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Studies on the Method for Long Term Environmental Monitoring

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

Research Report in 1980-1982
昭和55～57年度特別研究報告

Edited by Y. AMBE and K. FUWA
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ERRATA

Research Report from the National Institute for Environmental Studies, No. 79.

Studies on the method for long term environmental monitoring

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Page	Line	Read	Corrected
v	10	Tsugio	Tsuguo
2	2*	Ssud	Stud
6	23	laboratiry	laboratory
〃	1*	pollutinn	pollution
9	5*	sourced	sources
〃	4*	NO^x	NO_x
10	15	rep-resentative	representative
〃	1*	way	away
11	21*	site at	site is
〃	20*	Plain is	Plain, which is
〃	9*	from away	away from
〃	4*	Precipitations	Precipitation
12	3	restautant	restaurant
38	22*	resevoirs	reservoirs
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47	4	easten	eastern
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56	Table 4	leavels	levels
59	21	Iba	Ibe
65	1*	averge	average
70	4	pyrrolidlinedithiocarbamate	pyrrolidinedithiocarbamate
73	11	dithioncarbamate	dithiocarbamate
78	4	homogenous	homogeneous
133	5	Spectroscopy	spectroscopy
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Preface

When we talk about the environment, the argument should be based upon precise data. However the pollutants in atmosphere, in soil and water and in biosphere are hard to detect and the concentration of pollutants is usually very low. Consequently, the chemical analysis of the pollutants in environments is a matter of difficulty.

The second problem is to determine the appropriate place to monitor the environmental pollution on the earth. In other word, we should find the place where the environment are not contaminated by the human activities, in order to find the background level of pollutants.

The pollutants emitted into the environments stay and accumulate a long time when the substances are chemically stable. Consequently it is pointed that the pollution of the earth is gradually increasing due to the world wide increase of energy and material consumption in recent years.

The special research program "Studies on the Methods for Long-Term Environmental Monitoring" started in 1980 aiming to investigate better methods to solve above problems. The papers included in this volume are results obtained in the initial stage of the program.

We hope that the report will stimulate discussion among scientists in the fields of environmental research and the results will be useful for the program of the global environmental monitoring.

Jiro Kondo, D.Eng.
Director of the National Institute
for Environmental Studies

Jiro Kondo

January 1985

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Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

Outline of the Research Project

Yoshinari AMBE[1] and Keiichiro FUWA[1]

The change of the environment caused by pollution occurs in various temporal and spatial scale. The survey and monitoring on environmental pollution so far have been mainly focussed on rather local and short term variation of the environment. It is feared that the local scale of pollution is expanding to regional or national size covering all area of Japan Islands and further to global scale. The wider and the longer the scale of pollution is, the harder becomes the countermeasure against it. The need to assess a global scale environmental pollution has been widely recognized and several international activities relating to this problem have started recently.

As to the global environmental monitoring, the Earth Watch Program by UNEP cooperated with WHO, WMO, FAO and other UN organizations and the establishment of Monitoring and Assessment Research Center by SCOPE are noticed among these activities. In Japan, an advisory committee which discuss global scale environmental problems was set up in the Environment Agency. Based on the recommendation of this committee, a proposal to establish a special committee in UN on the global environmental policy in the 21st century was presented by Japan at the special meeting of UNEP executive committee held in May 1982. This proposal was adopted and the first meeting of this new committee was held in October 1984.

In many cases so far, the survey and investigation of environmental pollution have been performed after the phenomenon and its effect occurred, and because of the delayed survey the countermeasures were always insufficient. It is needless to say that the foregoing surveilance and care are the most important and effective way in the solution of environmental problems. However, at present, informations on the national wide or worldwide environmental change are very rare as well as monitoring system, and, above all, the methodology for monitoring of these scales of environmental pollution is insufficient.

Under such situation, a special research project was programmed at our institute (NIES) aiming to develop the methodology for long term environmental monitoring in national wide scale which is considered to be basically important to understand and to monitor the process of expanding local pollution to national scale and to the whole earth.

It is fundamental to know the value of so-called background level of pollutants as a base-line to find out the change of pollutant concentration in long term and national wide environmental monitoring in Japan Islands.

As the environmental monitoring systems existing in Japan are restricted in the highly polluted urban and industrial areas, the information on the national wide background levels of pollutant concentrations are quite lacking and the establishment of national wide background monitoring system is needed.

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Therefore, the methodology to set up a background region of national wide pollution and to know the background level of pollutant concentration was studied in the first step. Secondly, problems relating to environmental specimen banking were investigated, in which various enviromental specimens are stored to be used in future for the retrospective analysis to detect long term change of pollutant concentration. In this respect, the availability of the bank and the preservability of the stored samples were studied and a small pilot specimen bank was built and operated to examine the problems in practical operation. The selection of environmental indices to be monitored and that of environmental samples to be stored were the problems which should be studied previous to the studies on background monitoring and storing of the samples.

Further, in order to accomplish the studies above mentioned more exactly, several investigations on chemical analysis such as identification of trace organic compounds in the environment and developments of instrumentations for trace pollutant analysis were performed.

The research project was carried out with the participation of the members of the Division of Chemistry and Physics and several other divisions in the institute, under the subprograms as follows.

1) Studies relating to the selection of samples and sampling method for long term environmental monitoring.
2) Studies on the method for monitoring background level of pollution.
3) Studies on the method for long term storage of environmental samples.
4) Survey of unidentified or unknown trace organic substances in the environment.
5) Studies on the highly sensitive methods for trace pollutant analysis.

The first stage of the project was over in 1982, a part of the results of this research program was published in 1982 (Res. Rep. Natl. Inst. Environ. Stud. No. 36) and a general outline of the project was reported in 1984 (Res. Rep. Natl. Inst. Environ. Ssud. No. 58) both in Japanese.

The present volume is the collection of the papers on the results compiled after that. The research activities on this line is still going on, and the final results will be reported after several years.

研究計画の概要

安部喜也[1]・不破敬一郎[1]

汚染に基づく環境の変化には空間的・時間的にさまざまの規模のものがある。これまで環境汚染の状況に関する追跡はどちらかといえば，局地的，短期的な変動に注目して行われていたが，同時に日本全域，さらに地球全体にわたるより長期的規模の環境汚染が進行していることが予想される。汚染は規模が大きくなり長期的なものになるほど，対応は困難になる。

地球的規模の汚染についても近年世界的な関心が高まり，国際的な各種の活動がはじまっている。

環境変化への対策をたてるには問題が起こる前にあらかじめ監視をしておくことが必要であるが，国規模，地球規模の現象に対しては今のところモニタリングの体制がほとんどできてないのみならず，その方法論すら確立されていないといってよい。

本研究は以上のような状況を踏まえて，国規模の長期的環境モニタリングの方法論を確立することを目指して計画された。

国規模の汚染は，局地的な汚染が全地球的な汚染に拡大する中間の過程として重要な位置を占める。ここにおいて従来特に研究の欠けている二つの課題を中心にとりあげた。第一は，日本列島の長期的な環境汚染をモニターする際に変化を検出する基準となるベースラインとして，汚染物質に関するバックグラウンド値を明らかにすることを目標とした。すなわちバックグラウンドに相当する地域を設定する手法の確立，及び，そこにおけるバックグラウンド値を求めるための方法論の検討を行った。

第二に，長期的環境汚染モニタリングの一つの手法としての環境試料バンクをとりあげ，試料の保存性，保存方法，その他関連する諸問題について検討するとともに，小規模のバンクを設置してその有効性を検討した。

以上二つの課題と関連して，測定すべき環境指標項目及び保存すべき試料をいかに選定するかという問題が生じる。これについても長期モニタリングの観点から検討を加えた。

さらに，上記の目的をより高度に達成するために，環境中に存在する各種の未確認物質をモニターするための分析方法を確立する研究，並びに，測定の高感度化，高精度化のため機器分析手法の開発を行った。

本研究には計測技術部を中心として各部の研究者が参加した。成果の一部については既に中間報告として，また概要については総合報告として出版している。本報告書はその後の成果をまとめた論文集である。本特別研究の目的に沿った研究は引き続いて行われており，成果は順次まとめられる予定である。

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Ⅰ. Introduction

Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

Principles and Scope of Environmental Monitoring

Keiichiro FUWA[1]

The environmental monitoring in wider term has been carried out from the beginning of the history of mankind, as they had to survive by observing their environment, or the weather including natural disasters, fully utilizing their instinctive capabilities. The modern environmental monitoring in narrow term has essentially the same purpose, but differs entirely from the old one, as the methods of observation of the environment have vastly changed. Besides some meteorological observations, the monitoring of chemical species in the environment is the most characteristic. Table 1 gives a brief history of the environmental problems related to the monitoring.

Asian Research Center for Environmental Monitoring (ARCEM) has been planned and considered by the group of the national SCOPE/MAB committee and NIES was picked by the committee for the location of the organization. It is not yet, however, realized for any concrete base.

The background levels of environmental monitoring can be taken as the normal range of values of measurement of any species in the environment, and they are most important for both long term and short term of monitorings.

Lake Mashu was selected by our group as the most unpolluted hydrospheric location in Japan and the analysis of the lake water has been carried out. Some of the detailed results are described in this report. A repeated measurement of the

Table 1 Brief history of the environmental problems

1962	Publication of "Silent Spring" by Dr. R. Carson
1964	IBP/ICSU 1st meeting (Paris)
1965	Minamata Disease, Auch-Auch Disease, recognition of the causes.
1969	SCOPE/ICSU, MARC Chelsea, establishment of.
1970	EPA/USA ; Special research project "Human Survival"/Dept. Ed., Japan, starts of.
1971	Environment Agency/Japan ; PCB Act/Japan ; MAB/UNESCO.
1972	UN Stockholm Conference ; UNEP, Earth Watch, GEMS, starts of.
1973	Acts related to Chemical Substance/Japan
1974	NIES/EA, Japan ; ERDA/USA, establishment of.
1975	HESC/SCOPE, UNEP (Tokyo)
1977	Special research project "Environmental Science"/Dept. Ed., Japan, start of.
1981	ISMIED/MAB (Tokyo)
1984	10th anniversary of NIES ; MICE/MAB (Tokyo)

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sample obtained from the same location in a certain interval is the essence of the environmental monitoring, and, therefore, we intend to continue the observation and investigation of the water of Lake Mashu in this project and in future project.

Some methodological improvement or investigation have been carried out in relation to this background monitoring project, as are reported in this volume.

The requirements of the method for the environmental monitoring of chemical species are neccessarily similar, first of all, to those of analytical chemistry in general. And they are:

1. Accuracy
2. Precision
    reproducibility
    repeatability
3 Sensitivity
4 Specificity
5. Speed, easiness

The definition of accuracy in chemical analysis is expressed by the difference between the "true value" and the found value. Since the "true value" of a sample is not known or can not be obtained, a certain statistical treatment is usually required, such as inter-laboratoris calibration. One of the most reliable way of ascertaining accuracy is to obtain standard reference matirial, the analytical values of which are already certified by fully designed statistical menthod. Therefore, we started a project of the preparation of environmental standard reference materials right after the laboratiry's start. The process of the preparation including homogenization of dried material and that of the certification which needs the cooperation of many experts in varied institutes were completed on the materials such as, Pepperbush, Pond Sediment, Chlorella, Human Hair, Human Serum and Mussel.

Electrochemical analytical method has usually a good repeatability and reproducibility and probably the most suitable method for hydrospheric monitoring.

Ion selective electrode may be the most promising of all, as the procedure is the simplest with in situ insertion into the sample water. The response can be recorded continuously with automatic operation system. It has, however, a drawback in the property of specificity. The change of sensitivity at the active surface, i.e. the interference by micro-organism growth on the surface is another point to be considered. The further development is expected to overcome these short-comings.

Inductively coupled plasma emission spectrometer, the newest apparatus for metalic elemental analysis, has made possible the simultaneous analysis of forty to fifty elements at the level of ppb or less. It is most powerful for elemental monitoring of environmental materials, but the careful pretreatment of samples is required, and the cost as well as the size of the machine is not as small as being wanted for some monitoring purpose.

A semi-conducter laser light source has been developed and has become one of most promising light source for the absorption measurement at infrared region of some atmospheric compositions, including nitrogen oxides, carbon dioxide and hydrocarbons. The line width is extremely narrow from the laser, so that both the sepcificity towards the chemical species to be observed and the resulting sensitivity can be very high. The method could be a new one for in situ easy measurement of background level pollutinns of the atmosphere.

環境モニタリングの原理と展望

不破敬一郎[1]

広義の環境モニタリングは人類の歴史とともに行われてきた。しかし最近の急速な環境汚染に伴ったモニタリングでその様相を一変した。

モニタリングに要求される条件としては

1．正確さ
2．精度
3．感度
4．特異性
5．速度，実行の容易さ

などがあげられ，これらを達成するために多くの研究が行われている。環境標準試料の調製，バックグラウンド値の測定等はその例である。さらに今後広くモニタリングのために利用されるべき手法として，各種の電気化学的分析法，ICP 発光分光法，半導体レーザー光源による分光法の応用が考えられる。

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Ⅱ. Research Method for Background Level of Pollution

Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

II — 1

Background Air Pollutant Measurements and Selection of Background Sites in Japan

Tsuguo MIZOGUCHI[1], Masayuki KUNUGI[1],

and Masataka NISHIKAWA[1]

ABSTRACT

At several clean remote locations in Japan air pollutants such as SO_2, NO_x, O_3 and other species were measured for determination of background air pollution levels, Main pollutants except ozone were barely detectable, so background levels could not be directly estimated by these parameters. The relative standard deviation of O_3 concentration may well be a more accurate indicator of background air pollution levels because there are negligible amounts of substances which react to ozone in clean remote atmospheres. The concentration of certain elements in aerosols and variation in the chemical composition of precipitation were studied to determine if these factors could be qualified as reliable indicators of pollution levels.

1 . INTRODUCTION

For detection of the concentration and variation in global air pollution, it is necessary to monitor background air pollution for a long period of time.

Background air pollution monitoring has been carried out by the Organization for Economic Cooperation and Development (OECD) and the World Meteorological Organization (WMO) since the late 1960s[1,2)]. At Mauna Loa in Hawaii, the CO_2 concentration in the atmosphere has been measured for 20 years to detect the behavior of air pollutants over a global range[3-7)]. In Japan, air pollution has been monitored for nearly 20 years over anthropogenic polluted areas. Various data have been analyzed to clarify behavior of air pollution and sourced of emission. Of course, the variation in air pollutants such as SO_2, NO^x and CO should be monitored over clean remote areas.

In this study, the attempts were made to measure air pollutant concentration and select a suitable site for monitoring air quality in a clean atmosphere.

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2 . SITE SELECTION

WMO[1,8,9] defines the criteria for baseline air pollution stations as follows:

1) The station should be located in an area where no significant changes in land-use practices are anticipated for at least 50 years within 100 km in all diretions from the station.

2) It should be located away from major population centers, major highways and air routes, preferably an isolated island or on mountains above the tree line.

3) The site should experience infrequent effects from natural phenomena such as volcanic activity, forest fires, dust and sand storms.

There are few places which satisfy the WMO criteria in Japan except for an island in the Pacific Ocean. If air qualities must be monitored continuously, a station with difficult access, would not be satisfactory. Thus, in Japan a remote clean station for term monitoring will necessarily have a higher pollution level than WMO background stations.

The location of a site may be of crucial importance for determining rep-resentative background air pollutant concentration.

The criteria for site selection includes the following[10].

1) The site must be situated at a sufficient distance from urban areas.

2) There should be no local emission of anthropogenic air pollutants near the site.

3) The site should be as far way from main roads as possible.

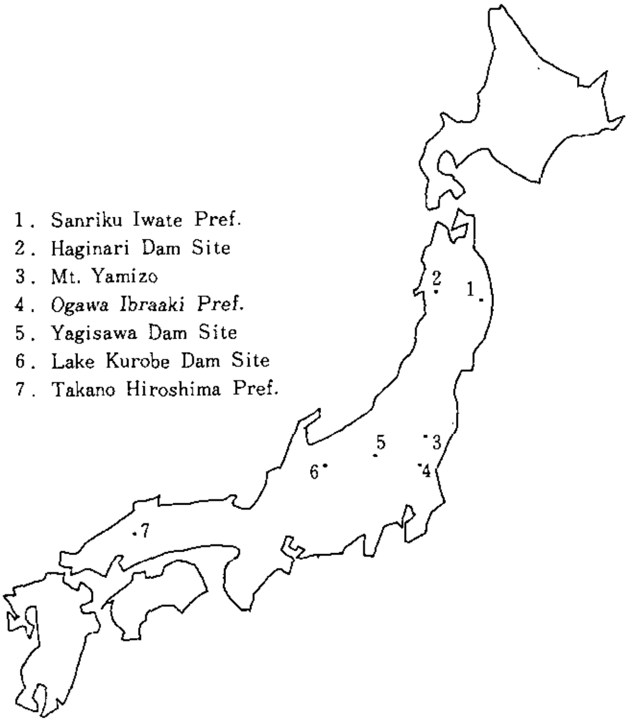


Fig. 1 Location of non-urban stations for this study

There must be a room for the measurement instruments, and a power supply available. The site should be reasonably accessable.

There are such stations on the Main Island of Japan (Fig. 1). Station No. 1 (Fig. 1) is located in northeast Japan. The site is on a small mountaintop about 450m above sea level. The Pacific Ocean is about 2km east of the station. There are mountains on all sides except the east. The WMO regional station of Japan, Ryori, is about 15km southeast. Air pollutant concentrations of station No. 1 were presumed as low as those of Ryori. There are few anthropogenic sources in the area, but a large ironworks is forward around 15km to the north. Thus, a north wind may bring pollution. The wind direction was usually from the west when air pollutant measurements were made.

Station, No. 2 is also located in northeast Japan. The site is situated over 100km from the No. 1 and to its west. The Sea of Japan is about 30km west of this site. Akita city with a population of about 300 thousands is around 30km to the south. There are a few local emission sources 10-20km away, and a spring area is situated about 10km to the east.

Dam sites are suitable for monitoring background air pollution in Japan, because they are generally in mountain regions or forest far from major pollution centers, and they have buildings and power facilities. Consequently three dam sites were chosen *i,e.* Haginari (No. 2), Yagisawa (No. 5) and Kurobe (No. 6).

Station No. 3 is Mt. Yamizo located about 130km northeast of the Tokyo metropolitan area and over 1000m above sea level. The station is near a mountaintop. Large emission sources are situated some 20-30km away. This station is very suitable for monitoring background air pollution.

Station No. 4 is a forest about 50km south of Mt. Yamizo. This site at the northeast end of the Kanto Plain is the largest in Japan and has the largest industries in the southern area. The site is around 100km away from the largest industrial area so that effects may be slight. A few anthropogenic emission sources are located about several dozen km away.

Station No. 5 is a dam site located about 150km north of the Tokyo metropolitan area. Mountains are not too far from here. This station is considered an unpolluted site.

Station No. 6 is also a dam site and located in central Japan. The largest dam in Japan, it is considered to be the cleanest area on the Main Island of Japan. In winter, however access is difficult.

Station No. 7 is the only one on the westside of Japan surrounded by farm land, it is over 80km from away large emission sourced.

3 . RESULTS AND DISCUSSION[11-18]

Table 1 shows the parameters and techniques employed for all measurements. Elements in aerosols were measured by X-ray flourescent spectrometry and neutron activation analysis.

Precipitations was analyzed by elemental analysis, inductively coupled plasma atomic emission spectroscopy and ion chromatography. A summary of the results is shown in Table 2. The results at stations No. 4 and No. 5 show slightly higher values than the others.

Table 1 Measurement method

Parameter	Instrument
Sulfur dioxide (SO_2)	Ultraviolet flurometric Analyzer
Nitrogen oxides (NO, NO_2)	Chemiluminescent Analyzer
Ozone (O_3)	Ultraviolet absorption photometer
Carbon monoxide (CO)	Nondispersive infrared spectrometer
Methane (CH_4)	Flame ionization detector
Non-methane hydrocarbon (NMHC)	Flame ionization detector
Total suspended particulate matter (TSP)	High (low) volume sampler

Air pollution at station No. 4 may be affected by emission sources from the south Kanto plain. Pollution at station No. 5 must be due to local sources such as automobile and restautant exhausts. The other results may be generally reliable.

Major air pollutants except ozone are barely detectable using the monitoring instruments indicated in Table 2. Thus, the levels of background air pollution must not be estimated directly by these data. To estimate background air pollution levels, the following indicators were tested by physical and chemical procedures.

1) Evaluation by the variation coefficient of O_3 concentration.
2) Estimation model by the total major air pollutant concentration.
3) Estimation by total suspended particulates.
4) Estimation by ratio of special components in aerosols.
5) Estimation by component variation in precipitation.

1) O_3 in an ambient atmosphere is assumed to issue from both the troposphere and the stratosphere. In remote clean areas, where O_3 is scarcely generated by photochemical reaction processes and hardly transported from anthropogenic polluted district in the troposphere, where O_3 injected from the stratosphere is usually constant and there is no component to react with it, clearly the smaller the variation in O_3 concentration, the cleaner is the site. On this basis, the following equations is defined as an indicator:

$$O_{RS}=\frac{1}{N}\sum_{j}^{N}\left(\frac{S}{\bar{x}}\right)_j \qquad (1)$$

where O_{RS} is the average of the relative standard deviation indicating the background air polltion level; Small O_{RS} indicates a higher background pollution level; N is the number of measurement days; S is the standard deviation per hour in O_3 concentration; and $\bar{x}$ is the average value per hour of O_3 concentration.

Table 3 shows O_3 data measured and calculated at 7 background and 4 anthropogenic polluted stations for comparison of background and polluted sites. O_{RS} calculated in Table 3 would appear to be a very effective indicator of background air pollution levels.

2) It is quite difficult to estimate background air pollution levels by such pollutants as SO_2, NO_x, CO and HC, respectively.

Table 2 Summary of measurement results

unit : ppb

Site	Component	Concentration Range	Average Concentration	Periods
Sanriku Iwate Pref.	SO_2	0～9.9 #	1.4	8 -11 Oct. 1980
	NO	0～27.5 #	2.5	
	NO_2	0～39.0 #	2.0	
	O_3	12.5～52	36	
	CH_4	1.62～1.71	1.67*	
	NMHC		(0.03)*	
	SPM		13.08**	
Ogawa Ibaraki Pref.	SO_2	0～26	4.2	17-21 Nov. 1980
	NO	0.9～7.0	1.83	17-21 Nov. 1980
	NO_2	0.5～12.9	4.2	17-21 Nov. 1980
	O_3	2～33	12.9	17-21 Nov. 1980
	CH_4	1.66～1.88	1.70*	18-21 Nov. 1980
	NMHC	0.18～0.55	0.30*	18-21 Nov. 1980
	SPM		38.42**	17-21 Nov. 1980
Kurobe Dam	SO_2	0～15	3	18-20 Aug. 1981
	NO	0～3	1.0	18-20 Aug. 1981
	NO_2	0～1	(0)	18-20 Aug. 1981
	O_3	13～48	29.4	17-21 Aug. 1981
	CH_4	1.6～1.75	1.64*	17-20 Aug. 1981
	NMHC	0.07～0.18	0.11*	17-20 Aug. 1981
	SPM		14.0**	17-21 Aug. 1981
Haginari Dam	SO_2	3.6～28.8	12.2	6 - 9 Oct. 1981
	NO	0～7.6	3.6	
	NO_2	0～6	1.6	
	O_3	10～48	28	
	CH_4	1.63～1.69	1.67*	
	NMHC	0.06～0.15	0.10*	
	SPM		9.55**	
Yagisawa Dam	SO_2	0.6～9.5	3.6	26-30 Jul. 1982
	NO	3.4～10.6	6.5	
	NO_2	2.0～8.6	5.0	
	O_3	7.0～44.0	26.3	
	CH_4	1.6～1.8	1.7*	
	NMHC	0.1～0.4	0.18*	
	SPM		11.7**	
Takano Hiroshima Pref.	SO_2	0～11	2.1	1 Jul.-12 Aug. 1982
	NO	0～3	0.5	1 -16 Jul. 1982
	NO_2	1～8	2.2	1 -16 Jul. 1982
	O_3	2～74	26.9	1 Jul.-12 Aug. 1982
	CH_4	1.60～2.20	1.74*	1 Jul.-12 Aug. 1982
	NMHC	0.07～0.24	0.12*	1 Jul.-12 Aug. 1982
	CO	0～6	2.3*	1 Jul.-12 Aug. 1982
Mt. Yamizo	O_3	15～60	31.4	29 Jun.-6 Jul. 1981
	SPM		15.3**	14-21 May 1981

* =ppm ** =$\mu g/m^3$

It would seem that the maximum values were affected by specific local emissions

Table 3 Summary of ozone measurement at selected sites

site \ item	measurement periods	O_3 max ppb	O_3 min ppb	O_3 ave ppb	σ ppb	Ors %
Sanriku Iwate Pref.	8-11 Oct. 1980	52	12.5	36.1	5.80	16
Ogawa Ibaraki Pref.	17-21 Nov. 1980	33	2	13	8.42	65
Mt. Yamizo	29 Jun.-6 Jul. 1981	60	15	31.4	8.45	27
Kurobe Dam Site	17-21 Aug. 1981	48	13	28.9	8.57	30
Haginari Dam Site	6-9 Oct. 1981	48	10	28.0	11.20	40
Yagisawa Dam Site	26-30 Jul. 1982	44.0	7.0	26.3	8.67	33
Takano Hiroshima Pref.	13 Jul.-11 Aug. 1982	49	6	24.1	7.59	32
Tsukuba Ibaraki Pref.	27-30 Sep. 1981	39.0	2.0	18.0	12.40	69
Osaka Pref.[*1]	9-13 Jun. 1979	47.6	1.0	16.0	17.80	111
Mt. Daisetsu[*2]	19-28 Apr. 1981	87	35	55.5	5.2	10
South Pole[*3]	18-24 Mar. 1982	27	23	24.4	0.66	3

*1 measured by Osaka Pref.
*2 measured by Okita *et al.*
*3 measured by Chubachi.

Therefore, in order to evaluate clean levels, the following equation is proposed.

$$P_r = \sin \frac{2\pi}{n} \sum_{i}^{n} (P_i P_{i+1}) \tag{2}$$

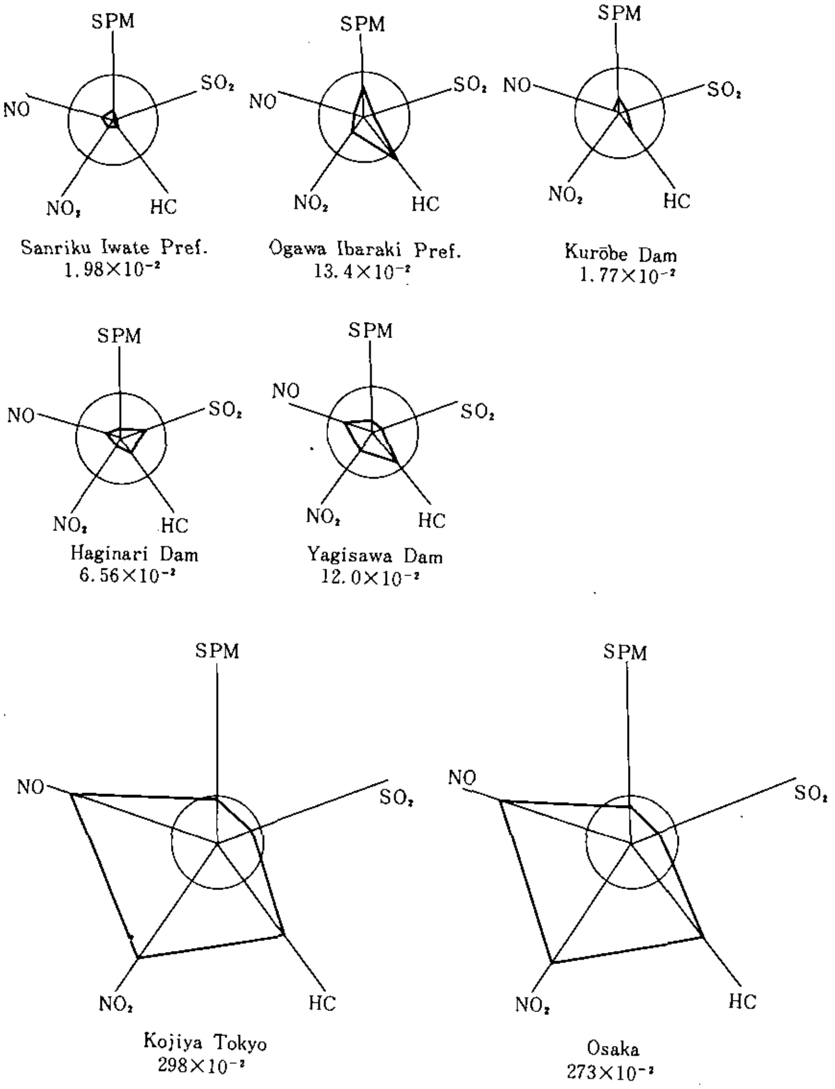
where P_r (Pollution Rose *i.e.*, pollution levels shown in area) is the indicator of background air pollution levels. The smaller P_r value is, the cleaner.

P_i is i pollutant value per environmental quality standard value of i pollutant. If the environmental quality standard value of a pollutant is not defind, reasonable value can be given. Therefore, the values of NO and NMHC were given 20 ppb and 500 ppb, respectively, n is the number of pollutants. P_r levels measured at 5 background and 2 polluted stations are shown in Fig. 2.

3) The present automatic instruments for measuring suspended paticulates are not so effective at clean areas. A high volume sampler or a low volume sampler may be effective if the sampler is used to collect airborne particulates for a sufficient period of time.

If enough suspended particulate quantities are collected, it should be possible to estimate background air pollution levels directly. It is very difficult to use a high-volume or low-volume sampler without precise and continuous operation. Hence, neither is suitable for background site monitoring.

4) Tables 4 and 5 show the results of element analysis of suspended particulates by neutron activation analysis and carbon ratio by elemental analysis, respectively, Al, Zn and Cu, which come from anthropogenic sources, may be



Sanriku Iwate Pref.
1.98×10^{-2}

Ogawa Ibaraki Pref.
13.4×10^{-2}

Kurōbe Dam
1.77×10^{-2}

Haginari Dam
6.56×10^{-2}

Yagisawa Dam
12.0×10^{-2}

Kojiya Tokyo
298×10^{-2}

Osaka
273×10^{-2}

Fig. 2 Pollution levels shown in area

Table 4 Analysis of elements in aerosol by NAA

unit : (ng/m³)

Site	Sanriku Iwate Pref.	Kojiya Tokyo	Tsukuba Ibaraki Pref.	Haginari Dam	Kurobe Dam	Yagisawa Dam	Mt. Yamizo
Periods	*8-11 Oct. 1980*	*20-23 Feb. 1981*	*9-17 Apr. 1981*	*6-8 Oct. 1981*	*17-21 Aug. 1981*	*26-30 Jul. 1982*	*4-29 Jun. 1981*
Volume (m³)	85.4	82.0	288.8	69.36	101.2	106.6	748.8
TSP (mg)	0.69	7.24	7.49	0.80	1.42	1.29	9.58
TSP (μg/m³)	8.08	88.29	32.74	11.53	14.03	12.1	12.8
Na	980.	1400.	420.	130.	91.	95.	48.
Al	110.	2300.	550.	100.	140.	89.	88.
Cl	1100.	4600.	220.	100.	<20.	140.	120.
K	200.	870.	200.	100.	80.	40.	140.
Ca	300.	1900.	380.	70.	100.	200.	20.
Sc	0.022	0.55	0.09	0.019	0.018	0.010	0.020
Ti	<10.	200.	50.	<10.	<9.	10.	8.
V	1.0	15.	0.3	0.66	1.0	0.98	0.69
Cr	<1.	27.	1.6	3.3	3.0	4.1	1.2
Mn	3.5	95.	17.	2.6	3.8	3.4	2.8
Fe	98.	3300.	430.	83.	110.	51.	61.
Co	0.17	2.4	0.22	0.093	0.086	0.10	0.72
Ni	4.	52.	<2.	5.8	10.	3.7	24.
Cu	9.	130.	20.	<6.	<4.	19.	260.
Zn	<7.	600.	84.	<9.	<6.	20.	910.
As	0.92	5.8	4.8	0.69	0.68	<0.04	0.46
Se	<0.4	9.8	0.95	0.26	0.25	0.06	0.1
Br	1.8	15.	1.8	2.3	1.5	1.7	0.77
Rb	<0.3	3.1	1.2	0.4	0.4	<0.2	0.3
Mo	<0.2	4.2	0.74	<0.1	<0.1	<0.06	<0.02
Ag	0.36	1.4	0.53	0.04	0.06	0.08	<0.04
Cd	<0.7	11.	1.3	<0.4	<0.3	0.4	1.3
Sn	<8.	<20.	<7.	<3.	<3.	<9.	10.
Sb	0.24	5.6	1.4	0.18	0.28	0.46	0.48
I	0.8	4.1	3.5	2.	1.	0.7	0.42
Cs	0.02	0.18	0.068	0.02	0.02	<0.01	<0.3
Ba	<3.	30.	<2.	<3.	5.	<2.	<2.
La	0.06	1.5	0.24	0.07	0.07	0.03	0.055
Ce	0.1	2.5	0.46	0.23	0.1	<0.04	0.098
Sm	0.008	0.16	0.034	0.0067	0.0093	0.0065	0.0062
Eu	<0.008	0.02	0.008	0.005	<0.002	<0.004	<0.002
Yb	<0.02	0.20	<0.001	<0.009	<0.008	<0.01	<0.007
Lu	<0.0009	0.016	0.002	<0.004	<0.004	0.001	<0.0008
Hf	<0.01	<0.04	<0.01	0.01	0.01	<0.01	<0.008
Ta	<0.03	0.63	<0.2	<0.005	<0.009	<0.01	<0.006
W	<0.09	5.2	0.26	<0.06	<0.04	0.04	0.06
Hg	<0.09	<0.009	<0.003	0.01	0.017	0.002	0.01
Th	0.02	0.24	0.060	0.04	0.055	0.02	0.01

Table 5 Ratio of carbon in aerosol

site	aerosol concentration	ratio of Carbon
Omiya Route 17	82.4 (μg/m³)	50.1 (%)
Kojiya Tokyo	110.0	16.9
Tsukuba	58.5	18.1
Mt. Yamizo	23.9	18.6
Sanriku Iwate	23.4	9.8

Table 6 Analysis in precipitation

site	rainfall mm	SO_4^{2-} ppm	Cl^- ppm	NO_3^- ppm	Na^+ ppb	K^+ ppb	Mg^{2+} ppb	Ca^{2+} ppb	PH	conductivity μs/cm
Lake Kurobe	(0~1)	0.3	0.05	1.20	30	50	10	22	5.1	5.7
	(1~3)	1.0	N.D.	1.0	30	50	10	35	4.7	7.7
Tsukuba	0~1	4.9	1.39	2.7	860	150	179	700	4.1	28
	1~3	2.5	0.20	0.8	61	50	30	100	4.3	19

expected to be good indicators for estimating background air pollution levels.

5) There are many reports on the chemical composition of precipitation in remote clean areas for background air pollution analysis. A direct estimation of background levels on the basis of precipitation should be avoided, because the rain mechnism is not clarified. Thus, in this study, two samples collected at the beginning and end of a rain were analyzed by ion chromatography and inductively coupled plasma atomic emission spectroscopy. Variation in the samples was examined.

Table 6 shows chemical compositions of precipitation sampled at Lake Kurobe and Tsukuba.

All measurements were carried out for different short terms. Though the basis for the estimation of the background air pollution levels, was only the results of this investigation, it would appear that the coefficient variation per hour in ozone concentration is a very good indicator of background levels, judging from the results in Table 2, Fig. 2 and the other data. The other indicators proposed should be subjected to further testing.

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Neutral activation analysis was conducted by A. Mizohata.

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大気汚染成分のバックグラウンドレベルの測定とバックグラウンド地点の評価手法の研究

溝口次夫[1]・切刀正行[1]・西川雅高[1]

我が国における大気汚染成分のバックグラウンド濃度レベルを明らかにすること及び大気域のバックグラウンドレベルを推定するための手法を検討することを目的として本研究を行った。

本州内の人為的汚染の影響が極めて少ないと思われる山岳，林野地域に7地点を選定し，1980～1982年の3か年間に，それぞれ極めて短期間ではあったが大気成分の測定を行った。測定項目はSO_2，NO，NO_2，CO，O_3 (O_x)，CH_4，NMHC及びTSPである．TSPはその中に含まれている主な元素成分の分析も行った。また，黒部ダムサイトでは降雨をサンプリングし，その成分分析も行った。測定項目のうち，O_3，CH_4以外の汚染成分は微量であるため，一般に用いられている大気汚染モニタリング装置では検出限界あるいはそれ以下であるため，これらの測定結果だけでは，正確なバックグラウンド値を求めるのは困難であった。

非汚染地域7地点での測定の結果及びこれまでの文献値などから判断して，本州内での大気汚染成分のバックグラウンド濃度はそれぞれ次の範囲にあるものと推定される。

$SO_2<10$ppb，NO<5 ppb，$NO_2<8$ ppb，$CH_4$1.5～1.8ppm，NMHC<0.3ppm，
TSP<15$\mu g/m^3$

非汚染地域のバックグラウンドレベルを推定するために，種々の手法を検討した結果，いくつかの指標成分を選定したが，そのうち，オゾン濃度の変動係数が最も有効なバックグラウンドレベル評価指標の一つであることを明確にした。エアロゾル中の特定な元素成分，降雨成分の変動等もかなり有効な指標となりうる可能性があることを確認したが，サンプル数が少ないため，結論を得るには至っていない。

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II — 2

Measurements of Physical Size Distribution of Atmospheric Submicron Aerosols in Urban, Suburban and Rural Areas

Yoko YOKOUCHI[1], Hitoshi MUKAI[1], Toshihiro FUJII[1]

and Yoshinari AMBE[1]

ABSTRACT

The aerosol size distribution was measured at Kiyosumi (rural area), Shinjuku (urban area) and Tsukuba (suburban area) using a CNC and a diffusion battery. The number size-distributions with a maximum in the range smaller than 0.004μm were observed at Tsukuba and at Kiyosumi, at night and directly after the aerosols probably transported from the polluted areas were reduced, respectively. These observations were possibly explained by considering that nucleation exceeded the coagulation and condensation growth of the nucleic mode when the concentration of aerosols to be adsorbed was relatively low and there were some gaseous pollutants or their reaction products likely to nucleate.

1. INTRODUCTION

Atmospheric aerosols resulting from human activity have been increasing throughout the world. The environmental effect of the increase of aerosols should be studied immediately, because aerosols are strongly concerned with climate through scattering the solar radiation or formation of cloud drops. Observations on the size distribution of atmospheric aerosols have been considered to be valuable for the understanding of the behavior of aerosols.

Particle sizes of atmospheric aerosols range $10^{-3}\mu$m to $10^{1}\mu$m, and are generally distributed in the trimodal mode as shown in Fig. 1. Particles in the Aitken nuclei mode, 0.005-0.05μm dia. are formed by condensation of vapors produced either by high temperature or chemical processes. The accumulation mode, which includes particles from 0.05 to 2μm dia., is formed by coagulation of particles in the nuclei mode and by growth of particles in the nuclei mode through condensation of vapors onto the particles. Coarse particles are formed by mechanical processes such as

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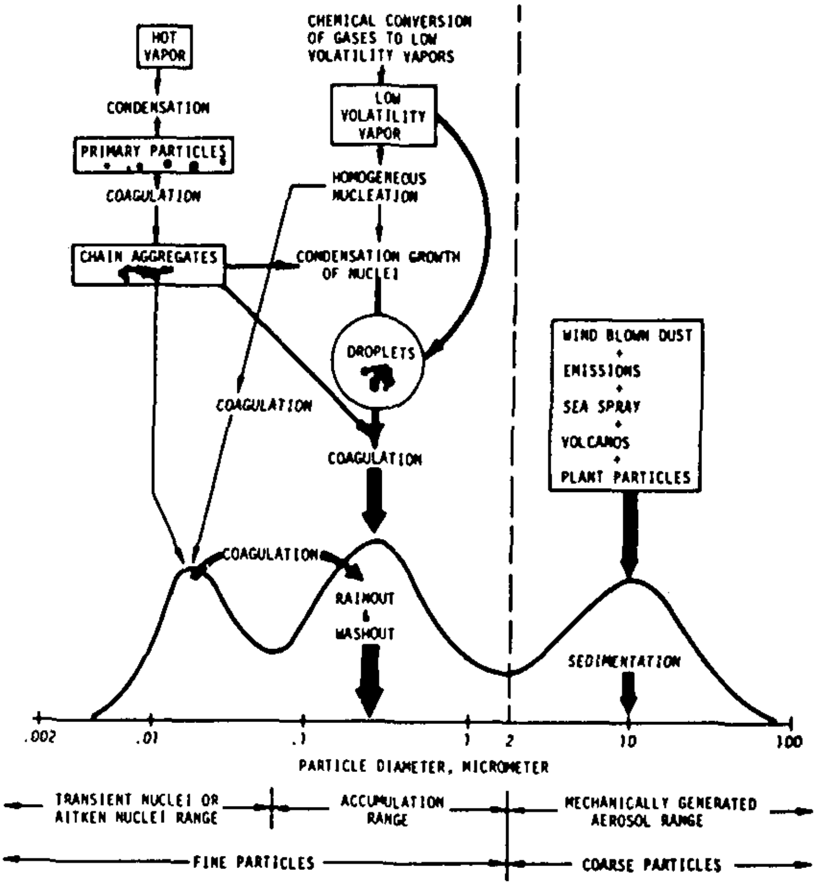

Fig. 1 Schematic of an atmospheric aerosol surface area disribution showing the three modes, main source of mass for each mode, the principal processes involved in inserting mass into each mode, and the principal removal mechanisms[1)]

grinding or rubbing (*e.g.*, soil, street dust and rubber tire wear), and by evaporation of liquid droplets. There is a distinct separation between "fine particles" ($D_p < 2\mu m$) and "coarse particles" ($D_p > 2\mu m$), which originate separately, are transformed separately, and are removed separately. As for the fine particle fraction in which most anthropogenic aerosols are found, there are some unresolved problems including the question why the nuclei and accumulation modes are usually separate in spite of the fact that both of them are formed directly or indirectly by condensation.

In the subject of "background atmosphere," the fine particles are important because they participate in long-range transport of anthropogenic pollutants. However, much of their behavior, including the variation of their concentration and size-distribution, has been unclear. The present study seeks to present in detail the diurnal variations of the number size distribution in the fine particle fraction measured by CNC (condensation nucleus counter) at several areas, and to determine factors affecting the size distribution. Some problems of the measuring method for the size distribution of sub-micron aerosols are also discussed.

2 . EXPERIMENTAL

2.1 Instrumentation

The system for measuring the size distribution of sub-micron aerosols consists of 1) a multiple screen diffusion battery (Nihon Kagaku Kogyo Co., Ltd.), 2) a continuous flow non-pulsing condensation nucleus counter (CNC), and 3) a switching valve to allow the CNC to detect the concentration at each battery port, as shown in Fig. 2. The details of the system have been described by Sem *et al.*[2]. The diffusion battery consists of 55 four-cm-dia. stainless steel screens with 250 wires per cm. Four 1 min^{-1} of air is drawn through the screens in series. The screens are mounted in 10 groups so that a CNC can measure the aerosol concentration upstream and downstream of each group. The CNC draws 300 cm^3 min^{-1} of air through a saturation chamber where the air becomes nearly saturated with butanol at 35°C. The nearly saturated air then passes through a 10°C condensation tube which condenses butanol onto the particles, growing them into supermicron droplets. The droplets then pass through the sensing zone of a forward scattering optical particle detector. The valving system allowed a single CNC to sample, in sequence,

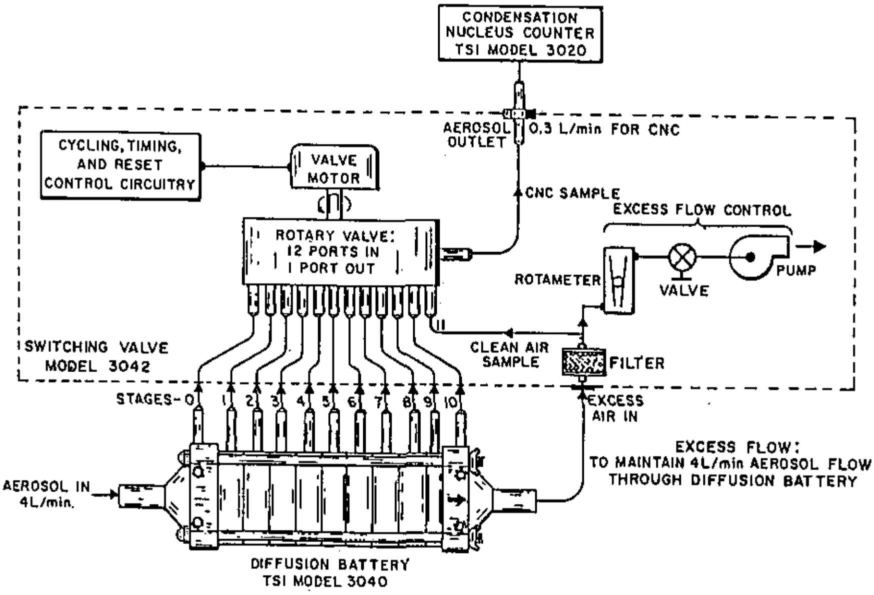

Fig. 2 Schematic diagram of the diffusion battery, switching valve, and condensation nucleus counter aerosol sizing system[2]

each of the sample ports of a diffusion battery.

For several days' run, the system was automatically controlled by a personal computer. The length of time on each port was set to be 15 s, while 100 measurements were repeated, and the average data were transferred onto a mini-floppy disk with the information on the measurement time and the stage.

2.2 Data reduction

The data reduction method used for the diffusion battery was a slightly modified version of the non-linear iterative inversion suggested by Twomey$^{3)}$ and adapted for use on diffusion battery data by Knutson and Sinclair$^{4)}$ and Sem *et al.*$^{2)}$. The program by Sem *et al.*$^{2)}$ used for this work was slightly modified as to the format of input data. The program uses the diffusion battery calibration of Sinclair *et al.*$^{5,6)}$ in a matrix developed by Kapadia$^{7)}$. It also corrects the CNC data for the detection efficiency using the CNC efficiency data of Agarwal and Sem$^{8)}$. A test for the quality of fit of the experimental data with the computed solution was included in the program. The program stopped when a chi squared value using the simulated raw data which would exactly result in the computed solution and the actual experimental raw data is less than 0.001 or 105 cycles of iteration have been completed.

Typical output of the program is shown in Table 1 and Fig.3. Number (DNDLGD), surface (DSDLGD) and volume (DVDLGD) concentration of particles at each size interval are listed in the form of $dN/d(\log D_p)$, $dS/d(\log D_p)$ and $dV/d(\log D_p)$ and in the units of particles/cm^3, $(\mu m)^2/cm^3$ and $(\mu m)^3/cm^3$, respectively, and are presented in the log-log form in Fig. 3.

2.3 Measurements of atmospheric aerosol size distribution

The measurements for aerosol size distribution were conducted in Kiyosumi (rural area) in Chiba Prefecture in August, in Shinjuku (urban area) in Tokyo in October, and in Tsukuba (suburban area) in Ibaraki Prefecture in December of 1982. The instruments were always operated at a height of 1 m above ground level. During the measurements at Kiyosumi and Tsukuba, the levels of other meteorological elements and environmental factors such as temperature, humidity and the concentrations of ozone and non-methane hydrocarbons (NMHC) were also observed.

3. RESULTS AND DISCUSSION

3.1 Aerosols in Tsukuba (suburban area)

The variation of the experimental total number concentration of the aerosols at Tsukuba is shown in Fig. 4, with the data for the concentration of ozone and nitrogen oxides. The number concentration usually showed a significant diurnal pattern with maxima late in the morning and in the afternoon, with minima around noon and during the night-time hours. The minimum around noon was not observed on cloudy days, suggesting that active mixing in the low troposphere at mid-day reduced the number concentration of aerosols resulting in minima around noon on the fine days. This diurnal variation was similar to that for NO_x and was, in part, inversely related to the ozone concentration. This suggests that aerosols and NO_x at

Table 1 Typical computer printout for a particle sizing run of the diffusion battery and CNC system

```
DATE=804  JIKOKU=1350
 PORT NO.      CNC DATA       CAL DATA
    0            6862.          6869.
    1            6318.          6281.
    2            5407.          5403.
    3            4440.          4508.
    4            3703.          3705.
    5            3023.          3014.
    6            2472.          2429.
    7            1975.          1939.
    8            1572.          1538.
    9            1179.          1213.
   10             950.           955.

MID  PT.
  DIA          DNDLGD              DSDLGD              DVDLGD
 0.0042    0.162625916E+03    0.907910615E-02    0.637642370E-05
 0.0075    0.159196582E+04    0.281052232E+00    0.351011287E-03
 0.0133    0.390685156E+04    0.218112659E+01    0.484412163E-02
 0.0237    0.328070508E+04    0.579191113E+01    0.228747539E-01
 0.0422    0.437632422E+04    0.244323273E+02    0.171593070E+00
 0.0750    0.819394531E+04    0.144660141E+03    0.180668926E+01
 0.1333    0.600846094E+04    0.335443115E+03    0.744996643E+01
 0.2371    0.185002148E+04    0.326612549E+03    0.128993626E+02
 0.4217    0.495514160E+03    0.276638672E+03    0.194289093E+02
 0.7498    0.184160950E+03    0.325128662E+03    0.406060944E+02
 TOTALS    0.751416406E+04    0.368798096E+03    0.224862518E+02

  NO. OF ITERATONS=80    CHISQ=0.495827943E-02
```

Tsukuba might have common sources. The correlation coefficients of the computed total number concentration of aerosols and NO_x, and that of their surface area concentration and NO_x were calculated to be 0.25 and 0.70, respectively, using 200 hourly data throughout the observation period.

This can be accounted for by the following explanations : (1) The emission of fine aerosols in the nuclei mode, not dominating surface area size-distribution in spite of weighting number size-distribution, are not strongly correlated with the emission of NO_x. (2) The coagulation or adsorption of fine aerosols while travelling, and the number of particles on the emission from the source are reflected in the surface area of the aged aerosols rather than in their number. (3) Or, there may be a correlation between the surface area concentration of the aerosols and NO_x on the emission. In the first case, the correlation between the number of the larger aerosols than 0.01 μm and NO_x would be expected to be larger than that for all the aerosols, and it was calculated to be 0.57.

Typical diurnal variation of aerosol size-distribution is shown in Fig. 5. The form log dN/d logD_p vs. log D_p is usually dominated by the aerosol with $D_p=0.05$

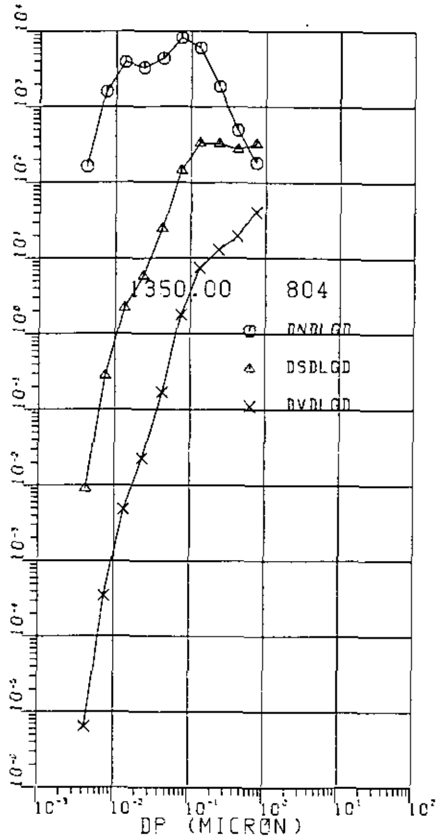

Fig. 3 *Number, surface area and volume distributions measured by diffusion battery of atmospheric aerosols*

~0.07 μm, and in some time the nucleic mode around 0.01 μm was also evident. Two distinct modes usually observed in the daytime correspond to the model for "the background aged urban plume influenced aerosols" presented by Whitby *et al.*[1]. It is interesting that the size distributions at night occasionaly exhibited a pronounced maximum at less than 0.004 μm (the lower limit of the size measured with the present diffusion battery method). One possible explanation for this is that at night the number of larger particles was reduced due to their sedimentation etc., increasing the relative importance of these ultra fine particles in the size distribution. However, in some case, the numbers of these ultra fine particles at night exceeded those observed during the daytime. Therefore, there should be a mechanism of increasing ultra fine particles at night. It would be probable that nucleation exceeded the coagulation and condensation growth of the nucleic mode at night when aerosol concentration was reduced because of little anthropogenic emission. This consideration is supported by the fact that a rather high concentration of ultra fine particles was also observed in the daytime of Dec. 19 (Sunday) and Dec. 23 (after rainfall) when this area was rather unpolluted.

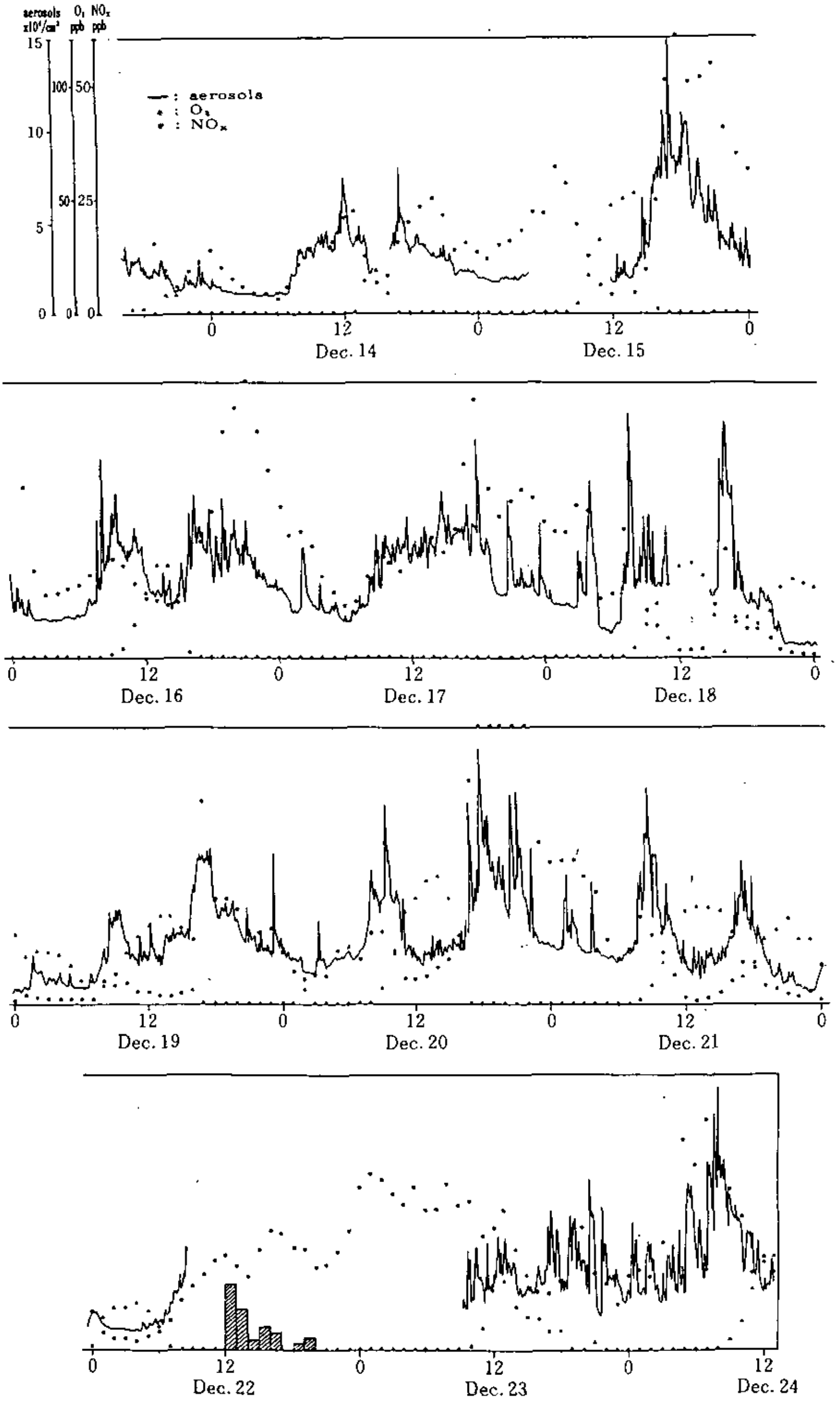

Fig. 4 Variation of the experimental number concentration of the aerosols in Tsukuba (Dec. 14 - Dec. 24, 1982)

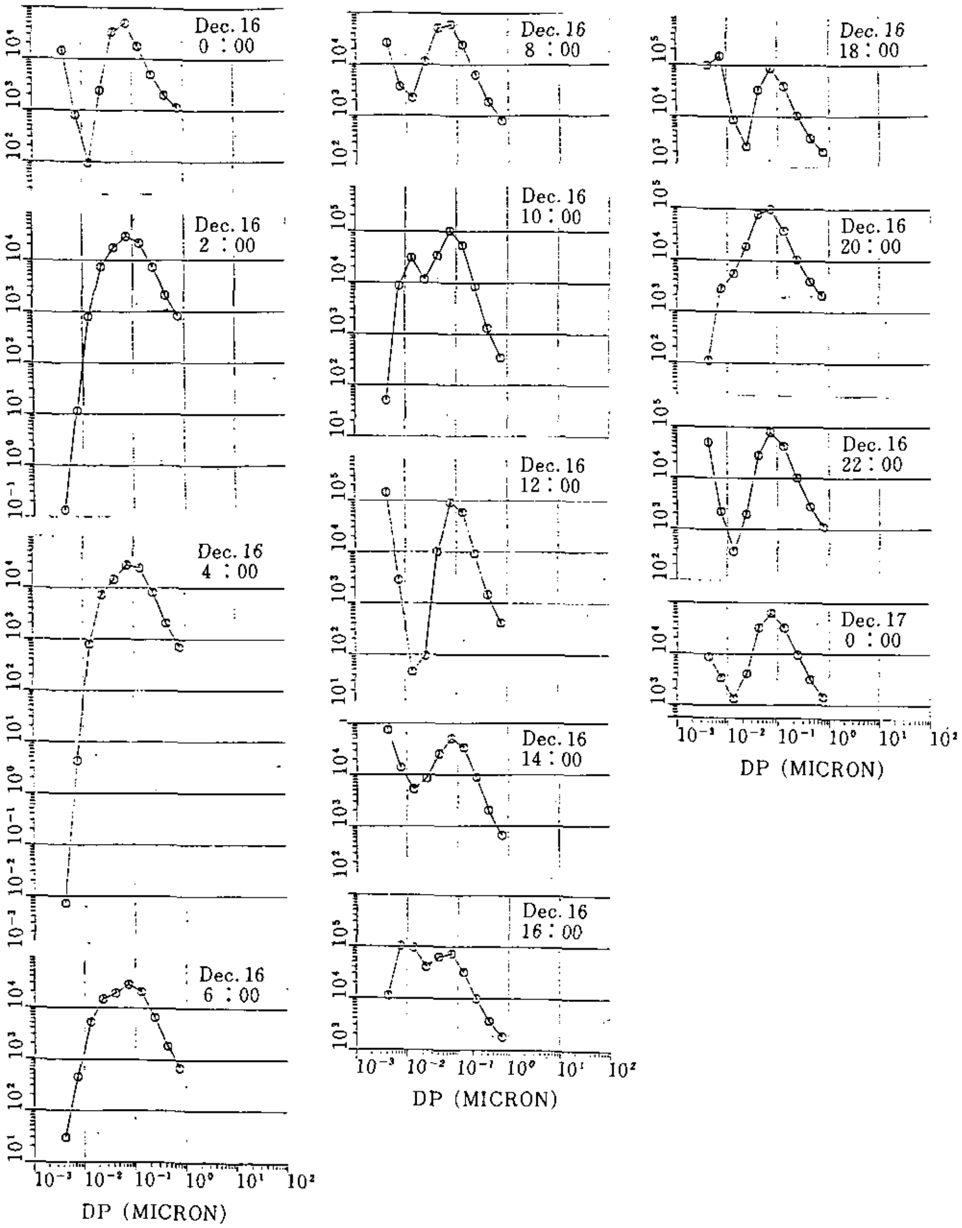

Fig. 5 Diurnal variation of the number size-distribution of the aerosols in Tsukuba (Dec. 16, 1982)

From the foregoing, it can be concluded that aerosols larger than 0.01 μm are emitted into the atmosphere from the same sources for NO_x ; they are probably from automobiles passing at a distance from this area, and the smaller ones are not necessarily connected with these sources. As for the origin of the smaller aerosols at this area, the nucleic aerosols produced from the condensation of the long range transported pollutants or their reaction products are more likely than those emitted directly from automobiles, considering their small correlation with NO_x which is a typical automobile pollutant.

3.2 Aerosols in Shinjuku (urban area)

Measurements were conducted near a heavy travelled road for one day (Oct. 6 - Oct. 7). The diurnal variation of the number concentration and the size-distribution of aerosols are shown in Fig. 6 and 7. Although these variations might not be typical because of the rainfall (all day on Oct. 6), the number concentration in the daytime was much larger than at night. The significance of ultra fine particles (<0.01 μm) was also observed in Shinfuku, in the daytime rather than at night. As most of the aerosols at this measuring site were considered to originate from automobiles, the observed size distribution of the atmospheric aerosols in the daytime are considered to reflect that of the automobile exhaust. At night, decrease of the exhaust and

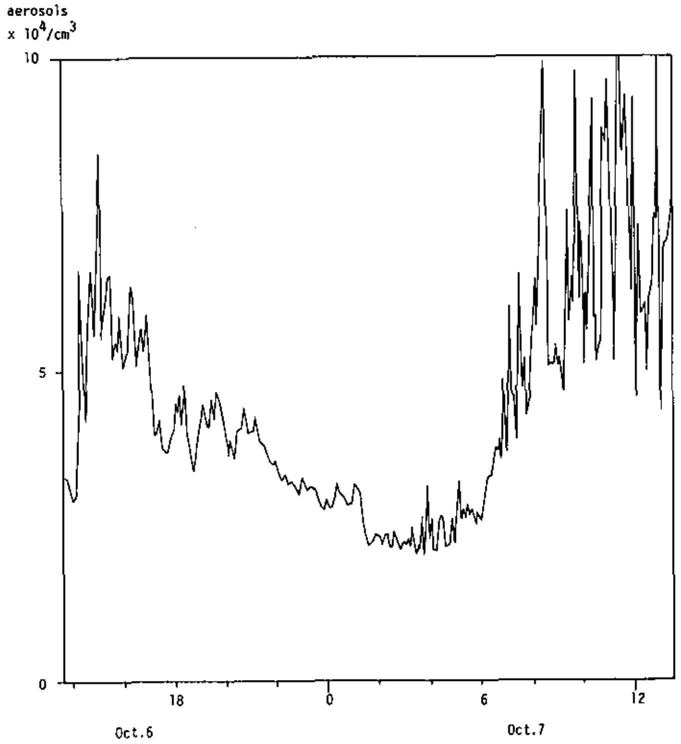

Fig. 6 Variation of the experimental number concentration of the aerosols in Shinjuku (Oct. 6 - Oct. 7, 1982)

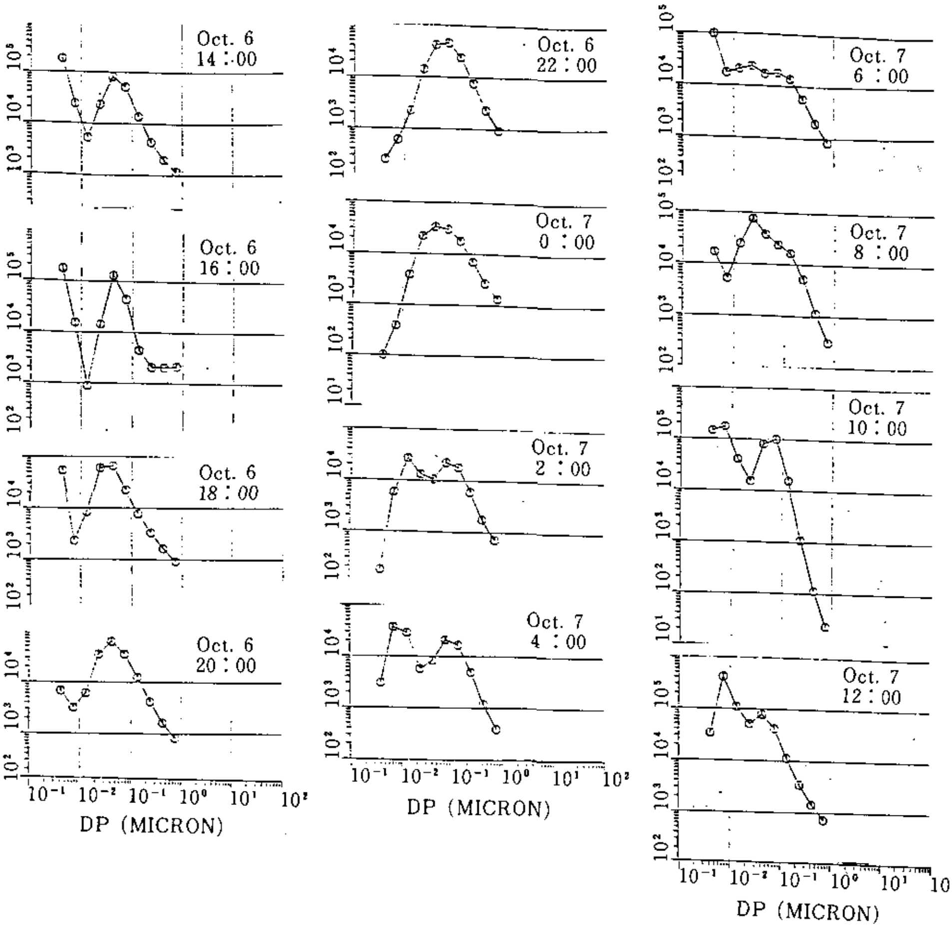

Fig. 7 Variation of the number size-distribution of the aerosols in Shinjuku (Oct. 6 - Oct. 7, 1982)

coagulation of the aerosols in the nuclei mode caused the dominance of the accumulation mode.

3.3 Aerosols in Kiyosumi (rural area)

Kiyosumi is 50 km south of Chiba City and represents a rural environment. The measurement was conducted at an open space surrounded by forests. Fig. 8 and 9 show the variations of the number concentration of aerosols during Aug. 3 - Aug. 6 and the diurnal variation of the number size-distribution on Aug. 5 respectively. The number concentration was almost one tenth of those in Tsukuba and Shinjuku. As for the number size distribution, the concentration in the accumulation mode was greater than in the nuclei mode at night, showing one modal distribution called the "clean background no nuclei mode" of Whitby *et al.*[1]. Directly after sunrise, the smaller aerosols were more prominent than at night, resulting in two modal distributions. This can be explained by considering that nucleation of the photochemical

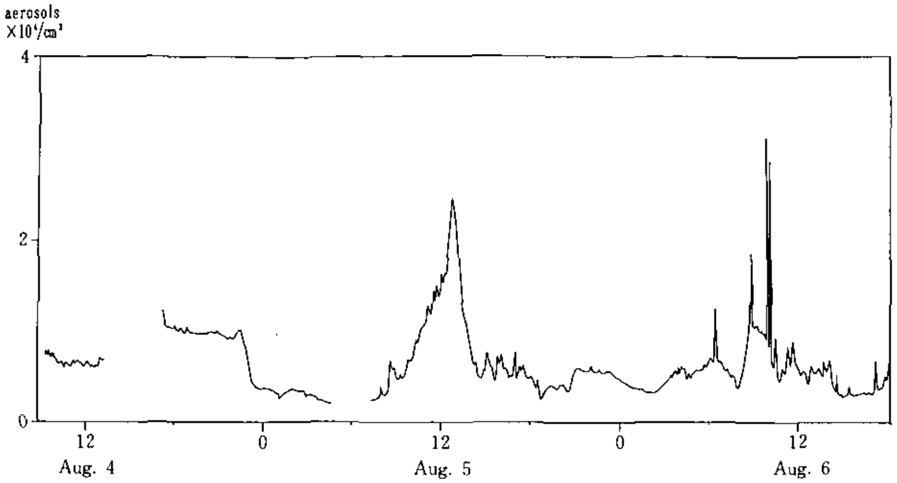

Fig. 8 Variation of the experimental number concentration of the aerosols in Kiyosumi (Aug. 4 - Aug. 6, 1982)

products of terpenes emitted into the atmosphere from the surrounding forest occurs in the daytime. At 10 : 00 - 14 : 00 on Aug. 5, an extremely large number of aerosols which were probably transported from urban area, was observed, and it is noticeable that significant increase of ultra fine particle ($<0.01\ \mu$m) was observed around 17 : 00 after the number concentration was reduced as before. This is consistent with Tsukuba's case, where the ultra fine aerosols increased at night after the anthropogenic aerosol emission was reduced. The sharp increase of the aerosols found on Aug. 6 in Fig. 8 was due to the local pollution of bonfire which size distribution is also shown in Fig. 10.

3.4 Measurement errors

The present system for the measurement of aerosol size-distribution using a CNC, a diffusion battery and a switching valve, requires five minutes for one run. During the time, there might be some change in the aerosol concentration in the atmosphere. Fig.11 shows how the size-distribution as shown in the left upper of the figure would be erroneously computed, in case there is a 10% increase in number concentration between the two measurements at the adjacent sample ports of the diffusion battery preserving the same size-distribution. As can be seen, the computed number concentration of nucleation mode particles is very sensitive to the errors resulting from the fluctuation of aerosol concentration during measurement. The best way to be free from these errors might be to prepare eleven CNCs to count the number of aerosols at each of the sample ports simultaneously. However, it would be too expensive and occupy too much space. Careful selection of the data would be another way requiring no modification of the present system. Thus, the data aquisition run should be repeated continuously, and the successive data with large difference in the total numbers and/or size-distributions should be avoided.

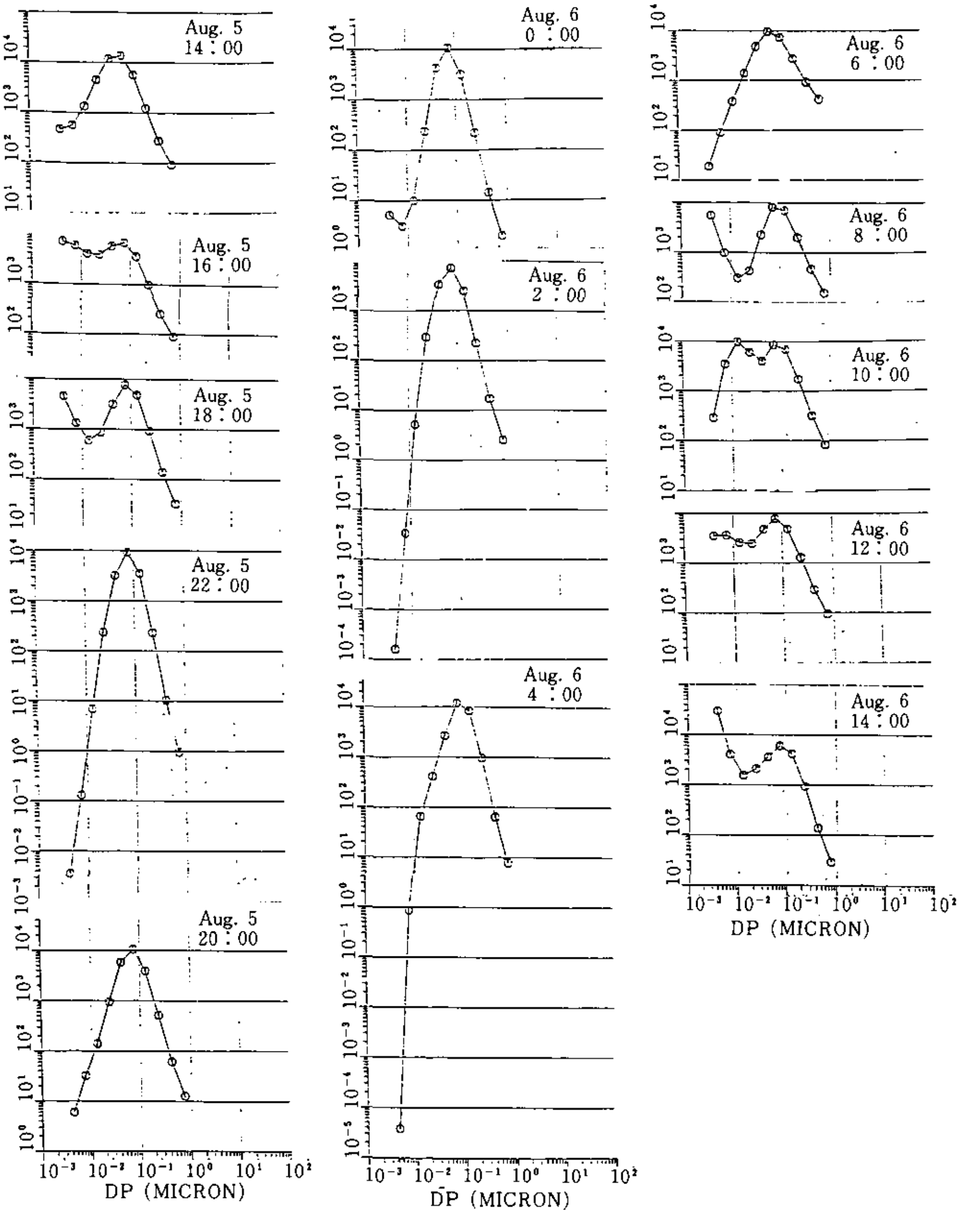

Fig. 9 Diurnal variation of the number size-distribution of the aerosols at Kiyosumi (Aug. 5, 1982)

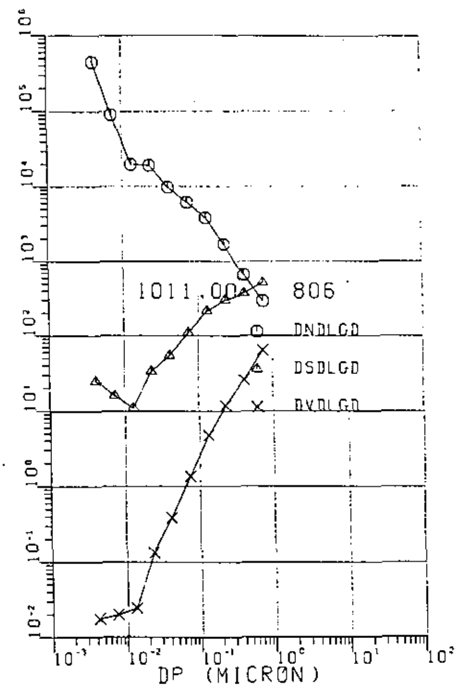

Fig. 10 Number size distribution of the aerosols strongly affected by fires at Kiyosumi (Aug. 6 10 : 00 a.m., 1982)

4 . CONCLUSION

The number size distribution of aerosols with a maximum at less than 0.004 μm, which does not belong to any distribution for a variety of location categories reported by Whitby *et al.*[1] was often observed at night in Tsukuba, and in the daytime in Shinjuku and Kiyosumi. Apart from the case in Shinjuku, where the aerosols directly resulting from auto exhaust, these size distribution of aerosols with a maximum at ultra fine range was considered to result from that nucleation exceeded the coagulation and condensation growth of the nucleic mode aerosols under the condition of less anthropogenic aerosol emission. However, in case there is also little gas to condense or nucleate, like at night in Kiyosumi, the number size distribution showed one modal distribution with a maximum in the accumulation mode.

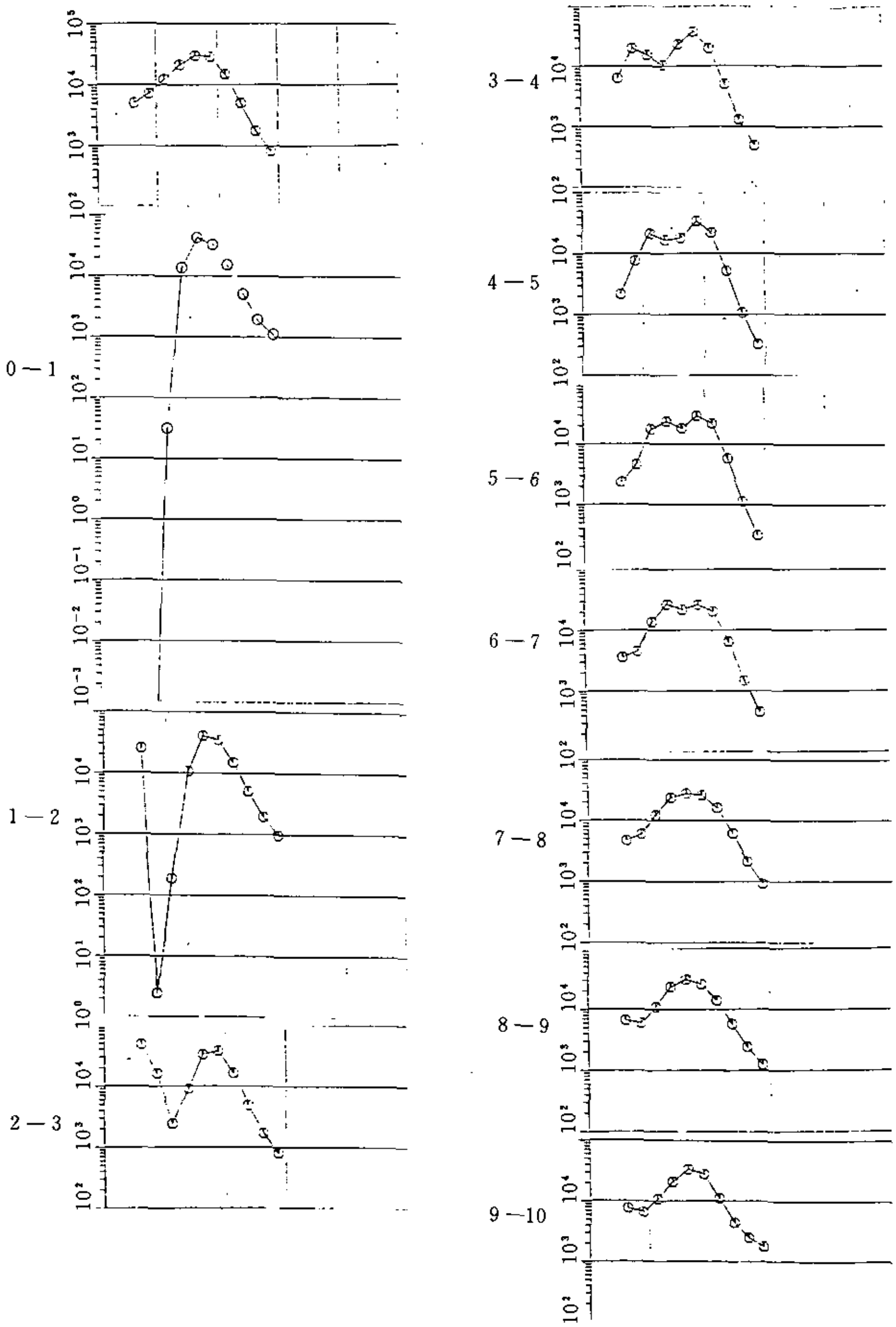

Fig. 11 Computed number size-distributions in the case that the number concentration of the aerosols with the size distribution as shown at the left upper increased by 10% between the measurement of n th and (n+1) th sample port. The "n" is shown in the left of each figure

As for the origin of ultra fine aerosols ($D_p < 0.01\ \mu m$), the nucleic aerosols produced from the condensation of the gases are more probable sources than those emitted directly from automobiles, considering their low correlation with NO_x which is typical automobile pollutant, and from the above-mentioned findings on size distribution. In the vegetation area, terpene was considered to be one origin of ultra fine aerosols.

It can be said that the anthropogenic emission of aerosols possibly affects the size distribution of atmospheric aerosols drastically through providing the particles on which gases condense instead of nucleation.

Further studies for correlating the size distribution and the origin of aerosols are necessary.

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都市及び非都市域におけるサブミクロンエーロゾルの粒径分布の測定

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エーロゾルの粒径分布を汚染度の異なる地域（清澄，筑波，新宿）において測定し，その変動要因を解析することによって，エーロゾルの挙動に関する知見を得た。エーロゾル粒径分布の測定は，凝縮核測定器(CNC)とディフュージョンバッテリーの組合せによって行った。0.004μm以下に極大をもつような数濃度粒径分布が筑波で夜間に，また，清澄では，汚染地域からもたらされたと思われるエーロゾルが減少した直後に観測された。このことは，ガス→エーロゾル変換の際，吸着すべきエーロゾル濃度が低くて，核化しやすい凝縮性のガスあるいは反応生成物がある場合には，核化による新しいエーロゾル生成の方が，核領域エーロゾルの凝集や凝縮による成長より優勢となるためとして説明された。

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II — 3

A Procedure for the Selection of Lakes as Background Level Monitoring Station of Pollutants for National and Global Environmental Monitoring

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ABSTRACT

Thirteen lakes with a surface area of more than 4 km^2 and a mean depth of more than 20 m were examined for national and global environmental monitoring stations, using limnological parameters, natural and simply determinable socio-economic factors.

Limnological parameters include the ratio of surface area to watershed area, the ratio of water volume to watershed area and hydraulic residence time. Natural factors are inflow of hot spring water, the effect of volcanic activities, forest fires, and geographical and geological considerations. Socio-economic factors are population density within watershed, number of city with 50,000 population within 50km around, the presence of highway within watershed and airport and airline within 10km, the presence of sightseeing launch and motorboat, agricultural use, fishery activities and others.

The results suggest that Lakes Mashu and Kuttara would be the most suitable long-term monitoring stations for national and global environmental pollution.

1. INTRODUCTION

Many recent reports point out that global environmental pollution is gradually progressing, including the increase in carbon dioxide concentration in air. Therefore, a world-wide linkage of national and regional environmental monitoring networks is needed to watch the global environmental pollution and also to provide information necessary to ensure the present and future protection of human health and safety and wise management of the environment and the resources.

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International Council of Scientific Unions (ICSU) has established the Scientific Committee on Problems of the Environment (SCOPE) in 1969, providing a Global Environmental Monitoring System (GEMS) which was recommended to United Nations Environment Programme (UNEP). GEMS reported by SCOPE covers the monitoring of the atmosphere, oceans, rivers, lakes, groundwater, soils, vegetations and forests in the remote, intermediate and impact areas[1]. For national and global environmental monitoring, GEMS recommends that the baseline monitoring stations should be located in the remote area which is the best place to provide early warning of significant environmental changes, and where no significant changes in land-use practices are anticipated for at least 50 years within 100km in all directions from the station. Lakes involved should have hydraulic basins which are not upstream of man-made sources of pollutants arising from agricultural, industrial or urban activities. However, it is difficult to meet such conditions in Japan.

To determine national and global environmental pollution through the monitoring of lakes, it is necessay, as the first step, to develop a procedure for the selection of lakes that can offer a suitale backgroud level station for monitoring pollutants in inland water before the pilot monitoring will be started.

2. METHOD

2. 1 Criteria for background level monitoring sites of inland water

To monitor national and global environmental pollution by means of inland water, certain criteria should be met. Although lakes, reservoirs, rivers and groundwater are possible candidates, only lakes present advantages. Water quality in rivers and resevoirs, for example, shows a relatively large day-to-day variability, depending upon the amount of precipitation. On the other hand. groundwater cannot sensitively reflect the change in the concentration of pollutants because the pollutants may be adsorbed on the surface of soil particles during the percolation process and then be decomposed by microorganisms in soil. Therefore, a lake with a water volume of more than a certain size would be most suitable for background level station to monitor inland water.

In the present study, the following criteria rather than the International Hydrological Decade program criteria used by GEMS are employed: the lake should have more than 4 km^2 in surface area and more than 20 m in mean depth. Consequently, thirteen lakes were listed in Table 1[2].

2. 1. 1 Limnological parameters

Water quality in lakes is strongly influenced by external input from watershed, but the atmosphers is the source of pollutants to watch in global environmental pollution. Therefore, the following factors should be considered:

1) The lower the concentrations of pollutants in the lake water, the more suitable is the lake for a background level monitoring station.
2) The greater the ratio of lake surface area to watershed area, the more suitable is the lake.
3) The greater the ratio of lake volume to watershed area, the more suitable is the lake.
4) The longer the residence time of lake water, the more suitable is the lake.

5) The higher the lake level above sea level, the more suitable is the lake.

No. 1, 2 and 3 were considered to minimize the effect of human activities near the lake, while No. 4 would mean the cumulative effect of input; No. 5 also means that the effect of human activities would be reduced in a mountainous area.

2. 1. 2 Natural factors

The origin of lakes in Japan is mostly volcanic activities. Thus, when considering change in the concentration of heavy metals, the effect of a hot spring water input may be an important factor. Effects of the following must be considered.

a) Inputs of hot spring water and waste water from mining companies.
b) Volcanic gases.
c) Forest fires.
d) Geographical and geological factors.

Mountain lakes sometimes receive the inflow of waste water from mining companies. Lakes Towada and Inawashiro, for example, are known to have received the inflow of waste waters from a mining company. The geographical factor embrances the geography of watershed, which means the presence of human activities.

2. 1. 3 Socio-economic factors

It is necessary to estimate the degree of human activities from simply determinable items within the watershed and neighbouring area. Thus the following factors should be considered:

a) Population density within the watershed.
b) The number of cities with 50,000 population within a radius of 50 km.
c) The number of companies with more than 100 workers within the watershed.
d) Highways within the watershed.
e) Airports and Air traffic within 10 km.
f) Sightseeing launch and motorboat.
g) Fishculture activity.
h) Fishery activities.
i) Agricultural land-use within the watershed and/or irrigation.
j) Artificial water control activities.
k) Guarantees that no significant changes in land-use practices will occur for at least 50 years within 10 km in all directions.

3 . RESULTS AND DISCUSSION

3. 1 Selection of lakes according to limnological parameters

All lakes listed in Table 1 were oligotrophic before 20 years[3], but now Lake Biwa, especially the south basin, and Lake Ashinoko, are reportedly mesotrophic. Since all lakes have a longer residence time than 3 years, they appear to be within the necessary limnolohgical parameters. Fig. 1 shows the ratio of surface area to watershed area and that of water volume to watershed area in the listed lakes. The result suggests that Lakes Mashu, Kuttara and Ikeda would be suitable for background level monitoring station. Lakes Towada and Tazawa have been greatly

Table 1 Limnological parameters of selected lakes in Japan (Environment Agency, 1980)

Parameter Lakes	Prefecture	Surface area S(km²)	Watershed area[3] W(km²)	Maximum depth (m)	Lake volume V(km³)	Mean depth (m)	Residence time (year)	Population within watershed (×10³)	Height of lake level (m)	S/W	V/W (m)	Origin
Biwa	Shiga	674	3126	103	27.5	41.2	4.8	850	8.5	0.216	8.79	Land elevation
Inawashiro	Fukushima	104	482	93.5	5.40	51.9	3.7	27.7	514	0.216	11.2	Caldera
Kussharo	Kushiro	77.5	136	120	2.20	28.4	12	2.96	121	0.570	16.1	Caldera
Shikotsu	Ishikari	77.3	142	363	19.5	256	(3.3)[1]	0.37	248	0.544	137	Caldera
Touya	Iburi	69.4	107	179	8.19	117	9.3	7.08	84	0.648	76.5	Caldera
Towada	Aomori, Akita	59.0	60 (160)[6]	334	4.19	71.0	8.5	1.10	401	0.268 (0.983)[4]	19.0 (69.8)[4]	Caldera
Tazawa	Akita	25.5	22.3 (400)[6]	423	7.20	280	7.9	0	249	0.060 (1.14)[4]	17.0 (322)[4]	Caldera
Mashu	Kushiro	19.6	12.9[5]	212	2.70	137	(—)[2]	0	351	1.52	209	Caldera
Chuzenji	Tochigi	11.5	58.5	172	1.10	94.6	7.2	1.90	1269	0.196	18.8	Caldera
Ikeda	Kagoshima	11.1	12	233	1.38	125	53	1064	66	0.925	115	Caldera
Ashinoko	Kanagawa	6.9	19	40.6	0.175	25.0	(4.5)[1]	3.10	722	0.363	9.2	Caldera
Motosu	Yamanashi	5.1	61	133	0.360	65.3	6.5	0.80	900	0.084	5.9	Caldera
Kuttara	Iburi	4.3	3.2	147	0.456	105	(—)[2]	0.002	260	1.34	142	Caldera

1) Estimation from outflow rate
2) No inflow and outflow
3) Lake surface area is not contained
4) Calculation from original watershed area
5) Horiuchi (1983)
6) Water-conveving

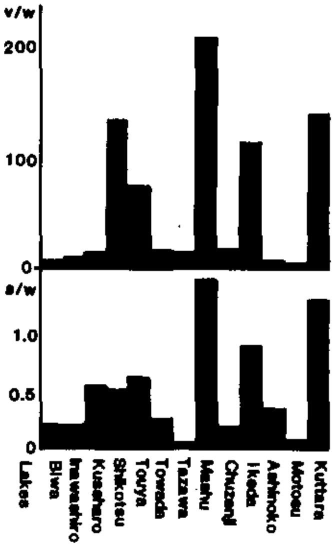

Fig. 1 The ratios of surface area to watershed area, and water volume to watershed area

changed by water-conveying construction to provide water for a power plant. Thus both were disqualified.

3. 2 Selection of lakes according to natural and socio-economic factors

The origin of the listed lakes is calderas, except for Lake Biwa, which is due to land elevation. Therefore, it would be very important to consider the effect of volcanic activities when monitoring the change in the concentration of heavy metals, especially Hg, for more than 50 years. Lakes Toya and Inawashiro are not only oligotrophic, but also acidic lakes. Lake Toya has been influenced by water-conveying construction for a power plant and became acidic lake after 1955. It is also affected now by input of large amounts of volcanic ash from current volcanic activity. Lake Inawashiro is also influenced by input from acidic stream. There is no inflow to Lakes Mashu, Ikeda, Motosu, and Kuttara. However, there is no evidence that input, from the lake bottom due to volcanic activities do not exist.

Table 2 shows the results of the evaluation of listed lakes by natural and simply determinable, socio-economic factors (Environment Agency, 1972-1977)[4]. Population density within the watershed of Lakes Shikotsu, Mashu, and Kuttara was zero or less than 5. Although Lakes Tazawa and Towada also have a low population density, both had to be excluded because their watershed has been greatly changed by water-conveying construction. Most lakes listed have been used as recreational areas, with sightseeing lauch and motorboats. Lakes Mashu and Kuttara are exceptions. In all lakes in Japan, the release of fry has been tried, but in Lake Mashu it was stopped in 1976. Net pen culture of carp and eel in Lake Ikeda is reported to be causing eutrophication. On the other hand, in several lakes lake water is recycled for a water power plant, and the same thing occurs in irrigation. Another important point is guarantees that no significant changes in land-use practices are anticipated

Table 2 Evaluation of selected lakes by natural and simply determinable, socio-economical facters

Items	Natural factor3)				Socio-economical factor4)										
Lakes	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
Biwa	−	−	−	not	272	11 (Osaka, Kyoto)2)	many	+	−	+	+	+	+	+	no
Inawashiro	+	±	−	not	57	8 (Fukushima, Koriyama)	many	+	−	+	−	+	+	+	no
Kussharo	+	±	−	yes	22	2 (Abashiri, Kitami)	0	±	−	+	−	+	−	−	yes
Shikotsu	±	±	−	yes	2.6	8 (Sapporo, Muroran)	0	±	±	+	−	+	−	−	yes
Touya	+	+	±	yes	66	3 (Muroran, Kucchan)	0	±	−	+	−	+	−	±	yes
Towada	±	−	−	yes	5.0	8 (Aomori, Hirosaki)	1	±	−	+	−	+	+	±	yes
Tazawa	+	−	−	yes	0	5 (Akita, Morioka)	0	±	−	+	−	−	−	+	no
Mashu	−	±	−	yes	0	0	0	−	−	−	−	±	−	−	yes
Chuzenji	+	−	−	yes	32	9 (Utsunomiya, Tochigi)	0	±	−	+	−	+	−	±	yes
Ikeda	−	±	−	yes	137	6 (Kagoshima, Ibusuki)	0	±	−	+	+	+	+	−	no
Ashinoko	+	±	−	yes	163	13 (Mishima, Odawara)	0	+	−	+	−	+	−	−	yes
Motosu	−	±	−	yes	13	9 (Numazu, Otsuki)	0	±	−	+	−	+	−	±	yes
Kuttara	−	±	−	yes	0.6	3 (Muroran, Tomakomai)	0	±	−	−	−	+	−	−	yes

1) Evaluation + Yes
± Yes or no
− No

2) Name of Major city

3) See 2.1.2

4) See 2.1.3

for at least 100 years within 10 km in all directions. It was assumed that no such development would be allowed within a national park area, for this is Environment Agency Policy.

From the viewpoint of natural and simply determinable, socio-economic factors, the results suggest taht Lakes Mashu and Kuttara are candidates for background level monitoring stations.

4 . CONCLUSION

The authors developed a procedure for the selection of lakes as background level monitoring stations to watch national and global environmental pollution through the monitoring of inland waters. According to this procedure, Lakes Mashu and Kuttara would be candidates. However, since the Muroran and Tomakomai industrial zone, which is 30 km south of Lake Kuttara, is developing, Lake Kuttara may have to be disallowed.

The present procedure should be used before pilot monitoring is started, and the feasibility should be examined, after the selection of lakes.

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陸水域バックグラウンドモニタリングステーションの選定方法

── 特に湖沼について ──

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全国的，地球的規模の環境汚染を陸水域のモニタリングを通して監視するためには，まず陸水域における汚染物質のバックグラウンドレベル（ベースライン）を知っておくことが不可欠である。

本報告では，対象として湖沼を選び，汚染物質のバックグラウンドモニタリング地点としてどの湖沼を選定したら良いか，湖沼学的条件，自然条件，人文地理学的条件から検討した。

その結果，それらの条件から判断すると，摩周湖，倶多楽湖がバックグラウンドモニタリング候補地として選定された。次のステップとして，本候補地における汚染物質の濃度の測定を行うことにより，本方法による選定の妥当性を検証することが必要である。

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II — 4

Morphological and Hydrological Characteristics of Lake Mashu

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ABSTRACT

Using an echo-sounding device a new bathymetric map of Lake Mashu, which describes its basin form in more detail, was prepared, and based on it, several morphometric parameters were calculated and some topographical characteristics of the lake were disclosed.

From the data of water level gauge and precipitation, the hydrological balance of lake water was estimated as that rainfalls in June to September contribute to the annual rise of water level and rainfalls in other months cause the rise of short term and the increased water escaped gradually as a leakage in a few days and hardly reserved in the lake. By analyzing the water level records, two types of leakage were distinguished. One was the rapid leakage right after the rapid increase of water level caused by rainfall and the other was the following slow leakage having 1-5mm/day of leakage rate, which increased at higher water stage and decreased below a critical level showing that leakage occurred mainly above the average water level.

1. INTRODUCTION

Lake Mashu has been studied for its suitability as a representative base-line lake to monitor the national scale pollution of inland water in Japan[1)]. Monitoring of water pollution of a lake can be performed based on the knowledge of hydrological conditions (*e.g.* variation of water mass and water budget) which are essential to evaluate water quality data. Little limnological research has been reported on Lake Mashu, and available data on water stage are very few.

Therefore, hydrological and morphological studies were carried out parallel to the hydrochemical studies in this research project. The previous morphometry of the lake basin of Lake Mashu by Tanakadate[2,3)], Takayasu *et al.*[4)] and Okazaki *et al.*[5)]

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were performed using a sounding lead and the measured bottom topography was not sufficiently detailed to discuss the formation of the lake basin or to calculate the exact volume of lake water.

The process of leakage of lake water is considered to play a very important role in the hydrology of this lake. As has been pointed out, the massive spring in the Nishibetsu River comes from the leakage water of Lake Mashu. The annual leakage loss from Lake Mashu was estimated as about 1200mm/y (Horiuchi & Ambe[10]) and the rate of leakage is thought to be a function of the lake water level. Okazaki *et al.*[5] suggested that the water level fell several meters in the past, but it has not yet been confirmed.

The primary aim of the present study is to describe the topographical characteriscics of this lake basin, which is the key to its limnological study and calculation of the water budget. A bathymetric map was prepared from the measurement of the depth using an echo-sounding device. Based on this map, various morphometric parameters such as shore development, area and volume hypsometric curve were obtained.

The secondary aim is to disclose the hydrological characteristics of the lake including the water cycle in the lake basin. A water stage gauge was installed on the lake shore, and interesting facts were found from the analysis of the records of water level so far available.

2. GEOGRAPHICAL DESCRIPTION OF THE LAKE

The surface area of Lake Mashu measures 19.6km^2 as shown in Table 1.

The maximum depth is 212 m, and steep caldera walls, about 150-350 m high above water surface, surround the lake.

The altitude of water surface above the mean sea level was 351.24m at the time of measurement. The lake is a closed lake having neither inflowing nor outflowing

Table 1 Morphometric characteristics of Lake Mashu based on bathymetric map

Altitude of water suface (Sept. 11, 1982)	351.24 m
Intake area	32.4 km^2
Surface area	19.6 km^2
Maximum depth	212.0 m
Mean depth	145.9 m
Volume	2.86 km^3
Length of shore	20.0 km
Maximum length	6.7 km
Maximum breadth	4.3 km
Shore development	1.27
Volume development	2.07
Volume of central cone	0.077 km^3
Area of bottnm central plane	7.2 km^2

rivers. Near the lake is a small island called Kamuishu, the area of the island is 0.0002km^2 and the height is 34.9m. This island is a volcanic cone formed by the eruption after the formation of Mashu caldera. The lake basin is a caldera formed first by eruption and the following depression in the easten end of Kussharo caldera. This intake area occupying only the Mashu caldera walls, covers 32.4 km^2 including the lake surface. The geohydrological situation of the crater of Mt. Kamuinupuri is questionable at present. If it is included in the intake area, the whole area covers to 33.8 km^2. The difference, however, is very small compared to the surface area as shown in Table 1.

As to the geology of this region, Mashu lava and the welded tuff of Kussharo volcano can be observed as the base rock on the crater walls in the northern part of the lake where collapse is quite conspicuous. Mashu lava is dense and impermeable, as pointed out by Konoya *et al.*(6) and Katsui(7-9), while welded tuff is breakable. Kamuinupuri lava covers the caldera walls in the eastern part of the lake.

Many springs appear around the outside of the somma of Lake Mashu caldera and the biggest one is in Nishibetsu area. The discharge from it is about 1.53m^3/s. In the Kenebetsu River and the west part of Lake Mashu more springs are encountered. These springs have also been considered as the seepage water from the lake, though no confirmed evidence is available.

As the total amount of spring water is too much as compared to the estimated amount of total seepage, 0.75m^3/s(10)from Lake Mashu, the mixing of water from another source should be considered.

Vegetation on the caldera walls is dense. Subalpine deciduous broad veaf forest covers in the area west of the lake and *quercus mongolia var. gross-eserrataacer* mono forest is found in the east of the lake.(11) After stormy rain, sometimes many trees fell into the lake by collapse and land slides of the caldera wallls.

3 . METHODS

3. 1 Bathymetric sounding

For the bathymetry of the lake basin, an ultrasonic echo-sounding device was used on a motorboat. The position was determined by measuring the angle between the two fixed points on the caldera walls from the boat.

This measurement was conducted every single minute along sounding tracks. The intervals of the tracks 300m-1000m does not always seem sufficient to compose a complete bathymetric map of a lake of this size. Considering the fact, however, that the basin is not so complicated, this does not cause much of a problem. The sounding was conducted on September 11 and 12, 1982.

3. 2 Water level change

A long-term (6 months) recording water level gauge has been installed at the point shown in Fig. 1 since June 1981 to observe the change of water level. To eliminate the effect of wind wave, the gauge was set on a well (1 m deep) which was dug on lake shore and connected with the lake through a small channel to keep the water levels of both the same.

The altitude of the water level which was used as the base line for sounding was determined from the distance between the bench marks on the caldera wall and the gauging station using a laser ranger. The water level was read every hour excluding cases in which the reading was heavily affected by wind generated waves.

Because of the difficulties of in maintaining the instrument, the obtained records could partially be used. The data on hourly precipitation at Teshikaga, which is the nearest meteorological station, 10km south from Lake Mashu, were used for the hydrological study.

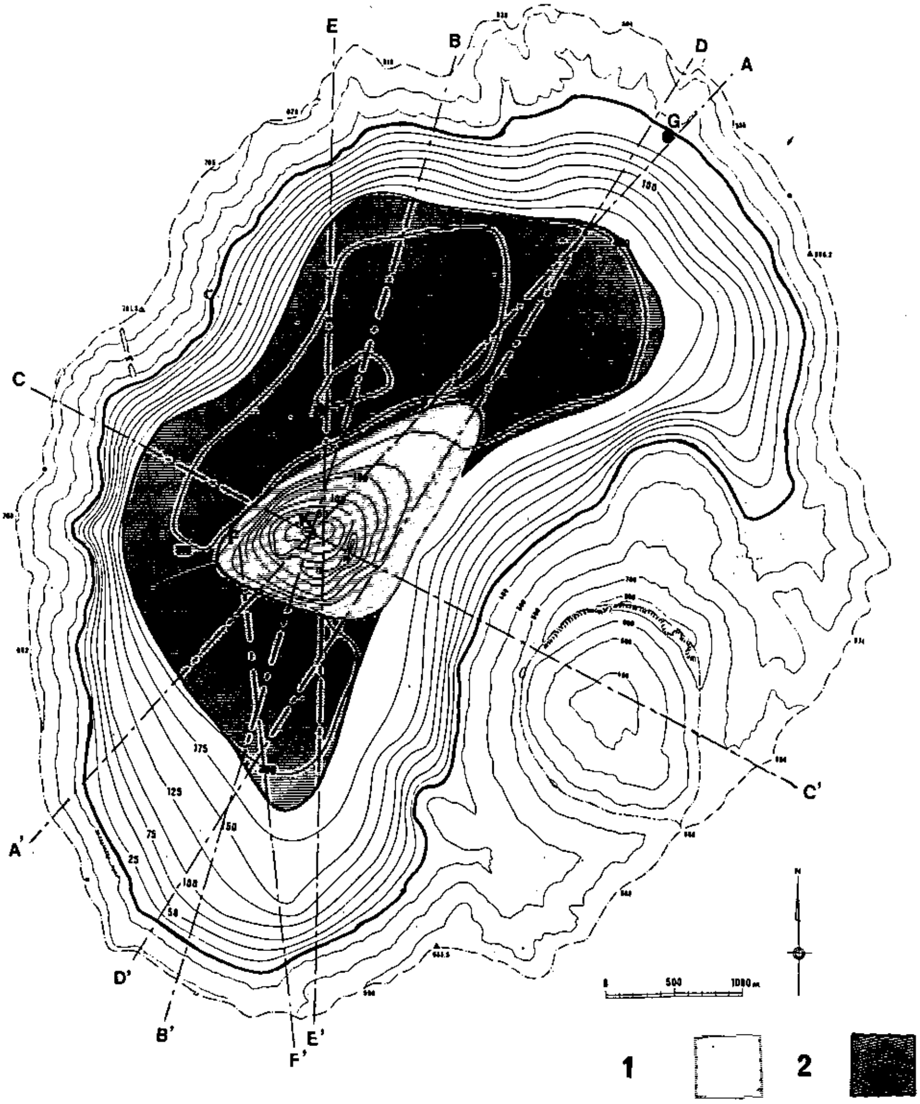

Fig. 1 Bathymetric map of Lake Mashu
1: the area of central cone (Kamuishu) 2: the area of central plain.

4 . RESULTS AND DISCUSSIONS

4. 1 Morphology of lake basin

Fig. 1 shows the bathymetric map of Lake Mashu measured in this study. There was no significant difference in major topographical features in this study and the earlier reported ones[2,4-5].The continuous records of the echo-sounding, however, made it possible to detect more detailed bottom topography such as the clear-cut line between the steep slope of caldera wall and the central plain in the basin which is very flat and nearly horizontal, (197-212 m depth).

In the most of the lake shore, the gradient of the steep slope of the caldera wall above and under the water surface was similar. Nothing significant was noted in shore process. At Uramashu, however, the northern area of Lake Mashu, the slope below the water surface only becomes steep at 25 m. It is considered to be composed of fan-like sediments due to the collapse and land slides of the breakable Kussharo tuff in the caldera wall. Kamuishu Island, a volcanic cone located in the central plain, has an elliptically shaped bottom whose long axis is from NE to SW. It has not been confirmed yet whether or not the flat part south east of Kamuishu Island, 75 m deep, was formed by the change of water level as pointed out by Okazaki. *et, al.*[5] These detailed topographical characteristics are indicated clearly in the longitudal and sectional profiles as shown in Fig. 2 and 3 (a,b and c).

The section of the steep slope at the western and northern area is straight, but that of south and west of Mt. Kamuinupuri is rather irregular, suggesting that the former was formed by the depression of caldera and the latter was covered by the lava of Mt. Kamuinupuri. A tallus form is noticed at the lower part of the slope as shown in the left part of Fig. 3a.

The values of shore development and other morphometric parameters of Lake

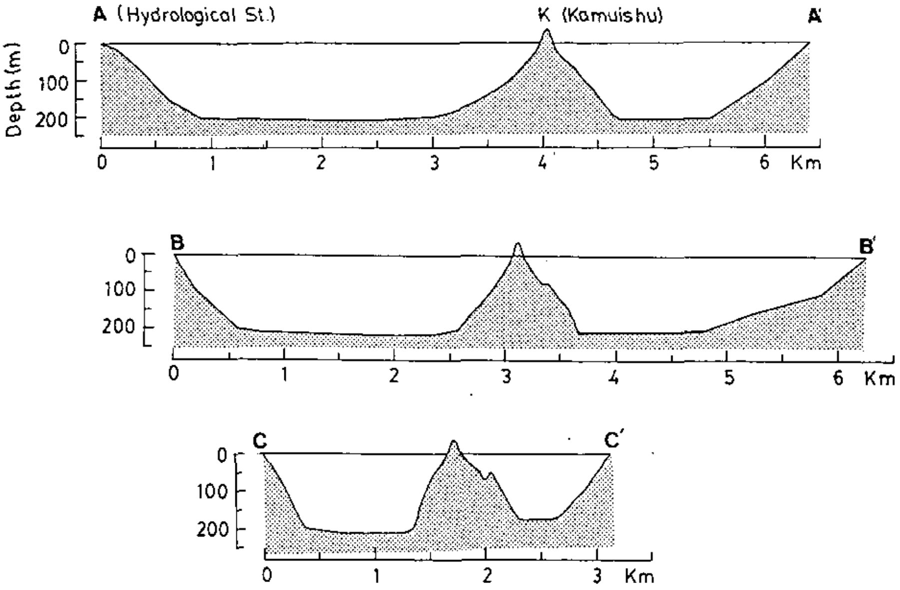

Fig. 2 Profiles of Lake Mashu

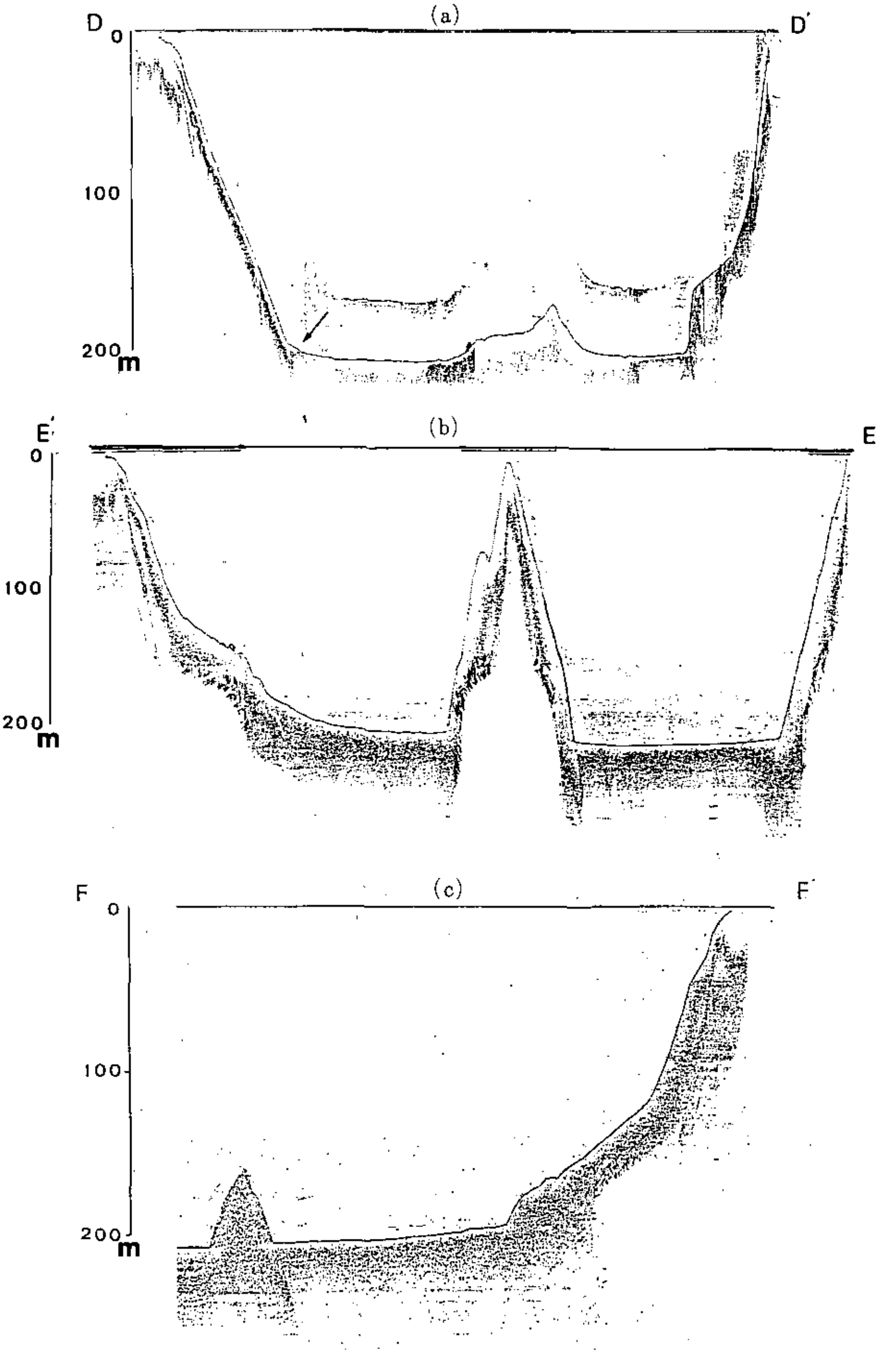

Fig. 3 (a,b *and* c) Profiles drawn by echograms of Lake Mashu: (a) shows the tallus deposits near the bottom(←), (b) shows the rough cliff of Kamuinupuri (left) and steep straight cliff of caldera wall (right) These figures show the detailed bottom topography, but vertical and horizontal scales are not so accurate.

Mashu were calculated based on the bathymetric map to compare with those of other lakes as shown in Table 1 and 2, where the lake volume and intake area are somewhat different from the previous data[3-5]The ratio of the intake area to the lake surface was estimated to be only 0.65 : 1 in this lake. This fact evidently means that the direct precipitation on the lake surface is a decisive factor in water supply, while inflow has minimal impact. The volume development of Lake Mushu is high compared to those of the other major lakes like the ratio of depth to surface area.

Thus, little water supply and a large water volume of 2.86 km^3 make a longer resident time of lake water, as has been estimated approximately as 100 years[10]. Area and volume hypsometric curves indicate that this lake has a concave form basin, a so-called bowl shaped type (Fig. 4-(a, b) and Håkansons[12]).

4. 2 Relationship between precipitation and water stage

Changes of water level are caused by the water supply and water loss including seepage and evaporation from the lake surface. The relationship between the precipitation and the water stage was analyzed for seven rainfalls of more than 20mm total precipitation as compiled in Table 3, except for those during the winter snow season. The stage rise is defined as the difference between the highest stage and the stage before rain, while the stage fall is the difference between the highest stage and the stationary stage.

In many cases the stage rise was 1.25-1.52 times as much as the precipitation. Evaporation loss was regarded as negligible during rainfall.

Supposing all rainfall in the intake area flows into the lake, the rise of water stage is expected to become 1.65 times as much as precipitation from the ratio of the intake area to the lake surface. From the ratio of the rise/precipitation, 1.25-1.52, the run-off coefficient of the intake area was calculated as 0.4-0.8, with a mean value of 0.59.

The fact that the ratio of rise/precipitation was greater than 1.65 indicates that the effect of the previous rainfall must have remained.

The decrease from the maximum stage to normal stationary stage is considered to be mostly due to the leakage of water from the lake having a 4.6 mm/h decreasing rate. It is clear that this leakage occurs during rising time of the water stage as well as the decreasing time. Supposing from the hydrograph that leakage occurs not right after the beginning of the rise of water stage but three hours thereafter, the net

Table 2 Volume development and the ratio of maximum depth to the surface of the selected major lakes in Japan

Lake	Volume development 3 md/mxd	Mean gradient mxd/$\sqrt{A}$	Maximum depth mxd (m)	Mean depth md (m)	Surface area A (km^2)
Tazawa	2.0	83.9	423.4	280.0	25.5
Shikotsu	2.1	41.0	360.1	255.9	77.3
Towada	0.7	42.3	326.8	71.0	59.8
Ikeda	1.6	70.3	233.0	125.0	11.0
Mashu	2.1	47.9	212.0	145.9	19.6
Kussharo	0.7	14.0	117.5	28.4	79.7
Biwa	1.2	4.0	103.8	41.2	673.8
Inawashiro	1.7	9.2	93.5	51.5	103.9
Suwa	1.6	2.0	7.6	4.1	14.1
Akan	1.2	12.6	44.8	17.8	12.7

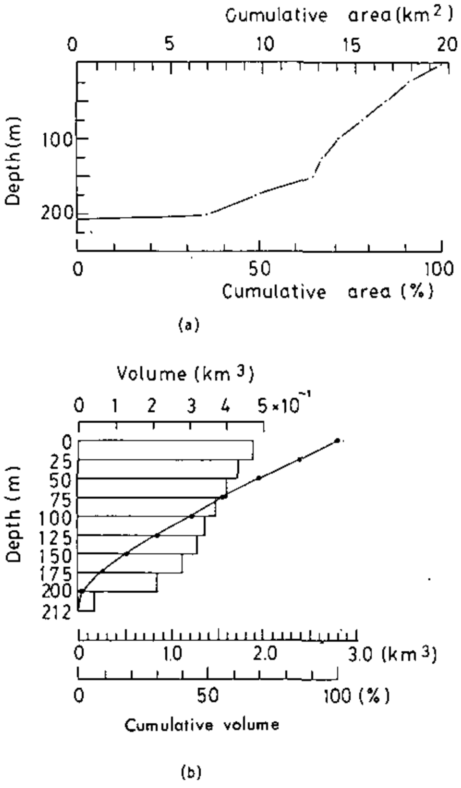

Fig. 4 Percentage area (a) and volume (b) hypsographic curves of Lake Mashu

change of lake level by inflow should be adjusted by 30% more than the values previously calculated. Thus, the ratio of rise/precipitation becomes 1.38-1.80 and the mean value of run-off coefficient is 0.79 as shown in Table 3.

In winter the ratio is very small because snow accumulates on the intake area, and a further survey is necessary for the inflows in winter snow season.

Fig. 5 shows some examples of stage hydrograph of hourly change of water stage during rainfall. The curves are smoothed, eliminating the effects of wind and wave. Rapid rise and fall of water stage corresponding to the rainfall are the most characteristic feature of Lake Mashu. Fig. 5 also shows that the level rise begins two or three hours after the beginning of rain and rapidly reaches the maximum stage.

The stage fall is relatively slow and water settles at the stationary stage within 10 hours after the rain stops. This pattern of change is more likely in an open lake with surface outflow than in a closed lake.

The major part of the increased water is lost by leakage within several hours, and the rest is stored in the lake, thereby raising the water level.

Table 3 The change of levels of Lake Mashu, recession rate and the ratio of surface rise to precipitation in the periods with heavy precipitation. Adjusted value is estimated on the assumption that leakage began three hours after the beginning of the rise.
The calculated run-off coefficient is (rise/precipitation−1)/0.65.

Date	Change of water level (m)	Precipitation (mm)	Rise (mm)	Fall (mm)	Net Rise (mm)	Leakage (mm/h)	Rise/Precip.	Adjusted Rise/Precip.
Jun. 27, 1982	351.050—.080	40	50	20	30	2.5	1.25	1.38
Jul. 12	.080—.090	22	30	20	10	2.5	1.36	1.59
Jul. 17	.120—.140	44	65	45	20	3.5	1.48	1.64
Aug. 29	.105—.240	132	185	50	135	4.1	1.40	1.46
Sept. 12	.270—.295	69	105	80	25	10.0	1.52	(1.80)
Oct. 20	.195—.205	66	85	75	10	5.0	1.29	1.44
Nov. 22	.170—.170	22	30	30	0	4.3	1.36	1.55
Mean						4.6	1.38	1.51*

Mean run-off coefficient 0.59, adjusted mean run-off coefficient 0.79
*excluding 1.80

As shown in Fig. 5a, 5b and 5c, with plentiful rainfall, the water stages did not drop back to the initial level after the rise and decrease following the rainfall episode and nearly 30% of water supply remained in the lake. When rainfall was not so plentiful, the water stage before and after the rain was nearly equal as indicated in Fig. 5d. About 70% of the increased water by rain was lost within 10 hours after the rain stopped, and this rapid seepage loss is the reason why the water level of Lake Mashu is kept relatively stationary.

4. 3 Leakage of water from Lake Mashu

Water escapes Lake Mashu only through leakage and evaporation. As stated by Horiuchi *et al*[10]., the water of Lake Mashu is continuously lost by seepage when precipitation exceeds evaporation and the water level is kept stationary. There are two types of leakage from Lake Mashu, one of which is slow leakage during the nearly stationary stage of water and the other is rapid leakage following rapid rise of water level caused by rainfall as shown in stage hydrographs. To estimate the loss by the former type of leakage, the change of water levels from November to February was selected and analyzed when the air and water temperature was so low that evaporation was negligibly small. In this period there was also little precipitation. The daily fall of the water level in the selected eleven periods with no precipitation was 1-5 mm, which is quite small compared to other lakes in Japan[13]. The relationship between the daily fall of water level, daily leakage loss and water stage is shown in Fig. 6. The leakage increases at higher water stages and decreases at low stages. The critical level is approximately 351.20 m. The decreasing rate of the water level reduced to 1-2 mm/day when the water level fell below this level. This value is considered to represent the leakage loss only.

This leakage process can be explained by geological features of the caldara walls. In the north of the caldera wall adjacent to the lake surface, welded tuff, the base of Kussharo caldara, is observed, relatively greater leakage loss from the

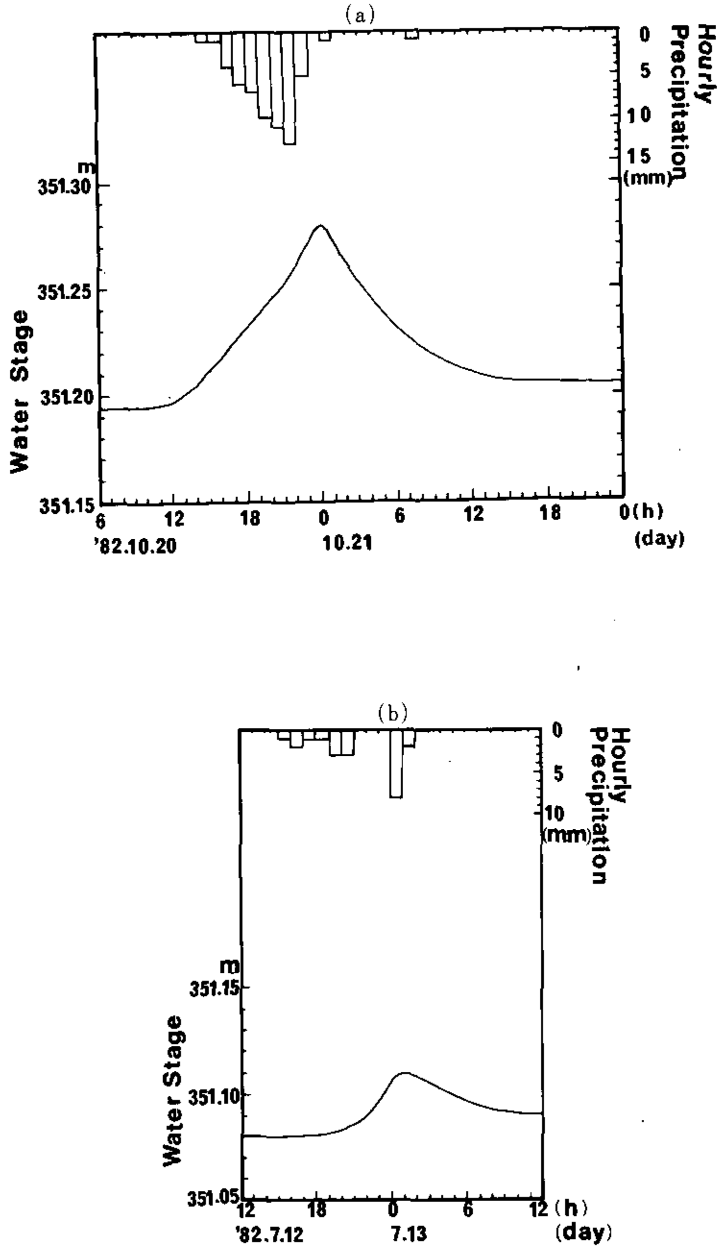

Fig. 5 Simplified smooth stage hydrograph and hourly precipitation on Lake Mashu, based on selected data in 1982

The stage of water surface before and after rainfalls are equal in (d) and not in (a), (b) and (c).

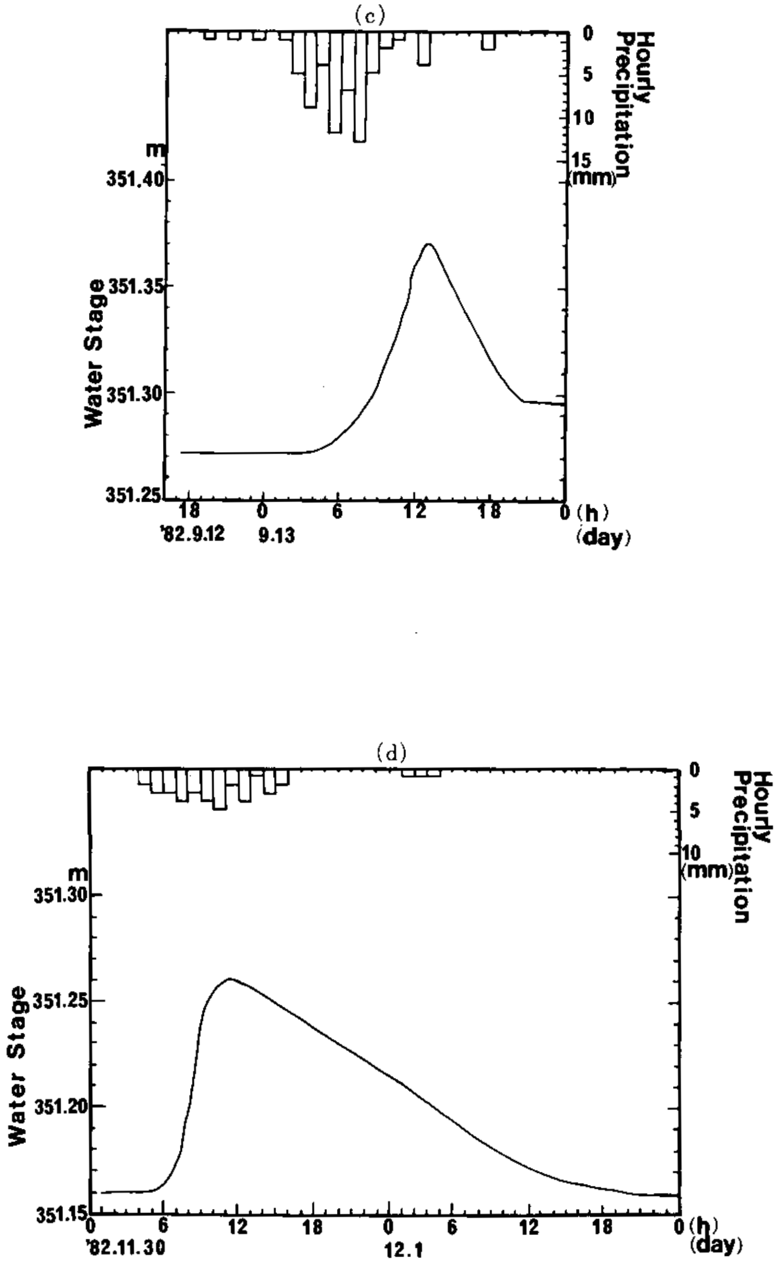

Fig. 5 (Continued)

Table 4 Monthly water balance of Lake Mashu from June in 1982 to January in 1983

I is amount of inflow from the intake area with run-off coefficient, 0.79. Leakage loss includes leakage and evaporation. dH is amount of rise or fall in leavels of water surface. P is monthly precipitation.

	June 1982	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan. 1983	Total for 8 months
Water level on the first day of the month (m)	351.040	.070	.130	.300	.250	.210	.230	.165	.095 (Feb, 1983)
P (mm)	79	82	191	95	117	107	29	30	730
I (mm)	40	41	96	48	59	54	15	15	368
P+I (mm)	119	123	287	143	176	161	44	45	1098
dH (mm)	+30	+60	+170	−50	−40	+20	−65	−70	+55 (=+280−225)
Leakage loss (mm)	89	63	117	193	216	141	109	115	1043

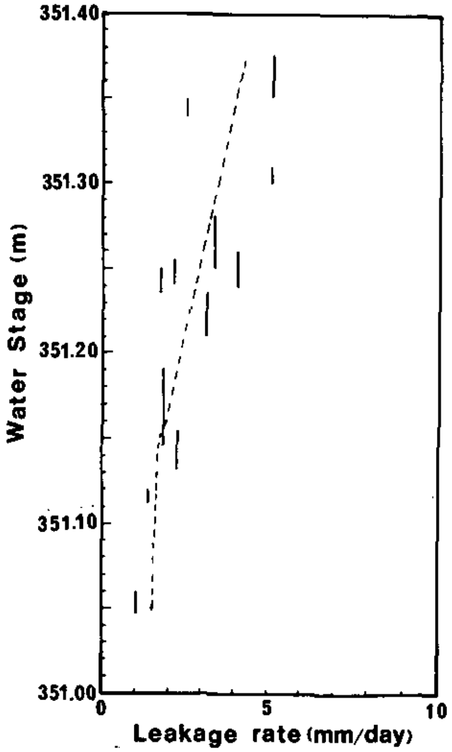

Fig. 6 The relationship between the water stage and leakage from Lake Mashu in the cold periods with no precipitation. (The lenghth of line denotes the range of lowering of water stage during observed period)

boundary between tuff and lava of Mashu is likely to occur.

Another type of leakage is due to the rapid rise of water stage having the leakage rate 2.5-10.0 mm/h, averaging 4.6 mm/h, more than 30 times as high as that of the former type of leakage at the normal water stage as shown in Table 4.

The increase of partial hydraulic gradient of the water seepage can be considered for this type of increased leakage. When the seepage water has a constant hydraulic gradient at the normal water level, the latter rises with precipitation by 50-100mm. Following this, the hydraulic gradiennt increases only near the lake shore and the leakage loss increases too.

4. 4 Long term change of water stage and water balance of Lake Mashu

The observed data from November 2, 1981 to February 15, 1982 and from June 12, 1982 to February 10, 1983 were referred. Monthly water stage observed on the first day of each month and monthly total precipitation are shown in Fig. 7. During the observed period, the highest stage was 351.43 m on November 3, 1981, and the lowest was 351.04 m on June 10, 1982. The difference between these two was 390 mm. The annual lowest stage seems to have occurred in the middle of February to June if the observation was performed continuously. Table 4 gives a brief summary of water balance from 1982 to 1983. Surface inflow is calculated by the following equation.

$$I=P\times R.\ I.\times R.\ C \qquad (1)$$

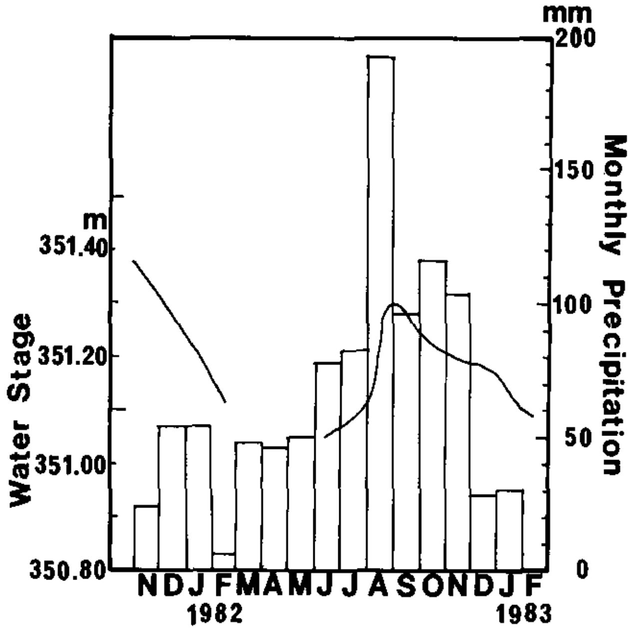

Fig. 7 Monthly changes of water stage and monthly precipitation from Sept. 1982 to Jan. 1983

Where I is inflow, P is monthly precitation on lake surface, and R. I. is the ratio of the intake area, excluding lake surface, to the lake surface. R.C. is 0.79 as run-off coefficient of the intake area. The monthly change of the stage is calculated as the difference between the stage on the first day of the month and that of the following months.

Leakage loss is calculated according to the following equation.

$$L.L. \fallingdotseq I+P-dH \tag{2}$$

Where L.L. is leakage loss from the lake including evaporation loss, dH is monthly stage change (unit: mm/month)

As shown in Fig. 7, the water stage rose in June, July, August and slightly in November and fell in September, October 1982 and January 1983. Leakage loss during the falling months was greater than that of rising month. Calculated leakage loss includes both slow leakage at the nearly stationary stage and leakage following rains as well as monthly evaporation (below 50 mm/month at the highest).

The water stage fell in September and October in spite of a great deal of income, demonstrating that leakage loss increases materially at higher water stages. The gross rise of water stage of 260 mm from June to August was equivalent to 50% of the total income (529mm). This 260mm of water is stored in the lake to slowly escape by seepage. From September to January, probably to May, the leakage predominated the income and the water stage lowered. Total gross rise of 280mm from June to January was equivalent to 38% of total precipitation and 26% of total income. At least 38% of annual total precipitation is stored in the lake during this period, and the same amount was lost by slow leakage through the whole year. Consequently, the lake remained at its level.

In the previous works the intake area of Lake Mashu has been estimated as 40-50km². The area shown in Table 1 is 32.4 km² in this study. The allowance is due to whether or not the crater of Mt. Kamuinupri should be included as the intake area and also to the difference of the method to calculate the intake area, though the same topographical map by the Geographical Survey Institute was used.

The area of the crater is 1.3km² with an altitude of the bottom at 369m, which is 10m higher than the surface of Lake Mashu. From this point, the crater may be included in the intake area. However, from the geological and topographical point of view, precipitation on Mt. Kamuinupuri may be mainly lost to the eastern rivers and does not remain as inflow to Lake Mashu by seepage.

5 . CONCLUSION

Distinctive features of the basin topography of the lake are the smooth steep slope in the west formed by depression of the caldera and the rough slope in the east formed by eruption of Mt. Kamuinupuri. The volume of the lake is larger than the previously reported one[4] and the mean depth is by 10 m deeper. The configuration of the lake basin is concave with a remarkable flat central plain 197-200m deep.

The small annual change of lake stage during the observation period is due to the smallness of the intake area and the relatively heavy leakage compared with that of other lakes without surface outflow.

The mechanism of leakage can be classified into two types.

One is the leakage, 1-5 mm/day, at the nearly stationary stage, which increases at higher stage and decreases at the lower stage having 351.15 m as the critical point of height. This is the evidence that leakage occurs mainly around the lake surface level. The other is the rapid leakage right after rain having 4.6 mm/h of leakage rate.

The water stage rises for a short time after rain due to the increase in the hydraulic gradient of the seepage water.

In this case the water is lost around the boundary between Mashu lava and Kussharo tuff where permeability is high. Thus, the leakage loss and water stage correlate with each other.

It has been disclosed by the calculated long-term water balance that rainfalls in June to September contribute to the rise of long-term water level, rainfalls in other months a short-term rise. The increased water escapes gradually as leakage in a few days and hardly reserved in the lake. About 5% of the total inflow was stored in the lake for eight month from June to January raising the water level by 55mm. From these hydrological observations, Lake Mashu is considered more likely to be an open lake than a closed lake in a strict sense.

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摩周湖の地形学的・水文学的特性に関する研究

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摩周湖において音響測深機を用いて測深を行い，既存のものに比べて精密な湖盆図を作製した。それに基づき，摩周湖の湖盆の計測を行い，湖盆に関する各種の諸元を求めた。また湖盆に関する形態的な特色を明らかにした。

長期間にわたる水位及び降水量の記録から，摩周湖の長期水収支の推定を行った。その結果主として６月～９月までの降水が湖の水位上昇をもたらし，それ以外の期間の降水は湖水中にはほとんどとどまらないことが明らかとなった。

水位記録の解析の結果，摩周湖からの湖水の滲出は降水に伴う水位上昇に引き続く急速な滲出と，長期にわたる緩やかな滲出（１～５ mm/d）の二つに分けられる。さらに後者はある水位以上の時の比較的速やかな滲出と，それ以下の水位でのより遅い滲出の二つに分けられることが明らかになった。

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II — 5

Determination of Trace Metals in the Water of Lake Mashu and Their Background Levels in Fresh Water Environment

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ABSTRACT

Trace metals (Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in the water of Lake Mashu were analyzed. Preconcentration were performed by adsorption of the complexes of these metals and 8-hydroxyquinoline to C_{18} chemically bonded silica gel. Simultaneous multielement analysis of the eluate with inductively coupled plasma emission spectrometry (ICPES) ensures the necessary sensitivity to measure the trace metals at concentration ranges from $\mu g\ l^{-1}$ (ppb) to ng l^{-1}(ppt) in natural water samples. The trace metal concentrations measured in Lake Mashu were extremely low: Fe 2.6; Al 1.2; Mn 0.76; Zn 0.63; V 0.15; Cu 0.069; Ti 0.06; Pb 0.05; Ni 0.027; Cd <0.006 and Co <0.004 $\mu g\ l^{-1}$.

1. INTRODUCTION

The procedure of the selection of Lake Mashu as the background level monitoring station was presented in other paper in this research report[1]. For background level monitoring purposes, a sensitive analytical method without contamination and offering the possibility of multielement analysis must be developed. Recently, the application of inductively coupled plasma emission spectrometry (ICPES) to the analysis of trace metals in natural water has been developed with various preconcentration methods[2-5] especially for seawater analysis. To use ICPES effectively for water analysis and take advantage of its simultaneous multielement capability, simultaneous preconcentation of as many as possible of the target trace metals is required. In this study, the method developed by Watanabe *et al*[5]. was adapted for the analysis of trace levels of metals in a lake water sample. Simultaneous multielement preconcentration and analysis of eleven elements was possible for the water sample of Lake Mashu.

Comparing the analytical results with reference data for other lakes around the world, the competense of Lake Mashu for a background level monitoring station for

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global environmental pollution is discussed.

2 . METHODS

2.1 Apparatus

A Jarrell-Ash Plasma Atomcomp II direct-reading ICP emission spectrometer was used for trace metal measurements. An atomic absorption spectrometer (Model 251 by Instrumentation Laboratory Inc.) with a graphite furnace atomizer (Model 555 by Instrumentation Laboratory Inc.) was used for the comparison of analytical values of natural water samples.

2.2 Reagent

Distilled water was further deionized and filtered by Milli-Q water purification system (Millipore Co.). In all analytical procedure, Milli-Q water (MQW) was used. Concentrated nitric acid for the acidification was prepared by sub-boiling distillation in a quartz still from electric industry grade reagent in a clean bench. Other reagents were analytical grade ones. 8-Hydoroxyquinoline was dissolved in 0.1 N hydrochloric acid and 1% solution was prepared. Neutral red as a pH indicator was prepared as a 0.1% solution in 70% ethanol. Multielement standard solutions were prepared from single element stock soulutions (1000 mg l^{-1}, for atomic absorption grade, by Kanto Chem. Co.) by appropriate dilutions.

2.3 Fresh water and seawater sampling

Fresh water samples were obtained from Lake Mashu. Lake Mashu is a deep oligotrophic lake (max, 212 m; mean deppth, 138 m), covering an area of 19.6 km^2at an altitude of 351 m in Hokkaido, Japan. The highest Secchi disk transparency value of 41.6 m was recorded in August, 1931 by Takayasu and Kondo[6]. Recently, the transparency has slightly decreased but it is still exceptionally high. The environment of the whole catchment area is protected as wilderness area and designated as a national park. No irrigation work, fishing boats, buildings or roadways are found in its catchment area. Lake water was sampled using a Teflon coated 10 l Go-Flo sampler (General Oceanic Co.). The sampling site was the center of Lake Mashu, the deepest point in the lake (about 210 m). Samples (8l) were immediately acidified with quartz distilled nitric acid (30 ml). Surface coastal seawater sample was obtained 18 km off the coast of Kashima Harbor (Ibaraki prefecture, Japan, January 1982) overlooking the Pacific, and sub-surface (8 m depth) lake water sample was obtained from the center of Lake Biwa (Shiga, Japan, December 1981).

2.4 Preconcentration procedure

About 1000 g of acidified lake water was weighed and taken in a Pyrex flask. It was evaporated to about 100 g using rotary evaporator at 50°C. Sample and washing water were transfered into a Pyrex beaker. One ml of 8-hydroxyquinoline solution and 0.03 ml of neutral red solution were added. The pH was adjusted to 7.0 using ammonia solution. After standing overnight, the sample solution was taken in a glass syringe and passed through a Sep-Pak C_{18} cartridge (Waters Scientific Ltd.). This cartrige was thoroughly washed with methanol and MQW. Sample solution flow rate was about 50 ml min^{-1}. Then the column was washed twice with 10 ml of MQW. Metal chelates of 8-hydroxyquinoline adsorbed to the column were eluted by

2 ml (3 times the column volume) of methanol. The eluate was taken into a preweighted Teflon PFA bottle and 0.1 ml of hydrochloric acid added. It was evaporated slowly nealy to dryness on a hot plate. Nitric acid (0.1 ml) was added to the residue and the solution was again evaporated on the hot plate. After repeating the addition of nitric acid and evaporation three times, organic material was completely decomposed. The residue was dissolved in 2 ml of 0.1 N nitric acid. The digestion procedure was performed on a clean bench. Using this solution, simultaneous multielement analysis was performed with the ICP emission spectrometer. The blank values were obtained by taking 20 ml of MQW through the same experimental procedure.

3 . RESULTS AND DISCUSSION

3.1 Preconcentration efficiency

8-Hydroxyquinoline forms stable metal chelates with many metal ions. In this study, recoveries of Al(III), Ti(IV), V(V), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Mo(VI), Cd(II), and Pb(II) ions, which seem to be principal existing forms in a fresh water sample acidified and preserved with nitric acid, were investigated over the pH range of 4 to 9. Five μg of each of these above-mentioned trace metals, 4 mg of magnesium and 8 mg of calcium were added to 100 ml of acidified MQW and the preconcentration procedure was carried out. Chelating and adsorption pH was adjusted with ammonia solution. For simultaneous multielement preconcentration, a compromise adsorption pH was chosen to be 7, considering the high recoveries of trace metals and low recovery of magnesium. At pH 7, quantitative concentration over 90% recovery can be carried out for about nine (Al, Ti, V, Fe, Co, Ni, Cu, Zn, and Pb) of the above-mentioned twelve elements. In the following analytical data for aluminum, titanium, vanadium, iron, cobalt, nickel, copper, zinc and lead, 100% recoveries of the metals were assumed. For manganese and cadmium, 71 and 78% recoveries, respectively, were used for the calculation of concentration. For molybdenum, recovery varied from 10 to 40% at the compromise pH, so another preconcentration at lower pH will be necessary.

Analytical blanks of the eleven elements were obtained from the same preconcentration procedure as for fresh water sample using 20 ml of MQW and all the reagents except for evaporation procedure with rotary evaporator. When 1000 ml of sample solution is used, the final concentration factor is 500. Thus the analytical values of the blank sample are divided by 500, and shown in Table 1, together with the detection limits of ICP analysis, also divided by the final concentration factor. As method sensitivity depends upon the blank reproducibility, twice the standard deviation of blank value from ten replicate determinations is shown in Table 1 as the practical detection limit. For vanadium, manganese, cobalt and cadmium, blank values are lower than ICPES detection limits, and ICPES detection limits divided by 500 represent practical detection limits. Blank values for copper and lead are nearly equal to ICPES detection limits. For aluminum, titanium, iron and zinc, the method sensitivies depend on the blank deviations.

To investigate the accuracy of this preconcentration method, four replicate preconcentrations and analyses of a subsurface water sample of Lake Biwa were carried out. The results, averge, standard deviation and relative standard deviation

Table 1 Analytical blank and detection limit for lake water analysis at 500-fold preconcentration

Element	[a]DL-ICP	[b]Analytical blank	[c]DL-practical
	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$
Al	0.04	0.12 ± 0.08	0.15
Ti	0.001	0.050 ± 0.018	0.036
V	0.004	<0.004	0.004
Mn	0.006	<0.006	0.006
Fe	0.004	0.045 ± 0.016	0.031
Co	0.004	<0.004	0.004
Ni	0.012	<0.012	0.012
Cu	0.002	0.005 ± 0.003	0.005
Zn	0.008	0.34 ± 0.14	0.28
Cd	0.006	<0.006	0.006
Pb	0.04	0.051 ± 0.016	0.034

a) ; detection limit of ICPES is divided by the concentration factor (500).
b) ; average and standard deviation of ten replicate blank operations
c) ; practical detection limit; twice the blank deviation
a, b, c) ; For Mn and Cd, each value is corrected with the recovery of each element.

Table 2 Method precision by replicate analysis of water sample of Lake Biwa

Element	Concentraition	RSD
	$\mu g\ l^{-1}$	%
Al	8.42 ± 0.28	3
Ti	0.144 ± 0.021	15
V	0.213 ± 0.012	6
Mn	5.00 ± 0.28	6
Fe	11.44 ± 0.15	1
Co	0.012 ± 0.001	12
Ni	0.019 ± 0.002	11
Cu	0.49 ± 0.01	2
Zn	0.30 ± 0.13	43
Cd	0.022 ± 0.019	86
Pb	0.053 ± 0.011	21

(RSD), are shown in Table 2 where blank subtraction was performed for the elements with measurable blank values. When the concentration in lake water sample is higher than ten times the method sensitivity, RSD is less than 6%. For iron and copper, whose concentrations are one hundred times higher than method sensitivity levels, RSDs are less than 2%. As the ratio of the concentration in the lake water sample to the method sensitivity becomes lower, RSD increases.

3.2 Analysis of Lake Mashu water sample

The average concentrations of major and minor elements in Lake Mashu were as follows; Na 13, Ca 8.1, Si 5.1, Mg 3.5, K 0.9, B 0.11 and Sr 0.02 mg l^{-1} (analyzed by ICPES, flame emission spectrometry or flame atomic absorption spectrometry), chloride-Cl 6.7 and sulfate-S 4.0 mgl^{-1} (analyzed by ion chromatography), pH 4.8 alkalinity 0.80 meq l^{-1} (analyzed by titration). The distribution of these components was thoroughly uniform from the surface to the bottom. The pH value of surface water was about 6.8 and slightly decreased as depth increased. The water was almost saturated with dissolved oxygen from the surface to the bottom. Lake Mashu is a typical oligotrophic lake and its nutrient concentrations are particularly low; the total dissolved phosphorus and total dissolved nitrogen were lower than 0.002 mgl^{-1} and 0.07 mgl^{-1}, respectively (analyzed by colorimetry). The biological activity is low, so the suspended substances (SS) concentration was about 0.3 mg l^{-1} for surface lake water.

Analysis of Lake Mashu water was performed by the procedure described, and the results are shown in Table 3. In this case, filtration was not necessary at all, because of the low concentration of SS. Lake water acidified for preservation was directly presented for analysis. Samples from a depth of 5 and 10 m were collected with metal free pump sampling device. When two bottles of 5 m sample and three of 10 m were analyzed, the analytical values of all five samples had no significant difference. These values were averaged and are shown with their standard deviations. Other samples (*i. e.*, 2, 50, 100, 150 and 200 m samples) were collected with the Go-Flo sampler. Considering the ICPES sensitivity, the concentration factor (about 500) was sufficient for the determination of alminum, vanadium, manganese, iron and zinc. For other elements, it was not sufficient and relatively large analytical errors existed. The large analytical errors of zinc and titanium resulted from the analytical blanks. Concentrations of iron and manganese for the sample obtained close to the bottom were higher than in other samples. For aluminum, nickel, copper, zinc and lead, surface water (2 m) concentrations were relatively higher, but

Table 3 Analytical results of trace elements in Lake Mashu water sample (μg l^{-1})

	Depth (m)					
	2	5 -10	50	100	150	200
Al	1.39	1.24 ± 0.16	1.04	1.11	0.97	1.04
Ti	0.05	0.06 ± 0.04	0.06	0.09	0.06	0.05
V	0.16	0.15 ± 0.02	0.16	0.16	0.15	0.15
Mn	0.79	0.76 ± 0.01	0.78	0.82	0.80	1.38
Fe	2.63	2.64 ± 0.24	2.67	2.94	2.81	8.89
Co	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Ni	0.036	0.027 ± 0.006	0.024	0.015	0.019	0.018
Cu	0.091	0.069 ± 0.028	0.050	0.052	0.045	0.065
Zn	0.93	0.63 ± 0.06	0.53	0.48	0.45	0.42
Cd	0.006	<0.006	0.008	<0.006	<0.006	0.006
Pb	0.18	0.05 ± 0.03	0.06	<0.04	<0.04	0.06

that may be due to the effect of fallout or contamination from the boat. For other depths, the distributions of these trace elements were quite uniform.

3.3 Direct analysis of Lake Mashu water

Manganese and iron in Lake Mashu water samples were determined directly with graphite furnace atonic absorption spectrometry (GFAAS), because of the high sensitivities of GFAAS for these elements and relatively high concentrations in the samples. Ten μl of acidified lake water sample (not filtered one) was injected onto the carbon atomizer rod and analyzed with background correction using a deutrium lamp. For these two elements, high ashing temperature can be applied (about 1000°C) to evaporate the salt matrix and reduce the background interfence. The concentrations giving 1% absorption pearks were 0.08 $\mu g\ l^{-1}$ for manganese and 0.4 $\mu g\ l^{-1}$ for iron, and detection limits were nearly equal to these values. The results were shown in Table 4. Analytical errors of manganese and iron at average concentrations were about 0.07 and 0.6 $\mu g\ l^{-1}$, respectively. Most of the results were in good agreement between the two independent methods within the range of error.

Since the cadmium concentration in 500-fold concentrated sample of Lake Mashu water was nearly equal to the detection limit of ICPES, it was analyzed also by GFAAS. Concentration of $0.007 \pm 0.003\ \mu g l^{-1}$ was determined as an average of 5 -10m samples. It corresponds to the practical detection limit of ICPES analysis after preconcentration (0.006 $\mu g l^{-1}$). Determination of cadmium for sample concentrated 20-fold by evaporation was tried with GFAAS. The results was $0.004 \pm 0.004\ \mu g\ l^{-1}$. Reproducibility was not good because of the deposition of silica in preconcentration procedure.

Table 4 Analytical results obtained from GFAAS direct analysis and ICPES with 500-fold preconcentration

	concentration ($\mu g\ l^{-1}$)						
depth (m)	2	5	10	50	100	150	200
Mn GFAAS	0.89	0.92	0.82	0.86	0.86	0.81	1.53
Mn ICPES	0.79	0.76	0.77	0.78	0.82	0.80	1.38
Fe GFAAS	2.7	2.0	2.1	3.3	2.5	2.7	8.6
Fe ICPES	2.63	2.66	2.60	2.67	2.94	2.81	8.89

3.4 Comparison to other lakes

Determination of trace metals in unpolluted natural waters has previously been hampered by the lack of sensitivity of analytical methods. Since reliable analytical data for trace metals in natural fresh waters are scarce, earlier analytical data have to be closely examined with respect to the sampling, preconcentration and analytical methods. Selected reference of trace metal investigations are summarized in Table 5 taking into account the accuracy of analysis. These reference values are mostly total metal concentration with acid digestion or labile metal concentration with the determination after long preservation with the addition of acid.

Investigation of the High Sierra area, where there are thousands of lakes covering a vast wilderness, by Bradford *et al.*[7] is one of the earliest available reports

Table 5 Reference data of trace metal concentration ($\mu g l^{-1}$) in lake waters

	170 High Sierra lakes Bradford (1968)		Lake Constance Hegi (1976)	Norwegian Pristine lakes Henriksen (1978)		Lake Superior Poldoski (1978)	
	range	median	mean	range	median	range	mean
Al	<15-40	<15	—	—	—	—	—
Ti	—	—	—	—	—	—	—
V	<0.3-1.7	<0.3	—	—	—	—	—
Cr	<5	<5	0.3	—	—	—	—
Mn	<0.3-21.7	<0.3	2	—	—	—	—
Fe	0.5-30.0	1.3	7	—	—	—	—
Co	<0.3-0.9	<0.3	—	—	—	—	—
Ni	<0.3-1.8	<0.3	—	—	—	—	—
Cu	0.4-5.0	1.2	<1	<0.5-2.0	1	0.5-3.4	1.25
Zn	0.3-100.0	1.5	5	0.5-12.0	5	—	—
Mo	<0.3-100.0	0.4	—	—	—	—	—
Ag	<0.03-6.0	0.1	—	—	—	—	—
Cd	<3-33	<3	<0.1	0.1-0.5	0.3	0.006-0.034	0.019
Pb	<0.3-4.0	0.5	<1	<0.5-2.0	1.5	0.10-0.30	0.18

Table 5 (Continued)

	Masurian Lake District Wieclawski (1972)		Lake Windermere Davison (1980)	Lake Ontario Nriagu (1981)	Lake Mashu this study
	range	median	mean	range	mean
Al	—	—	—	—	1.2
Ti	—	—	—	—	0.06
V	—	—	—	—	0.15
Cr	—	—	—	—	—
Mn	<0.1-9.8	0.5	—	—	0.76
Fe	—	—	—	—	2.6
Co	—	—	—	—	<0.004
Ni	—	—	—	0.85-1.13	0.027
Cu	0.1-4.5	0.5	0.3	1.10-1.65	0.069
Zn	0.5-9.7	1.9	2.1	—	0.63
Mo	—	—	—	—	(0.3)
Ag	—	—	—	—	—
Cd	<0.1-0.2	<0.1	<0.05	0.033-0.069	<0.006
Pb	0.3-1.2	0.7	<0.1	<0.43	0.05

with an estimation of natural background levels of trace metals in lake water. Surface water samples were collected by lowering a plastic container from a helicopter. 3000-Fold preconcentration (evaporation and extraction with Ammonium pyrrolidlinedithiocarbamate (APDC) chelates) was performed, and trace metals were measured by spark emission spectrometric analysis. Except for iron, zinc, and copper, concentrations of other trace metals (nickel, vanadium, manganese, molybdenum, lead, and silver) were sometimes lower than the detection limits. Though the spark emission spectrometric analysis was not sufficiently sensitive, it was found that most of trace metals exist at $\mu g l^{-1}$or below concentration levels in unpolluted lakes in mountainous districts.

Hegi[8)] measured monthly fluctuations of seven trace metals in the oligo-mesotrophic Obersee of Lake Constance with GFAAS. The concentrations indicated in Table 5 are the averages of monthly determinations for surface water. Manganese, iron, and zinc were in the $\mu g\ l^{-1}$range but others were below than $\mu g\ l^{-1}$. In shallow Untersee of Lake Constance, the usual cyclical fluctuations were observed for manganese and iron depending on redox conditions in the hypolimnion. High concentrations were observed for bottom water in summer and autumn.

Henriksen and Wright[9)] collected samples at about 200 small pristine lakes in Norway and determined the concentrations of copper, zinc, cadmium, and lead with GFAAS. They selected lakes without disturbance by agriculture, silviculture, or lake-level regulation. From the results for the lakes in central and northern Norway, natural backgound levels were estimated, including the global-scale depoition of trace heavy metals from the atmosphere. Considering that the background level concentrations were nearly equal to the analytical detection limits, the same authors commented that these estimates were the upper limits for the natural background levels.

Poldoski and Glass[10)] measured waters collected at western Lake Superior and streams of Superior National Forest in the wilderness area in Minnesota. Concentration differences were not observed between the two locations, and the range and mean values were reported. The detection limit of the analytical method (anode stripping voltammetry) was low enough for the determination.

Davison[11)] determined the total soluble concentrations of copper, zinc, cadmium, and lead for filtered water of Windermere Lake with anode stripping voltammetry analysis after ultra-violet radiation treatment. Except for zinc, the measured concentrations were very low and nearly equal to the data from "background level" areas. Similar results were obtained by Wieclawski[12)] for selected lakes in the Masurian Lake District. Trace heavy metals in soluble ionic forms were collected with a dithizone column, and polarographic determinations were performed. The data shown in Table 5 are summarized from Wieclawski's monthly determination. These lakes are not in an oligotrophic state.

In the Great Lakes, the concentration of labile metals was measured by Nriagu[13)] with flame atomic absorption spectrometry after Co-APDC coprecipitation method. Data indicated in Table 5 are from three open lake stations, where the distributions of four trace metals was uniform. Muhlbaier and Tisue[14)] determined cadmium in the waters of Lake Michigan with isotope dilution mass spectrometry, which appears to be the most reliable analytical technique at present. The results obtained were in the range from 0.012 to 0.046 $\mu g l^{-1}$.

The last column of Table 5 indicates the analytical data of Lake Mashu for the shallow water (average of 5-10 m samples). The measured concentration of each element in Lake Mashu water is herewith discussed. Aluminum in natural fresh waters has recently been widely investigated in relation to lake acidification by acidic precipitation, but no data comparable to Lake Mashu were obtained in this study. Very few data on titanium and vanadium are available in the literature. The manganese and iron concentrations of Lake Mashu are not especially low compared with those of other lakes. The levels are typical values for unpolluted oligotrophic lakes containing ample dissolved oxygen. The cobalt concentration in natural fresh water is usually very low. A more sensitive analytical method should be developed to discuss the nature of cobalt. Sometimes, it may be related to bioactive compounds like vitamin B_{12}. Nickel is one of the indices of pollution form petroleum and its combustion processes. Though atmospheric fall-out may be one possible source, it is difficult to justify the vertical distribution of nickel in Lake Mashu (Table 3), where the concentration of shallow lake waters showed a slight increase over deep lake waters. The concentration of nickel in open ocean seawater is rather higher than in Lake Mashu water (0.2-0.7 $\mu g\ l^{-1}$ after Bruland *et al.*[15]) and the effect of pollution from petroleum and its combustion is not so severe in Lake Mashu.

Reference data on copper and zinc are plentiful, because these elements are important in both biological and toxic senses. In Hegi's monthly monitoring data for Lake Constance[8], these elements showed an unsystematic seasonal fluctuation. However, Lake Mashu dose not have a river water inflow, and the water level is sustained only by precipitation inflow. The water volume is very large compared to the annual precipitation, which means a long water residence time (calculated to be about about 117 years). Hence the fluctuation of concentrations seems to be less. A low copper concentration will be evidence of low contamination from pollution, but this will not necessarily be the case for zinc, since biological transportation can be a large decisive factor in the zinc concentration. Data for Lake Biwa (Table 2) showed the lowest concentration.

The molybdenum recovery obtained with our preconcentration method is not entire satisfactory, but the concentration level in Lake Mashu can be estimated. The value (0.3 $\mu g\ l^{-1}$) was similar to the result obtained by Bradford *et al.*[7].

Though cadmium and lead in lake water have been widely investigated, natural background levels are especially low and difficult to analyze. All of the above-mentioned studies deal with these two elements, but some of them could not determine the analytical value. Cadmium concentrations in Norwegian small lakes, Lake Superior, Lake Michigan and Lake Ontario were readily analyzed above the detection limits. The Norwegian lakes showed rather high concentrations, which appears to be a geological effect. In the Great Lakes, cadmium concentration increases along the flow of water (*i.e.*, Lake Superior is the lowest, and Lake Ontario the highest). Our results from Lake Mashu water reflect the lowest of any levels cited in the literatures. Lead determination is also difficult and not able to be performed in some of the studies reported. The Norwegian study again showed the highest value, and that on Lake Mashu displayed the lowest. From the vertical distribution in Lake Mashu, lead seems to originated mainly from atmospheric fall-out.

From this survey of trace metals in natural lake waters, the concentration determined in Lake Mashu appears to be similar to approximate the lowest reported values in the world.

3.5 Application to seawater analysis

The present method is also applicable to the analysis of trace metals in seawater. Using 200 m*l* of seawater sample, the same preconcentration procedure was carried out except for evaporation with the rotary evaporator, since seawater has a high salt concentration. Surface seawater sample was immediately brought to laboratory, filtered through a 0.4 μm Nuclepore membrane filter, acidified with 14 N nitric acid (30 m*l* to 8 *l* sample) and stored for about two months.

As the concentration factor (about 100) was different from that of lake water, the analytical blanks and sensitivities were also different. The recoveries of 20 μg of elements added to the seawater (chelating and adsorption pH was 7.0), the practical detection limits of this method as obtained from the deviation of blank values, and the concentrations determined in this coastal surface seawater are shown in Table 6. Additional recoveries were almost the same as for the lake water matrix, but recoveries of some elements decreased, especially those of lead and nickel. On the other hand, recoveries of manganese and cadmium increased. Sensitivities, except for zinc, are about five times lower than for lake water analysis, because of the dependence on the ratios of concentration factors.

Table 6 Additional recovery, practical detection limit, and determined concentration for seawater analysis

Element	Recovery	DL-practical	Concentration
	%	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$
Al	97	0.6	1.10
Ti	89	0.14	0.53
V	97	0.015	1.90
Mn	83	0.04	0.12
Fe	92	0.17	0.45
Co	91	0.03	0.04
Ni	86	0.06	0.34
Cu	97	0.04	0.21
Zn	95	0.3	0.56
Cd	89	0.02	0.11
Pb	64	0.3	<0.3

4 . CONCLUSIONS

Satisfactory performance was confirmed for a preconcentration method for trace metals in natural waters using chelation to 8-hydroxyquinoline followed by adsorption to C_{18} chemically bonded silica gel. This procedure has the advantages of rapid sample treatment, few sample manipulations, low analytical blanks and simultaneous multielement preconcentration ability at a single set of treatment conditions. The combination with ICPES analysis gives sufficient sensitivity and reproducibility for many elements in natural water samples. From the results, the competence of Lake Mashu as a background level monitoring station was assessed in comparison with other reference data for trace elements in lake waters around the world. On-site preconcentration could be possible considering the strong adsorption of 8-hydroxyquinoline chelates on C_{18} chemically-bonded silica gel. Exclusion of sample preservation should result in lower contamination and analytical blank.

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摩周湖水中の微量金属の定量とその陸水環境におけるバックグラウンドレベルについて

野尻　幸宏[1]・河合　崇欣[1]・大槻　晃[1]

摩周湖水中の微量金属（Al, Tl, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb）の定量を行った。前濃縮には，8-ヒドロキシキノリンの金属キレートをC_{18}化学結合型シリカゲルに吸着させる方法を用いた。溶離液を高周波誘導結合プラズマ(ICPES)によって分析することにより，天然水中のppbからpptの濃度範囲にある多くの微量金属の定量が可能となった。摩周湖水中(深度5-10m）の微量金属の濃度(ppb)は次のとおりであった。Fe 2.6；Al 1.2；Mn 0.76；Zn 0.63；V 0.15；Cu 0.069；Ti 0.06；Pb 0.05；Ni 0.027；Cd <0.006；Co< 0.004。このように摩周湖水中の微量金属濃度は著しく低く，これまでの世界各地の湖沼に関する報告と比較した結果，摩周湖がバックグラウンドレベルモニタリングステーションとして，適していると考えられた。

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Ⅲ. Method for Long Term Storage of Environmental Samples

Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

III— 1

A Preliminary Study on the Preservability of Benzo〔*a*〕pyrene in Stored Atmospheric Particulate Matter Samples

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and Yoko YOKOUCHI[1]

ABSTRACT

To examine the preservability of benzo〔*a*〕pyrene in the stored sample of atmospheric particulate matter, a storage experiment was designed.

Atmospheric particulate matter collected on the quartz glass fiber filter was stored in the following four conditions; (1) +20°C, air. (2) +20°C, argon gas. (3) −20°C, air. (4) −20°C, argon gas. Benzo〔*a*〕pyrene concentration in each sample was analyzed after 6 months, one year and 2 years from the start to trace the change during the storage.

After two years, benzo〔*a*〕pyrene in the samples stored in +20°C decreased by 28% of the initial value and in −20°C it decreased by 12% showing the effect of temperature. The difference of the atmosphere in the storage box showed no significant effect on storage.

The experiment is still going on and the final results will be obtained after one year or so. From the results obtained so far, however, it was concluded tentatively that the storage method applied in this study cannot always keep benzo〔*a*〕pyrene in the atmospheric particles samples unchanged. Other storage conditions should be studied furthermore.

1. INTRODUCTION

The need for a so-called environmental specimen bank for retrospective studies to monitor long term environmental pollution has been discussed for several years. In connection with PAH and other pollutants contents, atmospheric particulate matter has been considered as one of the important specimens to be stored in such a bank. However, the establishment of the actual bank involves several problems which must be studied prior to start a full-scale banking system[1-3]. The preservability of the sample materials and substances in the bank is one of the key

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problems to be investigated as well as the selection of samples to be stored in the bank as indicators of environmental changes.

The information on the preservability of most environmental samples during the long term storage over months is limited, and this is also true of atmospheric particulate matter. However, in regard to the stability of PAH in the atmospheric particulate matter on the filter during the sampling time, several studies have indicated that some degradation of PAH occurs on the filters presumably affected by UV-radiation, NO_x, O_3 and other oxidants in the atmosphere[4-8].

Tomingas[4] reported that nearly 50% of benzo[*a*]pyrene collected on glass fiber filter diminished after one year storage in the room condition.

These results suggest that protection from such factors is necessary for long term storage of PAH in atmospheric particulate matter. The present experiment was designed to investigate the preservablity of benzo[*a*]pyrene in the atmospheric particulate matter on the sampling filter stored for a long time in several storage conditions as a means to find a more suitable method of storage.

2. EXPERIMENTAL

2.1 Samples

Atmospheric particulate matter was sampled at the roadside near Shinjuku Gyoen Park, Tokyo, in June 1981. The road had heavy car traffic, and high particulate matter content and PAH from vehicular exhaust gas was expected in the samples. Samples were collected on four sheets of quartz glass fiber filter (Palliflex 2500 QAOT) through which air passed for 70 hours using simultaeously four sets of high volume air samplers which were set side by side. Sampling was done twice to prepare two series of sample filters having different particulate matter and benzo[*a*] pyrene contents.

From one sheet of sampled filter (20cm×25cm), 12 pieces of small discs (5cm diameter) were cut out as analytical samples using a stainless steel punch.

2.2 Analytical procedure

The analytical sample filter disc was folded and dissected into 5mm wide strips with a stainless steel scissors and put into a 10ml centrifuging tube. After adding 10ml of acetonitril and ultra-sonic extraction for 15 minutes, the solvent was centrifuged for 7 minutes (3000 rpm). The extracted benzo[*a*]pyrene in the supernatant solvent was analyzed by HPLC coupled with fluorescence detector under the following conditions[9-11].

Instrument: HPLC (Waters 700A)
Column: Micro-Bondapak (i.d. 1/8 in. ×1 ft.)
Solvent: Acetonitril/water 80/20
Flow rate: 2.0ml/min
Detector: Fluorescent detector (Hitachi 10LC) (excitation wave length 366 nm, fluorescence wave length 403 nm)

The analytical result was expressed as benzo[*a*]pyrene weight per weight (ppm) of atmospheric particulate matter which was kept in the room with 50% relative humidity and temperature 20°C until the weight become constant.

2.3 Storage experiment

The experiment was designed to check the effects of temperature and oxgen on the stability of benzo[*a*]pyrene in the samples during storage, using the following four conditions.

(1) +20°C in air
(2) +20°C in argon gas
(3) −20°C in air
(4) −20°C in argon gas

The sample filters were placed on the stainless steel plate (20×25cm) and set in the airtight staineless steel boxes (30×30×50cm) filled with air or argon gas and stored in the 20°C or −20°C storage room.

A sufficient volume of argon gas to replace air in the container was introduced through a pipe connected to the container box. The replaced air was discharged from the pipe on the side of the box. Twelve pieces of analytical sample filter discs were stored in each of the four conditions and two each discs were programmed to be taken out from each containers to analyze the benzo[*a*]pyrene content after 6 months, 1 year, 2 years and 3 years from the start of the experiment.

The determination was done in duplicate for each analytical smaple disc.

Two series of samples with different benzo[*a*]pyrene content which had been sampled at a different time, were used in this experiment.

Since the similarity of the stored samples at the start of the experiment is essential for comparison of the analytical results after the storage to find a secular change of it, the homogeneity of the distribution of benzo[*a*]pyrene in the sample filters was examined prior to the storage experiment.

3. RESULTS AND DISCUSSION

3.1 Recovery and blank test

The recovery of benzo[*a*]pyrene in this analytical method was determined by adding a small amount of benzo[*a*]pyrene solution on the sampling filters and analyzing by the same procedure. As shown in Table 1, the percent of recovery was over 92% for each run. The blank value of the filter for benzo[*a*]pyrene was 0.0 ppm.

Table 1 Recovery test for benzo[*a*]pyrene on the atmospheric particulate matter on the filter

run	present	added	observed	recovery
1	46.3 ng	51.6 ng	93.9 ng	92 %
2	56.4	154.8	201.6	94
3	56.4	154.8	199.8	92

3.2 Distribution of particulate matter and benzo[*a*]pyrene concentration on

sampled filters

The mean coefficient of variance of the weights of particulate matter of 12 analytical sample discs cut from one sheet of filter was 1.4% and that of benzo〔*a*〕pyrene was 4.5%, both reflecting nearly homogenous distribution on the filter. The concentrations of benzo〔*a*〕pyrene of four sheets of filters were approximately equal as shown in Table 2. This also assured a reliable homogeneity in the samples at the start of the experiment.

Table 2 Comparison of the concentrations of benzo〔*a*〕pyrene in the simultaneously sampled four filters. Sampling was performed twice (1st and 2nd run)

Filter No.	Sampling run	
	1st	2nd
1	5.2 ppm	8.4 ppm
2	5.2	8.6
3	5.4	8.2
4	5.2	8.7
mean	5.3	8.5
c.v. (%)	2.9	2.2

Table 3 Change of benzo〔*a*〕pyrene concentration in the atmospheric particulate matter after two years storage in various conditions

Temp.	Atmosphere	Filter	A (1982/6/25)	B (1982/12/17)	C (1983/6/27)	D (1984/6/27)	$\frac{(A-D))}{A}\times 100$
20°C	Air	I	5.2 ppm	4.4 ppm	4.1 ppm	3.9 ppm	25 %
		II	8.7	7.4	6.9	5.9	22
	Ar	I	5.4	4.6	4.1	3.8	30
		II	8.2	6.9	6.3	5.9	28
−20°C	Air	I	5.2	4.8	4.7	4.7	10
		II	8.5	7.7	7.4	7.6	11
	Ar	I	5.2	4.7	4.4	4.6	12
		II	8.5	7.7	7.2	7.2	15

3.3 Storage experiment

Table 3 shows the analytical results of benzo〔*a*〕pyrene concentration in the atmospheric particulate matter at the start of the experiment, after 6 months, 1 year and 2 years, respectively for each series of samples stored in each of the four storing conditions. The duplicate analysis for each disc agreed within +2% tolerance. The

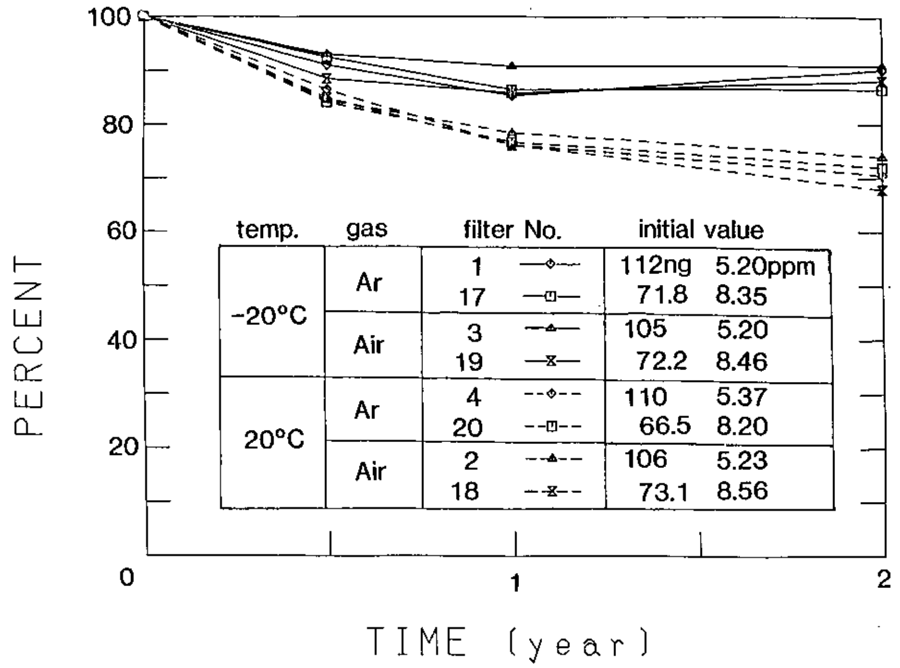

Fig. 1 Change of benzo[a]pyrene contents in the atmospheric particulate matter on the filters during the storage

trends of changes expressed as a percentasge of the initial values (100%) are illustrated in Fig. 1. The two series of tested samples gave nearly similar results, both evidencing decreased benzo[a]pyrene concentrations according to the storage conditions.

The average rate of benzo[a]pyrene decrease during the test period (2 years) was higher for the samples stored at 20°C, reaching 28% of the initial value. The samples in −20°C, on the other hand, were both reduced by an average of 12% of the initial value. Thus, the effect of the difference of temperature was significant. The difference of the atmosphere in the storage box did not show any remarkable effect in this experiment. However, a problem remains as to whether the argon gas in the container was completely reserved during the experiment, and further studies are needed.

The reasons for the decrease of benzo[a]pyrene in this experiment cannot be exactly explained as yet. The box was closed and dark inside, no effect of light can be considered to occur. From these differences in the behavior of benzo[a]pyrene in the different temperature conditions, it is estimated that some effects of biochemical or chemical reactions other than the decomposition by the reaction with oxidant or by photochemical reactions might occur, provided that no escape of benzo[a]pyrene occurs.

Another possibility is the evaporation loss of bezo[a]pyrene from the filters during long storage time. Considering, however, that the vapor pressure of this

Table 4 Rate of decrease of benzo〔*a*〕pyrene concentration during the storage time

Temp.	Atmosphere	Filter	1st 6 months	2nd 6 months	the next 1 year
20°C	Air	I	−15 %	− 7 %	− 5 %
		II	−15 %	− 7 %	−14 %
	Ar	I	−15 %	−11 %	− 7 %
		II	−16 %	− 9 %	− 6 %
−20°C	Air	I	−10 %	− 2 %	0 %
		II	− 9 %	− 4 %	+ 3 %
	Ar	I	− 8 %	− 6 %	+ 4 %
		II	− 9 %	− 6 %	0 %

substance is very low, this explanation seems less probable. The rate of decrease during the first 6 months and that of the following periods are compared in Table 4, which shows that in the first 6 months storage the decreasing rate was approximntely twice that in the next 6 months, during the following 1 year the decrease rate bacame almost zero in −20°C condition and in 20°C it still decreased by several percents. This suggests that benzo〔*a*〕pyrene in the atmospheric particulate matter consists of comparatively changeable part and more stable part.

Though it seems unlikely, a question remains if a part of benzo〔*a*〕pyrene changed its form to an unextractabe one and consequently the apparent concentration decreased after the storage. Another experiment is necessary to answer this problem.

4. CONCLUSION

This experiment is still going on and the final results will be obtained after one year or so. From the results obtained so far, however, it was concluded tentatively that the storage method applied in this study cannot always keep benzo〔*a*〕pyrene in the atmospheric particles samples unchanged. Other storage conditions should be studied furthermore.

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大気浮遊粒子試料中のベンゾ〔*a*〕パイレンの長期保存性に関する予察的研究

安部喜也[1]・向井人史[1]・安原昭夫[1]・横内陽子[1]

将来の環境試料バンクのための基礎として大気浮遊粒子試料中のベンゾ〔*a*〕パイレンの長期保存性を検討する実験を開始した。

石英ガラスファイバーフィルター上に採取した大気粒子試料を(1)＋20°C，空気中 (2)＋20°C，アルゴンガス中 (3)−20°C，空気中 (4)−20°Cアルゴンガス中の４条件で保存し，６か月，１年，２年後の変化を測定した。２年間にベンゾ〔*a*〕パイレン濃度は＋20°Cの場合28%，−20°Cでは12%ほぼ減少した。温度条件の差は明らかであったが，保存雰囲気の差は明瞭でなかった。

実験はなお継続中であるが，少なくとも今までの結果では，ここで行った保存法は，かかる試料の長期的保存法としては完全なものとはいえず，さらに各種の条件での保存法の検討が必要であることがわかった。

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Ⅳ. Survey and Analysis of Unidentified Trace Organic Substances in the Environment

Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

IV—1

A Survey Analysis of Resistant Organic Chemicals in Water by High Resolution Gas Chromatography/Mass Spectrometry

Hiroaki SHIRAISHI[1] and Akira OTSUKI[1]

ABSTRACT

Non-polar organic componds in an effluent from a domestic waste water treatment plant were analysed by high resolution gas chromatograph/mass spectrometry. About seventy compounds were identifed. The presence of halogenated methoxybenzenes and dimethoxybenzenes (fungicide), oxadiazon (herbicide), methylated triclosan (disinfectant), alkylphenol ethoxylates and diethoxylates (surfactant) was indicated.

1. INTRODUCTION

Many synthetic organic compounds have been discharged into the environment through disposal, only to cause local and global water pollution problems. So many synthetic organic compounds have been manufactured that it is necessary to select specific compounds for monitoring in order to safeguard water quality. The EPA's "priority pollutants"[1)] are one example of a list of compounds for monitoring industrial waste water discharge. Priority pollutants are 129 specific compounds including 114 organic (with 17 pesticides and 7 PCBs) and 15 inorganic metals or ions. Among them 71 compounds are halogenated organic compounds. However, the priority pollutants in the EPA list are only the beginning of the monitoring of industral wastewater discharges. It is desirable to identify organic compounds which are discharged into the water environment and decide whether add those compounds to the list after consideration of the levels present and the likely environmental impact, for monitoring not only industrial waste water but also natural water systems.

The object of the present study is to identify unknown resistant organic pollutants in water, in a so-called survey analysis of organic compounds. High priority was given to persistent organic chemicals, which will remain in the water environment for longer periods. Effluent from biologically activated sludge plants contains

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many persistent organic chemicals, because the biological degradation process is one of the important routes for removal of degradable organic chemicals from the water. Thus, effluent from biologically activated sludge was examined in this study.

Since many compounds are expected to be present in a very low concentration of less than 10^{-9} g per liter, a pre-concentration was required before analysis. Many methods for concentration of solutes from water at trace levels have been developed[2]. An extraction technique is usually selected from among liquid-liquid extraction[3], reverse osmosis[4], closed loop stripping (CLS)[5], head space sampling[6,7], or resin adsorption techniques[8], depending upon the properies and concentrations of compounds to be analyzed. The XAD-2 resin adsorption technique seems most convenient to handle several hundred liters of water, and has been successfully applied to water analysis. But it is sometimes reported that the presence of impurities in blanks from the XAD-2 resin makes it impossible to lower the detection limit[9,10]. A continuous liquid-liquid extraction method[11~13], often used in pesticide analysis, can conveniently handle several hundred liters of water and provide an exsremely low reagent blank, because it requires only one or two hundred milliliters of organic solvent. A continuous liquid-liquid extractor of the kind was used in the present study, with some modifications to extract non-polar organic compounds in a domestic waste water treatment plant.

Hexane extracts were still a quite complex mixture, and the concentrations of compounds were extremely low. The present investigators used fused silica capillary GC/MS for identification and semi-quantification. More than one hundred mass spectra can be measured in one GC/MS run, but they were not always found in the mass spectrum data base[14]. Identification of the exact molecular structures of the compounds, on the basis of the interpritation of mass spectrum, is accompanied by some difficulties. Collection of additional information is required, such as liquid or gas chromatographic behavior, or classification of compounds based upon their acidity and polarity. Other spectroscopic studies, such as nuclear magnetic resonance and infra-red spectroscopy, were not sufficiently sensitive for diluted complex mixtures. The knowledge of sources on what types of company discharge into this water treatment plant, may be very helpful, but this plant treats only domestic water.

The present study attempts to determine how GC/MS play a role in the elucidation of molecular structures, and reports the results of some efforts to find new pollutants in the effluent from activated sludge plants.

2 . EXPERIMENTAL

2. 1 Modification of extractor

As reported by Stachel *et al*[13], the decrease in water level which occurred during extraction made operation of the Ahnoff and Josefsson extractor[11] difficult. In order to overcome this undesirable phenomenon, the continuous liquid-liquid extracsor (see Fig. 1) was modified to regulate the water level. A commercial automatic water level controller (Nissin Rika Co., Model AL-66r) operating in on-off delay mode was used. The water level is monitored by an infra-red sensor on the side arm of the extractor. If the water level drops, air is pumped out through a one-way glass valve, thus causing a partial vacuum inside the extractor. The flow rate

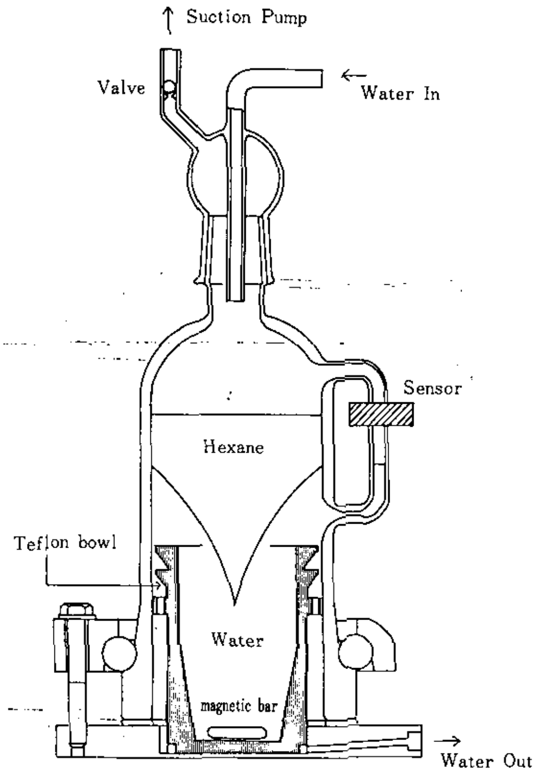

Fig. 1 A modified continuous liquid-liquid extractor

of water into the extractor then increases. The pumping speed and delay time were adjusted so as to prevent chattering of the water level. To facilitate changing of the extractor head, a transparent glass joint was adopted instead of the stainless steel flange originally used[11].

2. 2 Sampling

Two hundred liters of effluent was extracted by 150 mL of hexane on July 6th -8th, 1983 at the Kasumigaura Kohoku Regional Sewerage Plant. The flow rate of the effluent in the extractor was 68 ml/min. Recovery of hexane was about 0.14 l (more than 94%). The hexane extract was dried by sodium sulfate (about 5 g) and concentrated to a few milliliters on a rotary evaporator, and then to 1.0 ml under a nitrogen stream at room temperature. After the concentrate was analyzed by GC and GC/MS, it was further separated into three fractions by silica gel chromatography. The extract was eluted by hexane, dichoromethane, and finally ether. Each fraction gave a much more resolved peak in GC and GC/MS.

Fig. 2 shows the sewer service area of the Kasumigaura Kohoku regional sewerage system. Principal water treatment facilities are grit chambers, pumps, primary settling tanks, aeration tunks, secondary settling tanks, dual media filters, and a chlorination tank.

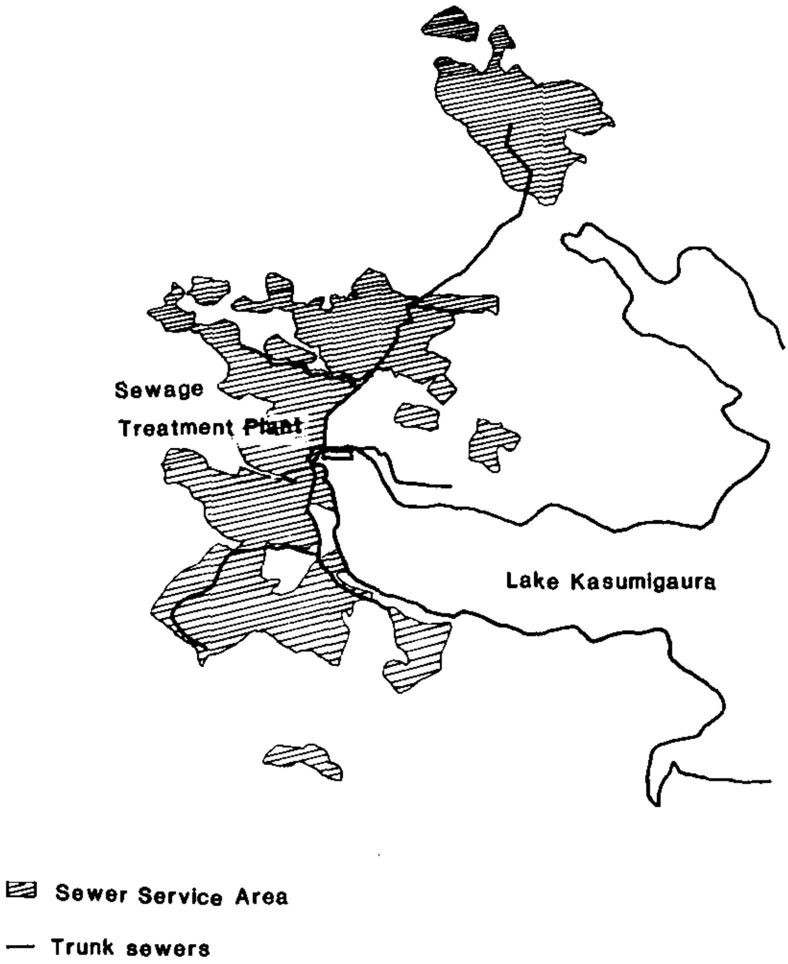

Fig. 2 Sewer service area of Kasumigaura Kohoku regional sewerage system

2. 3 Apparatus

The gas chromatograph was a Shimadzu GC 7A with flame ionization detector and a universal capillary inlet system (SGE, Australia). Helium was used as the carrier gas. Flexible capillary columns (25 m), methyl silicone, (Hewlett-Packard) and CP Sil 5 CB (Chrompak, Netherlands) were used. Mass spectrometry was performed on a DX-300 double focusing mass spectrometer (JEOL, Japan) fitted with a Hewlett-Packard 5700 model GC. The column was directly coupled to the mass spectrometer. The column temperature was set at 40 °C for 4 min, followed by an increase to 250 °C at a rate of 8 °C/min, and then held at 250 °C. The injector temperature was 250 °C and the head pressure of the column was 1.0 kg/cm^2. The mass spectrometric conditions were as follows : accelarating voltage, 3 kV ; ionizing current, 300 μA ; ionizing voltage, 70 V ; scan range, m/z 10 to 400 ; scan interval, 2 s. A JMS-3500 mass data analysis system (JEOL, Japan) was used. Chemical ionization (CI) mass spectrometry was performed using methane and isobutane as the reagent gases.

2. 4 Materials

The hexane was pesticide grade (Wako Pure Chem, Ind., Ltd) and required no further purification before use. Distilled water was purified by a Milli-Q system (Millipore Corp.).

4-Chloro-1-(2, 4-dichlorophenoxy)-2-methoxybenzene (methyl triclosan) was prepared from triclosan (Irgasan DP300, Ciba-Geigy) by methylation with diazomethane.

Styrene was chlorinated as follows : Concentrated hydrogen chloride solution was added into a 20 % sodium hypochloride solution and chlorine was trapped by chloroform. Chloroform solution of chlorine was added to the chloroform solution (25 m*l*) of styrene (2 g) at 0 °C. Chlorine was evaporated and the reaction mixture was analyzed by GC/MS without any further treatment.

The other chemicals used in this study were purchased from Wako Pure Chem. Ind., Ltd and Tokyo Chem. Ind. Co., Ltd.

2. 5 Recovery test

The extractor was fitted with a small reservoir and a Hershberg type dropping funnel. Water (100 m*l*) was poured into the funnel and then 5 μl of a standard methanol solution (0.5 mg/m*l*) of PAHs was added to the water. This solution was dynamically diluted by adding it dropwise to a glass reservoir through which water was flowing at 55 m*l*/min. The dilution factor in the cell was 250, so that the net concentration flowing through the extractor was 100 ng/*l* per component. The total volume of water extracted was 25 *l*. Recoveries (%) of naphthalehe, fluorene, phenanthrene, and fluoranthene were 84, 85, 88 and 85, respectively.

3 . RESULTS AND DISCUSSION

Fig. 3 shows a reconstructed ion chromatogram (RIC) of the effluent extract, and Table 1 lists the compounds identified. Halogenated organic compounds found in the extract were tetrachloroethylene, chlorohexane, dichlorobenzene, hexachlorocyclohexane isomer, chlorinated and brominated anisoles, chlorinated and brominated dimethoxybenzenes, chlorinated methoxytoluene, trichloroaniline, and mass spectra having characteristics of chlorinated unknown compounds were measured. 2,6-Di-t-butyl-benzoquinone, 3-t-butyl-4-hydroxy anisole, 2,6-di-t-butyl-4-methylphenol are antioxydizer and its oxidation product. The presence of 3,3-dimethyl-1, 5-di-t-butylbicyclo(4,1,0)hexane-2-one in river water was already reported[15]. Polynuclear aromatic hydrocarbons (PAHs) found in the extract were naphthalene, dibenzofuran, fluorene, phenanthrene, fluorantene, pyrene and chrysene. The levels of these PAHs were all below 10 ng/*l*.

GC/MS analysis revealed there fairly large amounts of chlorinated methoxy benzene derivatives in the extract. Their mass spectra showed the presence of intense molecular ion $(M)^+$ with chlorine isotope ion, and M -15 (CH_3), M $-15-28$ (CO) ions. Then $(M)^+$ and its isotope ion peak $(M+2)^+$ were selected for these

Table 1 List of

No	Name	R.T.	diagonostic ions
1	Tetrachloroethylene		
2	Chlorohexane	3'02	57, 43, 41, 91, 93
3	Dichlorobenzene, p	5'26	146(M), 148, 111, 113
4	Hexyl ether, i	8'34	85, 43, 73, 69
5	Hexyl ether, i	8'40	85, 43, 73, 69
6	Hexyl ether, i	8'44	85, 43, 129, 111
	+Naphthalene		128(M)
7	Dichloroanisole, i	8'58	176(M), 161, 178, 163
8	Hexyl ether, i	9'36	43, 85, 73, 69
9	Hexyl ether, i	9'42	43, 85, 129, 57
10	Dichloroanisole, i	10'24	176(M), 178, 133, 135
11	Dichloroanisole, i	10'32	176(M), 161, 178, 163
12	2-Methylnaphtalene	10'42	142(M), 141
13	Hexyl ether, n-	10'48	85, 43, 56, 57
14	Dichloromethylanisole, i	10'58	190(M), 175, 192, 177
	+1-Methylnaphthalene		142(M), 141
15	Dichloromethylanisole, i	11'04	190(M), 192, 175, 177
16	Trichloroanisole, i	11'20	195, 197, 210(M), 212
17	Dichlorodimethxybenzene, i	11'34	206(M), 208, 191, 193
18	Dibromoanisole, i	11'58	266, 264(M), 268, 251
19	Biphenyl	12'08	154(M), 153, 77
20	Trichloroaniline, i	12'32	195(M), 197, 199
21	Bromodichloroanisole, i	12'50	256(M), 241, 254, 239
22	Dichlorodimethoxybenzene, i	12'58	206(M), 191, 208, 193
23	Dichlorodimethoxybenzene, i	13'10	191, 193, 206(M), 208
24	Trichloroanisole, 2,4,5-	13'18	210(M), 212, 195, 197
25	Bromodichloroanisole, i	13'28	256, 254(M), 241, 258
26	Trichloromethylanisole, i	13'34	209, 211, 224(M), 226
27	Chlorodimethoxyxylene, i	13'40	200(M), 185, 202, 157
28	2,6-di-t-butylbenzoquinone	13'46	220(M), 177, 205
	+Acenapthene		154, 153
29	3-t-Butyl-4-hydroxyanisole	14'00	180(M), 165
	+3,3-dimethyl-1,5-di-t-butyl-bicyclo(4,1,0)hexan-2-one		221, 236(M)
30	Dibenzofuran	14'18	168(M), 139
	+Dibromochloroanisole, i		300, 302, 285, 298(M)
31	2,6-di-t-butyl-4-methylphenol	14'34	205, 220(M)

i means isomer. ? indicates tentative identification.

R.T. means Retention Time (min'sec). The column was 25 m CP Sil 5 CB.

M/z is listed in the order of relative intensities. M means molecular ion.

OP-1 and OP-2 mean octylphenol ethoxylate and octylphenol diethoxylate, respectively.

NP-1 and NP-2 mean nonylphenol ethoxylate and nonylphenol diethoxylate, respectively.

Peak No. refers to Fig. 3-8.

compound identified

No	Name	R.T.	diagonostic ions
	+Tetrachloroanisole, i +unknown		246, 244(M), 248, 231
32	Bromodichloroanisole, i	14'48	256, 254(M), 241, 258
33	Bromodimethoxyxylene, ?	15'04	244(M), 246
34	Fluorene	15'18	166(M), 167
35	Dibromodimethoxybenzene, i	15'42	296, 294(M), 298, 281
36	Tribromoanisole, i	15'48	344, 346, 329, 331, 342(M)
37	Dibromodimethoxybenzene, i	15'50	281, 296, 279, 283, 294(M)
38	Benzophenone	15'58	105, 77, 182(M), 135
39	Trichlorodimetoxybenzene. ?	16'12	240(M), 242
40	Tetrachloroanisole, i	16'30	246, 244(M), 248, 231
41	α-BHC	16'50	219, 217, 183, 181, 288(M)
42	Pentachloroanisole	17'26	280, 275, 273, 282, 278(M)
43	Phenanthrene	18'04	178(M)
44	OP-1	19'24	179, 135, 215, 250(M)
45	NP-1	20'10	179, 135, 264(M)
46	Anthraquinone	20'24	208(M), 180, 152
47	NP-1	20'34	207, 165, 221, 264(M)
48	Dibutylphthalate	20'40	149, 223, 205, 278(M)
49	NP-1	20'56	193, 165, 107, 235, 264(M)
50	NP-1	21'06	207, 193, 107, 264(M)
51	NP-1	21'14	207, 165, 107, 264(M)
52	unknown	21'30	139, 107, 103, 141, 245
53	unknown	21'40	139, 107, 103, 141, 245
54	Methyl-triclosan	22'32	302(M), 304, 252, 254
55	OP-2	22'58	223, 135, 45, 57, 294(M)
56	Oxadiazon	23'28	175, 177, 258, 302, 344(M)
57	NP-2	23'54	251, 265, 209, 121, 308(M)
58	NP-2	24'06	237, 279, 107, 45, 308(M)
59	NP-2	24'10	237, 45, 308(M)
60	NP-2	24'16	237, 45, 209, 279, 308(M)
61	NP-2	24'22	251, 45, 107, 121, 308(M)
62	NP-2	24'24	237, 45, 149, 308(M)
63	Chrysene	25'58	228(M)
64	Phthalate	26'14	149
65	Phthalate	26'40	149
66	Diethylhexylphthalate	27'16	149, 167, 279

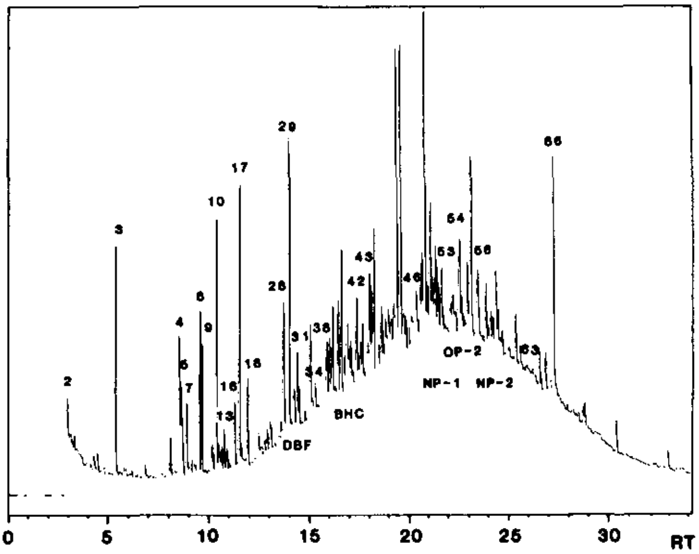

Fig. 3 The reconstructed ion chromatogram (RIC) of the effluent extract (The column was 25 m CP Sil 5 CB.)

halogenated aromatics, and a qualitative survey was done on the mass chromatography.

Fig. 4, 5 and 6 show mass chromatograms of chlorinated anisoles, dimethoxy benzenes, and methyl anisoles, respectively. Dichloroanisole, trichloroanisole, tetrachloroanisole, and pentachloroanisole, dichloro- and trichloro- derivatives of dimethoxy benzene and methyl anisole were found. Brominated methoxybenzenes found in the extracts were bromodichloroanisole, chlorodibromoanisole, dibromoanisole, tribromoanisole, bromodichlorodimethoxybenzene, and dibromodimethoxybenzene. The mass chromatogram of brominated derivatives is shown in Fig. 7 and 8. The result of semi-quantification of methoxybenzene derivatives in the effluent is shown in Table 2. It was known that biological methylation of chlorophenols takes place. Hence, chlorinated hydroxybenzene derivatives were presumed to exist but were not detected in the extract by means of mass chromatography. This suggests that polyhalogenated phenols may be effectively removed by the activated sladge plant. Miyazaki *et al.*[16] reported the presence of polyhalogenated anisoles and phenols in oysters collected from Tokyo Bay. They found trichloroanisole, tetrachloroanisoles, pentachloroanisole, bromodichloroanisole, chlorodibromoanisole, and tribromoanisole in the oysters. All compounds were also detected in this study. Pentachloroanisole may be derived from pentachlorophenol, which has been widely used as a herbicide in paddy fields until about twenty years ago, and it is still used as a fungicide in wood products. Di-, tri-, and tetrachloroanisoles may be degradation

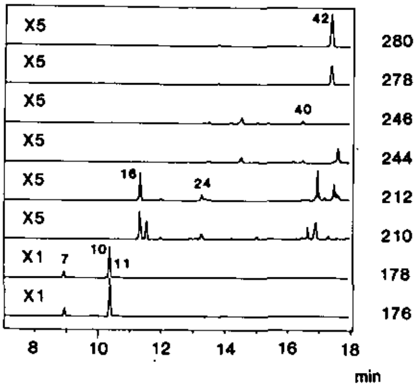

Fig. 4 Mass chromatogram of chloroanisoles
Dichloroanisole (m/z 176, 178): Trichloroanisole (m/z 210, 212):
Tetrachloroanisole (m/z 244, 246): Pentachloroanisole (m/z 278, 280)

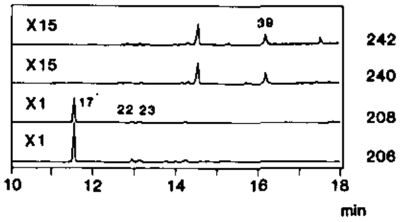

Fig. 5 Mass chromatogram of dimethoxybenzenes
Dichlorodimethoxybenzene (m/z 206, 208)
Trichlorodimethoxybenzene (m/z 240, 242)

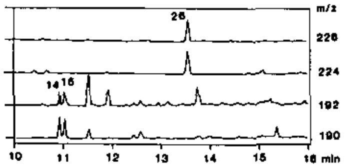

Fig. 6 Mass chromatogram of chloromethylanisoles
Dichloromethylanisole (m/z 190, 192)
Trichloromethylanisole (m/z 224, 226)

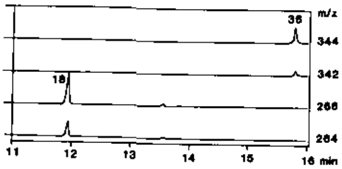

Fig. 7 Mass chromatogram of bromoanisoles
Dibromoanisole (m/z 264, 266)
Tribromonisole (m/z 342, 344)

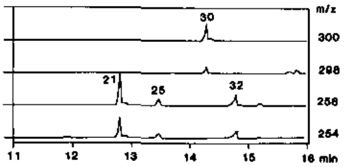

Fig. 8 Mass chromatogram of bromochloroanisoles
Bromodichloroanisole (m/z 254, 256)
Chlorodibromoanisole (m/z 298, 300)

Table 2 Semi-quantification of Halogenated methoxybenzene derivatives in the effluent (ng/*l*) (Based on relative peak area of molecular ions to 2,6-dichloroanisole: Recovery is not corrected.)

a) Halogenated Anisoles

Br＼Cl	0	1	2	3	4	5
0	ND	ND	91	13	0.8	8.5
1	ND	ND	2.6	ND	ND	×
2	1.9	0.5	ND	ND	×	×
3	0.7	ND	ND	×	×	×

b) Halogenated Dimethoxybenzenes

Br＼Cl	0	1	2	3	4
0	ND	ND	73	1.4	ND
1	ND	ND	tr	ND	×
2	0.6	ND	ND	×	×

ND=Not Detected. tr=trace

products[17] or impurities of pentachlorophenol and other agricultral chemicals, such as 2,4-D. Since the presence of brominated derivatives in oysters was reported, this type of compound may be commonly present in water environment. Sources for brominated methoxy benzenes are at present unclear.

Fig. 9 shows the mass spectrum of another chlorinated organic compound found in the extract. CI mass spectrum shows intense $(M+H)^+$ ion at m/z 345. Fragment ions having characteristics of chlorine isotope ion peak were found in EI mass spectrum at m/z 302 (M-42), 258 (M−42−44), 202, and 175 (base peak), and in the lower mass region intense ions were at m/z 41, 43 and 57. The mass spectra indicate that molecular weight was 344 and the molecule may contain two chlorine, dichlorophenoxy, carboxy group, butyl, and propyl groups. Although the structure could not be deduced from the mass spectrum, it was found by consulting with a list of pesticides that 2-butyl-2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazolin-5-one (Oxadiazon, herbicide) consisted of the above interpretations, and this identification

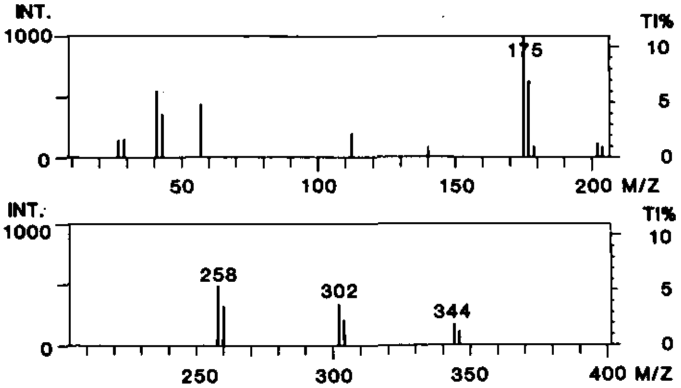

Fig. 9 Mass spectrum of oxadiazon extracted from the effluent

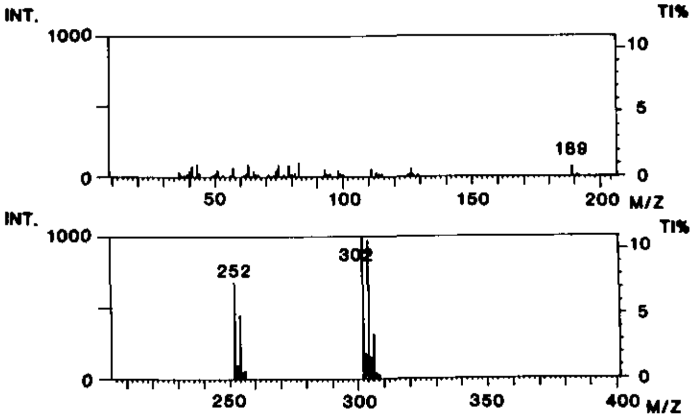

Fig. 10 Mass spectrum of methyl-triclosan extracted from the effluent

was confirmed by comparison of its GC retention time and mass spectrum with that of the standard. Oxadiazon has been widely used as a pre-emergence herbicide in paddy fields[18], and it has been reported in surface and tap water. There are paddy fields in the sewer service area of this plant, so oxadiazon, halogenated anisoles and dimetoxybenzenes may derive from agricultural run-off and can be carried by sewers.

Fig. 10 shows mass spectum of an unknown halogenated compound found in the extract. Ion clusters at m/z 302 were shifted by one mass unit in methane and isobutane CI mass spectrum. This indicates that molecular ion is m/z 302, and has three chlorines per molecule. Fragment ion at 252 may be due to (M-Cl-CH_3) or (M-CH_2Cl-H), but no fragment ions due to (M-Cl) or (M-CH_3) were found. Small fragment ion at m/z 217 and m/z 232 may reflect the loss of three and two chlorine atoms, respectively, from a molecular ion. Ion at m/z 189 may be interpreted as the loss of CO plus chlorine atom from m/z 252 fragment ion. No significant ion was found in the lower mass region, so this unknown compound was assumed to be an aromatic compound, and the CH_2 chain may not be included in the molecule. The loss of CO may indicate the presence of phenoxy group. Then a possible molecular formula is $C_{13}H_9Cl_3O_2$. No loss of chlorine from the molecular ion was observed, so the CH_2Cl group may not be present. The ion at m/z 252 may be due to the loss of Cl plus CH_3. Then the unknown compound may have three chlorine atoms, one phenoxy, one methyl, one phenyl, and one oxygen atom. Many isomers are possible, but 4-chloro-1-(2,4-dichloropheoxy)-2-methoxybenzene may be the most probable, because unmethylated derivative (5-chloro-2-(2,4-dichorophenoxy) phenol, Triclosan) is an antibacterial agent which has been widely used as a preservative in cosmetic and detergent preparations. This was confirmed by comparison of the mass spectrum and GC retention time with that of synthesized authentic standard. Triclosan has been found in industrial waste waters[19], and very recently methylated tricosan was detected in freshwater fish from the Tama River feeding Tokyo Bay[20]. However, this may well be the first time methylated tricosan has been demonstrated in the effluent from a domestic waste water treatment plant.

The other class of compounds identified was octylphenol ethoxylates and nonylphenol ethoxylates. Fig. 11 shows mass spectra of octylphenol ethoxylate (OP-1) and octylphenol diethoxylates (OP-2). Alkylphenol ethoxylates were known as degradation products of poly (oxyethylene) alkylphenyl ether, nonionic surfactant, which were already detected in river water[21]. Persistence of alkylphenol ethoxylate in sewage effluent was reported[22]. Mass spectra of octylphenol ethoxylate (OP-1) and octylphenol diethoxylate (OP-2) showed a base peak at m/z 179 and 223, respectively. These ions can can be explained by a rupture of benzylic bond in the octyl side chain resulting in a loss of C_5H_{11} from the molecular ion. Hence, OP-1 and OP-2 have α, α-dimethyl structure in the alkyl side chain. The remaining part of the alkyl group could not be deduced from the mass spectrum, but the mass spectra of OP-1 and OP-2 are analogous to the mass spectrum of 4-(1,1,3,3,-tetramethylbutyl) phenol triethoxylate reported by Sheldon and Hite[23]. Though no other isomeric OP derivatives was detected, there were many isomers of nonylphenol ethoxylates. Taking into account the fact that rupture of benzylic bond is favored in alkylphenol ethoxylate, it was concluded that α, α-ethylmethyl and α, α-diethyl (or α, α-propylmethyl) structures were abundant than α, α-dimethyl structure in the nonyl side chain (Table 1, Fig. 12). It may be first time that alkylphenyl ethoxylate was found from a nitrified effluent of biological sewage treatment.

Mass spectra having characteristics of halogenated compound were still found. Fig. 13 shows one of the mass spectrum of an unknown halogenated organic compound. Two similar spectra were obtained, so at least two isomers were present. The fragmentation pattern of the mass spectrum suggests that the compound may be chlorinated aromatics. Ions of the highest m/z value were found at m/z 245 and at m/z 247 (isotope ion). No additional ion peak was found in the higher mass region in methane and isobutane Cl mass spectrum of the extract. Three significant fragment ions were seen at m/z 139, 107, and 103. Fragment ions of m/z 139 and 141 may have one benzene ring and one chlorine atom. A possible formula for this ion may be C_7H_4ClO or C_8H_8Cl. Absence of 139-28 (CO) peak suggests that the latter is more probable. Fragment ion of m/z 103 may be due to the loss of HCl from m/z 139, and its possible formula is C_7H_3O or C_8H_7. This ion also suggests that m/z 139 may be due to C_8H_8Cl, because it may be more likely to lose HCl. A possible formula for ion at m/z 107 is C_7H_9N or C_7H_8O. If m/z 245 is considered a molecular ion, then

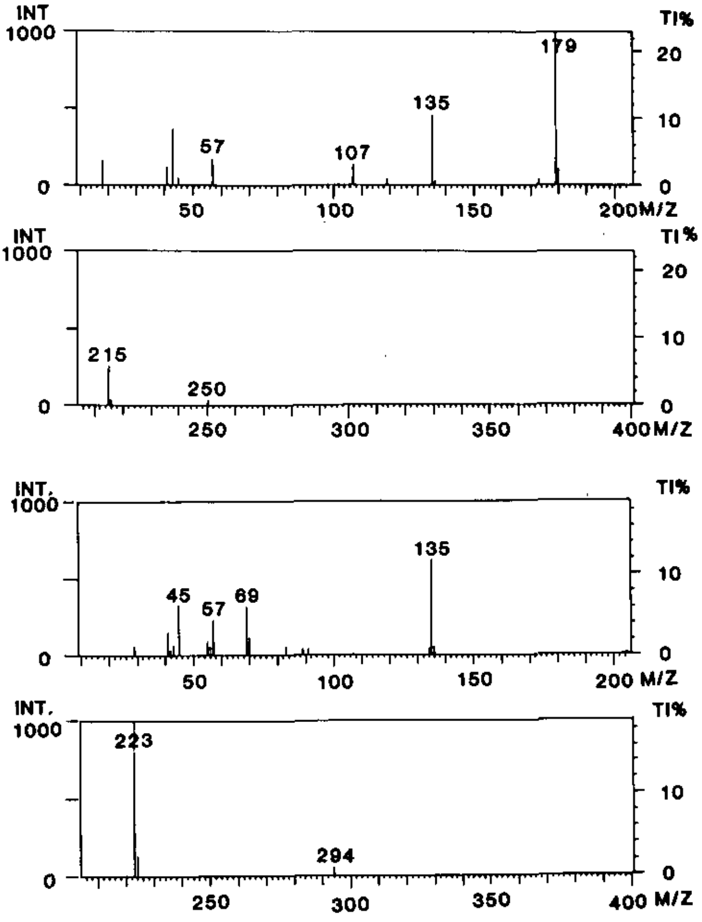

Fig. 11 Mass spectra of (a) octylphenol mono- and (b) di-ethoxylate

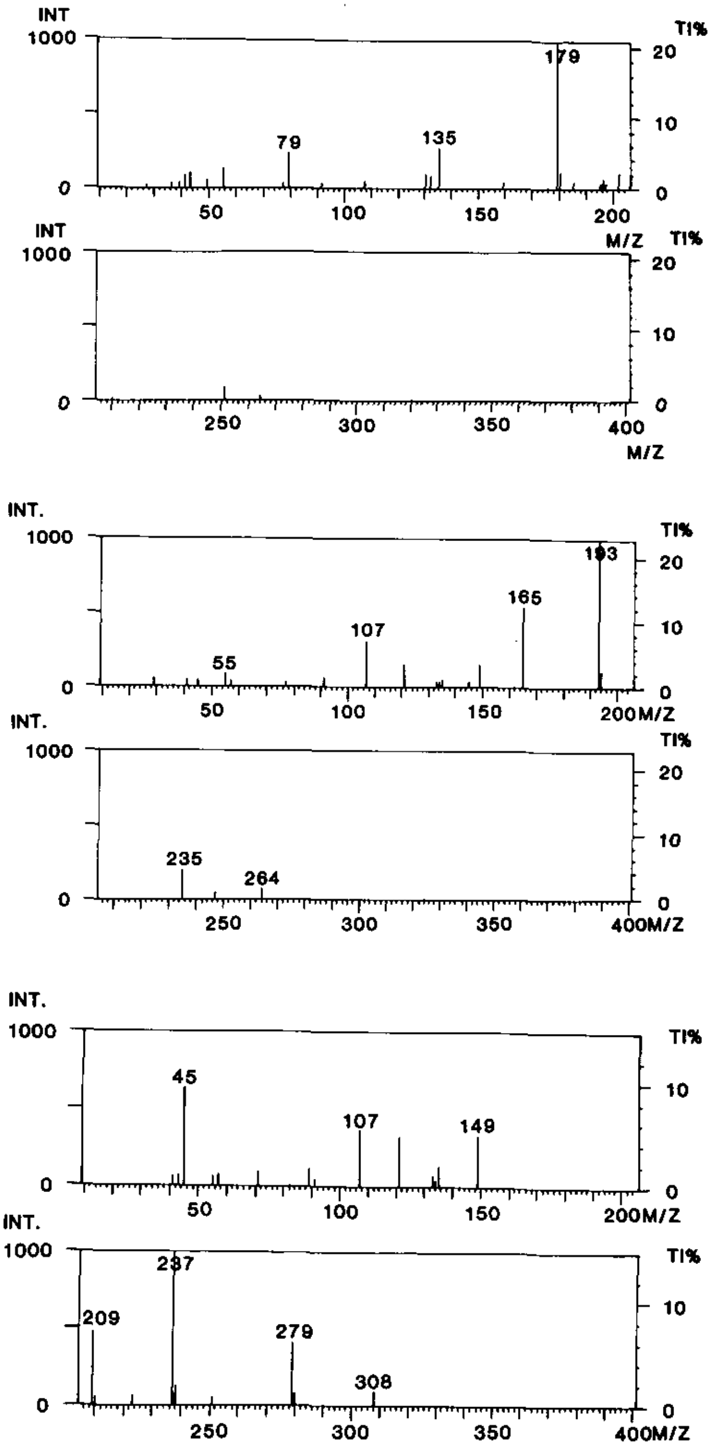

Fig. 12 Mass spectra of (a, b) nonylphenol mono- and (c) di-ethoxylate

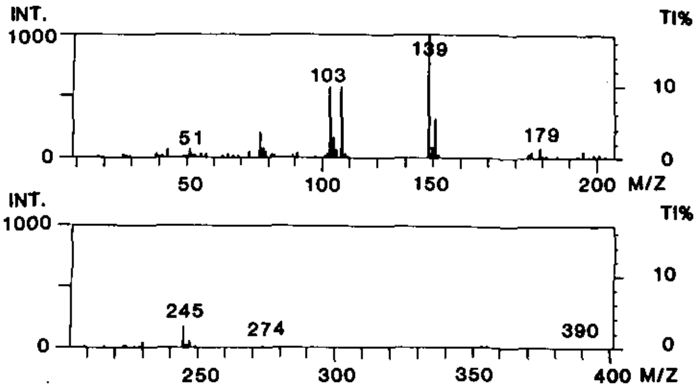

Fig. 13 Mass spectrum of unknown compound found in the effluent extract

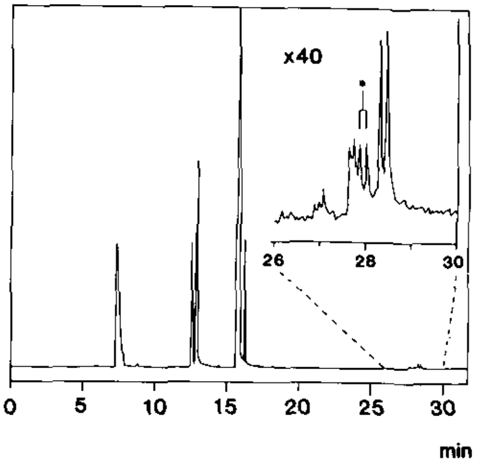

Fig. 14 Reconstructed ion chromatogram of chlorination product of styrene

unknown compounds should contain odd-numbered nitrogen atom and one chlorine atom and possible formula is $C_{14}H_{13}ClNO$ or $C_{15}H_{17}ClN$. From the consideration of the fragmentation pattern, N-methylphenyl-p-chlorobenzamide, N-(4-methyphenyl) -1-chloromethylbenzylamine were prepared as authentic standards, but both their mass spectrum and GC retention time did not match those of unknown compounds. Thus, it was considered that m/z 245 is not molecular ion and no nitrogen is contained, because an even number of fragment ions were not found in the mass spectrum. Fortunately, unknown compounds were found in the chlorination products of styrene. Fig. 14 shows an RIC chromatogram of chlorination products of styrene. Chloroethenylbenzenes and 1,2-dichloroethylbenzene were major products, and trace amounts of by-products were found from 26 to 30 minutes. Fig. 15 shows a mass

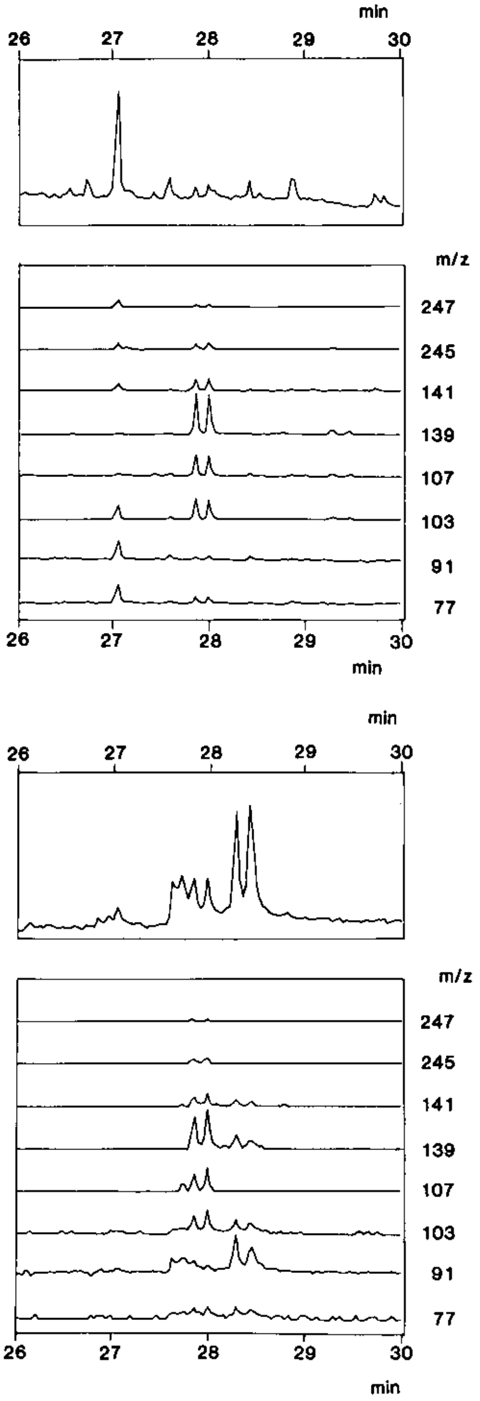

Fig. 15 Mass chromatogram of unknown compound
(a) the effluent extract: (b) the products of chlorination of styrene.

chromatogram of unknown compounds found in the extracts and by-products on the chlorination reaction of styrene. It was found that GC retention times and mass spectrum were exactly matched with each other. But the exact structure could not be determined at this stage.

4 . CONCLUSION

The analysis of hexane extractive organic compounds in the effluent of a sewage treatment plant indicated the presence of many synthetic organic compounds. Alkylphenol mono- and di-ethoxylate may be degradation products of poly (oxyethylene) alkylphenyl ethers, which are used for household detergent or pesticide emulsifier. Halogenated methoxybenzene derivatives and oxadiazon, which may be derived from agricultural run-off, were detected. Methylated triclosan may be derived from triclosan, which is used in cosmetics or detergents.

ACKNOWLEDGMENTS

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高分離能ガスクロマトグラフ／質量分析法による水中の未確認汚染物質の検索

白石　寛明[1]・大槻　晃[1]

連続液々抽出法により水中の有機化合物をヘキサン中に抽出した。抽出物をキャピラリーカラムを用いたガスクロマトグラフ質量分析法により分析した結果，ハロゲン化メトキシベンゼン，ジクロロベンゼン，ヘキサクロロシクロヘキサン，メチル化トリクロサンやオキサジアゾンなどの多くのハロゲン化有機化合物が検出され，更に，非イオン界面活性剤てして使用されているポリオキシエチレンアルキルフェニルエーテルの分解物と考えられる数種のアルキルフェノールエトキシレートの存在が明らかとなった。

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IV— 2

Analysis of Organic Substances in Soot

Akio YASUHARA[1] and Masatoshi MORITA[1]

ABSTRACT

Soot is one of important constituents in airborne particulate matter. In this study, naphthonaphthacene and nitropyrene derivative in soot were investigated from view point of carcinogenicity or mutagenicity.

Naphtho[2,1,8-*qra*]naphthacene (I), a higher homologue of benzo[*a*]pyrene, which is know to be carcinogenic, was detected in the soot from a public garbage furnace (14.9 μg/g) and from a home furnace (0.15 μg/g), both by gas chromatography-mass spectrometry and high performance liquid chromatography-fluorescence spectrometry.

1-Nitropyrene (**II**), which is found in fairly large amounts in diesel exhaust, is very mutagenic and unstable in light or heat. It was verified that a structure of a photolysis product (**III**) from **II** was 1-nitro-2-pyrenol on the basis of various spectrometric data. **III** has not been detected in the environment to date.

1 . INTRODUCTION

Although much information and many analytical methods on organic components in airborne particulate matter, soot and exhaust have already been reported[1-4], they are very complex and not fully understood. There also remain many problems as to the toxicity of these organic materials. Much attention has been paid to the carcinogenic or mutagenic compounds, but results have been clear only for several compounds including benzo[*a*]pyrene and benzo[*a*]anthracene. Therefore, it seems important to search and characterize unknown compounds in these materials in order to assess the danger to human health and to establish a monitoring system for the environment.

Soot is one of important constituents in airborne particulate matter. Many interesting compounds might exist in soot, since soot is formed during combustion process of various kinds of organic materials. The present research was undertaken on two compounds, naphtho[2,1,8-*qra*]naphthacene (I) and a derivative of 1-nitropyrene. It was of interest to determine whether **I**, a higher homologue of benzo [*a*]-pyrene, whose alternate name are naphtho[2,3-*a*]pyrene and 2,3-naphtho-1,2-

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pyrene, is carcinogenic. I, prepared by Cook and Hewett[5] firstly, showed clear carcinogenicity[6-8]. The possibility of I in airborne particulate matter was shown by Sawicki *et al.*[9,10]. Recently, Pierce and Katz[11] detected I in atmospheric aerosols by a combination of thin-layer chromatography and fluorescence spectrometry.

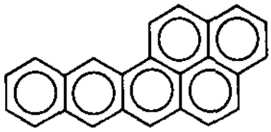
It is well known that strongly carcinogenic and mutagenic 1-nitropyrene (II) exists in diesel exhaust and airborne particulate matter[12-16]. It was confirmed that II is formed from pyrene by nitration with NO_x[17-19]. Some analytical techniques have been developed for determination of II[20-22]. Since II is fairly unstable and reactive against heat or light, it is important to know what occurs by thermolysis or photolysis and whether the reaction products are carcinogenic or mutagenic.

This report describes the determination of I in soot and the elucidation of the product from II by photolysis.

2. EXPERIMENTAL

2. 1 Synthesis of naphtho[2,1,8-*qra*]naphthacene (I)

1,2-(*o*-Phthaloyl)pyrene (3.59 g), which was prepared from pyrene according to the literature[2], was extracted from a Soxhlet apparatus into a suspended solution of $LiAlH_4$ (4.95 g) in boiling tetrahydrofuran (350 m*l*) for 17 h. The excess hydride was decomposed with moist ether (50 m*l*), and then 6M HCl solution (50 m*l*) was added. After the mixture was refluxed for 30 min to complete the decomposition, the aqueous layer was separated from the organic one and extracted several times with benzene. The combined organic layer was concentrated to dryness under reduced pressure after drying on anhydrous potassium carbonate. Deep red crystals of I (2.63 g) were obtained by a recrystallization of the crude product from benzene, yield 80.4 %. These crystals were dissolved in boiling xylene and rapidly passed through a short column of alumina (Merck) with heat in order to eliminate trace amounts of contaminants. The filtrate was recrystallized from xylene to give deep orange leaflets of I: mp 273-275°C (lit. mp[5]273°C); IR (KBr disk) 3040, 900, 880, 840, 825, 745, 740, 690, 480 cm^{-1}. Anal. Calcd. for $C_{24}H_{14}$: C, 95.33;H, 4.67. Found: C, 95.12; H, 4.71.



Naphtho[2,1,8-qra]naphthacene (I)

Scheme 1

2. 2 Extraction of PAHs in soot samples

Soot was collected from the lower part of a public garbage furnace chimney where a heavy oil had been used. Soluble matter was extracted with boiling benzene (200 m*l*) for 24 h from the soot (1.83 g), the extracts were concentrated and the precipitated matter was filtered. The filtrate was directly analyzed without separation. Another soot sample was obtained at the bottom of a home furnace chimney where firewood was burnt every day. Organic materials were extracted by the same method as described above from this soot (13.57 g). The extracts were chromatographed on alumina (Merck, 30 g). The first fraction, eluted with hexane (300 m*l*), contained mainly aliphatic hydrocarbons. All PAHs were involved in the second fraction, which was eluted with benzene (500 m*l*). The second fraction was concentrated and separated further by preparative thin-layer chromatography using silica-gel plate and a 1:1 benzene/hexane solvent. The part corresponding to **I** was scratched off and PAHs were extracted with ethyl ether. All solvents used were of pesticide grade and redistilled before use.

2. 3 Gas chromatography-mass spectrometry (GC/MS)

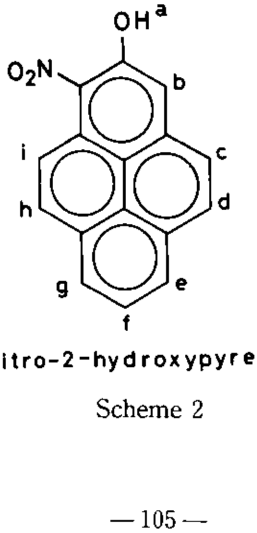
Mass spectra were measured by using a JEOL Model JMS-DX300 mass spectrometer connected with a Hewlett Packard 5710A gas chromatograph and a JEOL JMA-3500 mass data analysis system. Gas-chromatographic conditions were as follows: column, 1 % OV-1 (1 m × 3 mm i.d.); column temperature, 200°C for 2 min followed by an increase to 310°C at a rate of 8°C/min; injection temperature, 350°C; helium flow rate, 18 ml/min. Mass-spectrometric conditions were as follows: ion-source temperature, 310°C; ion-source pressure, 1×10^{-6}Torr; ionizing current, 300 μA; ionizing energy, 70 ev; accelerating voltage, 3 kV; scan range, m/z 100-400; scan speed, 1.5 s/scan; repetition time, 3.0 s.

2. 4 High performance liquid chromatography-fluorescence spectrometry (HPLC/FLS)

A Waters Model 7000A high performance liquid chromatograph was used with a HITACHI 650-10LC fluorescence detector. The operating conditions were as follows: column, μ-Bondapak C_{18} (1/8 in × 1 ft); solvent, 80:20 acetonitrile/water; flow rate, 2.0 m*l* /min: excitation wavelength, 294.4 or 335.0 nm (slit width, 10 nm); emission wavelength, 463.2 nm (slit width, 10 nm).

2. 5 Photolysis of 1-nitropyrene (II)

II (0.490 g), prepared according to the literature[23],was dissolved in acetonitrile



1-Nitro-2-hydroxypyrene (III)

Scheme 2

(1000 m*l*) and the solution was irradiated with a 400-W high-pressure mercury lamp, which emits the light of wavelength over 250 nm, under exposure to air for 5h.

2. 6 Isolation of photolysis product (III)

Reaction products were checked with thin-layer silica-gel chromatography, where the solvent was carbon tetrachloride. Two spots were observed. The spot with the Rf value of 0.42 coincided with the reference spot of **II**. A new compound (**III**) with the Rf value of 0.53 was separated from **II** by column chromatography using silica-gel (Merck, 140 g), where carbon tetrachloride was used as an elution solvent. The amount of recovered **II** was 0.282 g. Deep red needles of **III** (0.167 g), which were easily sublimated, were obtained by recrystallization from benzene: mp 227-229°C. Anal. Found: C, 72.86; H, 3.48; N, 5.20. IR, UV, mass and NMR spectra were measured with HITACHI Model 285 Grating Infrared Spectrophotometer, HITACHI Model 323 Recording Spectrophotometer, JEOL Model JMS-DX300 Mass Spectrometer and JEOL Model JNM-GX400 FT NMR Spectrometer, respectively.

3 . RESULTS AND DISCUSSION

GC/MS or HPLC/FLS is expected to be better than the previous method[11] to analize naphtho[2,1,8-*qra*]naphthacene (**I**). The mass spectrum of **I** is shown in Fig. 1. Molecular and double-charged ions were prominently observed, being a characteristic pattern of PAHs. Combination of separation technique by GC and selective detection by MS is extremely effective for the determination of **I** even in the presence of various PAHs. Mass chromatography at m/z 392, 300 and 151 was performed for identification. Typical mass chromatograms are shown in Fig. 2. The peak due to **I** appeared strongly at retention time 12.14 min in the mass chromatogram of m/z 302. It was confirmed with peak enhancement by spiking a standard sample. Also, mass spectra at the retention time corresponding to that of

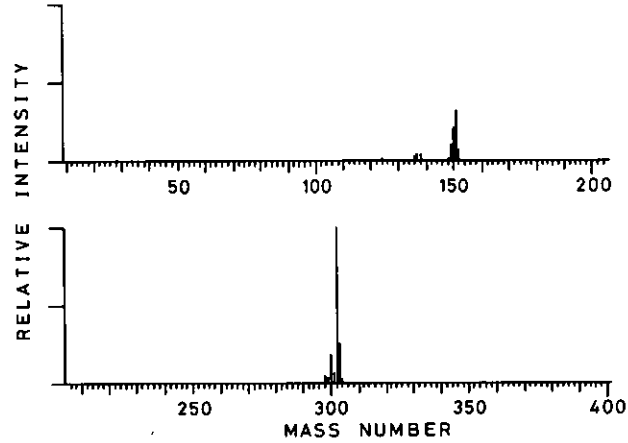


Fig. 1 Mass spectrum of naphtho[2, 1, 8-*qra*]naphthacene (**I**)

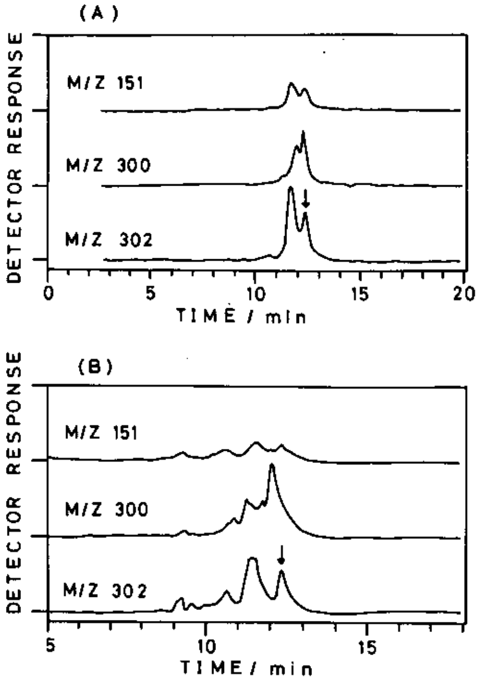


Fig. 2 Mass chromatograms of the extracts from soot samples
(A) soot from the public garbage furnace: (B) soot from the home furnace. Peaks indicated with arrow correspond to I.

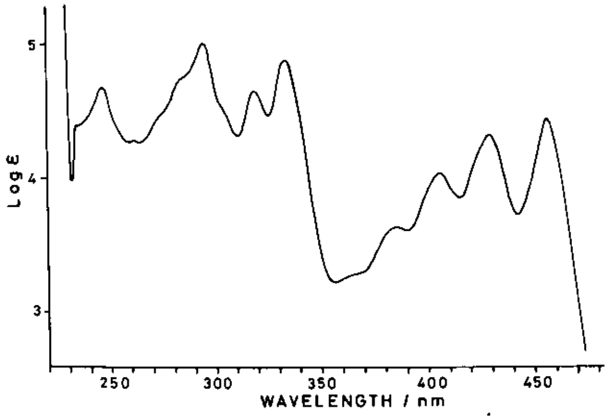


Fig. 3 Ultraviolet and visible absorption spectrum of I in tetrahydrofuran

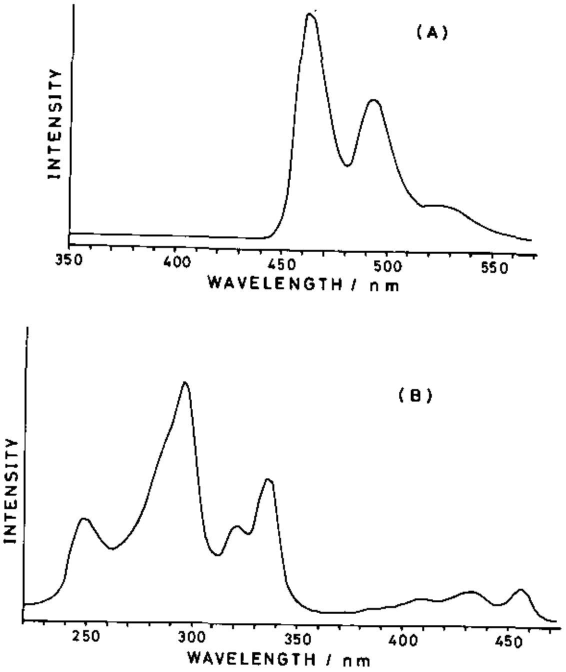


Fig. 4 Fluorescence emission spectrum (A; excitation wavelength of 294. 4 nm) and excitation spectrum (B; emission wavelength of 463. 2 nm) of **I**

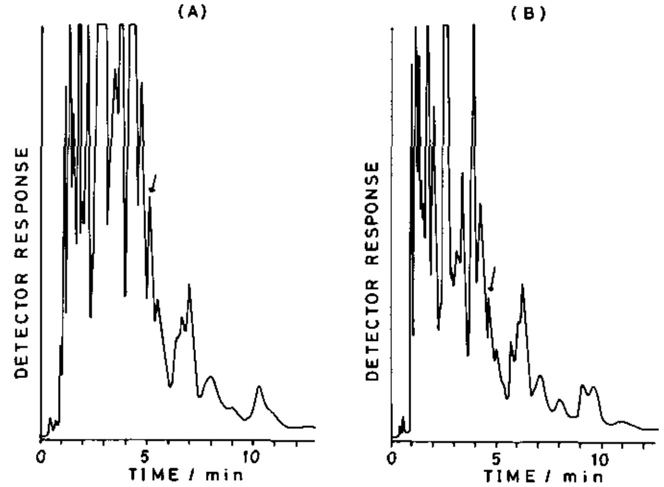


Fig. 5 High performance liquid chromatograms of soot extractsfrom the public garbage furnace with a fluorescence detection of 463 nm
(A) excitation wavelength of 294 nm: (B) excitation wavelength of 335 nm. Peaks indicated with arrow correspond to **I**.

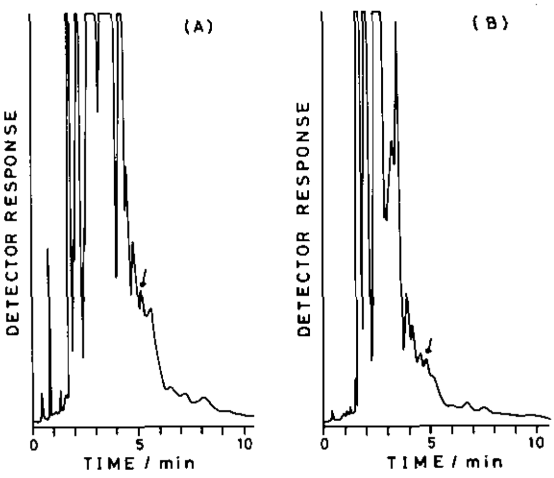


Fig. 6 High performace liquid chromatograms of soot extracts from the home furnace with the fluorescence detection of 463 nm
(A) excitation wavelength of 294 nm: (B) excitation wavelength of 335 nm. Peaks indicated with arrow correspond to I.

I agreed with the mass spectrum of a standard sample.

An ion of m/z 302 can come from $C_{24}H_{14}$(mol. wt 302) and $C_{24}H_{12}$ (mol. wt 300) species. In order to distinguish $C_{24}H_{14}$ from $C_{24}H_{12}$, a mass chromatogram at m/z 300 was needed. The major peak in the mass chromatogram at m/z 300 was assigned to coronene. Therefore, the peak of the same retention time as that of coronene in the mass chromatogram at m/z 302 was ascribed to coronene. Another small peak in the m/z 302 mass chromatogram was thought to be one of the equal molecular weight isomers of I. Pierce and Katz$^{11)}$ detected four hexacyclic compounds having the same molecular formulas of $C_{24}H_{14}$, including I, in the extracts from airborne particulate matter. The detection limit of I by GC/MS was subnanograms in the standard sample.

Further confirmation was carried out by HPLC/FLS where reverse-phase column shows high resolution and fluorescence spectrometry provides high selectivity and sensitivity for the analysis of PAHs. Ultraviolet and visible absorption spectrum and fluorescence emission and excitation spectra of I in tetrahydrofuran are shown in Fig. 3 and 4. The detection limit was estimated to be 1 pg for pure standard sample with S/N=2 by using 294- or 335-nm excitation wavelength and 463-nm emission wavelength. Figs. 5 and 6 show the chromatograms of soot samples obtained with 294- and 335-nm excitation wavelength. Peak assignment and quantification were made by the standard addition method. It is noteworthy that the chromatogram is not simple even with the high resolution (N=4500) by HPLC and selective fluorescence spectrometric detection.

Contamination in extraction and fractionation processes was not observed. Recovery from airborne particulate matter was quantitative (100.9 %). The existence of I in soot was verified both by GC/MS and HPLC/FLS methods. Analytical results by HPLC/FLS (excitation wavelength, 335 nm) were 14.9 μg/g for soot from

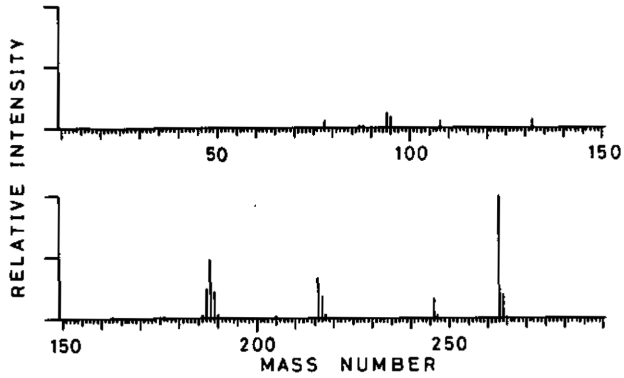


Fig. 7 Mass spectrum of photolysis product (III)

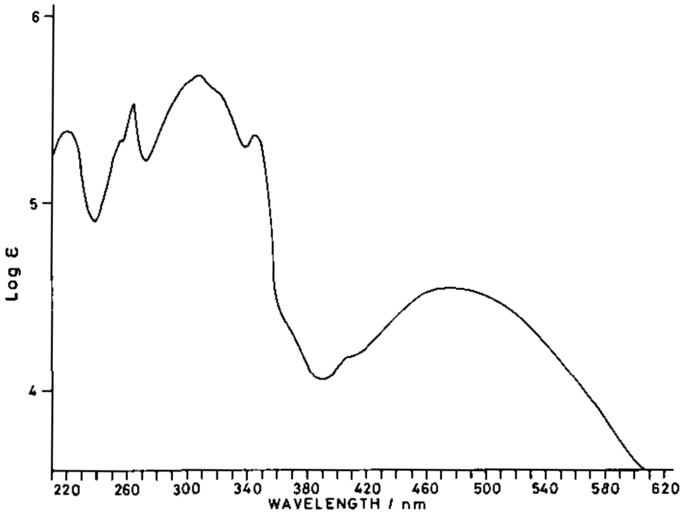


Fig. 8 Ultraviolet and visible absorption spectrum of III in tetrahydrofuran

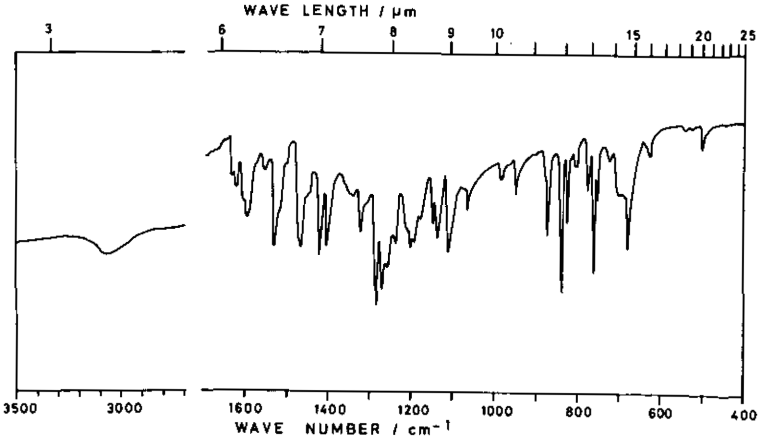


Fig. 9 Infrared absorption spectrum of III (KBr disk)

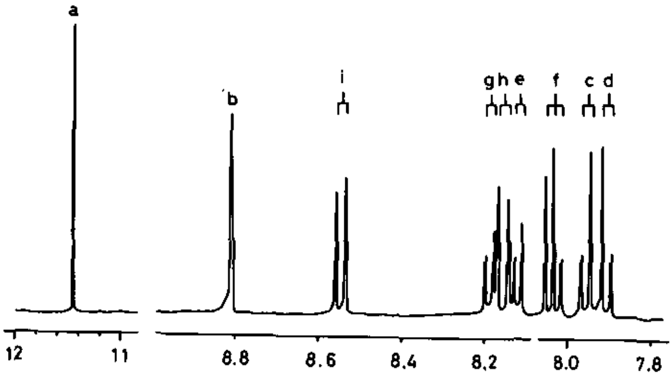


Fig. 10 400 MHz ^{1}H-NMR spectrum of III in tetrahydrofuran-d_8

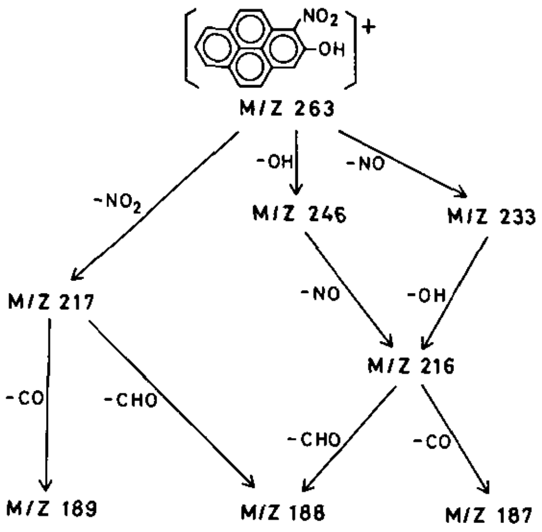


Fig. 11 Interpretation of fragmentation in mass spectrum of **III**

the public garbage furnace and 0.15 μg/g for soot from the home furnace. I was not detected in airborne particulate matter sampled near a bypass at Ohomiya nor in dust accumulated on a filter of the air-conditioner at the National Institute for Environmental Studies. Since soot is one source of environmental contamination by PAHs, further investigation is necessary to establish a routine analytical procedure and to estimate its concentration in the environment.

Photolysis product (**III**) of 1-nitropyrene (**II**) was fairly stable in light, but easily decomposed in solution by heating. **III** was converted to a dark tar-like substance by contact with active alumina. Figs. 7, 8, 9 and 10 show mass, ultraviolet and visible, infrared and 400 MHz ^{1}H-NMR spectra, respectively. The molecular

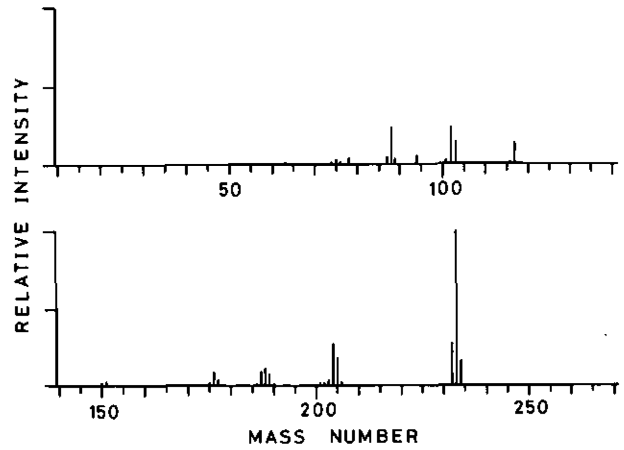


Fig. 12 Mass spectrum of reduction product of **III**

formula of **III** was suggested to be $C_{16}H_9NO_3$ based on element analysis. This estimation was assured by interpretation of mass spectrum. Molecular ion was observed at m/z 263, and the number of carbon atoms in a molecule of **III** was calculated to be 16, based on isotopic ratio at m/z264 vs. 263. The mass spectrum was interpreted as shown in Fig. 11. The presence of nitro group was also demonstrated by infrared spectrum.

It was very significant for the structural elucidation that the Rf value of **III** was higher than that of **II** in thin-layer chromatography and that there was a bathochromic shift in the UV spectrum of **III**. These facts agreed with vicinal position of the nitro and hydroxyl groups. The ^{1}H-NMR spectrum was interpreted as shown in the scheme. Further confirmation was carried out by means of reduction of **III** with hydrogen and palladium/charcoal at room temperature for 10 min. The mass spectrum of the reduction product is shown in Figure 12. Isotopic ratio of peaks at m/z 234 vs. 233 and fairly strong peak at m/z 232 indicated that this product was 1-amino-2-pyrenol. On the basis of these results and estimations, **III** was determined to be 1-nitro-2-pyrenol.

A few trials to detect **III** in airborne particulate matter and soot were unsuccessful because no suitable analytical method was available. Adsorption or thermal decomposition of **III** in GC/MS was observed and **III** did not show strong fluorescence in HPLC/FLS.

Since intropyrenols are anticipated to show greater carcinogenicity than nitropyrene[24)], it is of great interest to study **III** for its possible mutagenicity. According to the experiments by Löfroth *et al.*[25)], mutagenicity of **III** has been similar to that of benzo[*a*]pyrene. The determination of **III** in the environment will be the next subject for study.

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すす中の有機物質の分析

安原昭夫[1]・森田昌敏[1]

大気粉じんの重要なひとつであるすすに関連して，発がん性あるいは変異原性を有するナフトナフタセン及びニトロピレンを研究した。

ベンゾ［*a*］ピレンの高級同族体であるナフト〔2,1,8-*qra*〕ナフタセン(I)は発がん性を有することが既に確かめられている。この研究ではガスクロマトグラフィー質量分析法及び高速液体クロマトグラフィーけい光分光法を用いて，ゴミ焼却場及び家庭のかまどの煙突から採取したすすから，14.9及び0.15μg/gのIを検出した。

ディーゼルエンジンの排ガス中にかなり含まれている1-ニトロピレン(II)は強い変異原性を有する化合物で，光や熱に対して不安定であると言われている。この研究ではアセトニトリル中，IIに光を照射したときの生成物が1-ニトロ-2-ピレノール(III)であることを機器分析により決定した。現在，環境中からIIIは検出されていない。

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V. Highly Sensitive Methods for Trace Pollution Analysis

Res. Rep. Natl. Inst. Environ. Stud., Jpn., No. 79, 1985.

V－1

Determination of Ultratrace Polycyclic Aromatic Hydrocarbons in the Water of Lake Mashu with HPLC/Time-resolved Fluorometry

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ABSTRACT

By replacing the Xe lamp of a conventinal fluorometer with a N_2 laser-pumped dye laser as an excitation source, a time-resolved fluorescence measurement system was developed. The measurement system was used as a detector for high performance liquid chromatography (HPLC).

A detection limit, which is defined as the amount to produce a signal three times the standard deviation of the background noise, of 180 fg was achieved for benzo[*a*]pyrene. The measurement precision was 3.9%. The developed instrument was applied to the determination of ultratrace polycyclic aromatic hydrocarbons (PAHs) in the water of Lake Mashu.

After allowing for extraction efficiency, analytical results of 0.009 ng/*l*, 0.007 ng/*l*, and 0.014 ng/*l* were obtained for benzo[*k*]fluoranthene, benzo[*a*]-pyrence, and benzo[*ghi*]perylene, respectively.

1. INTRODUCTION

Some polycyclic aromatic hydrocarbons (PAHs) are known to be mutagenic and carcinogenic[1)]. Biosynthesized by plants and soil bacteria, they are also produced in high temperature reactions of forest fires and volcanic activities. On the other hand, far greater quatities of PAHs originating from man-induced combustion processes are released to the atmosphere. A significant proportion of PAHs, formed by either natural sources or human activities, is decomposed by photo-oxidation. However, some PAHs, which are not decomposed, contaminate the upper layers of the earth, where fallout of PAHs occurs. Some of this fallout will be carried to rivers, lakes, and, eventually, oceans[2)]. Until the beginning of the present century, a natural balance between formation and degradation of PAHs ensured a low and constant natural background concentration. However, with increasing industrial development, the PAHs originating from human activities have disturbed the balance,

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leading gradually to increased environmental concentrations[3]. The PAH concentrations can be used as an indication of the pollution existing in a given district. In such cases, the concentrations of PAHs existing under natural conditions are used as the background level of PAHs. According to recent reviews concerning PAHs in the aquatic environment[4,5], the PAH concentration in unpolluted water can be estimated to be less than 1 ng/l (ppt). To deternine such low PAH levels, improved analytical methods are necessary[6].

A fluorescence measurement system utilizing a pulsed laser has been developed for extremely sensitive detection of PAHs. There is no doubt that laser fluorometry has a big advantage with respect to sensitivity in the determination of PAHs at ultratrace levels. However, even more selectivity is necessary when the laser fluorometry is applied to measure PAHs in environmental samples. In recent years, together with gas chromatography (GC), the technique for separation of PAHs with high-performance liquid chromatography (HPLC) has been improved[7], and separation with HPLC has been widely applied to the determination of PAHs in the aquatic environment[8,9]. The use of lasers as a detection system for HPLC is generating great interest[10,11]. Diebold and Zare[12] have succeeded in obtaining a detection limit (S/N = 2) of 750 fg for aflatoxin, and Folestad *et al.*[13] have established a minimum detection limit (S/N = 10) of 20 fg for fluoranthene by utilizing HPLC separation followed by CW laser-induced fluorescence detection. A major shortcoming of these fluorometers is less flexibility in wavelength selection due to a CW laser. Tunability is much larger with a pulsed laser through a wider selection of both dyes and doubling crystals. In this study, time-resolved fluorometry based on a pulsed laser was used as a detection system for HPLC.

2 . EXPERIMENTAL SECTION

2.1 Instrumentation

A block diagram of the instrument is shown in Fig. 1. The pumping source of the dye laser was a Molectron Model UV-14 nitrogen laser. The peak power and the pulse duration of the N_2 laser were 425 kW and 10 ns, respectively. It was operated at a repetition rate of 16 Hz. The dye laser used was a Molectron Model DL14. The two dyes used for tuning the laser were PBD [2-(1,1'-biphenyl)-4-yl-5-phenyl-1,3,4-oxadiazole]and BBQ[4,4'''-bis[(2-butyloctyl)oxy]quaterphenyl], respectively, for the 360-386 nm and 373-399 nm wavelength regions. The energy of the dye laser measured with a Molectron J3 pyroelecric joulmeter was 0.4 mJ at 366 nm and 0.96 mJ at 386 nm. A small portion of the N_2 laser beam was detected by a photodiode to provide a trigger pulse for a digital boxcar integrator (Model BX-531, NF Circuit Design Block Co., Japan). The laser-induced fluorescence was collected at right angles to the laser beam and was dispersed by a monochromator with a Rowland circle of 15 cm diameter. A side-on photomultiplier (Hamamatsu R446) with base wiring modification[14] was employed at an applied voltage of 1 kV with a Model PH-7A (Japan Electronic Measuring Instrument Co., Japan) power supply. The fluorescence signal was delayed for 150 ns by a Tektronix Model 7M11 delay line to circumvent the inherent boxcar gate pulse delay (150 ns for the digital boxcar used), and then fed into the digital boxcar. The digital boxcar enables measurement of the fluorescence signal during the gate width with an appropriate

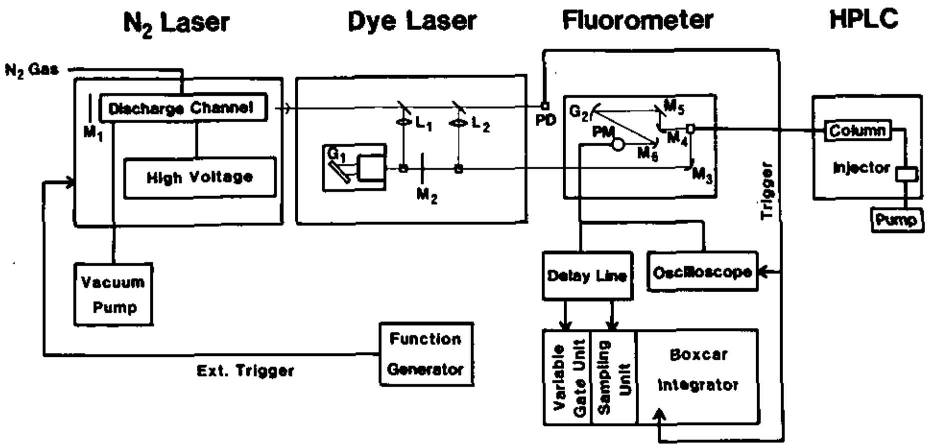

Fig. 1 Laser-induced fluorescence measurement system in conjunction with HPLC
M_1, mirror for N_2 laser ; M_2, mirror for dye laser ; M_3 and M_4, toroidal mirrors ; M_5, plain mirror ; M_6, spherical mirror ; L_1 and L_2, cylindrical lenses ; G_1, ruled grating ; G_2, concave grating ; PM, photomultiplier ; PD, photodiode.

delay time after the trigger pulse is acquired. There are two gate units: a Tektronix S-5 sampling head unit which has a fixed gate width of 1 ns, and a NF Circuit Design Block variable gate unit whose gate width range is 10 ns to 5 ms. In this experiment, the quantitative measurement of PAHs was carried out with a gate width of 10 ns.

The HPLC consisted of a Waters Associates Model M-6000 liquid chromatograph pump and Model U6K injector. The column used was a Waters Associates Radialpak A (8 mm×10 cm) and μBondapak C_{18} (4 mm×30 cm). The sample chamber consisted of a Model FP-1030 (Japan Spectroscopic Co., Japan) flow cell system. The active volum of the flow cell was 15 μl.

2.2 Sampling

Lake Mashu is situated in the northern part of Japan; it has the highest recorded value of transparency depth (41.6 m) in the world. There is no river flowing into it and no road near the lake, so it is little exposed to the effects of human activies. A special device was constructed to collect water samples of Lake Mashu directly into a 3 *l* separating funnel. The water sample was collected at a depth of 5 m in the center of the lake on Sept. 9, 1982.

2.3 Extraction procedures

The water sample of 2 *l* was placed in a 3 *l* separating funnel, and 100 m*l* of redistilled cyclohexane was added as an extraction solvent, at the shore of Lake Mashu. The separating funnel was fixed in a rugged, lighttight box, and brought back to the laboratory by car. In fact, the funnel had been thoroughly shaken during transport for 6 days until the extraction procedure could be conducted in the laboratory. After the separating funnel was shaken for 30 min by a shaker, the emulsion was allowed to stand for 1 day. The cyclohexane layer was collected into a 200 ml distilling flask through a prewashed anhydrous sodium sulfate layer. After the cyclohexane layer was separated, the separating funnel was rinsed with 20 ml of redistilled cyclohexane. The combined cyclohexane solutions were evaporated to small volume by distillation in a rotating evaporator. The concentrated solution was transferred to a 10 ml Kuderna-Danish tube. After the solution was transferred, the 200 ml distilling flask was rinsed with 5 ml of redistilled cyclohexane. The combined cyclohexane solutions were evaporated to dryness and 0.5 ml of acetonitrile was added. For the extraction procedure blank, 100 ml of redistilled cyclohexane was added to a 3 l separating funnel without a water sample, and the same extraction procedures as described above were conducted. For the extraction procedure, 125 ml of redistilled cyclohexane was used. Therefore, in order to check the solvent blank, 125 ml of redistilled cyclohexane was evaporated to dryness and dissolved in 0.5 ml of acetonitrile.

2.4 Recovery

For the recovery experiment of PAHs at ultratrace levels, organically free water was prepared. Distilled water was purified by the Millipore Corp. Milli-Q system equipped with two ion-exchange resin cartridges (Ion-Ex) and one activated carbon cartridge (Organex-Q). The water so collected was passed through a trace organic removal cartridge (Millipore Norganic) and then filtered under vacuum through a Nucleopore 1 μm filter. The NBS Standard Reference Material (SRM 1647), which contained 16 PAHs at μg/ml levels in acetonitrile, was used for the recovery experiment. Two liters of the organically free water was taken in a 3 l separating funnel, and a 1 ml portion of SRM 1647 acetonitrile solution diluted by a factor of 25000 was added. The separating funnel was then shaken continuously for 1 day to mix thoroughly. In order to reproduce the analytical conditions used for the Lake Mashu water sample, the separating funnel was allowed to stand for 6 days after the addition of 100 ml of redistilled cyclohexane. The subsequent extraction procedures were also the same as those used for the Lake Mashu water sample.

2.5 Reagents and glassware

Ethanol and acetonitrile used in this experiment were purchased from Wako Pure Chemical Industries, Ltd. The former was guaranteed reagent grade and the latter was a guaranteed grade for the analysis of pesticides. They were used without further purification. Cyclohexane was ultraviolet spectrometric grade obtained from Wako Pure Chemical Industries, Ltd. and was distilled twice at 26 °C under vacuum in a rotating evaporator. Anhydrous sodium sulfate was also obtained from Wako Pure Chemical Industries, Ltd., and was fluorescence spectrometric grade. All PAH compounds were obtained from commercial sources and used without further purification; naphthalene, phenathrene, acenaphthene, acenaphthylene, anthracene, pyrene, benz[*a*]anthracene, benzo[*a*]pyrene, and dibenz[*a,h*]anthracene (all from Wako Pure Chemical Industries, Ltd.), fluorene, fluoranthene, triphenylene, chrysene, and perylene (all from Nakarai Chemicals, Ltd.), benzo[*b*]fluoranthene, benzo[*j*]fluoranthne, and benzo[*k*]fluoranthene (all from P. K. Chemical, Ltd.), benzo[*e*]pyrene and benzo[*ghi*]perylene (all from Aldrich Chemical Co., Ltd.), and indeno [1,2,3-*cd*] pyrene (Tokyo Kasei Kogyo Co., Ltd.).

All glassware was cleaned with acetone and detergents, and then thoroughly rinsed with distilled water. The cleaned glassware remained in contact with a solution of potassium dichromate for more than 1 week, and prior to use was rinsed with deionized and redistilled water.

3. RESULTS AND DISCSSION

3.1 Time-resolved fluorometry as a detection system for HPLC

Time-resolved fluorescence chromatograms obtained at different delay times are shown in Fig. 2. The NBS standard (SRM 1647) was diluted with acetonitrile by a factor of 250, and 25 μl of the solution was injected into the HPLC column. The separation of PAHs was performed by a Radialpak A column with the use of isocratic elution (80% acetonitrile in water) at a flow rate of 3.0 ml/min. By use of a PBD dye, a tuned dye laser irradiated the eluent at 366 nm, and the induced fluorescence was measured at 403 nm. With a delay time from 0 ns to 10 ns after excitation, strong base line drift results from drift of stray light, Raman scattering, and short-lived fluorescence from the HPLC eluent. With a delay time from 20 ns to 30 ns, the baseline drift decreased, and the chromatogram with the best S/N ratio was obtained. After 40 ns delay, the S/N ratio decreased because the fluorescence intensity decreased. With a delay time adjusted from 0 ns to 20 ns, the chromatogram peak observed at a retention time of 3.8 min is assigned to anthracene. Since anthracene has a relatively short fluorescence lifetime of 4.9 ns[15], the fluorescence is greatly reduced in magnitude after a 30 ns delay. It is clear from Fig. 2 that even with the moderate gate width of 10 ns, short-lived PAHs can be distinguished from long-lived PAHs. However, more precise separation of PAHs by using the lifetime difference requires the improvement of time resolution of the total system. Imasaka

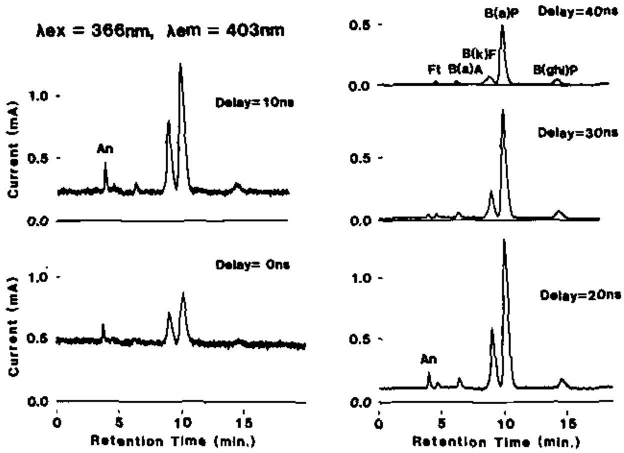

Fig. 2 Liquid chromatograms for a mixture of 16 PAHs (SRM 1647) with time-resolved fluorometry
Chromatographic conditions were as follows : Radialpak A column ; 80 : 20 (v/v) acetonitrile-water ; flow rate, 3.0 ml/min. Fluorescence detection conditions were as follows : bandwidth, 5 nm ; time constant, 1 s.

et al.[16] constructed a transversely excited atmospheric-pressure N_2 laser and achieved a time resolution of 1.4 ns by using a subnanosecond tunable dye laser as an excitation source, a subnanosecond response photomultiplier, and a sampling oscilloscope with a bandwidth of 1 GHz.

Optimum operating conditions for the determination of B(*a*)P were determined by changing parameters such as the delay time, the column, the dye, the time constant of the boxcar integrator, and the bandwidth of the monochromator. Compared with a Radialpak A column, μBondapak C_{18} column gave poorer separation performance for B(*a*)P and B(*k*)F, but it was nevertheless used for the PAH separation because the fluorescence signal was twice as large due to a lower flow rate. As the pulse energy of a BBQ dye is higher than that of a PBD dye, the detection capability was improved by using a BBQ dye. Detection limits of B(*a*)P were obtained by optimizing the time constant of the boxcar integrator and the bandwidth of the monochromator. Table 1 summarizes the detection limits obtained by a cuvette cell and a flow cell, respectively. The detection limits were improved by increasing the bandwidth from 5 nm to 10 nm, and were almost inversely proportional to the square root of the time constants. When a cuvette cell is used, a fast response is not required because the sample concentration does not change rapidly with time. Therefore, lower detection limits can be obtained by increasing the time constants. Detection of 0.003 ng/m*l* of B(*a*)P could be achieved with a S/N ratio of better than 2. The detection limit was improved by 1 to 2 orders of magnitude as compared with that of a conventional fluorometer equipped with a Xe lamp[17]. On the other hand, when a flow cell is used, reasonably fast response is required to follow the sample change. When isocratic elution was used at a flow rate of 0.8 m*l*/min, the flourescence response was too slow with the time constant of 16 s. Therefore, the time constant of 4 s was used. Although lower detection limits can be achieved by increasing the injection volume, excessive injection results in decreased column efficiency. Comparison of the detection limits obtained by the cuvette cell with those obtained by the flow cell indicates that the sample dilution factor due to

Table 1 Comparison of detection limits (S/N = 2) of B(*a*)P obtained by using a cuvette cell and a flow cell (ng/m*l*)

	cuvette cell		flow cell		
injection volume			25 μl		50 μl
bandwidth (nm) λ_{em} (403 nm)	5	10	5	10	10
time constants (s)					
0.25	0.043	0.033	0.168 (4.2pg)$^{a)}$	0.100 (2.5pg)$^{a)}$	0.055 (2.7pg)$^{a)}$
1	0.020	0.014	0.065 (1.6pg)$^{a)}$	0.045 (1.1pg)$^{a)}$	0.030 (1.5pg)$^{a)}$
4	0.009	0.005	0.035 (0.9pg)$^{a)}$	0.033 (0.8pg)$^{a)}$	0.015 (0.75pg)$^{a)}$
16	0.008	0.003	——$^{b)}$	——$^{b)}$	——$^{b)}$

a) Values in parentheses represent the injected amount of B(*a*)P.

b) Fluorescence response was too slow with the time constant of 16 s.

the mobile phase is 4 to 5 with an injection volume of 25 μl, and 2 to 3 with an injection volume of 50 μl.

Under optimun operating conditions for B(*a*)P, the linearity of the instrument was checked. As shown in Fig. 3, a linear dependence between fluorescence intensity and concentration extends over 2 orders of magnitude. The chromatogram obtained at the lowest concentration is shown in Fig. 4. If the detection limit is defined as the amount which produces a signal equivalent to twice the noise (S/N=

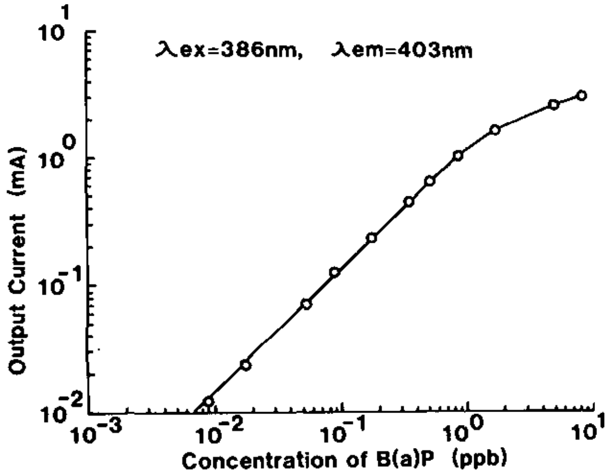

Fig. 3 Linearity of HPLC/time-resolved fluorometry
Chromatographic conditions were as follows : μBondapak C_{18} column ; 80 : 20 (v/v) acetonitrile-water ; flow rate, 0.8 ml/min. Fluorescence detection conditions were as follows : bandwidth, 10 nm ; time constant, 4 s.

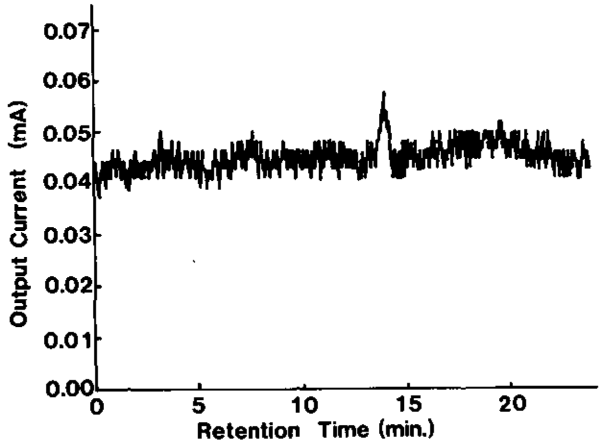

Fig. 4 Time-resolved fluorescence chromatogram for the injection of 50 μl of 0.0088 ng/ml B(*a*)P (440 fg)
Chromatographic and fluorescence detection conditions were the same as in Fig. 3.

2), a detection limit is 750 fg for B(*a*)P, while a detection limit of 180 fg can be achieved if it is defined as the amount which produces a signal three times the standard deviation of the background noise (3σ). Richardson *et al.*[18] obtained detection limits ($S/N=2$) of 10 pg and 4 pg for fluoranthene and pyrene, respectively. The detection limits are almost the same as those obtained in this work when molar absorptivities and quantum yields of the PAHs are considered. The measurement of 2.65 pg of B(*a*)P by HPLC was repeated seven times. The measurement precisions expressed by % relative standard deviations (RSD) were 0.37% and 3.9% for the retention time and the fluorescence intensity, respectively.

3.2 Determination of B(*a*)P in the NBS standard

The 16 PAHs in the SRM 1647 and the other 4 PAHs commonly encountered in the aquatic environment[19] were chosen and standard solutions of the 20 PAHs were prepared by dissolving the PAHs in acetonitrile. Excitation and fluorescence spectra for the 20 PAHs were measured by a Xe lamp, and optimum excitation and fluorescence wavelengths were determined for each PAH. Table 2 shows retention times and relative fluorescence intensities for the 20 PAHs together with the

Table 2 Retention time and relative fluorescence intensity obtained under optimum conditions for each PAH

No.	compound	abbreviation	λ_{ex} (nm)	λ_{em} (nm)	retention time (min)	rel fluoresc. intens
1	naphthalene[a]	Nph	276.4	334.7	5.68	0.063
2	fluorene[a]	Fl	266.0	303.0	6.70	0.63
3	phenanthrene[a]	Phe	268.6	304.0	6.72	0.12
4	acenaphthene[a]	Ace	689.6	323.0	6.80	0.17
5	acenphthylene[a]	Act	288.7	336.4	6.88	0.0064
6	anthracene[a]	An	251.2	400.5	7.40	0.75
7	fluoranthene[a]	Ft	284.0	467.1	8.44	0.092
8	pyrene[a]	Py	333.0	373.0	8.80	0.27
9	triphenylene	Tr	285.5	353.1	9.68	0.036
10	chrysene[a]	Chy	267.1	381.8	9.99	0.32
11	benz[*a*]anthracene[a]	B(*a*)A	286.0	387.0	10.15	0.55
12	benzo[*b*]fluoranthene[a]	B(*b*)F	298.5	428.6	12.34	0.16
13	benzo[*e*]pyrene	B(*e*)P	329.5	397.2	12.42	0.085
14	perylene	Per	407.0	437.0	12.48	2.8
15	benzo[*j*]fluoranthene	B(*j*)F	408.2	437.9	12.66	0.10
16	benzo[*k*]fluoranthene[a]	B(*k*)F	306.5	410.0	12.84	1.85
17	benzo[*a*]pyrene[a]	B(*a*)P	382.5	404.6	13.41	1.00
18	dibenz[*a*,*h*]anthrancene[a]	D(*a*,*h*)A	395.5	395.0	15.03	0.43
19	indeno[1,2,3-*cd*]pyrene[a]	IP	379.4	503.0	16.68	0.049
20	benzo[*ghi*]perylene[a]	B(*ghi*)P	381.0	406.4	17.28	0.17

a) Represents 16 PAHs contained in the NBS standard (SRM 1647).

abbreviations used in the present study and the optimum wavelengths. The relative fluorescence intensities listed in the last column were calculated by reference to B(*a*)P and obtained without correction for the wavelength dependence of the Xe lamp intensity and the photomultiplier sensitivity. The relative fluorescence data imply that Per and B(*k*)F will give lower detection limits than B(*a*)P due to high molar absorptivities and high quantum yields. The excitation and fluorescence spectra and retention times listed in Table 2 provided useful information for the assignment of chromatogram peaks.

In order to evaluate the accuracy of the instrument, SRM 1647 was diluted with acetonitrile by a factor of 12500, 25000, and 50000, and B(*a*)P in those samples was quantitatively analyzed as unknown samples. Fig. 5 shows the time-resolved fluorescence chromatograms obtained by injecting 50 *μl* of the diluted NBS standard (SRM 1647) into the HPLC column. The concentration of B(*a*)P in the diluted NBS standard was determined using the analytical curve shown in Fig. 3. The data summarized in Table 3 attest to the accuracy of the developed instrument. There is excellent agreement of the determined values with the certified NBS values.

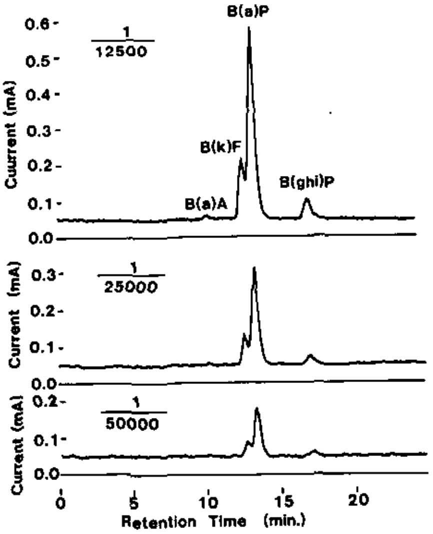

Fig. 5 Time-resolved fluorescence chromatograms for the diluted NBS standard (SRM 1647)
Chromatographic and fluorescence detection conditions were the same as in Fig. 3.

Table 3 B(*a*)P concentration of the NBS standard

	concentration (ng/m*l*)	
SRM 1647	determined	certified
1/12500	0.43	0.424
1/25000	0.21	0.212
1/50000	0.10	0.106

3.3 Determination of PAHs in water of Lake Mashu

Time-resolved fluorescence chromatograms for the sample extracted from the water of Lake Mashu were obtained by injecting 50 μl of the extract into the HPLC column. The measurement of the chromatograms was performed under optimum operating conditions for B(*a*)P. Four extraction experments were carried out independently, and the chromatograms obtained are shown in Fig. 6 as well as those obtained by blank experiments. The chromatogram peak observed at a retention time of 5.42 min is due to impurity found in anhydrous sodium sulfate. Assignment of the other peaks was performed by means of the excitation and fluorescence spectra, and retention times for the 20 PAHs listed in Table 2. The concentration of B(*a*)P was determined using the analytical curve shown in Fig. 3, and the concentrations of B(*k*)F and B(*ghi*)P were derived from chromatograms for the diluted NBS standard shown in Fig. 5. Table 4 summarizes the analytical results for 3 PAHs present in the water of Lake Mashu, as well as the retention times for each chromatogram peak. These times are shorter than those obtained earlier (Table 2) due to slight deterioration of column performance with time. The % relative standard deviation of the four extraction experiments were 32%, 18%, and 32% for B(*k*)F, B(*a*)P, and B(*ghi*)P, respectively. The blank of extraction procedures is equivalent to the concentration of 0.004 ng/*l*, 0.003 ng/*l*, and 0.010 ng/*l* for B(*k*)F, B(*a*)P, and B(*ghi*)P, respectively. Therefore, the concentration of PAHs determined in the water of Lake Mashu corresponds to about twice the blank.

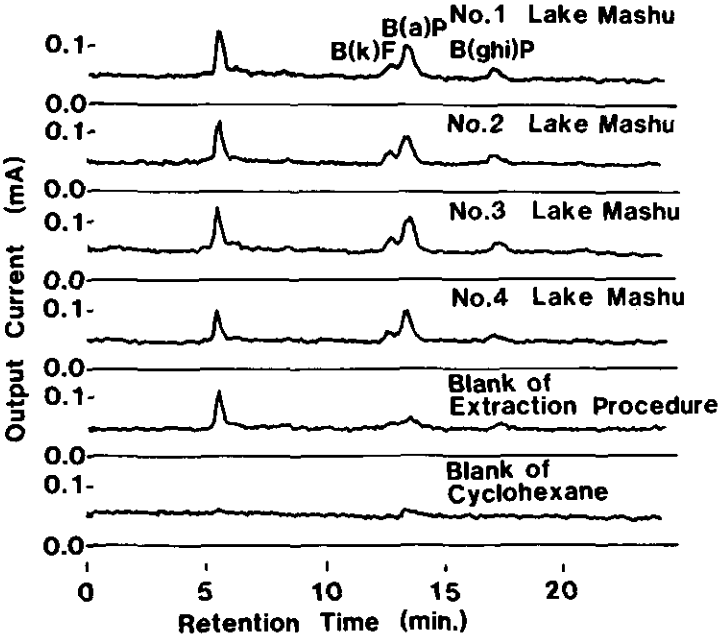

Fig. 6 Time-resolved fluorescence chromatograms for the samples extracted form Lake Mashu and the blanks
Chromatographic and fluorescence detection conditions were the same as in Fig. 3.

Table 4 Analytical results of PAHs in water of Lake Mashu (without correction for extraction efficiency)

	retention time(min)	B(*k*)F (ng/*l*)	retention time(min)	B(*a*)P (ng/*l*)	retention time(min)	B(*ghi*)P (ng/*l*)
standards	12.6±0.07		13.36±0.20		17.05±0.06	
No. 1	12.64	0.0078	13.35	0.0064	17.02	0.020
No. 2	12.66	0.0088	13.36	0.0049	17.08	0.013
No. 3	12.70	0.012	13.48	0.0074	17.17	0.015
No. 4	12.56	0.0055	13.34	0.0056	17.10	0.009
av		0.0085		0.0061		0.014
RSD		32%		18%		32%

Table 5 Extraction efficiency of PAHs spiked in 2*l* water

	0.20ng B(*k*)F spiked		0.21ng B(*a*)P spiked		0.16ng B(*ghi*)P spiked	
	found(ng)	yield(%)	found(ng)	yield(%)	found(ng)	yield(%)
No. 1	0.18	90	0.18	84	0.10	63
No. 2	0.18	87	0.17	80	0.13	81
No. 3	0.21	103	0.20	96	0.21	128
No. 4	0.21	104	0.21	96	0.20	126
av	0.19	96	0.19	89	0.16	100
RSD		9.2		9.7		33
blank	0.028		0.020		0.130	

The reliability of analytical results at ultratrace levels depends on the extraction efficiency. The extraction efficiency has been determined at about 100 times higher concentration than the analytical value because it is very difficult to remove trace organics from water[20]. Extraction efficiencies obtained by using the organically free water are summarized in Table 5. The recovery experiment was conducted at about 10 times higher concentration than the analytical value of Lake Mashu. Four recovery experiments were carried out independently, and the % relative standard deviations of 9.2%, 9.7%, and 33% were obtained for B(*k*)F, B(*a*)P, and B(*ghi*)P, respectively. The poorer relative standard deviation for B(*ghi*)P results from the blank contained in the organically free water.

Table 6 summarizes literature values for B(*a*)P measured in various lake waters. B(*a*)P present in lake water has seldom been determined, so few data have been published to date. Lake Erie is one of the Great in the U.S.A. and is contaminated with industrial discharge. A concentration of 0.3 ng/*l* of B(*a*)P has been found in its waters[21]. Basu and Saxena[21] considered that the low level of B(*a*)P obtained may be traced to the fact that sampling was undertaken in a severe snowstorm period. Lake Constance, which is situated between West Germany and Switzerland,

Table 6 Concentration ranges of B(a)P in various lake waters

	B(a)P (ng/l)	sampling volume (l)	date
Lake Erie[a), at Buffalo, USA	0.3	30	12-1976
Lake Boden[b), GFR (Lake Constance)	1.3	500	5-1964
Lake Zürich[c), Switzerland			
lake surface	0.5-5.4		1970-1976
30-m depth	0.4-1.5		1970-1979
Zhizhitskoe Lakes[d) at Pskov, USSR	0.01-0.1		1971
Lake Mashu[e), Japan	0.007	2	9-1982

a) Cited from Ref. 21, b) Cited from Ref. 22, c) Cited from Ref. 23, d) Cited from Ref. 24, e) This work

is famous for sightseeing. The lake water has been found to contain 1.3 ng/l of B(a)P[22). Borneff and Kunte[23) investigated Lake Zürich at weekly intervals from 1970 to 1979. The concentration of B(a)P ranged from 0.5 to 5.4 ng/l for the lake surface and from 0.4 to 1.5 ng/l for the 30-m depth. The highest concentrations always occurred in the first months of the year, presumably due to the snow melting in the Alps.

Pskov, which is located 160 miles south from Leningrad, is the least polluted region in the USSR. Less than 0.01-0.1 ng/l of B(a)P has been reported by Russian workers[24) as the background level of B(a)P. The data of Lake Mashu (0.007 ng/l) are analytical results obtained from this study after correction for extraction efficiency. It should be noted that the sampling volume has a big influence. Analytical procedures for the data of Pskov were not described in detail, but for the others the data were obtained with conventional fluorometry except for Lake Mashu. When conventional fluorometry was used, a large sample volume of 30 or 500 l was necessary to extract a detectable amount of B(a)P. In this work, the detection capability is improved by 1 to 2 orders of magnitude by replacing the Xe lamp with the pulsed laser, so that the required sample volume is reduced to 2 l. A small sample volume makes the analytical procedures simple and enables PAHs at ultratrace levels to be determined more precisely.

4 . CONCLUSIONS

It has been verified that time-resolved fluorometry based on a pulsed laser in conjunction with HPLC provides not only high sensitivity but also high selectivity for the determination of PAHs. By utilizing HPLC/time-resolved fluorometry, a detection limit of 180 fg could be achieved for B(a)P. With even more powerful dye laser systems (some of which provide more than 2 orders of magnitude greater pulse energy than the laser used in this work) and more efficient flow cells with a smaller active volume[13,25), one should be able to improve the detection limit. Ideally, PAH in natural water should be determined directly without preconcentration, but because the sensitivity is insufficient at the present stage, an extraction procedure is necessary. In this study, Lake Mashu was chosen as a lake free from pollution by human activities in Japan. By extracting PAHs from 2 *l* of the water sample, and taking into account the extraction efficiency, analytical results of 0.009 ng/*l*, 0.007 ng/*l*, and 0.014 ng/*l* obtained for B(*k*)F, B(*a*)P, and B(*ghi*)P, respectively. These values establish the background level of PAHs existing in natural lake water. The degree of pollution of a given lake water can be estimated by reference to these values.

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ＨＰＬＣ／時間分解けい光法による摩周湖の水の中に含まれる超微量多環芳香族炭化水素の測定

古田直紀[1]・大槻　晃[1]

従来のけい光分光光度計で，光源として用いられているXeランプを，チッ素レーザー励起のパルス色素レーザーに置き換えて，時間分解けい光測定系を開発し，その測定系を，高速液体クロマトグラフィー(HPLC)の検出器として用いた。本システムの検出限界は，検出限界を，バックグラウンドノイズの標準偏差の3倍のシグナルを与える濃度と定義すると，180fgで，検出限界の100倍程度の濃度のサンプルを測定した際の繰り返し精度は，3.9％であった。

本システムを，摩周湖の水の中に含まれる超微量多環芳香族炭化水素の測定に応用した。摩周湖の水2 *l* を採水し，溶媒抽出の抽出効率を考慮した結果，ベンゾ[*k*]フルオランテン，ベンゾ[*a*]ピレン，ベンゾ[*ghi*]ペリレンに対し，それぞれ，0.009ng/*l*，0.007ng/*l*，0.014ng/*l* の分析結果を得た。

摩周湖は，人間活動によって汚染されていない湖として考えられるので，これらの分析結果は，今後，湖水の汚染の程度を推測する際の参照値として用いられるであろう。

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V－2

Raman Spectroscopic Analysis of Coal Fly Ash Particles

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ABSTRACT

Raman Spectrscopy has been applied to the analysis of coal fly ash in two different modes. Firstly, Raman spectra of individual particles (Raman micro-analysis) have shown that most of particles consist of α-quartz, alumino-silicate glass or amorphous carbon. Secondly, quantitative total analysis of α -quartz in coal fly ash has been attempted. The results agree with those obtained by the X-ray diffraction method. Accordingly, Raman spectroscopy has been demonstrated to be a useful method in characterizing the chemical composition of environmental particle samples.

1. INTRODUCTION

Recently, laser Raman spectroscopy has been employed as an important technique for the structural determination of molecules including biologically interesting molecules or adsorbed species on metals$^{1)}$. The important practical analytical application of laser Raman spectroscopy may include :

(1) Replacing the absorption photometric detection by use of resonance Raman effect with much more structural information.
(2) Analysis of solid samples (often powder), Raman method being free from the difficulties inherent in the optical absorption spectrometry.
(3) Analysis of individual fine particles using a small laser spot, often referred to as Raman micro-analysis or Raman microprobe.

At present, however, its analytical application has been quite limited, especially in the quantitative analysis of solid samples$^{2)}$. In environmental problems, solid samples are generally the mixture of several kinds of particles, then qualitative and quantiative determinations of each component without pretreatment are highly desirable. Laser Raman spectroscopy should certainly be an attractive approach as suggested by its applicability mentioned above. After the Mount St. Helens ash eruption in 1980, there has been a great deal of concern in the U.S.A. regarding the content of crystalline silica of the ash, because crystalline silica, if significantly contained in respirable-size airbone particles (less than 10 μm), can induce respi-

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ratory disease. However, the analyses by IR or X-ray diffraction techniques by several groups revealed conflicting results[3]. Therefore, a new analytical method without the sample pretreatment procedure was sought and analytical Raman spectroscopy was recognized as a candidate[2,4].

Raman micro-analysis is the method to observe the Raman spectrum of individual fine particles. Measurements of particles as small as 1 μm are possible[5-7]. Recently, several kinds of microprobe analysis are available, but most of these techniques offer information on elemental composition. Raman microprobe (Raman micro-analysis) is characteristically capable of providing information on molecular components. In the analysis of powdered soild environmental samples, most analysis has been conducted on bulk samples or gross collection of particles. From single particle studies the heterogeneity in the powder is ascertained at the microscopic level. The results may give a more precise definition of the chemical species present, while offering a more conclusive identification of sources and particle transformation processes in the environment.

In this report, using coal fly ash as an example of environmental particulate samples, studies concerning above items (2) and (3) are described. Quantitative determination of α-quartz in coal fly ash using laser Raman spectroscopy was attempted, and some problems in the quantitative measurement for coloured soild samples, often encountered in environmental samples, were considered. Also Raman micro-analysis was attempted for individual particles of coal fly ash using a conventional Raman spectrophotometer. Raman spectra of individual particles whose morphologies were characterized by scanning electron micrograph were obtained.

2 . EXPERIMENTAL

Coal fly ashes measured were those sampled from an electric power plant, whose portions sieved through a 200 mesh (74 μm) standard sieve were distributed by Japan Environmental Agency for the quality survey of institutions for environmental analysis (EA-S57 & EA-S56), and US National Bureau of Standards (NBS) standard reference material for environmental analysis (NBS-1633a). Commercial quartz (Wako Chemical Industries Ltd.) was crushed and powderd in an agate mortar and particles of diameter less than 0.044 mm were obtained.

The laser Raman spectrophotometer used is a JRS 400T spectrophotometer with a NEC Model GLG 3300 argon ion laser. All spectra were measured using the 514.5 nm line of argon ion laser with the nonlasing plasma lines removed by a narrow band-pass interference filter. The laser power measured at the sample was 50 mW and slit width was 5 cm^{-1}.

The sample pellet was oriented at a 60° angle to the incident beam and Raman scattered light was viewed at an angle of 90° to the laser beam. During the measurement the sample was kept fixed or spinning in the laser beam path. In the spinning method, the ash sample was spread on a KBr disc and pressed to prevent the breakdown during the spinning at 1000 rpm.

Raman spectra for the analysis of an individual particle were measured using the same conventional Raman spectrometer, and the laser beam was focused onto the sample having diameter of 20-50 μm. Raman light from the particle less than 20 μm was too weak to detect because of the dispersion of scattered light.

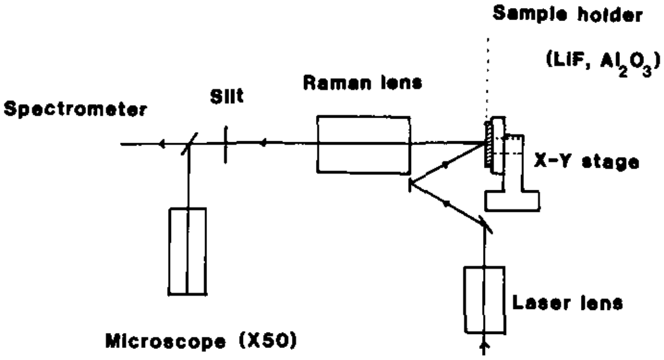

Fig. 1 Schematic diagram of a Raman spectrometer for micro-analysis

A schematic diagram of the sample compartment of the spectrometer is shown in Fig. 1. A single crystal of high purity sapphire (α-Al_2O_3) or lithium fluoride was used as a substrate material of sample holder, which was chosen because of weak background scattering. The incident beam was at an angle of 60° to the sample. The orientation of sample holder was restricted to the vertical due to the arrangement in the compartment, and the poor cohesion of sample particles to the substrate gave a limitation to the measurement. Thus particles larger than 50 μm would be held on the vertical substrate plane only with difficulty. XY mechanical stage was used to adjust the position of a particle on the laser beam spot by the viewing microscope (magnification, 50x) which was arranged inside a slit of the spectrophotometer (Fig. 1).

A Rigaku X-ray diffractometer RAD-IIA, equipped with a copper-anode X-ray tube and a Ni-filter was used for the quantitative X-ray diffraction analysis. All the experiments were carried out with a tube power of 40 kV, 20 mA, and the intensities were recorded at a rate of 0.01° (2θ) $\min^{-1}$ with 1° divergence slit and 0.3mm receiving slit. The amount of α-quartz in the coal fly ash was determined from integrated intensity measurents of (100) line of the sample spiked with a known amount of commercial α-quartz, normalized by mullite (110) line as the internal standard. Mullite, an alumino-silicate mineral, is known to be formed during the combustion of coal[8)].

3 . RESULTS AND DISCUSSION

3.1 Analysis of individual particles by Raman spectroscopy

Most fly ash particles are spherical as shown in the scanning electron micrograph of Fig. 2, especially in the finer fractions. Irregularly shaped particles and spheres packed with smaller spheres are also observed. The observation by polarized light microscope demonstrates that most spherical particles are glassy and crystals are present as angular particles or as embedded within glass spheres. Black lacy carbon coats the particles.

Raman spectrum typical for a spherical particle is shown in Fig. 3 (a). Such a broad spectrum is characteristic of alumino-silicate glass which is rather alumina

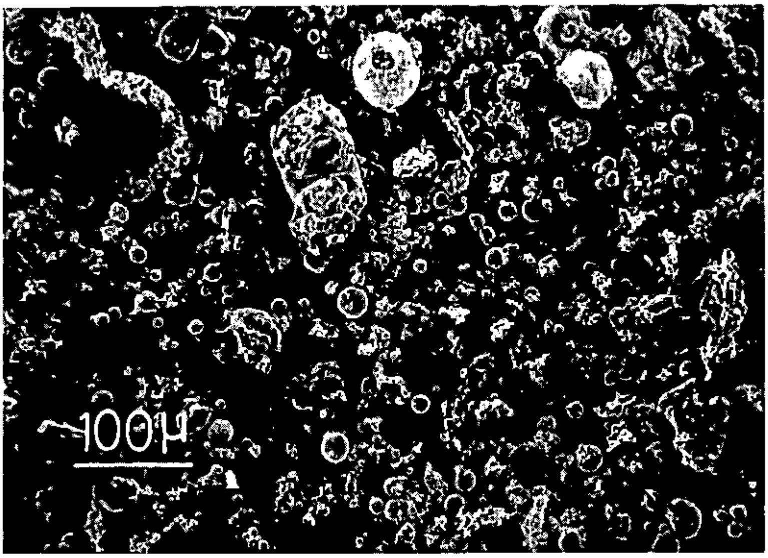

Fig. 2 Scanning electron micrograph of coal fly ash EA-S57

rich ($SiO_2/Al_2O_3=2$-4) and contains Ca^{2+} or Fe^{3+} ion[9,10]. Raman bands observed in the frequency range of 800 to 1100 cm^{-1} are considered due to Al-O and Si-O stretching, and the bands observed lower than 500 cm^{-1} can be assigned to O-Si-O or O-Al-O deformation vibration.

The spectrum of a crystalline angular particle is consistent with that of α-quartz as shown in Fig. 3 (b). An intense band at 465 cm^{-1} is due to O-Si-O deformation belonging to the A_1 species of D_3 symmetry group, and other bands are also assigned to A_1 (358, 190) or E (400, 120) symmesry species[11].

The black carbonaceous part which coats the particle gives a spectrum shown in (c), that is characteristic of amorphous carbon[12]. The Raman band at 1575 cm^{-1} is present in a single crystal of graphite, and a band at 1355 cm^{-1} appears when the graphite structure becomes disordered. The size of ordered graphite network in the carbonaceous material can be estimated from the intensity ratio of these two bands[12]. From their calibration curve the size of the graphite part of carbon in our coal fly ash EA-S56 is estimated to be less than 4 nm, so the carbon on this coal fly ash is essentially amorphous.

3.2 Calibration method and some problems in the quantitative analysis by laser Raman spectroscopy

The band at 1075 cm^{-1} of calcium carbonate (calcite) was used as the internal standard for the quantitative analysis of α-quartz contained in coal fly ash. To obtain the calibration curve, the spectra of α-quartz and calcium carbonate, mechanically mixed in an agate mortar or a vibrating blender, were measured and the ratio of integrated intensities of the band at 1075 cm^{-1} (CO_3^{2-}) and that at 465 cm^{-1} (SiO_2) was plotted against the composition. The intensity ratio measured by the fixed method gave about 70% uncertainty from point to point on the sample, indicating that the composition of mechanically mixed sample measured micro-

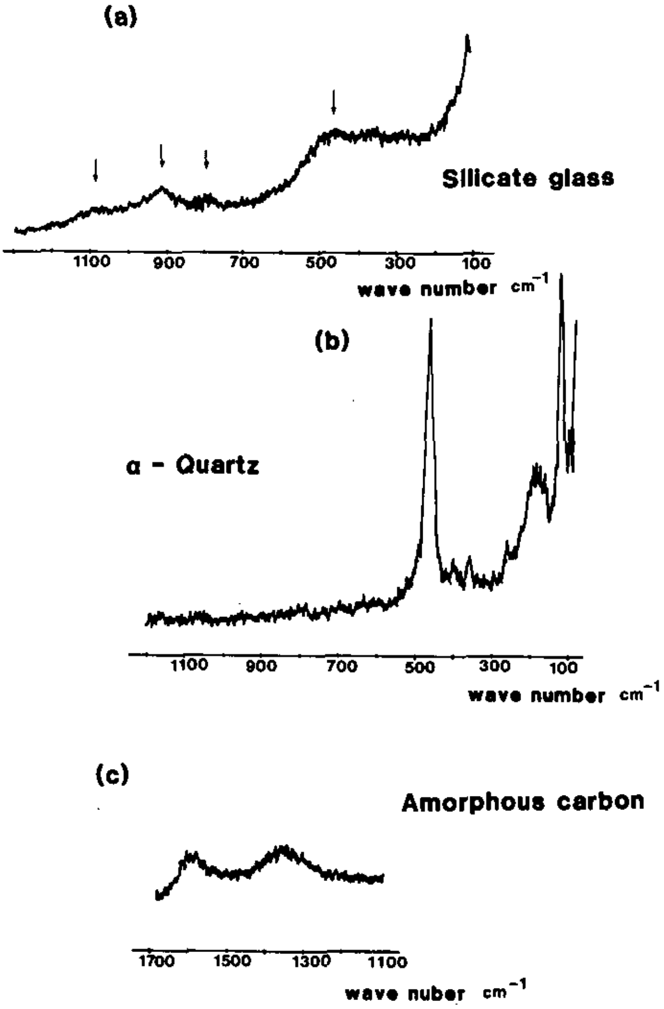

Fig. 3 Raman spectra of individual particles in coal fly ash EA-S56
(a) silicate glass (b) α-quartz (c) amorphous carbon

scopically by the size of laser spot was not sufficiently homogeneous. Therefore the spinning method was applied to determine the intensity ratio of CO_3^{2-} and α-quartz bands, where the divergence was less than 6% in one sample.

The effect of the coexistence of strongly light-absorbing material like carbon on Raman band intensities of α-quartz or calcium carbonate was studied, by adding graphite powder or activated charcoal to the sample mixture. The effect of the content of graphite powder on the Raman band intensity of α-quartz (465cm^{-1}) is shown in Fig.4, where the measurement was performed under the same experimental condition ; the laser power was 50 mW at the sample, slit width was 5 cm^{-1} and the spinning rate was 1000 rpm. The intensity of the Raman band decreases drastically

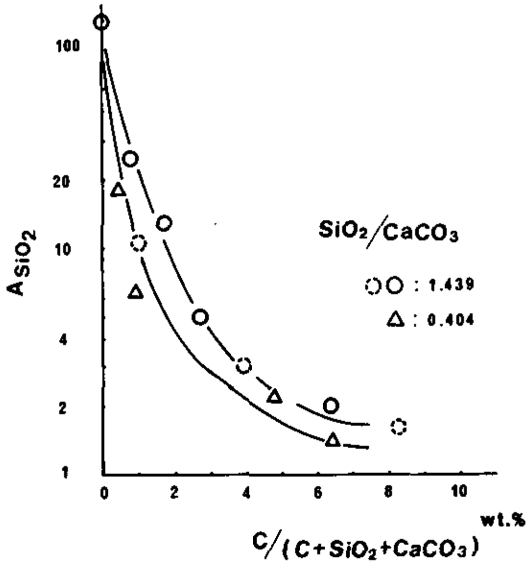

Fig. 4 The effect of carbon content on the Raman band intensity of α-quartz at 465 cm^{-1}

with addition of graphite. Since the content of carbon in coal fly ash is about 3 wt %, the observed Raman band intensity is considered to be less than 5 % of the same material without carbon. In the fixed method the intensity of the Raman band also decreases in the presence of carbon, but becomes constant when carbon content is greater than 2 wt%.This would be due to the burning-off of carbon under the laser illumination which is noticed by the decoloration of the spot.

The intensity ratio of α-quartz and carbonate bands as a function of the content of graphite powder is shown in Fig. 5. As far as the $SiO_2/CaCO_3$ ratio is constant, the observed intensity ratio is kept almost constant despite the decrease of the intensity of each band with the carbon content. When activated charcoal was added instead of graphite, the remarkable line broadening occurred in α-quartz and carbonate bands. This would be due to the interaction between α-quartz or calcium carbonate and activated charcoal which has a large surface area.

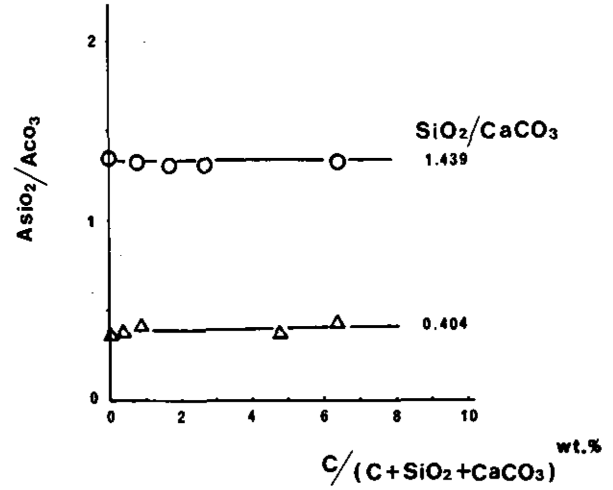

Fig. 5 The effect of carbon content on the intensity ratio of α-quartz band at 465 cm^{-1} and calcium carbonate band at 1075 cm^{-1}

3.3 Quantitative analysis of α-quartz in coal fly ash

According to the elemental composition of coal fly ash which was used for the Raman measurement, carbon content is 3.37 wt% in EA-S57. SiO_2 and Al_2O_3 are 61.18, 27.15 % in EA-S57 and 48.9, 26.4% in NBS-1633a[13]. Large parts of these Si and Al elements exist in the form of aluminosilicate glass as shown in Fig. 3 (a).

Raman spectrum of untreated EA-S57 is shown in Fig. 6 (a). The sharp band of α-quartz at 465 cm^{-1} and weak broad bands at 1580 and 1350 cm^{-1} assigned due to carbon are observed. However, other species are not identified due to the overlap of broad silicate glass spectrum. The Raman bands ascribable to the mullite evident in the X-ray diffraction analysis are only occasionally recognized and not clearly. Fig. 6(*b*) is the spectrum of EA-S57 treated with nitric acid and perchloric acid, a

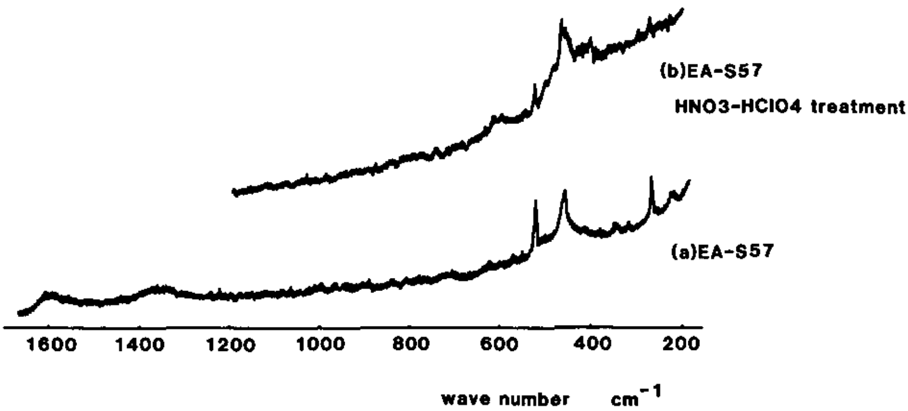

Fig. 6 Raman spectra of coal fly ash EA-S57
(a) untreated (b) treated with HNO_3 -$HClO_4$.

treatment which removes carbon from the ash and decolors the ash. The Raman spectrum does not show any significant difference from (a) except for the absence of the carbon bands.

Quantitative analyses of α-quartz in coal fly ash, EA-57, NBS-1633a and EA-S57 treated with nitric acid-perchloric acid, were performed using the Raman band at 465 cm^{-1} by the spinning method. Calcium carbonate was added as an internal standard, and the weight of calcium carbonate added was about half of the fly ash. The intensity ratio of 465 cm^{-1} (α-quartz) and 1075 cm^{-1} (carbonate) bands were determined, then the the quartz/carbonate ratio was calculated according to the calibration procedures described in the previous section. The results are presented in Table 1, where those obtained by the fixed method for EA-S57 after the acid treatment are also shown.

Table 1 The content of α-quartz in coal fly ashes (wt. %)

		Raman* (fixed)	Raman* (spinning)	XRD**
EA-S57			12± 1	11.2±0.6
EA-S57	(1)	17± 1	13± 1	
(HNO_3-$HClO_4$ treatment)	(2)		10± 2	
	(3)	11± 1	11± 2	
NBS-1633a			7± 4	7.5±0.7

* $CaCO_3$ was added as the internal standard.

** α-quartz was spiked and (110) peak of mullite in ashes was used as the standard reference peak.

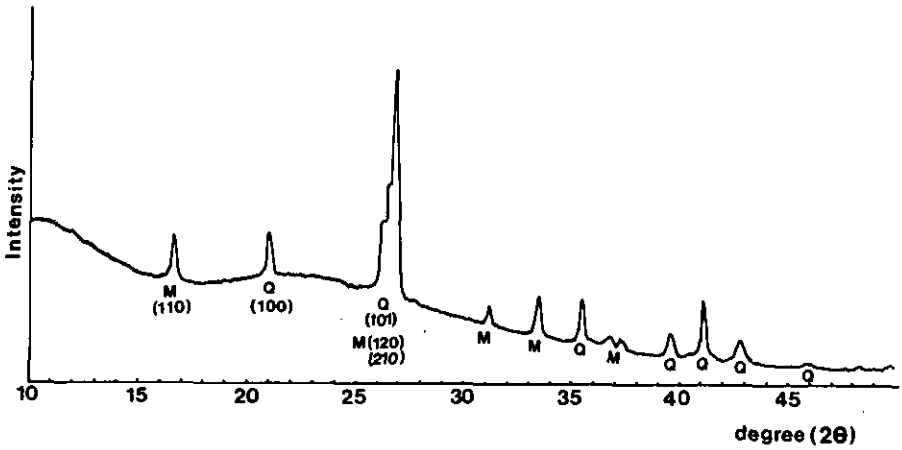

Fig. 7 X-ray powder diffraction pattern of coal fly ash EA-S57
M: Mullite, Q : α-quartz.

The X-ray powder diffraction pattern of EA-S57 is shown in Fig. 7, where α-quartz and mullite peaks are indentified[14]. NBS-1633a ash shows the similar diffraction pattern with the content of mullite slightly higher than in EA-S57. Quantitative analysis of α-quartz was performed using (100) peak of the samples spiked with a known amount of commercial α-quartz, whereby a mullite (110) peak was used as the internal standard for the diffraction intensity.

As shown in Table 1, quantitative analysis by Raman spectroscopy and XRD agree satisfactorily. α-Quartz in coal fly ash is 11 wt% in EA-S57 and the amount in NBS-1633a is a little less than that in EA-S57, so about one-fifth of the silica exists as quartz. The content of α-quartz in fly ash treated with HNO_3-$HClO_4$ does not show any significant difference, in accordance with the fact that only a small part of coal fly ash is dissolved by HNO_3-$HClO_4$ treatment.

The white ash, EA-S57 from which carbon was removed, shows the same value in the spinning and fixed methods. Therefore, the fixed method is also applicable for the quantitative measurement of colourless compounds.

4 . CONCLUSION

Raman micro-analysis of individual particles of solid environmental samples has been demonstrated to be useful for the qualitative analysis of each particles, although there are some limitations ; dispersion of Raman light because of various particle shapes makes the intensity insufficient to the measurement of fine particles, or the strong light absorption by coloured species such as carbon may cause melting or vaporization of sample by laser light. In the analysis of particles which contain amorphous noncrystalline solids, the increase of background level makes the XRD measurement difficult. On the other hand, Raman spectroscopy is capable to distinguish between crystals and glass, as shown in Fig. 3.

Quantitative analysis of α-quartz in coal fly ash using Raman spectroscopy showed the similar sensitivity level with that by X-ray diffraction method, although it may depend on samples. Fine crystals less than 10 nm show line broadening in XRD and those less than 3 nm are inefficient to XRD, while Raman spectra will not show little particle size effect. Therefore conflicts between IR and XRD data on St. Helens volcano ash are attributable to the presence of very small particles in crystalline silica[3].

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ラマン分光法による石炭フライアッシュ粒子の分析

相馬悠子[1]・相馬光之[1]

ラマン分光法により石炭フライアッシュの分析を粉末回転測定法とマイクロアナリシス法を応用して行なった。個々の粒子を観測するラマンスペクトル（ラマンマイクロアナリシス法）により、フライアッシュ粒子は，α-石英，ガラス状シリカアルミナや無定形炭素が多い事を見た。次に石炭フライアッシュ中の α-石英のラマンスペクトルによる定量分析を試み，X線回折法による結果と一致する値を得た。

以上の結果から，ラマン分光法が環境中の粒子状試料の化学組成を決定するのに有用な方法である事が示された。

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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）

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第 5 号　芳香族炭化水素一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）

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※ 第 7 号　A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)

（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）

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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）── 霞ヶ浦（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）── 霞ヶ浦流域の地形，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）── 霞ヶ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）── 霞ヶ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
別研究報告.（1983）

第 41 号　土壌環境の遠隔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 w
description of 15 new species.

Part 6. Description of species of the subfamily Orthocladiinae recovered from the main strea
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　特別研究中間報告.（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53～55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）── 湯ノ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1）── 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 morphological 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）

第 75 号　Limnological and environmental studies of elements in the sediment of Lake Biwa. (1985)
（琵琶湖底泥中の元素に関する陸水学及び環境化学的研究）

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）

第 77 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58年度　特別研究報告．（1985）

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)
（環境汚染の長期的モニタリング手法に関する研究）

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)

No. 9* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1978. (1979)

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)

※ No.15* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1977-1978. (1980)

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)

No.37* Study on supporting technology for systems analysis of environmental policy – The evaluation laboratory of Man-environment Systems. (1982)

No.38 Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)

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)

No.49* The development and evaluation of remote measurement method for environmental pollution – Research report in 1982. (1984)

No.50* Comprehensive studies on the eutrophication control of freshwaters – Estimation of input loading of 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)

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