PROCEEDINGS

FOURTH US-JAPAN CONFERENCE

ON

PHOTOCHEMICAL AIR POLLUTION

February 28-March 2, 1978
East-West Center
Honolulu, Hawaii

US DELEGATION

Dr. A.P. Altshuller, Chairman
Environmental Sciences Research
Laboratory
USEPA

Dr. B. Dimitriades
Environmental Sciences Research
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JAPANESE DELEGATION

Mr. Shoji Takeno, Chairman
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PREFACE

This conference is a part of the activities fostered under the US-Japan Environmental Agreement negotiated between the two countries in August, 1975. Purpose of the Environmental Agreement and associated activities is to develop environmental awareness and to promote cooperation between the US and Japan in effort to reduce air pollution. Cooperative activities pertaining to photochemical air pollution were commenced in June, 1973, when the First US-Japan Conference on Photochemical Air Pollution was held in Tokyo, Japan. The Second Conference was held in Tokyo also, in November, 1975; the Third Conference took place in Research Triangle Park, N.C., in September 1976.

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Technical Papers

INTRODUCTION

Dr. Altshuller, head of the US Delegation, welcomed the delegates and discussed briefly the exchange in correspondence of mutual interest. Such interests are on recent legislative and research developments in the areas of the oxidant, sulfate and nitrate problems and constitute the subjects of this Fourth Conference.

AGENDA

FOURTH US-JAPAN CONFERENCE

ON

PHOTOCHEMICAL AIR POLLUTION

East-West Center   February 28 - March 2, 1978

Honolulu, Hawaii

<u>Tuesday, February 28, 1978</u>   Session Chairman: Dr. Altshuller

10:00 -- 10:30 a.m.   Welcome   A.P. Altshuller

                          Introduction of Participants

                          Election of Session Chairmen

                          Approval of Conference Program

10:30 -- 11:00 a.m.   Refreshments

11:00 -- 12:00 N   Legislative Developments in   A.P. Altshuller
                          Photochemical Pollution Area   U.S. EPA

12:00 -- 1:00 p.m.   Lunch

1:00 -- 3:00 p.m. NO_x and HC Control Measures   S. Takeno
                          in Japan   Japan Environment
                                                           Agency

3:00 -- 4:00 p.m.   Scientific Issues Related   B. Dimitriades
                          to Oxidant Control   U.S. EPA

Wednesday, March 1, 1978   Session Chairman: Mr. Takeno

9:00 -- 10:00 a.m.   Trend of Photochemical   S. Imai
                          Oxidants in Japan   Japan Environment
                                                          Agency

10:00 -- 10:30 a.m.   Refreshments

10:30 -- 12:00 N   Emissions to Oxidant and   B. Dimitriades
                          NO_2 Air Quality Relationships U.S. EPA

12:00 -- 1:00 p.m.   Lunch

1:00 -- 2:00 p.m.   Photochemical Ozone Formation in M. Okuda
                          Propylene-Nitrogen Oxide-Dry   Japan National
                          System   Institute for
                                                            Environmental Studie

2:00 -- 2:30 p.m.   Refreshments

2:30 -- 4:00 p.m.   Photochemical Sulfate and   A.P. Altshuller
                          Nitrate Research in the US   U.S. EPA

Thursday, March 2, 1978   Session Chairman: Dr. Altshuller

9:00 -- 10:00 a.m.   Sulfate, Nitrate and Nitric   M. Okuda
                          Acid Research in Kanto Area   Japan National
                                                          Institute for
                                                          Environmental Studie

10:00 -- 10:30 a.m.   Refreshments

10:30 -- 12:00 N   Discussion

12:00 -- 1:00 p.m.   Lunch

                                            Session Chairman: Mr. Takeno

1:00 -- 2:00 p.m.   Plans for Future Activities

2:00 -- 3:30 p.m.   Preparation of Joint Communiqué

                          Conclusion of Meeting

ACKNOWLEDGMENT

We wish to express our greatest appreciation to Dr. R. Carpenter and Mr. H. Ajiroji for the time and effort they took to assist us in organizing this Conference and in locating interpreters. The success of the Conference was largely due to the excellent facilities and services made available to the Conferees by the East-West Center of the University of Hawaii through the efforts of Messrs. Carpenter and Ajiroji. We are grateful.

A.P. Altshuller

Chairman of the host

US Delegation

JOINT COMMUNIQUE

The Fourth US-Japan Conference on Photochemical Air Pollution was
held in Honolulu, Hawaii, on February 28 - March 2, 1978, at the
premises of the EAST-WEST Center.

The Japanese delegation included: Mr. Shoji Takeno, General Chair-
man, Environment Agency; Dr. Michio Okuda, National Institute for
Environment Studies, and Mr. Senro Imai, Environment Agency.

The United States delegates were: Dr. A. P. Altshuller, General
Chairman, Environmental Protection Agency; and Dr. B. Dimitriades,
Environmental Protection Agency.

Discussions were centered around subjects agreed upon by the two
delegations during the Third Conference held in September 8-10,
1976 and in subsequent communications exchanged by the two dele-
gations. Such subjects included:

-- NO_x and HC Control Measures in Japan
-- Trends of Photochemical Oxidants in Japan
-- Photochemical Ozone Formation in Propylene-Nitrogen Oxide
   Dry Air System (Smog Chamber Studies)
-- Sulfate, Nitrate and Nitric Acid Research in Kanto Area
-- Legislative Developments in Photochemical Pollution Area
   in the U.S.
-- Scientific Issues Related to Oxidant Problem in the U.S.
-- Emissions to Oxidant/Ozone Air Quality Relationships in
   the U.S.
-- Recent U.S. Studies on Ambient NO_2 Problem
-- Photochemical Sulfate and Nitrate Research in the U.S.
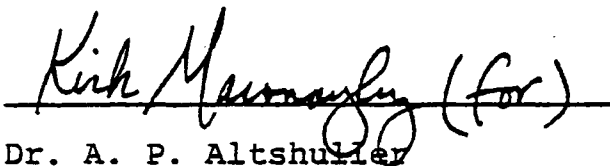
Highlights of the presentations and discussions held in the Con-
ference and conclusions reached are summarized as follows:

1. The two delegations expressed general agreement with the
    strategies adopted by the two countries for photochemical
    pollution control with respect to both NO_x and HC.
2. Being aware of the importance to prevent the adverse health
    effects by NO_2, both Japan and U.S. are now enforcing
    nationwide NO_x emission controls on both mobile and sta-
    tionary sources to reduce ambient NO_2 concentrations.
3. To reduce ambient oxidant concentrations, Japan is pres-
    ently enforcing organic emission controls on mobile sources
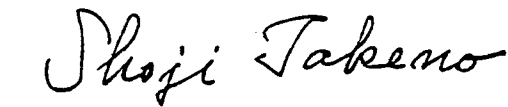   only; controls on stationary sources are contemplated.

4. Data available suggest that on-going controls in Japan on particulate and SO_2 emissions resulted in reduction of ambient sulfates. The impact, however, of the more recently initiated NOx controls on ambient NO_2 and nitrates has not been detected yet. Therefore, it is recognized that Japan as well as the U.S. have to make an effort to verify such interpretations of the emissions and air quality trends through more systematic and in-depth analyses. In this sense, the need of further research especially on photochemical nitrates in both countries is recognized.

5. The delegates agreed to exchange additional information on subjects discussed, including smog chamber data for modeling use, U.S. criteria documents (drafts) for ozone, oxidants and for NO_2, and other requested EPA reports.

6. The delegates agreed on a continuing cooperative program with immediate and specific interest in exchange of scientific evidence on
    (a) emission and air quality trends and their interpretation in terms of impact of emission control on ambient air quality;
    (b) the chemistry and transport processes associated with the ambient sulfate and nitrate problems;
    (c) question of monitoring station siting;
    (d) smog chamber methodology.

Overall, it was agreed to continue the effort to generate and exchange scientific data including possible exchange of scientific personnel.

It was tentatively agreed to call the next meeting in 1979 in Tokyo.

_____ (for)
Dr. A. P. Altshuller
General Chairman
U.S. Delegation

_____
Mr. Shoji Takeno
General Chairman
Japanese Delegation

Date: March, 1978

LEGISLATIVE DEVELOPMENT IN PHOTOCHEMICAL POLLUTION AREA

presented by A.P. Altshuller

Environmental Protection Agency

United States

LEGISLATIVE DEVELOPMENT IN PHOTOCHEMICAL POLLUTION AREA

The Clean Air Act Amendment, Public law 95-95 was enacted in August 1977. A number of provisions of this Act directly relate to photochemical pollution. Section 106 concerns air quality standards. It requires review of all existing standards before December 31, 1989 with subsequent review at 5 year intervals. The National Ambient Air Quality Standard for Oxidants is currently under review. The air quality criteria document has been rewritten and reviewed by technical experts, revised, and has been submitted and discussed with EPA's science advisory board. At the same time, a working group on Photochemical Oxidants was set up, concerned with the standard for oxidants. The preparation of the criteria document lies with the Research and Development Office of our agency, but the actual development of the standard itself is the responsibility of the Office of Air Quality Planning and Standards. This office sets up a working group which contains representatives from all interested portions of the agency. The working group uses the criteria document draft as the scientific input to its work, but it is then concerned with the form of the standard itself.

After the working group has established recommendations, there are public hearings held concerning these, and the first of these was held a few weeks ago in Washington. These hearings allow representatives from our state and local governments and representatives of industry to comment on the proposals.

To get to the technical recommendations themselves, the first of these is that the standard be redesignated from oxidants to ozone. The reasons for this are several. The most important is that the health information that we have obtained in recent years from toxicological experiments, both animal and human is for ozone, not oxidants. The measurement technique for the original standard (chemiluminescence) was for ozone rather than for oxidants. So, in view of the fact that the only additional scientific data concerning oxidants concerned ozone and NO_2, it is appropriate to have an ozone standard. In the internal discussions of the working group, as well as scientific materials discussed with experts, the question came up as to whether it would be appropriate to set a separate standard for PANs. The proposal is not to set a separate standard at this time for PAN. The reasons for thinking it best not to set a separate standard are several. First, we lack health information on the effects of PAN; there has been little additional work in recent years. The only effect which received some attention in past years was the effect of PANs on eye irritation. But in our working group discussions, it was decided, subject to reviewing this with health experts, not to consider eye irritation as a health effect but as a nuisance, more of a welfare effect. Although we do have measurement techniques for PAN, they have not, at least in our experience, been acceptable for monitoring by local agencies because of the scientific complexities of the methods.

A third recommendation was to redefine the standard in a statistical form, and fourthly, to retain the 1 hour averaging time for the standard. Review of the health evidence suggests that the range of the standard definitely lies between 8 and 15 pphm [ozone, 1 hour average]. There are several problems in making a decision within this range of concentration from the scientific standpoint. This is because we have no direct toxicological results which demonstrate an effect within the range of 8-15 pphm. On the other hand, the law in the U.S. is stated so as to protect not only the average person but also individuals who are particularly sensitive to the effects of ozone. As you know, one such group is asthmatics. One cannot take individuals with serious asthma problems and expose them in clinical chamber studies. The threshold effect from those subjects that can be studied is between 15-25 pphm, but how do we estimate the threshold for those who we cannot study, with severe asthma? We will probably maintain that the number of exceedances of the standard shall not exceed 1 per year. This term "exceedance" now refers to a statistical-type approach. There has been discussion and some investigation into the possibility that unusual meteorological events, such as stratospheric intrusions of ozone at ground level, could result in ozone levels above the standard. Estimating the statistical probability of these occurrences is very difficult. Some consideration has been given to the possibility of permitting a day of hourly values above the standard to allow for rare meteorolgoical conditions. [one day rather than one hour would be excluded] Based on those estimates we can make, this would seem to provide an allowance for this sort of event occurring at any given geographical location.

Section 106 also contains the provision that not later than 1 year after enactment a National Primary Ambient Air Quality Standard for NO_2 shall be promulgated. The wording suggests that a period of not more than 3 hours should be considered unless there is no significant evidence to support the need for such a standard to protect public health. It was believed that enough scientific evidence was available to proceed to prepare a revised health criteria document for NO_2 and a draft criteria document has been prepared for review. This document emphasizes health aspects concerning the short term effects of NO_2. This document and associated standards must go through the same process described for oxidant and ozone.

It's believed that a standard will be proposed in the 1-3 hour range, but one matter to be resolved is whether the adverse short term exposures should be considered on a one-time or repeated basis. Here again, this would strongly affect the statistical form of the standard as it is finally promulgated. It is an intention to revise the entire NO_2 Criteria document in all its aspects, and some discussion of other aspects on health are in the present revision; but it is anticipated that these will be enlarged upon later. The problem is partly associated with the deadline in the Clean Air Act of 1 year, so we're concerned with concentrating the efforts on the health effects to meet what was considered the primary legal mandate in the Act. It is clear, it follows, that understanding the role of mobile and stationary sources in contributing through their emissions to producing such short term NO_2 concentrations is a major concern. Unless we can properly define the relationships between emissions and short term air

quality for NO_2, we will not be able to promulgate the standard after it is written properly; and again, our colleagues at the Office of Planning and Air Quality Standards are trying to assemble the technical information related to this problem. Within the Act itself, there is a provision under a section 202a which is closely related to the present discussion. This requires that "the EPA administrator shall conduct a study of public health implications of obtaining an emission standard of the oxides of nitrogen of light-duty vehicles of 0.4 gm per vehicle mile, the cost and technical capabilities of such a standard, and the need for such a standard to protect the public health and welfare. The administrator shall submit a report to the Congress together with recommendations not later than July 1, 1980."

So, this provision reflects the continuing concern and controversy whether the vehicles sold in the U.S. can meet the standard of 0.4 gm/mile, taking into consideration deterioration, and fuel economy aspects which we have to face in other laws in the U.S.

Turning to another major portion of this act which is concerned with significant deterioration of air quality. This provision of the Act is directed at preserving and protecting air quality in national parks, wilderness areas, and similar type areas. Numerical provisions with respect to concentration levels for SO_2 and TSP are already provided for in the Act. However, it is important to note that within 2 years, provisions must be promulgated to prevent deterioration by the other criteria pollutants including photochemical oxidants and nitrogen oxides.

Emphasizing the concern of our Congress about the effects of oxidants on significant deterioration there is an added provision in section 169 in that portion of the Act concerning significant deterioration. This section requires a guidance document to include recommended strategies for controlling photochemical oxidants on a regional or multistate basis. This section represents the appreciation by our Congress of the transport of oxidants, particularly ozone. The report must also include recommendations for legislative change necessary to implement strategies for controlling photochemical oxidants on a regional or multistate basis.

Another very interesting section of the Act provides for the establishment of a National Commission on Air Quality. The composition of this commission includes a number of important members of Senate and House committees concerned with air pollution problems, as well as members of the public appointed by the President by and with the consent of the Senate. This would make this commission a very high level organization [not more than 1/3 of the public members may have any interest in any business or activities regulated by this Act]. The law gives a long list of assignments to the Commission concerned with oxidants and NO_x. For example, they are asked to report on the technical capabilities of achieving or not achieving the control levels for mobile and stationary sources for oxides and NO_x. In doing this, they are supposed to consider the economy, energy, environmental, and health aspects.

NO_x AND HC CONTROL MEASURES

IN JAPAN

presented by S. Takeno

Environment Agency

Japan

C O N T E N T S

I. BASIC CONCEPT

The basic concept of atmospheric Ox control measures in Japan is to reduce the Ox concentration in the atmospheric air to a level harmless to human health through the bilateral reduction of NOx and HC.

As regards the NOx control measures, in particular, an ambient air quality standard for NO_2 has already been established for the purpose of preventing the adverse effect of NO_2 on human health, and all NOx control measures described in II (A) are being conceived and implemented to achieve this standard. Therefore, in Japan, there is an existing NO target level (daily average value: 0.02 ppm) and the basic Ox control concept is based on this NOx control scheme and the HC control scheme to be described in III.

II. BASIC CONCEPT OF NOx ABATEMENT SCHEME

(A) Controls on Emissions from Stationary Sources

1. General

With respect to stationary NOx sources, the Environmental Quality Standard for NO_2 was established in May 1973, and, within the framework of this standard, the 1st stage regulation was enforced on large establishments in August 1973, the 2nd stage regulation was enforced to enlarge the scope of application in December 1975, and

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the 3rd stage regulation was enforced to apply the emission standard to smaller establishments in June 1977. Fig. 1 shows the NOx emission standards for the 3rd regulation.

These emission standards are national minimum emission standards based on the Air Pollution Control Law and are applicable to all areas in Japan, comprising the permissibl emission concentrations determined for various types and sizes of smoke-and soot-emitting facilities, and the types of fuel used.

Where the intended environmental quality level cannot be achieved even though all the applicable facilities adhere to these emission standards, additional stringent emission standards are scheduled to be enforced by local governments; and where the air pollution conditions are not improved even by these stringent emission standards, the total mass emission regulation in the area is scheduled to be enforced, with the total permissible emission in the area to achieve the ambient air quality target calculated by means of pollution simulation models, and this total permissible emission will be allocated to all the plants within the area possessing smoke-and soot-emitting facilities.

Such total mass emission regulation systems as this are in force in Japan for SOx with the following basic

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concepts:

1) In contrast to the emission standard scheme and the stringent emission standard scheme which are applicable to individual smoke and soot-emitting facilities, the total mass emission regulation standards are applied to individual factories within the limit determined from the total permissible amount within the area. Therefore, the owners of smoke-and soot-emitting facilities are at liberty to arrange the facilities of the factories as long as the total emission for the plant is kept within the permissible amount. This means that despite very strict control levels, the owners of the factories are able to satisfy them by installing smoke-and soot-treatment equipment without modifying all the plant facilities.

2) The total mass emission regulation standards to be allocated to individual factories are sure to achieve the ambient air quality goal using pollution simulation models.

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Table 1. The 3rd Regulations Emission Standards for NOx

	Existing Facilities			Newly Built Facilities		
Types of Facilities		New Std	Old Std		New Std	Old Std
Boilers Gas combustion	(Unit: 1,000 Nm³/h) Over 500 100 - 500 40 - 100 10 - 40 5 - 10	130 ppm 130 130 150 150	130 ppm 130 130 150 –	(Unit: 1,000 Nm³/h) Over 500 100 - 500 40 - 100 10 - 40 5 - 10 Up to 5	60 ppm 100 100 130 150 150	100 ppm 100 130 130 – –
Solid material combustion	Over 100 40 - 100 10 - 40 5 - 10	480* 600(750) 600(750) 480	600(750) 600(750) 600(750) –	Over 100 40 - 100 10 - 40 5 - 10 Up to 5	400 400 400 400 400	480 480 480 – –
Others (Liquid combustion)	Over 1,000 500 - 1,000 100 - 500 40 - 100 10 - 40 5 - 10	180 180(210) 190(210) 190(210) 230(250) 250(280)	230(280)** 230(280)** 230(280)** 190*(280)** – (250)** –	Over 500 100 - 500 40 - 100 10 - 40 5 - 10 Up to 5	130 150 150 150 180* 180*	150 150 150 150 – –
Sintering Furnace	Over 100 Up to 100	260 270	– –	Over 100 Over 100 (Alumina Calcination Furnace)	220 200	– –
Metal Heating Furnace	Over 100 40 - 100 10 - 40 5 - 10	160(200) 170(200) 200 170(200)	220 220 200	Over 100 40 - 100 10 - 40 5 - 10 Up to 5	100 100 130(150)(180) 150* 130(150)(180) 150* 150* 180*	– –
Petroleum Heating Furnace	Over 100 40 - 100 10 - 40 5 - 10	170 170** 180*** 180(190)	210* 210* 180*	Over 100 40 - 100 10 - 40 5 - 10 Up to 5	100 100 130 100 130 150 180	150 – –
Cement Calcination Furnace		480	–	Over 100 Up to 100	250 350	250 –
Coke Furnace		350	–	Over 100 Up to 100	170 170	200 –
Waste Incinerator				Over 40	250	–

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Remarks

(1) Reference to Boiler-Solid Material Combustion category, marked * in the "existing" column shows 650 ppm for ceiling burner and 550 ppm for divided wall type. ( ) are applied for low-grade coal combustion burners.

(2) Reference to Boiler-Others (Liquid Combustion), ( ) in the "existing" column are applied for the ones equipped with stack gas desulfurization facilities. Marked * indicates excluding the ones equipped with desulfurizer.
Mark ( )** are for crude oil combustion burners, and the standards marked * in the "newly built facilities" are applied from September 10, 1977.

(3) Reference to Sintering Furnace, "existing" does not cover Pellet sintering furnaces.

(4) Reference to Metal Heating Furnaces, "existing" does not cover the heating furnaces for welded steel pipe. ( ) are applied for heating furnaces of the radiant tube type. Marked * in the "newly built" column shows not including heating furnaces for welded steel pipe. ( ) in the "newly built" column are applied for radiant tube type heating furnaces. ( ) are applied for heating furnaces for welded steel pipe.

(5) Marked * in the "existing" column of Petroleum Heating Furnace are not applied for Ethylene Resolving

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Furnaces, independent super-heating furnaces, methanol refining furnaces and ammonium refining furnaces. Marked ** are not applied for independent super heating furnaces and methanol refining furnaces Marked *** are not applied for ethylene resolving furnaces. ( ) are applied for those equipped with a stack gas desulfurization facility.

(6) Reference to Cement Calcination Furnace, standards in the "existing" column are not applied for wet type furnaces, and application from April 1, 1981.

(7) Reference to Coke Furnaces, standards in the "existin(column are not applied for Otto type furnaces.

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The flow chart for the enforcement process of the SOx total emission regulation scheme is shown in Fig. 2.
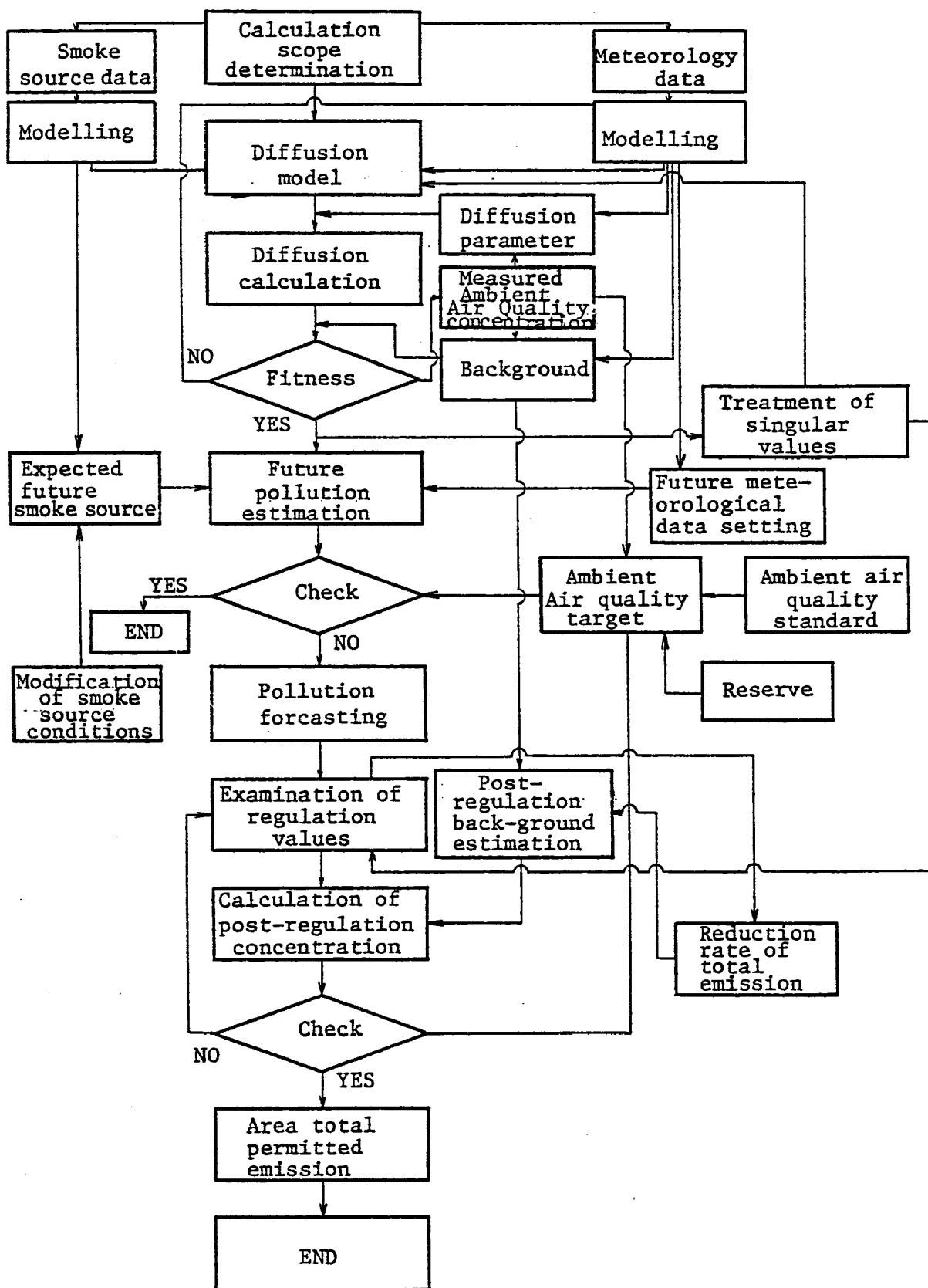

Figure 2 Flow chart for SOx
          total emission regulation scheme

2. Problems in NOx Total Mass Emission Regulation

For a NOx total mass emission regulation scheme to be effective, the following problems seem to require solutions:

1) Pollution estimation technique

Unlike the case of SO_x, the establishment of NOx pollution estimation involves the following problems: As NOx is formed in all combustion processes by the oxidation of not only nitrogen in the fuel but also of N_2 in the air, its source including ordinary households is varied and complicated. In addition to smoke- and soot-emitting facilities, automobiles also contribute much to atmospheric pollution, and the dispersion in the air layer near the ground surface must also be taken into consideration. Finally, immediately after discharge, all NOx in the discharged gas is in the form of NO, and therefore, its conversion into NO_2 must be taken into consideration.

Therefore, at present, efforts are being made in many related fields to establish good techniques of estimating NOx pollution that can contribute to the rational control of NO_x pollution.

For this purpose, continuous efforts must be made in the following directions:

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(1) Obtaining reliable information about the actual NOx emission conditions from small and medium stationary sources and mobile sources.

(2) Establishment of methods for estimating the diffusion of NOx emitted from these sources (establishment of low altitude or local diffusion models).

(3) Obtaining precise information about the conversion process from NO to NO_2.

(4) Obtaining precise information about the background concentration.

(5) Obtaining reliable information about the ambient air quality concentration.

2) Precise information about emission data

Needless to say, precise information about the volume of emitted NOx is required, and at present, various emission sources are under investigation by various authorities as listed below. A comprehensive nation-wide NOx emission survey is scheduled to be made by the Environment Agency in 1978.

```
Stationary        ⎡ Large smoke ———— In principle, actual measure-
sources          ⎢ sources           ments
                 ⎢
                 ⎢ Small and ———— Estimation based on emission
                 ⎢ medium smoke      factor (many data of Environment
                 ⎣ sources           Agency, etc. available)


Mobile            ⎡ Automobiles ———— Estimation based on emission
sources          ⎢                   factor (many data of Environment
                 ⎢                   Agency, etc. available)
                 ⎢
                 ⎢ Ships ———————— Estimation based on emission
                 ⎢                   factor (data of Environment
                 ⎢                   Agency, Transport Ministry,
                 ⎢                   and Kanagawa Pref. are available.)
                 ⎢
                 ⎣ Aircraft —————— Estimation based on emission
                                     factor (data of Environment
                                     Agency and Osaka Pref. are
                                     available.)


Many small ————————————————— Estimation based on emission
sources                              factor (Environment Agency
                                     data are available.)

Background ——————————————————— Actual measurement by urban
                                     types (Environment Agency
                                     data are available.)
```

3)   Development of diffusion models

Mobile sources, especially automobiles, are said to

be drastically different in the mode of diffusion from

the emitted NOx from stationary sources, so that new

types of diffusion models are under study for automobile

exhaust gas entirely different from the model used for

the total mass emission regulation scheme for SOx.

At present, several modified total mass emission

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regulation models based on the data obtained from an actual on-road tracer experiment (assigned to Osaka Pref. 51' - 53') modified by initial diffusion range, etc., and non-normal models are under comprehensive study.

As to the study in diffusion models incorporating $NO - NO_2$ conversion, although several models have been proposed based on NO decay functions derived from reaction velocity theory viewpoints and derived from statistical treatment of the measured concentrations of NO, NO_2 and NOx, none has provided reliable proof, and further experience in other areas and further studies are required to obtain reliable models.

3. The Present State and Problems of Exhaust Gas Denitrification Technology

As for the exhaust gas denitrification technology, the last year's report said that there were no technical problems about the "clean exhaust gases" (containing none or extremely small quantities of SOx and dust) which are emitted from the soot and smoke emitting facilities using LPG and LNG for fuels. Such being the case, in the last hearings, emphasis was placed on the survey to find what advances had so far been made in the development of the denitrification technology for what is called the dirty

exhaust gases containing higher concentrations of SOx
and dust.

As the point of time when the report was completed
in October 1975, there were eleven pieces of denitrification
equipment in actual operation and moreover they were for
the most part designed for handling the clean exhaust gases.
The last survey has revealed that the number of denitri-
fication equipment in operation increased to 35 or more,
including an increasing number of those for dirty exhaust
gases.

(1) Speaking about the dry type (ammonia catalytic reduction
type) of exhaust gas denitrification equipment, there
are 26 units now in operation (with a combined capacity
amounting to 4,300,000 Nm^3/h), including those which
are used for C heavy oil-burning boilers and various
kinds of heating furnaces.

The operating records of such equipment show that
there are no problems about the exhaust gases as
dirty as those which are emitted by the combustion
of C heavy oil in the respect of catalytic activity
for such reasons that SOx-resistant catalysts have
been put to practical use. The problem of catalystic
being clogged by dust has also been solved, making
so much progress in the practical usefulness of this

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type of exhaust gas denitrification technology.

What is needed in the future is a further improve-
ment in the economy of this type of denitrification
system and an increased reliability by solving the
problem of the safety of the combustion facility
itself which arises from the deposition of acid
ammonium sulfate onto the heat exchangers.

On the other hand, no such advances have yet been
made in the development of denitrification technology
for the dirtier exhaust gases emitted by sintering
furnaces, glass melting furnaces and the like. Though
there are some denitrification equipment of this type
now in operation but they are equipped with various
attachments disregarding the operating economy to
some extent. Such being the case, it is still
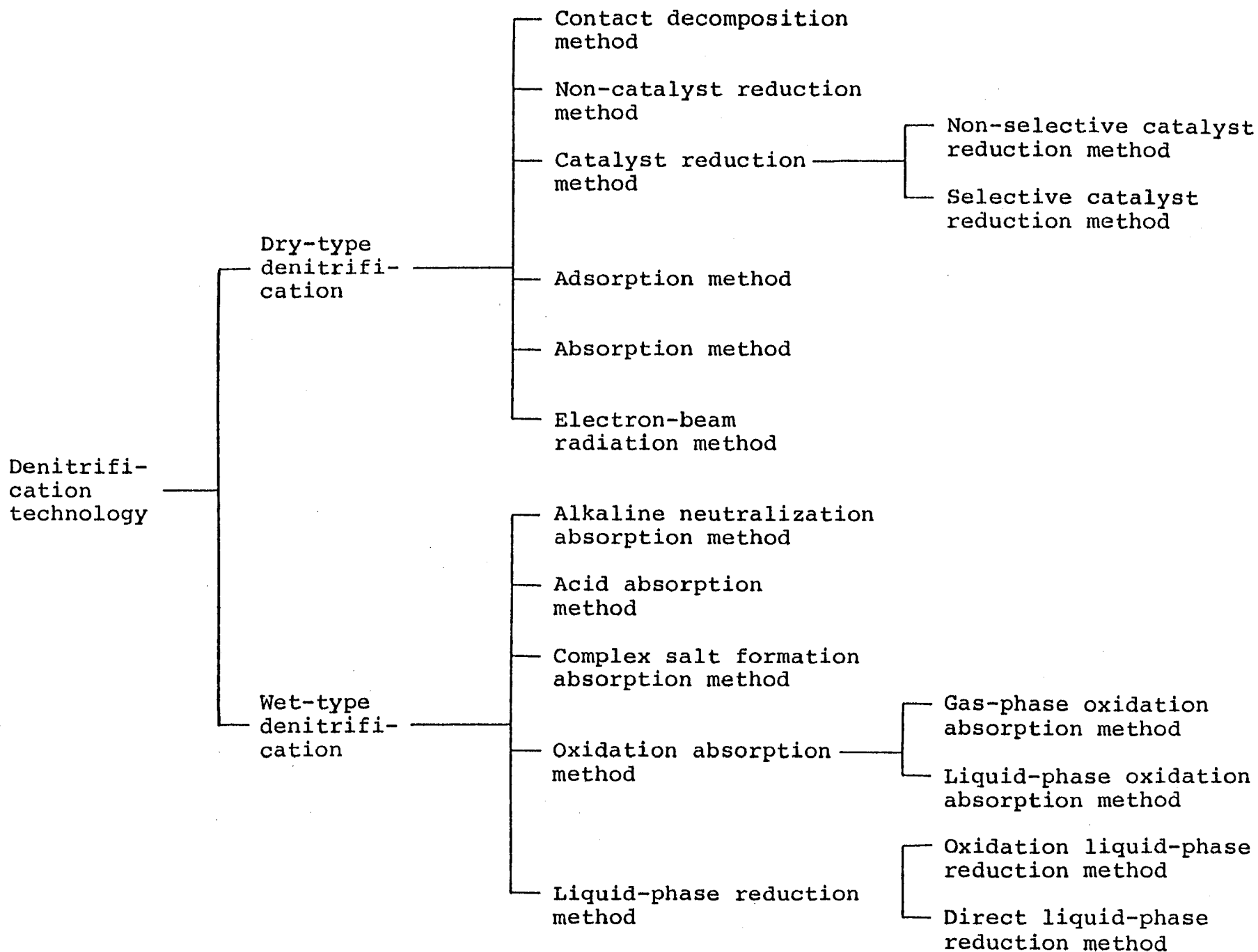premature to evaluate it to have reached the stage
of practical usefulness.

Figure 1   Classification of exhaust gas denitrification technologies

Table 1 Development state of smoke denitrification devices
(NH₃ Catalyst reduction method) (Dry-type practical size devices)

Developing firm	Source	Fuel type	Capacity	Gas pre-treatment	Type of catalyst bed	SV	Reaction temperature	Operation date
Sumitomo Chenicals	Ammonia improvement furnace	LPG	Nm³/h 200,000	none	Fixed-bed box type	SV = 10,000	300 ∿ 350°C	April 1975 ∿
	Methanol improvement furnace	"	200,000	"	Fixed-bed cylindrical type	SV = 7,000	"	May 1974 ∿
	Ammonia improvement furnace	"	250,000	"	Fixed-bed cylindrical type	SV = 6,000	"	Jan. 1975 ∿
	Boiler	"	100,000	"	Fixed-bed cylindrical type	SV = 7,000	"	Jul. 1975 ∿
	Boiler	"	200,000	"	"	SV = 7,000	"	April 1975 ∿
	Metal heating furnace	"	10,000	"	"	SV = 7,000 ∿10,000	"	Sept. 1975 ∿
	Boiler	C-fuel oil	30,000	Dust collector (Cottrell)	"	SV = 4,000	"	Jul. 1973 ∿
	Boiler	"	240,000	E.P	Fixed-bed box type	SV = 5,000	350°C	Mar. 1976 ∿
	"	"	300,000	E.P	Moving bed	SV = 5,000	"	Nov. 1976 ∿
Mitsubishi Kakoki	Metal heating furnace	LNG	5,000	none	Vertical cylinder	SV = 3,100	400 ∿ 450°C	Feb. 1976 ∿
	Boiler	C-fuel oil	14,000	none(temp. rise only)	"	SV = 3,000	350 ∿ 400°C	Jul. 1976 ∿
Hitachi Ltd.	Boiler	C-fuel oil	15,000	none	Intermittent moving bed	SV = 6,000	335°C	Oct. 1976 ∿
	Coke furnace	MG	500,000	none(temp. rise only)	"	SV = 6,200	335°C	Nov. 1976 ∿
Japan Gasoline	Boiler	C-fuel oil	125,000	none	Fixed-bed cylindrical type (2-tower type)	-	400°C	Aug. 1975 ∿
	Petroleum heating furnace	C-fuel oil + gas	50,000	none	Parallel passage	SV = 4,000	390 ∿ 400°C	Nov. 1975 ∿
	Boiler	FCC discharge gas (CO)	70,000	none	"	SV = 5,000	390 ∿ 400°C	Jul. 1976 ∿

Developing firm	Source	Fuel type	Capacity	Gas pre-treatment	Type of catalyst bed	SV	Reaction temperature	Operation date
Mitsui Ship-building	Boiler	FCC dis-charge gas (CO)	Nm³/h 240,000	E.P	Fixed bed	SV = 3,000	350 ∿ 400°C	Oct. 1975 ∿
Kurashiki Spinning	Boiler	C-fuel oil	30,000	none	Moving bed	SV = 10,000	350°C	Aug. 1975 ∿
Hitachi Ship-building	Catalyst bak-king furnace	LPG	10,000	none	Vertical wall type			
	Petroleum heating furnace	FCC discharge gas LBG (Butane)	350,000	E.P	Radial flow type			Oct. 1975 ∿
	Power gene-rator boiler	C-fuel oil	440,000	E.P desul-furization	"			Nov. 1975 ∿
	Plante annealing furnace	LPG	6,000	none (cooling)	Vertical wall type	SV = 4,000 ∿5,000	350 ∿ 420°C	Oct. 1975 ∿
	Metal heating furnace	Kerosine	70,900	"	Radial flow type			May 1976 ∿
	Sintering furnace	–	762,000	E.p desul-furization	Screen type			Nov. 1976 ∿
	Metal heating furnace	Light oil	10,000	none				Dec. 1976 ∿
Asahi Glass	Glass melting furnace	Heavy oil	75,000	Dust removal, desulfuri-zation		Under experiment	under experiment	Feb. 1976 ∿

(Non-catalyst reduction method)

Tonen Technology	Boiler	Heavy oil	450,000	none	Non-catalyst denitrification	–	700∿1,100°C	Oct. 1975 ∿
	Petroleum heating furnace	"	200,000	"		–	"	Jul. 1975 ∿

(2) As for the wet type of exhaust gas denitrification
equipment, they are for the most part still in the
testing stage but there are seven units (with a total
capacity of 350,000 Nm^3/h) in operation, which can
be evaluated as practically useful. The wet system
is capable of a denitrifying rate of more than 90%
and the remaining problem is the treatment of waste
fluid and the improvement of economy. With regard to
the treatment of waste fluid, the development of a
system is under way. In this respect, the develop-
ment of a system which does not allow nitric acid
radical to remain in the waste fluid is desired.
Now under way is the development of such wet type
denitrification equipment that they are be readily
attached to the existing desulfurization equipment
and are capable of easily and economically performing
simultaneously such functions as desulfurization,
denitrification and dust removal. Attention should
be paid to further technological advances to be made
in this particular field.

Compared with the time of the hearing of 1975, both
dry and wet systems have reduce the cost of exhaust
gas denitrification considerably.

Table 2 Development state of smoke denitrification devices.
(Wet-type practical size devices)   (as of August 1976)

Developing firm									
Fuji Kasui	Oxidation absorption method	Chlorine dioxide	$NaOH-Na_2SO_3$	Boiler	C-fuel oil	62,000	90 ∿ 95%	99.5%	21,000 hrs.
	"	"	"	Metal heat-ing furnace	B.C-fuel oil	85,000	90 ∿ 93%	–	8,400
	"	"	"	"	"	100,000	"	–	10,500
	"	"	"	Boiler	"	39,000	"	–	14,000
	"	"	"	Metal heat-ing furnace	"	39,000	"	–	12,600
	"	Ozone	"	"	"	12,000	85 ∿ 90%	–	5,900
	"	"	"	Boiler	"	16,000	85 ∿ 90%	–	7,600

4. The Present State and Problems of Low NOx Combustion

    Technology

The nitrogen oxides (NOx) are not only the fuel NOx
produced by the reaction of the nitrogen compounds contained
in the fuel itself (hereafter referred to as "N content")
and oxygen in the air during the process of combustion but
also the thermal NOx produced by the reaction of nitrogen
and oxygen present in the air at high temperatures.

Such being the case, the measures to be taken for
reducing the NOx emissions may be classified into the
following three types.

(1) To reduce the N content in the fuel or switch
over to a fuel having less N content. (2) To make the
combustion conditions difficult for the production of NOx.
(3) To remove NOx from combustion exhaust gases.

As for (1), the techniques for removing the N content
selectively from a fuel as the desulfurization of a heavy
oil, still remain to be developed in the future. At the
present time, it is only known that the N content is
partially removed as a secondary effect of the desulfuri-
zation of a heavy oil. As for (2), several techniques
have been developed for low NOx combustion. With regard
to (3), various techniques for exhaust gas denitrification
have been developed as mentioned earlier.

5. Principle and Problems of Low NOx Combustion Techniques

(1) Switching to low-NOx fuels

Generally speaking, the various fuels can be arranged as follows according to the amounts of NOx they causes when burnt.

Coal > Asphalt > C heavy oil > B heavy oil > A heavy oil > Gas oil > Kerosene > LPG > LNG > City gas > Co Methanol > H_2. The above order is also applicable to the ratios of NOx contents in the fuels, and therefore the best way to reduce NOx emissions is to use fuels having lower N content.

The switching to the use of better-quality fuels involves such economical problem as the increase in cost of fuel and also such technical problems as the alterations to be made to the combustion equipment as required by the use of such new fuels.

The utilization of the byproduct gases, as is done in the iron manufacturing and chemical industries, is an effective way to reduce NOx emissions.

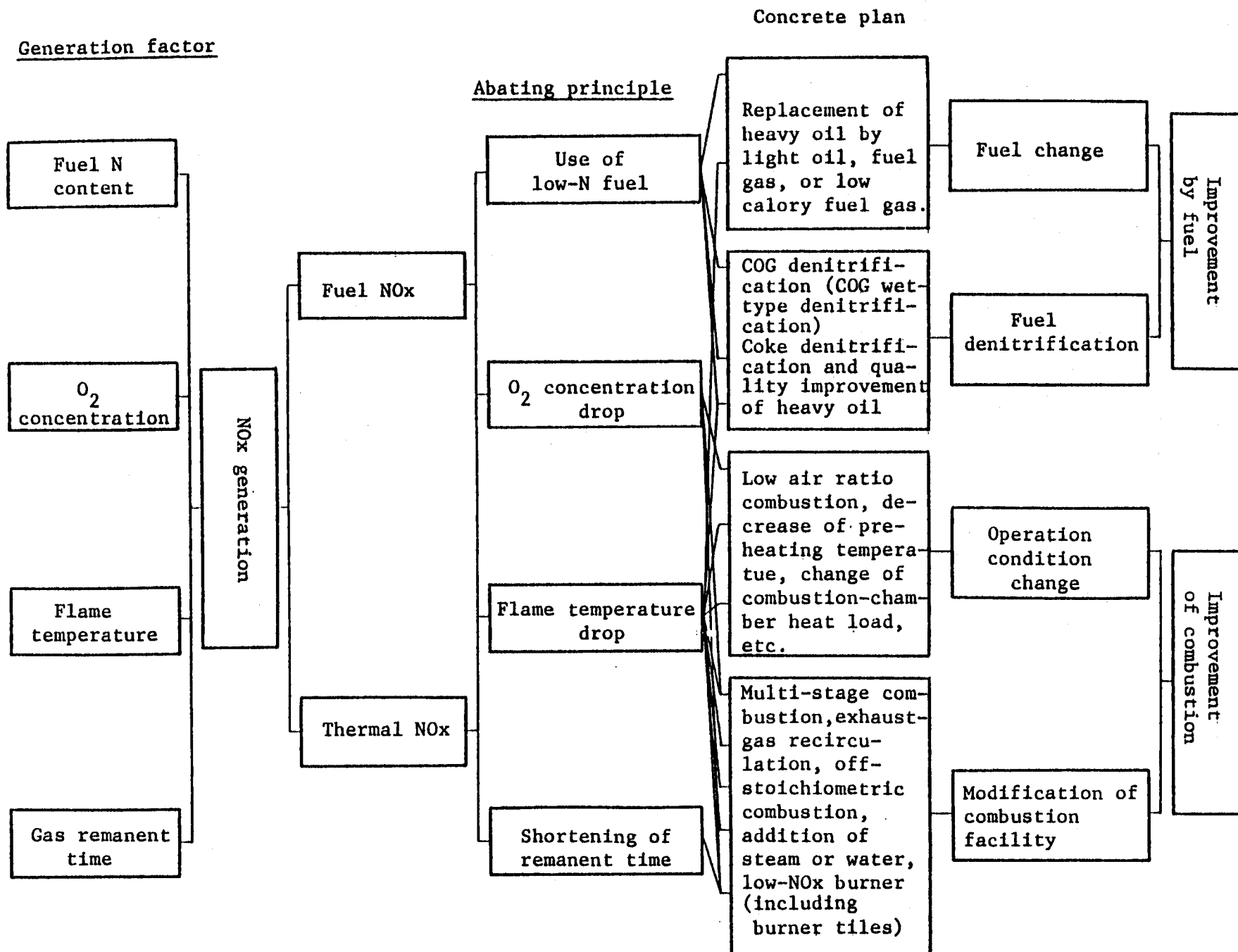(2) Principle and problems of low NOx combustion techniques

As was mentioned earlier, if NOx emissions are to be reduced, it is necessary to reduce the production of fuel NOx and thermal NOx.

First, the N content in the fuels, which causes the
production of fuel NOx, is not completely converted
into NOx through the process of combustion but its
rate of conversion is generally governed by the
combustion conditions. It is known particularly that
the conversion rate is decreased when combustion takes
place in the air with low oxygen concentrations.
The production of thermal NOx can be reduced by (1)
lowering the air ratio, (2) lowering the flame temperature,
and (3) shortening the time the combustion gases and
exposed to high temperatures. These methods can be
used independently or in combination for decreasing
the amounts of NOx to be produced in the process of
combustion.

i) Combustion at a low air ratio (Combustion at low
    oxygen concentration)

    Generally, combustion is caused to take place in
    an oxidizing atmosphere with an excess air but a
    lower air ratio will results in the reduction of
    fuel NOx and thermal NOx. However, if the air
    ratio* is lowered excessively, it will cause
    incomplete combustion, thus increasing the emissions
    of soot and smoke, carbon monoxide, and hydrocarbons
    remaining unburnt and so forth.

Generation factor

Abating principle

Concrete plan

Generation factor		Abating principle	Concrete plan		
Fuel N content	Fuel NOx	Use of low-N fuel	Replacement of heavy oil by light oil, fuel gas, or low calory fuel gas.	Fuel change	Improvement by fuel
O₂ concentration		O₂ concentration drop	COG denitrification (COG wet-type denitrification) Coke denitrification and quality improvement of heavy oil	Fuel denitrification	
Flame temperature	NOx generation	Flame temperature drop	Low air ratio combustion, decrease of preheating tempera-tue, change of combustion-chamber heat load, etc.	Operation condition change	Improvement of combustion
Gas remanent time	Thermal NOx	Shortening of remanent time	Multi-stage combustion,exhaust-gas recircu-lation, off-stoichiometric combustion, addition of steam or water, low-NOx burner (including burner tiles)	Modification of combustion facility	

* (Note)   The ratio of the amount of theoretical
           air to the amount of air which is actually
           used for combustion.

Therefore, the NOx reducing measures in the form
of combustion at a low air ratio include (1) a
method in which the excess air is reduced to the
lowest level possible to reduce the production of
soot and (2) a method in which the air ratio is
first lowered to gasify the fuel and then additional
air is injected to cause the complete combustion
of the fuel.

This concept is used in the following applications.

(1)   Changing the air ratio ..... Combustion is
      caused to take place at the lowest air ratio
      possible.

(2)   Changing the mixture characteristic .....
      The mixture of air and fuel is changed by
      the change of air resistor, etc. to obtain
      the lowest air ratio possible.

(3)   Use of low NOx burner

         Mixture acceleration type ..... The mixture
            of fuel and air is accelerated to cause
            combustion at a low air ratio.

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Split flame type ..... A flame is split

into smaller independent flames, thereby

to increase the radiation of heat from

the flame and to accelerate the combustion

at a low air ratio.

Self-circulation type ..... High-temperature

combustion gas is circulated within the

burner to gasify the fuel at low oxygen

concentrations.

Staged combustion assembly type ..... Low

and high air ratio combustion burners

and two-stage combustion burners are

assembled.

(4)   Staged combustion

Off-stoichiometric combustion ..... Low air

ratio burner and high air ratio burner

are used in combination.

Two-stage Combustion ..... Low air ratio

combustion in the first stage and complete

combustion in the second stage.

ii)   Lowering of combustion temperature

Generally speaking, the previous furnaces have been

designed mainly to make them compact in size and

to produce a high thermal efficiency by complete

combustion of the fuel, and therefore the temperature tends to rise so much higher within them and produce high concentrations of NOx. This being so, the production of NOx, particularly thermal NOx, can be reduced generally by lowering the combustion gas temperature, except for some special furnaces which require high temperatures. This concept is used in the following methods.

(1) Low air ratio combustion ..... In the case of low air ratio combustion as mentioned in (1), combustion progresses gradually, therefore, combustion gas temperature lowers accordingly.

(2) Low thermal load combustion ..... The temperature within the furnace can be lowered by burning at a low thermal load.

(3) Exhaust gas recirculation ..... If part of exhaust gas is recirculated, the amount of generated heat per unit volume of gas is so much reduced and combustion temperature is lowered accordingly.

(4) Use of low-temperature preheated air ..... Usually preheated air is used to facilitate combustion or for surplus heat utilization. Low-temperature air is used for this purpose

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to lower the combustion temperature.

(5) Water or water vapor mixing ..... Water or

water vapor with a large thermal capacity

and heat-removing effects are mixed to

lower the combustion temperature.

iii) Shortening of the stay in the high-temperature zone

The production of thermal NOx can be reduced by

shortening the time the combustion gas stay in

the high-temperature zone.

It may be considered that most of the NOx reducing

measures so far described incorporate the principle

of NOx reduction by the shortening of the stay of

combustion gases in the high-temperature zones.

As we have just discussed, there are various low

NOx combustion techniques in which various principles

are used in combination to eliminate the shortcomings

of the individual methods. Fig. III-1 shows such

techniques classified by the NOx reducing methods

employed.

Below, the guarantee values, target values, and

the NOx decrease effect in actual application on

existing smoke emitting facilities, of the makers

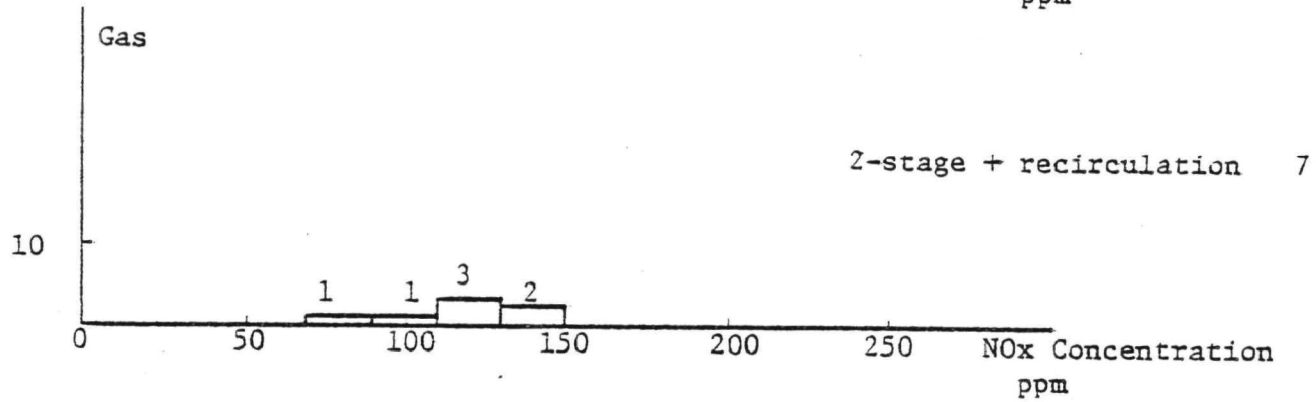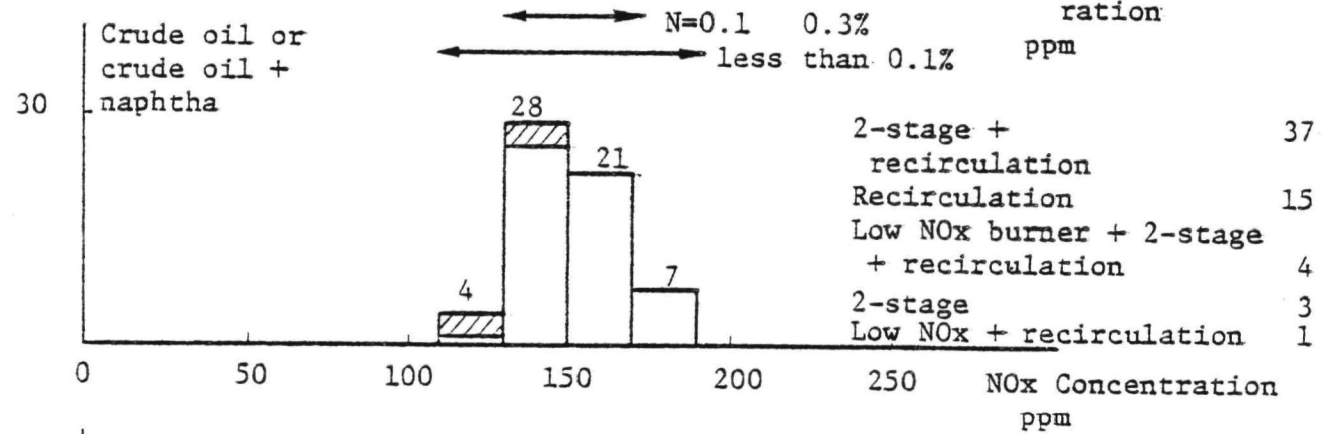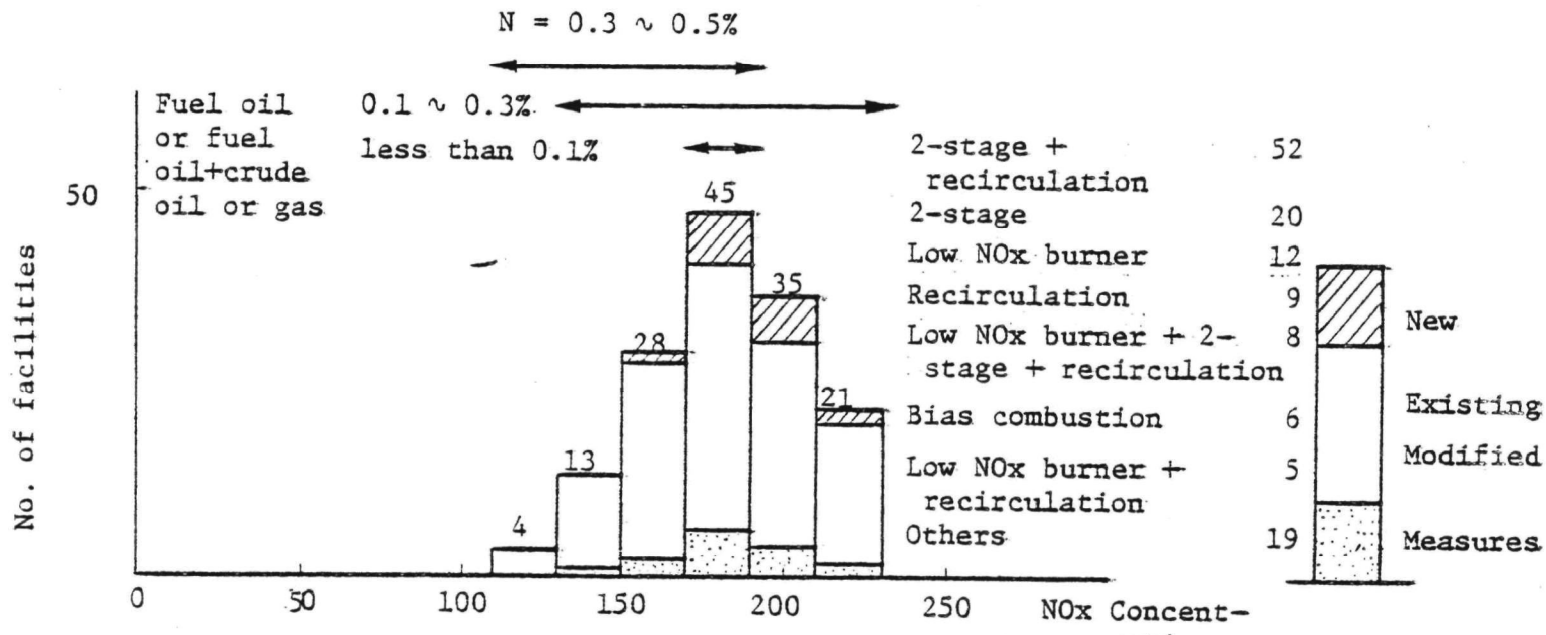developing low-NOx combustion technologies by types

of facilities.

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Table 3 Guarantee values of makers developing low-NOx combustion technologies for boilers

(in ppm)

Type of measure	C fuel oil	B fuel oil	A fuel oil	Light oil, kerosine	Gas	Note
Self-recirculating type low-NOx burner	(N 0.2 0.25%)	(N 0.05%)				
(1)	150 ~ 160		65	55	50	
(2)	120 ~ 165	100 ~ 135	50 ~ 65			Target value
(3)	Minasu fuel oil 50 ~ 70		40	30	LPG 20 ~ 40	Target value for medium boiler
Low-NOx burner+exhaust gas recirculation or 2-stage combustion				80	70	Large boiler
Low-NOx burner+exhaust gas recirculation 2-stage combustion	140 (Crude oil 130)					"
2-stage combustion+exhaust gas recirculation	150					Medium boiler
2-stage combustion	150					Small boiler
In-furnace exhaust-gas recirculation+steam injection	130 ~ 159	83 ~ 94	60 ~ 72	43 ~ 51	50	Empirical value
In-furnace exhaust gas recirculation+emersion fuel	100 ~ 140	100 ~ 140	38 ~ 57	35 ~ 55		"
2-stabe combustion+steam injection (user)	120 ~ 160	120 ~ 160	60 ~ 80			
Low-NOx burner with built-in 2-stage combustion	N 0.17% 6	N 0.17% 63		28 ~ 34	12 ~ 32	Empirical value

$N = 0.3 \sim 0.5\%$

Fuel oil
or fuel
oil+crude
oil or gas

$0.1 \sim 0.3\%$

less than 0.1%

No. of facilities

50

45

35

28

13

21

4

2-stage + recirculation	52
2-stage	20
Low NOx burner	12
Recirculation	9
Low NOx burner + 2-stage + recirculation	8
Bias combustion	6
Low NOx burner + recirculation	5
Others	19

New

Existing
Modified
Measures

0   50   100   150   200   250   NOx Concentration
ppm

Crude oil or
crude oil +
naphtha

30

$N=0.1$ 0.3%
less than 0.1%

28

21

7

4

2-stage + recirculation	37
Recirculation	15
Low NOx burner + 2-stage + recirculation	4
2-stage	3
Low NOx + recirculation	1

0   50   100   150   200   250   NOx Concentration
ppm

Gas

10

1   1   3   2

2-stage + recirculation   7

0   50   100   150   200   250   NOx Concentration
ppm

Coal or
coal mixed

2-stage	13
2-stage + low-NOx burner	3
Bias combustion	2
Low-NOx burner	1

10

10   9   4   5   4

0    $\sim$ 300   400   500   600   700   NOx Concentration

Table 4 Guarantee value of makers developing low-NOx combustion technology for metal heating furnace
(in ppm)

Type of measure		C fuel oil	A fuel oil	Light oil, kerosine	Gas	Note
Self-recirculating type low-NOx burner	(1)	85 ∿ 90	45 ∿ 50		20 ∿ 50	
	(2)	Minasu crude oil 50 ∿ 80	50	50	<LPG> 35 ∿ 55	Target value
	(3)				74 ∿ 77	Empirical value
Low-NOx burner with built-in 2-stage combustion		105		60	<COG> 50 ∿ 85	Empirical value

Table 5 Examples of metal heating furnaces adopting low-NOx burner

Name of facility	Size of exhaust gas volume (Nm^3/hr)	Fuel	NOx concentration (converted for O_2 11%)		Reduction rate (%)
			Before measure	After measure	
Soaking furnace	33,000	BFG + CPG	New	110	–
Hot-rolling heating furnace	63,400	Heavy oil + COG	200 140	110 75	45 46
Heating furnace (W.B. continuous)	196,000	Heavy oil	New	70	–
Heating furnace (W.B. continuous)	131,000	BFG + COG ± Heavy oil	150	100	33
Medium pipe heating furnace	65,700	LPG	New	70	–
Medium pipe heat-treatment furnace	48,400	LPG	New	70	–
Quenching furnace (W.B. continuous)	14,800	Kerosine + LPG	New	20	–
Annealing furnace (W.B. continuous)	13,300	Kerosine + LPG	New	20	–

Note) Facilities with * marks are low in furnace temperature and use light fuel. Its exhaust gas has an intringically low NOx concentration as compared with conventional furnaces, so that after the process, NOx concentration is made especially low.

Table 6 Guarantee value of makers developing low-NOx combustion technologies for petroleum heating furnace

Type of measure	C fuel oil	A fuel oil	Light oil kerosine	Gas
Self-recirculating-type low-NOx burner	123 ~ 150 ppm	70 ~ 90 ppm	50 ~ 60 ppm	50 ~ 60 ppm

Table 7 After-measure NOx concentration for petroleum heating furnace by fuel type and measure type

(Note) Numbers indicate No. of facilities, new (existing)

Fuel	Measure	Max -50	50 ~ 70	70 ~ 90	90 ~ 110	110 ~ 130	130 ~ 150	150 ~ 170	170 ~ 190	Total
C fuel oil (N = 0.08 ~ 0.2%)	LNB			1	(6)	4 (3)		(1)		5 (10)
	EGR		1	3	1					5 (0)
	LNB + EGR				1		1			2 (0)
	Low O_2				(1)	(2)	(1)			0 (4)
	Sub-total		1 (0)	4 (0)	2 (7)	4 (5)	1 (1)	0 (1)		12 (14)
C fuel oil + gas	LNB		(1)	2	3 (1)	2 (1)	2 (2)			9 (5)
	EGR			1	1					2 (0)
	LNB + EGR				1					1 (0)
	Low O_2				(1)	(3)				0 (4)
	Sub-total		0 (1)	3 (0)	5 (2)	2 (4)	2 (2)			12 (9)
Light oil	LNB		1 (2)							1 (2)
Gas	LNB	2 (1)	5	4 (1)	2	1				14 (2)
	EGR		1							1 (0)
	LNB + EGR	1	1							2 (0)
	Low O_2	(1)			(2)	(1)				0 (4)
	Sub-total	3 (2)	7 (0)	4 (1)	2 (2)	1 (1)				17 (6)
	Total	3 (2)	9 (3)	11 (1)	9 (11)	7 (10)	3 (3)	0 (1)		42 (31)

(B)   Controls on Emissions from Motor Vehicle

On December 26, 1977, the Central Council for Control of Environmental Pollution submitted to the State Minister and Director-General of the Environment Agency a recommendation pertaining to the Long-Term Policy for Establishment of Maximum Permissible Limits of Motor Vehicle Emissions. The recommendation set forth the targets to be attained in two stages as regards the maximum permissible limits of nitrogen oxides (NOx) emissions by motor vehicles, other than gasoline-fueled passenger cars, for which the Fiscal 1978 Emission Controls are scheduled to be enforced as from April this year.

In line with the recommendation, the Environment Agency issued a public notice on January 30 this year regarding the maximum permissible limits of NOx emissions for the first stage (dubbed 1979 Emission Controls) (Notification of the Environment Agency No. 5, Jan. 30, 1978).

At the same time, the Agency issued another notice as regards the strengthened controls on motor vehicle noise (dubbed 1979 Noise Controls) (Notification of the Environment Agency No. 4, Jan. 30, 1978). This was based on a recommendation submitted by the said Council on June 15, 1976 with respect to the long-term targets for the maximum permissible limits of automobile noise.

Following is a gist of the recommendation pertaining
to the Long-Term Policy for Establishment of Maximum
Permissible Limits of Motor Vehicle Emissions, the notifi-
cation of the Environment Agency concerning the maximum
permissible limits of NOx emissions (1979 Emission Controls)
and the notification of the Environment Agency concerning
the maximum permissible limits of automobile noise (1979
Noise Controls):

1.   Recommendation:

With reference to the request for a recommendation
pertaining to the Long-Term Policy for Establishment of
Maximum permissible Limits of Motor Vehicle Emissions
(dated September 18, 1971), this Council submitted recommen-
dations to the State Minister and Director-General of
Environmental Agency concerning gasoline- and liquefied
petroleum gas (LPG)-fueled passenger cars on October 3,
1972 and again on December 27, 1974. However, in view
of the necessity of stiffening emission controls on other
types of motor vehicles as well, the Council's Expert
Committee on Motor Vehicle Pollution studied the matter
for about two years and a half, and recently came up with
a report as per attached hereto.

The Air Quality Subcommittee of this Council received
and deliberated on the report, and consequently, decided

to accept the report as the Long-Term Policy for Establishment of Maximum Permissible Limits of Motor Vehicle Emissions. At the same time, the Subcommittee concluded it is desirable to further promote comprehensive measures for the prevention of air pollution due to automobile exhaust gas.

Accordingly, this Council hereby recommends the Government to protect the living environment in areas adjacent to roads as soon as possible by attaining the targets for maximum permissible levels of motor vehicle emissions as specified in the following Seciton 1, and at the same time, taking measures for the prevention of air pollution due to automobile exhaust emissions as referred to in Seciton 2.

Section 1.   Establishment of Long-Term Targets for Maximum
             Permissible Limits and Dates of Attainment

It is considered appropriate to attain the target values for maximum permissible limits of nitrogen oxides (NOx) emissions (average values) in two stages as indicated in the following table:

Category of Motor Vehicle		Target Values of Maximum Permissible Limits (average values)		Measurement Method
		1st Stage	2nd Stage	
Diesel-oil-fueled ordinary or small-size motor vehicles	Direct injection type	540 ppm	470 ppm	Diesel 6-mode
	Indirect Injection type	340 ppm	290 ppm	
Gasoline- or LPG-fueled ordinary motor vehicles & small-size motor vehicles (excluding those exclusively used for carrying passengers with a riding capacity of 10 persons or less)	With gross vehicle weight (GVW) exceeding 2,500 kg	1,100 ppm	750 ppm	6-mode
	With GVW of exceeding 1,700 kg and up to 2,500 kg	12g/km	0.9g/km	10-mode
	With GVW of 1,700 kg or less	1.0g/km	0.6g/km	
Light motor vehicles (excluding those exclusively used for carrying passengers or equipped with two-stroke engine		1.2g km	0.9g/km	

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The target values for the first stage should be attained in 1979. The reason is that this Council considers it proper that they be achieved simultaneously with the first-stage targets under the long-term policy for establishment of maximum permissible limits of motor vehicle noise, recommended earlier by this Council.

To attain the second-stage target values for gasoline-fueled motor vehicles, it is essential to develop related technologies, centering on the large-scale adoption of emission-reducing techniques as developed for passenger cars. As regards diesel-powered vehicles, various measures are now under study, including a further injection retard, installation of supercharger and exhaust gas recirculation (EGR).

Some of these techniques still defy prediction as to how soon they will become practically applicable. Therefore, in the enforcement of the emission controls, full consideration needs to be given to the diversity of the types of vehicles subject to the controls, and this makes it difficult to forecast precisely when the target values for the second stage could be attained.

Nevertheless, the current state of air pollution due to nitrogen dioxide is such that even when the emission controls for the second-stage targets are enforced with full effectiveness, it would presumably be very difficult

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to achieve even the intermediate targets of the environ-
mental quality standards in those areas where the degree
of pollution is especially high. This being the case,
this Council considers it necessary to put the second-
stage emission controls into practice within several
years after the enforcement of the first-stage controls
or by the first half of the 1980s at the latest.

Section 2. Measures for Lessening Air Pollution Due to
Automobile Exhaust Emissions Other than
Controlling Exhast Gases of Individual Motor
Vehicles

In those cities whose air is exceedingly polluted
due to heavy motor traffic, it is desirable to further
promote the following measures throughout the country
with the object of restricting the total volume of
vehicular traffic and ensuring a smooth traffic flow
while resolving various related problems, in addition
to controlling exhaust gases of individual motor vehicles.

(1) It is essential to step up measures mainly geared
     to improvement of roads, such as the elimination of
     traffic bottlenecks through construction of bypasses,
     adoption of grade separation, expansion of road width,
     etc., and establishment of green buffer zones to
     mitigate the effects of automobile exhaust emissions

upon local inhabitants. In a long-range perspective, moreover, it is desirable to take such measures as the restriction of the establishment or expansion of workshops, and the relocation of those facilities which contribute to sharply increasing motor traffic.

(2)   Mass transit systems like railroads and bus services should be expanded, and measures taken to encourage the public to use such means of transport with a view to facilitating a diversion of transport needs from passenger cars, etc.

(3)   As for the transport of goods, the traffic volume of trucks, etc. should be reduced by such means as the streamlining of freight collection and distribution, and the introduction of a freight transit information system.

(4)   Traffic control measures should be further intensified through the comprehensive regulation of urban traffic, the traffic control systems, etc. so as to curb the total volume of motor traffic and to ensure a smooth flow of vehicular traffic.

Section 3.   Conclusion

This Council has worked out the present recommendation regarding nitrogen oxides emitted by automobiles in the

belief that the allowable limits should be made as strict as possible in consideration of the current state of development in regard to techniques for reducing exhaust emissions of trucks, etc. and the outlook for the practical application of such techniques. But the current state of air pollution is such that even in the event all the vehicles subject to the emission controls achieve the second-stage targets, the situation would not be fully improved to the extent of reaching the present intermediate targets of the environmental quality standards in those districts where air pollution has assumed especially serious proportions.

In these circumstances, it is believed imperative to further strengthen the controls on the emission of nitrogen oxides and to carry out various measures for the prevention of air pollution, and studies to these ends should be conducted without interruption. However, although the Council's deliberations this time have been primarily devoted to reducing the emissions of nitrogen oxides, it is also essential to study the necessity of imposing or strengthening controls on other substances emitted by motor vehicles. At present, this Council is deliberating on the conditions for assessment of the effects of nitrogen dioxide upon human health. Therefore, it must be pointed out that the results of deliberations on the matter should also be given full consideration in the implementation

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of the control as specified in the present recommendation and the promotion of various related measures.

Revision of Maximum Permissible Limits of Motor Vehicle Emissions (summary)

The Environment Agency decided to stiffen the controls on the emissions of nitrogen oxides from vehicles other than gasoline- or LPG-fueled passenger-cars as from 1979 in conformity with a recommendation submitted by the Central Council for Control of Environmental Pollution in December 1977. Consequently, on January 30, 1978, it issued a public notice (Notification of the Environment Agency No. 5) for partial amendment of the Maximum Permissible Limits of Motor Vehicle Emissions (Notification of the Environment Agency No. 1, January 21, 1974). The revised limits are as follows:

Classification of automobile		Measurement Method (Unit)	1979 Controls		1975 Controls	
			Maximum Permissible Limits	Average Value (A)	Maximum Permissible Limits	Average Value (B)
Gasoline- or LPG-fueled light-duty vehicles (ordinary or small-size motor vehicles with a gross vehicle weight (GVW) of 1.7 tons or less, excluding those exclusively used for the carrying passengers with a riding capacity of 10 persons or less)		10-mode (g/km)	1.4	1.0	2.3	1.8
		11-mode (g/test)	10.0	8.0	20.0	15.0
Gasoline- or LPG-fueled medium-duty vehicles (ordinary or samll-size motor vehicles with GVW of over 1.7 tons and up to 2.5 tons, excluding those exclusively used for carrying passengers with a riding capacity of 10 persons or less) and light motor vehicles (excluding those exclusively used for carrying passengers and those equipped with two-stroke engines)		10-mode (g/km)	1.6	1.2	2.3	1.8
		11-mode (g/test)	11.0	9.0	20.0	15.0
Gasoline- or LPG-fueled heavy-duty vehicles (ordinary or samll-size motor vehicles with GVW of more than 2.5 tones, excluding those exclusively used for carrying passengers with a riding capacity of 10 persons or less)		6-mode (ppm)	1,390	1.100	1,850	1,550
Diesel-oil-fueled vehicles	Direct injection type	Diesel 6-mode (ppm)	700	540	850	650
	Indirect injection type		450	340	500	380

Changes of Effect of Automobile Exhaust Control

(Average of NO$_x$ Emission Volume)

I   Gasoline or LPG -fueled ordinary motor vehicles
    & small-size motor vehicles

(1)   With gross vehicle weight (GVW) of 1,700 kg or less
      1,700 kg or less

100%	Before April, 1973
71%	April, 1973
59%	April, 1975
32%	First Stage
19%	Second Stage
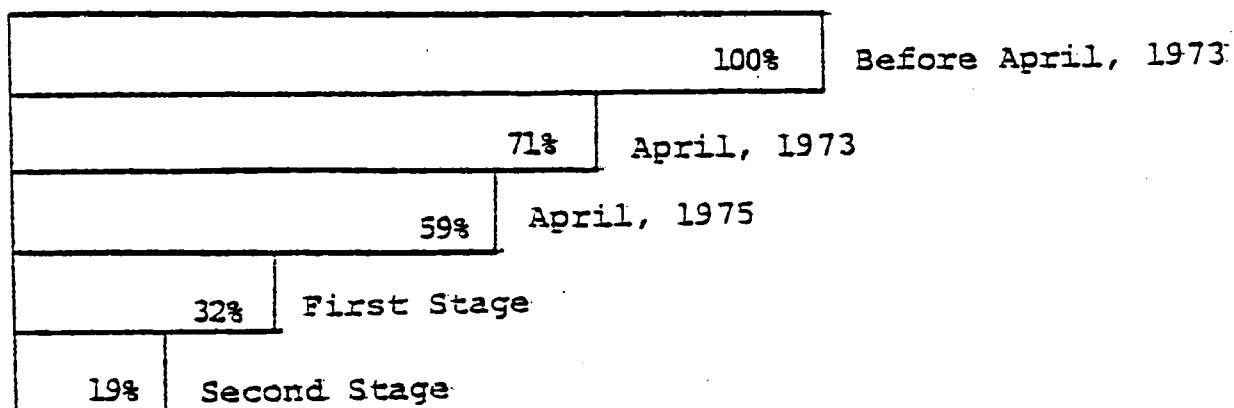
(2)   With GVW exceeding 1,700 kg and up to 2,500 kg

100%	Before April, 1973
71%	April, 1973
59%	April, 1975
39%	First Stage
29%	Second Stage

Annex-1

(3). With GVW exceeding 2,500 kg

100% Before April, 1973

70% April, 1973

59% August, 1977

42% First Stage

29% Sacond Stage
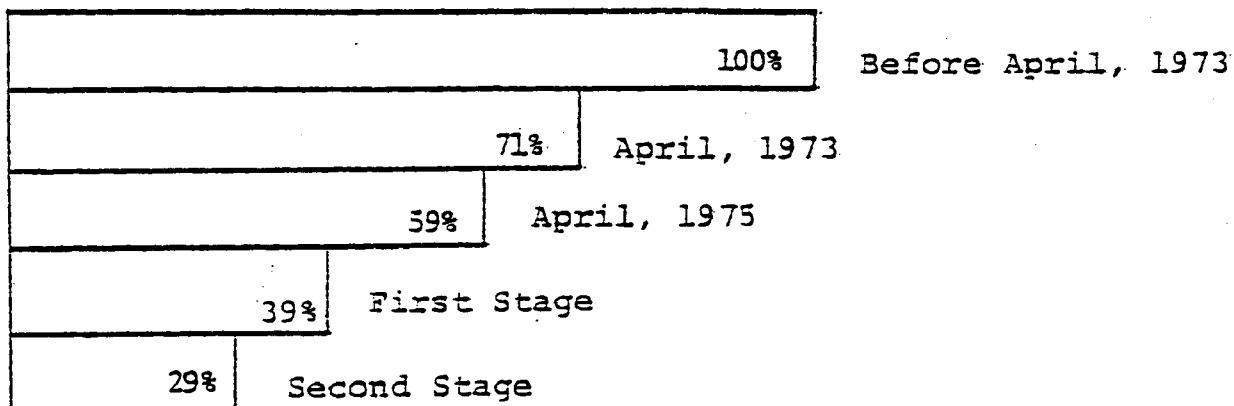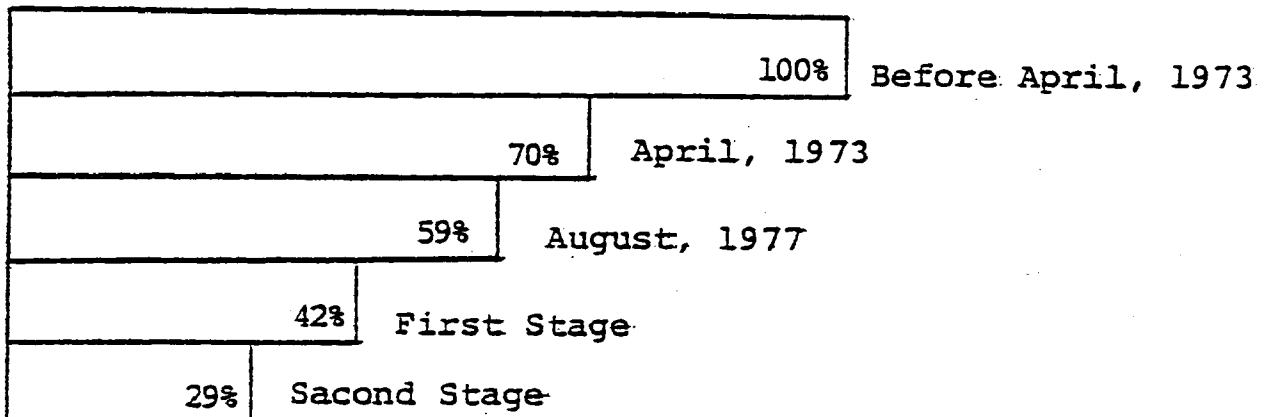
2   Diesel-oil-fuelded ordinary or small-size motor vehicles.

(1) Direct injection type

100% Before September, 1974

80% September, 1974

68% August, 1977

56% First Stage

49% Second Stage

(2) Indirect injection type

100% Before September, 1974

80% September, 1974

68% August, 1977

60% First Stage
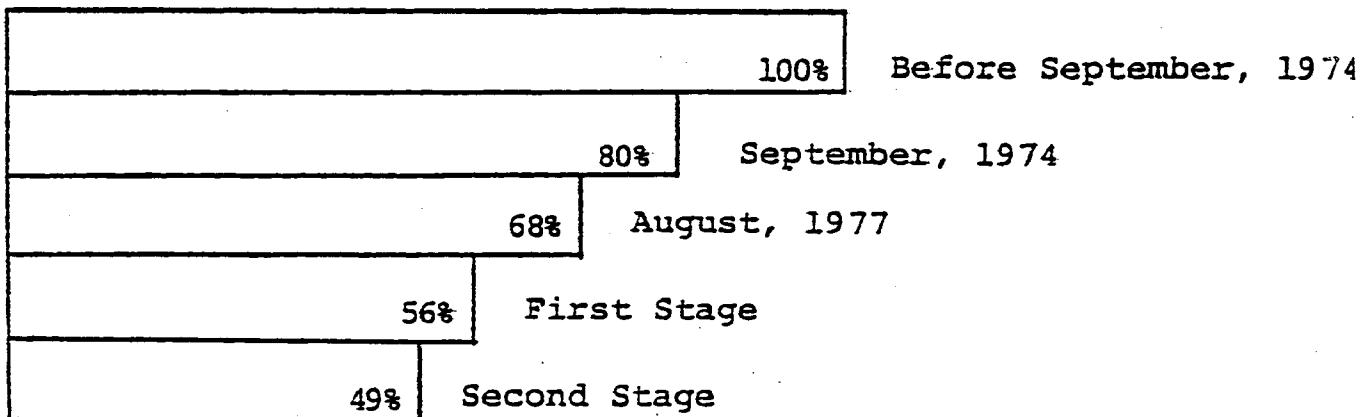
52% Second Stage
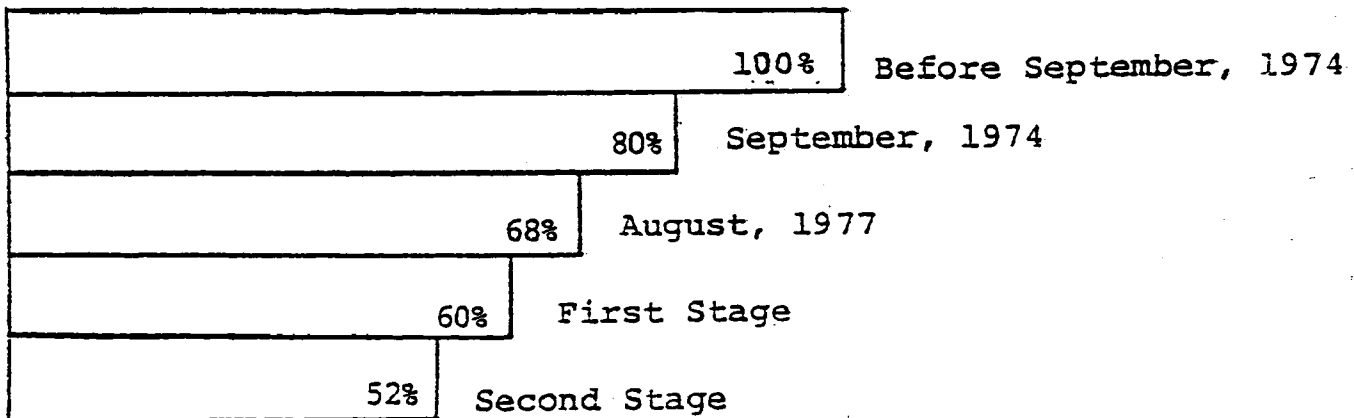
III. CONTROL MEASURES AGAINST EMISSION OF HYDROCARBONS FROM
     STATIONARY SOURCES

1.

   Hydrocarbons along with nitrogen oxides are precursors
for creating photochemical oxidants. Regarding nitrogen
oxides, emission controls have already been enforced because
of their inherent toxicity. But as for hydrocarbons, only
automobile exhaust gas is subject to control, and no national-
level controls are in force concerning the emission of
hydrocarbons from stationary sources, such as factories and
so on.

   The Environment Agency has set up the investigation group
on measures to reduce the emission of hydrocarbons from
stationary sources. Recently, it has announced the result
of the group's study conducted for about a year from October
1976. Major points of the report are as follows:

(1) Current level and evaluation of techniques for reducing
     the emission of hydrocarbons

(2) Information available as of now in regard to the
     photochemical reactivity of hydrocarbons

(3) Recommendations about future measures to reduce the
     emission of hydrocarbons from stationary sources

(4) Others

(i) Present state of application of emission control
techniques for hydrocarbons and problems involved,
as based on inquiries to the industries concerned

(ii) An outline of controls enforced by local governments.

As for the contents of emission control techniques
mentioned in (1), the present techniques applied to different
sources, such as storage facilities, distribution processes,
painting and printing processes are evaluated conceptually.

As for (2) information on photochemical reactivity of
hydrocarbons is collected; the degree of reactivity is divided
into five classes for each type of hydrocarbon on the basis of
various experimental data thus far obtained and announced.
Regarding recommendations on emission control measures mentioned
in (3), it is noted that hydrocarbons are emitted not only from
such stationary sources as oil tanks, but also from various
sources, including paints, printing ink, adhesives and cleaning
solvent. Therefore, measures for emission control will neces-
sarily vary in the degree of difficulty, and full consideration
should be given in working out appropriate control measures.
The report points out such measures will also conceivably have
to take account of the season and time when photochemical oxidant
emerges and areas where it occurs. For the present, it says,
measures should preferably by taken according to the following
guidelines:

(1)　To prevent the emission of hydrocarbons from tanks
storing them, such as petroleum, and the emission of
hydrocarbons in transferring them from tanks.

(2)　To prevent the evaporation of hydrocarbons from factories
and other workshops where hydrocarbons are used, such
as painting and printing factories.

(3)　To promote research and development of low-emission
paints and printing ink and enlarge the scope of their
use.

(4)　To step up a PR drive for encouraging painters and
printers to use low-emisison materials.

In addition, the report points up the need for effective
measures to prevent the emission of hydrocarbons from
petrochemical and other plants, since such emission cannot
be neglected in some areas.

At is noted in the report, hydrocarbons are emitted from
a large variety of sources, such as organic solvents contained
in paints, printing ink and adhesives, as well as the storage
facilities and distribution process of petroleum products,
and moreover, there are a large number of such sources.
Accordingly, the Environment Agency will have to take this
fact into full account in working out and enforcing administrative
measures to reduce hydrocarbon emission.

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In preparation for establishment of controlling the emission of hydrocarbons from stationary sources, the Agency intends to investigate the actual state of emission from each type of source, improve the monitoring system of non-methane hydrocarbons and examine concrete strategies for control.

For the immediate future, the Agency will take the following steps:

(1) Reduction of organic solvents contained in paints, etc. is essentially an effective means for preventing the emission of hydrocarbons. Moreover, it is also desirable from a viewpoint of saving resources. Therefore, the Agency requires the private quarters concerned and public research institutes to step up their research and development efforts for the practical and extensive use of low-emission paints and printing ink, centering on those with a low content of organic solvents.

(2) The Agency requires private quarters concerned to widen the use of low-emission paints, printing ink, etc. Besides, public agencies will be required to use such low-emission materials.

(3) The Agency requires private quarters handling hydro-carbons to cooperate in the prevention of hydrocarbon emission through their trade associations so that they may respond smoothly once legislative controls are introduced.

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(4) The Agency requires local governments to take steps in
     conformity with this report, when they intend to set up
     the regulations of hydrocarbon emission under local laws.

     In addition, the Agency will further promote researches
and investigations so far made in regard to the behavior of
hydrocarbons in the air.

     (1) Emission survey by materials, by types of facilities,
          and by sizes of facilities.

     (2) Survey on HC measurements

     (3) Fact-finding surveys in HC treatment installations.

2. Basic Concept of Emission Control

   1) Necessity for regulating the emission of hydrocarbons

          Hydrocarbons are substances that produce photochemical

     oxidants together with NOx. The Specialist Committee

     for Environmental Hydrocarbon Quality Standard of the

     Central Council for Environmental Problems reported that

     to maintain the concentration of photochemical oxidants

     within the relevant environmental quality standard, the

     concentration of hydrocarbons excluding mathane (referred

     to as "non-methane hydrocarbon" hereafter) must be kept

     below 0.20 - 0.31 ppmC in the three-hour average between

     6 and 9 AM, and this report was accepted by the Central

     Council (report submitted on August 13, 1976).

     According to the available monitoring data, generally,

the 3-hour average values of non-methane hydrocarbons
are 0.5 - 0.6 ppmC, with concentrations as high as
1 ppmC monitored from time to time, indicating the need
to drastically reduce the hydrocarbon emission. Legal
control of automobile hydrocarbon emission was first
enforced in 1970 with the regulations progressively
tightened, and from April 1975, the present regulation
requiring passenger cars not to emit 0.23 g/km of
hydrocarbons, an emission level corresponding to a
reduction of 93 % compared to the un-controlled level.
However, stationary sources for hydrocarbons are at
present only regulated by local government regulations.
With photochemical oxidant alarms issued several times
every year, and victims reported, it is very important
to regulate the emission of hydrocarbons, an important
precursor of photochemical oxidants, from sources other
than automobiles as early as possible.

2)   Preferable hydrocarbon regulation measures

Some odorous hydrocarbons have already been legally
regulated, but other hydrocarbons in themselves are
considered to be harmless to human health in the
concentrations in which they are contained in the
atmospheric air. This means that they need only be
regulated because of their causative effect on

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photochemical oxidants. However, hydrocarbons are
evaporated into the air from a great variety of
facilities such as paints, printing inks, adhesives,
and laundry solvents, in addition to such stationary
sources as petroleum tanks, and their control measures
also differ greatly in their difficulty of control
measures; so when selecting measures, the degree of
difficulty of application and the seasons and areas
most related to the generation of photochemical
oxidants must be taken into consideration.

For the time being, measures should desirably be taken
along the following guidelines:

(i)   To prevent the emission or hydrocarbons from tanks
      storing them, such as petroleum, and the emission
      of hydrocarbons in transferring them from tanks.

(ii) To prevent the evaporation of hydrocarbons from
      factories and other workshops where hydrocarbons
      are used, such as painting and printing factories.

(iii) To promote research and development of low-emission
      paints and printing ink and enlarge the scope of
      their use.

(iv) To step up a PR drive for encouraging painters and
      printers to use low-emission materials.

In addition to these measures, in areas where industrial plants such as petrochemical works account for the major portion of emission, effective measures must be taken at these works.

3. Emission Control Technology

1) Outline of emission control technology

Hydrocarbon emission control technologies are classified into two major groups: vaporization-prevention technology to prevent emission by modifying the structure of the hydrocarbon-containing facilities, and processing technology to eliminate emitted hydrocarbons by some means.

2) Evaporation-prevention devices

Evaporation-prevention devices are applied to the storage installations in refineries, oil tanks, and oil supply facilities. Principal device are floating roofs, internal floating roofs for fixed roof tanks, and vapor return devices.

Floating roofs and internal floating roofs are covers floating on the surface of oil, and are capable or rising and lowering as the oil surface rises and lowers.

Floating roofs are already in use in large tanks and have proved that loss of hydrocarbons during oil supply is negligible with tanks with floating roofs, and the larger the tanks, the smaller the breathing loss becomes compared

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with fixed roof tanks. For this reason, tanks over 1000 liters in capacity should preferably be floating roof tanks. Internal floating roofs are simply installed in the existing fixed roof tanks without special reinforcement, but have an evaporation-prevention effect comparable with floating roofs, except for simple ones.

Vapor return devices are mostly used in the gasoline transportation stage. They are used at the gasoline storage facilities and gasoline stations to collect the escaping hydrocarbon vapor from the receiving side, during gasoline transfer from tank lorries to the storage tanks, and to return the collected vapor to the supplying side, thus preventing its escape into the atmosphere.

This device is expected to prove effective when it is used at the storage stations when loading tank lorries with gasoline, to be more beneficial, it should preferably also be used by the gasoline stations in supplying automobiles with gasoline, because emission is great in this final stage of gasoline supply.

In vapor return devices, mostly absorpting techniques with solution are used to recover vaporized hydrocarbons.

3) Processing devices

Vapor processing devices are based on one of the following techniques: adsorption technique, solution

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technique, condensation technique, direct combustion technique, and catalyzer oxidation technique.

The adsorption technique utilizes the adsorption of hydrocarbons on the surface of a porous substance. Mostly activated carbon is used as the porous substance. When a predetermined amount of hydrocarbon has been adsorbed onto the porous substance, it is heated by steam to drive off the hydrocarbons and to renew the adsorbent.

Activated carbon adsorbent is used either in the fixed bed system or in the fluid bed system. Although differing in the absorption efficiency according to the type of hydrocarbons, almost all hydrocarbons are adsorbed by activated carbon with a high degree of efficiency, so that it is widely used in painting facilities, printing facilities, etc.

The solution technique is based on the dissolving of hydrocarbon vapor in absorbent liquid. As the absorbent liquid, mostly hydrocarbons having a high affinity with the vapor to be adsorbed are used; but for processing hydrophilic hydrocarbons, water containing additives is used.

In some vapor return devices used in oil storage stations, the returning hydrocarbon vapor is recovered by the solution technique.

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The condensation technique is based on the removal of
hydrocarbon vapor through condensation by means of a coolant.
As this technique is advantageous in recovering high-
concentration hydrocarbon vapor, it is more often used in
the pre-treatment devices attached in adsorption devices
or solution devices than as indipendent units.

The direct combustion technique is based on the com-
bustion of discharge gas containing hydrocarbons with the
aid of combustion additives. This technique is suited
to treat exhaust gas which contains many types of hydrocarbons
and therefore is not suitable for recovery, and/or which
contains resin powder or oil mist. Its efficiency is
generally high.

The catalyzer oxidation technique is based on the
oxidation of hydrocarbon vapor of very low concentration
in preheated gas which is sent through the layer of
catalyzer. If metal powder or resin powder is contained
in the gas to be processed in catalyzer oxidation devices,
the metal or resin powder adheres to the catalyzer and
deteriorates its oxidation power. For this reason, the
gas to be treated in catelyzer oxidation devices must be
free from these harmful powder materials. Although this
technique requires the gas to be preheated, if hydrocarbons
are contained in the gas in high concentration,
preheating fuel can be saved. If the hydrocarbon concent-
ration of the gas is too high, it must be diluted before
treatment.

This technique is capable of treating gas with a
wide range of hydrocarbon concentration at high treat-
ment efficiency, and is used in the petrochemical
industry and printing industry, etc.

4. Low Emission Paint

The FY 1975 national total consumption of paint
is approx. 1.2 million tons, and the breakdown of FY 1976
national consumption by major application classifications
is as shown in Table 4.1.

Table 4-1 Breakdown of 1976 total paint consumption
by application classifications

Classification	Percentage (%)
1. Roads and vehicles	20.3
2. Buildings	19.4
3. Marine	11.3
4. Metal products	9.1
5. Wood products	7.4
6. Structures	6.3
7. Electrical machinery	5.3
8. Machinery	4.2
9. Household use	3.9
10. Road signs	2.2
11. Export	1.6
12. Rolling stock	1.3
13. Government and public	1.0
14. Others	6.1
Total	100

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Most paints used today are resin-type paints containing
solvents. As these paints consist of body resins dissolved
in approximately equal amount of hydrocarbon solvents, when
they form a coating film, most solvents are freed into the
atmosphere. As low-emission paints, containing little or
no organic solvent, the following types are in use or under
development:

   i)   Powder paint

  ii)   Water-borne paint

 iii)   High-solid paint

  iv)   Other paints (Multi-liquid paint, inorganic paint,
        dry-oil type paint, ultraviolet radiation curing
        paint, electron-beam radiation curing paint, and
        solvent replacement type paint)

Although some of these paints have been in use for
years because of their other features, the majority of
them were developed as resources-saving type paints. Their
total consumption in FY 1975 is shown in Table 4.2.

In FY 1975, approx. 20.8% of the total national paint
consumption is accounted for by low-emission paints, but
they are mostly conventional dry-oil type paints and
water-borne emulsion type paints, and newly developed ones
are used in only very small amounts.

Table 4.3 shows the present state of development of
low-emission paints.

Although many low-emission paints have been developed already, they are used only to a limited extent, and the cause for this seems to be as follows:

(1)   The coating films of these new paints are not quite equal to those of conventional paints in some performance features.

(2)   Most of them require modification of the existing painting facilities.

(3)   Their cost is higher than that of conventional paints.

(4)   Many new paints are being developed, and it is difficult to predict which one will become the main paint type.

(5)   The future direction of legal regulations is unpredictable.

(6)   Their application range is limited as compared with conventional paints.

Table 4-2   1975 low-emission paint demand

Paint type		Amount (tons)	%
Low-emission paints	Powder pain	3,000	0.25
	Water-borne paint	153,000	13.0
	High-solid paint	-	-
	Multi-liquid solid	45,000	3.8
	Inorganic paint	3,000	0.25
	Dry-oil type paint	41,000	3.5
Sub-total		245,000	20.8
Conventional paint		714,000	60.6
Thinner		220,000	18.6
Grand total		1,179,000	100

Table 4-3 Development and application of low-emission paint

		Low-emission paints							
		Powder paint	Water-borne paint	High-solid paint	Multi-liquid paint	Inorganic paint	Dry-oil paint	Ultraviolet ray radiation curing & electron-beam radiation curing paints	Solvent replace-ment type paint
Usage	Steel bridges (steel structure)		△	△	o				△
	Buildings (building material)		o	△	o	△	△		△
	Automobiles — Top coat	o	△	△					△
	Automobiles — Undercoat	o	o	△					△
	Light electrical appliances	o	o	△	△				△
	Industrial machinery	△	△	△					△
	Ships		△	△	△				△

Note: o Used in limited areas

△ Applicable or application possibility is under study

No mark: Difficult to apply or not be developed

4. Low-Emission Ink

As hydrocarbons are freed into the atmosphere in the printing process, the use of low-emission inks in place of conventional solvent type inks is a positive measure towards controlling photochemical oxident generation. At the same time, the use of low-emission inks is positively recommendable from the viewpoint of reducing the use of imported petroleum products and of improving working environments.

Today, printing inks are used not only in books and posters, but also in many items used in daily life such as food packages, and building materials, and the trend is towards more elaborated printing processes such as gravure printing in parallel with the rise of living standard of the people.

Table 4 shows major printing inks and coating varnishes used today that are expected to constitute significant hydro-carbon emission sources, because of their amount of use and printing process.

As can be seen in this table, the printing process involves not only paper but also many other sheet materials such as cellophane, plastic, building material, and metal. But among them, gravure inks used such as in book printing, package printing, building material printing, and metal coating varnish are used in much larger amounts than other

materials and are considered to free larger amounts of hydrocarbons into the atmosphere than other materials. For youf reason, the replacement of these materials with suitable low-emission materials is desirable.

For the purpose of preventing emission of solvent hydrocarbons from these printing inks and coating varnishes, the following measures are under consideration and partly in use.

1. Replace the currently used solvents by low photochemical-reaction solvents.

2. Use the mixture of water and a small amount of low photochemical-reaction solvent as solvents.

3. Develop new type of resin or resin despersant to obtain high solid inks containing 80% or more solid constituents.

4. Eliminate the use of solvent.

    The industry-wide states of technical development on the problem of printing ink types and coating varnish type in the measures 1 through 4 mentioned above are roughly shown in Table 4.

    As can be seen is Table 4, the progress in control technology for these inks is in the order of the replacement of conventional solvent by low photochemical-reaction solvents,

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use of water-borne solvents, elimination of solvent, and use of high-solid paints.

However, because of a large number of applications, properties of printed sheets and printing methods, these technologies have not been fully developed for use with all types of printing inks and coating varnishes that require measures.

Table 4 Printing inks and coating varnishes applications liable to emit
hydrocarbons and state of conversion into low-emission substitutes

Printing ink & coating varnish	Applications of printed or coated sheets
Web offset ink (heat set type)	School text book, magazine, publication, leaflet, catalogue, business forms
Flexiso ink	Bags, craft paper bags for cement, fertilizer, etc., corrugated cardboard and paper containers
Gravure ink (publication)	Weekly magazine, monthly magazine, books, newspaper, postage stamp, poster, calendar
Gravure ink (package)	General wrapping paper, packages for food-medicine, and other industrial products
Gravure ink (building material)	Decorative board for household electric appliance, building material and furniture, wall paper
Metal decoration ink	Can for food and beverage, decorative can, metal tube, toy
Metal coating varnish	Same as above
Screen ink	Poster, display, sign board, decorative bottle, clothes, toy, IC circuit board, measuring instrument, road sign
Paper coating varnish	Telephone directory, picture book, record jacket, glossing of book and magazine cover, glossing of poster, etc.

Note: (1) This table shows an overall survey of the states of developments
of the industry as a whole.

(2) ⊚ : In actual use to a considerable extent

o : Potentially usable or partly in actual use with products
already in existance

Δ : In research and experimental stage

× : Technically very difficult to use practically

× × : Expected to be totally out of the question from the
present stage of technical development

(3) * : Depending on the property, type, and application of the
printed sheets, sometimes impossible to adopt in
practice.

(4) Water-borne solvent means water containing a small amount
of low photochemical-reaction solvents such as alcohol-type
solvents.

Conversion into low photochemical reaction solvents	Water-borne solvent	Elimination of solvent (ultraviolet-ray radiation curing ink)	Use of high-solid ink
o	× ×	o *	Δ
◎	For paper ◎ * for plastic ×	Δ	× ×
Δ	o *	× ×	× ×
o *	For paper o * for plastic ×	Δ	× ×
o *	For paper o * for plastic × ×	× ×	× ×
Δ	× ×	o *	◎
Δ	Δ	Δ	Δ
Δ	×	o *	Δ
o	For offset printing ◎ *	Δ	× ×

Annex I

Total Amounts of Hydrocarbons, which are discharged
from Stationary Generation Sources, by Generation Source
(Summary Table) in FY 1973.

(in Tons)

Generation Sources		Discharged amounts	(Percents) %	Sub-total	(Percents) %
Petroleum Industry	Plants	12,100	-	198,000	(15.1)
	Oil-Manufacturing Plants : Tanks	67,000	(5.1)		
	Oil-Storing Facilities; Tanks	68,100	(5.2)		
	Oil-Fuelling Facilities	62,800	(4.8)		
Petro-chemical Industry	Plants	69,800	(5.3)	74,700	(5.7)
	Tanks	4,900	(0.4)		
Paint Industry	Manufacturing Processes	1,600	(0.1)	623,500	(47.4)
	Paint Solvents — Paint Solvents for Car Body	37,500	(2.9)		
	Paint Solvents — Paint Solvents for Ship-Building	19,900	(1.5)		
	Paint Solvents — Others	564,500	(42.9)		
Printing Ink Industry	Manufacturing Processes	200	-	109,800	(8.3)
	Ink Solvents	109,600	(8.3)		
Others	Solvents for Adhesive Materials	42,500	(3.2)	309,100	(23.5)
	Solvents for Removal of Fat on Metal	85,000	(6.5)		
	Solvents for Cleaning	116,500	(8.9)		
	Solvents for Rubber	51,200	(3.9)		
	Combustion Processes	13,900	(1.1)		
Total		1,315,100	(100)	-	-

Annex II   HC CONTROL TECHNOLOGIES

HC control technology		a. combustion technique		b. absorption technique, etc.			c. use of closed system	d. improvement in tank filling	e. improvement of products		
		direct combustion technique	oxidation technique with catalyzer	charcoal technique	solution technique	condensation technique	vapor return system etc.	floating roof, internal floating roof	paint	ink	others
degree of development		developed	developed	developed	developed	developed	developed	developed	under development		
reduction rate			more than 90 %	more than 95 %	80~95 % in summer	80 % in summer					
storaging and circulation of HC	tanks	△		○	○	△	◎	◎			
	loading and receiving facility	△		◎	◎	△	◎	◎			
painting	paint producing factories	○	○	◎	○	△	○				
	painting factories	◎	◎	◎	○	△			△		
printing	ink producing factories	○	○	◎	○	△	○				
	printing factories	◎	◎	◎	○	△					
general chemical factories		◎	◎	◎	○	△	○			△	△
cleaning laundry, rubber processing ind., metal degreasing ind., etc.		△	△	◎	○	△					△

◎: easy for adopting and very effective,   ○: possible for adopting,   △: possible for adopting among a few facilities

Annex III   COSTS REQUIRED FOR HC CONTROL

HC control technology		initial cost
a. combustion techniques	direct combustion technique	about 50 million yen for 20 thousand Nm^3/h exhaust gas
	oxidation technique with catalyzer	about 20 million yen for 6 thousand Nm^3/h exhaust gas

b. adsorption technique, etc.	charcoal technique	exhaust gas (Nm^3/h)	construction cost (million yen)
		1,000	1~3
		5,000	10~12
		10,000	20~45
		50,000	100~110
		100,000	180~200

	solution technique	60~70 million yen for 200~300 Nm^3/h exhaust gas
c. use of closed system	vapor return system	vapor return system at a gas station, 150~160 thousand yen per tube

d. improvement in tank filling system. — floating roof, internal floating roof

costs required for reconstructing a fixed tank to a floating roof tank or an internal floating roof tank   (million yen)

capacity	1,000 KL	10,000 KL	50,000 KL	
to a floating roof tank	12	35	95	
to an internal floating roof tank	8	23	60	

SCIENTIFIC ISSUES RELATED TO OXIDANT CONTROL

presented by B. Dimitriades

Environmental Protection Agency

United States

SCIENTIFIC ISSUES RELATED TO OXIDANT CONTROL

The emission control for oxidant reduction in the US started in the early 60's in Los Angeles. Nationwide control strategy was formally introduced by the federal government in 1971 when the states were asked to submit emission control standards for the control of oxidants. Shortly after, it was realized that these oxidant controls were extremely expensive and even threatened to disrupt the lifestyle. At the same time, we got reports of high oxidant readings in the rural areas, and we then discovered that the oxidant problem was not just an urban problem. In fact, violations of the oxidant standard were more frequent in the rural areas than in many urban areas. These two factors, to reiterate, the cost of control and the extent of the rural oxidant problem, are perhaps the two most important factors that led the technological community both within and outside the federal government to take another look at the oxidant problem. Thus, in the last 4-5 years, we have been reexamining the oxidant problem by conducting extensive field and laboratory studies, and by reassessing and analyzing new and old evidence. The first phase of the reexamination of the oxidant problem was an in-depth analysis of the problem, in which analysis we identified those aspects of the problem which were either little understood or they were subjects of controversial issues. The first phase is described in a published report [a] that presents and discusses the key issues as perceived by USEPA. In the second phase, which is a continuing one, we are doing research which is addressed to these issues and aims to resolving them. These issues and related studies and findings are as follows:

ISSUES

1. Measurement of oxidants

2. Importance of natural sources of oxidants

3. Role of oxidant transport

4. Optimum control strategy

5. Organic emission reactivity

6. Emission to air quality relationships

It's important to remember that these reports reflect not EPA's viewpoint; they reflect the viewpoints of experts that were contracted from universities and state agencies. We agree with some of these viewpoints, but we disagree with others. The EPA viewpoint can be found in the oxidant criteria document, a draft of which is now available, but it will be finalized by mid-1978.

On the ozone/oxidant measurement issue, one question of interest is whether it is ozone or oxidants that should be measured in the atmosphere. The EPA reference method is specific for ozone. The reasons why EPA preferred the specific method for ozone were that

a) Ozone was suspected to be the specific oxidant responsible for health effects.

b) Ozone forms hand-in-hand with other oxidants and therefore it can be viewed as a surrogate for those other oxidants.

c) Ozone can be measured much more reliably relative to the oxidant mixture.

More recent studies by EPA and non-EPA researchers convinced EPA that ozone is responsible for adverse health effects, and EPA is now ready to

abandon the oxidant concept altogether and promulgate a National Air Quality Standard for ozone, not oxidant. Thus, in the future, it is expected that both the measurement and air quality standard will refer to the same species, ozone.

On the issue of natural sources of oxidant, the question is how much of the oxidant and ozone at ground level comes from natural sources? The significance of this question is that the natural contribution to ground level ozone must be known if the benefits from anthropogenic emission control are to be estimated reliably. The EPA recognizes two natural sources: intrusions from the stratosphere and photochemical reactions of natural organic emissions.

In regards to stratospheric intrusion, recent studies have shown that on occasions, usually in the Spring months of the year, stratospheric ozone accumulation at ground level could reach as much as 0.2 ppm ozone or slightly above. During the smog season (summer and early fall), the frequency and intensity of intrusions are not known. From indirect evidence, we estimate the average stratospheric ozone during the smog season to be 30 ppb (at ground level). Recently, a new method has been developed by which stratospheric ozone concentrations can be measured directly during the smog season. This method is based on measuring radioactive beryllium (^{7}Be) and radioactive phosphorus (^{32}P). Some measurements have been made in a mountain site in New York, and we are about to start a measurement program in Houston, Texas.

On the other natural ozone source, photochemical reaction of natural organic emissions, EPA believes that some ozone may come from the reaction

of natural methane and some from vegetation-related emissions. We are
not sure about the magnitude of the methane contribution, perhaps 10 ppb
is the most we can expect. The vegetation emissions (terpenes) do not
seem to cause appreciable terpene concentrations in the ambient air, only
a few ppb at most. Considering this, and the oxidant reactivity of these
emissions, we have estimated that 10-20 ppb of O_3, at the most, can arise
from this source. Not everyone agrees with EPA. Some investigators claim
that they have measured natural organics at 1 ppm or more.

On the oxidant transport issue, the important question is how much of
the oxidant observed in an urban area originates from local sources, and
how much comes from outside the city. We must know this if we are to
estimate the impact of local emissions on urban air quality, and if we are
to decide whether controls need to be applied upon the upwind sources.

From recent studies, we have found that oxidant transport definitely
occurs at distances from a few km up to perhaps a thousand km. Short
range transport is usually seen in the form of urban ozone plumes which
have been observed very clearly through aircraft measurements to extend as
far as 100-150 miles. Long range (i.e. several hundred miles) transport
has been associated with high pressure, stagnating anticyclone systems.
These high pressure systems cause stagnation conditions over large areas
within which emissions persist with little dilution and react for a number
of days. The result is formation of an "ozone blanket" that covers the entire
high pressure cell area. While we understand the qualitative aspects of

this pollutant transport phenomenon, it is the quantitative aspects that
need further study. To explain, when oxidant in a city results from local
emissions (there is no extraneous ozone transported in), then the system
is simple and we have been able to quantify it, that is, we have derived
quantitative relationships between emissions and ambient ozone. Thus, for
this simple situation, the chemistry is well known, dispersion is relatively
limited, and the natural sources are unimportant. However, when considerable
part of the ozone observed is extraneous ozone transported in, then
quantitative relationships are not easy to derive. This is because (a) the
chemistry of such a system, which is reacting for several days, is not very
well known, (b) dispersion is a much more important factor now; and (c) it
is also conceivable that natural emissions or their reaction products may have
a role now. We are just now begining to explore this field in a quantitative
way by developing mathematical models that will treat long-range transport.

The two issues left to be discussed, pertain to the reactivity of organic
emissions, and to the emission to oxidant relationship. In regards to
the reactivity issue, the question is: in view of the pollutant (long range)
transport phenomenon, which organics should be exempted from control as
being truly unreactive. Alternatively, where do we draw the border line
separating the non-reactive organics from the reactive ones?

Two approaches have been offered to answer this question. One is the smog
chamber approach; the other is the modeling approach. By the smog chamber method,
organics are tested in the laboratory and are placed in an order of reactivity
based on the amount of ozone they produce in the smog chamber test. To obtain

such reactivity data, smog chamber experiments have to be conducted under a large variety of conditions (initial concentrations and ratio of organic and NO_x reactants). The problem with the smog chamber method is that the reactivities of the very unreactive reactants cannot be measured with confidence because the chamber artifacts interfere seriously with the measurement. Also, the chamber method yields data on the organic's reactivity in the smog chamber but not necessarily in the real atmosphere. By the modeling method, the reactivity of an organic could conceivably be estimated; however, the method is not ready yet to be used since the model method can be applied only on those organics for which the reaction mechanism is known. For the time being, we feel that the best way of answering the question at issue is through combined use of the smog chamber and modeling techniques. The smog chamber technique could be used to place the organics in an order of reactivity and the modeling method could be used to define one organic which is at the borderline separating the unreactive from reactive ones. Studies are continuing in the U.S. on these two approachs. We should mention that we have received from Japan a large number of reactivity data which we thought were excellent and of great help.

TREND OF PHOTOCHEMICAL OXIDANTS

IN JAPAN

presented by S. Imai

Environment Agency

Japan

Contents

1. Introduction

To examine the occurrence of photochemical oxidants and injuries resulting from it in 1977, the Bureau compiled related data from the last five years.

In view of the fact that the formation of photochemical oxidants is affected by geographical and meteorological conditions, we tried to ascertain not only national conditions as a whole but also trends in major areas. For this purpose, four areas were selected: the Tokyo Bay area, the Ise Bay area, the Osaka Bay area and the Seto Inland Sea area.

This study was conducted on the following points:

(1) Frequency of warnings issued by four major areas;

(2) Frequency of warnings issued simultaneously for wider areas;

(3) Maximum concentration of photochemical oxidants on days when a warning is issued;

(4) Frequency of warnings issued on the meteorologically potential days;

(5) Reports of affected people.

As a result of this study, we found that though the meteorological conditions in 1977 were conducive to the occurrence of photochemical oxidants, the frequency of warnings issued was lower than previous years both nationally and

- 1 -

regionally. Also, the generation of the oxidants in a wider area was found to decline, and maximum concentration went down.

The number of days when sufferers reported was considerably reduced, and the number of people reporting suffering per day remained on a similar level to 1976.

Year / Prefecture	'70	'71	'72	'73	'74	'75	'76	'77
1 Miyagi				3				
2 Fukushima						3	1	
3 Ibaragi			16	21	14	17	9	18
4 Tochigi				10	10	6	7	11
5 Gunma				1	4	11	1	
6. Saitama		23	15	45	29	44	15	26
7 Chiba		19	21	28	26	33	21	7
8 Tokyo	7	33	33	45	26	41	17	21
9 Kanagawa		11	31	30	26	27	17	12
10 Shizuoka				8	15	6	3	1
11 Aichi		1	5	8	2	6	3	2
12 Mie			4	6	7		3	1
13 Shiga				4	4	4	5	1
14 Kyoto			7	17	17	11	6	9
15 Osaka		4	18	26	27	23	25	25
16 Hyogo		7	19	23	19	11	3	4
17 Nara			1	6	3	9	3	3
18 Wakayama			1	11	1			
19 Okayama			3	14	16	5	1	5
20 Hiroshima				9	18	4	1	6
21 Yamaguchi					5	1	2	5
22 Tokushima					2	2	3	3
23 Kagawa				1	4	1		
24 Ehime			2	22	13	1	4	7
Total	7	98	176	328	288	266	150	167

Table 2. Frequency of oxidants warnings issued by month in 1977 (In number of days)

Month / Prefecture	3	4	5	6	7	8	9	10	Total
1 Miyagi									
2 Fukushima									
3 Ibaragi		1			10	4	2	1	18
4 Tochigi			2		7	2			11
5 Gunma									
6 Saitama	1	1	3	1	11	6	1	2	26
7 Chiba					3	2	1	1	7
8 Tokyo			4	2	11	4			21
9 Kanagawa		1	1	2	4	2		2	12
10 Shizuoka					1				1
11 Aichi					1	1			2
12 Mie						1			1
13 Shiga						1			1
14 Kyoto		1		1	3	3	1		9
15 Osaka			1	7	7	5	3	2	25
16 Hyogo				2	1	1			4
17 Nara				1	1	1			3
18 Wakayama									
19 Okayama					1	3	1		5
20 Hiroshima				2	3		1		6
21 Yamaguchi			1	1	1		2		5
22 Tokushima		1	1	1					3
23 Kagawa									
24 Ehime			3	4					7
Total	1	5	16	24	65	36	12	8	167

Table 3. Frequency of oxidants warnings issued by month:
1972 - 1977

Month \\ Year	3	4	5	6	7	8	9	10	Total
1972	0	5	14	34	31	54	25	13	176
1973	0	17	26	31	126	108	16	4	328
1974	0	11	52	81	28	90	17	9	288
1975	0	2	19	47	72	68	52	6	266
1976	0	6	21	22	29	47	12	13	150
1977	1	5	16	24	65	36	12	8	167

2. Frequency of warnings issued by four major areas
   (1972 - 1977)

It is considered that the formation of photochemical oxidant is considerably affected by different meteorological conditions, conditions of stationary sources, air advection patterns, and other regional conditions.

Considering this, we selected the following four regions as major areas:

Tokyo Bay area: Tokyo, Kanagawa, Chiba and Saitama;

Ise Bay area: Aichi and Mie;

Osaka Bay area: Osaka, Kyoto, Hyogo and Nara;

Seto Inland Sea area: Okayama, Hiroshima, Yamaguchi,

Kagawa and Ehime.

The combined total number of days in these four areas
when a warning is issued accounted for about 80 % of the
nation's total in 1977. In years 1973 to 1977, the number
of days when a warning is issued was greatest in the Tokyo
Bay area (about 40 % of the total), followed by the Osaka
Bay, the Seto Inland Sea, and the Ise Bay areas.

The fewest number of warning days in the past five
years was recorded in 1976 both for the nation and in each
of the four areas. The figure for 1977 was lower or on a
similar level compared with 1976, except in the Seto Inland
Sea area (Fig. 1).

In the Tokyo Bay, the Osaka Bay and the Seto Inland
Sea areas where the number of warning days has been
relatively high, when comparing the average monthly number
of warning days in the past five years with that in 1977,
the latter was less in each of the four areas (Figs. 2-1 -
2-4)

In general, the number of warning days has tended to
decline gradually. Offset against meteorological con-
ditions, as we discuss in 5. below, the declining trend is
evident.

Table 4. Number of warning days by year and month

	Month / Year	4	5	6	7	8	9	10	Total
National	1973	17	26	31	126	108	16	4	328
	1974	11	52	81	28	90	17	9	288
	1975	2	19	47	72	68	52	6	266
	1976	6	21	22	29	47	12	13	150
	1977	5	16	24	65	36	12	8	166
	5-year average	8	27	41	65	70	22	8	241
Tokyo Bay (Tokyo and 3 prefectures)	1973	15	14	9	51	46	11	2	148
	1974	7	21	21	13	34	7	4	107
	1975	2	11	24	29	43	32	4	145
	1976	3	10	6	15	23	6	7	70
	1977	2	8	5	29	14	2	5	65
	5-year average	6	13	13	27	32	12	4	107
Ise Bay (2 prefectures)	1973				7	7			14
	1974		1	4		4			9
	1975			1	4		1		6
	1976		1			5			6
	1977				1	2			3
	5-year average		–	1	2	4	–		8
Osaka Bay (4 prefectures)	1973	1	3	9	31	24	2	2	72
	1974	1	9	21	3	23	5	4	66
	1975		3	17	19	7	6	2	54
	1976	2	5	6	8	9	4	3	37
	1977	1	1	11	12	10	4	2	41
	5-year average	1	4	13	15	15	4	3	54
Seto Inland Sea (5 prefectures)	1973		2	12	20	11	1		46
	1974	1	10	22	7	14	2		56
	1975		1	3	3	2	3		12
	1976			6	1		1		8
	1977		4	7	5	3	4		23
	5-year average	–	3	10	7	6	2		29
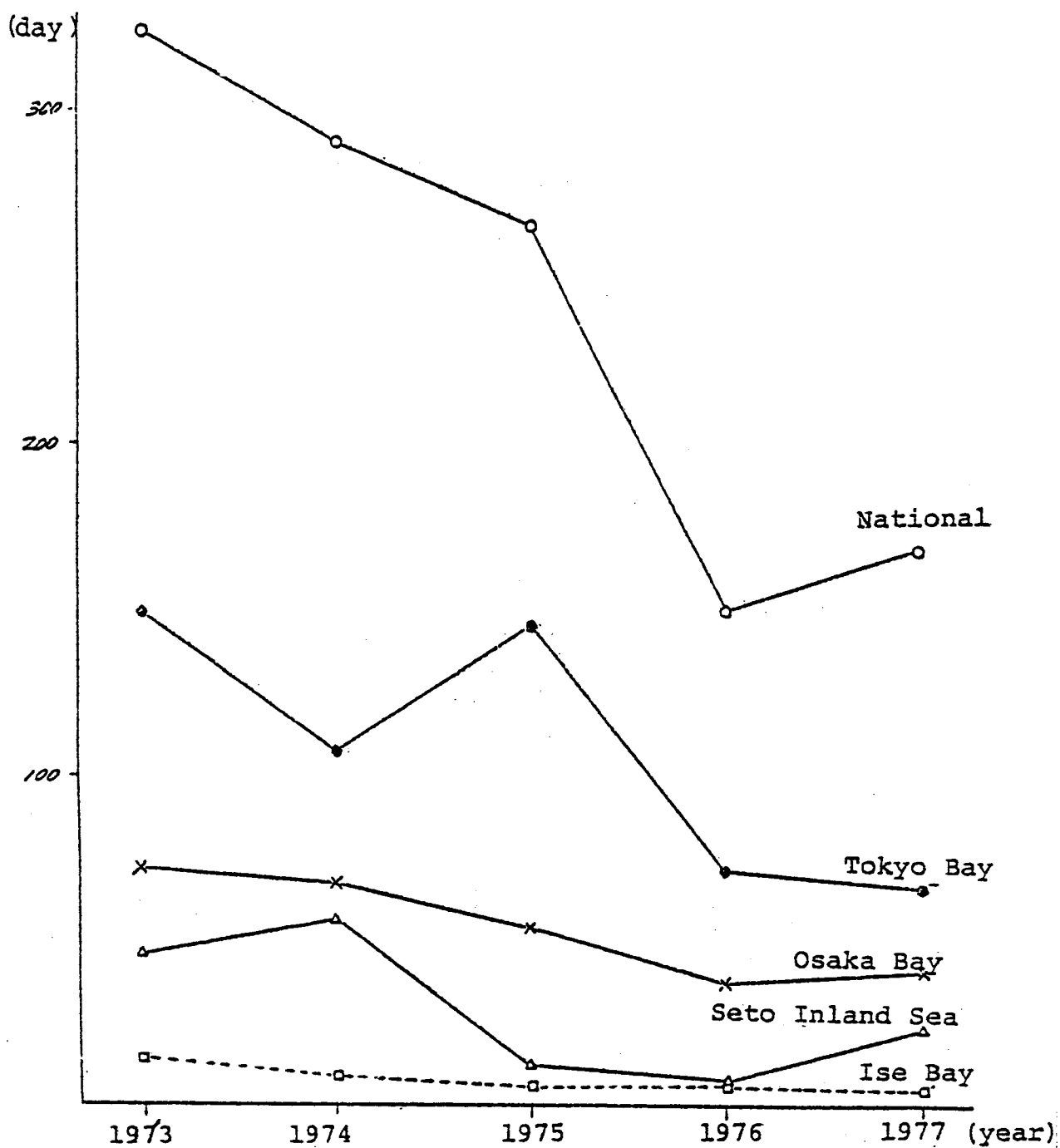
Fig. 1 Number of Warning Days from April to October:

(1973 - 1977)

Note: The number of warning days is the total of such
         days from April to October which is obtained by
         adding figures of prefectures comprising the
         whole nation and each area.
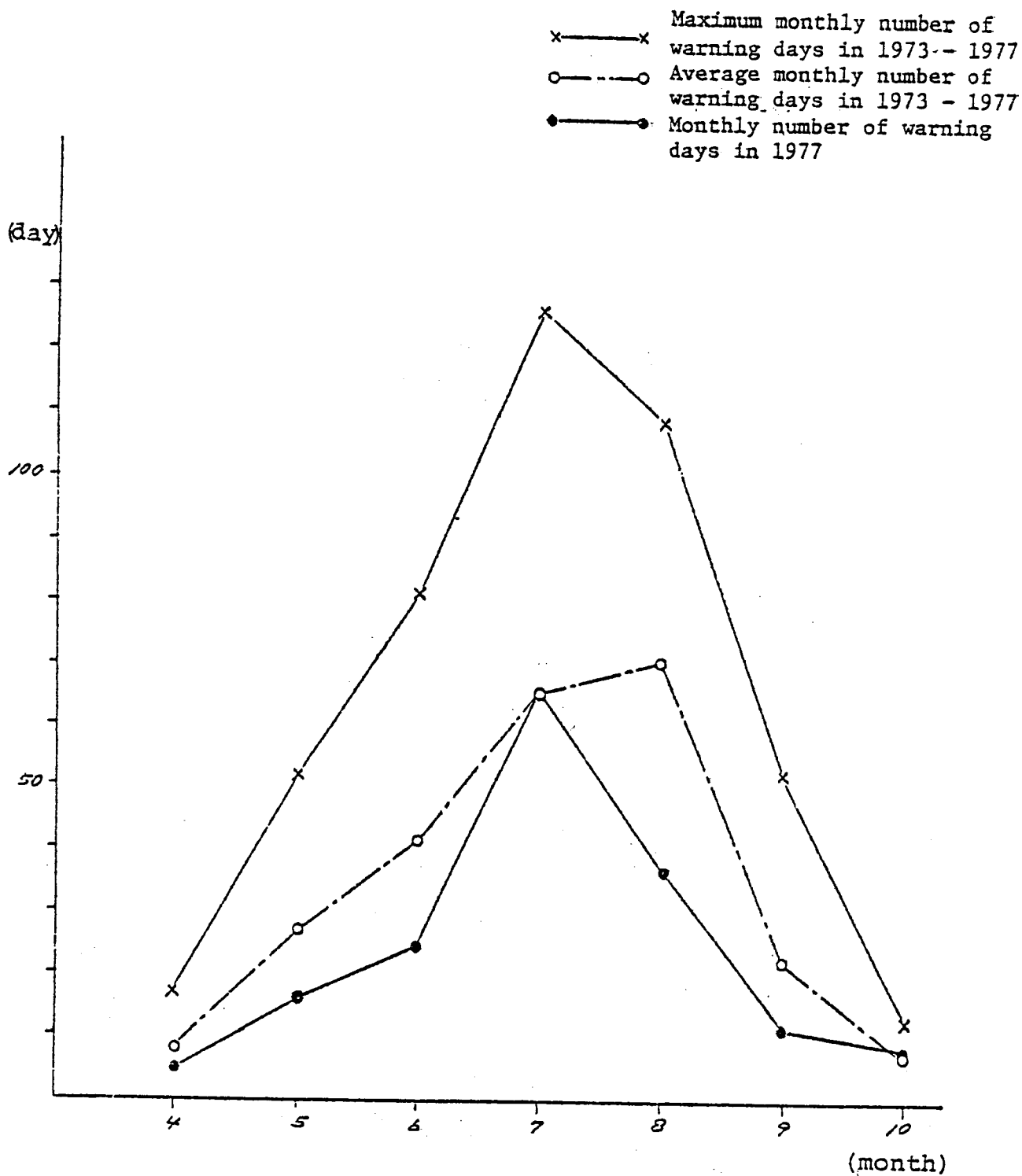
Fig. 2-1 Monthly Trend of the Number of Warning Days
(National)
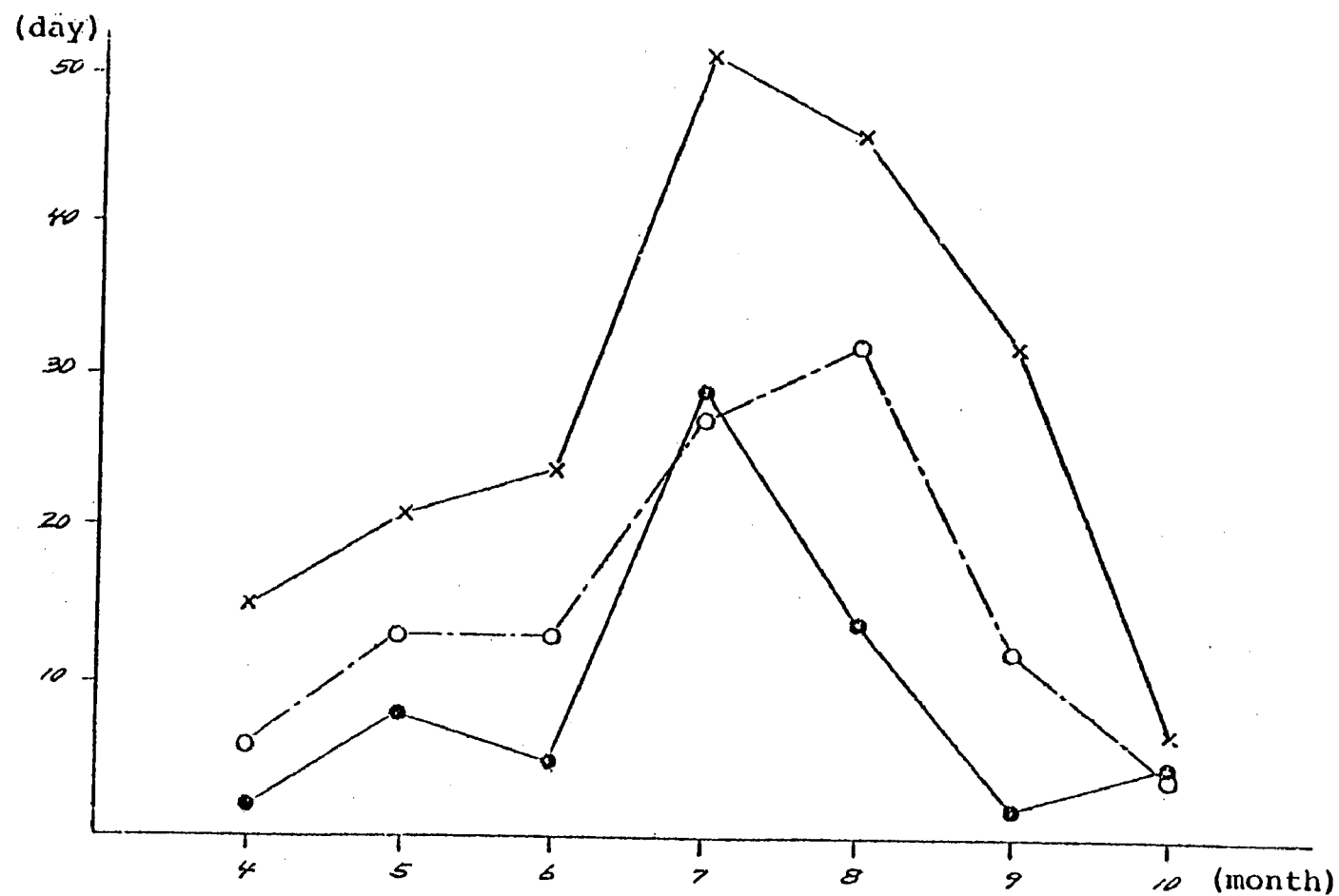
Fig. 2-2 Monthly Trend of the Number of Warning Days (Tokyo Bay Area)
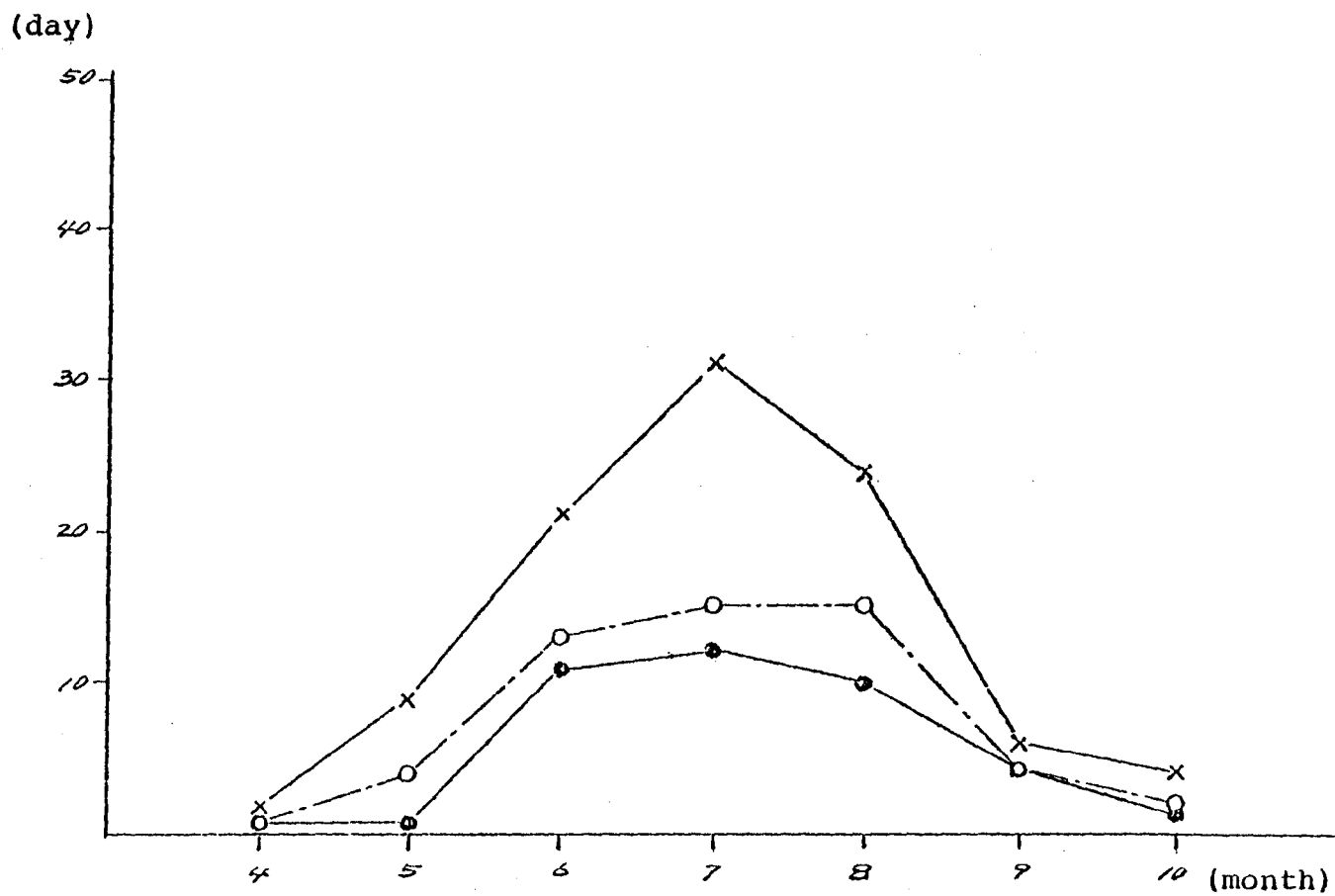
Fig. 2-3   Monthly Trend of the Number of Warning Days (Osaka Bay area)
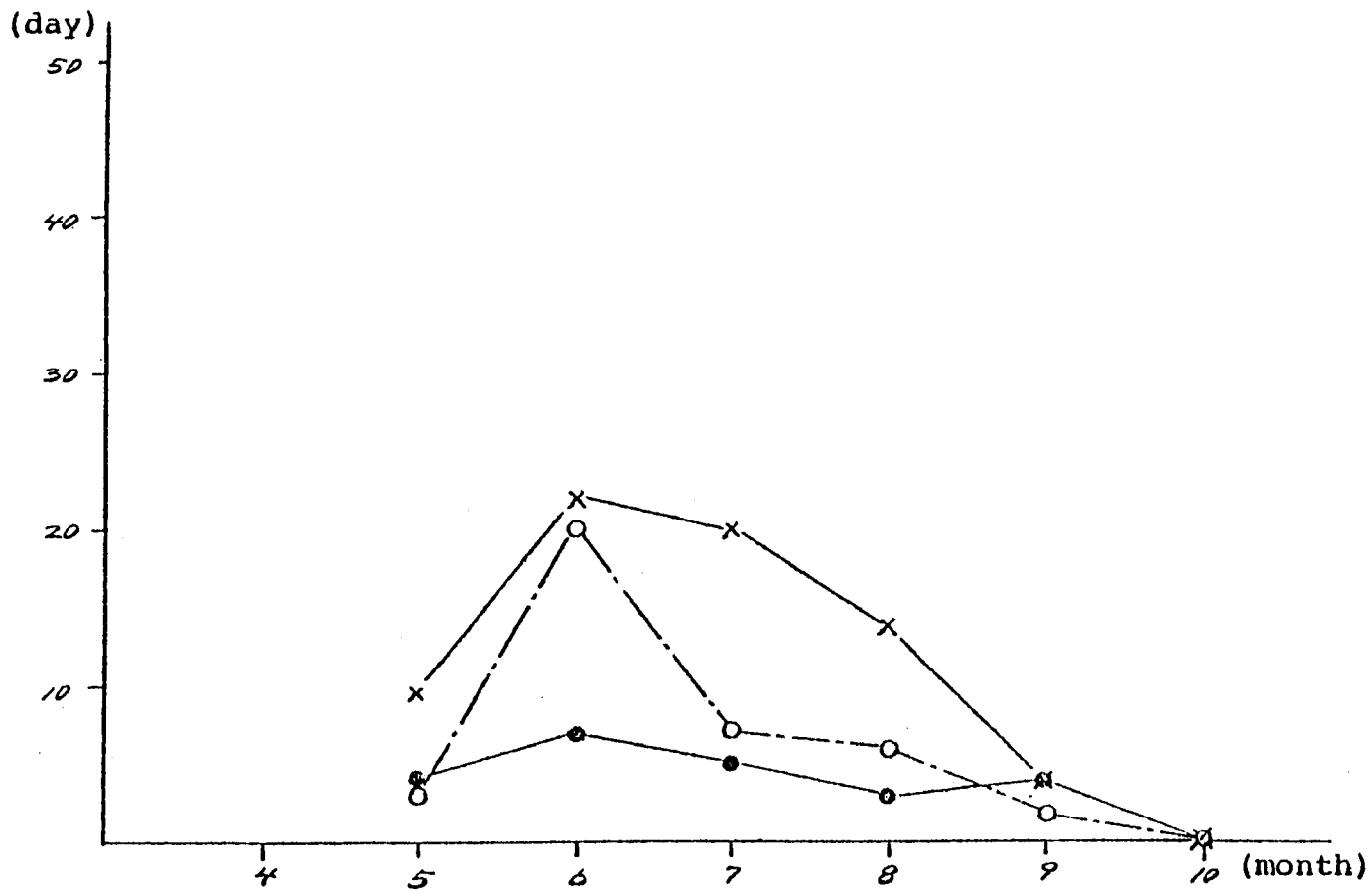
Fig. 2-4 Monthly Trend of the Number of Warning Days (Seto Inland Sea area)

3. Frequency of warnings issued simultaneously for wider areas
   (June - August, 1974 - 1977)

In the Tokyo Bay area where the number of warning days
is comparatively great and air advection phenomena are more
conspicuous, we studied the number of days when warnings
were issued simultaneously for wider areas.

In this area, the number of days when a warning was
issued for the total four prefectures was seven in 1974,
nine in 1975, four in 1976 and one in 1977, showing a
drastical decrease.

A similar declining tendency is observed in the case
of the number of days when a warning was issued for three
or two prefectures, and the percentage of warning days for
only one prefecture is increasing.

The maximum value of the average concentration of
oxidant [1] on the days when a warning was issued for the
total four prefectures was 21 pphm in 1974, 22 pphm in 1975,
22.8 pphm in 1976, and 18.3 pphm in 1977, again indicating
a substantial decrease.

Note: The maximum concentration of each prefecture on the
      day when a warning was issued for the total four
      prefectures is added and the total is divided by
      four. This figure is the maximum average concent-
      ration on the day in the area. The maximum value is
      the highest of such average maximum cencentrations.

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Table 7. Number of days when a warning was issued simultaneously for wider areas (June - August, 1974 - 1977)

Tokyo Bay Area

Pre-fectures warned \ Year	1974	1975	1976	1977
No. of days when the total 4 prefectures were warned.	7	9	4	1
Maximum value of average maximum concentration of oxidant. (pphm)	21	22	22.8	18.3
No. of days when three or more prefectures were warned.	13	19	7	6
No. of days when two or more prefectures were warned.	17	30	14	12
No. of days when a warning was issued for only one prefecture.	12	10	5	14

Table 8. Percentage of warning days in Saitama in the Tokyo Bay area (%)

Year \ Month	4	5	6	7	8	9	10	4 - 10
1973	53	43	11	29	28	0	100	30
1974	0	29	29	46	26	29	0	27
1975	0	18	33	45	30	25	0	30
1976	0	10	17	33	26	33	0	21
1977	50	38	20	38	43	50	40	39

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4. Concentration of photochemical oxidants on days when a warning is issued (June - August, 1974 - 1977)

As described above, it is observed that the number of warning days has been declining. So, how about the oxidants concentration on warning days? We studied this in the Tokyo Bay and the Osaka Bay areas where warnings were more frequent than other areas.

First, we found that in both areas the maximum concentration was lowest in 1977 in the previous years (1974 - 1977). In particular, in the Tokyo Bay area, the figure substantially declined in 1977, except in 1976 when both temperature and flux of solar radiation were abnormally low.

Next, we studied the relation between frequency of warnings and concentration on warning days. In the Tokyo Bay area, warnings were most frequently issued around 14 pphm and 18 pphm. But in 1977, there was no peak around 18 pphm, and as the concentration became higher, the number of warning days gradually declined. Also, the number of warning days showed a substantial decline in general in each grade of concentration (Fig. 3-1).

Similarly, in the Osaka Bay area (Fig. 3-2), two peaks were observed. But in 1977 there was only one peak at 16 pphm. This was higher than the peak at 14 pphm in 1974 - 1976, but in higher concentration grades, the figures in 1977 were lower than the previous three years.
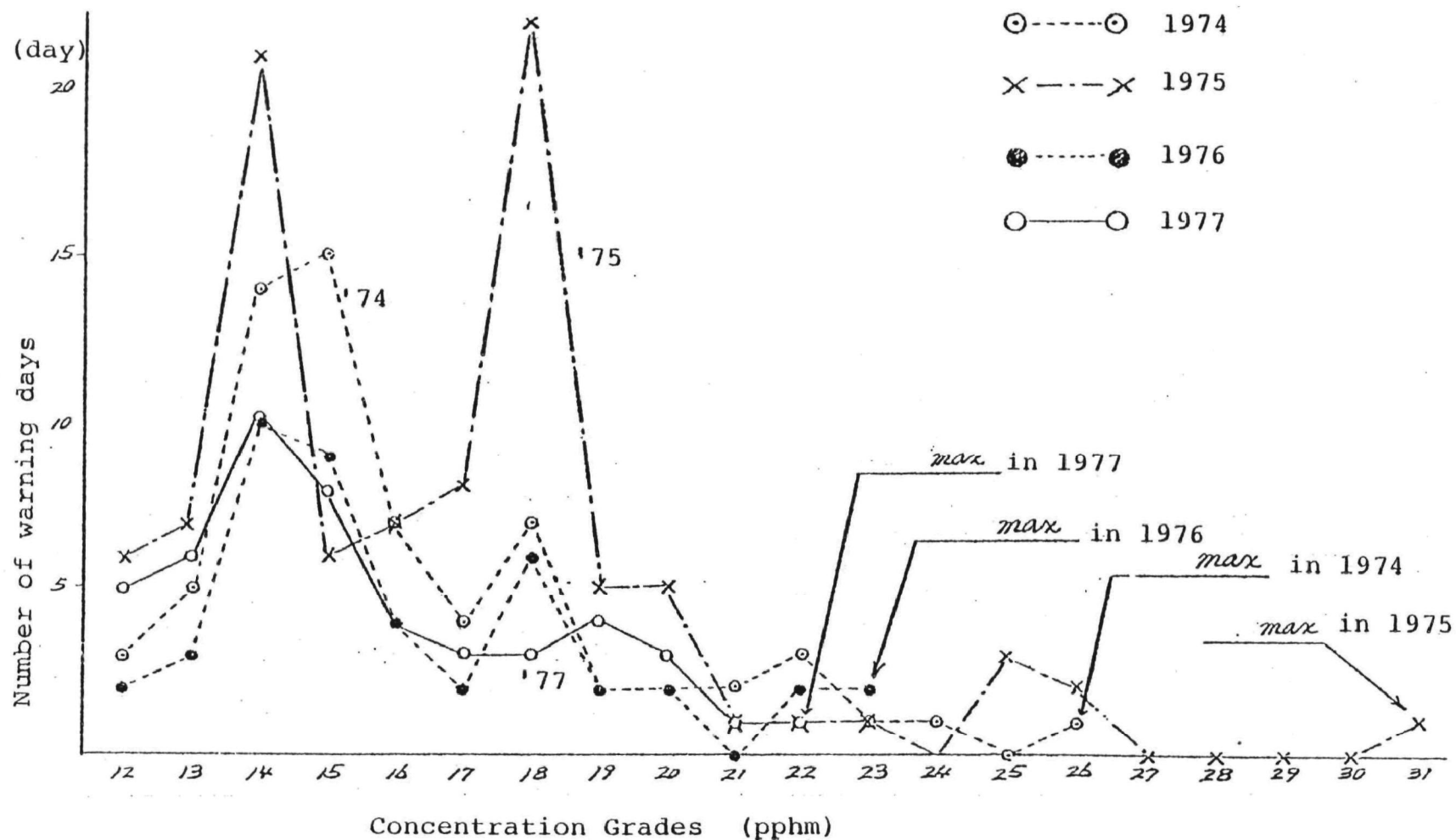
Fig. 3-1 Number of Warning Days by Concentration Grades

in the Tokyo Bay Area (June - August)
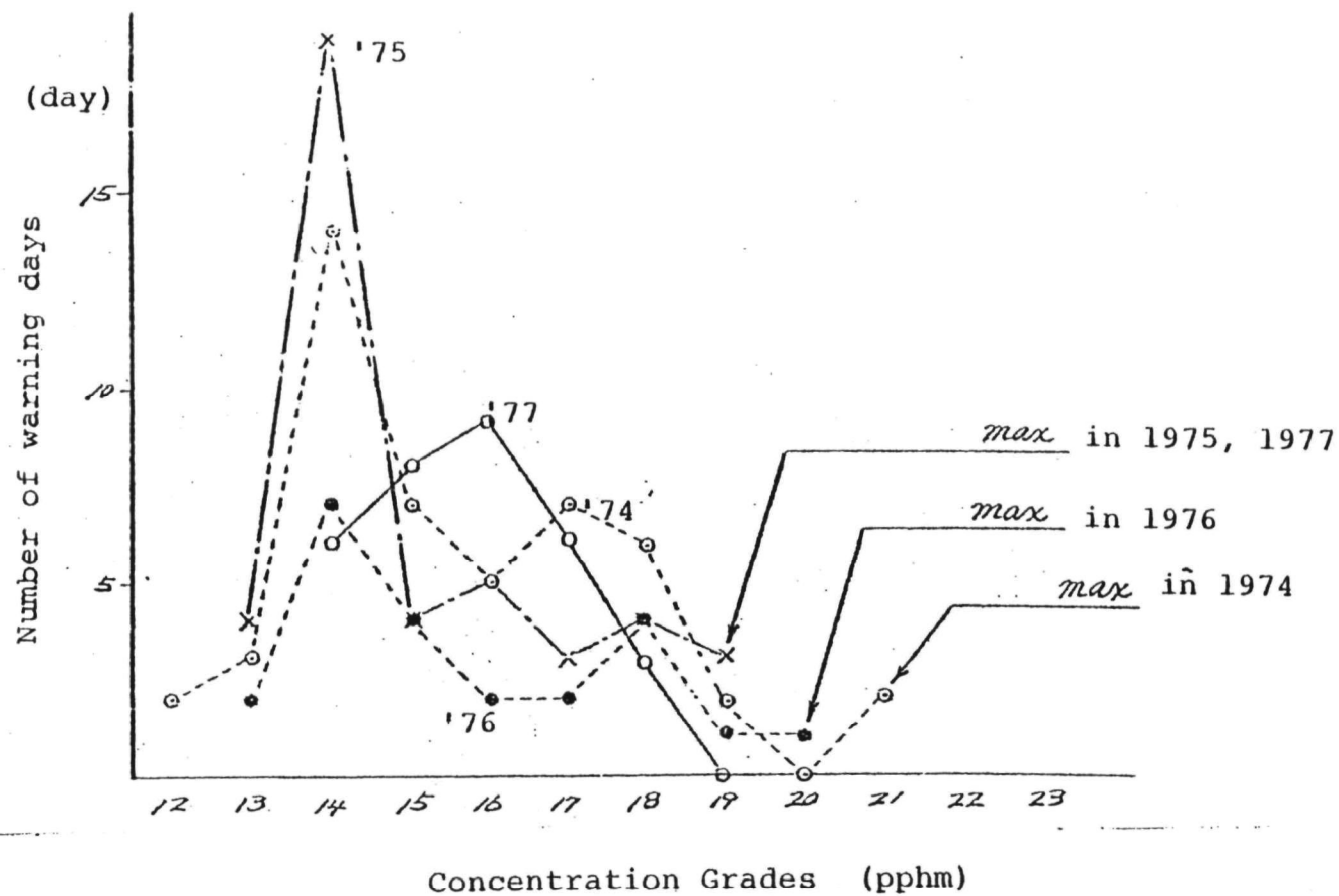
Fig. 3-2 Number of Warning Days by Concentration Grades
in the Osaka Bay Area (June − August)

5. Frequency of warnings issued on the meteorologically potential days

The occurrence of high-concentration oxidant has a close relation to weather conditions, especially, wind velocity, wind direction, temperature, flux of solar radiation and weather. In view of this fact, the Environment Agency compared and analyzed observation and weather data from the Tokyo District Meteorological Observatories and conditions of warnings issued in Tokyo and Saitama prefecture, and determined as meteorologically potential days those days which meet the following conditions:[1]

Factor	Description
Flux of global solar radiation(R)	2 hrs. or more of radiation of 30 cal/cm^2/h between 9:00 - 15:00.
Wind velocity (V)	An average velocity of 5 m/s or less at 9:00, 12:00, and 15:00.
Wind direction (D)	Wind with southerly component between 9:00 and 18:00.
Temperature (T)	A maximum temperature of 24 °C or higher
Weather (W)	Fine (including slightly cloudy) or cloudy at 9:00, 12:00 and 15:00.

The number of meteorologically potential days in 1977 was generally on a similar level in 1973 between June and August (Table 9).

However, the percentage of the number of warning days on potential days has declined. The figure in 1977 showed a substantial decrease when compared with averages of the past five years (Fig. 4).

Note (1): Report of Meteorological Observation Survey for Emergency Measures against Photochemical Air Pollution, Air Quality Bureau, Environment Agency, February, 1977.

Table 9. Relation between potential days and warning Days

Month / Year \ Item	June 48	49	50	51	52	July 48	49	50	51	52	August 48	49	50	51	52	Total 48	49	50	51	52
No. of potential days A	9	12	14	8	9	18	6	18	14	19	17	19	18	14	13	44	37	50	36	41
No. of warning days B	4	9	9	1	3	19	6	14	6	13	15	12	14	8	6	38	27	37	15	22
No. of waring days on a potential day C	4	7	9	1	3	16	6	14	6	11	14	11	14	6	6	34	24	37	13	20
No. of warning days on a non-potential day D	0	2	0	0	0	3	0	0	0	2	1	1	0	2	0	4	3	0	2	2
C/A (%)	44	58	64	13	33	89	100	78	43	58	82	58	78	43	46	77	65	74	36	49

(Note) 1. The number of potential days is calculated using data from the Tokyo District Meteorological Observatories.

2. The number of warning days is the total of warning days in Tokyo and Saitama prefecture minus overlapping days.
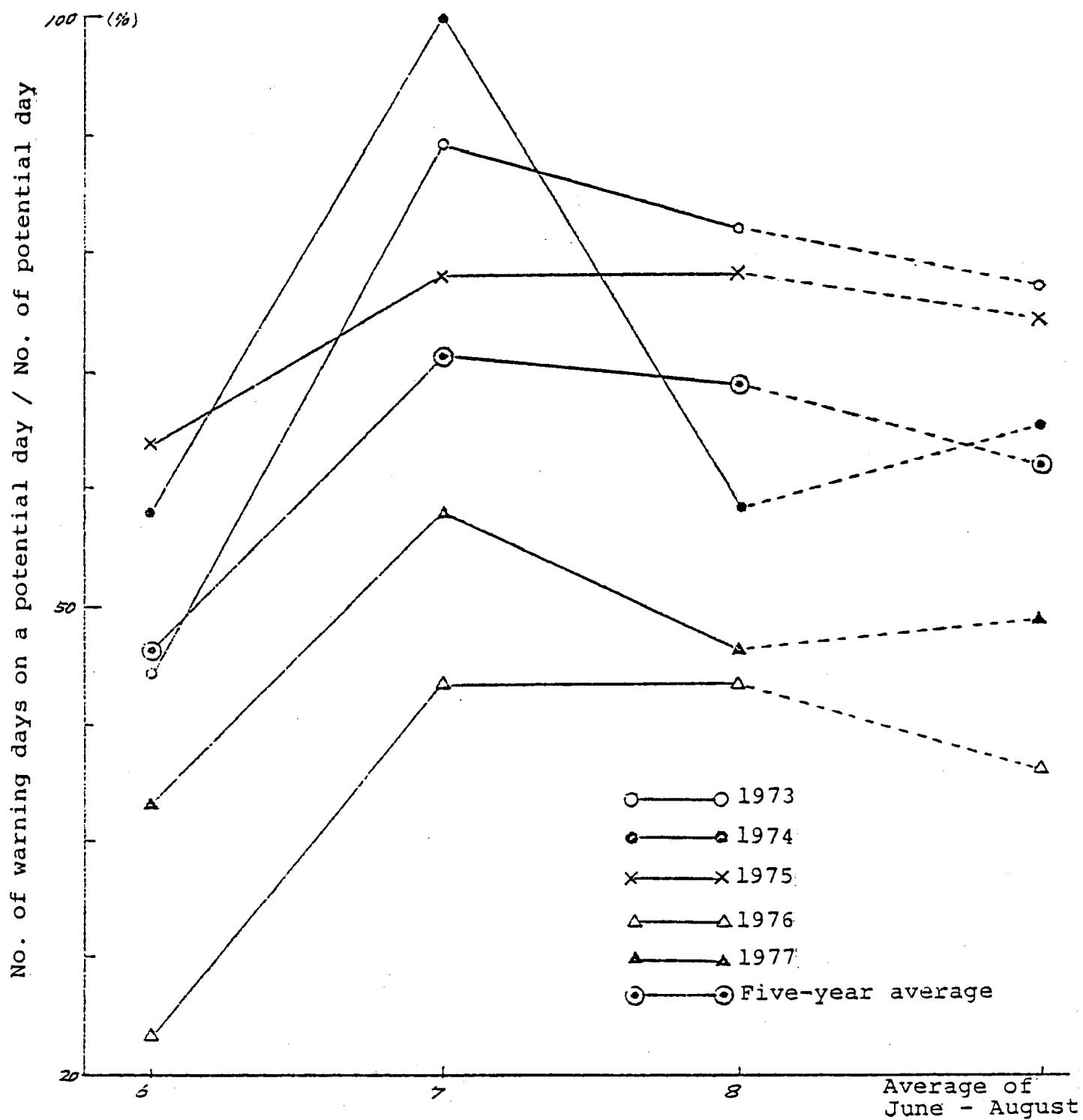
Fig.4   Percentage of Warning Days on a Potential Day

6. Reports of affected people

The number of people who were thought to be affected by oxidants decreased drastically in 1977. But as the number fluctuated up and down so sharply that it may not help observation of the actual trend, we used the number of days when any report of oxidant effects was made as the fundamental data for analysis.

The peak of the number of days when such a report was received came in 1975 when the number of people reporting oxidant effects was largest. After that, the figure tended to decline. This trend was observed both nationally and in the Tokyo Bay and the Ise Bay areas. Also, in each area, the number of days reported substantially decreased in 1977 compared with in 1974 (Fig. 1).

In the Tokyo Bay area, the number of days reported accounted for about 50 % of the nation's total, and its trend corresponded with the national tendency.

The Ise Bay area, where the number of warning days was the least of all four areas, was ranked second in terms of the number of days reported after the Tokyo Bay area.

The trend in the Osaka Bay and the Seto Inland Sea areas differed slightly from the other two: there was no peak in 1975.

The number of people reporting per day was the

highest in 1975, too, excluding the Osaka Bay and the

Seto Inland Sea areas. Nationally speaking, 1975 was the

year when oxidant effects had the greatest possibility of

occurring. (Fig. 2)

The condition in 1977 was at a similar level to 1976.

But, taking the weather conditions in 1977 into account,

we can say that some improvement is seen in 1977.

While in the Tokyo Bay and the Ise Bay areas the

condition was at a similar level in 1976 and 1977 after

a peak in 1975, in Osaka Bay and the Seto Inland Sea areas,

the figure in 1975 was far lower than that in 1974 and

thereafter gradually increased (in the Seto Inland Sea

area) or remained on a similar level (the Osaka Bay area).
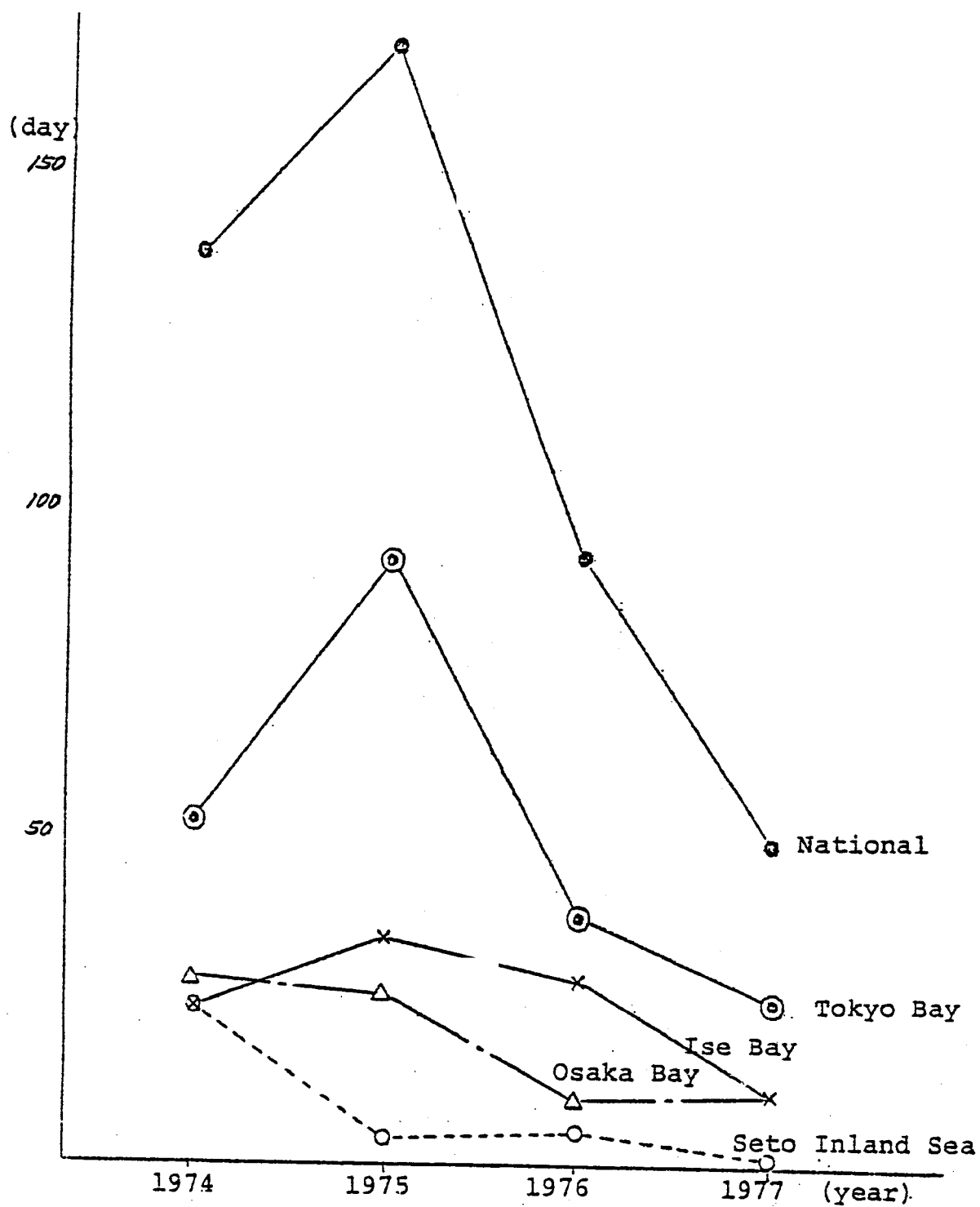
Table 1. Number of Days Reported (April - October)

(day)

300 —

200 —

Osaka Bay
area

Ise Bay
area

100 —

Tokyo Bay
area

National

Seto Inland
area

1974   1975   1976   1977   (year)
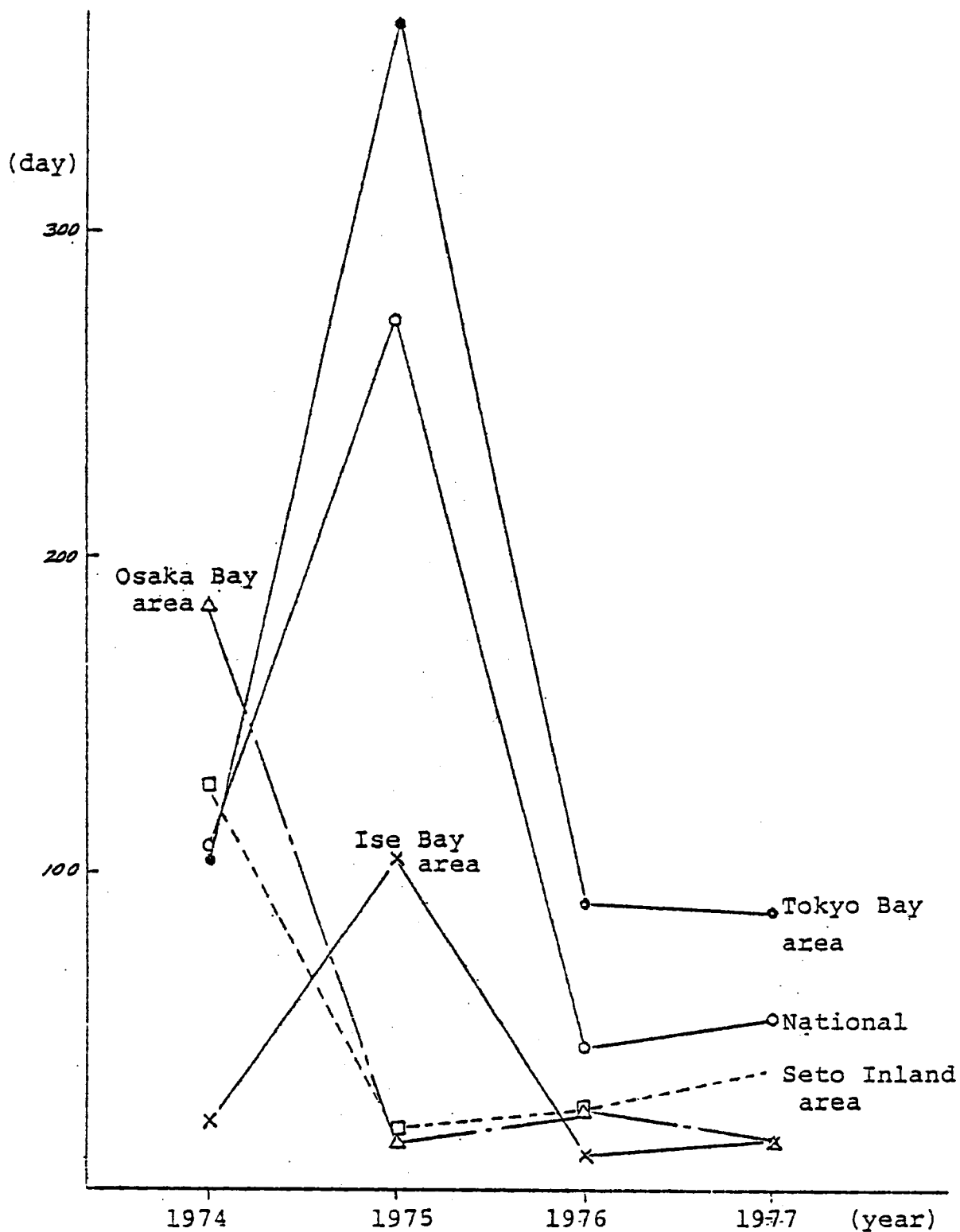
Table 2. Number of People Reporting/Number of Days Reported

(April - October)

Reference data:

1. Temperature, flux of solar radiation, and frequency
   of warnings in the Tokyo Bay area (April - October)

——— Monthly average temperature (°C)

——— Flux of global solar radiation (cal/cm^2/day)

----- Frequency of warning days (days/prefecture)

✳ Part of data not available

April

May

August

September

October

°C Cal/cm²

19

240

18

200

17

1

160

(day/pre-
fecture)

10

8

6

4

2

1973   1974   1975   1976   1977 (year)
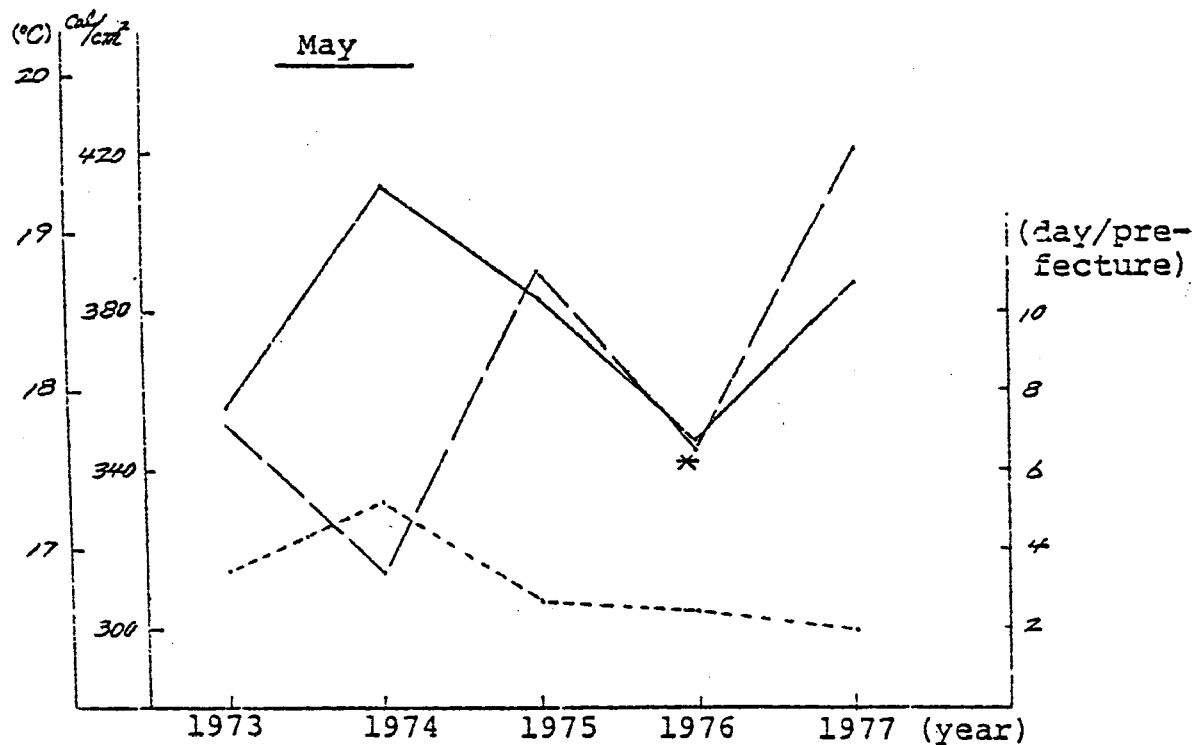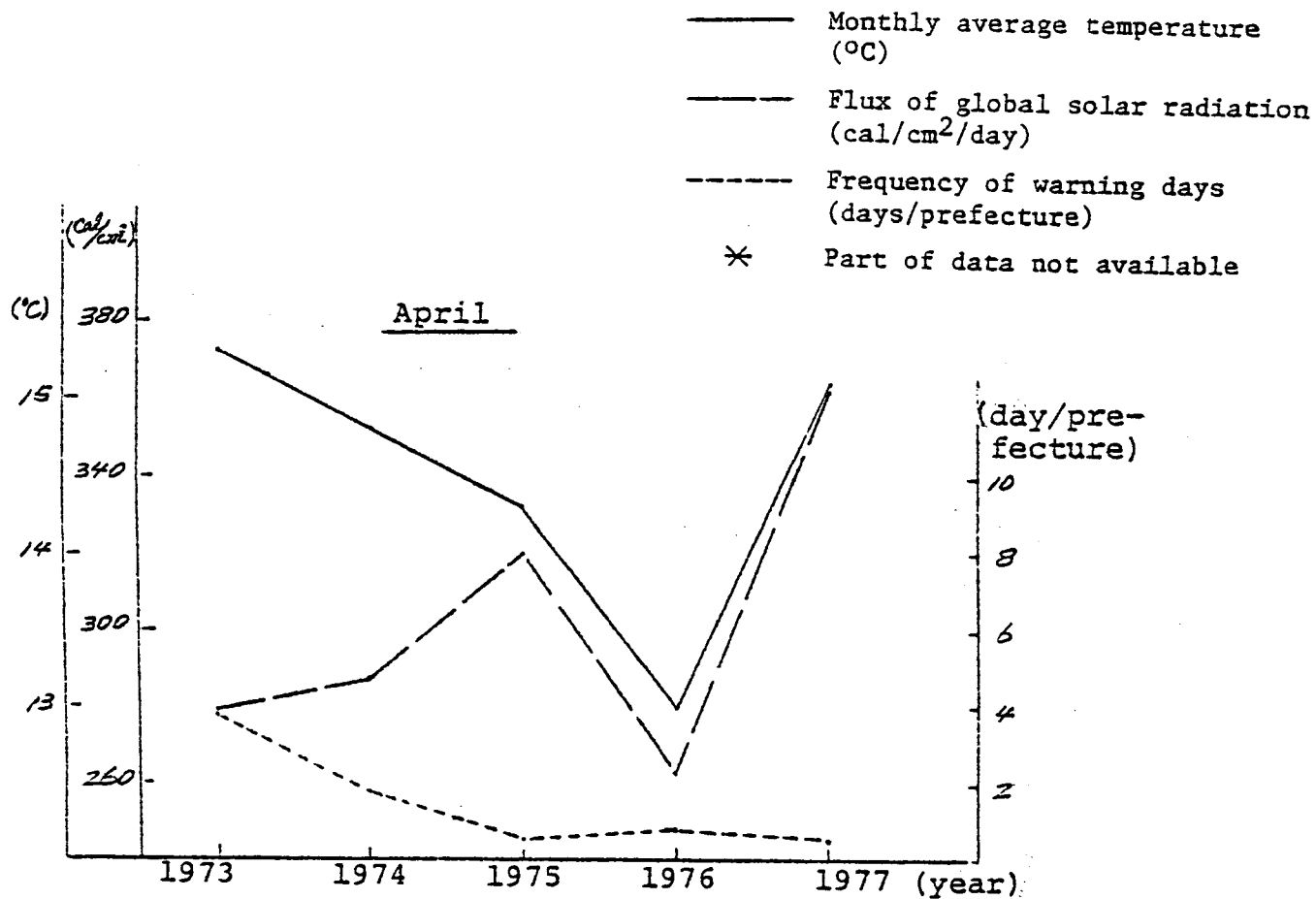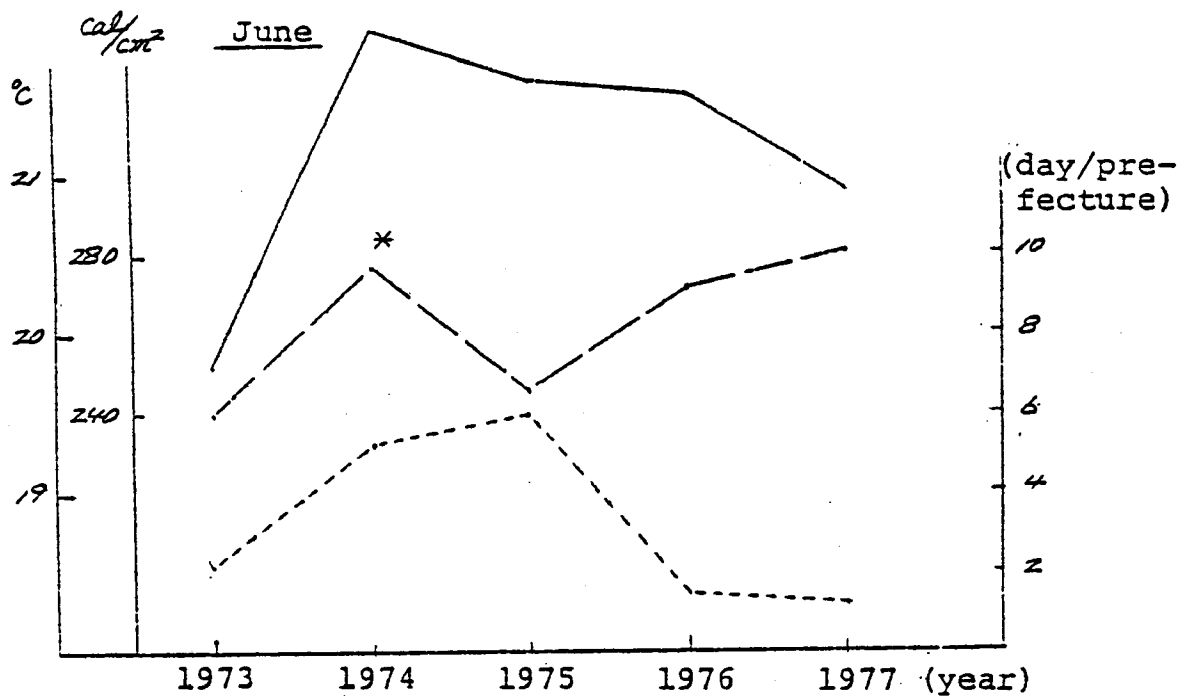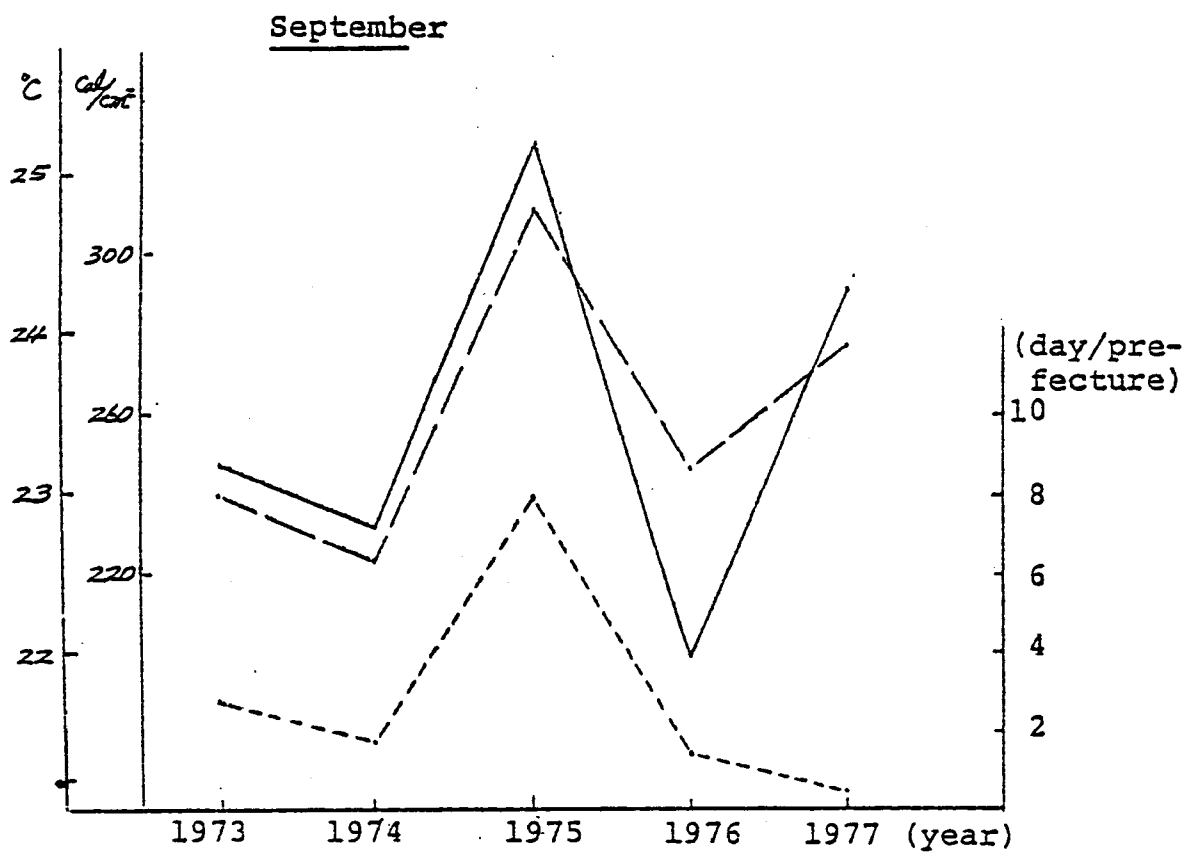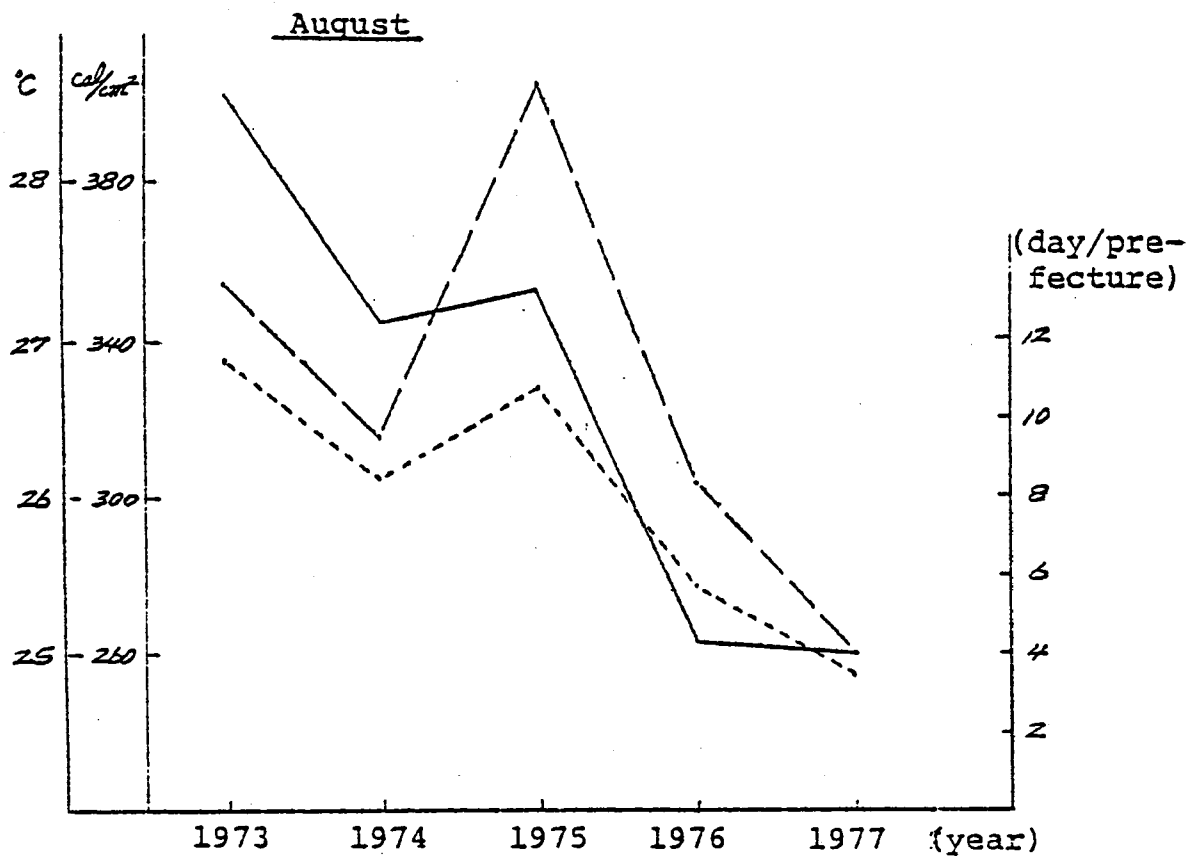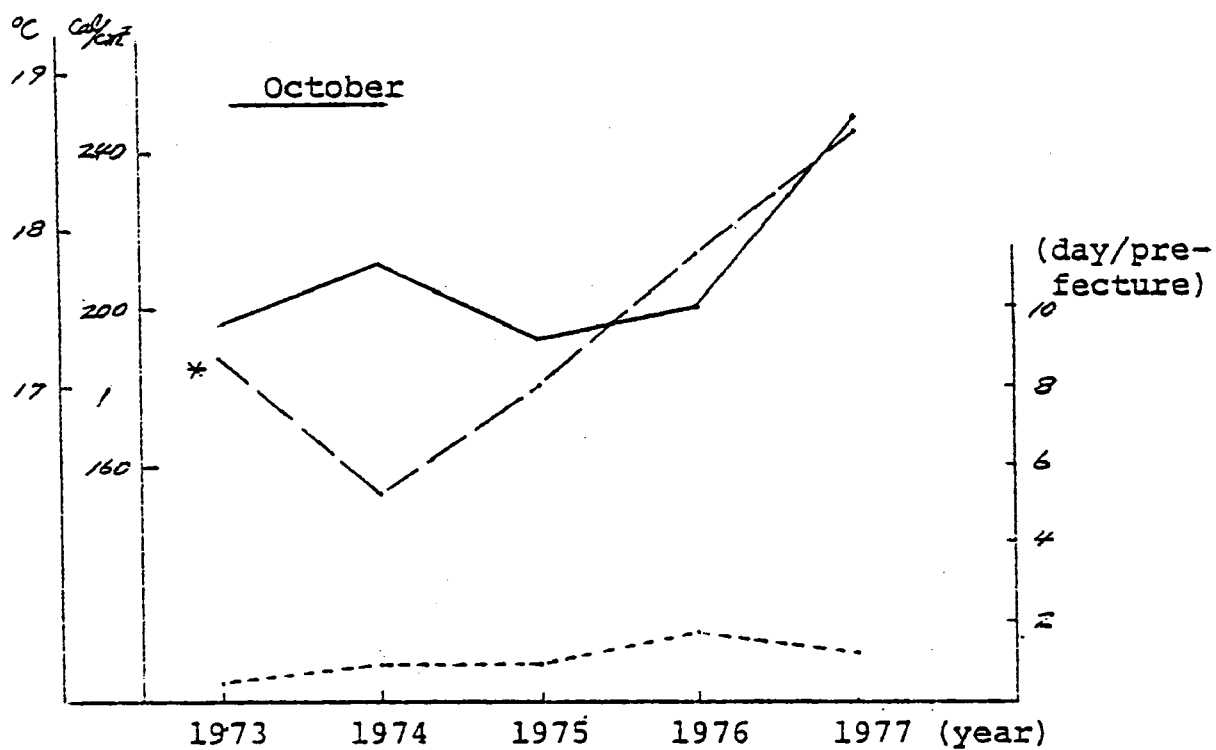
2. Relation between the meteorologically potential days and days when a warning is issued

(1) Introduction

In this section, we studied weather factors on days when an oxidant warning was issued in Tokyo and Saitama (in part of the analysis, including Kanagawa) in the past four years, and found the minimum or maximum conditions for each factor using the upper limit curve method.

Then, with reference to the minimum and maximum conditions, a standard was established by changing combinations of grades of factors.

As weather factors for this study, we used data on temperature, flux of solar radiation, wind direction, wind velocity and weather from the observation data of the Tokyo District Meteorological Observatories.

(2) Minimum values or conditions of weather factors

Figs. 1-a - 1-d show the minimum values of flux of solar radiation and wind velocity. Some differences are seen by years, but on average, the minimum value of maximum flux of solar radiation is about 30 $cal/cm^2/h$, and that of wind velocity about 5 m/s.

As indicated in Fig. 2, the minimum value of maximum temperature is 24.1 °C (Only figures in June are shown).

O_x concentration is apt to increase when there is a breeze off the land in the morning and then the wind changes to one from the sea. However, when a warning is issued in Saitama, there are a lot of cases when a wind with a southerly component blows from midnight and no land breeze is observed. Similar cases are seen in Tokyo too.

On the contrary, in Kanagawa, a northeasterly wind frequently blows when a warning is issued.

Thus, the minimum conditions of wind direction are hard to determine when we analyze a wider area. In this study, in which our subject is Tokyo and Saitama, we determined as the minimum condition "the existence of a wind with a southerly component in the daytime."

It seemed that there was no need to consider weather as one of the factors because it is directly or indirectly represented in flux of solar radiation and temperature. But as it is one of the representative weather factors, we added it as one factor to be analyzed.

An O_x warning is sometimes issued on a cloudy day, but it is rare on a rainy day (a day when it rains at 9:00, 12:00 and 15:00).

Therefore, the minimum condition of weather was determined as "a cloudy, rainless day".

(3) <u>Meteorologically potential days and their number</u>

The above-mentioned minimum values or conditions of weather factors are the minimum weather conditions observed on those days in the past four years when an O_x warning was issued. The number of days when the minimum conditions are met is very great, and it does not seem to be suitable for an analysis of photochemical smog. Therefore, we made each condition severer and considering the number of warning days to be included when the conditions become severer, determined standards of weather conditions which were considered the most suitable.
(Note 2.) (Table 4-1-3)

Note 2: We tried to find the best combination of the grade of each weather factor in determining the standards of weather conditions so that the percentage of the number of warning days on such days that meet the standards to the number of such days that meet the standards may be as high as possible, and so that the percentage of the number of warning days on such days that do not meet the standards to the number of such days that do not meet the standards may be as low as possible.
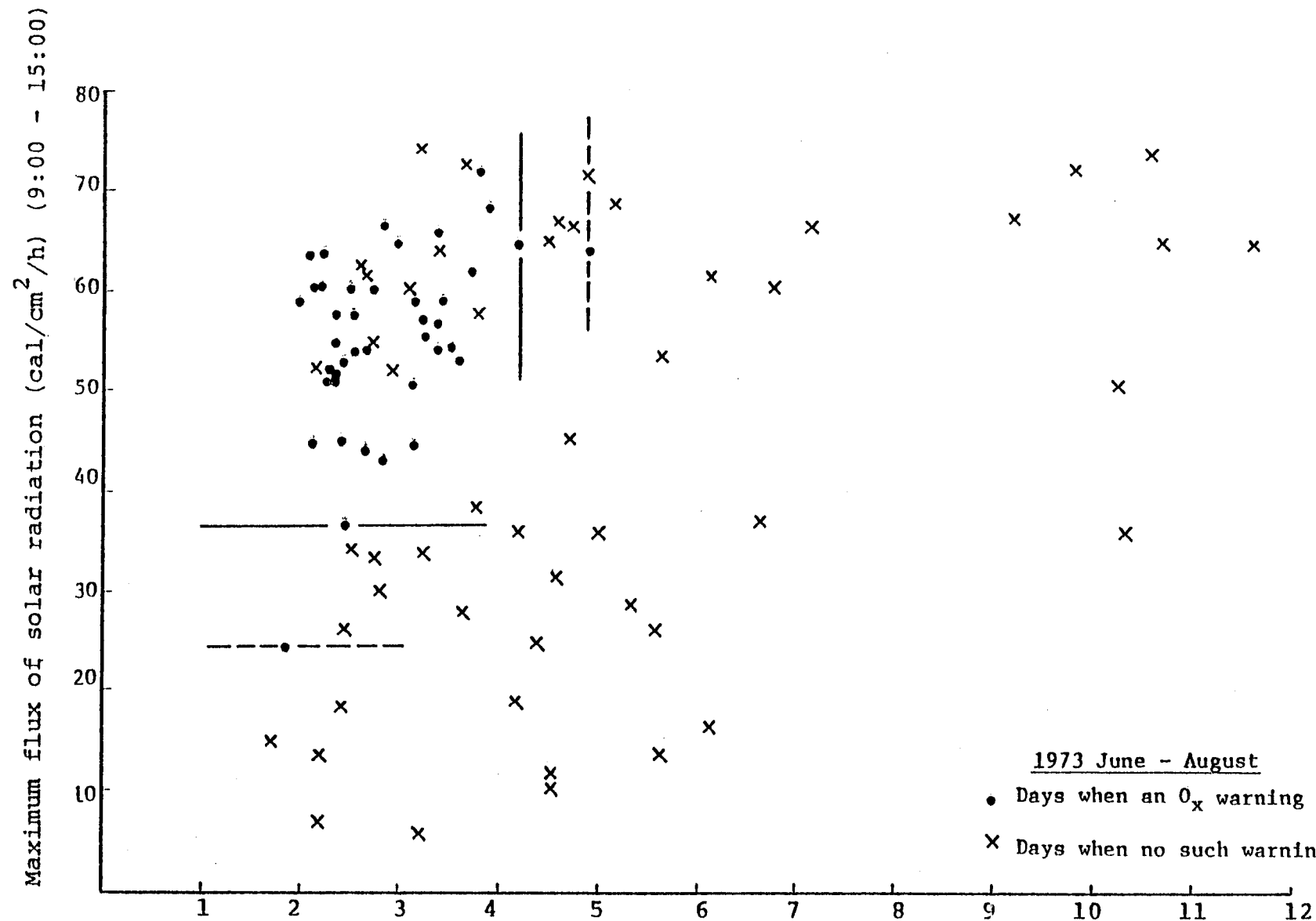
Fig. 1-a. <u>Maximum flux of solar radiation
and wind velocity</u>

Maximum flux of solar radiation $(cal/cm^2/h)$ (9:00 – 15:00)

Wind velocity (average
of values at 9:00, 12:00
and 15:00) (m/s)

<u>1973 June – August</u>

• Days when an O_x warning was issued.

✕ Days when no such warning was issued.

Fig. 1-b. **Maximum flux of solar radiation and wind velocity**

Wind velocity (average of values at 9:00, 12:00 and 15:00) (m/s)

1974 June - August

• Days when an O_x warning was issued.

✕ Days when no such warning was issued.

Fig. 1-c. __Maximum flux of solar radiation__
__and wind velocity__

1975 June – August

• Days when an O_x warning was issued.

✗ Days when no such waning was issued.

Wind velocity (average of
values at 9:00, 12:00
and 15:00) (m/s)

Maximum flux of solar radiation (cal/cm^2/h) (9:00 – 15:00)

Fig. 1-d **Maximum flux of solar radiation
and wind velocity**

1976 June - August
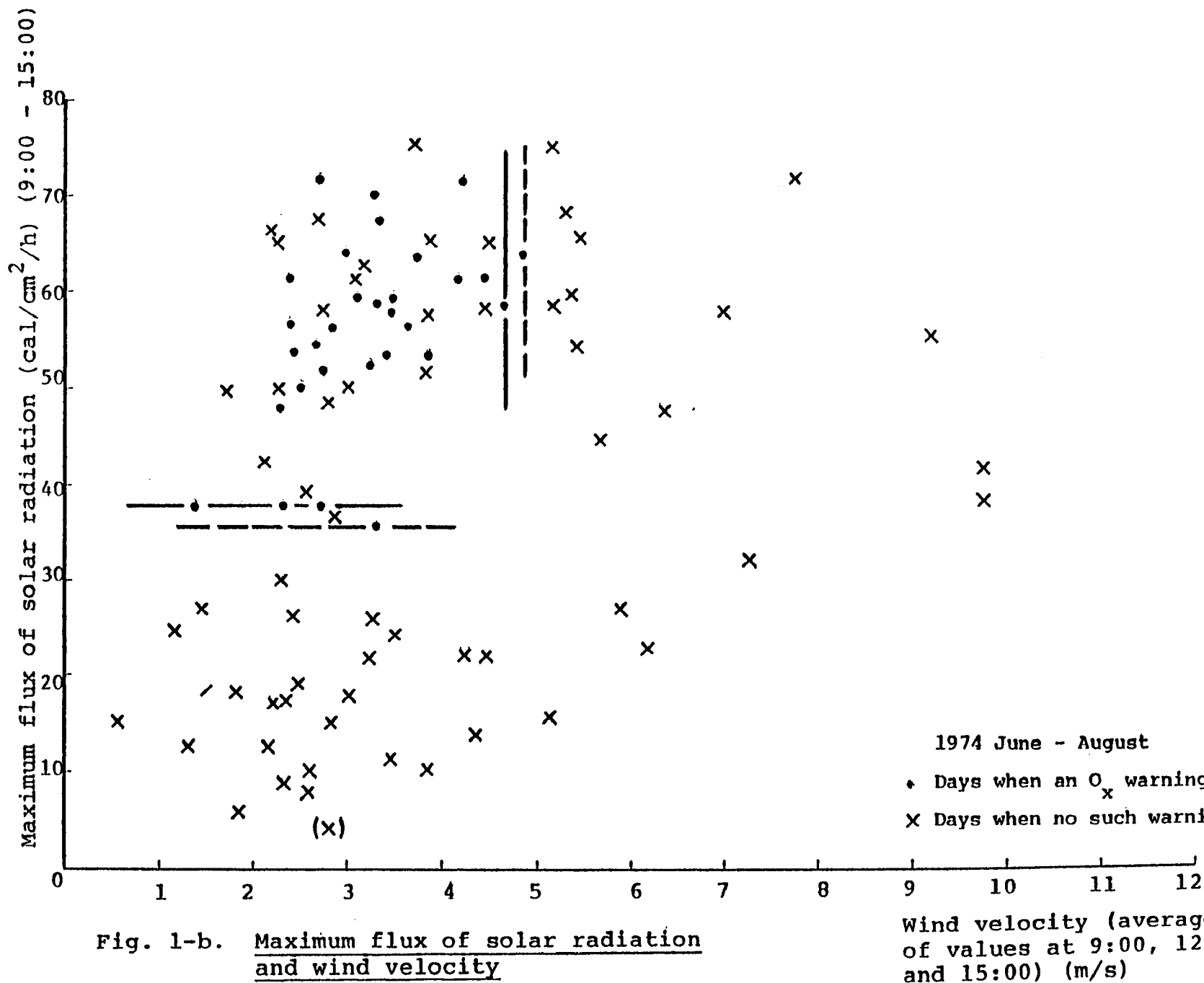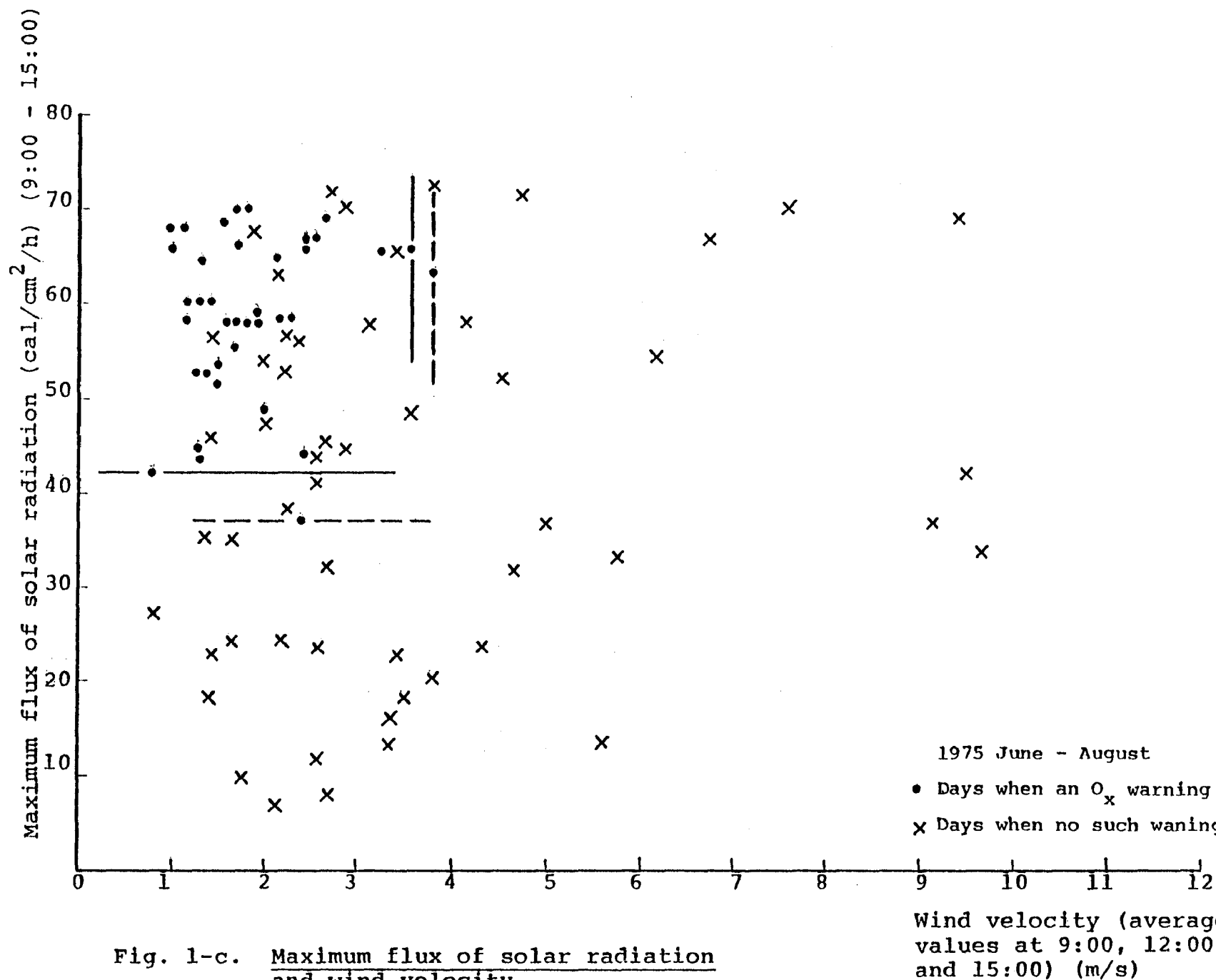
• Days when an O_x warning was issued.

✕ Days when no such warning was issued.
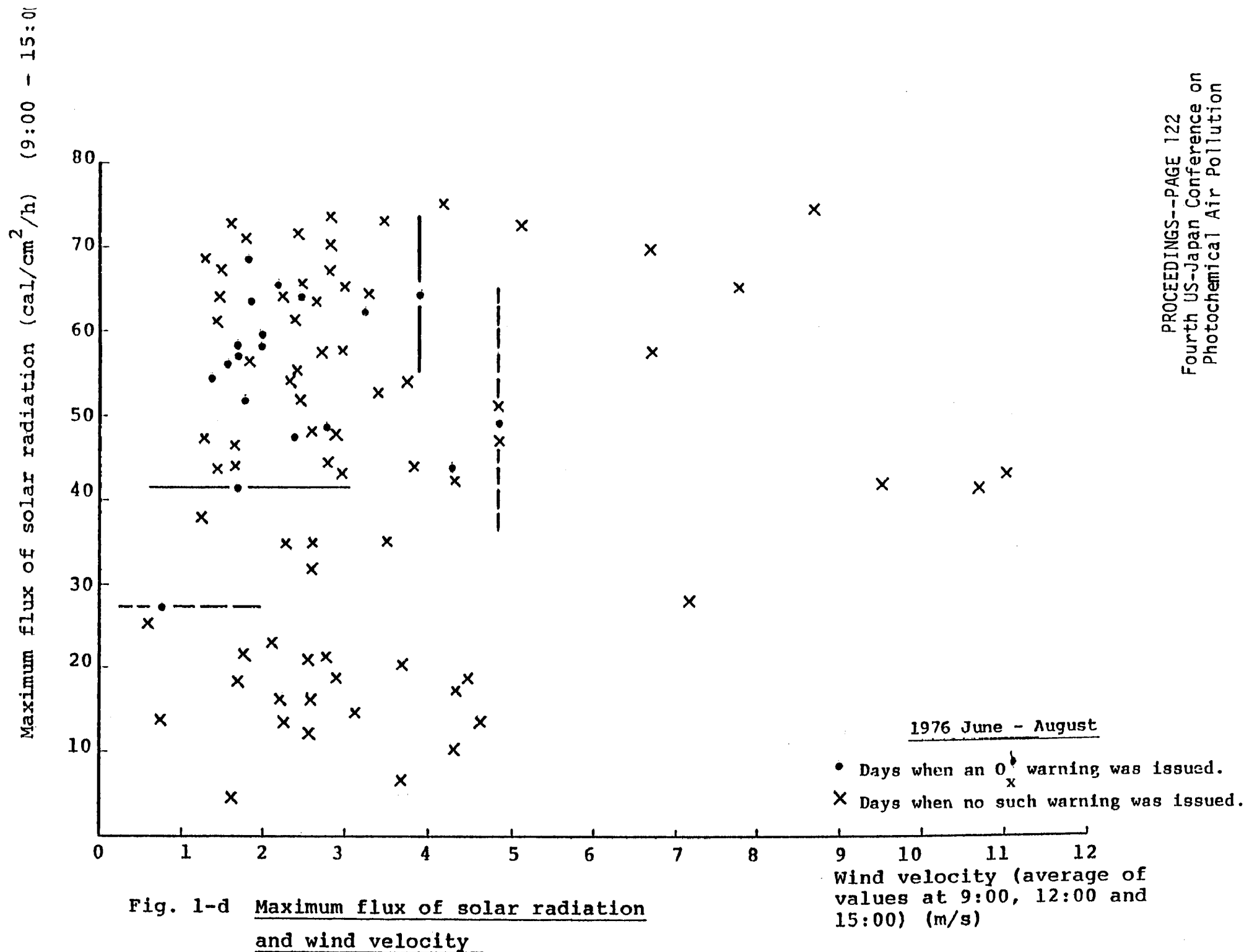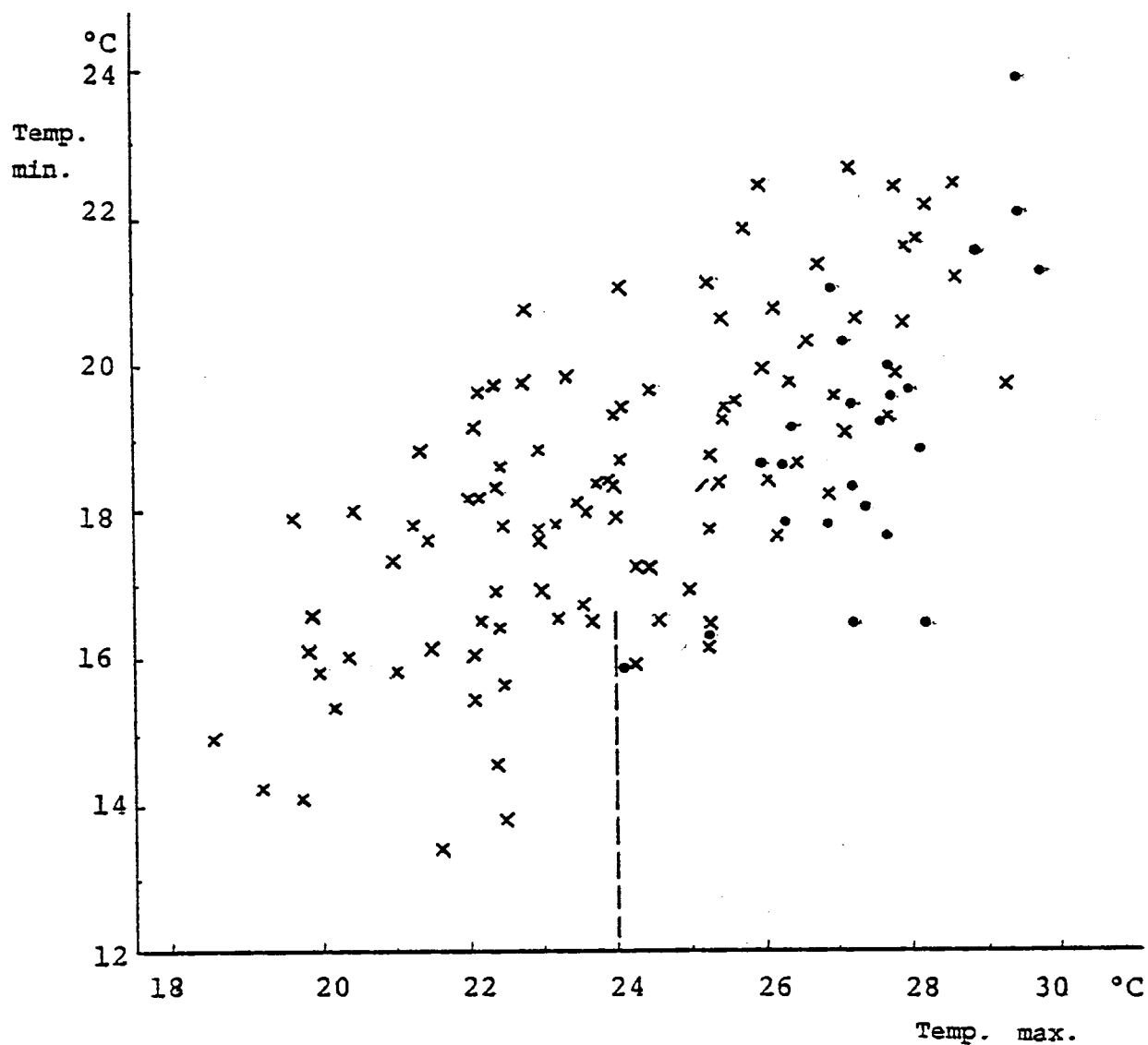
Fig. 2 Maximum temperature and minimum teperature
(June, 1973 - 1976)   • Days when an O_x warning was issued.
                       × Days when no such warning was
                          issued.

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Table 1.

Minimum values of maximum flux of solar radiation and average
wind velocity on warning days in Tokyo and Saitama prefecture

Factor / Year	Maximum flux of solar radiation cal/cm^2/h		Average wind velocity m/s	
	Minimum value	Second lowest value	Minimum value	Second lowest value
1973	26	37	4.9	4.1
1974	36	38	4.8	4.6
1975	37	42	3.7	3.4
1976	27	41	4.7	4.4
1977	32	40	4.5	4.1

Maximum flux of solar radiation: One-hour maximum value
between 9:00 and 15:00

Average wind velocity: Average value of velocity at
9:00, 12:00, and 15:00.

Table 2. Standards of meteorological conditions for Tokyo
and Saitama

Factor	Description
Flux of global solar radiation(R)	2 hrs. or more of radiation of 30 cal/cm^2/h between 9:00 - 15:00.
Wind velocity (V)	An average velocity of 5 m/s or less at 9:00, 12:00, and 15:00.
Wind direction (D)	Wind with southerly component between 9:00 and 18:00.
Temperature (T)	A maximum temperature of 24 °C or higher
Weather (W)	Fine (including slightly cloudy) or cloudy at 9:00, 12:00 and 15:00.

EMISSIONS TO OXIDANT AND NO$_2$ AIR QUALITY RELATIONSHIPS

presented by B. Dimitriades

Environmental Protection Agency

United States

EMISSIONS TO OXIDANT AND NO$_2$ AIR QUALITY RELATIONSHIPS

On the subject of methods for relating emissions to ambient ozone and NO$_2$, we wish to report here two significant developments: (a) EPA has developed a new method, the isopleth method, for relating emissions to ozone, and (b) in 1977, EPA removed the requirement that the Appendix J method be the only method to be used in the preparation of State Implementation Plans. EPA now feels that other methods can be used, for example, the rollback method, the isopleth method, and air quality simulation models. Of the methods pertaining to ozone, the rollback method and the Appendix J method are the least acceptable for 3 main reasons.

1. They are not based on cause-effect relationships

2. They do not consider the role of NO$_x$

3. They cannot be used in a variety of applications.

Furthermore, the modeling method has not been developed yet to the point where it can be used. Thus, for the time being the isopleth method is the most acceptable one.

The isopleth method, often called the EKMA (Empirical Kinetic Mechanism Approach) method, is based on the use of a mathematical method that predicts fairly accurately the photochemical behavior of the atmospheric HC-NO$_x$ reaction system. This mathematical model was validated using smog chamber data on HC-NO$_x$ mixtures similar to those found in the atmosphere. Thus, by specifying the sunlight intensity in a given specific city and prevailing dilution conditions (inversion data), the model will provide the quantitative relationships between ambient concentration of ozone and concentrations of NO$_x$ and HC.

To use the isopleth method we need:

1. A measure of ambient ozone air quality (second highest value observed in reference year).

2. The ratio of non-methane-HC to NO_x during 6-9 am.

3. A measure of NO_2 air quality, which in the U.S. is the annual mean NO_2 concentration.

The method has only relative validity and handles only atmospheric chemistry not dispersion. It does not relate precursor emission rates to oxidant, but ambient concentrations (of precursors) to oxidant. It can not treat the effect of ozone transported in from outside the city nor can it treat sink (removal) processes. However, it has the important advantages over the earlier methods that it is based on a cause-effect relationship between ozone and precursors and that it considers the role of NO_x.

Finally, the air quality simulation model (AQSM) method is based on a mathematical model of the dispersion, reaction, and removal processes, in the form of a mathematical equation that is known as the atmospheric diffusion equation. In order to solve this equation we need:

1. rates of HC and NO_x emissions with adequate spatial and temporal detail

2. meteorological data on atmospheric stability, wind, sunlight, and temperature

3. the atmospheric reaction mechanism

4. data on removal processes in the form of depostiion velocities

5. initial (early morning) and boundary conditions (concentrations of pollutants in air masses flowing into the model area)

3

The input is very large and complex, making the method difficult and expensive. However, it has two advantages:

1) It predicts absolute air quality -- an important advantage because it's possible, in principle at least, to validate the method using real atmospheric data.

2) It can be used in a wide variety or applications.

EPA has been engaged in developing AQSMs for the past several years. We have just completed a 5 yr study in St. Louis which was designed specifically to develop and validate this modeling approach. We are now using this information to validate several such models. At the end of 1978 or early in 1979 we will finish the first phase of the effort and will have a first assessment of the accuracy of these models. Following that, we will be testing the model(s) in cities outside of St. Louis. We are now in the process of gathering data in other cities for this purpose.

Recent studies concerned with the emissions-to-NO_2 relationships are briefly as follows:

EPA has been conducting studies on the occurrence and health effects of short term (s.t.) concentrations of NO_2 and has been exploring the need for a s.t. NO_2 standard. In one relevant study we examined the 1 hr. and annual mean NO_2 data available and specifically the ratio of maximum NO_2 to annual NO_2 concentration, and found that the max. NO_2 values can be as high as 0.4 ppm and that the ratio of max. to annual values ranged considerably from location to location and with time. This latter variation suggests that neither one of the two indices can represent the other, and that, therefore, we

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may need two standards. Another question of interest is whether the NO_2 concentrations are distributed uniformly within the urban area so that measurements from one or two stations within a city could provide a reliable measure of NO_2-related air quality. The results seem to indicate that the NO_2 is uniformly distributed within the city. However, there are some indications that there may be some hot spots in the heavily trafficked arteries, suggesting that the concentrations of NO_2 within roadways, streets, etc., should be explored further. Existing data, note, are not indicative of roadway concentrations because the measurement stations are off the roadways. We also observed that the concentration of NO_2 degrades rapidly as we move away from the city into the rural areas where the NO_2 is barely detectable.

Another study was addressed to the relative contributions of mobile to stationary sources to ambient NO_2. In that study it was assumed that

(1) CO represents auto exaust (mobile), and

(2) SO_2 represents stationary source emissions

Using statistical regression analysis to calculate the relative contributions of the mobile sources and the stationary sources, it was concluded tentatively that by far most of the NO_x comes from the mobile sources in the urban areas. For this reason, EPA is tentatively thinking of placing the NO_x control emphasis on the mobile sources.

In another study, we performed an analysis of smog chamber and atmospheric data in an effort to derive relationships between ambient NO_2, and HC and NO_x, and to determine the effects of HC and NO_x controls on ambient NO_2.

5

The results were:

1. NO_x control will probably result in an equal percent reduction in the maximum or annual NO_2.

2. HC control will result in a small effect on the maximum NO_2 and in no effect on the annual NO_2. The HC effect was found to be stronger during the winter time; however, the statistical analysis is such that the HC effect cannot be distinquished from the meteorological factors. This means that it's possible that there is no HC effect at all but the effect observed could be an effect from meteorological factors.

PHOTOCHEMICAL OZONE FORMATION IN PROPYLENE-NITROGEN OXIDE-DRY AIR SYSTEM

presented by M. Okuda

National Institute for Environmental Studies

Japan

Photochemical experiments were performed investigating the formation of ozone in propylene-nitrogen oxide-dry air (H_2O less than 1 ppm) system using an evacuable and bakable smog chamber. The maximum concentration of ozone reached ultimatly, $[O_3]_{max}$, were studied varing initial concentrations of C_3H_6 (0.1 - 0.5 ppm) and NO_x (0.0093 - 0.290 ppm), and also light intensity, k_1 (0.13 - 0.37 min^{-1}). When the initial concentration ratio of C_3H_6 and NO_x is larger than about two, the relationship, $[O_3]_{max} = (12.4 \pm 1.5)[O_3]_{ps}$ was obtained, where $[O_3]_{ps}$ is the photostationary state concentration of ozone in the absence of C_3H_6 for the same initial concentration of NO_2, as that of NO_x in the presence of C_3H_6. In this initial concentration region, $[O_3]_{max}$ was found to be proportional to $\sqrt{k_1}$, and the linear relationship between $[O_3]_{max}$ and $\sqrt{[NO_x]_0}$ was obtained.

Introduction

Using a so called "smog chamber" or "environmental chamber," a number of investigations (1 - 9) has been conducted on the photooxidation of hydrocarbon (HC)-nitrogen oxides (NO_x)-air system in order to evaluate the effect of initial mixture composition on oxidant or ozone

formation under simulated atmospheric conditions. Earlier studies have been reviewed by Altshuller and Bufalini (10,11). Although these studies have revealed some characteristic dependence of oxidant or ozone generation on the initial concentrations of HC and NO_x under the specific experimental conditions, they were not successful enough to obtain any general relationship between them due to the complex nature of the dependence. Recently, an effort to establish a general relationship between the amounts of ozone generated and the mixture composition for a cyclohexene-NO_x-air system has been attempted using a photochemical flow reactor (9).

The establishment of such general relationship in the smog chamber study is thought to be of critical importance for the understanding of ozone formation mechanism in the atmosphere, and also for proving the usefulness of smog chamber studies for the planning of ozone control strategies. From this viewpoint, the photooxidation of propylene (C_3H_6)-NO_x-air system, which is important as a basic photochemical smog reaction model, was reinvestigated in the present work. Although this reaction system has been studied (1, 2, 6) in some detail in view of obtaining the dependence of maximum oxident yield on the initial concentrations of C_3H_6 and NO_x, the influece of any reaction parameter on the amount of ozone generated has

not been well established. In this work, the photooxidation

was studied using an evacuable and bakable smog chamber at

the National Institute for Environmental Studies (NIES),

in the lower initial concentration region (C_3H_6; 0.1 - 0.5

ppm; NO_x; 0.01 - 0.5 ppm) than that for the earlier studies

(1, 2, 6). The object of this invistigation is to study

the effects of the initial concentration of C_3H_6 and NO_x,

and also of light intensity on the maximum yield of ozone,

and try to present their effects as   functions of

generalized parameters.

Experimental

Experiments were carried out using an evacuable and

bakable smog chamber system (12,13). The reaction chamber

is a Teflon-lined stainless steel cylinder, 1450 mm inner

diameter, 3500 mm long, and 6065 ℓ in volume. One end of

the chamber is sealed with nineteen quartz windows of 280

mmφ (effective diameter for light transmission, 250 mmφ)

each and 20 mm thick. The other end is sealed with

eighteen Pyrex and one quartz windows with the same size.

Irradiation is made through the nineteen quartz windows

on axis to the reaction chamber.

The pumping system consists of three oil rotary pumps

(950ℓ/min each) with a liq. N_2 foreline trap, a turbo-molecular pump (650ℓ/sec), two titanium getter pumps (10,000ℓ/sec each) and two sputter ion pumps (800ℓ/sec each). The chamber wall is bakable at the maximum temperature of 200°C and is also temperature controled at 0~40°C within ± 1°C with the circulation of heat transfer agent around the reaction chamber. Both ends of the chamber where the windows are flanged, are not temperature controlled but cooled with water to protect the Viton O-rings during baking.

After baking at 200°C under evacuation, the chamber wall was found to be "activated" for the decay of O_3 and NO_2. In order to "deactivate" the wall, the chamber was treated with a few ppm of O_3 for about 24 hours. After this procedure the decay rates of about 0.03 ppm of O_3, NO_2 and NO were 0.07 ± 0.01, 0.025 ± 0.005, and < 0.01 hr^{-1}, respectively. The decay rates for 2 ppm of O_3 was 0.04 hr^{-1} after the same procedure These decay rates did not change appreciably after the overnight evacuation so for as the chamber wall was not baked. The baking of the chamber wall was found to be of critical importance in order to sustain good reproducibility of a low concentration run, after the reaction chamber was exposed to the reactants, say, at ten times higher concentrations than those for the run. Therefore, the baking and the ozone

treatment were made occasionally during this study to maintain system integrity, and consecutive experimental runs of close initial concentrations were carried out evacuating the chamber down to 2×10^{-5} torr with a turbo-molecular pump without baking between runs. For data analysis, the corrections for the wall decay of O_3 and NO_x were not made in this work.

The irradiation source is external to the reaction chamber and is called a solar simulator. It consists of nineteen high pressure xenon arc lamps (1Kw nominal rating each, Wacom Co. KXL-1000). The light flux from each lamp is collimated and directed toward the chamber on axis using an elliptical mirror, a quartz integration lens and a quartz collimation lens. The center of each collimated beam is matched to the center of each quartz window of the reaction chamber. The beam size is 250 mm in diameter each at the front window and about 450 mm in diameter at the back window. A Pyrex 7740 filter (4 mm in thickness, 50 mmϕ) is installed just after the each integration lens in order to match the spectral distribution of the light source to the actinic irradiance of the real sun (14) in the near U.V. region. The spectral distribution of the solar simulator was measured with a spectroradiometer (Optronic Lab., Model 740A) which was calibrated by the manufacturer to the radiometric standards

supplied by the National Bureau of Standards. Figure 1
shows the relative spectral distribution (spectral bandwidth
5 nm) of the solar simulator as compared with the estimated
actinic irradiance for $Z = 20°$ given by Leighton (16).
Both distributions are normalized at 350 nm.

The effective U.V. light intensity inside the chamber
was measured by photolyzing about 0.1 ppm NO_2 in "purified
air". After the lamps were turned on and allowed to
stabilize for 30 min, the irradiation was started by
opening a shutter of the solar simulator. Since NO_2, NO
and O_3 reach the photostationary state within a couple of
minute (12), the k_1 value, the first order rate constant
for the reaction,

$$NO_2 + h\nu \longrightarrow NO + O \ , \tag{1}$$

was calculated by the following equation given by Wu
and Niki (15).

$$k_1 = k_2 \frac{[NO]_{ps}[O_3]_{ps}}{[NO_2]_{ps}} + k_3[O_3]_{ps} \tag{I}$$

Here, $[NO_2]_{ps}$, $[NO]_{ps}$, and $[O_3]_{ps}$ are photostationary state
concentration and k_2 and k_3 are the rate constants (15) of
the following reactions,

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad k_2 \approx 27.5 \ ppm^{-1}min^{-1} \tag{2}$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad k_3 = 6.8 \times 10^{-2} \text{ ppm}^{-1} \text{ min}^{-1} \quad (3)$$
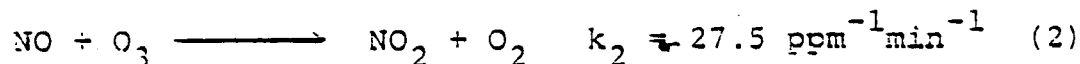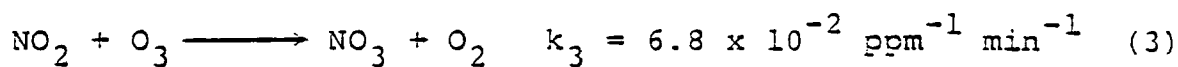
The light intensity was varied in this study by varing the discharge current of the lamps.

In our smog chamber system, "purified air" is obtained by passing crude cylinder air through a air purifier. The air purifier is composed of heated platinum catalyzer for the oxidation of hydrocarbons and NO, and molecular sieve adsorbent for the removal of CO_2, NO_2, SO_2, H_2O and etc. Impurities in the "purified air" were typically NO_x (~ 2 ppb), hydrocarbons (<10 ppbC), CO_2 (<1 ppm) and H_2O (<1 ppm).

Measurements of NO_x and NO (Monitor Labs, chemiluminescence analyzer, Model 8440L), and O_3 (Monitor Labs, chemiluminescence analyzer, Model 8410) were made continuously. The reaction mixture was sampled by means of a glass lined stainless steel tube (1/8" o.d.) or a Teflon tube (1/8" o.d.) probes extending 60 cm beyond the interior walls of the chamber. The NO_x analyzer was calibrated with a capillary flow calibrator (Standard Technology Inc., Model SGGU-14) using NO standard gas (Takachiho Co., 490 ppm). For the calibration of the ozone analyzer, the chamber was filled with zero air containing 0.5 - 5 ppm O_3 and concentrations of O_3 were simultaneously monitored with the chemiluminescent analyzer, an UV analyzer (DASIBI Co. Model 1003H) and a long path

(221.5 m) Fourier transform infrared spectometer (Block Engineering Co.) equipped to the chamber (12,13). The absolute concentrations of O_3 were determined by the IR photometry using the absorption coefficient, $\varepsilon = 4.06 \times 10^{-4}$ $ppm^{-1} \, m^{-1}$ at 1053 cm^{-1} (resolution 2 cm^{-1}) obtained by McAfee et al. (16). The chemiluminescent analyzer and the UV analyzer were standardized against the IR photometry. During the course of this work, the chemiluminescent analyzer was calibrated against the standardized UV analyzer occasionally. For several experimental runs, the concentration of C_3H_6 was monitored by using an automatic sampling gas chromatograph (Shimazu Co.).

Prior to each experiment, the "purified air" was introduced into the chamber at about 770 torr. The premeasured amounts of C_3H_6 and NO_x were then injected into the chamber using the "purified air" as carrier gas. The reaction mixture was stirred by a fan during the experiment. For each run, irradiation was continued until the maximum of ozone concentration was reached, so that real ozone formation potential of each mixture is obtained rather than the maximum concentration within a fixed irradiation time. Since the pressure of the reaction mixture decreased during a run due to sampling by the NO_x and O_3 analyzer, the pressure was monitored continuously by a capacitance manometer (M.K.S. Baratron, 1000 torr full scale), and the outputs of the

chemiluminescence analyzers and gas chromatograph were corrected to the value at 760 torr. All experiments were carried out at $30 \pm 1°C$.

Results

In the first series of experiments, the dependences of the maximum concentration of ozone formed on the initial concentrations of C_3H_6 and NO_x were studied. Throughout these runs the light intensity was kept constant at the level, $k_1 = 0.16 \pm 0.02$ min^{-1}. Typical variations of the concentrations of O_3, C_3H_6, NO and $NO_x - NO$ are shown in Figures 2(a)-(c). In these runs, the initial concentration of C_3H_6 and NO_x were kept constant at 0.1 ppm and about 0.04 ppm respectively, but the ratio of NO and NO_2 in the initial NO_x was changed. Thus, the initial contents of NO_x were essentially NO, NO/NO_2 (1:1) and essentially NO_2 for the runs shown in Figure 2(a)-(c), respectively. As shown in these figures, the difference in the NO_x contents only affected the time for O_3 to reach to the maximum but did not affect appreciably the maximum concentration of O_3 reached. Therefore, although some of the runs in this series were started with C_3H_6-NO-air mixtures in order to check the validity of this result, most of the runs were started

with C_3H_6-NO_2-air mixture from the reasons; (1) the
irradiation time could be shortened and (2) the constancy
of the initial phase of the photooxidation could be
attained easier for the latter system. When the irradiation
is started with C_3H_6-NO-air mixture, the initial rate of
the photooxidation reaction was influenced by the small
content of NO_2 in NO, which is somewhat difficult to
control, and the reproducibility of time variation was
poorer. Table I gives the experimental results of ozone
formation along with data on initial concentrations of
reactants. As shown in Table I, the initial concentrations
of C_3H_6 and NO_x were varied in a systematic manner. First,
the initial NO_x concentration was varied from 0.009 to 0.086
ppm, and from 0.045 to 0.29 ppm, while the initial C_3H_6
concentration was kept constant at 0.1 and 0.5 ppm,
respectively. Second, the initial C_3H_6 concentration was
varied from 0.05 to 0.4 ppm, and from 0.1 to 0.5 ppm, while
the initial NO_x concentration was kept constant at about
0.04 and 0.09 ppm, reapectively. The variation of the
maximum concentration of ozone generated ($[O_3]_{max}$) with the
initial concentration of NO_x ($[NO_x]_0$) for the constant
initial C_3H_6 concentration are shown in Figure 3. Similarly,
the variation of $[O_3]_{max}$ with the initial concentration of
C_3H_6 ($[C_3H_6]_0$) for the constant initial NO_x concentration
are shown in Figure 4. The reproducibulity of the $[O_3]_{max}$
for each run can be estimated to be $\pm$ 10%. Using the curves

given in Figure 3 and 4, equiconcentration contours of $[O_3]_{max}$ against the concentration coordinate of $[C_3H_6]_0$ and $[NO_x]_0$ for a fixed k_1 value can be drawn as Figure 5. It should be noted that the $[O_3]_{max}$ illustrated in Figure 3 $\sim$ 5 is the ultimate ozone concentration generated for the initial mixtures instead of maximum ozone concentration within a fixed irradiation time, as is sometimes presented (17,18).

In the second series of experiments, the dependence of $[O_3]_{max}$ on light intensity was studied for a fixed initial composition of C_3H_6 and NO_x. The selected initial composition was $[C_3H_6]_0 = 0.5$ ppm and $[NO_x]_0 \sim 0.076$ ppm. The experimental results with the detailed data on initial conditions are given in Table II. The time variations of the concentration of O_3 for these runs are shown in Figure 6.

Discussion

It has been well known (9,15,19,20,21) that irradiation of near U.V. light on a NO_2-dry-air mixture produces O_3 even in the absence of HC. When the initial concentration of NO_2 is low enough (< 1 ppm), the chemistry at the initial stage of the irradiation can be described simply by reactions,

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad (1)$$

$$O + O_2 + M \xrightarrow{k_4} O_3 + M \qquad (4)$$

$$O_3 + NO \xrightarrow{k_2} NO_2 + O_2 \qquad (2)$$
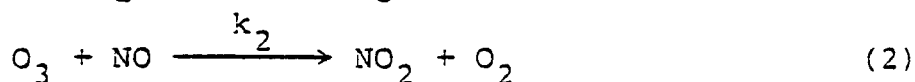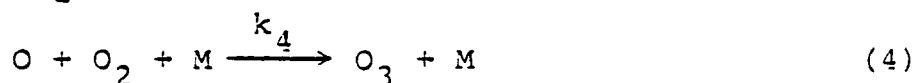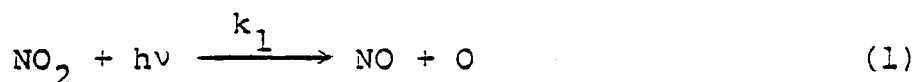
The reaction between O_3 and NO_2 (reaction (3)) is substantially negligible under these conditions. When the photoequilibrium between NO_2, NO and O_3 is reached, the photostationary state concentrations of these species may be written as

$$[O_3]_{ps} = [NO]_{ps} \qquad (I)$$

$$= \sqrt{\frac{k_1}{k_2} \{ [NO_2]_0 - [O_3]_{ps} \}} \qquad (II)$$

$$= \frac{-k_1 + \sqrt{k_1^2 + 4k_1 k_2 (NO_2)_0}}{2k_2} \qquad (IV)$$

$$[NO_2]_{ps} = [NO_2]_0 - [NO]_{ps} \qquad (V)$$

When $[O_3]_{ps}$ is much smaller than $[NO_2]_0$, as in the most practical situations, the equation (III) and (IV) may be approximated as

$$[O_3]_{ps} = \sqrt{\frac{k_1}{k_2} [NO_2]_0} \qquad (VI)$$

The deviation from equation (VI) should be observable when $(NO_2)_0$ is very low ($\leqslant 0.01$ ppm for $k_1 = 0.20$ min^{-1}).

When HC is added to the NO_2-dry air system, the NO-NO_2 photoequilibrium defined above is shifted to the NO_2 side due to the reaction,

$$RO_2 + NO \longrightarrow NO_2 + RO \qquad (5)$$
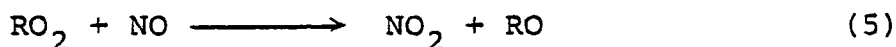
resulting in the increase of O_3. In our experimental system of the C_3H_6-NO_2-air mixture, for a given initial concentration of NO_2, $[O_3]_{max}$ first increased with increasing $[C_3H_6]_0$ and then leveled off as shown in Figure 4 and 5. The effect of initial increase in $[C_3H_6]_0$ is thought to build up RO_2 radicals which convert NO to NO_2 competing with reaction (2), resulting in the increase of $[O_3]_{max}$. However, naturally, $[O_3]_{max}$ cannot be increased infinitly with the increase of $[HC]_0$. The restricting factor to limit $[O_3]_{max}$ in the presence of enough hydrocarbon is thought to be the loss of NO_2 due to reactions,

$$O_3 + NO_2 \longrightarrow NO_3 + O_2 \qquad (3)$$
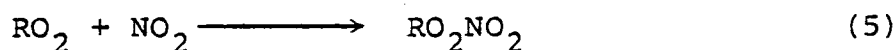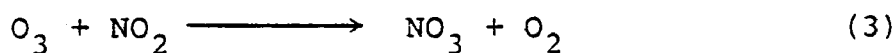
$$RO_2 + NO_2 \longrightarrow RO_2NO_2 \qquad (5)$$

where RO_2NO_2 should be taken as a stable NO_2 containig products such as peroxyacyl nitrates. Since NO_2 is removed from the reaction system, the recycling of NO and NO_2 to form O_3 cannot be continued infinitly and $[O_3]_{max}$ is limited to a certain level for a given $[NO_x]_0$. This would result in the leveling off of the curves in Figure 4 at the higher

$[C_3H_6]_0$. The concentration of $[C_3H_6]_0$ above which this leveling is observed apparently depends on $[NO_x]_0$, but seems to be fairly independent on the ratio of $[C_3H_6]_0/[NO_x]_0$. Thus, it can be seen in Figure 5, that the saturation occurs at the ratio higher than about $[C_3H_6]_0/[NO_x]_0 \simeq 3$. Therefore, this region where $[NO_x]_0$ is the restricting factor for $[O_3]_{max}$ may be defined as a C_3H_6 excess region.

In most of previous studies (1-3, 9-11) using higher initial concentrations of olefins and NO_x, it has been shown that $[O_3]_{max}$ for a given $[NO_x]_0$ has a rather sharp maximum at a certain initial concentration of HC, and an further increase in $[HC]_0$ beyond the value resulted in a decrease in $[O_3]_{max}$. The decrease of $[O_3]_{max}$ with increasing $[HC]_0$ was interpreted by the reaction of O_3 with olefins (9). In the present work, however, it is demonstrated that there is a substantial plateau region where $[O_3]_{max}$ for a given $[NO_x]_0$ is not varied with $[C_3H_6]_0$. In the case of hydrocarbon which is reactive to O_3, this behavior would be characteristic to the photooxidation reaction at the low initial concentrations of C_3H_6 and NO_x employed in this work. Similar behavior for the less reactive hydrocarbon or hydrocarbon mixtures has already been noted (4,18).

In the C_3H_6 excess region, $[O_3]_{max}$ for a given $[C_3H_6]_0$ increased with $[NO_x]_0$ as shown in Figures 3 and 5. In order to obtain generalized information on ozone formation in the

C_3H_6-NO_2-air system, an attempt is made to find out an analytical relationship between $[O_3]_{max}$ and $[NO_x]_0$ in this initial concentration region. Here we assume that $[O_3]_{max}$ reached in the presence of enough C_3H_6 is proportional to $[O_3]_{ps}$, the photostaionary state concentration of O_3 for the same initial concentration of NO_2 in the absence of C_3H_6. Thus, using equation (VI),

$$[O_3]_{max} \propto \sqrt{\frac{k_1}{k_3} [NO_2]_0} \qquad \text{(VII)}$$

Figure 7 shows the plot of $[O_3]_{max}$ vs. $\sqrt{[NO_x]_0}$ for the data given in Figure 3. The linear relationship between them can be seen for the two different set of data with $[C_3H_6]_0 = 0.5$ and 0.1 ppm. Although the plots do not pass through the coordinate origin, this may be due to the approximation used to derive equation (VI). When we use equation (V) instead of equation (VI) to calculate $[O_3]_{ps}$, better proportionality between $[O_3]_{max}$ and $[O_3]_{ps}$ can be confirmed as shown later. In Figure 7, the plots for $[C_3H_6]_0 = 0.5$ and 0.1 ppm did not overlap perfectly but shifted each other in near parallel. This is apparently due to the reason that the data points for $[C_3H_6]_0 = 0.1$ ppm does not belong to the true C_3H_6 excess region as can be seen in Figure 5.

Next, the validity of equation (VII) is evaluated by taking light intensity, k_1, as a variable. In Figure 8, $[O_3]_{max}$ given in Table II and shown in Figure 6 was plotted against $\sqrt{k_1}$. As show in Figure 8, the plot gives a linear line passing through the origin. The proportionality of $[O_3]_{max}$ vs. $\sqrt{k_1}$ has been predicted by Shen et. al.(9). Our result offers most clear experimental support for the prediction.

Since the linear dependence of $[O_3]_{max}$ on $\sqrt{[NO_x]_0}$ and $\sqrt{k_1}$ was obtained approximately, it is now worthwhile to evaluate the proportionality between $[O_3]_{max}$ and $[O_3]_{ps}$. For this purpose, $[O_3]_{max}$ obtained in two independent sets of data, one for variable $[NO_x]_0$ at constant values of $[C_3H_6]_0 = 0.5$ ppm, and $k_1 = 0.16$ min^{-1}, and another for variable k_1 at constant values of $[C_3H_6]_0 = 0.5$ ppm and $[NO_x]_0 \simeq 0.09$ ppm, were plotted against $[O_3]_{ps}$ calculated using equation (IV). Figure 9 shows the plot. As shown in Figure 9, the plots for two independent sets of data gives nearly a single linear line which passed through the origin. Although a slight difference in slope for each set of data, the slope being 11.5 and 13.3, is noted, the consistency is thought to be good enough to define a single proportionality factor. Thus, taking the average of the two slopes, the following relationship is obtained.

$$[O_3]_{max} = (12.4 \pm 1.5) [O_3]_{ps} \qquad \text{(VIII)}$$

The error limit given above is a rough estimate taking the reproducibility and scattering of the data into considaration.

Although the equation (VIII) was derived mostly from the data for C_3H_6-NO_2-air mixtures in this work, the relationship should be applicable more generally to C_3H_6-NO_x-air mixture since $[O_3]_{max}$ was found to be insensitive to the initial composition of NO_x as shown in Figures 3 and 4. Further, it is expected that such relationship can be applied to other types of hydrocarbons. When the corresponding proportionality constant is determined for each hydrocarbons and also for hydrocarbon mixtures, it can offer a new reliable scale of hydrocarbon reactivity in the sense of ozone formation potential.

In Figure 5, $[O_3]_{max}$ is seen to be more strongly dependent on $[C_3H_6]_0$ and less sensitive to $[NO_x]_0$ in the low ratio region of $[C_3H_6]_0/[NO_x]_0 \lesssim 2$. It has been often reported (1-11) that $[O_3]_{max}$ for a given initial concentration of HC first increased with increasing $[NO_x]_0$ but then decreased when $[NO_x]_0$ was further increased beyond a certain value. This would have been observed if $[NO_x]_0$ was further increased for the experiments shown in Figure 3. However, as the ratio of $[C_3H_6]_0/[NO_x]_0$ decresed, the time for O_3 to reach the maximum becomes longer, and it was not practical to study these behavior in the present study.

In the study of photochemical ozone formation in cyclohexene-NO_2-air mixtures using a flow reactor, Shen et

al.(9) has proposed a general relationship between $[O_3]_{max}/\sqrt{k_1[NO_2]_0/k_2}$ and $[HC]_0/[NO_2]_0$. According to the proposition, the plot of $[O_3]_{max}/\sqrt{k_1[NO_2]_0/k_2}$ vs. $[HC]_0/[NO_2]_0$ is expected to be fallen on a single curve for each hydrocarbon. The plot was attempted for the C_3H_6-NO_2-air system using the date shown in Table I and II. However, particularly, the data for $[C_3H_6]_0 = 0.1$ and 0.5 ppm (shown in Figure 3) were not fallen on a single curve but formed two different curves. Although this might be characteristic to the low initial concentration region, further data for different types of hydrocarbons are necessary to evaluate the generealization.

Conclusions

In the photooxidation of the C_3H_6-NO_x-dry air system, for the initial concentration region of excess C_3H_6, maximum level of ozone produced, $[O_3]_{max}$, was found to be approximately proportional to $[O_3]_{ps}$. Here $[O_3]_{ps}$ is the photostationary concentration of ozone in the absence of C_3H_6 for the same initial concentration of NO_2 as that of NO_x in the presence of C_3H_6. From the data reduction in the present study, the following relationship was obtained

$$[O_3]_{max} = (12.4 \pm 1.5)[O_3]_{ps}$$

The proportionality between $[O_3]_{max}$ and $\sqrt{k_1}$ and a liner relationship between $[O_3]_{max}$ and $\sqrt{[NO_x]_0}$ were also confirmed for the initial concentration region specified above. It is proposed that the above proportionality factor would be useful as a scale of ozone formation potential of each type of hydrocarbons.

Acknowledgement

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Table I Experimental data[a, b] of the dependence of $[O_3]_{max}$ on $[C_3H_6]_0$ and $[NO_x]_0$.

Run	$[C_3H_6]_0$ (ppm)	$[NO_x]_0$ (ppm)	$[NO]_0$ (ppm)	$[NO_2]_0$ (ppm)	$[C_3H_6]_0/[NO_x]_0$	$[O_3]_{max}$ (ppm)	t_{max} (min)
1	0.10	0.0093	0.0035	0.0058	10.8	0.0264	480
2	0.10	0.0196	0.0154	0.0042	5.10	0.0681	510
3	0.10	0.0260	0.0046	0.0214	3.85	0.0776	450
4	0.10	0.0342	0.0329	0.0013	2.92	0.116	720[c]
5	0.10	0.0359	0.0040	0.0319	2.79	0.106	540
6	0.10	0.0430	0.0217	0.0213	2.33	0.115	660
7	0.10	0.0516	0.0488	0.0028	1.94	0.126	720
8	0.10	0.0630	0.0478	0.0152	1.59	0.164	1160[c]
9	0.10	0.0864	0.0064	0.0800	1.16	0.148	1020[c]
10	0.50	0.0452	0.0040	0.0412	11.1	0.151	150
11	0.50	0.0896	0.0082	0.0814	5.58	0.236	160
12	0.50	0.0890	0.0811	0.0079	5.62	0.232	315
13	0.50	0.0901	0.0818	0.0083	5.55	0.217	315
14	0.50	0.187	0.0110	0.176	2.67	0.363	220
15	0.50	0.290	0.255	0.036	1.72	0.443	660
16	0.05	0.0382	0.0035	0.0347	1.31	0.0850	1020
6	0.10	0.0430	0.0217	0.0213	2.33	0.115	660
17	0.15	0.0393	0.0035	0.0359	3.82	0.139	420

continued

18	0.20	0.0396	0.0042	0.0353	5.05	0.136	280
19	0.30	0.0391	0.0049	0.0341	7.67	0.136	200
20	0.40	0.0393	0.0046	0.0347	10.2	0.139	170
9	0.10	0.0864	0.0064	0.0800	1.16	0.148	1020 [c]
21	0.20	0.0863	0.0092	0.0771	2.32	0.216	630
22	0.33	0.0912	0.0077	0.0835	3.62	0.232	270
11	0.50	0.0896	0.0082	0.0814	5.58	0.236	160
13	0.50	0.0901	0.0818	0.0083	5.55	0.217	315
12	0.50	0.0890	0.0811	0.0079	5.62	0.232	315

(a) Some of the runs are cited twice for convinience of reference.

(b) $k_1 = 0.16 \pm 0.02$ min^{-1} throughout runs.

(c) Ozone maximum has not been reached within the irradiation time.
However, $[O_3]_{max}$ observed at the given t_{max} is thought to be
more than 98% of the true maximum value.

Table II   Experimental data of the dependence of $[O_3]_{max}$ on light intensity

Run	$[C_3H_6]_0$ (ppm)	$[NO_x]_0$ (ppm)	$[NO]_0$ (ppm)	$[NO_2]_0$ (ppm)	k_1 (min^{-1})	$[O_3]_{max}$ (ppm)	t_{max} (min)
23	0.50	0.0850	0.0115	0.0735	0.367	0.390	120
24	0.50	0.0900	0.0120	0.0780	0.308	0.366	130
25	0.50	0.0889	0.0068	0.0821	0.247	0.307	135
26	0.50	0.0830	0.0094	0.0736	0.189	0.271	145
27	0.50	0.0881	0.0087	0.0794	0.130	0.233	170

Figure Captions

Figure 1. Spectral distribution of the solar simulator for the smog chamber at NIES (——), and the actinic irradiance of the sun at $Z = 20°$ after Leighton (14) (---).

Figure 2. Time variations of the concentrations of O_3, C_3H_6, NO and NO_x-NO after irradiation. $[C_3H_6]_0 = 0.1$ ppm, $k_1 = 0.16$ min^{-1}, in common. (a) $[NO_x]_0 = 0.0342$, $[NO]_0 = 0.0329$, $[NO_2]_0 = 0.0013$ ppm; (b) $[NO_x]_0 = 0.0430$, $[NO]_0 = 0.0217$, $[NO_2]_0 = 0.0213$ ppm; (c) $[NO_x]_0 = 0.0359$, $[NO]_0 = 0.0040$, $[NO_2]_0 = 0.0319$ ppm.

Figure 3. Variations of $[O_3]_{max}$ vs. $[NO_x]_0$ for the constant initial concentrations of C_3H_6. Initial composition of NO_x is almost entirely NO_2 ($O, \triangle$), nearly half and half ($\triangle$) and almost entirely NO ($\ominus, \blacktriangle$).

Figure 4. Variations of $[O_3]_{max}$ vs. $[(C_3H_6)]_0$ for the constant initial concentrations of NO_x. Initial composition of NO_x is almost entirely NO_2 ($O \triangle$), nearly half and half ($\oplus$) and almost entirely NO ($\ominus, \blacktriangle$).

Figure 5. Equiconcentration contours of $[O_3]_{max}$ composed using the curves in Figure 3 and 4.

Figure 6. Time variations of the concentration of O_3 after irradiation for different light intensities.

Figure 7. Plot of $[O_3]_{max}$ vs. $\sqrt{[NO_x]_0}$. The abscissa is in a square root scale. $k_1 = 0.16\ min^{-1}$.

Figure 8. Plot of $[O_3]_{max}$ vs. $\sqrt{k_1}$. The abscissa is in a square root scale. $[C_3H_6]_0 = 0.50$, $[NO_x]_0 = 0.09\ ppm$.

Figure 9. Plot of $[O_3]_{max}$ vs. $[O_3]_{ps}$. (a) $[NO_x]_0 = variable$, $[C_3H_6]_0 = 0.50\ ppm$, $k_1 = 0.16\ min^{-1}$ (O); (b) $k_1 = variable$, $[C_3H_6]_0 = 0.50\ ppm$, $[NO_x]_0 = 0.09$ ppm (●).
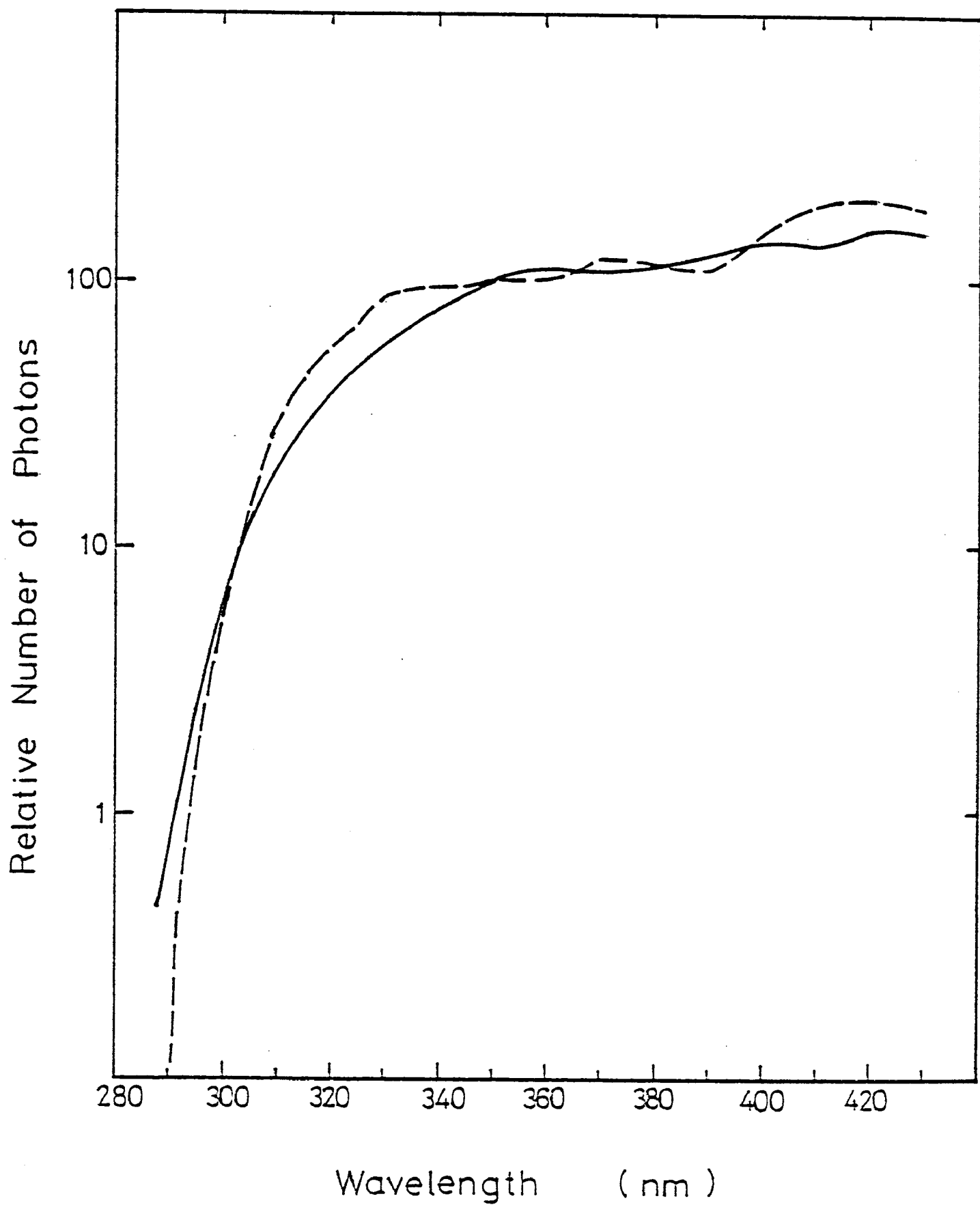
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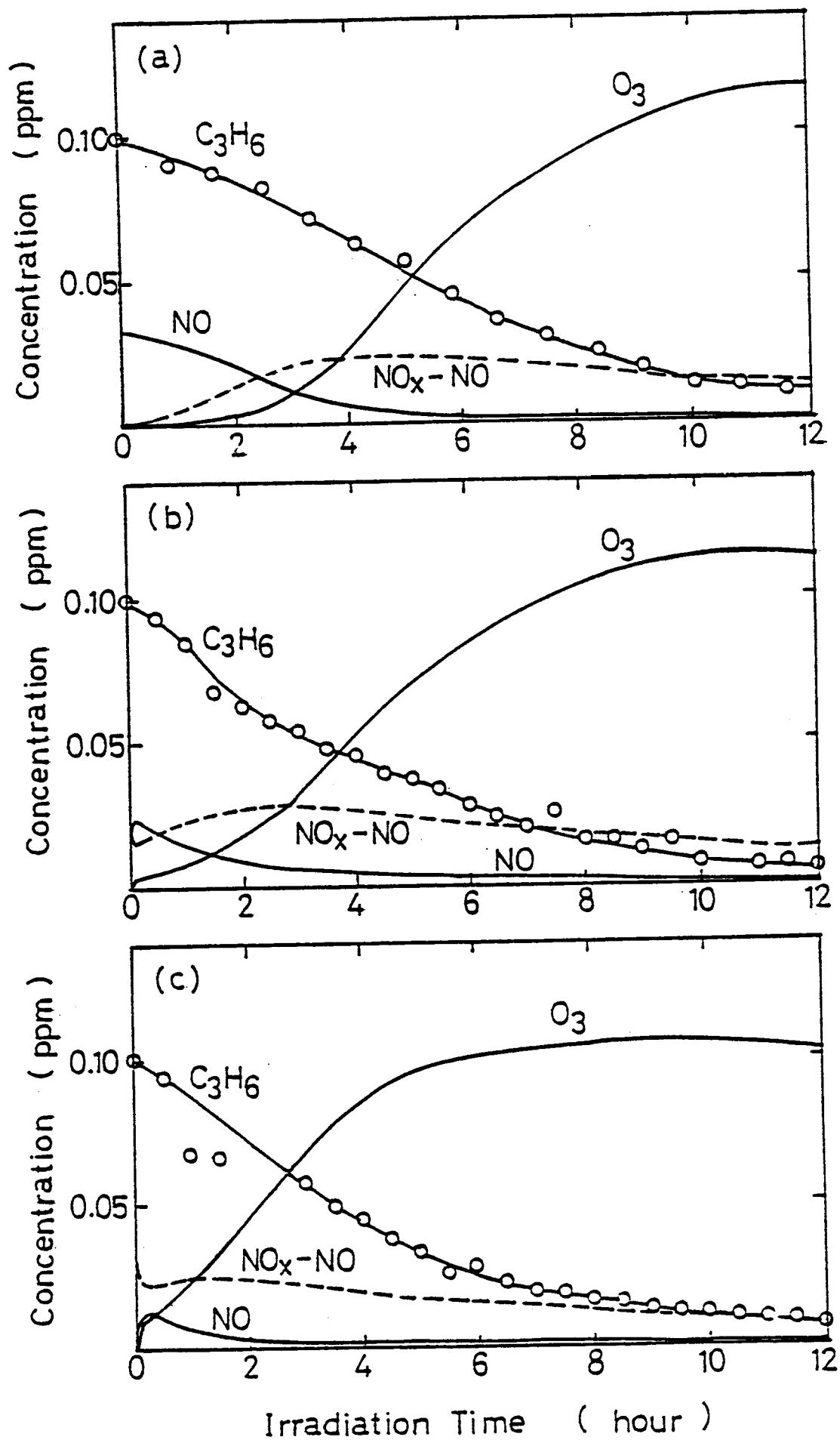
FIGURE 2   Fourth US-Japan Conference on
Photochemical Air Pollution
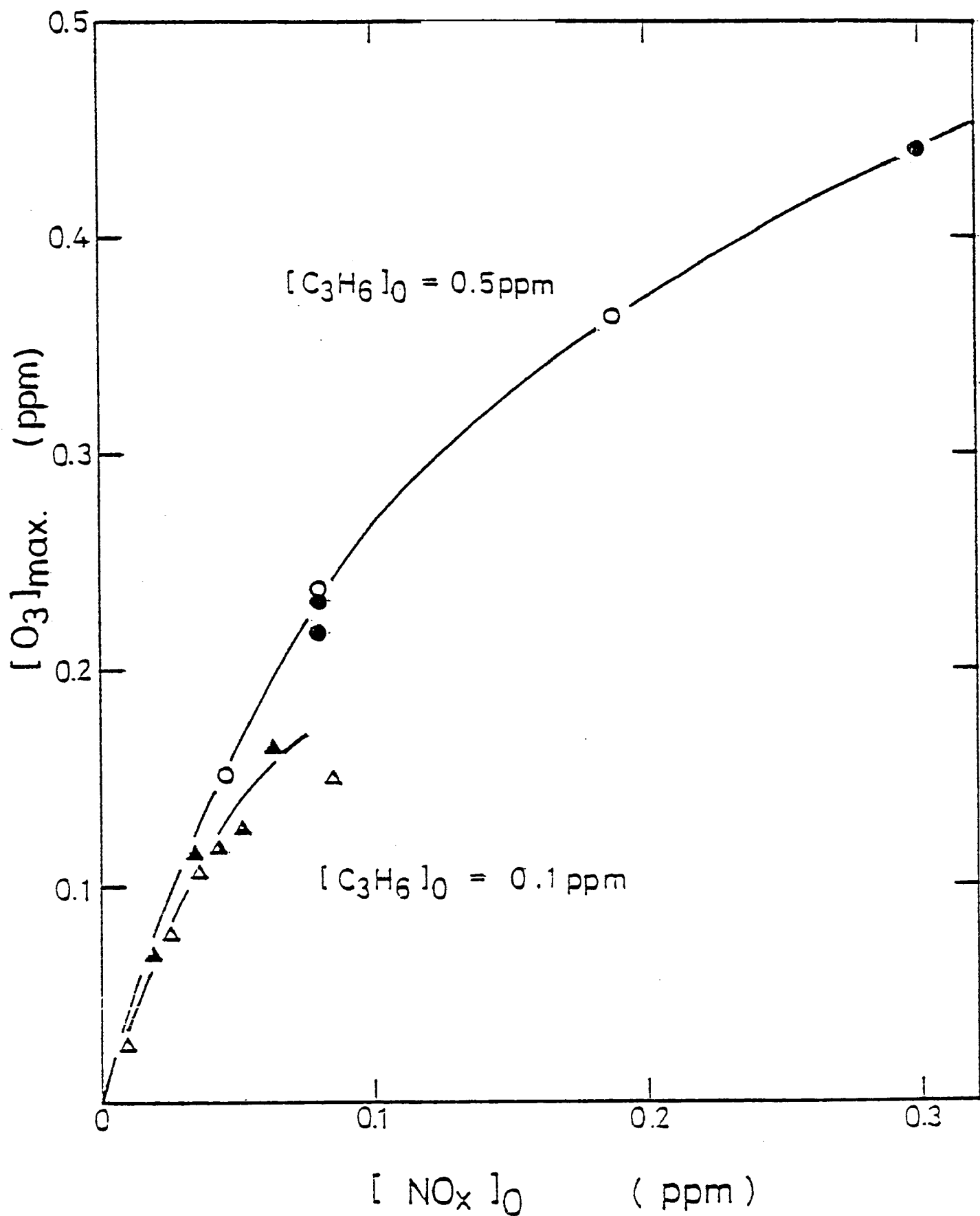
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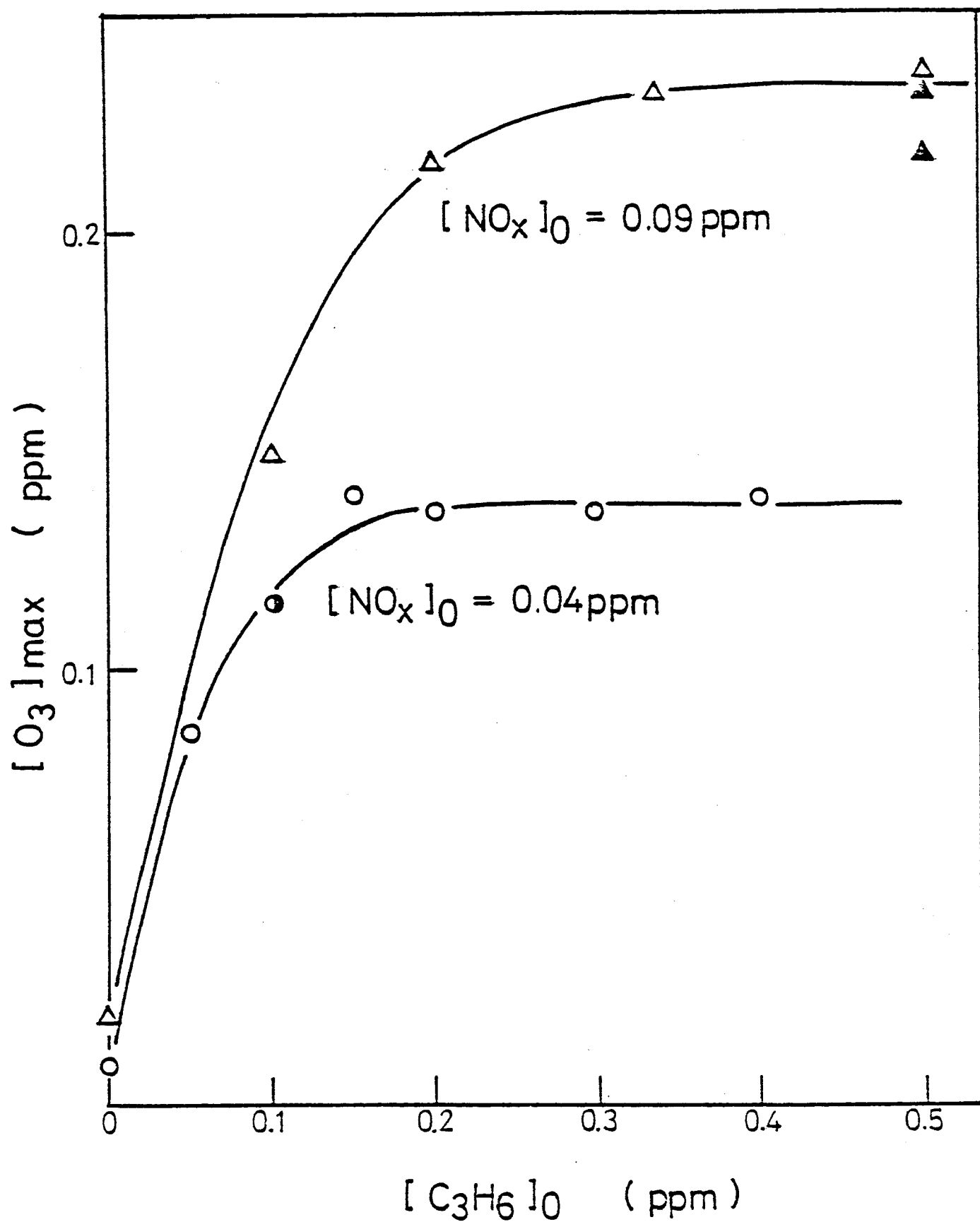
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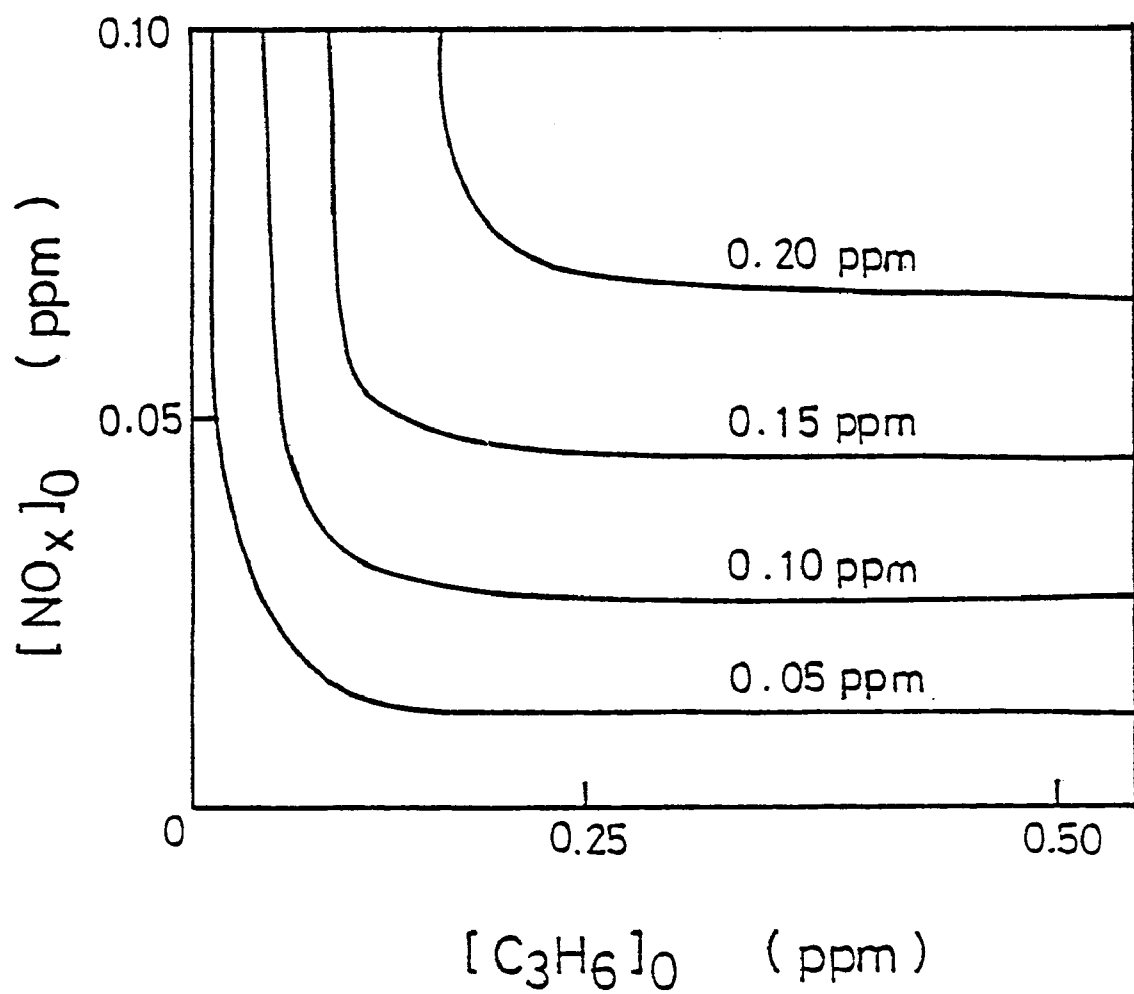
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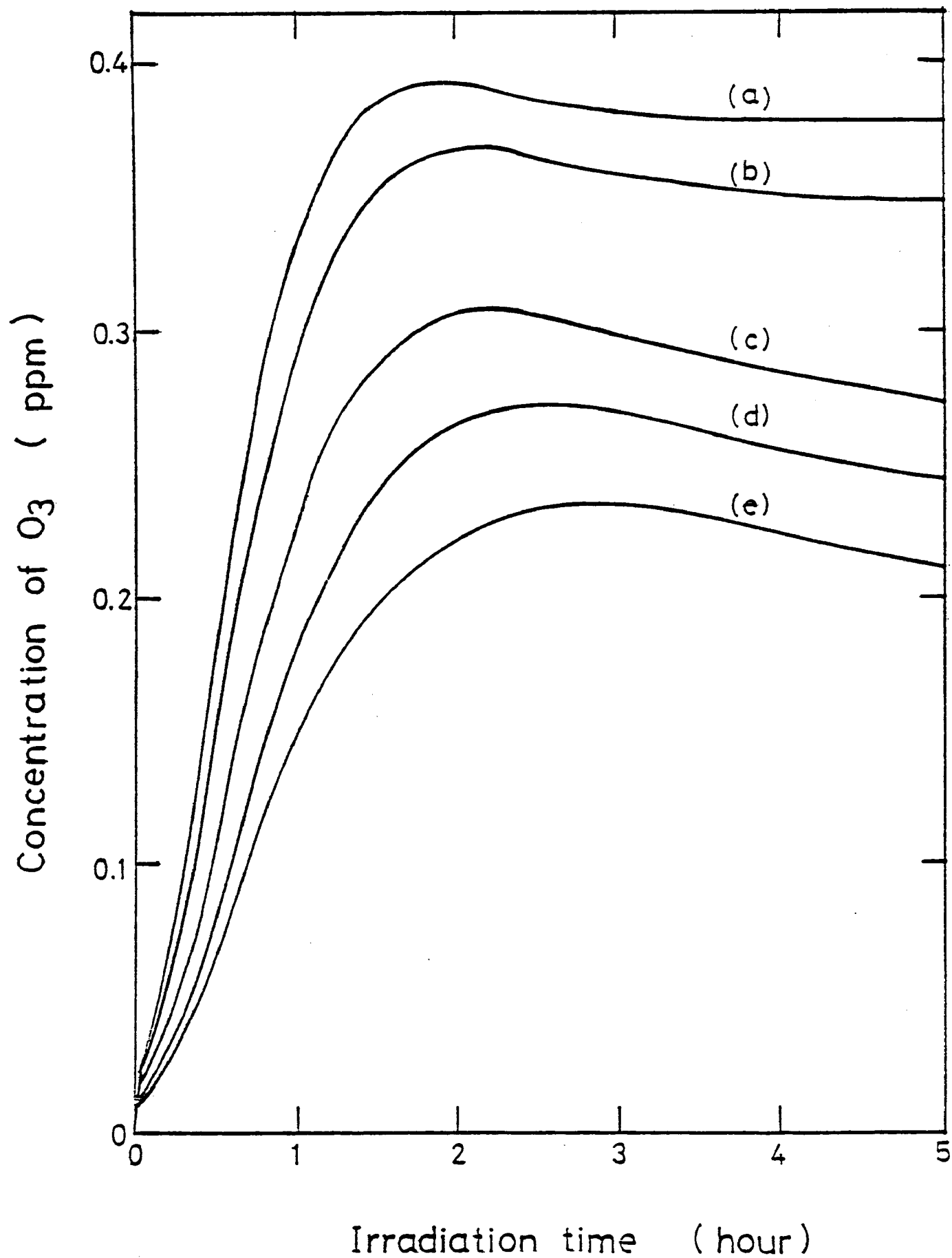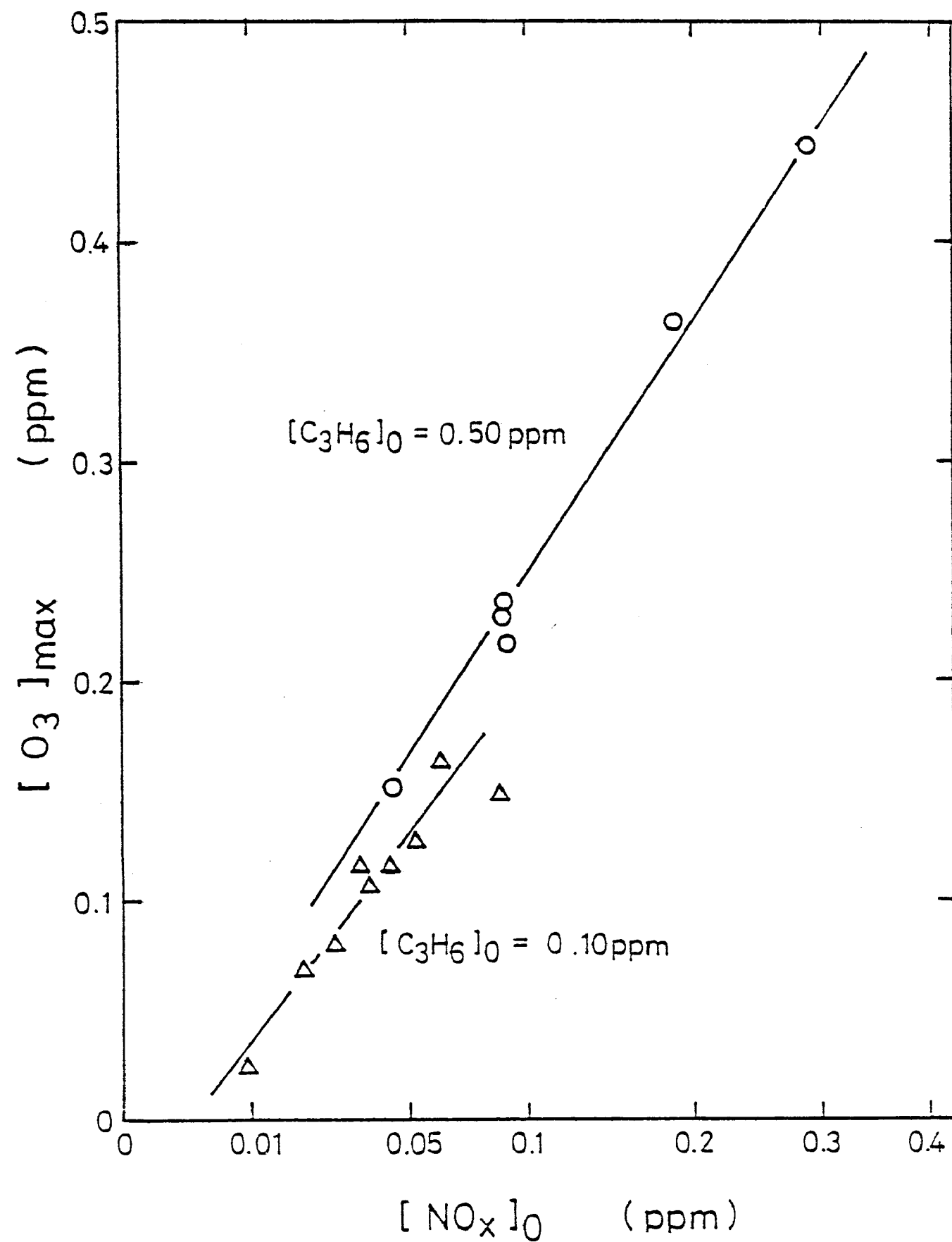
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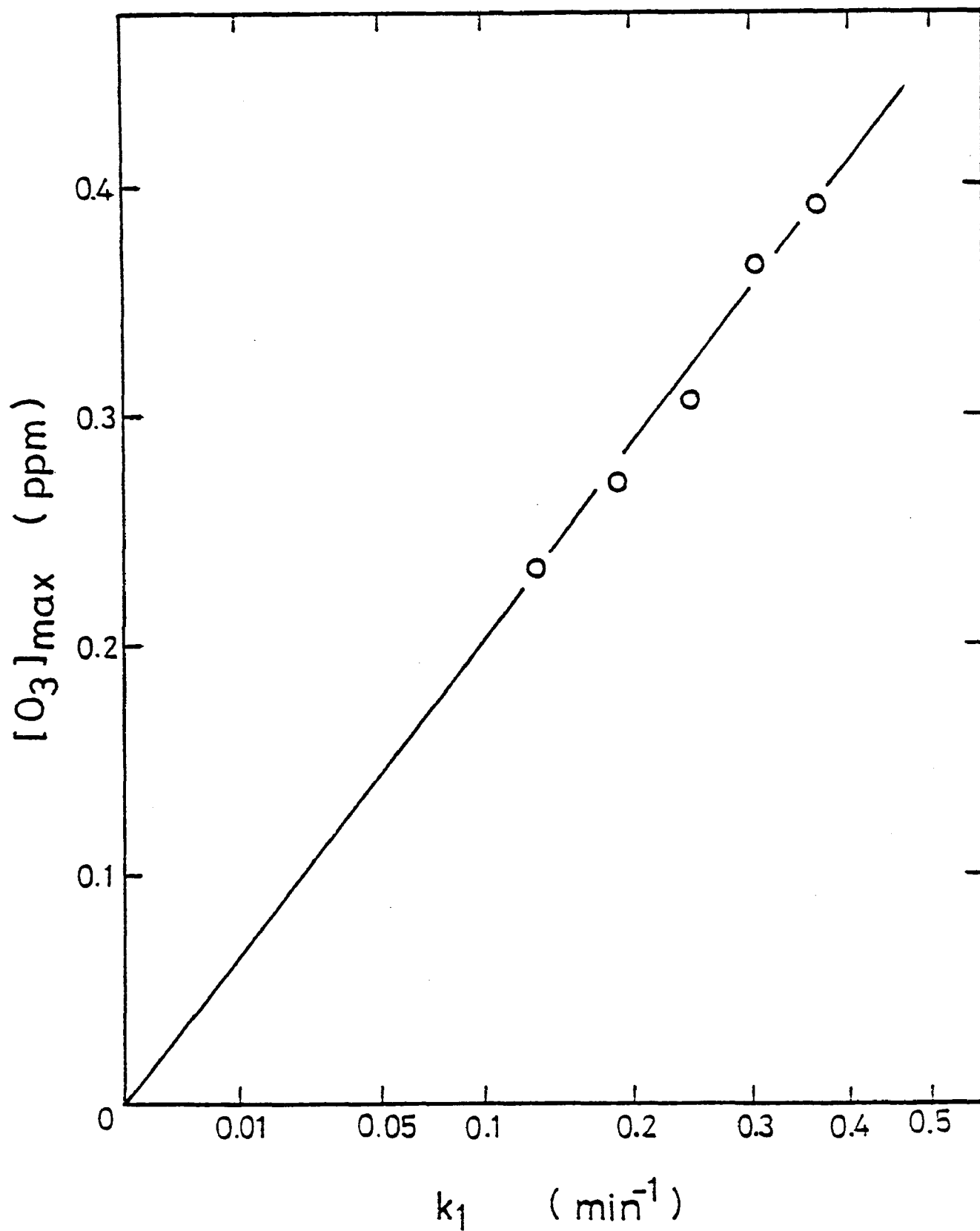
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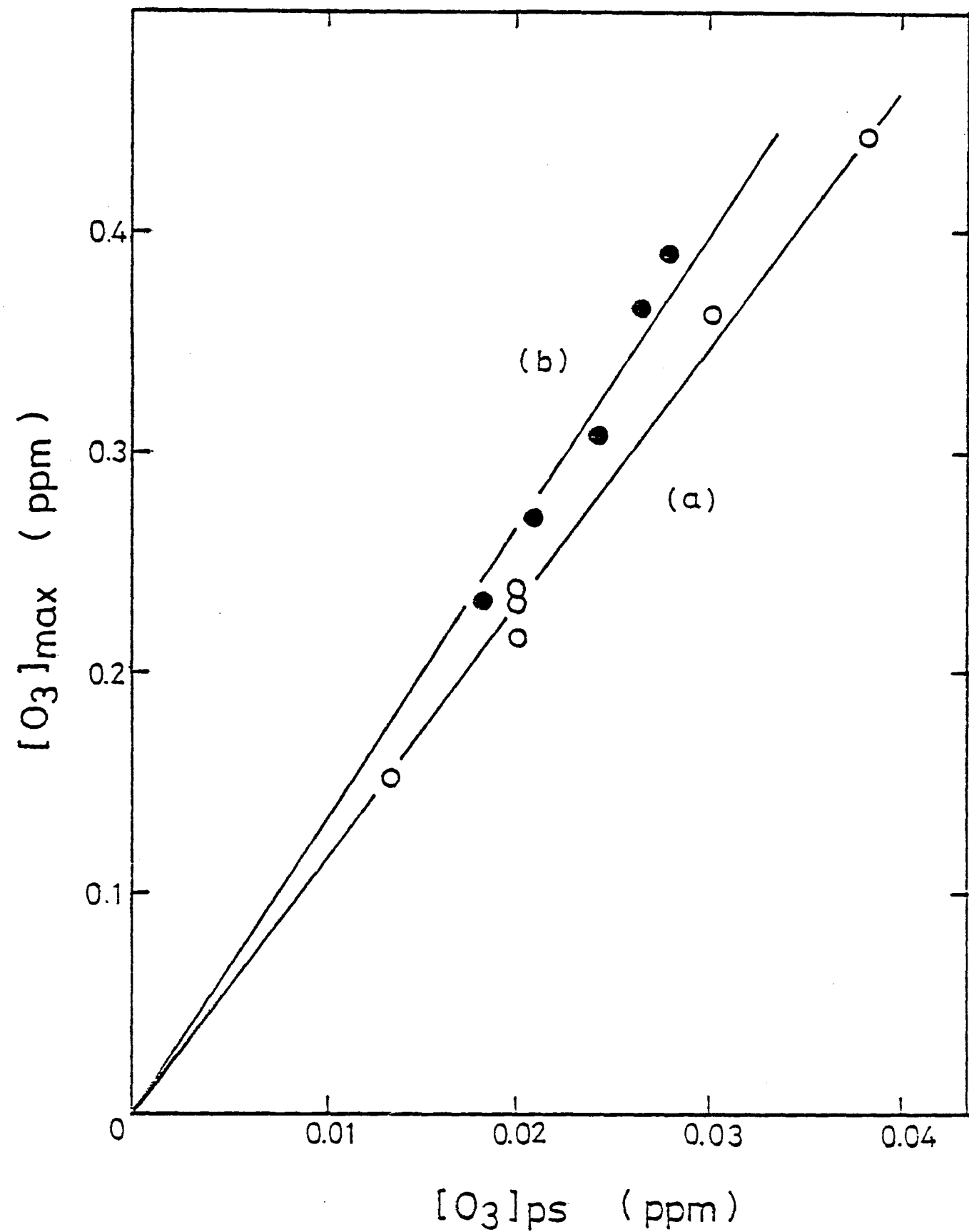
FIGURE 9

PHOTOCHEMICAL SULFATE AND NITRATE RESEARCH IN THE US

presented by A.P. Altshuller

Environmental Protection Agency

United States

PHOTOCHEMICAL SULFATE AND NITRATE RESEARCH IN THE US

Much of the earlier work done in the U.S. (1974-76) has either been published or will be out shortly. The work that has been published already appears in journals available in Japan (Atm. Environment & ES & T) or Science (journal of the AAS). There were a series of papers at the Dubrovnik conference on sulfates presented on U.S. work and my understanding is that these papers have been published as No. 1-3 in Volume 12 of Atmospheric Environment. Much of the work which has or will be published shortly resulted from experimental work conducted in and around St. Louis. These studies were connected within the Regional Air Pollution Study (RAPS) or from a closely associated program named MISTT. The results are in papers published by Charlson, Whitby, Dzubay, and Stevens. Dr. Wilson of our laboratory was the scientist who coordinated the MISTT programs. He also will be directing a followup EPA plume program - STATE. There now are some studies in power plant plumes funded by EPRI (Electric Power Research Institute). This is an organization in the San Francisco area which receives a large amount of funds from the U.S. utility industry and they have a number of different research projects associated with sulfates. One major aspect of their program has been to set up a number of monitoring stations in rural sites in the Eastern U.S. where SO_2, NO_x, ozone, and aerosols are measured. We supplied them with a number of continuous monitoring equipment from the RAPS program. We also are participating with them in making part of the aerosol compositions measurements at these monitoring sites. This EPRI program has the acronym of SURE. Additionally there

is carryover work from the AEC to the Energy Administration to our new

Department of Energy on sulfate measurements. This is sometimes called

MAP3S. Therefore, several governmental and non-governmental organizations

in the U.S. have programs involving the measurement, monitoring, and transport

properties of sulfates. These programs are informally coordinated by the

program managers for the various programs and there is interchange of

equipment and concurrent measurements. There may be a new program (under-

way next year) concerned with nitrates. There have been a small number

of programs in the U.S. on nitrates but not nearly as much as has been

done on sulfates. There is substantial agreement in the U.S. based on

ground level and aircraft measurements that sulfates can be transported.

These sorts of results are consistent with work done in Western Europe and

this is consistent with the physical and chemical properties of particles

of diameters near 0.2, μm, in the highest oxidation state and therefore stable

to further oxidation, and their deposition velocities are much smaller than

those of gases such as SO_2 or NO_2. The field experiments following plumes

making measurements over long trajectories verify that sulfates can be

transported over long distances. However, we need to know the portion of

the material transported. Also, the chemical composition of the sulfate.

We are interested in the extent to which sulfates removed by dry deposition

processes compared with wet deposition processes. Another proposed new

U.S. program is concerned with deposition of acid sulfates and nitrates.

One of the types of observations that has been made is that the sulfate concentrations are relatively uniform at urban and rural sites in the same geographical locations. For example, the sulfate concentrations at rural sites, outside of St. Louis were almost the same as the sulfate concentrations within the city itself. On the other hand, as weather fronts moved through any particular area, one sees large sulfate variations over periods of several weeks. In St. Louis, one could see concentrations as high as 20 or more $\mu g/m^3$ and as low as 2 $\mu g/m^3$ as various weather fronts went through. An important general conclusion is that both sulfate and ozone are distributed relatively evenly over large geographic U.S. areas. This, of course, would be readily understandable if they are formed by the same chemical mechanisms or by similar chemical mechanisms; and it does appear, at least during the summer months, that the formation of both ozone and sulfates is associated with photochemical reactions. This is also consistent with the fact that both species, sulfate and ozone are found together and found rather uniformly in large geographical regions. We need to do considerable additional work to better identify quantitatively the urban sources of sulfates as well as the contribution to sulfate from our large non-urban power plants in the U.S. In another program conducted in our laboratory, we have been measuring the primary emissions of sulfates from coal-and oil-fired boilers. What we found is that although we can confirm the amount of sulfur in the form of sulfate emitted from coal-fired power plants, we believe that the old data on oil-fired sources cannot be used. There is considerably more of the sulfur in the form of sulfate

from oil-fired sources than have been recorded in older literature. In oil fired-boilers, we find that 5% and as much as 10% sulfur as sulfate. This is very dependent on the operating conditions of the oil-fired boiler, and the fuel used in that facility. The higher values also are associated with a high vanadium content of the fuels used in the U.S. Conversely, a combination of low vanadium content and appropriate operating conditions can result in as little as 2% sulfur as fulfate from oil-fired sources. We have extended these measurements to measurements around oil fired facilities at ground level and we believe we have experimental evidence to show that immediately downwind of the oil-fired facilities, a significant fraction of the sulfate measured is directly emitted from the facility. This effect of direct emissions is possibly more important in the immediate vicinity of a given oil-fired facility than over large geographical areas. We have also measured a considerable amount of acidity in these emissions (sulfuric acid from SO_3 + H_2O or from acid on fly-ash particles).

We have also been working on the problem of reliably measuring the acidity in the atmosphere. We have been using the method used and developed by Professor Brosset in Sweden for the last several years. We have evidence that, at times, a significant fraction of the sulfate is not ammonium sulfate, but sulfuric acid or ammonium bisulfate. There is a very difficult analytical problem here. Unless one protects the sample as collected both in the field and the laboratory against reaction with ammonia, ammonia sulfate will form; and in some of our earlier work, we were finding almost all of the sulfate as ammonium sulfate. We now have doubts about these earlier results.

In work which we did very close to our laboratory at the Research Triangle Park, N.C., where we used special devices to protect the samples from reaction with ammonia and also took very careful precautions in the laboratory with the samples, we found a considerable fraction of the sulfate over a several-day period to be in the acid form sulfates. Some of these results were presented at the Dubrovnik meeting (by Stevens, Dzubay). Dr. Charlson earlier suggested, based on a completely different method of measurement using his nephelometer, that in the St. Louis area a considerable amount of the sulfate was acid in form. So results on acidity carried out in very different geographical areas seem to be consistent.

In our new programs, we will follow power plant plumes over longer distances and obtain much more meteorological data than we did in earlier programs so that we will have data in the form that can be used to validate sulfate air quality simulation models.

NITRATES

Let me now turn to nitrates. We have a few groups of investigators in the U.S. who have been involved in nitrates. The original monitoring work supposedly gave us a measure of nitrates in particulate form [samples collected on glass fiber filters]. As you know, there are now considerable doubts about the use of glass fiber filters for the collection of both sulfates and nitrates. Besides the reaction of SO_2 with the filters to form "artifact sulfate", the reactions of NO_2 and nitric acid with these filters to

6

form "artifac nitrate" is now rather well established as even a worse
problem than that of artifact sulfate. It appears that the measurement
on glass fiber filters of sulfates are probably usable within limits. In
rural areas where there is very little SO_2 present, the sulfate measurements
should be reasonably acceptable. Similarly, suflate measurements on a
relative basis in urban areas may be used for certain purposes. We are
even more concerned that it may be that the nitrate results which have
been obtained are not acceptable. A research group at Battelle Memorial
Institute in Columbus, Ohio, headed by Mr. Spicer, which both EPA and one of
the U.S. industrial associations, the Coordinating Research Council funded,
has been making a series of measurements for short periods of time in a
number of urban areas in the U.S., as well as lab studies. They have
compared field results on quartz filters with results on glass fiber filters
and have found much higher nitrate concentrations on the glass fiber than on
quartz filters. In a series of measurements which they reported several
months ago in a Note in Atmo. Envir. from LA, I believe that the average
ratio of nitrate on the quartz to glass fiber was something like 10:1.
There has been some work by Los Angeles Air Pollution Control District
investigators presented in a paper at the Spring 1978 ACS Meeting showing
substantial nitrate artifac on glass fiber filters, although they claim
that it is not nearly as large as that reported by Battelle. However, it
appears that their method may underestimate the artifact. We have obtained
data using dichotomous samplers equipped with teflon-type filters (virtual
impactors) on nitrates also showing much lower values than on glass fiber

filters. These impactors will be used extensively in a large network of these samplers in the U.S. These samplers which have been reported on both the Dubrovnik Conference and in papers in ES&T have several advantages over the high volume samplers. We used filters which do not have problems with respect to sulfate and nitrate artifacts. The sampler separates the particles into coarse and fine particles. Measurements can be made by X-ray fluorescence without manipulation of the material on the filter, as well as permitting more traditional chemical measurements for sulfates and nitrates. It also is possible to make the acidity measurements I was referring to earlier in the discussion. Finally they can be used to measure the mass of particles by beta-gauging or gravimetric techniques. So, they are very useful samplers for conducting wide range of measurements. All this seems to suggest that there is much less of the nitrate in the form of particles. Since we must account for the nitrogen oxides which are emitted from sources, either the gaseous and vapor forms of nitrate are much more important or the nitrogen oxides are being removed from the atmosphere by dry deposition very effectively. We have a substantial amount of measurements of peroxyacetyl nitrates (PAN's) in several locations in the U.S. but these have usually been made without measuring other forms of nitrate; and many of the measurements of particulate nitrate has been made without measuring the gaseous and vapor forms of nitrate. About the only work where all these forms were measured concurrently was again done by the Battelle group. They have concluded particularly from measurements in Los Angeles that the vapor forms of nitrate are far more important than the particulate forms. We do have independent confirmation

at Riverside, CA, of nitric acid by use of a Fourier Transform Spectrometer (FTS system) working over an open air path. This is one of the spectrometers in our laboratory that Dr. Hanst was using which we loaned to Dr. Pitts and his group to set up in an open air path. This is a very useful tool since we can measure a number of species including not only nitric acid but ammonia, ozone, PANs, and some of the other reaction products of photochemical reactions in the ambient atmosphere. What we need to do next in the U.S. is to make concurrent measurements by the chemical techniques of nitric acid and by this Fourier Transform Spectrometer technique to see how similar the concentrations of nitric acid are by the various measurement methods. One final remark on nitric is that nitric acid seems to be a quite important contributor to acid precipitation as it affects lakes and fish and other aquatic species and possibly forest and soil productivity. Discussions with U.S. investigators in this field as well as with European investigators indicate that perhaps one-third to one-half of the total acidity in precipitation may be associated with nitric acid. We can only speculate at the present time on the importance of nitric acid in dry deposition but since nitric acid is a vapor and a polar vapor which is easily absorbed on surfaces, it is possible that nitric acid is very important compared with acid sulfates in dry deposition. This is another aspect of the problem of sulfate and nitrates that we hope to quantitate.

SULFATE, NITRATE AND NITRIC ACID RESEARCH

IN KANTO AREA

presented by M. Okuda

Environment Agency

Japan

Sulfate, Nitrate and Nitric Acid

Research in Kanto Area

In June and July of 1973 to 1975 many people suffered from eye-, throat- and skin-irritations by contaminated drizzle (fog) droplets.

In order to study the case of the irritation the Japanese Environment Agency organized a study group. Several examples of the concentrations of sulfate, nitric acid and nitrate and other constituents measured by the group are as shown in Figs. 1 to 3.

Fig. 1 shows the ratios $R_S = C_{SO_4^{2-}} \cdot S / C_{SO_2} \cdot S$, $R_{NO_3^-} = C_{NO_3^-} \cdot N / C_{NO_2} \cdot N$ and $R_{HNO_3} = C_{HNO_3} \cdot N$ obtained in 1977 at five stations together with oxidant concentration and relative humidity where C is the each material's concentration. The methods of measurements are as follows.

SO$_2$: automatic electro-conductivity recorder

NO$_2$: automatic Saltzman's colorimetric recorder

SO_4^{2-} and NO_3^-: sampled on quartz fiber filter and analyzed by glycerine-alcohol method and sodium salicylate method[1] respectively.

Oxidant: automatic neutral buffered KI colorimetric recorder

- 1 -

HNO_3: Okita's impregnated filter method[2]

Aerosol and HNO_3 samplings were done between 10 A.M. and 4 P.M. everyday.

The figure indicates that usually the concentrations of R_S and R_{HNO_3} had peaks on June 28 and July 5 when oxidant concentration was high, suggesting that production of aerosol sulfate and nitric acid were highly associated with photochemical air pollutions.

Similar trends on the summit of Mt. Tsukuba are shown in Fig. 2 which exhibits the peaks of SO_4^{2-}, NH_4^+ and HNO_3 concentrations also on June 28 and July 5, 1977 together with on July 7 - 9, 1976 when oxidant concentration was also high.

As shown in Fig. 3 most of the sulfate would be $(NH_4)_2SO_4$ at Mt. Tsukuba.

$R_{NO_3^-}$ in Fig. 1 and NO_3^- concentration in Fig. 2, on the other hand, usually had no such peaks on the days of high oxidants concentration besides on July 7 - 9, 1976. It seems that in inland area the rate of production of nitrate aerosol was rather low.

In June and July of 1976 and 1977 airbone samplings of sulfate, nitric acid, nitrate and other constituents were conducted on helicopters.

Fig. 4 shows the concentrations of trace constituents

- 2 -

sampled on two helicopters at 270 and 670 m in the early afternoon of July 5, 1977. It was found that on the flight routes B_1 and B_2, SO_4^{2-} and HNO_3 concentrations were considerably high. Simultaneous measurements of O_3 by ultraviolet absorption on the helicopters indicate the O_3 concentration of 0.05 - 0.07 ppm and 0.1 ppm on the route A and B respectively. The presence of relatively high concentration of sulfate and nitric acid in the air coming from the north-east or east where no big pollution sources were located is also interesting.

Fig. 5 shows the vertical distributions of SO_x and NO_x measured at Ohira using tethered balloons and helicopters indicating that whereas SO_2 and NO_2 concentrations gradually decreased with height the concentrations of SO_4^{2-}, HNO_3 and NO_3^- had uniform distribution or peak concentration at several hundred meters above the ground. Such patterns presume that SO_2 and NO_2 come from nearly ground level sources whereas SO_4^{2-}, HNO_3 and NO_3^- would be formed during long distance transport of the pollutants.

The data of Fig. 6 obtained in 1976 at Ohira indicates that nitric acid concentration is highly correlated with O_3 and NO_2 concentrations, which also suggests that nitric acid was produced by photochemical reactions.

- 3 -

In conclusion, it seems that over the Kanto area near Tokyo high concentration of sulfate and nitric acid occur in photochemical air pollution and most of the sulfate would be ammonium sulfate. High concentration of nitric acid was frequently observed at several hundred meters above the ground. Aerosol nitrate had no association with oxidants concentration.

Reference

(1) Air Quality Control Division, Environment Agency: Acid Rain Research. March, 1978 (in Japanese)

(2) Toshiich Okita et al.: Measurement of Inorganic Gaseous and Particulate Nitrates in the Atmospher. Bull. Inst. Publ. Health, 24(2): 1975
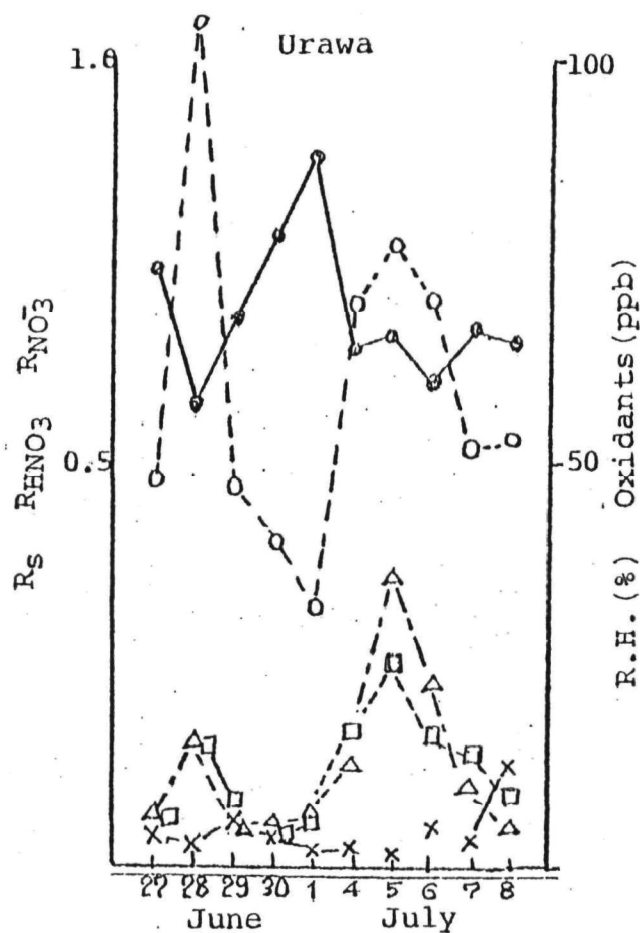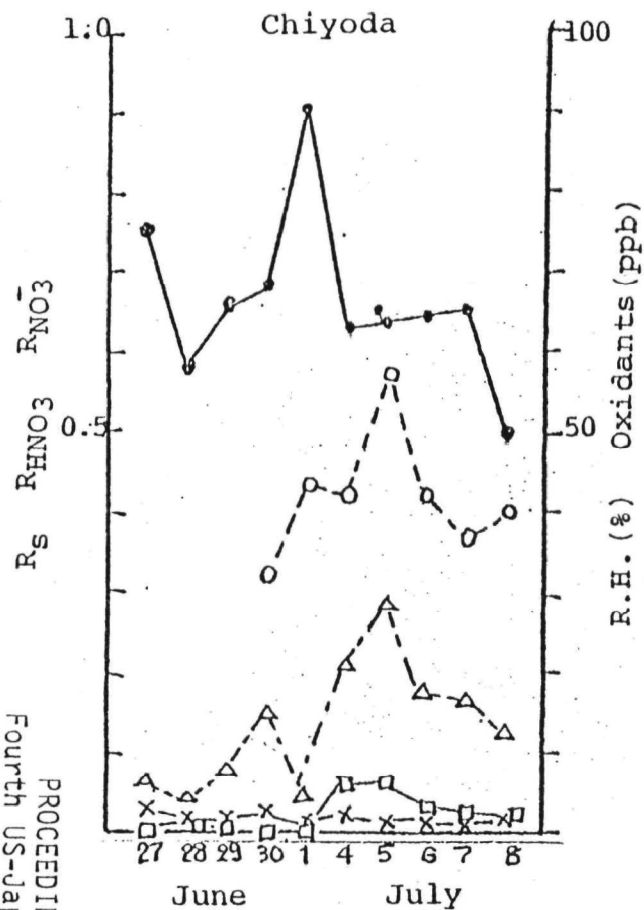
- 4 -

Chiyoda

Urawa

Kumagaya
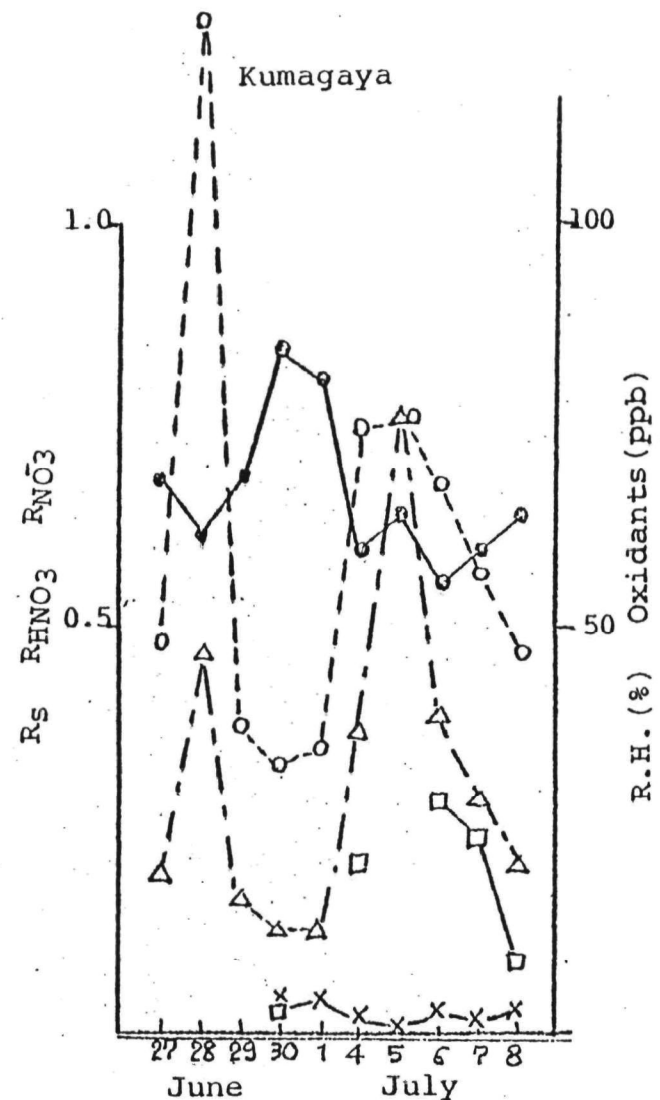
Fig.1(a) Relative Humidity, Oxidants R_S, R_{HNO_3} and $R_{NO_3^-}$ in Kanto Area (1977)

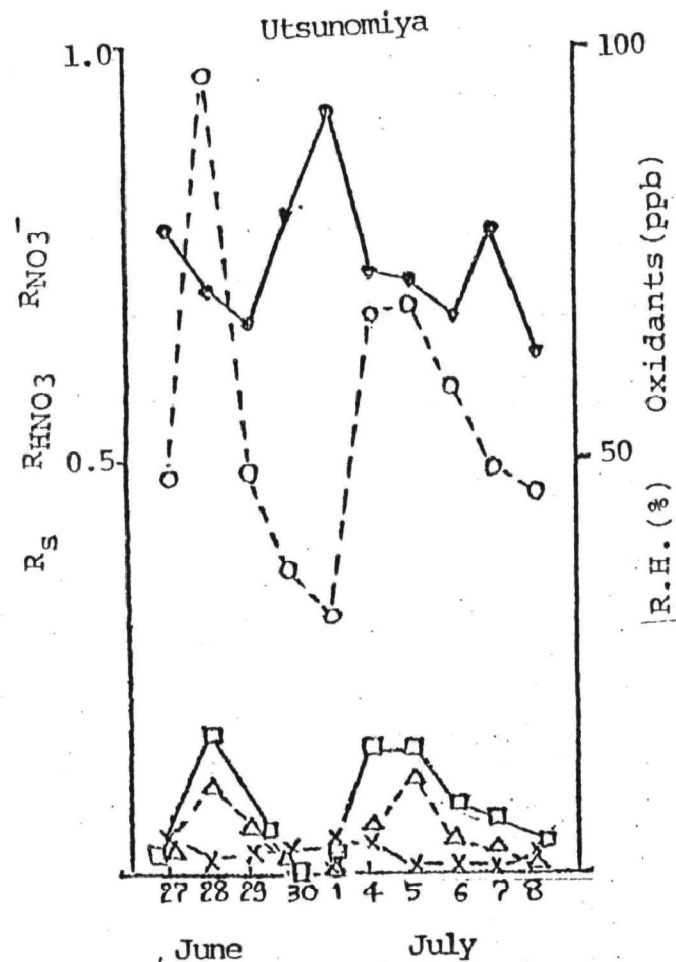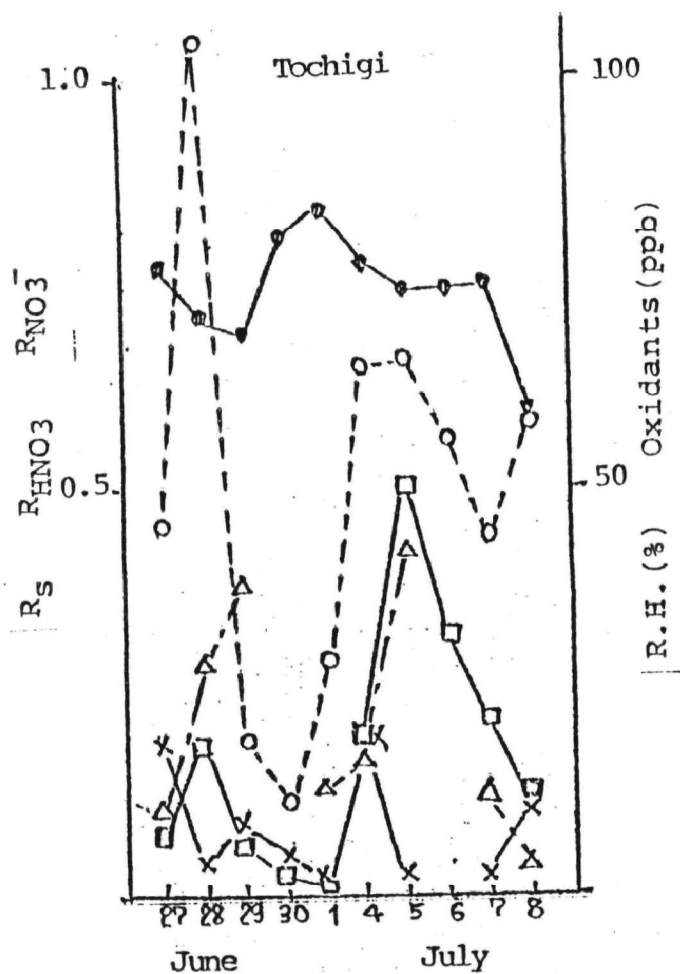● Relative Humidity
○ Oxidants
△ R_S
□ R_{HNO_3}
✕ $R_{NO_3^-}$

Fig.1(b)   Relative Humidity, Oxidants,
R_S, R_{HNO_3} and $R_{NO_3^-}$ in Kanto
Area   (1977)

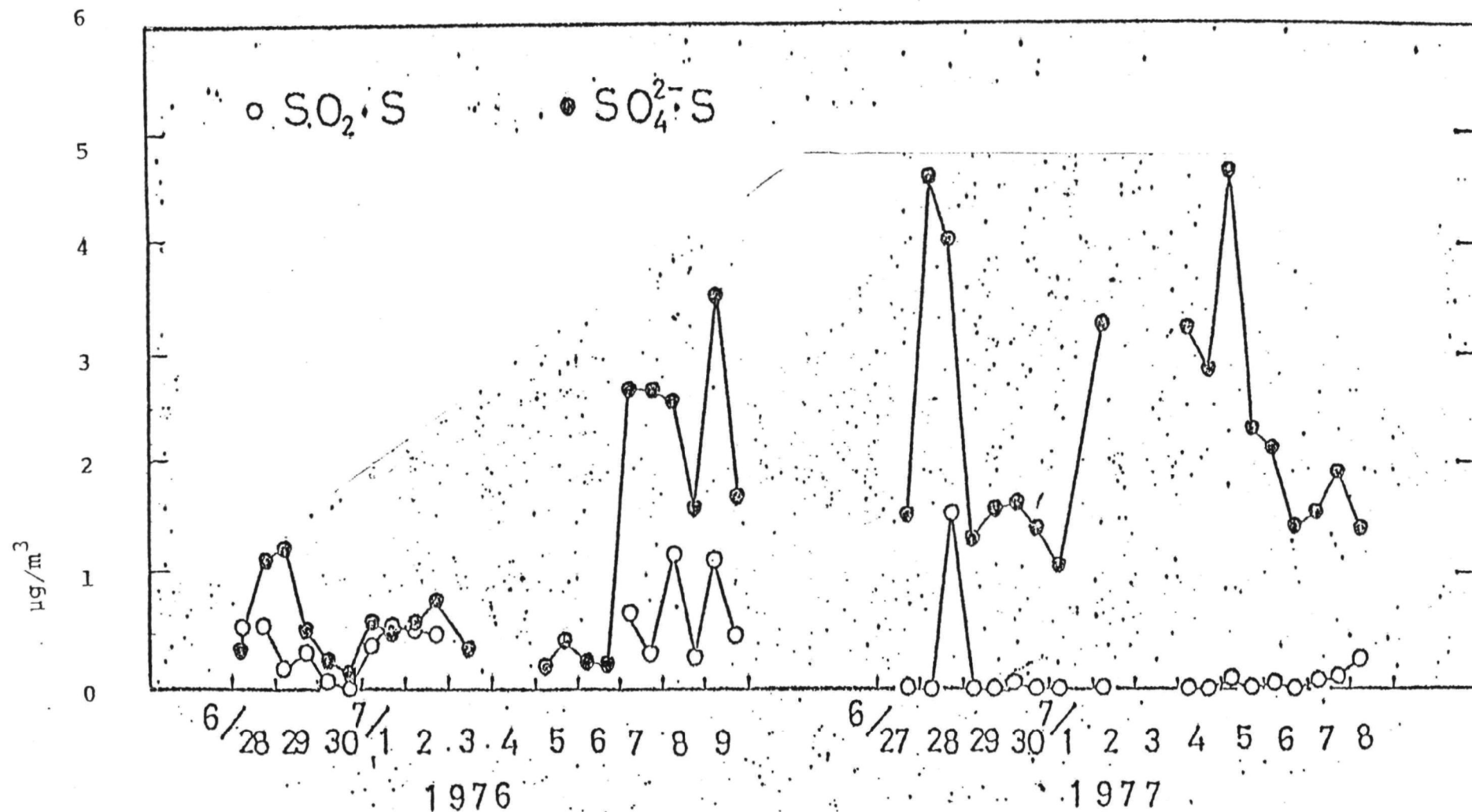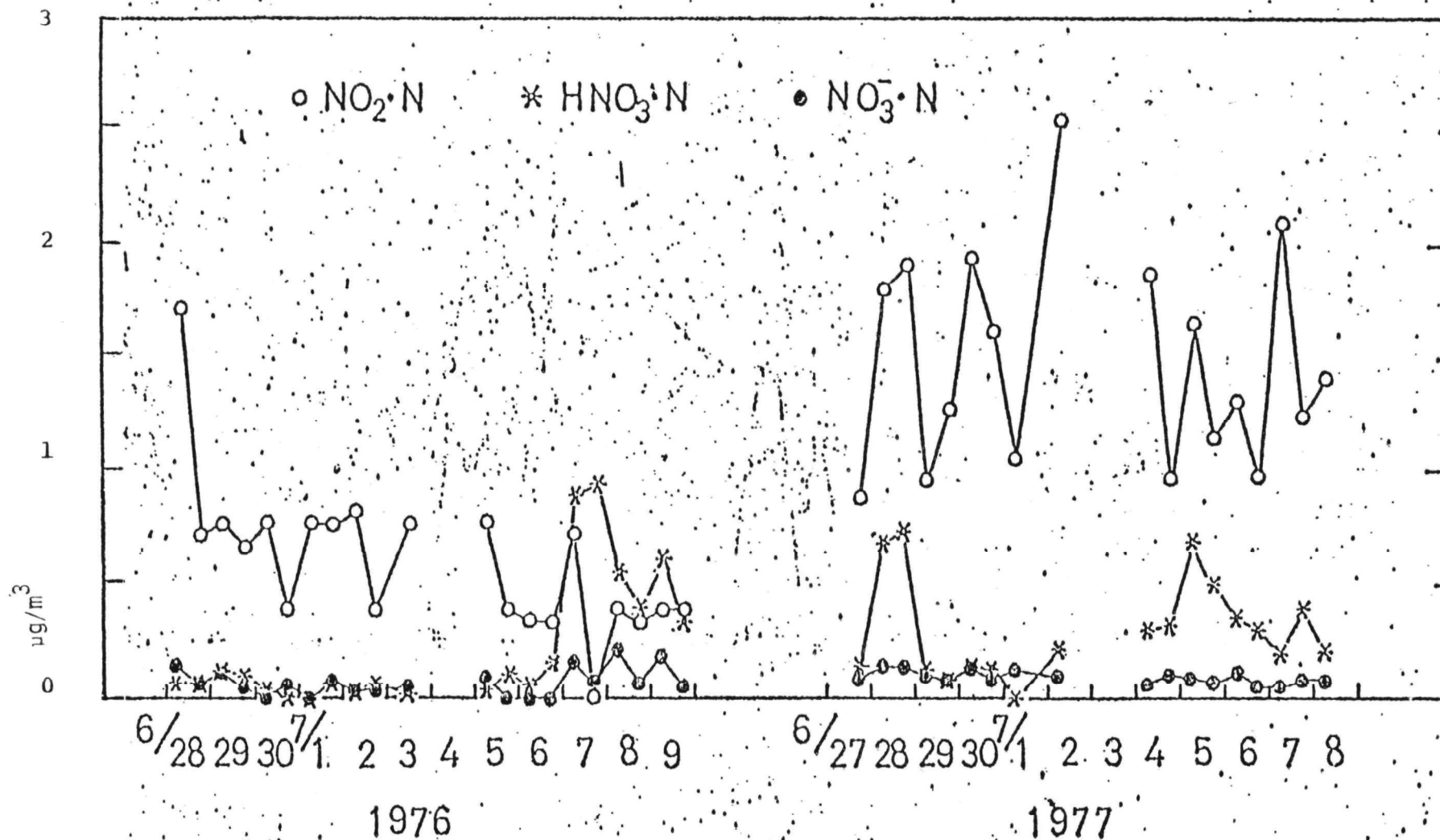● Relative Humidity
○ Oxidants
△ R_S
□ R_{HNO_3}
× $R_{NO_3^-}$

Fig. 2 (a) Fluctuation of SO_2 and SO_4^{2-} concentrations at the top of Mt.Tsukuba

Mt. TSUKUBA

Fig.2 (b) Fluctuation of NO_2, HNO_3, and NO_3^- concentrations at the top of Mt.Tsukuba
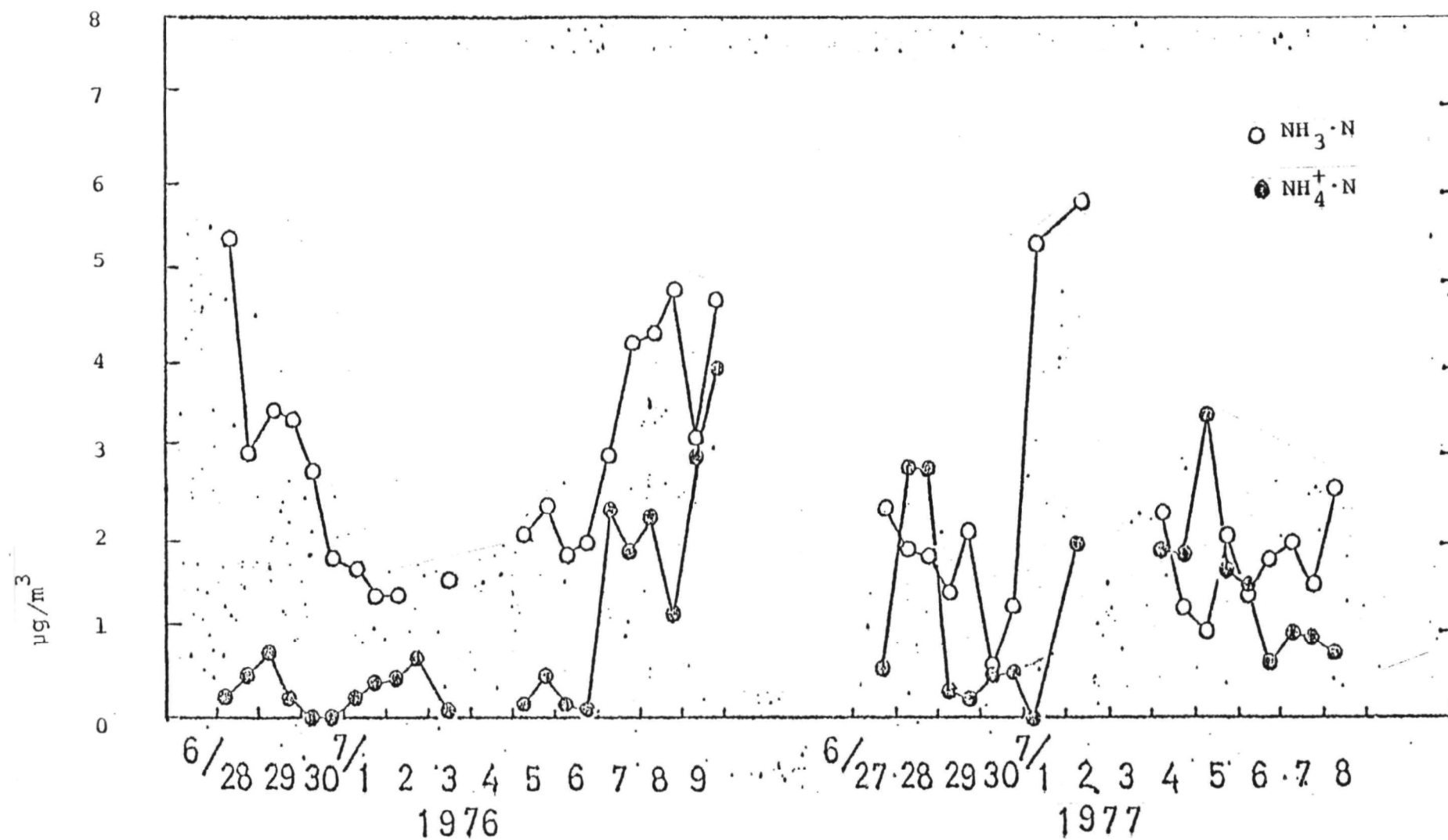
Mt. TSUKUBA

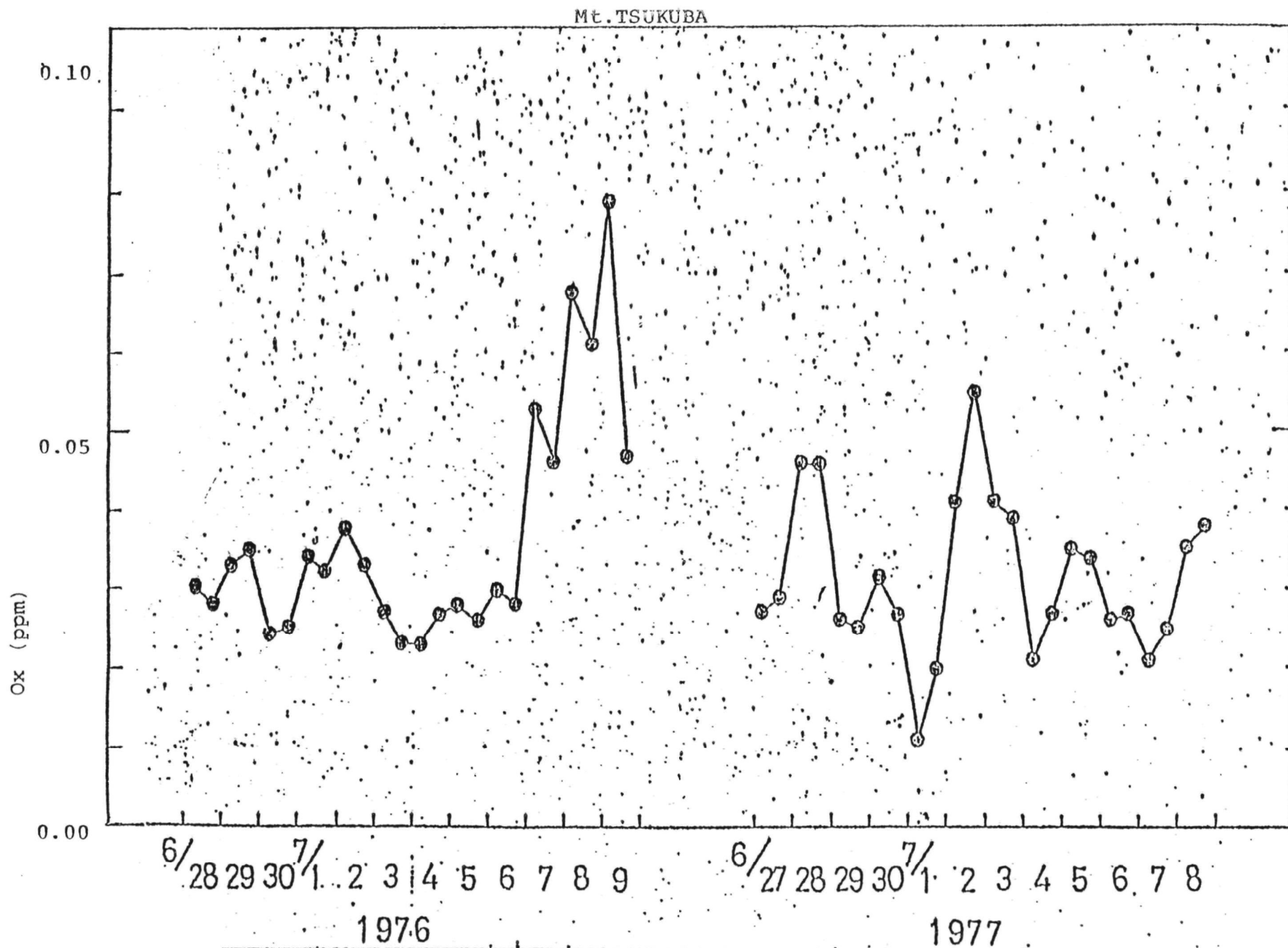Fig.2(c) Fluctuation of NH_3, NH_4^+ concentrations at the top of Mt.Tsukuba

Fig.2(d) Fluctuation of oxidant concentration as measured by Mt.TSUKUBA
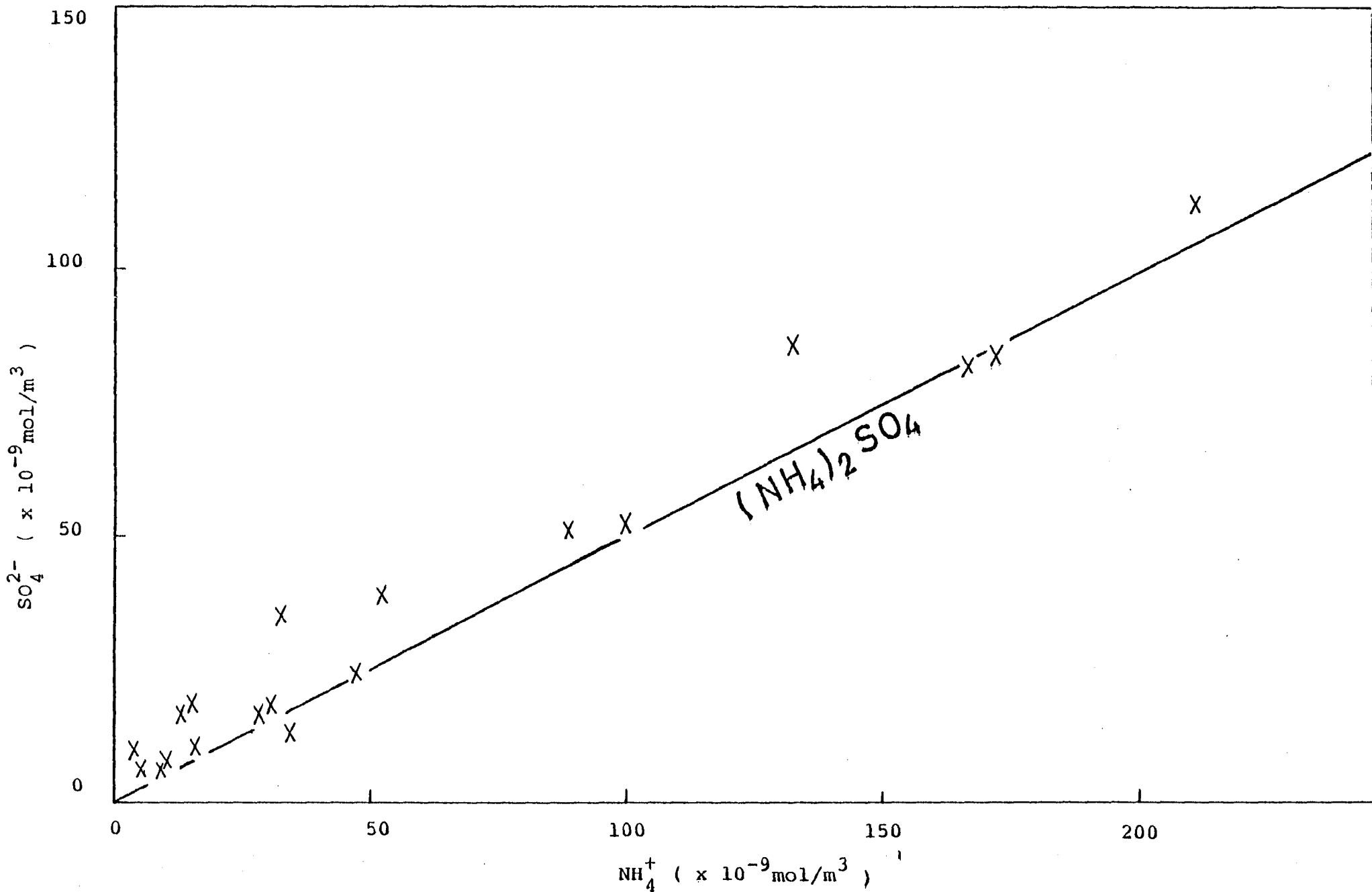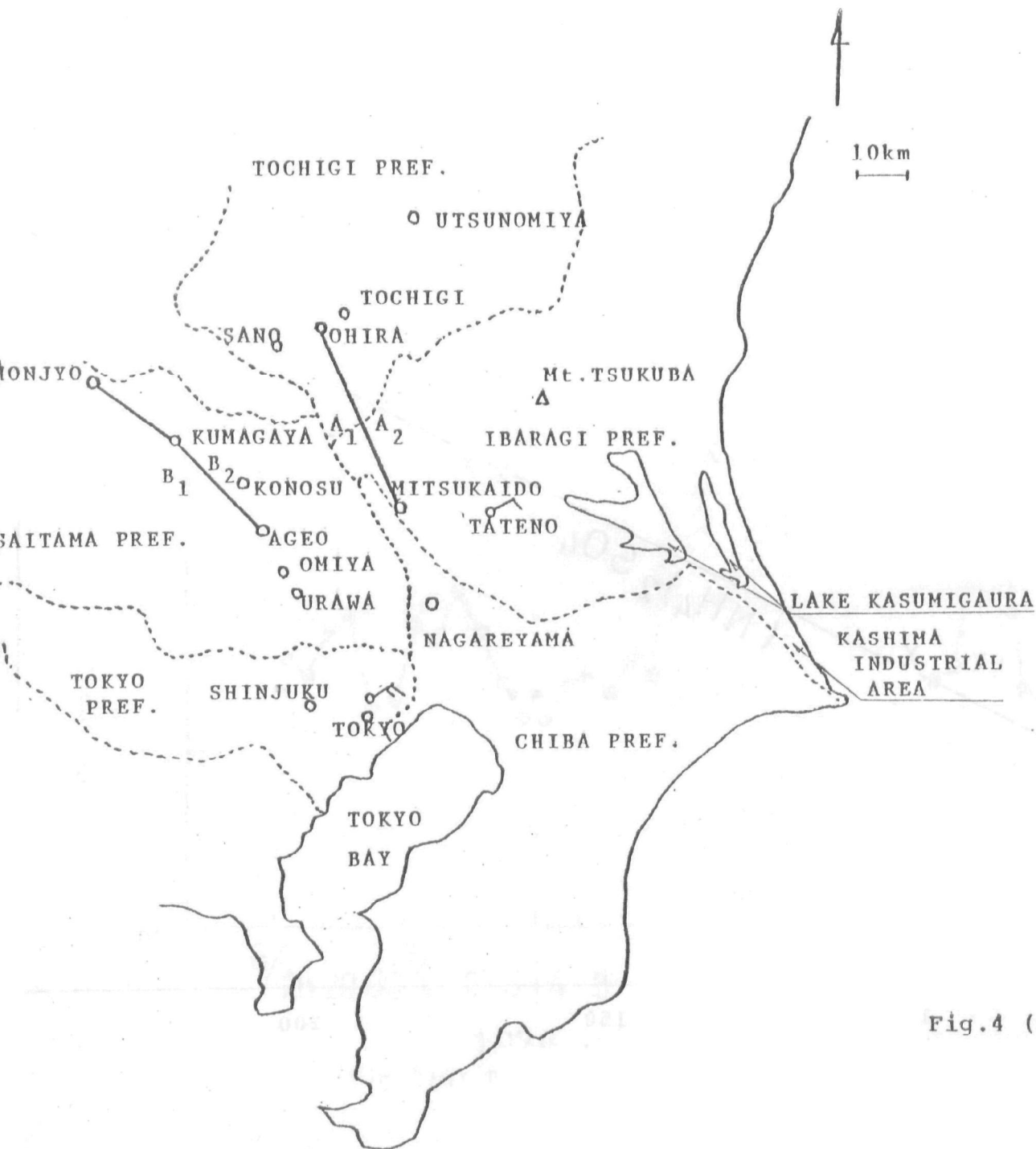National Measuring Station

Fig.3 NH_4^+ and SO_4^{2-} relationship

Flight route	Route	Time	Height
	A1	1214-1302	270 m
	A2	1311-1404	400 m
	B1	1206-1305	270 m
	B2	1310-1408	400 m

Mean Concentration

	A1	A2	B1	B2
SO_2	0.95	0.95	2.2	2.7
NO_2	9.0	8.5	9.3	7.5
HNO_3	5.9	16.5	12.1	19.5
NH_3	1.8	1.6	1.9	5.7
HCl	6.2	6.1	–	–
SO_4^{2-}	1.8	3.0	10.5	18.7
NO_3^-	0.17	<0.05	<0.05	0.81
NH_4^+	0.03	2.8	4.5	4.9
Cl^-	6.3	0.90	–	–

$(\mu g/m^3)$

Map labels:

TOCHIGI PREF.
O UTSUNOMIYA
TOCHIGI
SANO OHIRA
HONJYO
Mt.TSUKUBA
KUMAGAYA A1 A2
IBARAGI PREF.
B1 B2 KONOSU MITSUKAIDO
SAITAMA PREF. AGEO TATENO
O OMIYA
URAWA
LAKE KASUMIGAURA
NAGAREYAMA
KASHIMA INDUSTRIAL AREA
TOKYO PREF. SHINJUKU
TOKYO CHIBA PREF.
TOKYO BAY

Fig.4 (a) Survey by helicopter
(June 5, 1977)
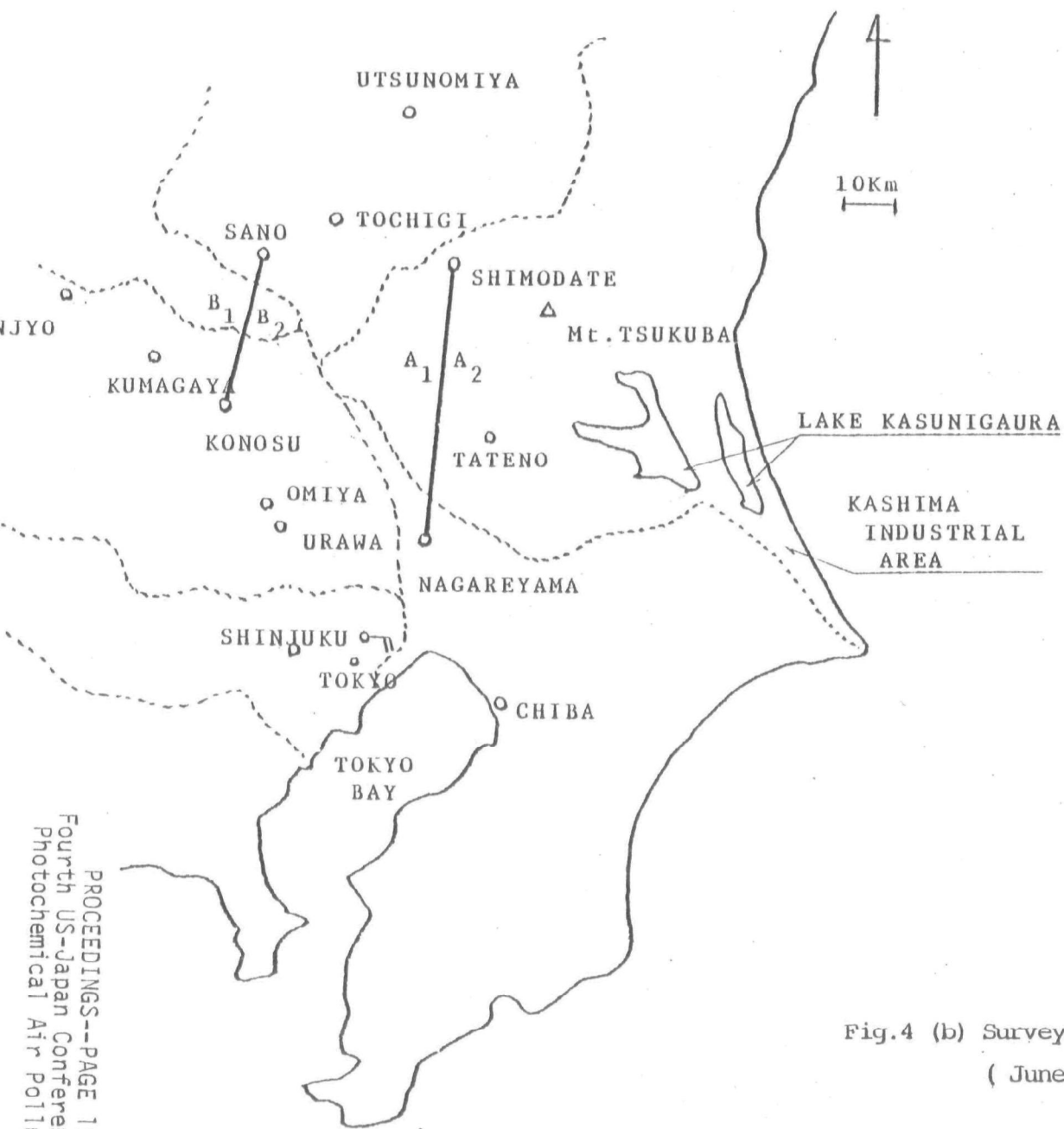
Flight route	Route	Time	Height
	A1	1525–1615	270 m
	A2	1623–1710	670 m
	B1	1528–1624	270 m
	B2	1628–1728	670 m

Mean Concentration

	A1	A2	B1	B2
SO_2	<0.1	<0.1	0.23	<0.1
NO_2	6.0	6.0	5.4	4.2
HNO_3	1.5	7.1	21.1	13.1
NH_3	3.8	2.1	—	—
HCl	4.7	5.4	6.2	4.4
SO_4^{2-}	<0.5	5.9	15.7	16.7
NO_3^-	0.40	<0.05	0.32	0.83
NH_4^+	0.06	1.7	—	—
Cl^-	4.0	5.4	5.1	6.0

$(\mu g/m^3)$

Fig.4 (b) Survey by helicopter

(June 28, 1977)

	$SO_2 \cdot S$	$SO_4^{2-} \cdot S$
A.M.	×	+
P.M.	○	△

Fig.5-a. Vertical Distribution of SOx

(June 28, 1977)

× $NO_2 \cdot N$

○ $HNO_3 \cdot N$

△ $NO_3^- \cdot N$

Fig.5-b. Vertical Distribution of NOx

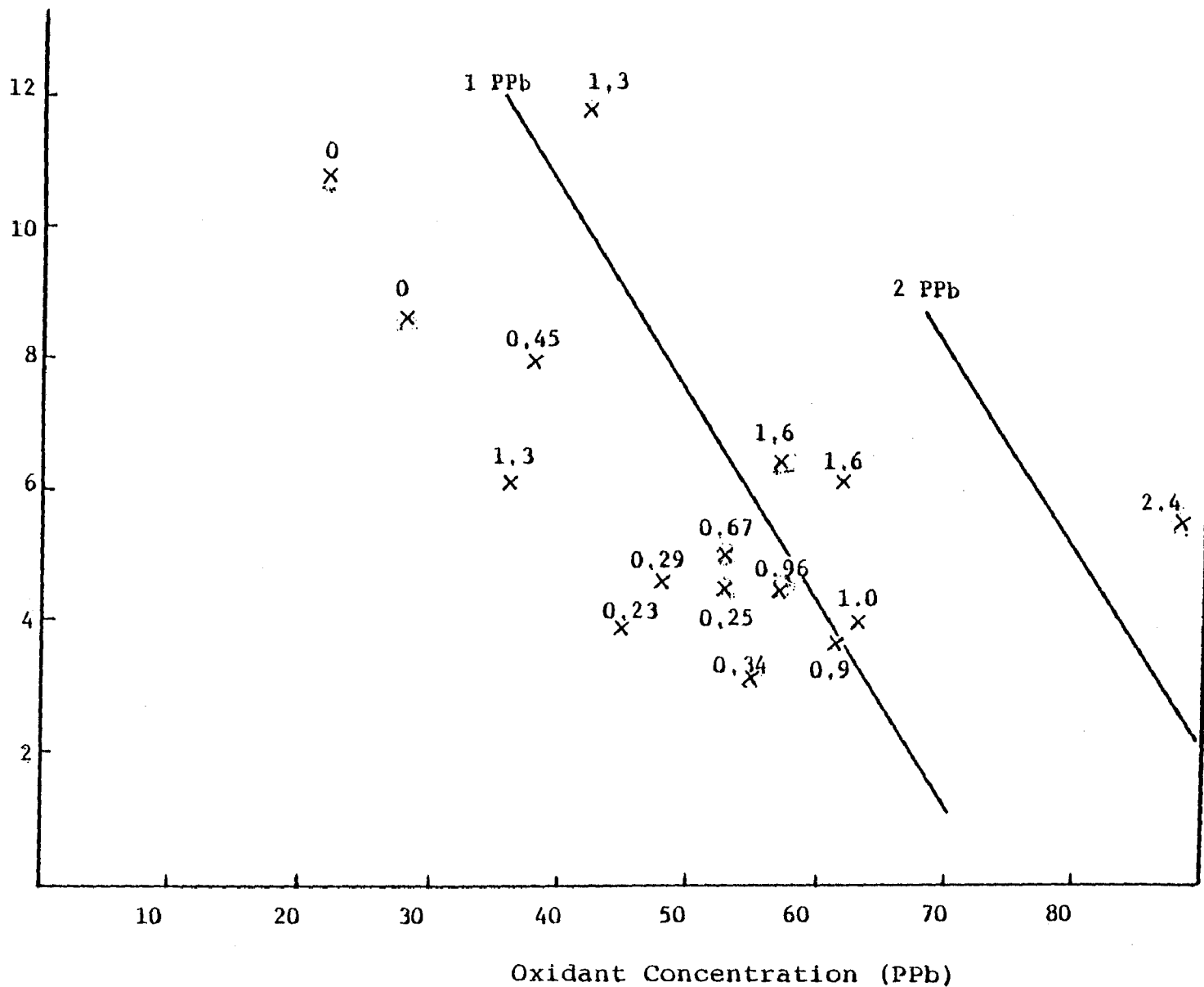(In the Morning of June 29, 1977)
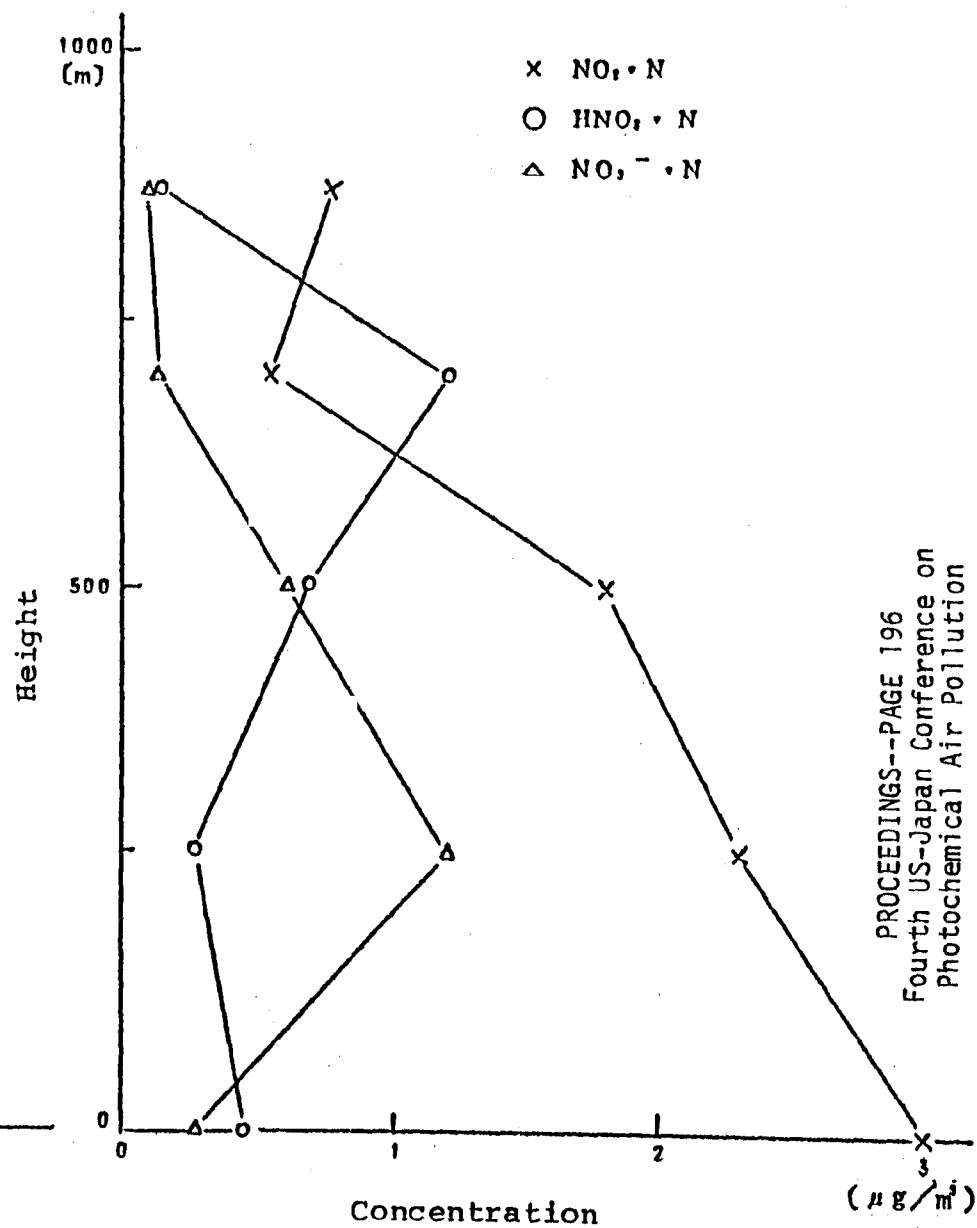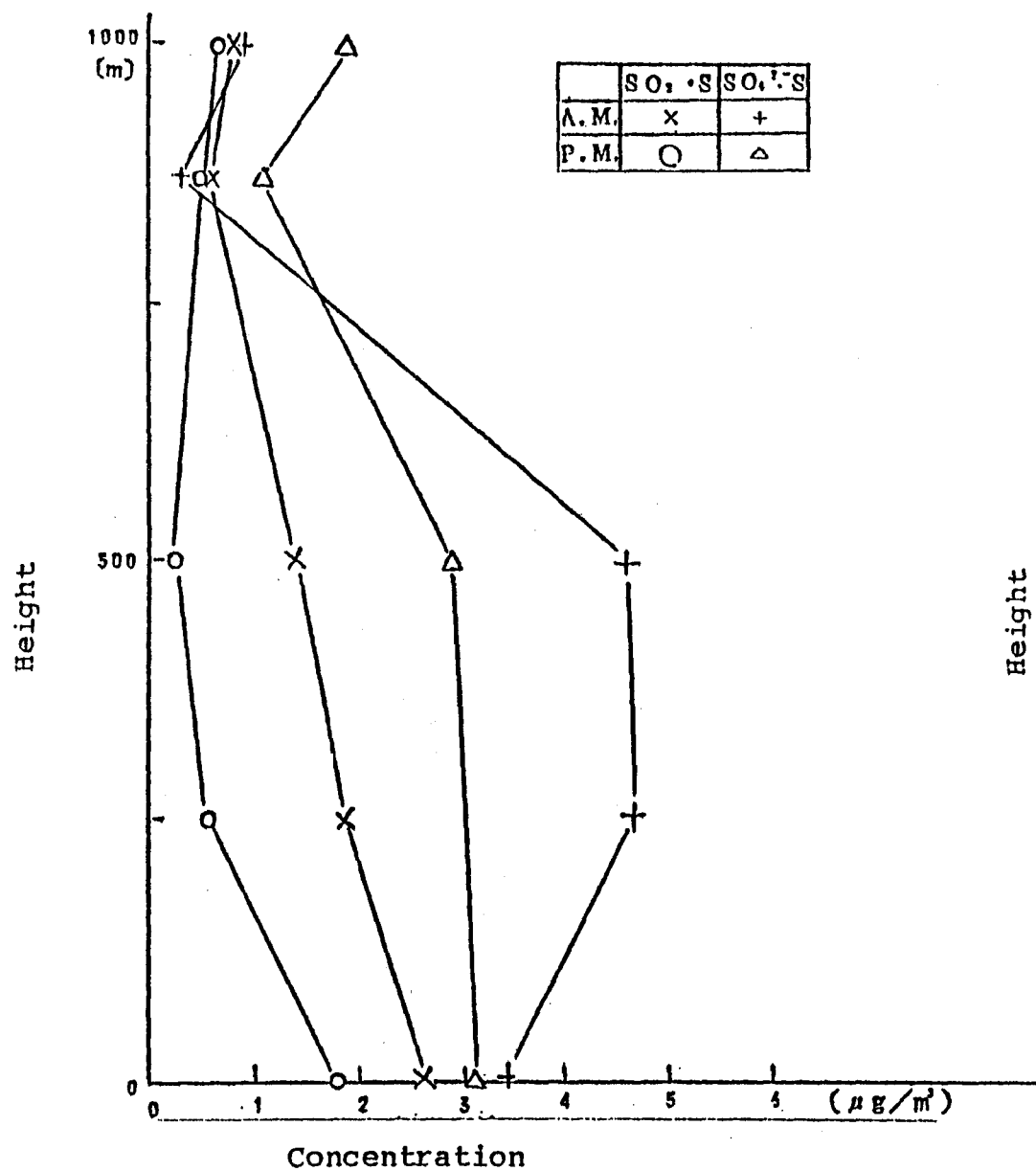
Fig.6   Relationship between HNO$_3$ generation concentration and NO$_2$ and Oxidant concentrations

Note)   Superior numerals of X marks are HNO$_3$ concentrations in ppb.

Particulate Matter, NH_4^+, NO_3^- and SO_4^{2-}

in Kanto Area (1977)

Part.
$NH_4^+ \bigcirc SO_4^{2-}$
NO_3^-

(UNIT: $\mu g/m^3$)

91
1.17 ⭕ 6.9
2.4

124
2.59 ⭕ 17.2
4.4

144
0.65 ⭕ 7.9
2.5

78
0.3 ⭕ 2.4
1.0

84
0.10 ⭕ 2.8
1.3

57
0.3 ⭕ 5.3
1.1

83
0.64 ⭕ 8.5
1.3

△ Mt. Tsukuba

113
0.2 ⭕ 9.1
1.9

81
0.17 ⭕ 5.4
0.4

190
1.36 ⭕ 6.2
8.1

68
0.04 ⭕ 6.1
0.9

272
2.08 ⭕ 27.9
9.6

66
<0.01 ⭕ 6.0
1.7

61
1.56 ⭕ 9.4
5.9

June 27, 1977

Part.
NH_4^+ ◯ SO_4^{2-}
NO_3^-

(UNIT: $\mu g/m^3$)

119
3.18 ◯ 25.4
1.1

144
5.71 ◯ 38.8
2.0

145
4.79 ◯ 31.3
1.5

97
2.17 ◯ 11.7
0.3

94
0.22 ◯ 3.4
1.7

57
0.30 ◯ 5.3
1.1

150
3.83 ◯ 33.5
1.0

174
2.14 ◯ 25.2
2.9

94
1.14 ◯ 19.0
2.6

168
0.77 ◯ 12.3
6.4

42
82 < 0.01 ◯ 1.0
0.33 ◯ 5.0   0.9
1.7

229
2.20 ◯ 31.9
6.8

58
0.33 ◯ 6.8
2.9
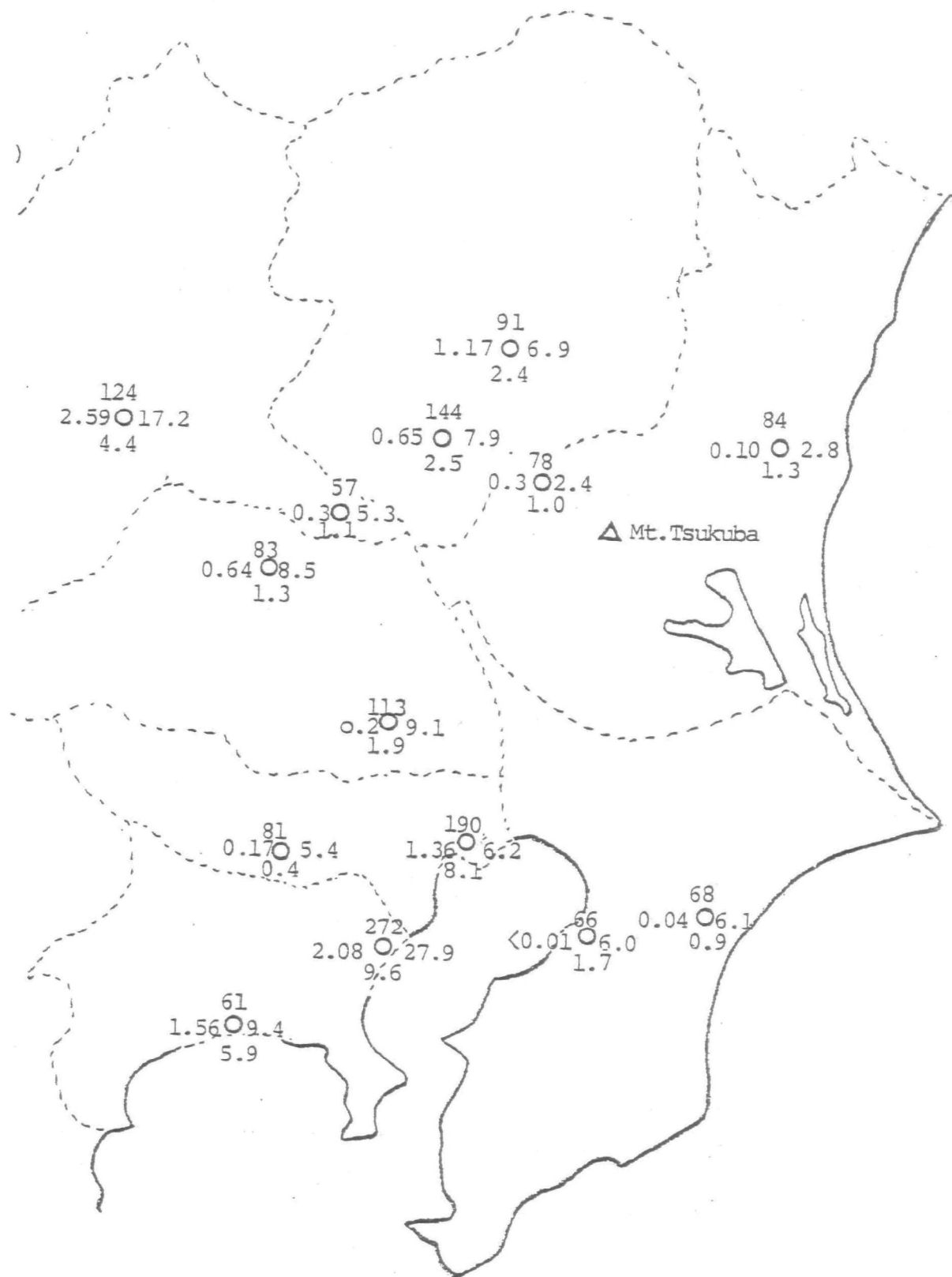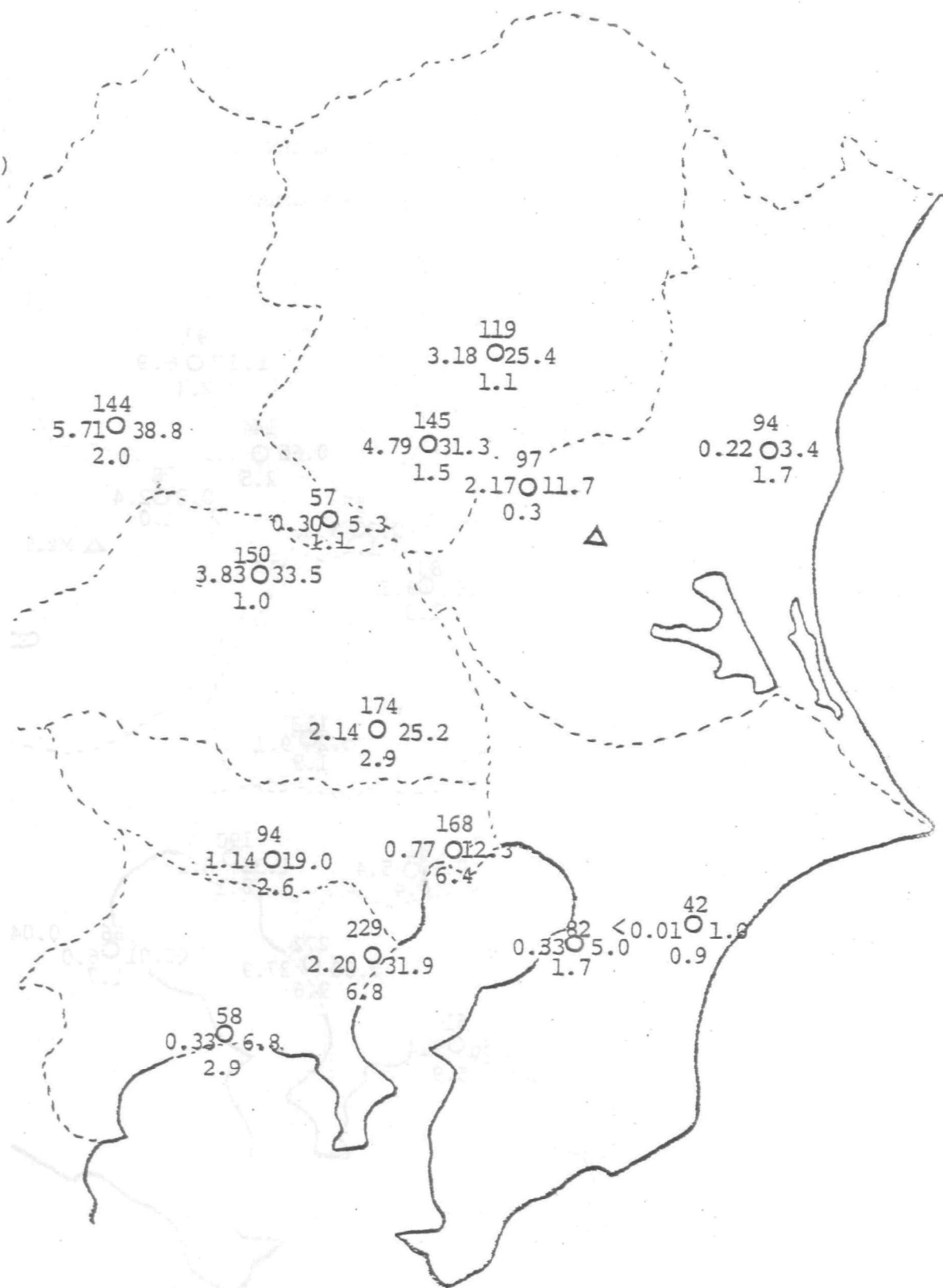
June 28, 1977

Part.

NH_4^+ ⃝ SO_4^{2-}
NO_3^-

(UNIT: $\mu g/m^3$)

86
1.91 ⃝ 12.4
1.1

104
2.71 ⃝ 15.6
0.6

119
2.86 ⃝ 19.7
2.9

70
1.93 ⃝ 8.8
0.9

73
0.31 ⃝ 3.7
1.0

59
0.26 ⃝ 5.3
0.6

96
1.93 ⃝ 15.8
0.8

91
1.19 ⃝ 11.1
0.7

110
1.56 ⃝ 29.5
0.5

213
1.52 ⃝ 19.4
5.7

91
< 0.01 ⃝ 9.6
1.8

88
1.55 ⃝ 6.1
0.9

187
2.64 ⃝ 21.9
5.3

117
2.48 ⃝ 14.2
3.1

July 4, 1977

Part.

NH_4^+ ◯ SO_4^{2-}

NO_3^-

(UNIT: $\mu g/m^3$)

110
3.00 ◯ 23.1
0.3

152
5.42 ◯ 35.8
0.7

147
4.80 ◯ 35.7
0.6

107
3.43 ◯ 22.4
0.5

94
1.22 ◯ 9.3
1.0

73
0.70 ◯ 8.4
0.7

141
5.40 ◯ 38.4
0.5

△

126
3.79 ◯ 30.7
0.4

169
3.68 ◯ 28.6
0.2

172
2.71 ◯ 23.9
4.5

84
<0.01 ◯ 5.7
1.5

124
0.53 ◯ 7.8
3.3

185
1.78 ◯ 13.0
5.3

138
3.61 ◯ 30.4
3.3

July 5, 1977

Part.

NH_4^+ ◯ SO_4^{2-}

NO_3^-

(UNIT: $\mu g/m^3$)

83
1.56 ◯ 9.8
0.2

127
3.21 ◯ 24.6
1.0

75
0.05 ◯ 3.4
1.2

67
0.21 ◯ 3.9
0.6

72
1.35 ◯ 5.5
0.7

107
2.90 ◯ 19.4
0.8

136
2.35 ◯ 19.0
1.5

134
2.38 ◯ 25.4
0.6

184
1.27 ◯ 16.4
7.9

93
<0.01 ◯ 8.4
1.1

179
1.91 ◯ 14.4
5.0

116
0.36 ◯ 5.3
2.6

131
4.04 ◯ 39.0
1.4

July 6, 1977

Part.

$NH_4^+ \bigcirc SO_4^{2-}$

NO_3^-

(UNIT: $\mu g/m^3$)

75
0.87 ◯ 6.7
0.2

108
2.10 ◯ 15.4
1.0

78
1.40 ◯ 11.0
0.6

41
0.13 ◯ 3.1
1.2

60
1.07 ◯ 4.7
0.8

59
0.24 ◯ 3.5
0.5

96
1.98 ◯ 11.9
0.5

△

87
1.30 ◯ 8.7
0.9

93
1.49 ◯ 27.4
0.5

112
1.03 ◯ 14.1
2.0

55
<0.01 ◯ 6.1
0.9

134
1.24 ◯ 9.0
3.5

75
1.16 ◯ 7.3
1.2

111
1.85 ◯ 13.6
4.9

July 7, 1977

Part.
NH_4^+ ◯ SO_4^{2-}
NO_3^-

(UNIT: $\mu g/m^3$)

84
0.82 ◯ 8.5
1.4

78
0.09 ◯ 3.5
1.8

69
0.10 ◯ 4.4
2.0

64
<0.01 ◯ 1.6
2.4

56
<0.01 ◯ 2.1
0.8

62
0.02 ◯ 3.1
2.2

△

78
0.87 ◯ 3.7
1.3

72
0.02 ◯ 3.7
2.3

80
0.14 ◯ 11.2
1.1

100
0.28 ◯ 11.1
3.4

54
<0.01 ◯ 10.3
1.3

114
0.47 ◯ 8.9
6.0

59
<0.01 ◯ 4.2
2.0

107
0.58 ◯ 10.4
5.6

July 8, 1977