for the sample from Kiyosumi. Compounds identified based on the mass spectra included more kinds of carboxylic acids, hydrocarbons, phthalic esters and alcohols, which have been usually found in urban aerosols. There were more carboxylic acids other than palmitic acid, oleaic acid and stearic acid. This sampling point, therefore, was considered to be rather polluted. As for terpene-origin compounds, pinon aldehyde was also detected, amounting to 2.6 ng/m^3 (w/v) in the atmosphere and 51 ppm (w/w) in the aerosol sample.

Terpene-origin aerosols

Terpene-origin aerosol, which has an important meaning for the study of terpene cycles in the atmosphere as described in the Introduction of this chapter, was found in the field. Pinon aldehyde, the main product of the α-pinene-O_3 reaction, was detected both in the pine forest at Tsukuba and in the cedar forest at Kiyosumi. The concentration was calculated to be 2~3ng/m^3(w/v). Analysis of the forest air by GC-MS showed that α-pinene was the most abundant monoterpene in the atmosphere in both cases. Although there was as much limonene as α-pinene at Kiyosumi and its reaction with ozone was more rapid, no limonene-O_3 reaction product was found in the aerosol samples. One possible explanation for this is that limonene-O_3 reaction products are divided into several compounds (cf. Section 5.2), and individual product compounds which might be present at low concentrations were not detected by the present method. It is noteworthy that pinonic acid (the only compound previously reported as a terpene reaction product detected in the atmosphere) was not found in the aerosols in these forests and that pinon aldehyde was detected in the field for the first time. Pinonic acid was not detected even by high-sensitive mass-chromatography, while pinon aldehyde was present in a sufficient quantity to be detected by TIM mode. From these results, it would be reasonable to consider that α-pinene in the atmosphere produces pinon aldehyde through its atmospheric reaction. As for the concentration of pinon aldehyde, the observed value should be considered the minimum of the real concentration because of sampling loss.This compound has a rather high vapor pressure, judging from its relatively short retention time (Fig. 5.15), and some pinon aldehyde might have escaped from the filter by evaporation while it was sampled by the high-volume sampler. Although pinon aldehyde amounted to only 0.5% of the particulate organics, and 65 ppm of the aerosol sampled at Kiyosumi, it is not necessarily conclusive that terpene-origin aerosols have little impact on air quality. Aerosol particles related to visibility or meteorology have diameters of the order of less than a micron, while all particles larger than one micron were collected with the present sampling method using filters. In order to draw a conclusion about the role of terpene-origin aerosols in the atmosphere, further work including the analysis of sub-micron aerosols will be necessary. However, the discovery of the common presence of pinon aldehyde in aerosols in forests is considered to advance an important step in the study of the fate of terpenes.

Conclusion

Some of the crucial processes in the atmospheric terpene cycle (Fig. 6.1) were established.

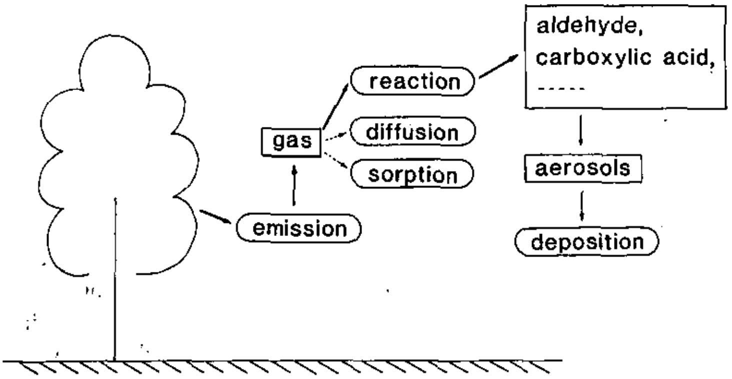


Fig. 6.1 A possible terpene cycle in the atmosphere

Emission : It was revealed by the study using a dynamic mass balance gas cabinet that monoterpene emission rate from plant depends on temperature in a log-linear manner and is also influenced by light. These observations were explained reasonably by the model that monoterpene emission rate depends on the monoterpene amount in the leaf oil and its saturated vapor pressure, and it was suggested that the seasonal variation of monoterpene emission rate should be estimated from those of photosynthetic rate and temperature. The measurements of monoterpene emission rate from a pine branch in the field showed a significant seasonal variation which was consistent with the above consideration. From the monoterpene emission data measured by a revised method, it was suggested that Zimmerman's estimate for the global emission rate of terpenes (8×10^8 t/y) must be revised downward by a factor of 10.

Atmospheric concentration : The concentration of monoterpenes in the atmosphere was found to be ~1 ppb at most in Japan. The concentration of monoterpenes varied greatly from day to day, and from season to season. It was high in summer and autumn, and relatively low during January to March. The concentration at night was much higher than that in the daytime. Using multiple regression analysis, the variation of monoterpene concentration was found to depend on those of ambient temperature and ozone concentration in the air.

Atmospheric reactions : Ozonolysis was proved to be the main pathway for disappearance of monoterpenes in the atmosphere, by the observation of monoterpene concentration and several environmental factors. This means that plant-origin terpenes play an ozone-destruction role rather than an ozone-producing role. Through the chamber experimets, it was found that the ozonolysis of α-pinene produces mainly pinon aldehyde and that of β-pinene produces mainly 6,6-dimethyl bicyclo [3.1.1] hept-2-one as their non-volatile reaction products.

Aerosol formation : The possibility of terpenes as the origin of forest aerosols was supported by detection of pinon aldehyde (α-pinene-O_3 reaction product) in forest aerosols. This compound was for the first time confirmed to exist in the atmosphere.

The present study revealed that (i) plant-origin terpenes play an ozone-destruction role rather than an ozone-producing role, (ii) their atmospheric concentration is dependent mainly on temperature and ozone concentration in the air, (iii) their emission rate is dependent on their amount in leaves and their vapor pressure, and (iv) terpene-origin aerosols exist commonly in forest air.

Future Problems

(1) To what extent terpene reaction products contribute to forest aerosols?

Pinon aldehyde (main product of α-pinene-O_3 reaction) was detected in forests at the concentration of 2 ng/m^3 in the atmosphere and 65 ppm of the sampled aerosols. As described in Section 5.3, these concentrations should be considered the minimum of the actual ones taking sampling loss into account. Further quantitative investigations are necessary to evaluate their impact on air quality.

Supposing that most of monoterpenes emitted from plants disappear through atmospheric reactions in a forest as discussed in Section 4.2, their reaction products (M.W. 150~180?) would be produced at the rate of 500 $\mu g/m^3 \cdot hr$ from monoterpenes (M.W. 136) emitted at 400 $\mu g/m^3 \cdot hr$ in summer. It is another important subject to estimate their ambient concentration based on this production rate and to confirm the possibility of their condensation into aerosols under the estimated concentration.

(2) The fate of terpene-origin aerosols

There has been no investigation about the fate of terpene-origin aerosols except the report by Went (1960), who suggested a possible relation to petroleum formation of terpene-origin aerosols returned to earth.

Although the lifetime of most of terpenes in the atmosphere is several hours at most due to their rapid reaction with O_3 and OH, their reaction products existing as aerosols are expected to have longer lifetime. Average residence time of aerosols has been considered to be a week or so. Therefore, they might be carried away to remote areas until they are removed by washout or dryout, or might participate in cloud formation as condensation nuclei. However, since terpene-origin aerosols are produced in a forest, their adsorption onto dense leaves is probably a prominent removal process. In this case, their lifetime might be much shorter than a week and their impact is limited to a local phenomenon.

It is also important for the study of geochemical cycle of terpenes to confirm whether their reaction products (~10^8 tons/y) are likely to be decomposed or accumulated in the soil.

(3) Terpene emission from tropical rain forest

There has been no data available on the terpene emission rate from tropical rain forests where plants grow most actively. Considering their large scale and their high plant activity, regional or global impacts of terpenes emitted from these areas and their resultant aerosols are of great interest. It is also indispensable for the reliable estimation of worldwide terpene emission rate to investigate their emission rate from tropical plants.

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大気中モノテルペンの挙動に関する研究

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地球上の多くの植物が大気中に揮発性のテルペン類を放出している。その量は，地球全体で年間数億トンにのぼるといわれている。これらは，二重結合をもつオレフィン化合物であるため，人為発生のオレフィンが光化学スモッグを引き起こすのと同様な現象を起こすことが考えられている。実際，多くのチェンバー実験により，窒素酸化物との光化学反応性，及びオゾンとの反応性がともに高いことが証明されている。このように量も多く，反応性も高いため，テルペンの挙動については，次に挙げるいくつかの問題が論じられている。それらは，a)テルペンが非都市地域で時折観測される高濃度オゾン発生の原因物質である可能性，b)成層圏からもたらされるオゾンの消費物質としての役割，c)森林地帯を夏期におおう青味がかったもやがテルペン起源のエーロゾルである可能性，ひいては，d)凝結核としての気象への影響などである。以上の諸点は，いずれも大気化学の面で重要な課題であると考えられるが，実際の測定データが著しく少ないため，未解決となっている。

そこで，本研究ではテルペンの環境大気中における挙動と役割を明らかにすることを目的として，大気中テルペン濃度の変動要因を知ることと，テルペン起源のエーロゾル成分を検出することを主眼に，以下の研究を行った。

i) sub-ppbレベルの大気中モノテルペンのGC-MS SIM法による分析法を確立。

ii) テルペン放出速度と環境因子との関連を環境コントロール大型チェンバーを用いた実験，及び放出ガスと精油中のテルペン組成の比較から解明。

特に前者の実験では環境条件を変化させた長時間後の影響も観測するよう留意した。

iii) 大気中モノテルペン濃度の変動の把握と要因の解析。

これまで知られていない大気中テルペン濃度の変動を松林内で1年間にわたって測定し，種々の気象・環境因子との関連を調べた。

iv) 森林内エーロゾル中のテルペン起源物質の検索。

テルペンの気相反応のメカニズム及び生成物が明らかでないので，まず，室内実験により，その主要生成物を同定した。森林内でハイボリュームサンプラーによって集めたエーロゾルをキャピラリーGC-MS法によって分析し，前記のテルペン反応生成物の検出を試みた。

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以上の測定において，森林内テルペン濃度とオゾン濃度との間に明らかな負の相関が見いだされ，テルペンは，オゾンとの反応により主に消滅していることが分かった。したがって，都市あるいは郊外において，テルペンは，オゾンの発生源としてよりむしろ消費物質として働いていることが明らかとなった。このことは，成層圏から下りてくるオゾンの消滅に，植物起源のテルペンが何らかの寄与をしていることを示すものである。

また，テルペン起源のエーロゾルに関しては，チェンバー実験などにおいても生成物の同定の研究は少なく，環境大気中の検出では，わずかに一例，α-ピネンの反応生成物として pinonic acid がEPAのレポートに報告されているにすぎなかった。本研究では，α-ピネンとオゾンとの反応実験によって pinon aldehyde が主に生成することを明らかにするとともに，これが夏期の針葉樹林内には，比較的ありふれていて，pptオーダー(以上)で存在することを初めて確認した。このことは，樹木から放出されたテルペンが林内で気相反応を受け，さらにエーロゾルへと変わっていくことを示すものであり，森林地帯のもやの原因になりうることを明らかにした点で重要な結果である。ただし，現段階では，定量的にすべてを説明できるには至っていない。

こうした環境へのインパクトを考える場合，その量が大きな問題となる。従来のテルペン放出速度は，木の枝に袋をかぶせ，一定時間後にその中の空気を全部吸引して測定されていた。この方法は，葉を物理的に傷つけやすいなど，大きな測定誤差を伴っていた。そこで，植物への影響を少なくし，精度よくテルペン放出速度を求めるため，大きな箱で枝全体をおおい，一定時間後にその一部を採取してテルペン濃度を測定し，箱の内容積を乗じて放出速度を求める方法を考案した。その結果，これまでの推定値を数分の１に下方修正する必要のあることが分かった。しかしなお，新たに見直した結果でも年間１億トン近いテルペンが放出されていることとなり，オゾン消費物質及びエーロゾルの原因物質としての役割は重要であると考える。

国立公害研究所特別研究成果報告

第 1 号　陸水域の富栄養化に関する総合研究 ── 霞ヶ浦を対象域として ── 昭和51年度.（1977）

第 2 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 ── 昭和51，52年度　研究報告.（1978）

（改　称）

国立公害研究所研究報告

※第 3 号　A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)
（日本産ユスリカ科　*Cironomus*　属9種の成虫，サナギ，幼虫の形態の比較）

第 4 号　スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 ── 昭和52年度　中間報告.（1978）

第 5 号　芳香族炭化水素－窒素酸化物系の光酸化反応機構と光酸化二次生成物の培養細胞に及ぼす影響に関する研究 ── 昭和51，52年度　研究報告.（1978）

第 6 号　陸水域の富栄養化に関する総合研究（II）── 霞ヶ浦を中心として. ── 昭和53年度.（1979）.

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（日本産ユスリカ科20種の成虫，サナギ，幼虫の形態学的研究）

※第 8 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和52，53年度　研究報告.（1979）

第 9 号　スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 ── 昭和53年度　中間報告.（1979）

第 10 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 ── 昭和51～53年度　特別研究報告.（1979）

※第 11 号　Studies on the effects of air pollutants on plants and mechanisms of phytotoxicity. (1980)
（大気汚染物質の植物影響およびその植物毒性の機構に関する研究）

第 12 号　Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)
（コンピュータ制御装置を利用したフレームおよび誘導結合プラズマ分光法による多元素同時分析）

第 13 号　Studies on chironomid midges of the Tama River. (1980)
Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.
Part 2. Description of 20 species of Chironominae recovered from a tributary.
（多摩川に発生するユスリカの研究
── 第1報　その一支流に見出されたユスリカ各種の分布と下水による汚染度との関係 ──
── 第2報　その一支流に見出された Chironominae 亜科の20種について ──）

第 14 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 ── 昭和53，54年度　特別研究報告.（1980）

※第 15 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和54年度　特別研究報告.（1980）

第 16 号　計測車レーザーレーダーによる大気汚染遠隔計測.（1980）

※第 17 号　流体の運動および輸送過程に及ぼす浮力効果 ── 臨海地域の気象特性と大気拡散現象の研究 ── 昭和53，54年度　特別研究報告.（1980）

第 18 号　Preparation, analysis and certification of PEPPERBUSH standard reference material. (*1980*)
(環境標準試料「リョウブ」の調製，分析および保証値)

※第 19 号　陸水域の富栄養化に関する総合研究（Ⅲ）── 霞ケ浦（西浦）の湖流 ── 昭和53，54年度.（1981）

第 20 号　陸水域の富栄養化に関する総合研究（Ⅳ）── 霞ケ浦流域の地形，気象水文特性およびその湖水環境に及ぼす影響 ── 昭和53，54年度.（1981）

第 21 号　陸水域の富栄養化に関する総合研究（Ⅴ）── 霞ケ浦流入河川の流出負荷量変化とその評価 ── 昭和53，54年度.（1981）

第 22 号　陸水域の富栄養化に関する総合研究（Ⅵ）── 霞ケ浦の生態系の構造と生物現存量 ── 昭和53，54年度.（1981）

第 23 号　陸水域の富栄養化に関する総合研究（Ⅶ）── 湖沼の富栄養化状態指標に関する基礎的研究 ── 昭和53，54年度.（1981）

第 24 号　陸水域の富栄養化に関する総合研究（Ⅷ）── 富栄養化が湖利用に及ぼす影響の定量化に関する研究 ── 昭和53，54年度.（1981）

第 25 号　陸水域の富栄養化に関する総合研究（Ⅸ）──［*Microcystis*｜（藍藻類）の増殖特性 ── 昭和53，54年度.（*1981*）

第 26 号　陸水域の富栄養化に関する総合研究（Ⅹ）── 藻類培養試験法によるＡＧＰの測定 ── 昭和53，54年度.（1981）

第 27 号　陸水域の富栄養化に関する総合研究（Ⅺ）── 研究総括 ── 昭和53，54年度.（1981）

第 28 号　複合大気汚染の植物影響に関する研究 ── 昭和54，55年度　特別研究報告.（1981）

第 29 号　Studies on chironomid midges of the Tama River. (*1981*)

Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.

Part 4. Chironomidae recorded at a winter survey.

(多摩川に発生するユスリカ類の研究

── 第３報　夏期の調査で見出されたエリユスリカ亜科Orthocladiinae 各種の記載と，その分布の下水汚染度との関係について ──

── 第４報　南浅川の冬期の調査で見出された各種の分布と記載 ──）

※第 30 号　海域における富栄養化と赤潮の発生機構に関する基礎的研究 ── 昭和54，55年度　特別研究報告.（1982）

第 31 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和55年度　特別研究報告.（1981）

第 32 号　スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 ── 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究１）── 昭和54年度　特別研究報告.（1982）

第 33 号　臨海地域の気象特性と大気拡散現象の研究 ── 大気運動と大気拡散過程のシミュレーション ── 昭和55年度　特別研究報告.（1982）

第 34 号　環境汚染の遠隔計測・評価手法の開発に関する研究 ── 昭和55年度　特別研究報告.（1982）

第 35 号　環境面よりみた地域交通体系の評価に関する総合解析研究.（1982）

第 36 号　環境試料による汚染の長期モニタリング手法に関する研究 ── 昭和55，56年度　特別研究報告.（1982）

第 37 号　環境施策のシステム分析支援技術の開発に関する研究.（1982）

第 38 号　Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)
(環境標準試料「池底質」の調製，分析及び保証値)

第 39 号　環境汚染の遠隔計測・評価手法の開発に関する研究 ── 昭和56年度　特別研究報告.（1982）

第40号　大気汚染物質の単一及び複合汚染の生体に対する影響に関する実験的研究——昭和56年度　特別研究報告．（1983）

第41号　土壌環境の計測と評価に関する統計学的研究．（1983）

※第42号　底泥の物性及び流送特性に関する実験的研究．（1983）

※第43号　Studies on chironomid midges of the Tama River. (1983)

Part 5. An observation on the distribution of Chironominae along the main stream in June with description of 15 new species.

Part 6. Description of species of the subfamily Orthocladiinae recovered from the main stream in the June survey.

Part 7. Additional species collected in winter from the main stream.

（多摩川に発生するユスリカ類の研究

——第5報　本流に発生するユスリカ類の分布に関する6月の調査成績とユスリカ亜科に属する15新種等の記録——

——第6報　多摩本流より6月に採集されたエリユスリカ亜科の各種について——

——第7報　多摩本流より3月に採集されたユスリカ科の各種について——）

第44号　スモッグチャンバーによる炭化水素−窒素酸化物系光化学反応の研究．——環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究2）——昭和54年度　特別研究中報告．（1983）

第45号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究——昭和53年〜55年度　特別研究報告．（1983）

第46号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究——昭和54，55年度　特別研究報告　第1分冊．（1983）

第47号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究——昭和54，55年度　特別研究報告　第2分冊．（1983）

※第48号　水質観測点の適正配置に関するシステム解析．（1983）

第49号　環境汚染の遠隔計測・評価手法の開発に関する研究——昭和57年度　特別研究報告．（1984）

第50号　陸水域の富栄養化防止に関する総合研究（Ⅰ）——霞ケ浦の流入負荷量の算定と評価——昭和55〜57年度　特別研究報告．（1984）

第51号　陸水域の富栄養化防止に関する総合研究（Ⅱ）——霞ケ浦の湖内物質循環とそれを支配する因子——昭和55〜57年度　特別研究報告．（1984）

第52号　陸水域の富栄養化防止に関する総合研究（Ⅲ）——霞ケ浦高浜入における隔離水界を利用した富栄養化防止手法の研究——昭和55〜57年度　特別研究報告．（1984）

第53号　陸水域の富栄養化防止に関する総合研究（Ⅳ）——霞ケ浦の魚類及び甲殻類現存量の季節変化と富栄養化——昭和55〜57年度　特別研究報告．（1984）

第54号　陸水域の富栄養化防止に関する総合研究（Ⅴ）——霞ケ浦の富栄養化現象のモデル化——昭和55〜57年度　特別研究報告．（1984）

第55号　陸水域の富栄養化防止に関する総合研究（Ⅵ）——富栄養化防止対策——昭和55〜57年度　特別研究報告．（1984）

第56号　陸水域の富栄養化防止に関する総合研究（Ⅶ）——湯の湖における富栄養化とその防止対策——昭和55〜57年度　特別研究報告．（1984）

第57号　陸水域の富栄養化防止に関する総合研究（Ⅷ）——総括報告——昭和55〜57年度　特別研究報告．（1984）

第58号　環境試料による汚染の長期的モニタリング手法に関する研究——昭和55〜57年度　特別研究総合報告．（1984）

第 59 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 ── 光化学スモッグチャンバーによるオゾン生成機構の研究 ── 大気中における有機化合物の光酸化反応機構の研究 ── 昭和55～57年度　特別研究報告（第1分冊）．（1984）

第 60 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 ── 光化学エアロゾル生成機構の研究 ── 昭和55～57年度　特別研究報告（第2分冊）．（1984）

第 61 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 ── 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究）── 昭和55～57年度　特別研究報告（第3分冊）．（1984）

第 62 号　有害汚染物質による水界生態系のかく乱と回復過程に関する研究 ── 昭和56～58年度　特別研究中間報告．（1984）

第 63 号　海域における富栄養化と赤潮の発生機構に関する基礎的研究 ── 昭和56年度　特別研究報告．（1984）

第 64 号　複合大気汚染の植物影響に関する研究 ── 昭和54～56年度　特別研究総合報告．（1984）

第 65 号　Studies on effects of air pollutant mixtures on plants—Part 1. (1984)
（複合大気汚染の植物に及ぼす影響 ── 第1分冊）

第 66 号　Studies on effects of air pollutant mixtures on plants—Part 2. (1984)
（複合大気汚染の植物に及ぼす影響 ── 第2分冊）

第 67 号　環境中の有害物質による人の慢性影響に関する基礎的研究 ── 昭和54～56年度　特別研究総合報告．（1984）

第 68 号　汚泥の土壌還元とその環境に関する研究 ── 昭和56～57年度　特別研究総合報告．（1984）

第 69 号　中禅寺湖の富栄養化現象に関する基礎的研究.（1984）

第 70 号　Studies on chironomid midges in lakes of the Nikko National Park (1984)
Part I.　Ecological studies on chironomids in lakes of the Nikko National Park.
Part II.　Taxonomical and mophological studies on the chironomid species collected from lakes in the Nikko National Park.
（日光国立公園の湖沼のユスリカに関する研究
── 第1部　日光国立公園の湖のユスリカの生態学的研究 ──
── 第2部　日光国立公園の湖沼に生息するユスリカ類の分類学的，形態学的研究 ──

第 71 号　リモートセンシングによる残雪及び雪田植生の分布解析．（1984）

第 72 号　炭化水素—窒素酸化物—硫黄酸化物系化学反応の研究．環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究2）—昭和55～57年度　特別研究報告（第4分冊）．（1985）

第 73 号　炭化水素—窒素酸化物—硫黄酸化物系化学反応の研究．—昭和55～57年度　特別研究総合報告．（1985）

第 74 号　都市域及びその周辺の自然環境に係る環境指標の開発に関する研究．環境指標—その考え方と作成方法—昭和59年度特別研究報告．（1984）

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第 76 号　Study on the behavior of monoterpenes in the atmosphere. (1985)
大気中モノテルペンの挙動に関する研究

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第 78 号　生活環境保全に果たす生活者の役割の解明. (1985)

第 79 号　Studies on the method for long term environmental monitoring — Research report 1980-1982. (1985)
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第 80 号　海域における赤潮発生のモデル化に関する研究—昭和57—58年度　特別研究報告. (1985)

第 81 号　環境影響評価制度の政策効果に関する研究—地方公共団体の制度運用を中心として. (1985)

第 82 号　植物の大気環境浄化機能に関する研究—昭和57〜58年度　特別研究報告. (1985)

第 83 号　Studies on chironomid midges of some lakes in Japan. (1985)
日本の湖に発生するユスリカ類の研究

※残部なし

Report of Special Research Project the National Institute for Environmental Studies

No. 1* Man activity and aquatic environment – with special references to Lake Kasumigaura – Progress report in 1976. (1977)

No. 2* Studies on evaluation and amelioration of air pollution by plants – Progress report in 1976-1977. (1978)

[Starting with Report No. 3, the new title for NIES Reports was changed to:]

Research Report from the National Institute for Environmental Studies

※ No. 3 A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)

No. 4* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1977. (1978)

No. 5* Studies on the photooxidation products of the alkylbenzene-nitrogen oxides system, and on their effects on Cultured Cells – Research report in 1976-1977. (1978)

No. 6* Man activity and aquatic environment – with special references to Lake Kasumigaura – Progress report in 1977-1978. (1979)

※ No. 7 A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)

※ No. 8* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1977-1978. (1979)

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No.10* Studies on evaluation and amelioration of air pollution by plants – Progress report in 1976-1978. (1979)

※ No.11 Studies on the effects of air pollutants on plants and mechanisms of phytotoxicity. (1980)

No.12 Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)

No.13 Studies on chironomid midges of the Tama River. (1980)

Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.

Part 2. Description of 20 species of Chironominae recovered from a tributary.

No.14* Studies on the effects of organic wastes on the soil ecosystem – Progress report in 1978-1979. (1980)

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No.16* Remote measurement of air pollution by a mobile laser radar. (1980)

※ No.17* Influence of buoyancy on fluid motions and transport processes – Meteorological characteristics and atmospheric diffusion phenomena in the coastal region – Progress report in 1978-1979. (1980)

No.18 Preparation, analysis and certification of PEPPERBUSH standard reference material. (1980)

※ No.19* Comprehensive studies on the eutrophication of fresh-water areas – Lake current of Kasumigaura (Nishiura) – 1978-1979. (1981)

No.20* Comprehensive studies on the eutrophication of fresh-water areas – Geomorphological and hydrometeorological characteristics of Kasumigaura watershed as related to the lake environment – 1978-1979. (1981)

No.21* Comprehensive studies on the eutrophication of fresh-water areas – Variation of pollutant load by influent rivers to Lake Kasumigaura – 1978-1979. (1981)

No.22* Comprehensive studies on the eutrophication of fresh-water areas – Structure of ecosystem and standing crops in Lake Kasumigaura – 1978-1979. (1981)

No.23* Comprehensive studies on the eutrophication of fresh-water areas – Applicability of trophic state indices for lakes – 1978-1979. (1981)

No.24* Comprehensive studies on the eutrophication of fresh-water areas – Quantitative analysis of eutrophication effects on main utilization of lake water resources – 1978-1979. (1981)

No.25* Comprehensive studies on the eutrophication of fresh-water areas – Growth characteristics of Blue-Green Algae, *Mycrocystis* – 1978-1979. (1981)

No.26* Comprehensive studies on the eutrophication of fresh-water areas – Determination of argal growth potential by algal assay procedure – 1978-1979. (1981)

No.27* Comprehensive studies on the eutrophication of fresh-water areas – Summary of researches – 1978-1979. (1981)

No.28* Studies on effects of air pollutant mixtures on plants – Progress repot in 1979-1980. (1981)

No.29 Studies on chironomid midges of the Tama River. (1981)

Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.

Part 4. Chironomidae recorded at a winter survey.

※ No.30* Eutrophication and red tides in the coastal marine environment – Progress report in 1979-1980. (1982)

No.31* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1980. (1981)

No.32* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1979 – Research on the photochemical secondary pollutants formation mechanism in the environmental atmosphere (Part 1). (1982)

No.33* Meteorological characteristics and atmospheric diffusion phenomena in the coastal region – Simulation of atmospheric motions and diffusion processes – Progress report in 1980. (1982)

No.34* The development and evaluation of remote measurement methods for environmental pollution – Research report in 1980. (1982)

No.35* Comprehensive evaluation of environmental impacts of road and traffic. (1982)

No.36* Studies on the method for long term environmental monitoring – Progress report in 1980-1981. (1982)

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No.39* The development and evaluation of remote measurement methods for environmental pollution – Research report in 1981. (1983)

No.40* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1981. (1983)

No.41* Statistical studies on methods of measurement and evaluation of chemical condition of soil. (1983)

※ No.42* Experimental studies on the physical properties of mud and the characteristics of mud transportation. (1983)

※ No.43 Studies on chironomid midges of the Tama River. (1983)

Part 5. An observation on the distribution of Chironominae along the main stream in June, with description of 15 new species.

Part 6. Description of species of the subfamily Orthocladiinae recovered from the main stream in the June survey.

Part 7. Additional species collected in winter from the main stream.

No.44* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1979 – Research on the photochemical secondary pollutants formation mechanism in the environmental atomosphere (Part 2). (1983)

No.45* Studies on the effect of organic wastes on the soil ecosystem – Outlines of special research project – 1978-1980. (1983)

No.46* Studies on the effect of organic wastes on the soil ecosystem – Research report in 1979-1980, Part 1. (1983)

No.47* Studies on the effect of organic wastes on the soil ecosystem – Research report in 1979-1980, Part 2. (1983)

※ No.48* Study on optimal allocation of water quality monitoring points. (1983)

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No.50* Comprehensive studies on the eutrophication control of freshwaters – Estimation of input loading in Lake Kasumigaura. – 1980-1982. (1984)

No.51* Comprehensive studies on the eutrophication control of freshwaters – The function of the ecosystem and the importance of sediment in national cycle in Lake Kasumigaura. – 1980-1982. (1984)

No.52* Comprehensive studies on the eutrophication control of freshwaters – Enclosure experiments for restoration of highly eutrophic shallow Lake Kasumigaura. – 1980-1982. (1984)

No.53* Comprehensive studies on the eutrophication control of freshwaters – Seasonal changes of the biomass of fish and crustacia in Lake Kasumigaura and its relation to the eutrophication. – 1980-1982. (1984)

No.54* Comprehensive studies on the eutrophication control of freshwaters – Modeling the eutrophication of Lake Kasumigaura. – 1980-1982. (1984)

No.55* Comprehensive studies on the eutrophication control of freshwaters – Measures for eutrophication control. – 1980-1982. (1984)

No.56* Comprehensive studies on the eutrophication control of freshwaters – Eutrophication in Lake Yunoko. – 1980-1982. (1984)

No.57* Comprehensive studies on the eutrophication control of freshwaters – Summary of researches. – 1980-1982. (1984)

No.58* Studies on the method for long term environmental monitoring – Outlines of special research project in 1980-1982. (1984)

No.59* Studies on photochemical reactions of hydrocarbon-nitrogen-sulfer oxides system – Photochemical ozone formation studied by the evacuable smog chamber – Atomospheric photooxidation mechanisms of selected organic compounds – Research report in 1980, 1982. (1984)

No.60* Studies on photochemical reactions of hydrocarbon-nitrogen-sulfer oxides system – Formation mechanisms of photochemical aerozol – Research report in 1980, 1982. (1984)

No.61* Studies on photochemical reactions of hydrocarbon-nitrogen-sulfer oxides system – Research on the photochemical secondary pollutants formation mechanism in the environmental atmosphere. – Research report in 1980, 1982. (1984)

No.62* Effects of toxic substances on aquatic ecosystems – Progress report in 1980-1983. (1984)

No.63* Eutrophication and red tides in the coastal marine environment – Progress report in 1981. (1984)

No.64* Studies on effects of air pollutant mixtures on plants – Final report in 1979-1981. (1984)

No.65 Studies on effects of air pollutant mixtures on plants – Part I. (1984)

No.66 Studies on effects of air pollutant mixtures on plants – Part 2. (1984)

No.67* Studies on unfavourable effects on human body regarding to several toxic materials in the environment, using epidemiological and analytical techniques – Project research report in 1979-1981. (1984)

No.68* Studies on the environmental effects of the application of sewage sludge to soil – Research report in 1981-1983. (1984)

No.69* Fundamental studies on the eutrophication of Lake Chuzenji – Basic research report. (1984)

No.70 Studies on chironomid midges in lakes of the Nikko National Park – Part 1. Ecological studies on chironomids in lakes of the Nikko National Park. – Part II. Taxonomical and morphological studies on the chironomid species collected from lakes in the Nikko National Park. (1984)

No.71* Analysis on distributions of remnant snowpack and snow patch vegetation by remote sensing. (1984)

No.72* Studies on photochemical reactions of hydrocarbon-nitrogen oxides-surfur oxides-system – Research on the photochemical secondary pollutants formation mechanism in the environmental atmosphere. – Research report in 1980-1982. (1985)

No.73* Studies on photochemical reactions of hydrocarbon-nitrogen oxides-surfur Oxides-system – Final report in 1980-1982. (1985)

No.74* A comprehensive study on the development of indices system for urban and suburban environmental quality. Environmental indices-basic notion formation – Research report 1984. (1984)

No.75 Limnological and environmental studies of elements in the sediment of Lake Biwa. (1985)

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No.80* Modeling of red tide blooms in the coastal sea – Research report 1982-1983. (1985)

No.81* A study on effects of implementing environmental impact assessment procedure – With particular reference to implementation by local governments. (1985)

No.82* Studies on the role of vegetation as a sink of air pollutants – Research report in 1982-1983. (1985)

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* in Japanese

※ out of stock