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Survey of some chemical background of the environment in Japan

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Abstract - Three subjects entitled: (i) monoterpenes in the atmosphere; (ii) ozone as an index for air quality; and (iii) Jungermannia vulcanicola Steph. as a biological indicator for heavy metals, are selected for discussion in this paper from recent problems investigated by the research members of Division of Chemistry and Physics of this institute.

INTRODUCTION

In order to monitor the environment, such as the analysis of chemical pollutions in atmosphere or hydrosphere, the background levels of any species of pollutants should be known for the comparison, or to estimate the levels of the pollution, the unpolluted value, or the normal level has to be first established. Hydrocarbons are one of the main pollutants and they come from combustions of fuels at factories of chemical industries and from that of automobile fuel. Besides these man-made pollutions of hydrocarbons, it is known that some species of hydrocarbones, such as terpens, are produced from forest trees and that it may contribute the background levels of the material.[1] On the other hand, these materials have been thought to cause so-called "blue haze" of forests as well as forest's smell. A study was carried out to establish the behavior of terpents, particularly monoterpenes, in atmosphere.[2]

Ozone has an unique nature in the sense that it would give a hazardous effect as one of main components of so-called oxidants in cities, which cause the photochemical smog effect to the people, whereas it composes an ozone layer in stratosphere which absorbs the ultra violet light from the sun to protect the human being from exposure to the strong UV radiation. According to this particular nature of the gas, ozone may serve as an indicator to evaluate the level of general pollution of atmosphere in both urban and rural area. This idea has been investigated.[4]

Several mosses have been studied for usefulness as a biological indicator for heavy metals in hydrosphere. Jungermannia vulcanicola Steph was found to have a nature of accumulation of unusually high concentration of mercury. The amount of the metal as well as the chemical form inside of the leaf, quality of the water where the moss is grown, and the environmental meanings were investigated.[5,6]

1. MONOTERPENES IN THE ATMOSPHERE (refs. 2, 3)

Biogenic terpenes in urban and rural area have been recently investigated on the base that terpenes may contribute a main portion of total nonmathane hydrocarbons in the atmosphere, which cause the oxidant formation. The emission rate of terpenes was estimated in world wide scale, and the value of $1.75\times10^{8}\sim8.3\times10^{8}$ t/y is more than that of man-made hydrocarbons, that is, 6.5×10^{7} t/y.[1] This estimation, however, should be reinvestigated farther with more data of better and more reliable measurements. Fig 1 shows the chemical structures of atmospheric terpenes , which has been determined so far by several investigators, with varied analytical methods such as GC and GC-MS.

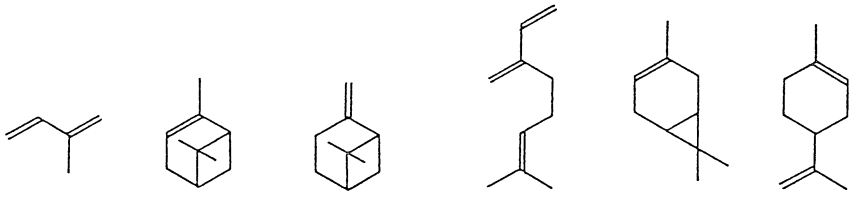

Fig. 1. Structures of atmospheric terpenes.

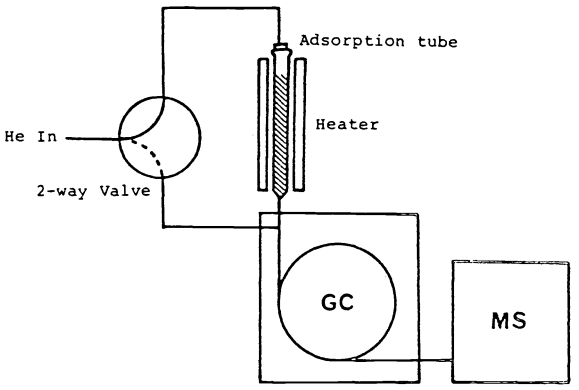

Fig. 2. Experimental GC-MS system

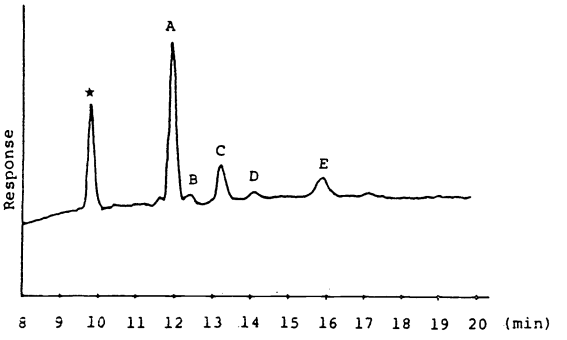

Fig. 3.
Selected ion chromatogram (m/z 93) of an air sample collected in a pine forest. Peaks: A = α-pinene, B = camphene, C = β-pinene, D = myrcene, E = β-phellandrene, the asterisk indicates an isotope of the molecular ion of toluene.

A sensitive and rapid GC-MS procedure of analysis of monoterpenes in atmosphere was developed by employing Tenax GC absorbent and a selected ion monitoring detection (SIM). Fig 2 gives the schematic system of the analysis.[2)]

With this analytical system, atmospheric monoterpenes were measured in the forests near the NIES, which located Tsukuba district in Japan, about 70Km northeast of Tokyo, as well as few other districts in Japan, during the period of 1979~1980. One of a typical chromatographic responses is given in Fig 3, which indicates well separated peaks of α-pinene, camphene, β-pinene, myrcene and β-phellandrene.

A set of data obtained from Tsukuba district is shown in Table 1. Most values are seen less than 1 ppb and are varied day by day, as well as due to the kind of trees in the forest, namely, pine, hinoki(cedar), or sugi(cypress).

Table 2 gives some values of α-pinene obtained at various districts of Japan ; Mashu in Hokkaido, Yaku in Kyushu and Kurobe in Nagano prefecture. All values are in sub-ppb range.

An example of diurnal variatin of α-pinene as well as that of ozone is given in Fig 4, and a seasonal variation of α-pinene measured everyday at 11am in the year of 1979 and 1980 in Fig 5. α-pinene consentratin is high at night, when the ozone concentration is low, and it is low and steady in winter season contrasting high and varied in summer and autumn season.

Table 1 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.

Table 2. 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

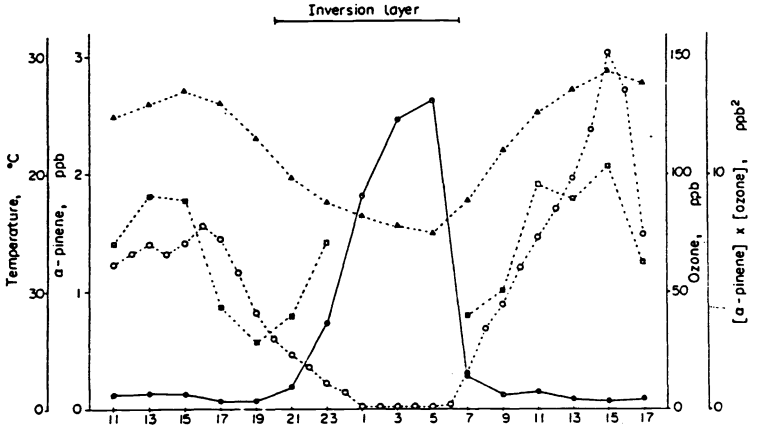

Fig. 4 Diurnal variation in the concentration of α-pinene in the air of a pine forest (5–6 June 1980). ●: α-pinene concentration, △: temperature, ○: ozone concentration, ■: the product of the concentration of α-pinene and ozone.

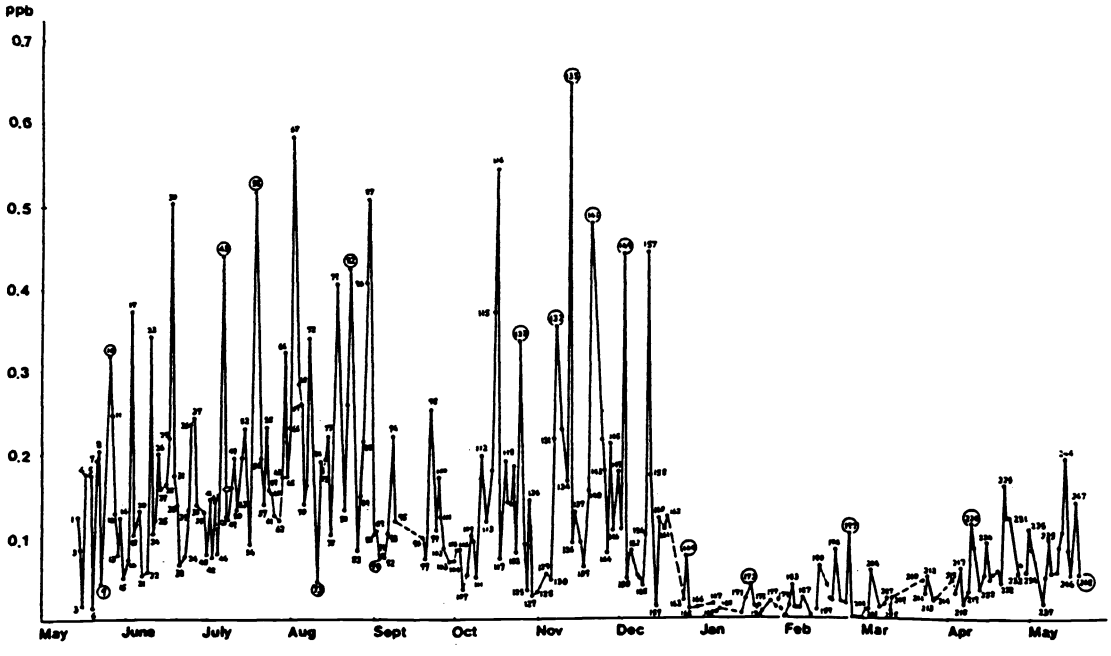

Fig.5. Seasonal variation of α-pinene in the air
(Pine forest, Tsukuba, 11:00a.m. 14 May 1980 — May 1981)

It is suggested from the study that (i) plant-origin terpenes play an ozone-destruction role rather than an ozone-producing role (ii) their atmospheric concentration and a total production may be lower than those preveously reported (8×10^8 t/y), and their local concentration is dependent on temperature and ozone concentration (iii) their emission rate depends on their amount in leaves and their vapor pressures, and (iv) terpen-origin aerosols exist commonly in forest air, as some compounds such as pinon aldehyde, one of decomposition products, were detected.

2. OZONE AS AN INDEX FOR AIR QUALITY (ref. 4)

A level of air pollution is generally given by concentrations of such pollutants as SO_2, NOx etc in any polluted area. However, these values may not be used in unpolluted area to show the air quality, since the values are substantially lower than the polluted area, so that analysis are not easy. Ozone is the species found in both polluted and unpolluted area, or it is one of the man-made pollutant and at the same time one of the naturally produced component of the air. Moreover, ozone concentration is higher in day time and lower at night at polluted places, whereas little diurnal variation at unpolluted places, as is clearly shown in Fig 6 for example.

There is a possibility, therefore, the ozone variation can be adopted as a single value index to show the air quality at any place, polluted or unpolluted. In order to test the idea actual data have been obtained and processed as is shown in Table 3.

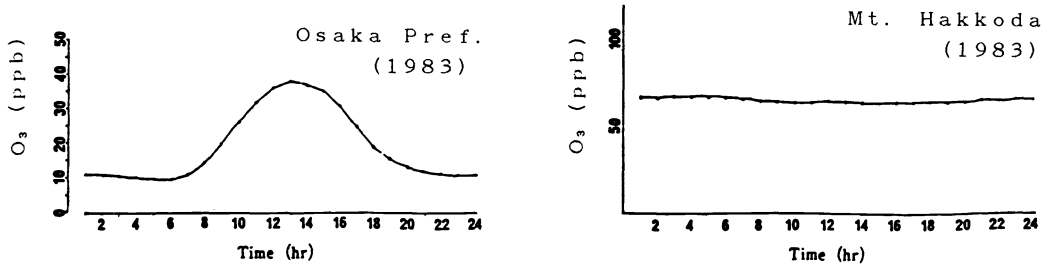

Fig. 6. Diurnal variations of ozone at both polluted and unpolluted sites.

Table 3. Scatter Diagram of PL vs SO_2, NO_2 and MP

(ppb)

place	date	Conc. O_3 max.	min.	av.	σ_n	PL	SO_2 av.	NO_2 av.
Sanriku, Iwate Pref.	1980.10. 8~11	52	12.5	36.1	5.80	16	1.2	1.5
Ogawa, Ibaraki Pref.	1980.11.17~21	33	2	13	8.42	65	4.2	4.2
Mt.Yamizo	1981. 6.29~7.26	60	15	31.4	8.45	27	-	-
Kurobe Damsite	1981. 8.17~21	48	13	28.9	8.57	30	3.0	-
Haginari Damsite, Akita Pref.	1981.10. 6~ 9	48	10	28.0	11.20	40	(12.2)	1.6
Yagisawa Damsite Gunma Pref.	1982. 7.26~30	44.0	7.0	26.3	8.67	33	(3.6)	(5.0)
Takano Hiroshima Pref.	1982. 7.13~8.11	49	6	24.	7.59	32	2.1	2.2
Tsukuba Ibaraki Pref.	1981. 9.27~30	39.0	2.0	18.0	12.40	69	7	10
Higashinari,Osaka Pref.	1979. 6. 9~13	47.6	1.0	16.0	17.80	111	13.9	33.3
Ikeda, Osaka Pref.	1983. 4~1984. 3	170	0	28.8	16.5	57	5	13
Yao, Osaka Pref.	〃	210	0	18.8	16.1	86	9	28
Sakai, Osaka Pref.	〃	123	0	21.7	16.5	76	7	22
Mt. Daisetsu.	1981. 4.19~28	87	35	55.5	5.2	10	-	-
Showa Station,Antarctic	1982. 3.18~24	27	23	24.4	0.66	3	-	-
Mt. Hakkoda.	1983. 4~1984. 3	113	2	44.7	2.6	5	-	-
Mt. Norikura.	1983. 7~1984. 3	90	5	46.3	2.4	8	-	-

σ : diurnal variation

PL : pollution level expressed by $PL = \frac{100}{v} \Sigma \left(\frac{\sigma_i}{x_i} \right)$; x : av. of O_3.

Fig 7 (a, b, c) shows the correlatin of measured O_3 variations expressed by PL, pollution level, $\frac{100}{n} \Sigma \left(\frac{\sigma}{\chi}\right)$, against measured values of SO_2 and NO_2 at same area. n is the number of observed days, σ is daily variation and χ is the average value of ozone.

The set of data indicates clearly that ozone concentrations could represent the air quality at any place including polluted urban sites and clear rural area.

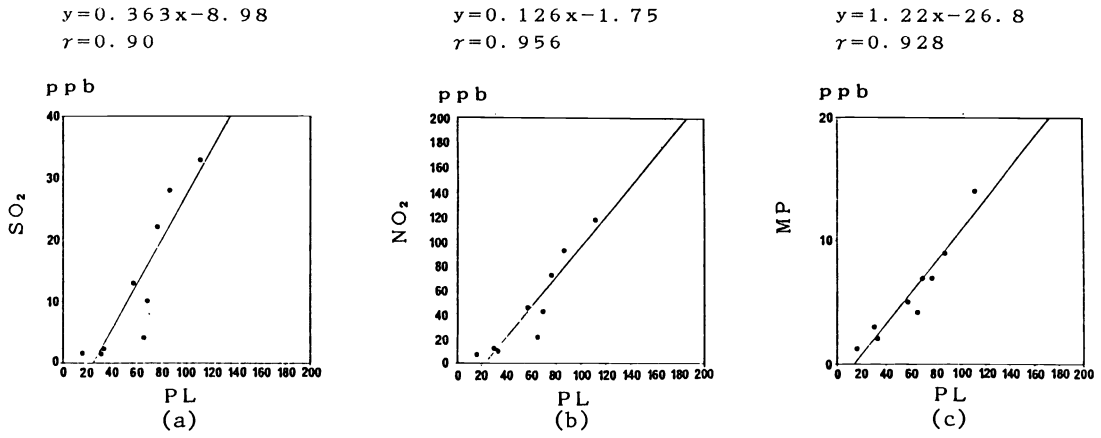

Fig. 7 Correlation of PL vs SO_2, NO_2 and MP
MP: multiple pollution level expressed by $MP=\frac{1}{2}\left(\frac{SO_2+NO_2}{40}\right)$

3. *JUNGERMANNIA VULCANICOLA* STEPH. AS A BIOLOGICAL INDICATOR FOR HEAVY METALS (refs. 5, 6)

Various species of plants have been investigated in order to find out any special one might be useful for environmental monitoring, or the plant for biological index for monitoring similar to the "mussel watch" project for the ocean coast monitoring. A particular liver-wort Jungermannia vulcanicola Steph grown in an mountain stream was found to accumulate mercury in fairly high amounts at a north part of Japan. The exact locatin of the stream, Kashiranashi river, and the sampling sites, 1~4, is shown in Fig 8.

The plant tissues and stream water as well as some sediments from the stream were analysed by various spectrometric analytical devices, such as Zeeman atomic absorption spectrometer, cold vapour atomic absorption spectrometer, energy dispersive X-ray fluorescence spectrometer and X-ray photoelectron spectrometer. A X-ray fluorescence spectrum of the tissue is shown in Fig 9.

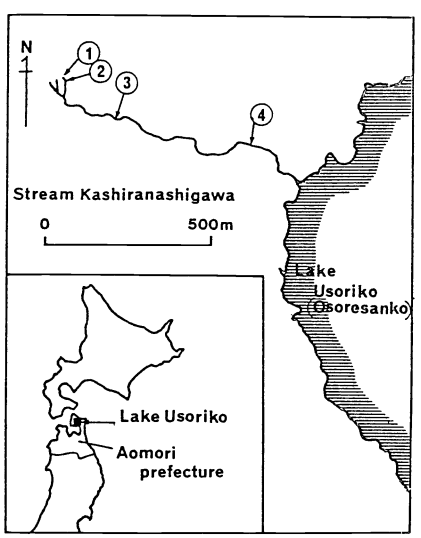

Fig. 8 Map of Stream Kashiranashigawa and Lake Usoriko.

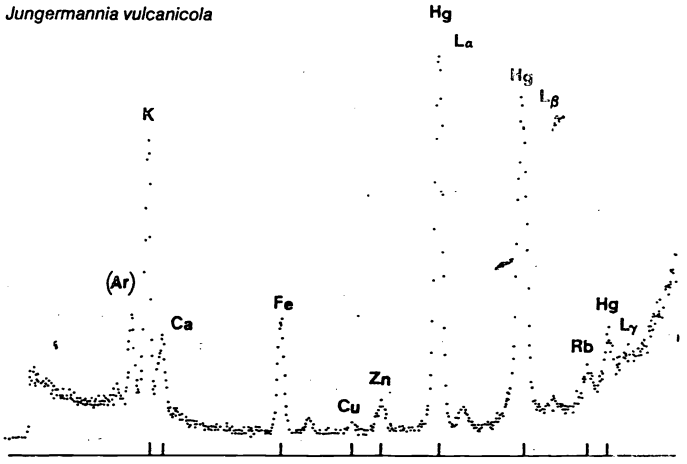

Fig.9. X-ray fluorescence spectra of the tissues of liverworts Jungermannia vulcanicola STEPH. sampled from upstream of stream Kashiranashigawa (Mo anode, Mo filter, anode voltage 45 KV, anode current 100μA).

Table 4. Mercury contents in the liverworts Jungermannia vulcanicola SPEPH, water and sediments sampled from the stream Kashiranashigawa (29 March, 1981; 11May, 1981).

Sample	Station	Mercury content	
		wet weight	dry weight
J. vulcanicola	2		
section			
0-1cm		39mg·kg^{-1}	780mg·kg^{-1}
1-2		217	4340
2-3		334	6680
3-4		549	11000
4-5		604	12100
5-6		528	10600
0-1(laterial bud)		95	1900
Spring water	1		0.7μg·l^{-1}
Stream water	2		0.6
Stream water	4		<0.015
Sediment	1		32-158mg·kg^{-1}
Sediment	2		53-121
Sediment	3		62-122
Sediment	4		16-34

The table 4 gives a set of data of mercury contents in these samples. The average value of Hg in the tissue of J. vulcanicola was calculated 3740~5320 mg·Kg^{-1} in dry weight base, which is extraordinary high, exceeding those of ordinary elements such as Na, Mg, P and Ca. The estimated accumulation factor from the water is 6.2×10^{6}, which is hundred times higher than that for K. The results of XPS analysis indicate that the state of Hg may have HgS Form, which is most stable and insoluble and suggests, therefore, a detoxification effect of mercury inside the liverwort.

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