PROCEEDINGS

THIRD US-JAPAN CONFERENCE

ON

PHOTOCHEMICAL AIR POLLUTION

September 8-10, 1976
USEPA Research Center
Research Triangle Park, N.C.

S DELEGATION

r. A.P. Altshuller, Chairman
vironmental Sciences Research Laboratory
SEPA

r. B. Dimitriades
vironmental Sciences Research Laboratory
SEPA

r. K. Maconaughey
fice of International Activities
SEPA

JAPANESE DELEGATION

Mr. Kei Yamazaki, Chairman
Environment Agency

Dr. Naomi Yamaki
Saitamo University

Dr. Michio Okuda
National Institute for
Environmental Studies

Dr. Machio Okita
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ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711 USA

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INTRODUCTION

Dr. Altshuller, head of the U.S. Delegation, welcomed the delegated and discussed briefly the history of the joint panel activities. He referred to the previous Conference conclusions, one of which was that the US and Japan exchange scientific information on the oxidant pollution problem. It was specifically agreed in the Second Conference that the scientific basis supporting the oxidant and NO_2 control strategies in the two countries should be described, and discussed by the respective delegations. Such discussions constitute the program of the Third Conference.

AGENDA

THIRD US-JAPAN CONFERENCE ON PHOTOCHEMICAL AIR POLLUTION

U.S. Environmental Protection Agency
Environmental Sciences Research Laboratory
Environmental Research Center
Research Triangle Park, N.C. 27711, USA

September 8-10, 1976

Wednesday, September 8, 1976: Session Chairman: Dr. Altshuller

10:00 a.m.	Welcome	A.P. Altshuller Kei Yamazaki Naomi Yamaki
	Introduction of Participants	A.P. Altshuller
	Election of Chairmen	
	Discussion and Approval of Meeting Program	
10:30 -- 11:00	Coffee -- Refreshments	
11:00 -- 11:30	Impact of Hydrocarbon Emission Control in the U.S. (Introduction)	A.P. Altshuller B. Dimitriades U.S. EPA
11:30 -- 12:00	Discussion	
12:00 -- 1:30	Lunch	
1:30 -- 2:00	Impact of Hydrocarbon Emission Control in the U.S.	B. Dimitriades U.S. EPA
2:00 -- 2:30	Discussion	
2:30 -- 3:00	Coffee -- Refreshments	
3:00 -- 4:00	Outdoor Smog Chamber Studies In the U.S.	H. Jeffries U. North Carolina
4:00 -- 4:30	Discussion	

Thursday, September 9, 1976: Session Chairman: Dr. Kei Yamazaki

9:00 -- 9:15	Opening Remarks	Dr. Kei Yamazaki
9:15 -- 9:45	Results of Smog Chamber Studies In Japan	Japanese Delegation
9:45 -- 10:15	Discussion	
10:15 -- 10:45	Coffee -- Refreshments	
10:45 -- 11;15	The Strategy for Oxidants and NO_2 Control in Japan	Japanese Delegation
11:15 -- 12:00	Discussion	
12:00 -- 1:30	Lunch	
1:30 -- 4:30	Tour, ERC - RTP Visit University of North Carolina and Research Triangle Institute Outdoor Smog Chamber Facilities	

Friday, September 10, 1976: Session Chairman: Dr. Altshuller

10:00 -- 10:15	Opening Remarks	Dr. Altshuller
10:15 -- 10:45	Results of Studies in Japan on Health Effects of Oxidants	Japanese Delegation
10:45 -- 11:15	Coffee -- Refreshments	
11:15 -- 12:00	Discussion	
12:00 -- 1:30	Lunch	
	Session Chairman: Dr. Kei Yamazaki	
1:30 -- 3:00	Plans for Future Activities	
3:00 -- 3:30	Coffee -- Refreshments	
3:00 -- 4:00	General Discussion Joint Communiqué Conclusion of Meeting	

JOINT COMMUNIQUE

The Third U.S. -- Japan Conference on Photochemical Air Pollution was held in Research Triangle Park, North Carolina on September 8-10, 1976.

The Japanese delegation included: Mr. Kei Yamazaki General Chairman, Environment Agency; Dr. Naoomi Yamaki -- Saitama University; Dr. Michio Okuda -- National Institute for Environmental Studies; Dr. Toshiichi Okita --Institute of Public Health; Dr. Isao Mizoguchi -- Tokyo Metropolitan Research Laboratory of Public Health and Mr. Toshiaki Shimazaki -- Environment Agency.

The principal United States delegates were: Dr. A.P. Altshuller, General Chairman, EPA; Dr. B. Dimitriades, EPA, and Mr. K. Maconaughey, EPA.

Discussions were centered around subjects agreed upon by the two delegations during the Second Conference held in November 17-21, 1976, and in subsequent communications exchanged by the two delegations. Such subjects included:

1. The Strategy for Oxidants and NO_2 Control in Japan

2. Results of Smog Chamber Studies in Japan

3. Results of Studies in Japan on Health Effects of Oxidants

4. Impact of Hydrocarbon Emission Control in the U.S.

5. Outdoor Smog Chamber Studies in the U.S.

The most notable scientific findings and viewpoints presented and discussed in the Conference are summarized as follows:

1. The current Japanese strategies for control of oxidant and of NO_2 evolved from consideration of several scientific findings. Principal scientific evidence relevant to the need for NO_2 control was obtained from studies of health effects associated with NO_2. The NO_2 control strategy is based on control of NO_x emissions. Evidence relevant to the question of oxidant control strategy consists of air monitoring and smog chamber data, and, overall, suggests HC control as an approach to ambient oxidant reduction.

2. The evidence currently available in the US strongly suggests that when sufficient and reliable data are available, it can be demonstrated that HC control in the last decade had a beneficial effect upon oxidant air quality in the core areas of urban centers.

The two delegations agreed on a continuing cooperative program with immediate and specific interest in exchange of scientific evidence and expertise in the area of smog chamber and field studies of the photochemical pollution problem. More specifically, it was agreed to continue the effort to generate and exchange comparable data and procedures including possible scientific personnel exchange.

It was tentatively agreed to call the next meeting in the fall of 1977.

A.P. Altshuller

Dr. A.P. Altshuller
General Chairman
U.S. Side

Kei Yamazaki

Mr. Kei Yamazaki
General Chairman
Japanese Side

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IMPACT OF HYDROCARBON EMISSION CONTROL IN THE U.S.

Basil Dimitriades
Environmental Sciences Research Laboratory
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ABSTRACT

Studies conducted in various parts of the US on the impact of hydrocarbon emission control upon oxidant air quality met with various degrees of success. Thus, observed air quality trends in some cases could and in others could not be explained by emission control. The latter diffculty appears to be caused by a host of interfering effects that cannot be delineated unless an abundance of valid air quality and emission data are available. In two areas -- Los Angeles and San Francisco, California --for which adequate data were available, it was shown (a) that urban air quality trends could be explained by emission changes, and (b) that hydrocarbon emission control was the cause of observed air quality improvement.

INTRODUCTION

Hydrocarbon emission control for ambient oxidant reduction was intitiated in the U.S. in 1961 when the automobile manufacturers voluntarily installed crankcase controls on all new 1961-model cars sold in California. Since then mandatory hydrocarbon control was enforced and expanded to cover the entire U.S. and to include most types of mobile and some types of stationary emission sources. With the passage of the Clean Air Act of 1970, EPA was empowered (a) to establish a NAAQS for oxidant/O_3 to be achieved through hydrocarbon emission control, and (b) to require a 90-percent control of hydrocarbon emissions from automobiles and (c) to set up a mechanism for air quality management (Submission of State Implementation Plans). Notwithstanding the controls in the 1960's the levels of hydrocarbon emissions in the US continued to increase as a result of growth, and began declining only in the early 1970's. Table 1 shows estimates of national emissions of hydrocarbons from mobile and stationary sources projected through 1985. The important deduction from these estimates is that the emissions from the stationary sources are becoming the dominant ones, and,hence, stationary sources are the most promising area where additional emission control can be achieved.

Table 1. Nationwide Hydrocarbon Emissions (millions of tons per year)

Year	Mobile Sources	Stationary Sources	Total HC Emissions
1972	16.6	12.5	29.1
1975	15.2	13.7	28.9
1985	10.4	14.7	25.1

From laboratory dtudies of the oxidant formation process it has been established unequivocally that for oridnary urban atmospheres control of the HC precursor will have a beneficial impact upon urban oxidant air quality. Aerometric data taken in real atmospheres verified the beneficial nature of the HC control effect but failed to provide reliable quantitative estimates. The reason for the latter problem is that in the real atmosphere the effect of HC reduction is masked, partially or totally, by effects from changes in NO_x emissions, from changes in HC, composition, from changes in meteorological conditions, and from shifts in population or industrial activity. The complexity of the problem is illustrated in several atmospheric studies conducted in the US in the recent years. These studies and their findings are summarized next.

ATMOSPHERIC STUDIES ON IMPACT OF HYDROCARBON CONTROL ON OXIDANT AIR QUALITY

The approach commonly used in the studies conducted to date on the impact of HC control consists of deriving air quality and precursor emissions trends in a locality and examining such trends for evidence suggestive of emissions effects. Obviously, this approach will be valid only in those cases for which local oxidant and emissions are linked through a cause-effect relationship that is, when the local emissions are the cause of the oxidant observed. When pollutant transport causes a significant part of the locally observed oxidant then air quality and emission trends, unless carefully examined in conjunction with air movement data, will be inconclusive.

The first systematic examinations of oxidant air quality trends were conducted and reported by the State of California (1) and by Altshuller (Figures 1-3) (2). The State of California reported Los Angeles basin data showing the oxidant levels to decline (in the recnet years) more rapidly in the coastal areas than in the inland areas. The Althsuller analysis showed that in the CAMP cities also, center-city oxidant levels declined in the recent years. The two reports made the following important observations:

1. Aerometric data on oxidant and precursor concentrations should be carefully examined for quality and completeness before they are used;

2. More than one indices for oxidant air quality should be used; e.g. highest or second highest oxidant concentration, number of days with oxidant exceeding 0.08 ppm, etc.;

3. Air quality trends in the source-intensive center-city areas are not necessarily the same -- in intensity or even direction -- as in the downwind suburb and/or rural areas.

While the two studies strognly suggested that the observed air quality trends reflected emission control impact, no attempt was made to quantitatively relate such trends to changes in emissions an/or other relevant factors.

In a subsequent study conducted by the California Institute of Technology, the researchers used a more rigorous and detailed investigative approach (3,4) Specifically, they derived air quality trends for several locations within the Los Angeles air basin and attempted to explain such trends in terms of effects from hydrocarbon emission control, NO_x emission control, emission source growth, geographical distribution of emissions, and meteorology. Findings from that study are summarized and illustrated in figures 4 - 10.

Figure 4 shows the area covered by the Los Angeles air basin and the geography of the six county sub-areas for which air quality and emission trends were derived. Figure 5 shows population and automobile traffic (VMT) growth rates within te basin and its subparts during 1967-1974. Fagures 6 and 7 percent the hydrocarbon and NO_x emission trends during the same decade. The NO_x increase reflects partly growth and partly a side effect of the control techniques used to reduce HC and CO from atuomobiles. From figures 5-7, two significant observations can be made:

(a) Growth rate is not uniform within the LA basin; it is low in downtown Los Angeles (DOLA) and high in the areas sourrounding DOLA.

(b) Consistent with these growth patterns and with the expected effects of emission control, hydrocarbon emissions decreased most in DOLA and least in surrounding areas; coversely, NO_x emissions increased most in the surrounding areas and least in DOLA.

Such non-uniform occurrence of emission changes should also have non-uniform effect upon the basin's air quality. However, before this is examined, it would be necessary to first verify that the trends in ambient HC and NO_x concentrations are consistent with the emission trends. These trends are shown in figures 8 and 9. These figures show excellent agreement between emission and ambient concentration trends for NO_x, and one case of disagreement between ambient HC trend in Azusa and ambient HC and emission trends elsewhere in the LA County (Fig 9).

Oxidant air quality trends are illustrated in figure 10 and are also compared with those in HC and NO_x emissions. The significant observations to be made from Figure 10 are as follows. First, basinwide, the ambient oxidant reduction is nearby equal to the HC emission reduction, namely, 19% and 18% respectively. Second, in the individual localities, oxidant changes and HC emission changes agree qualitatively, at least, in the sense that Los Angeles County experienced the greatest improvement in both oxidant concentration and HC emissions. Finally the coastal areas seem to have experienced greater improvement in oxidant air quality than the inland areas; in fact, in some inland localities air quality deteriorated.

These oxidant trends can be explained reasonably well based on what is known about the relative roles of the HC and NO_x precursors in the oxidant formation process. Thus, control of HC should cause oxidant

reduction in all localities where oxidant is caused by local emissions. Such localities are the ones in coastal areas; HC control did indeed cause oxidant reduction in those areas. Increase of NO_x is expected to have a beneficial effect in the coastal areas; in the inland areas the effect could be either beneficial or detrimental, as illustrated in Figure 11. This explains the small improvement or deterioration of air quality in the inland areas.

In conclusion, the Los Angeles data show:

(a) Significant reduction of HC emissions was achieved in the LA basin

(b) A degree of O_x reduction was observed that appears to be consistent with the expected effects of HC reduction and accompanied NO_x increase.

The LA situation makes perhaps the best case for the beneficial impact of HC control upon oxidant air quality; however, Los Angeles is not a typical urban area in the U.S. For a more reliable assessment of the effect of HC control it is necessary that other areas in the US be studied in a manner similar to the LA study. Such studies have been attempted recently but without much success, mainly because these studies have extremely high demands in air quality and emission data, and such complete data are not usually available. One such attempted study was conducted recently under EPA contract and is briefly summarized as follows (5).

The locations studied were:

Urban: San Francisco, Philadelphia, Denver

Non-urban: Redding, San Joaquin Valley, Salinas, Lancaster (all in California)

In the first attempt data were used that covered a 5 year period (1970-74). Results showed that only San Francisco and Denver experienced a significant downward trend in oxidant air quality. In the case of Denver the trend wasd weaker and was not paralleled by all oxidant indices (average daily maximum in year). Correlation between oxidant changes and emission changes were overall fairly good for SF, the correlation with HC/NO_x being much better than with HC alone. In Denver, the correlations were poor but the emission data available were also very inadequate, a fact that might be the cause of the poor correlations.

In a second attempt an analysis was made of data for San Francisco covering a longer period of 13 years (1962-1974). This analysis gave more conclusive results, namely:

1. Downward trend in oxidant was much better defined

2. Correlation between oxidant trend and HC/NO_x-emission trend was much better.

3. Weather variables did affect air quality trends; when data were used for days meeting the smogginess criteria (high T, low mixing height), the effects f emission changes could be seen much more clearly.

4. Coastal areas have less severe O_x problems than inland areas (ventilation, NO_x effect)

5. Monitoring data for a 5-year period are not enough to establish air quality trends for an individual monitoring station.

Overall, the main conclusions from this study were that(

(a) to reliably assess the impact of emission control in air quality, an abundance of data (stations, years) need to be used.

(b) when such data are available then the emission control impact can be assessed and it appears to relate to HC/NO_x change rather than to the HC-change.

It is perhaps because of the first conclusion that other studies failed to show significant relationship between emission changes and air quality changes. Thus, for example one and two-year studies in urban areas of Texas failed to show any significant correlation between ambient oxidant and emissions (figure 12) (6). Lack of such correlating may also result from failure to properly consider pollutant transport. Thus, there have been several studies of various parts of the U.S. that have shown no correlation betweeen local oxidant and locally observerd meteorological and emission factors (6). When all these interfering effects are understood and when there are sufficient data to permit delineation of these interfering effects, then the impact of emission control can be and has been determined.

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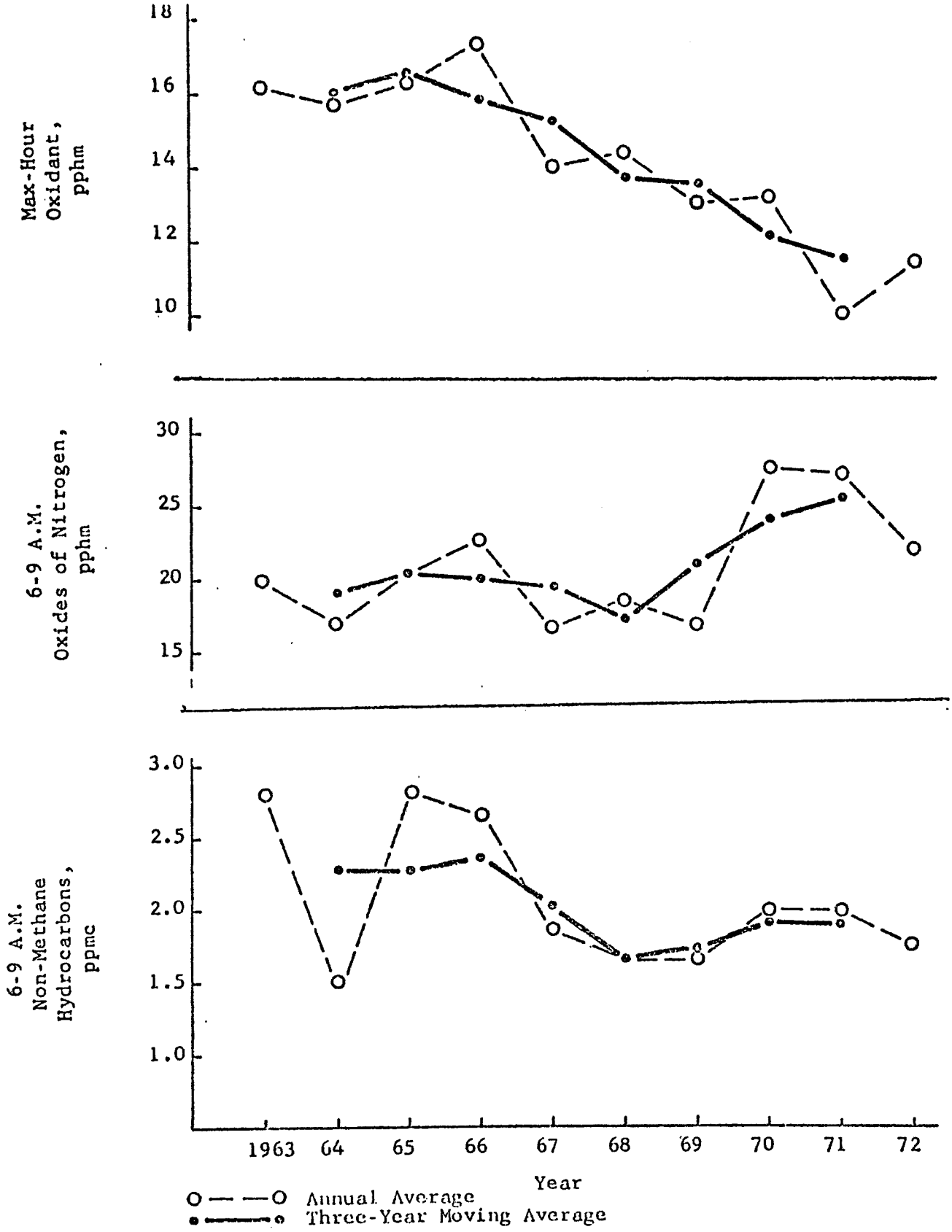


Figure 1

POLLUTANT TRENDS IN LOS ANGELES, 1963-1972
ANNUAL AND THREE-YEAR MOVING AVERAGES
FOR JULY, AUGUST & SEPTEMBER

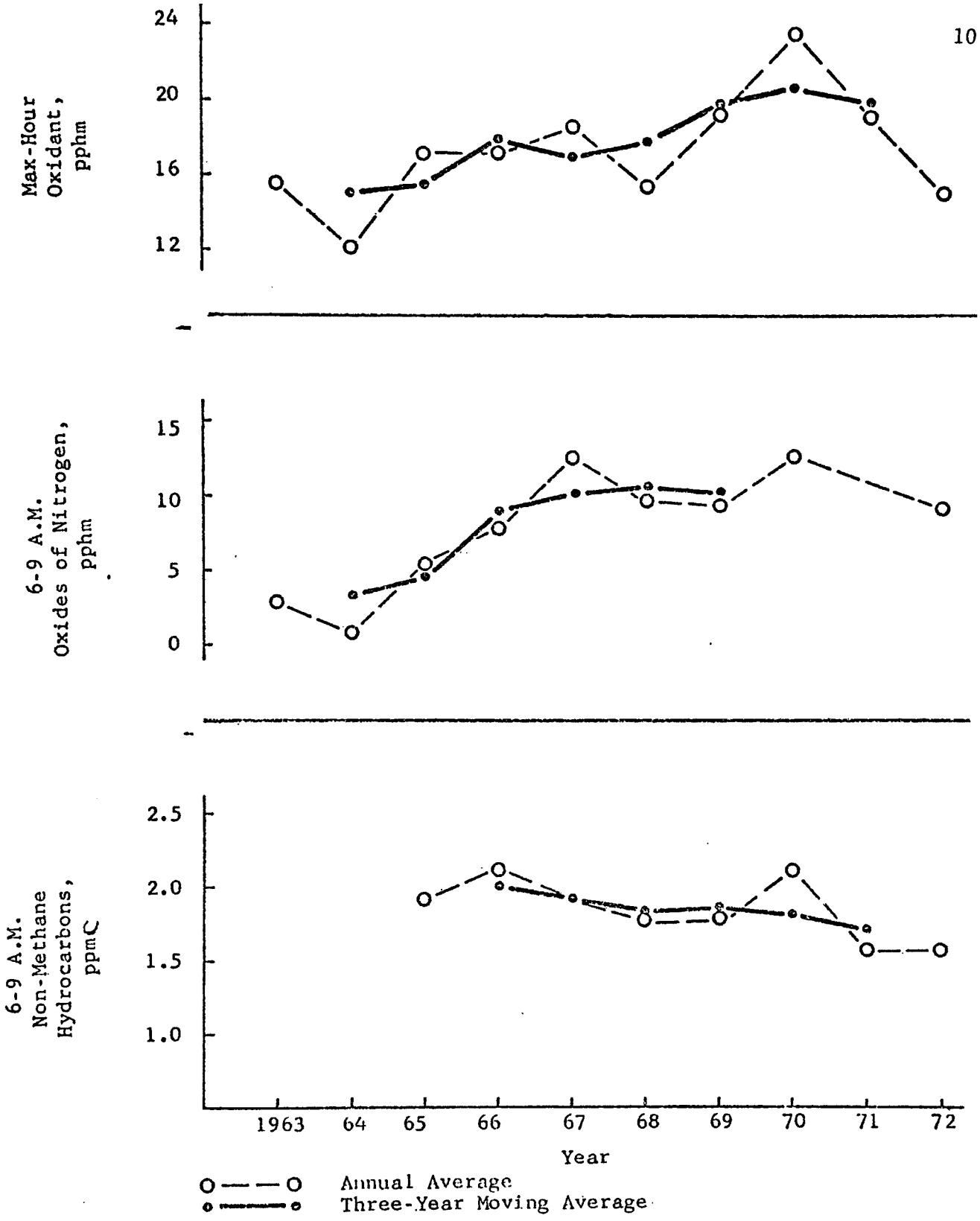


Figure 2

POLLUTANT TRENDS IN SAN BERNARDINO, 1963-1972
ANNUAL AND THREE-YEAR MOVING AVERAGES
FOR JULY, AUGUST & SEPTEMBER

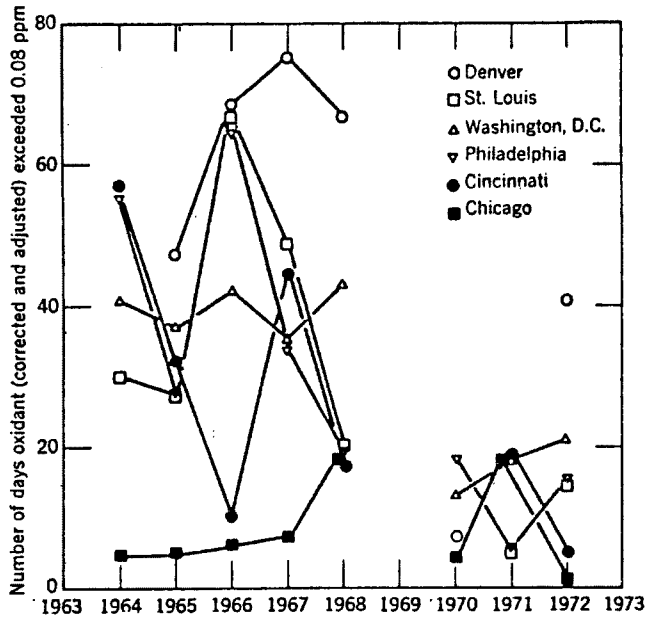
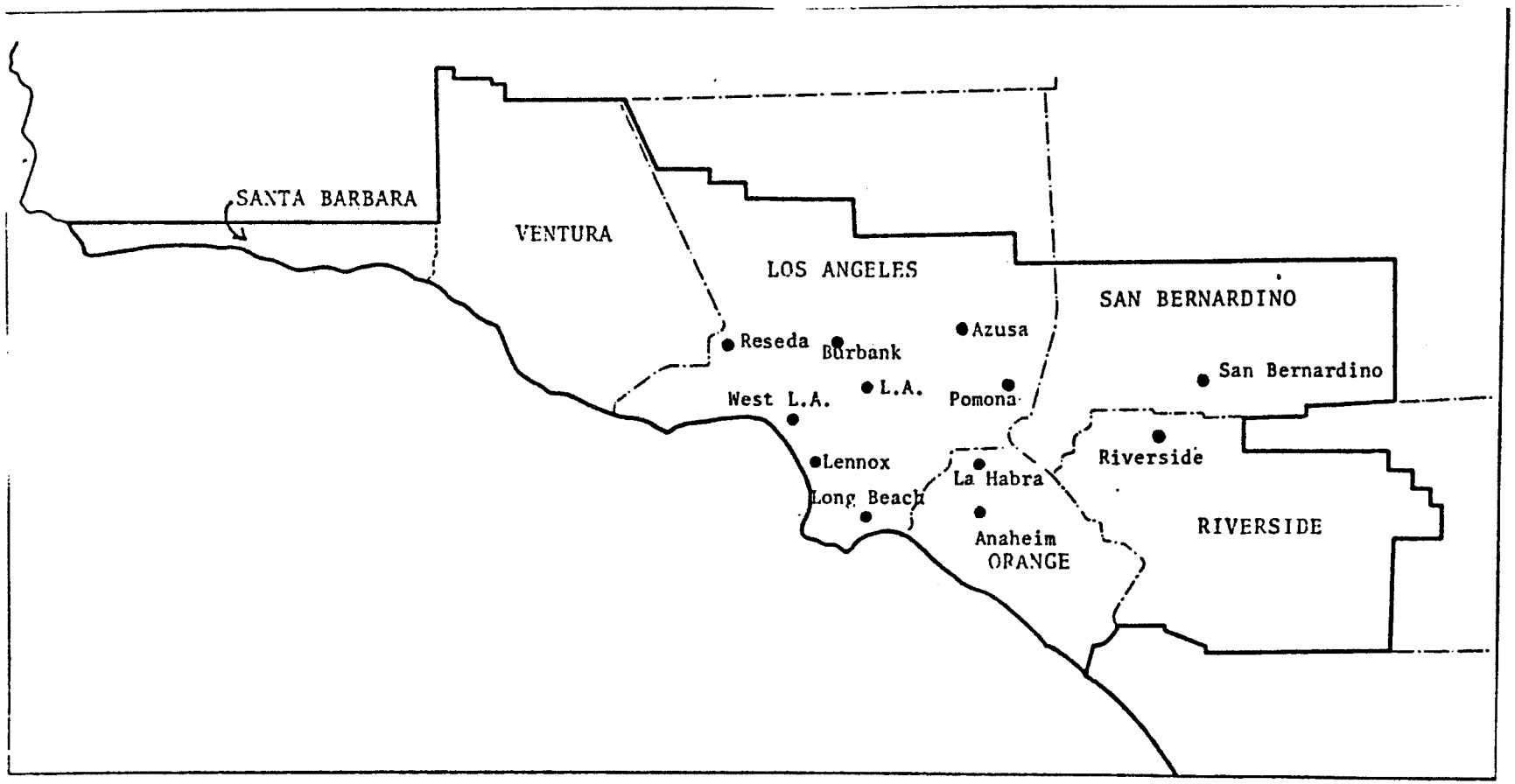
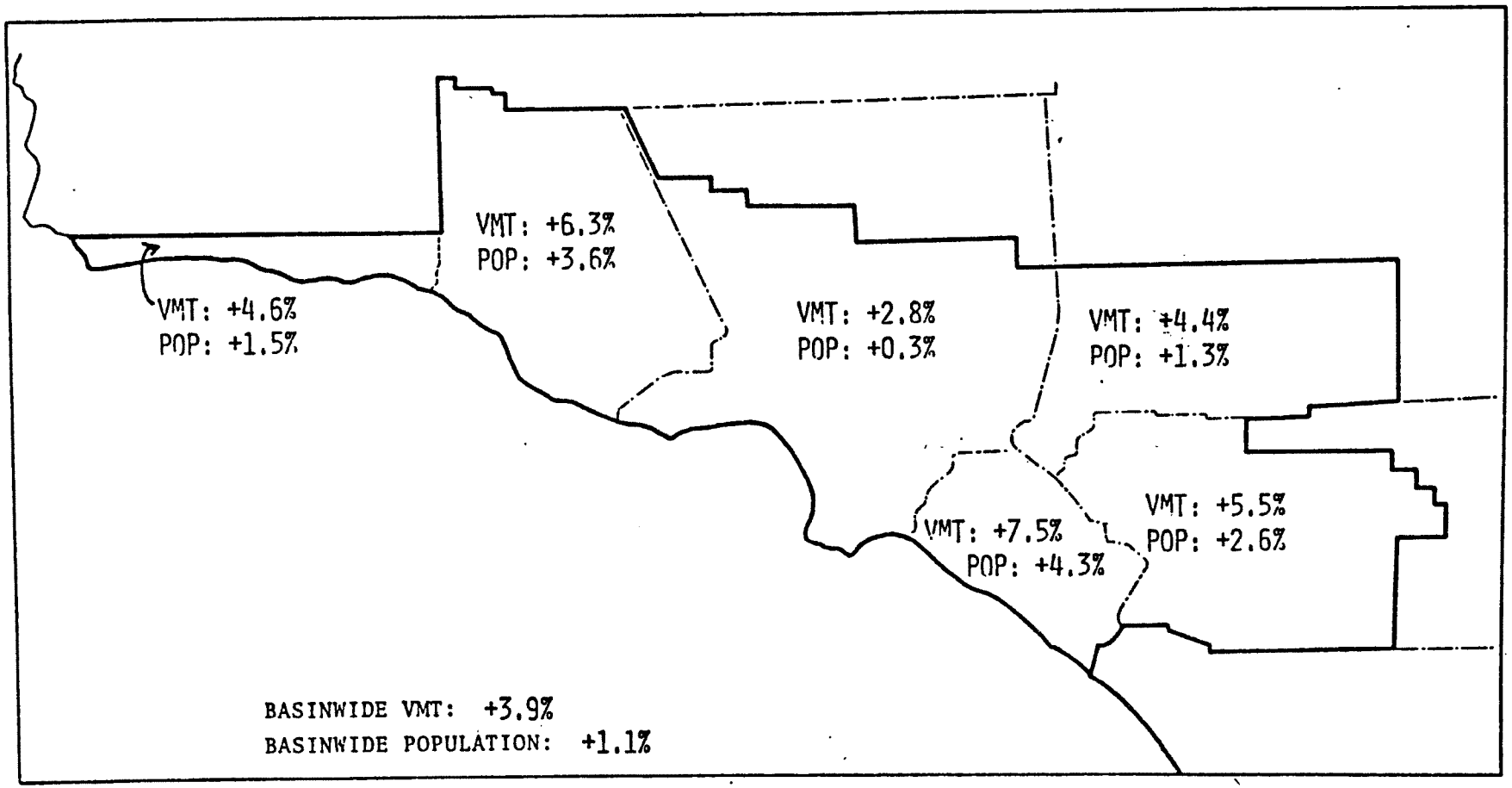


Figure 3. Trend in oxidant results by year at CAMP sites.



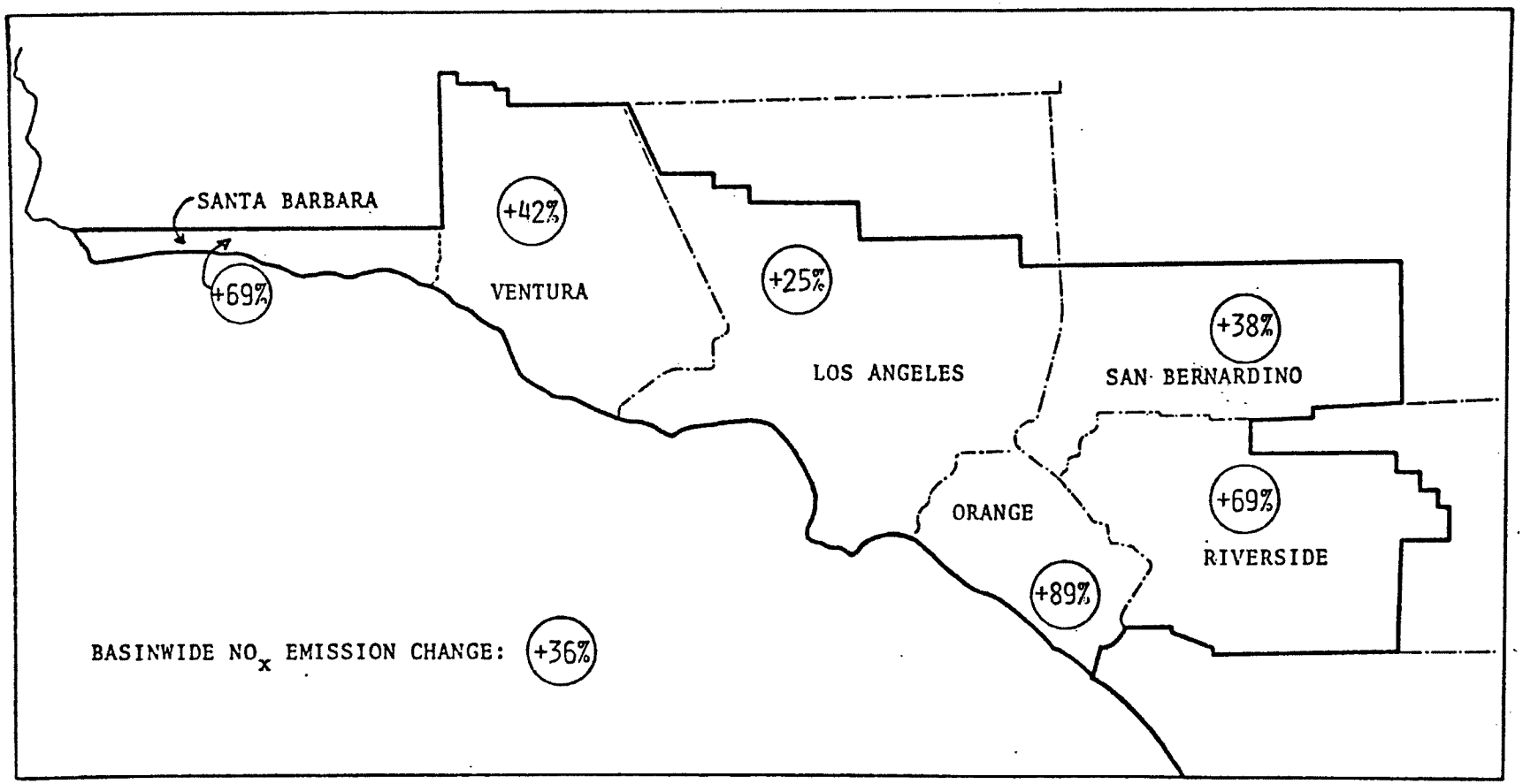
MAP OF SOUTH COAST AIR BASIN

FIGURE 4

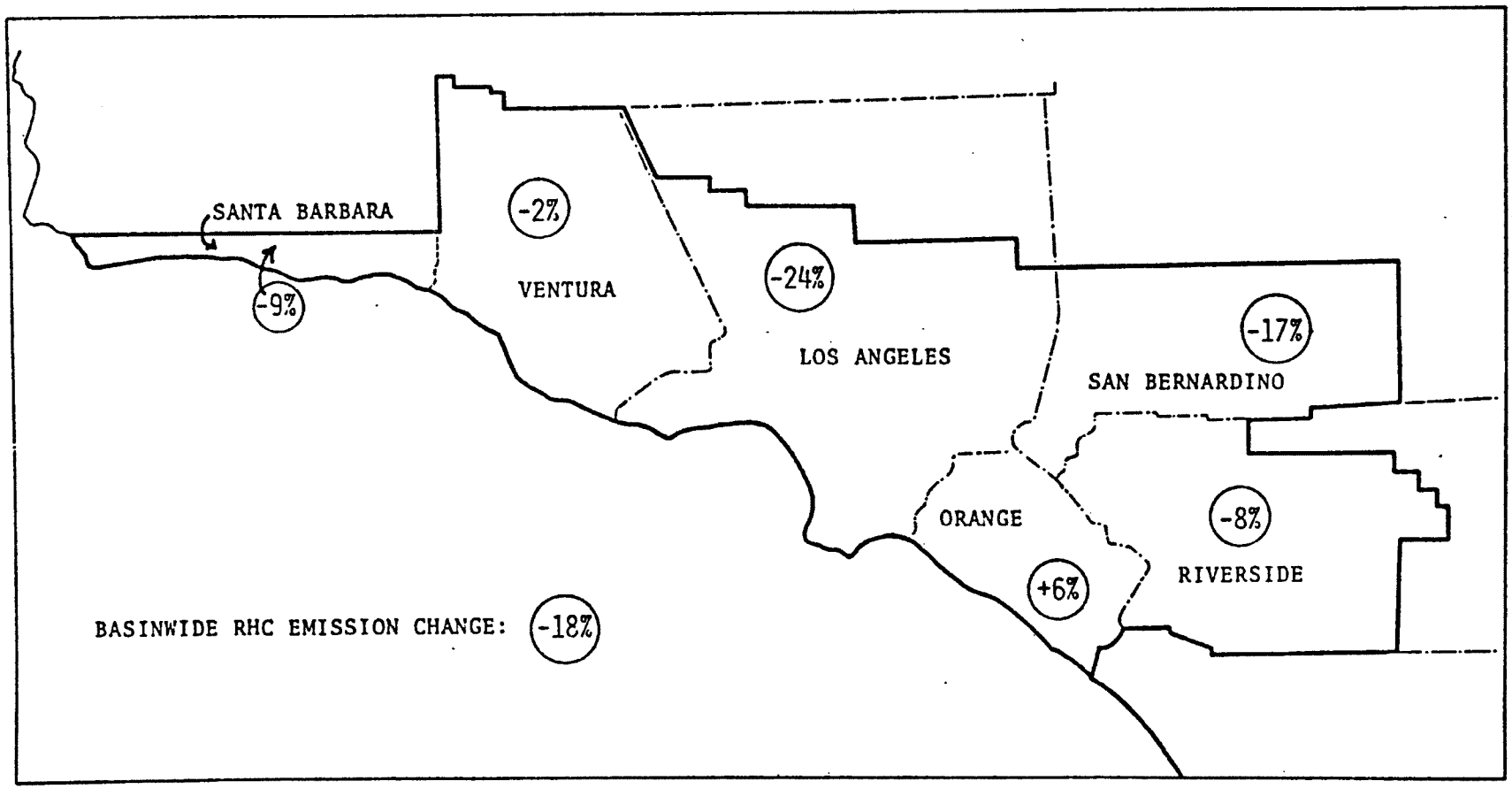


AVERAGE YEARLY VMT AND POPULATION GROWTH RATES, 1965-1974

FIGURE 5



TRENDS IN NO_x EMISSIONS, 1965-1974
FIGURE 6



TRENDS IN RHC EMISSIONS, 1965-1974
FIGURE 7

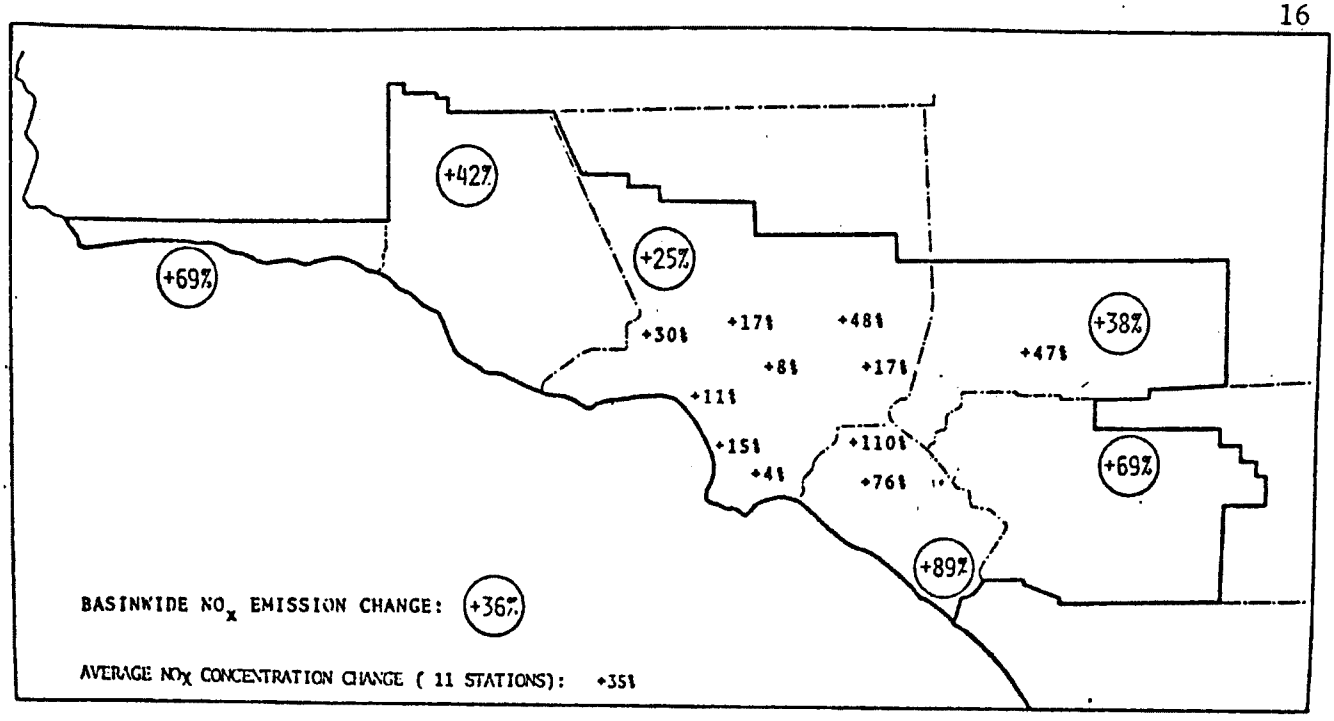


Figure 8 Trends in NO_x Emissions and Air Quality, 1965-1974

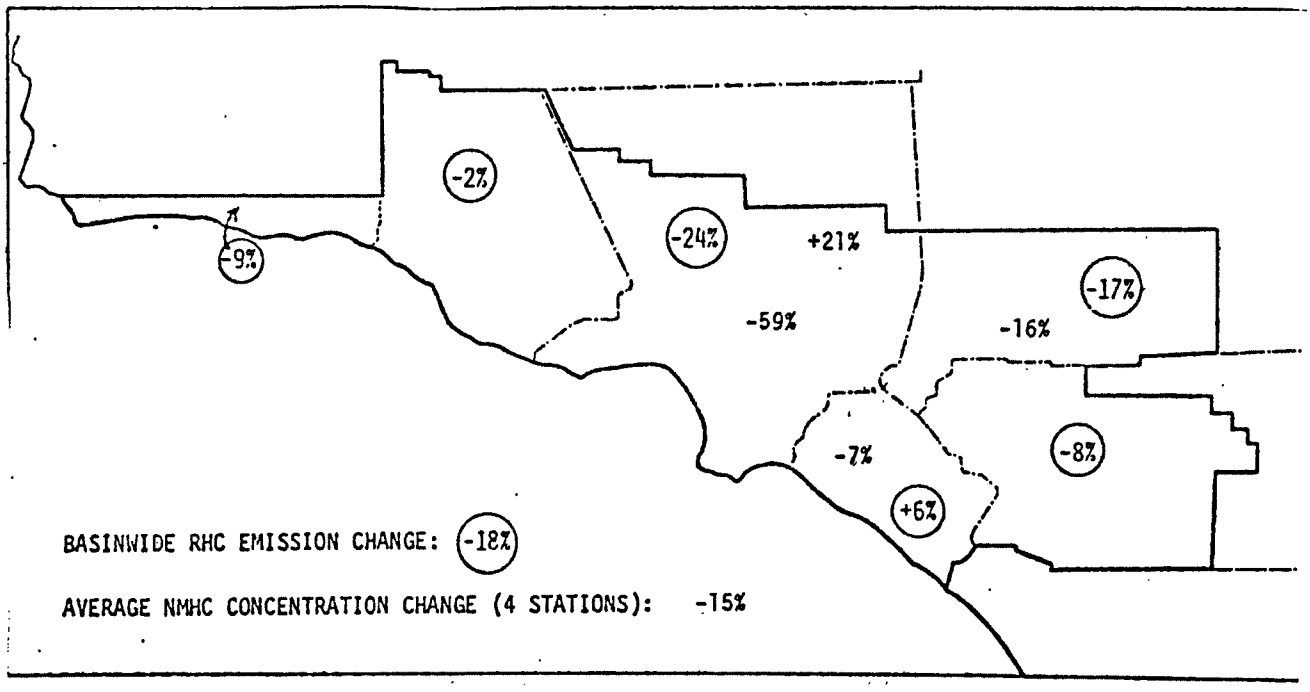
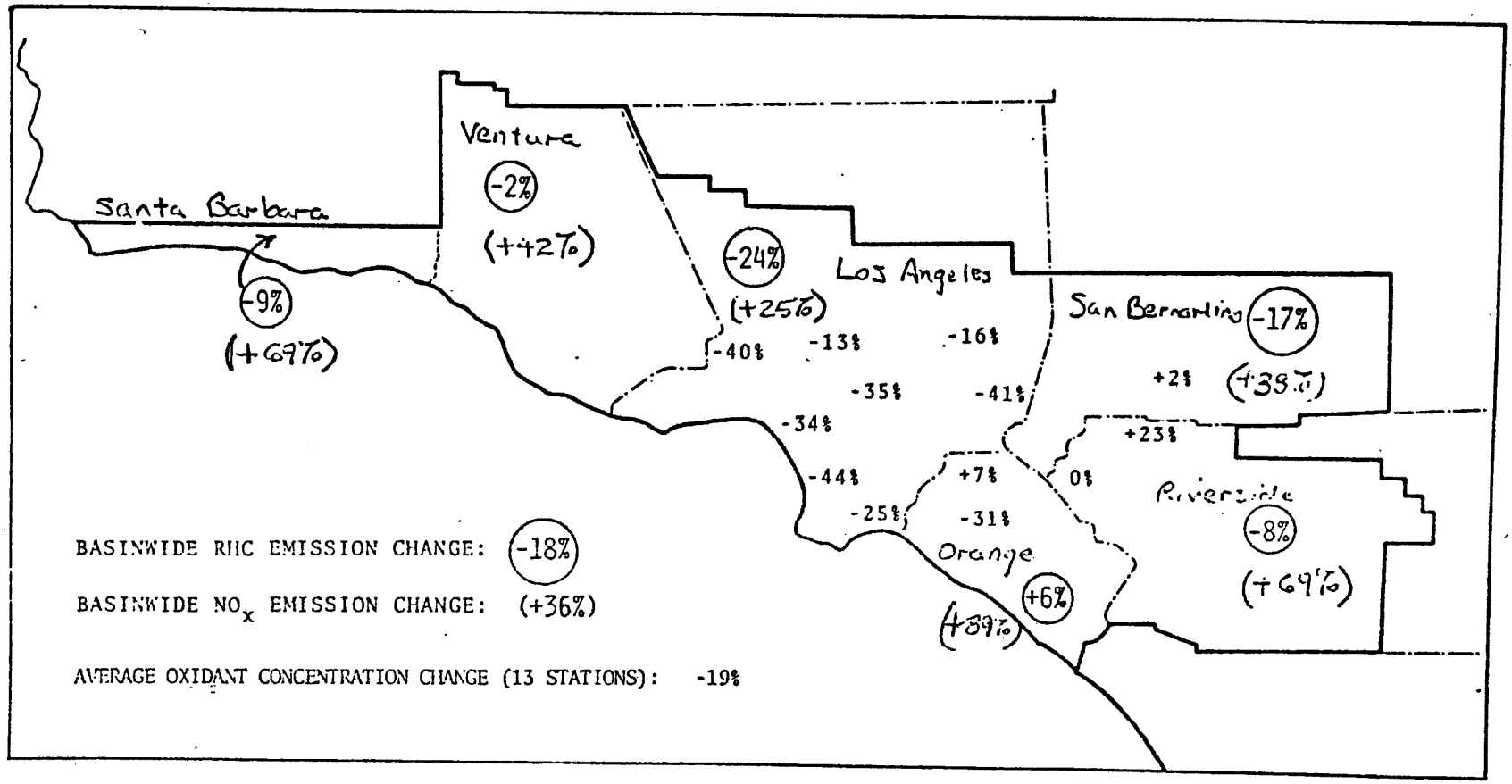
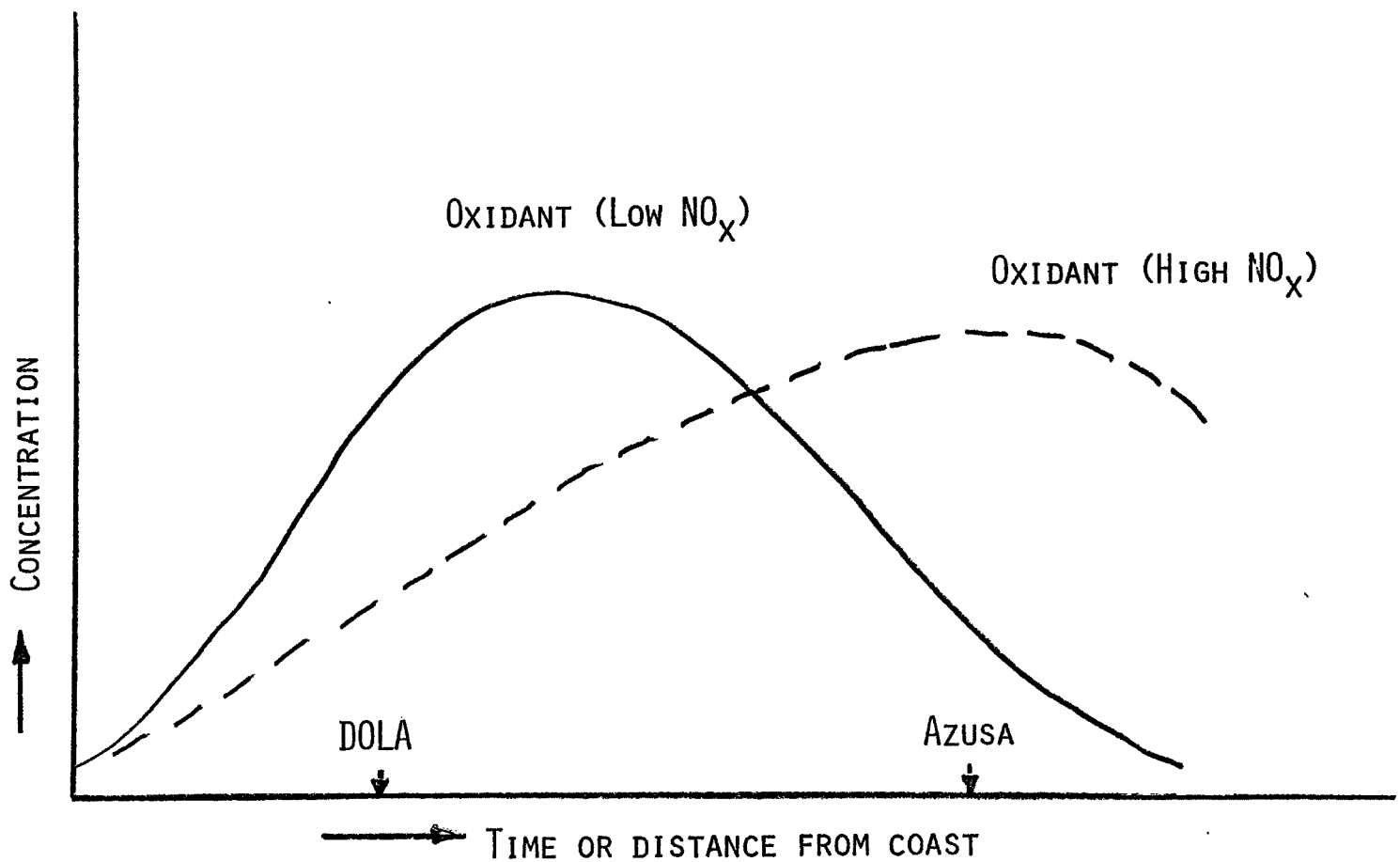


Figure 9 Trends in RHC Emissions and Air Quality, 1965-1974



TRENDS IN RHC EMISSIONS AND OXIDANT AIR QUALITY, 1965-1974
FIGURE 10

Figure 11. Effect of NO_x on peak-oxidant level and locations



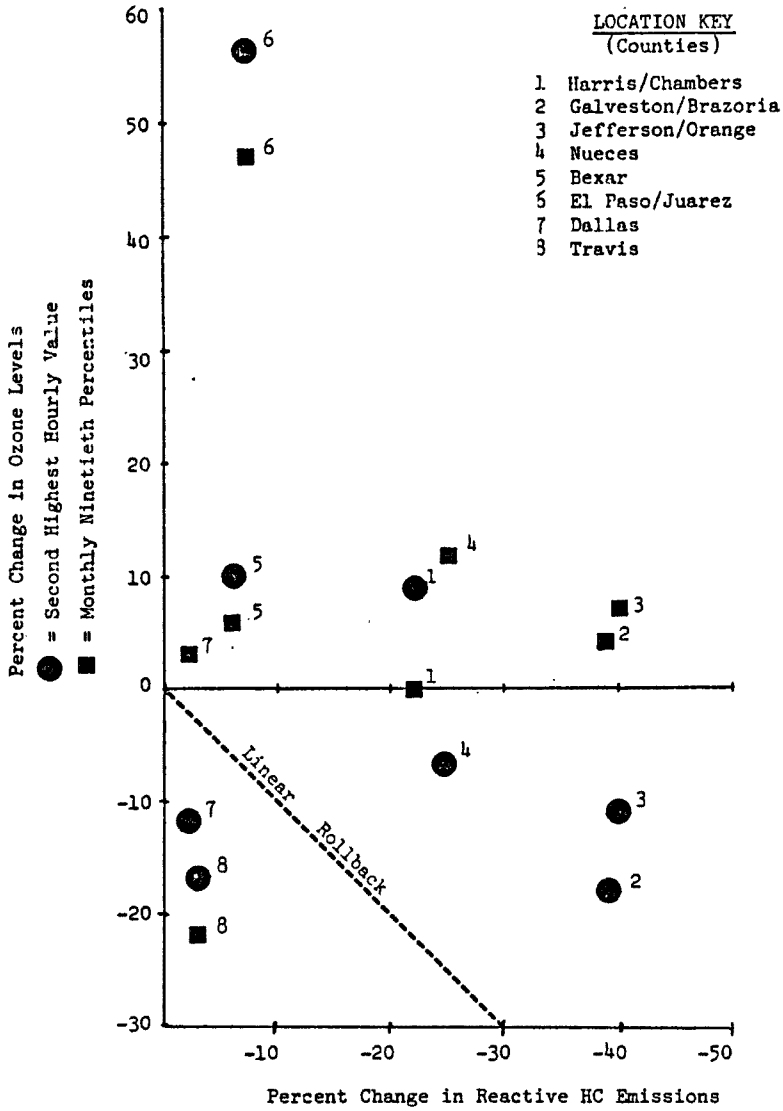


Figure 12 Scatterplot of Changes in Ozone Levels and in Man-Made Hydrocarbon (HC) Emissions (1974-75)

OUTDOOR SMOG CHAMBER STUDIES IN THE US

by

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INTRODUCTION

Outdoor smog chamber studies, sponsored by the Environmental Protection Agency (EPA), have concentrated on simulation aspects of air pollution control strategies under reasonably realistic conditions. Special emphasis has been placed on the effects of hydrocarbon concentration reductions on nitrogen dioxide (NO_2) and ozone (O_3) concentrations.

Presently, there are two groups of outdoor chambers, one set operated byt he University of North Carolina (UNC) at a rural site approximately 35 miles from the Research Triangle Park (RTP), and one set operated by the Research Triangle Institute (RTI), located in RTP.

CHAMBER DESCRIPTIONS

The UNC chambers consist of one dual compartment, very large chamber intended primarily for gas phase studies, and a slightly smaller, single compartment chamber, intended primarily for aerosol studies. The cahmbers are of similar design and construction, therefore, only the gas chamber will be described.

The UNC dual outdoor chamber, shown schematically in Figure 1, is constructed of 0.13 mm fluorinated ethylene propylene (FEP) Teflon film supported by an exterior wooden A-frame, 9.14 m wide, 12.19 m long, and 6.10 m high on a plywood platform 1.22 m above grouhd. It is divided into

two compartments each 148 m^3 by a center Teflon vertical panel. The interior surface is 98% Teflon and 2% aluminum and glass. The chamber operates with natural sunlight, temperature, and humidity, and the air source is natural rural background of very low reactivity. Instrumentation is located in a temperature-controlled laboratory adjacent to the chamber. Glass sampling manifolds, 3.75 cm in diameter, bring air from the chamber in to the laboratory at > 60 $l\text{-}min^{-1}$ and the excess air is returned to the chamber. Pollutants are injected from high concentration gas tanks into this return manifold air. Two large, 0.56 m diameter mixing fans in opposite corners assist in mixing the chamber; this mixing requires less than 2 minutes.

The UNC aerosol chamber is essentially identical to the gas chamber except that it has only one compartment and a volume of 200 m^3. Because of sampling requirements, the laboratory for the aerosol chamber is located below ground, under the chamber, and several vertical, short-sampling manifolds are used.

The four side-by-side outdoor chambers at RTI are of a different design. Each chamber is a cylinder, 3 m in diameter and 3.66 m high on a plywood platform. Aluminum channel is used as an interior framework and FEP Teflon film, heat sealed into a cylinder, is mounted around the aluminum frame. The four chambers are placed approximately 4.5 m apart in a clear area between two laboratory buildings. Each chamber is equipped with an air purification system that uses chemical scrubbers to remove water and oxides of nitrogen and a catalytic combustion system to remove hydrocarbons including methane. This was necessary because the ambient air at RTP contains traces of auto exhaust.

At the UNC chambers, a computer based data acquisition and control system fully automates chamber and instrument operation. A PDP 11/40 computer with 56 kilobytes of memory, a 2.4 millionbyte disk system, two terminals, digital clocks, a Hewlett Packard 5½ digit digital voltmeter, 200 channel, 3-wire analogue multiplexer, and solid state controlled ac power switches can operate chamber intakes and exhaust, fans, blowers, injection gases, strip charts, and sampling valves. It simultaneously

acquires data from instruments in both the gas and aerosol laboratories, carries out calculations, stores data and prints out data in real-time in physical units. The computer can carry out complex timing tasks necessary to simulate the continuous injection and dilution that occurs in the real atmosphere.

TYPES OF EXPERIMENTS IN UNC CHAMBER

There are four general types of experiments that have been performed in the UNC chamber: static, slow dilution, two types of dynamic, and full atmospheric simulation experiments.

Static experiments. In static experiments, all of the reactant mass is injected into the chamber before sunrise and the system remains closed for the duration of the run, usually until sunset. These are the simplest type of experiment that can be performed and they test the effect of varying initial reactants under conditions of diurnal light and temperature. In general, NO_x initial conditions are the same in the two chamber sides and initial hydrocarbon (HC) concentrations are different. Two types of hydrocarbons have generally been used, propylene in chamber testing experiments, and a simulated urban mix consisting of acetylene, five paraffins, and six olefins. An example of such an experiment is shown in Figure 2, taken from "Outdoor Smog Chamber Studies : Effect of Hydrocarbon Reduction on Nitrogen Dioxide" (EPA-650/3-75-011, June, 1975). This data graphically illustrates the effect of initial HC reduction while keeping initial NO_x constant.

Dilution Experiments. In these experiments, the initial chemical conditions are the same. One side of the chamber, however, is slowly diluted (9.5% h^{-1}). Figure 3, taken from "Ozone Transport Phenomena : Observed and Simulated" (paper no. 76-14.3 presented at Portland APCA meeting, June 1976) illustrates the outcome in such experiments. The diluted side makes more O_3 if the dilution rate is approximately equal to the NO to NO_2 conversion rate. This results in a more favorable NO_2 to NO ratio earlier in the diluted run and subsequently more O_3.

Another experiment in the aerosol chamber, using a high concentration propylene-NO_x system, illustrates how difficult it may be to dilute O_3 in a photochemically active system (Figure 4). Although the dilution rate was 50% h^{-1} after 1215 EDT, the O_3 decreases only slowly suggesting that O_3 formation was approximately 50% h^{-1}.

Dynamic Experiments. In dynamic experiments, the reactants are not added all at once in the beginning of the experiment, but rather they are added slowly over several hours (3 to 12 hours). In some experiments, the chamber was closed (that is, semi-batch) and in others, the chamber was simultaneously diluted while injection was occurring. These types of experiments are very simple simulations of urban atmospheric dynamics. Figures 5, 6, and 7 illustrate the results in ramp (semi-batch) type experiments. Although the NO, NO_2, and HC profiles are dissimilar, the O_3 profiles are very similar, suggesting that the total mass added controls the final O_3 concentration. Table 1 shows that this behavior holds over a wide range of initial conditions and HC to NO_x ratios. The maximum O_3 in dynamic experiments is approximately 90% of the maximum O_3 in static experiments.

In another type of dynamic experiment, called simulate, conditions are as follows: a) in the static side reactants are added all at once before sunrise, b) in the dynamic side, reactants are initially injected beginning at 6 a.m. at a constant HC to NO_x ratio and at a rate such that at 9 a.m. the masses on the two sides would be identical, c) beginning at 9 a.m. until 12 noon, the chamber is diluted so as to remove 50% of the mass and injection continues at a rate which would have doubled the injected mass by 12 noon, d) after 12 noon, both injection and dilution ceases and the chamber becomes a simple batch reactor. The results of such an experiment using the urban mix are illustrated in Figures 8-11. Although from 9 a.m. to 12 noon mass is being added and removed, the profiles for NO, NO_2, and O_3 are essentially identical.

Full Atmospheric Simulations. We are currently simulating an actual atmospheric event, Operation 33 from the Los Angeles Reactive Pollution Program (LARPP). In LARPP, tetroons were used to "tag" a trajectory for

an air mass and two instrumented helicopters were used to measure pollutant concentrations at 200, 400, 600, and 800 feet above ground level along the tetroon path. We have chosen one of these operation to simulate in the outdoor chamber. The helicopter data was subjected to extensive analysis and the results were used in a vertical transport model to compute vertical flux of pollutants. An analogy between a variable-volume continuous stirred tank reactor and the atmosphere allowed this flux to be converted into dilution rate and pollutant injection rate for the outdoor smog chamber that would result in very similar behavior of the chamber contents as that for emissions and atmospheric dynamics in the real situation.

The mean concentrations of NO, NO_2, and O_3 observed in individual helicopter patterns in the well-mixed region of the atmosphere are shown in Figure 12. Profiles from a chamber simulation run are shown in Figure 13. It was necessary to inject the NO_x into the chamber as 75% NO, 25% NO_2 to obtain reasonable O_3 formation in the chamber simulation. The integrated injected hydrocarbon (total mass injected up to a given time) and the effective chamber volume necessary to simulate LARPP 33 are shown in Figures 14 and 15. It would seem that, if operated similarly to the real atmosphere, smog chambers can reasonably duplicate atmospheric behavior.

EXPERIMENTS IN THE RTI CHAMBERS

The RTI chambers have been used to simulate the effects of dilution and transport on O_3 formation. These experiments typically last three days, begin with an urban type HC/NO_x system, are subjected to varying degrees of dilution (beginning on the first day and lasting 24 h). An example of such an experiment is shown in Figure 16. In this run, 95% of the mass was removed between NO-NO_2 crossover ($\sim$ 9 a.m. on the first day) and 9 a.m. on the second day. The remaining 5% of the mass was still able to make more than 0.3 ppm of O_3 on the second day and 0.25 ppm of O_3 on the third day.

Comparisons of O_3 profiles for second day irradiations at three different dilutions (100% of material remaining, 23% of material remaining, and 5% of material remaining) are shown in Figure 17. The O_3 maximum are reduced by 53 and 40% of the no dilution case. This suggests an increased yield of O_3 percursor molecule under these conditions.

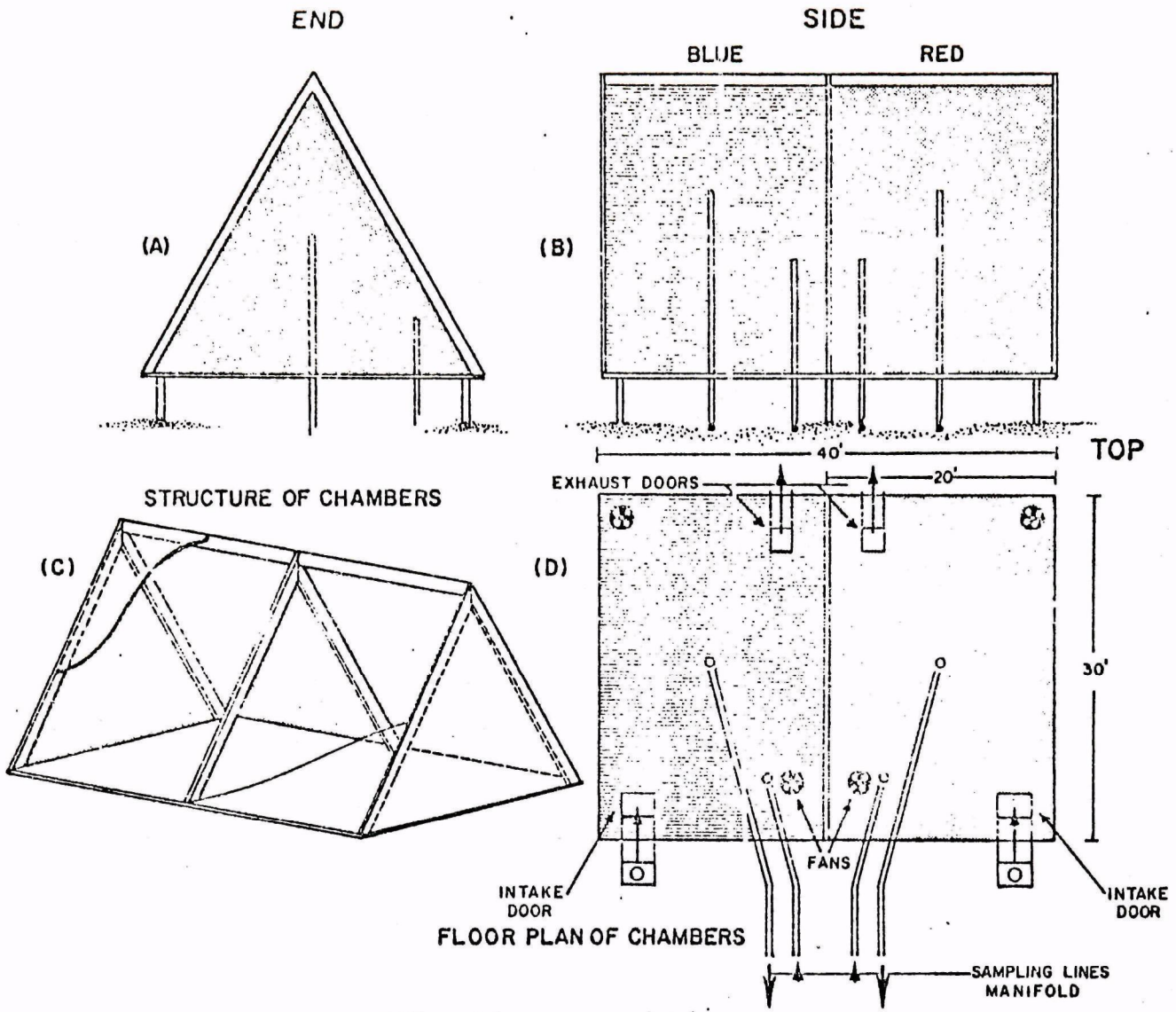


Figure 1. Schematic of UNC outdoor smog chamber.

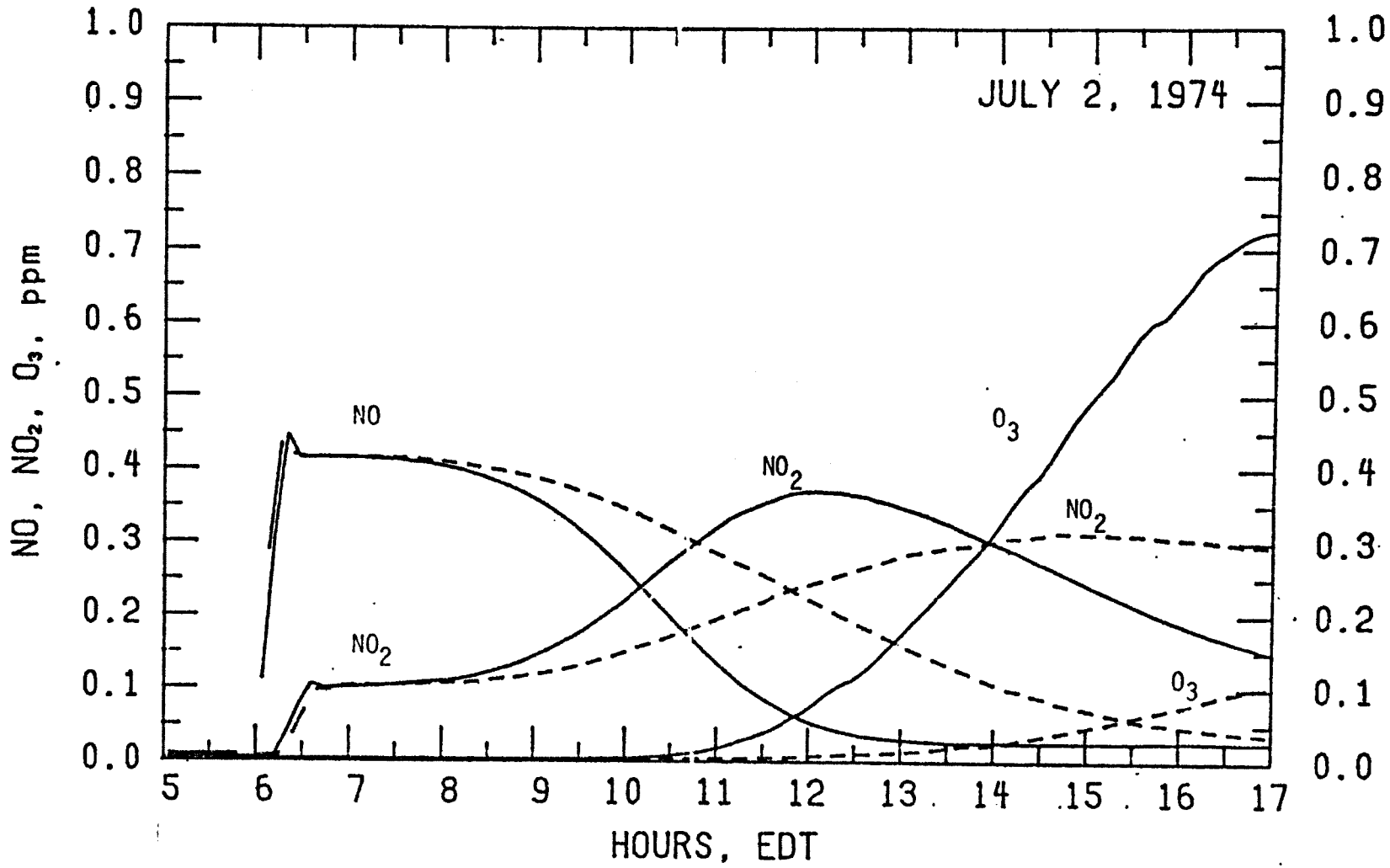


Figure 2. Profiles for dual run. Initial conditions: NO_x(—) 0.507, (---) 0.510 ppm; NO_2(—) 0.100, (---) 0.102 ppm; NMHC(—) 4.00, (---) 2.29 ppmC urban hydrocarbon mix in UNC outdoor smog chamber.

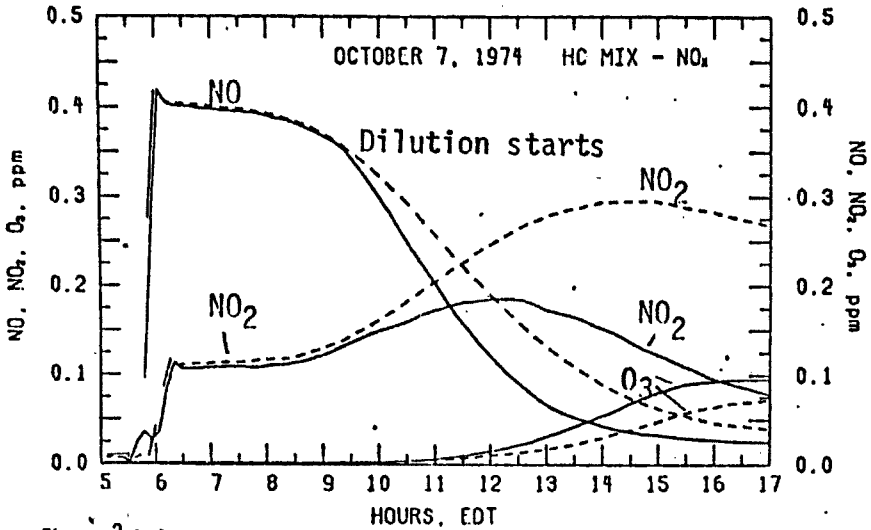


Figure 3 Dual run comparing dilution and no dilution. Initial Conditions: NO_x (—) 0.514, (---) 0.512 ppm; NO_2 (—) 0.106, (---) 0.111 ppm; NMHC (—) 2.39, (---) 2.43 ppmC urban hydrocarbon mix in UNC outdoor smog chamber. Dilution rate 9.5% hr^{-1}.

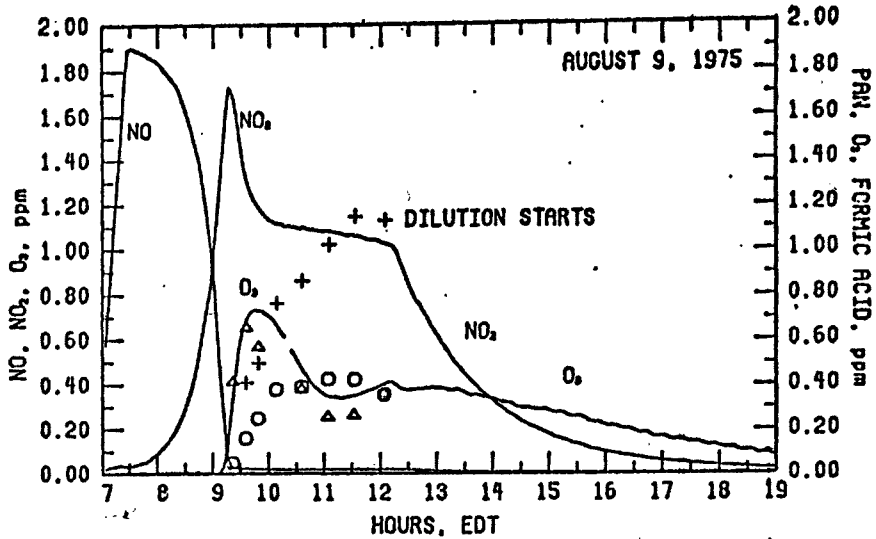


Figure 4 Effect of dilution in a high concentration run. Initial Conditions: NO_x = 1.95 ppm; NO_2 = 0.05 ppm; propylene = 23.3 ppmC in UNC outdoor aerosol chamber.

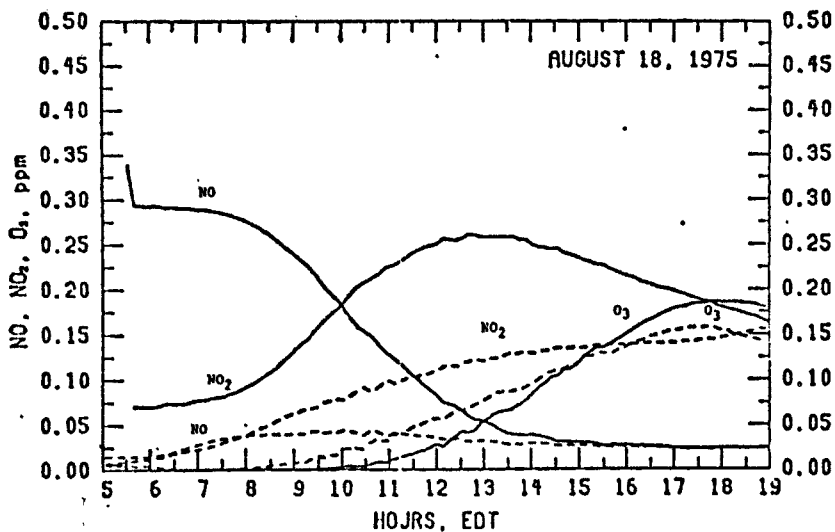


Figure 5 Static (—) and Ramp (---) injection Dual Run in UNC Outdoor Smog Chamber. Initial Conditions at 0545 in Static side (—): NO, 0.29 ppm; NO_2, 0.07 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC. Ramp side (---) would achieve: NO, 0.36 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC at 1800 hours if no reaction occurred.

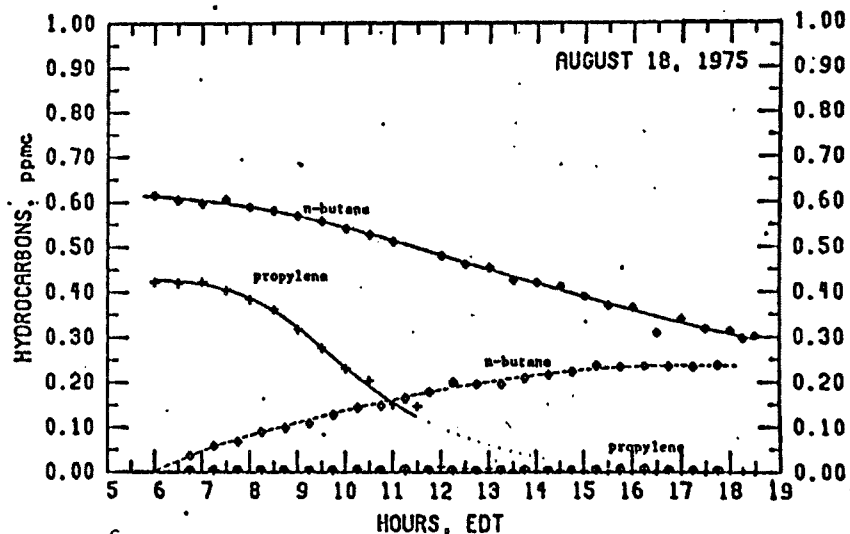


Figure 6 Static (—) and Ramp Injection (---) Dual Run in UNC Outdoor Smog Chamber. Initial conditions at 0545 in Static side (—): NO, 0.29 ppm; NO_2, 0.07 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC. Ramp side (---) would achieve: NO, 0.36 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC at 1800 hours if no reaction occurred.

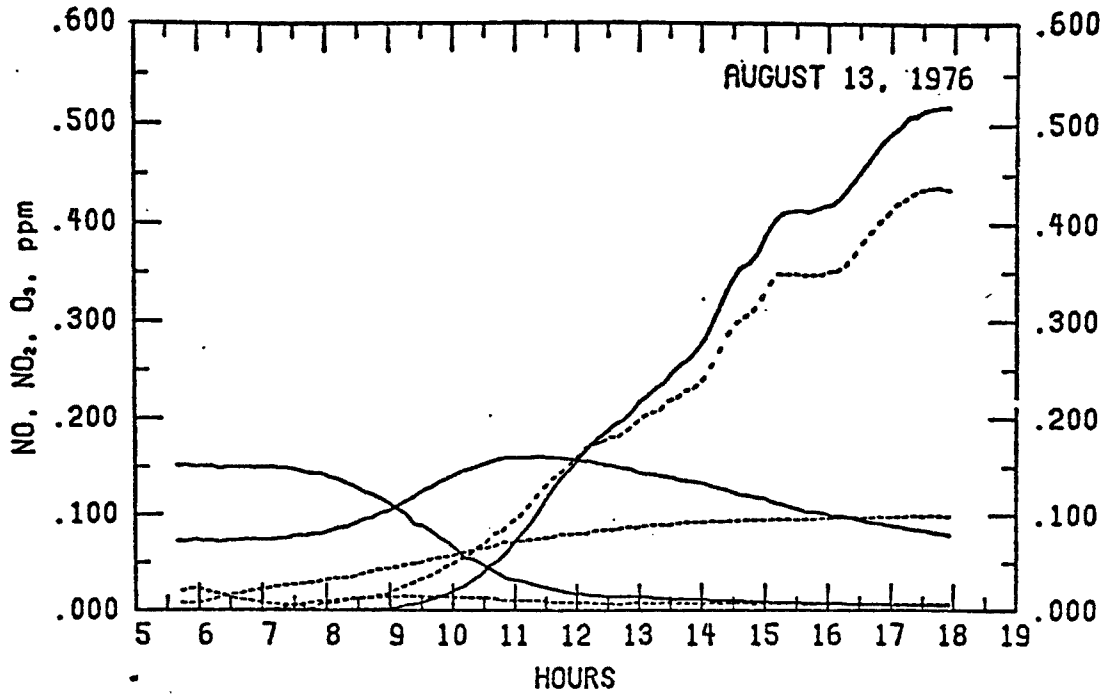


Figure 7 Static (—) and Ramp (---) injection dual run in UNC Outdoor Smog Chamber. Initial Conditions at 0540 in static side (—): NO, 0.151 ppm; NO_2, 0.072 ppm; 1.93 ppmC urban hydrocarbon mix. Ramp side (---) would achieve: NO, 0.22 ppm; 1.93 ppmC urban hydrocarbon mix at 1800 hours if no reaction occurred.

TABLE 1. Ozone Formation in Static and Ramp Injected Outdoor Smog Chamber Experiments

Date	Precursor Conditions[a] NO_x	HC	cmp[b]	HC/NO_x ppmC/ppm	O_3 max, ppm static	ramp	ramp/static %
8/16/75	0.37	0.98	P	2.65	0.68	0.48	71
8/17/75	0.36	1.00	B/P	2.78	0.28	0.25	89
8/18/75	0.36	1.00	B/P	2.78	0.18	0.16	89
8/4/76	0.35	0.97	M	2.70	0.05	0.05	100
8/5/76	0.31	1.93	M	6.23	0.24	0.32[c]	133
8/6/76	0.24	0.97	M	4.04	0.17	0.29[c]	171
8/12/76	0.24	1.93	M	8.04	0.72	0.65	90
8/13/76	0.24	1.93	M	8.04	0.49	0.41	84
8/24/75	0.38	4.00	M	10.53	0.57	0.46	81
8/30/76	0.36	4.56	M	12.00	0.74	0.65	88

[a] initial values for static experiments established at 0540 EDT and values that would have existed at 1800 EDT in ramp injected experiments if no reaction occurred.

[b] P, propylene; B/P, 60% n-butane-40% propylene by carbon; M, synthetic urban mixture of acetylene, paraffins, and olefins.

[c] NO injection rate for ramped side lower than required to give final NO_x value

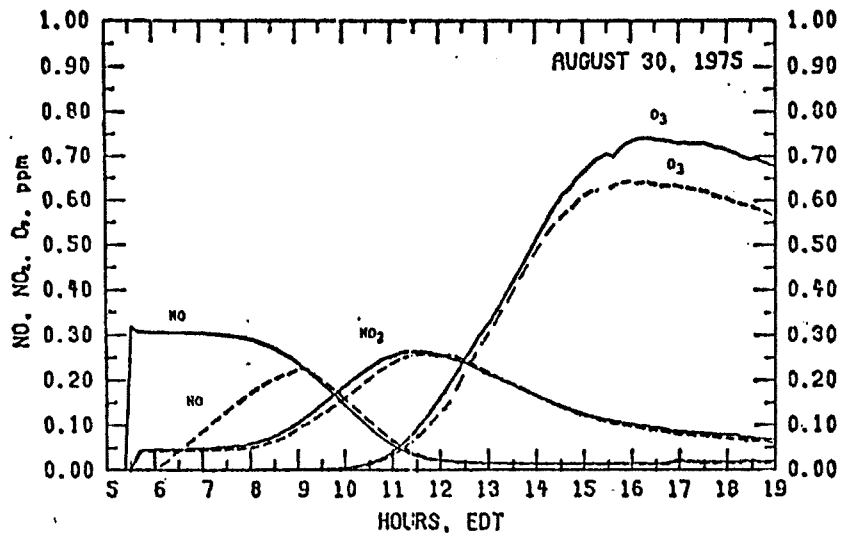


Figure 8 Static (—) and Ramp injection (0600-0900) with 50% dilution (0900-1200) and continued ramp injection (0900-1200) at rate equal to mass removal by dilution if no reaction (---). Initial conditions in static (—) side: NO, 0.31 ppm; NO_2, 0.05 ppm, Urban hydrocarbon mix, 4.56 ppmC. An initial condition of 0.05 ppm NO_2 was established in ramp (---) side. NO and mix injected in (---) so as to achieve same conditions at 0900.

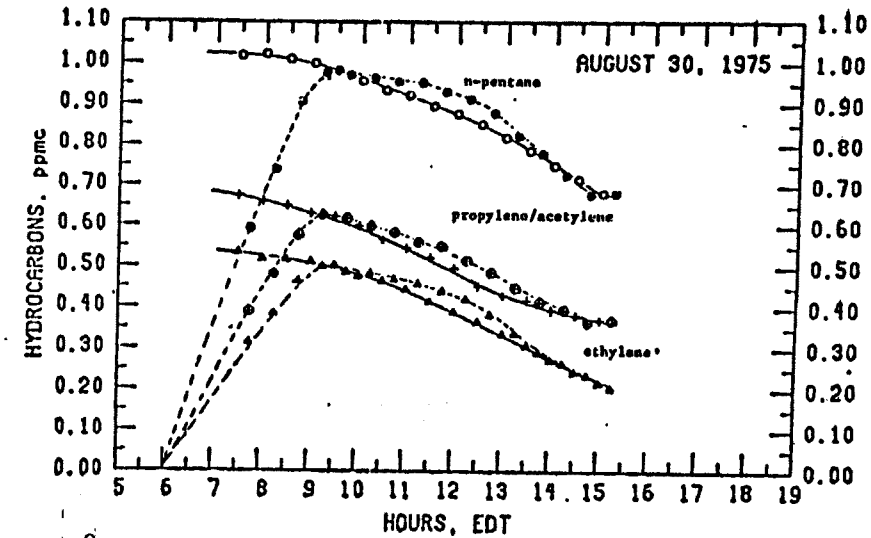


Figure 9 Selected hydrocarbon compounds in Urban hydrocarbon mix for Static (—) and Ramp injection (---) Dual Run in UNC Outdoor Smog Chamber.

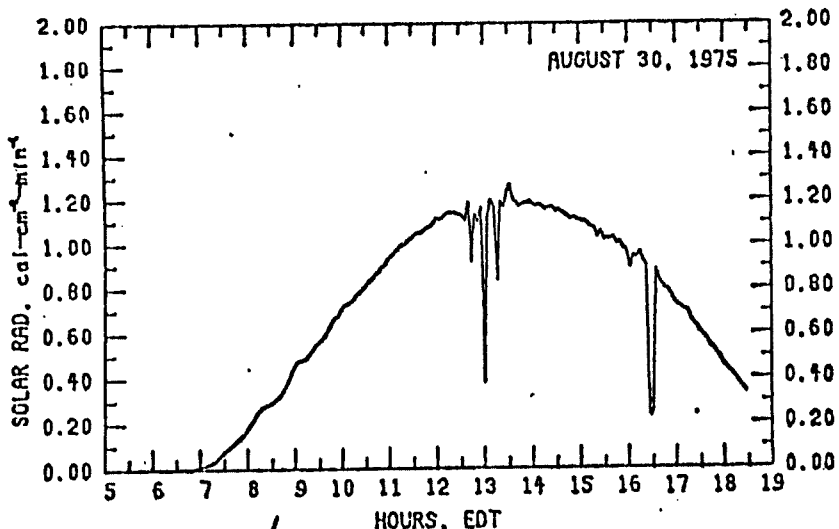


Figure 10 Solar radiation for August 30, 1975.

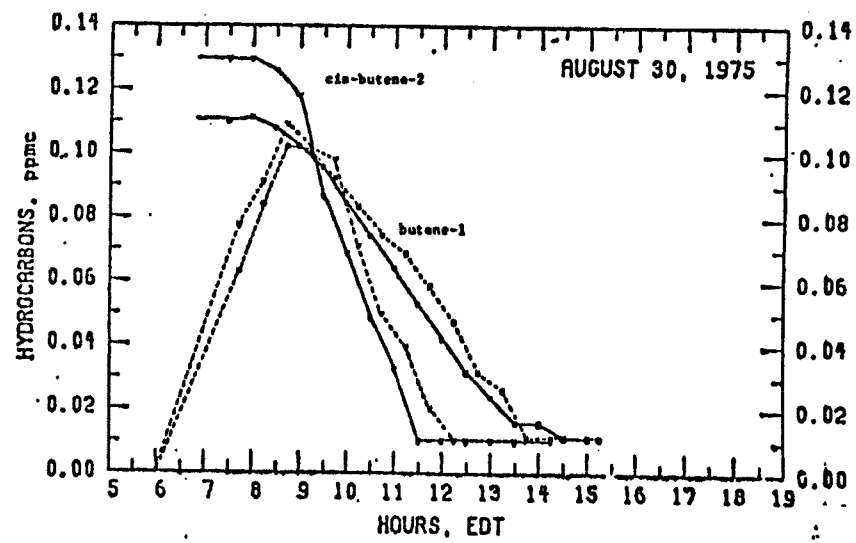


Figure 11 Selected hydrocarbon compounds in Urban hydrocarbon mix for Static (—) and Ramp injection (---) Dual Run in UNC Outdoor Smog Chamber.

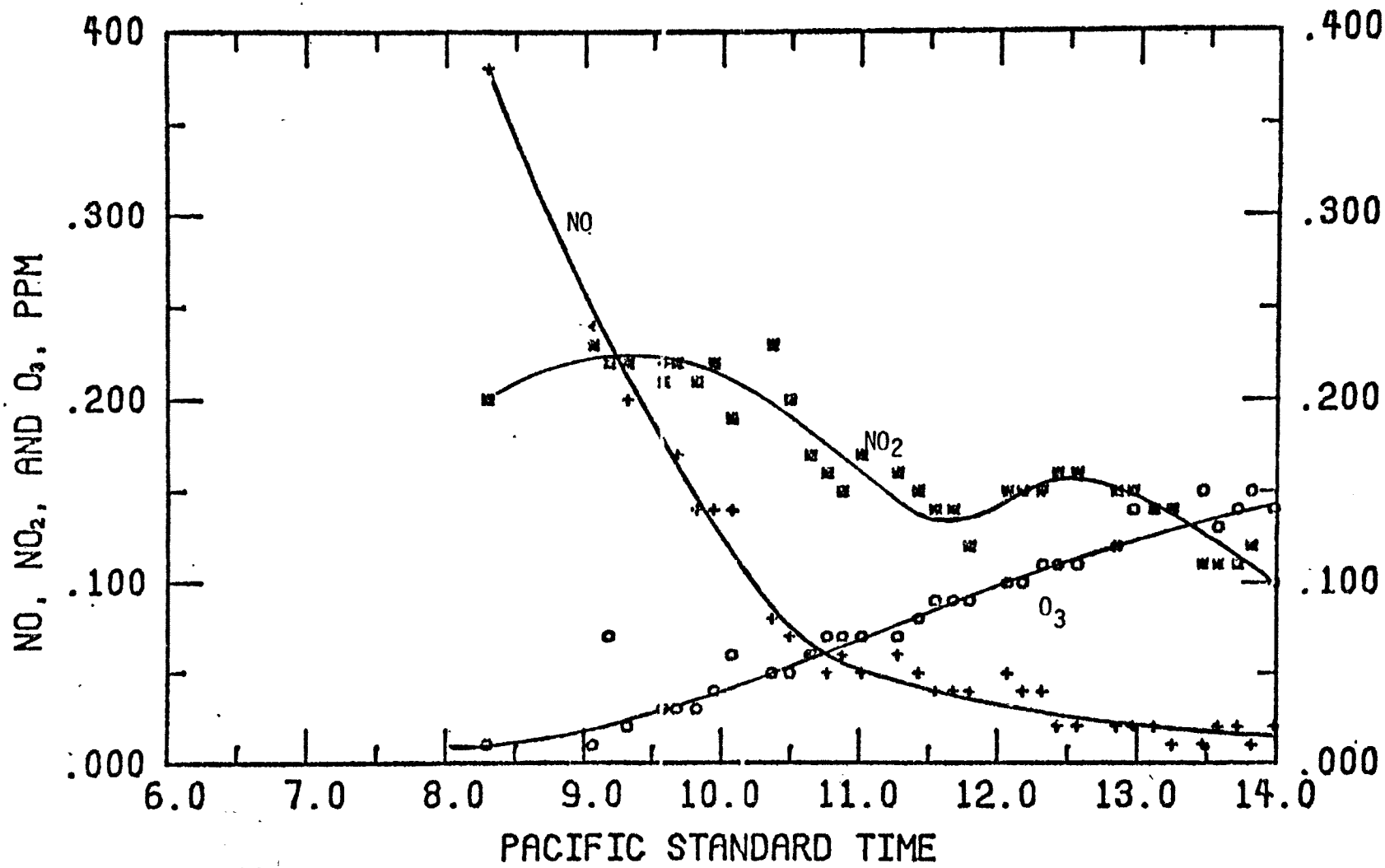


Figure 12. Mean concentrations of nitric oxide, nitrogen dioxide, and ozone around helicopter patterns within the well-mixed region.

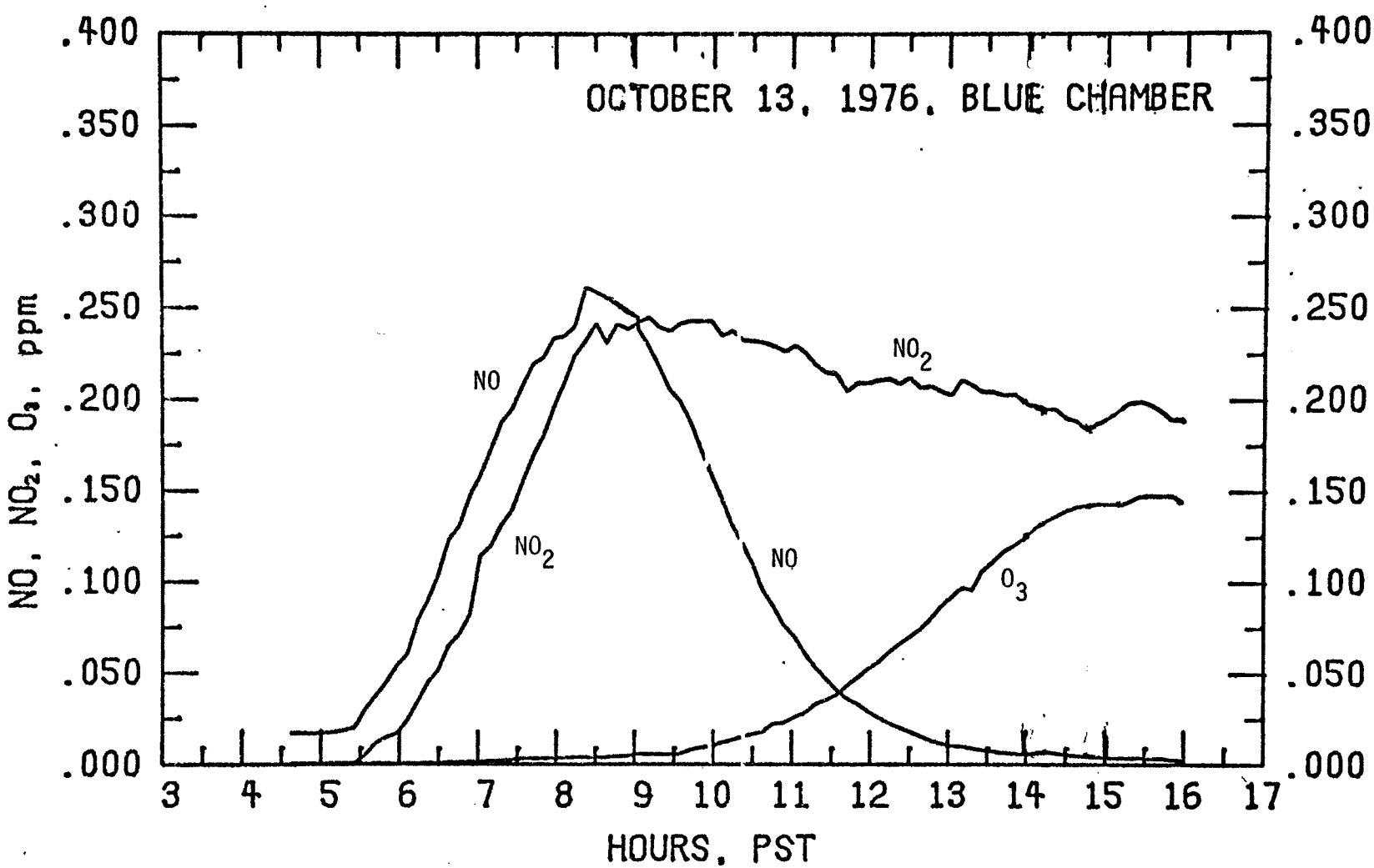


Figure 13 Chamber Simulation of LARPP Operation 33

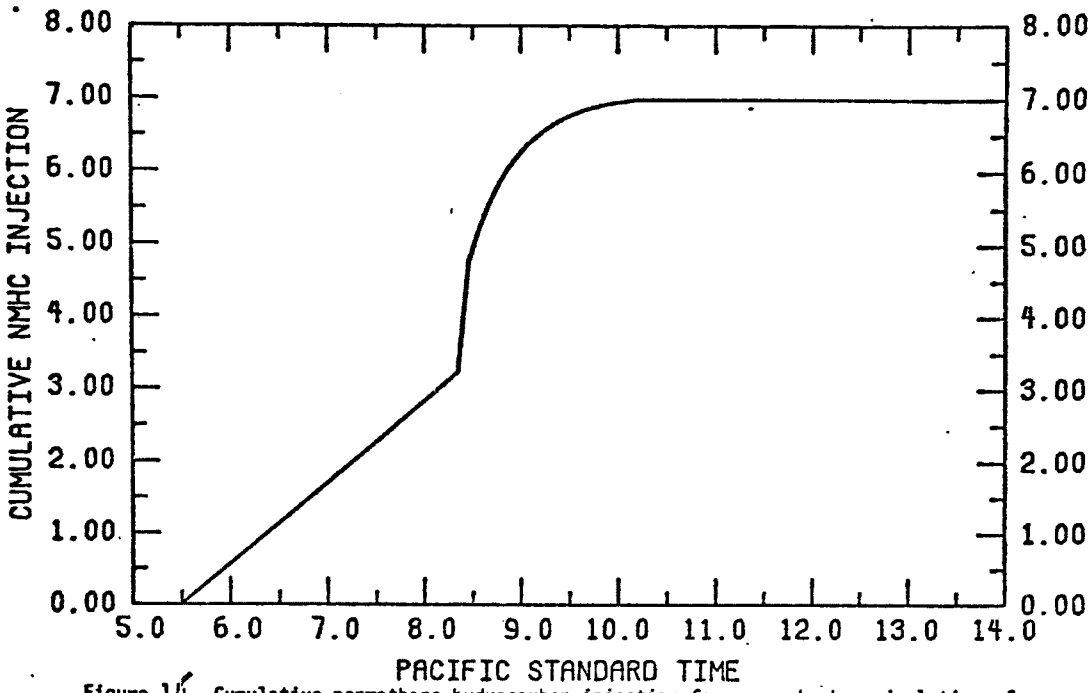


Figure 14. Cumulative nonmethane hydrocarbon injection for smog chamber simulation of LARPP Operation 33.

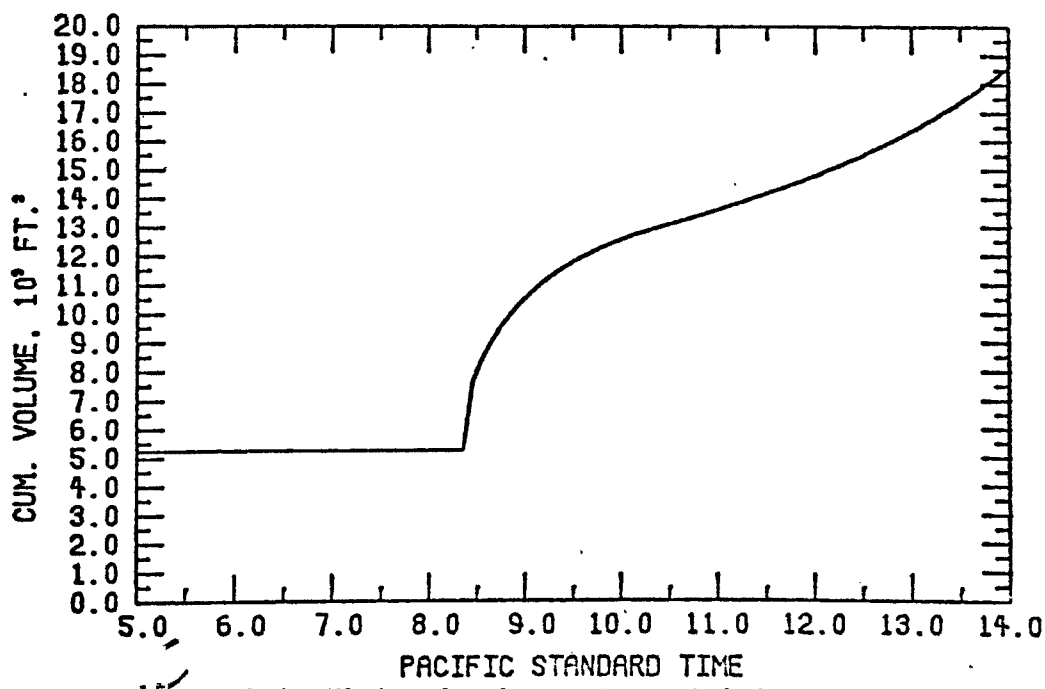


Figure 15. Cumulative dilution volume for smog chamber simulation of LARPP Operation 33.

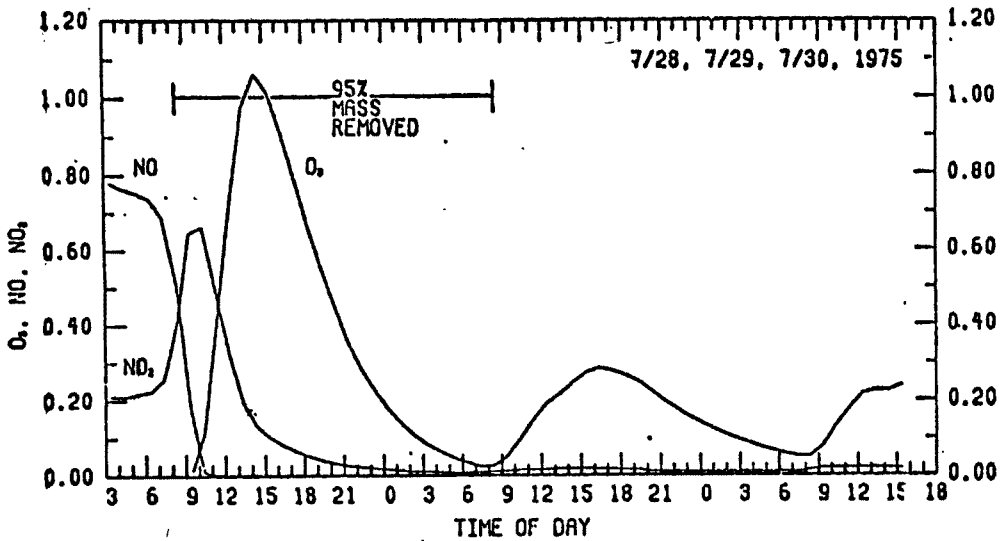


Figure 16 Three day outdoor run with dilution. Initial conditions: NO_x, 1.00 ppm; NO_2, 0.21 ppm; Urban mix, 7.02 ppmC in RTI outdoor smog chamber number 1. Dilution began at 0830, 7/28 and continued for 24 hours at a rate of 12% hr^{-1}.

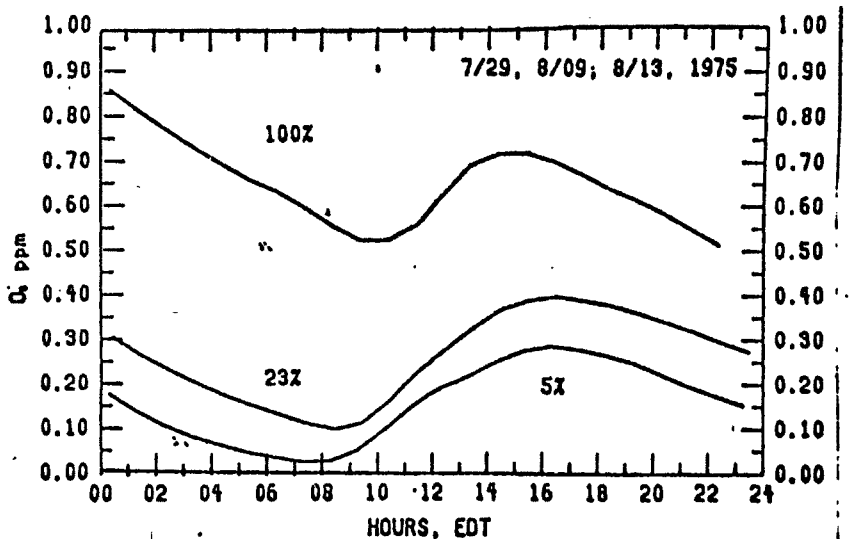


Figure 17 Second day ozone profiles for three dilutions at same first day initial condition (NO_x, 1.00 ppm; NO_2, 0.21 ppm; urban mix, 7.02 ppmC) in RTI outdoor chambers.

The Concept of Prevention of Photochemical Oxidants -- with Reference to Results of Smog Chamber Experiments

Japanese Delegation

1. On Results of Smog Chamber Experiments; Japanese and Overseas

1.1 Air Pollution by Photochemical Reaction

Photochemical air pollution is defined as the mixture of hydrocarbons and nitrogen oxides in the atmosphere subjected to the radiation of sun light (especially the ultraviolet component of sunlight). The product of this mixture is the formation of new compounds such as photochemical oxidants. The reaction mechanism of the photochemical air pollution in the environmental atmosphere is very complicated, and the characteristics of the reaction process can be summarized in the results of previous smog chamber experiments as shown in the following.

(a) Rapid oxidation of nitric oxide to nitrogen dioxide.

(b) Decrease of initial hydrocarbons.

(c) Increase of aldehydes.

(d) Increased concentration of ozone.

(e) Decrease of nitrogen dioxide.

(f) Increase of nitrates.

(g) Increase of aerosol.

However the coexisted substances such as sulfur dioxide, etc. participate in the photochemical reaction in the environmental atmosphere in addition to the hydrocarbons and the

nitrogen oxides, thus the process covering the whole reaction system is very complicated.

In order to qualitatively, as well as quantitatively, explain the photochemical reactions of non methan hydrocarbons and nitrogen oxide complexes in environmental atmospheres, studies using the following methods have been actively carried out to date:

a) 1. a method to measure hourly changes of reactants and generated products by irradiating mixtures of nonmethane hydrocarbons and nitrogen oxides with artificial light (or sunlight) in a smog chamber.

a) 2. a method similar to the above a)1, in which environmental air samples will be collected in a smog chamber. Since the Environment Agency is conducting experiments with a smog chamber loaded in a car, these are called the mobile smog chamber experiments.)

b) a method whereby the photochemical reactions will be modelled and the calculation of numerical values will be made according to a series of the modelled reaction formula, thereby quantitatively estimating the reaction process.

c) Not only the concentration and the composition of reactants as well as the intensity of ultraviolet ray change

in terms of time and space, but also such conditions as climate and geography are complicatedly intermixed, which will inevitably contribute to the generation of photochemical oxidants. This is an analysis method by using the environmental measurement data which express comprehensively such phenomenon.

1.2 On Different Smog Chamber Experiments

A detailed review of smog chamber experiments on photochemical air pollution reveals that different conditions are applied for different experiments. They can be categorized as follows:

1) Samples
   a) NMHC and/or NO_x, independent or mixed
   b) Diluted automotive exhaust gas
   c) Ambient air
2) Irradiation: type and intensity
   a) Artificial light
   b) Natural light
3) Materials and size of the smog chamber
4) Methods of measurement and analysis of reactants and products.
5) Conditions of experimentation: initial concentration of reactants; temperature; humidity; agitation (or no agitation); duration of experiment.

6) Replenishment (or no replenishment) of air samples for measurement and analysis consumed in the chamber.

A straightforward comparison of the results of experiments without due consideration to above-mentioned variations in their conditions would be meaningless. This is a point that calls for attention in utilizing any experimental data.

1.3 Outline of the Results of Photochemical Reaction Experiments by a Smog Chamber

The smog chamber experiments conducted both in U.S.A. AND Japan have clarified the following points concerning the generation of ozone or photochemical oxidants.

a) The rate with which ozone will be formed is accelerated according to the increase in the initial concentration of nonmethane hydrocarbons and subsequently decelerated when the initial concentration of nitrogen oxides is steadily fixed and the composition of nonmethane hydrocarbons is common. (Fig. 1)

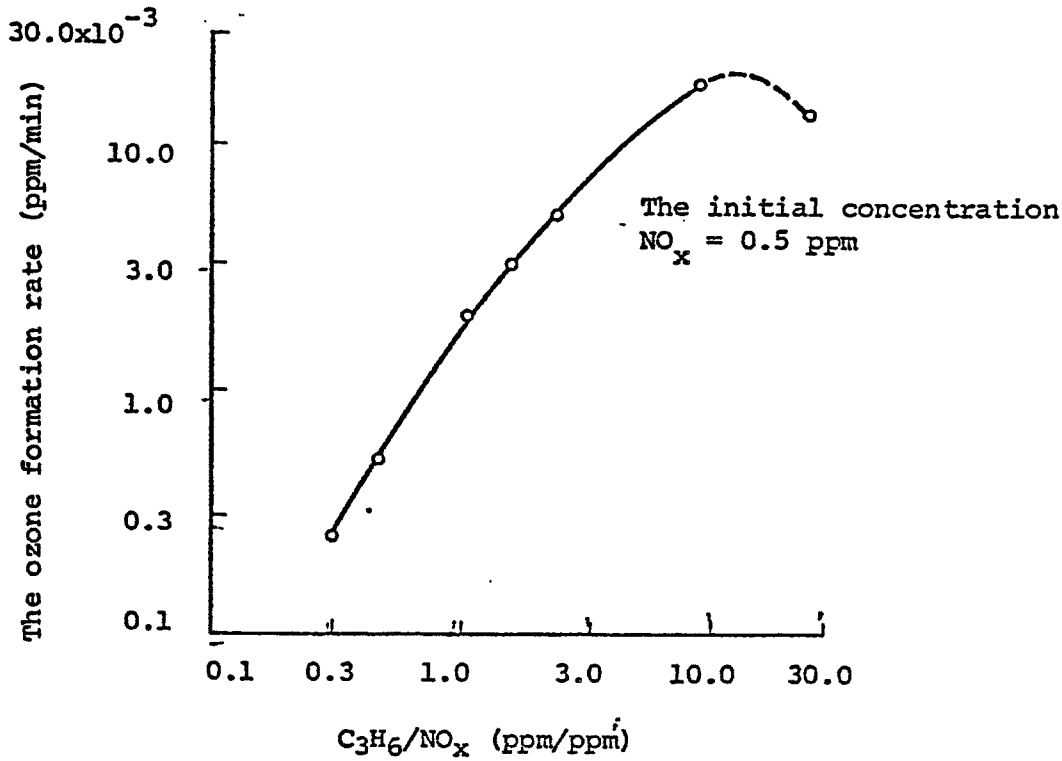


Fig. 1 The ozone (O_3) formation rate when the initial concentration of nonmethane hydrocarbons is steadily fixed and the concentration of propylene is altered (source: Yanagihara ....., 1975)

Note: Figures 1-3 show the results of experiments using propylene as one example, but similar relations have been elucidated by experiments using hydrocarbons other than propylene or automotive exhaust gas.

b) The higher the initial concentration or nitrogen oxides, the higher the maximum concentration of ozone when nonmethane hydrocarbon concentrations are high and the reactivity is sufficiently large. (Fig. 2)

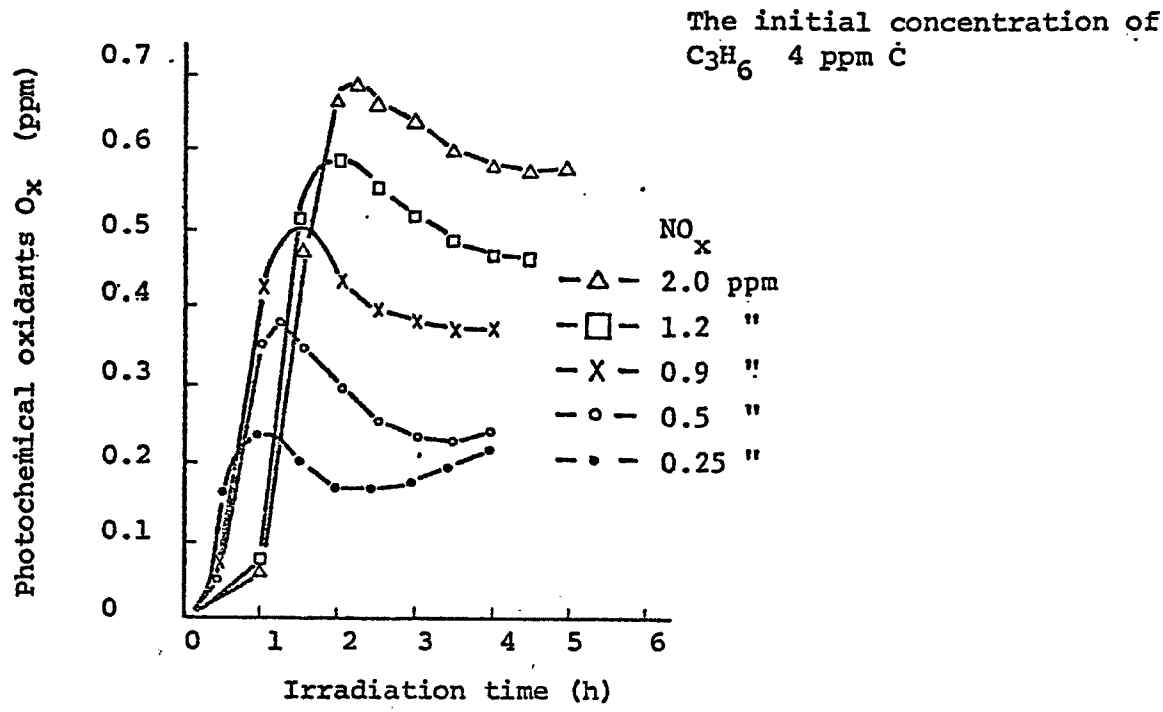


Fig. 2 The formation of photochemical oxidants when the initial concentration of propylene is steadily fixed and the concentration of NO_x is altered (source: Yanagihara....., 1971)

:) The maximum concentration of ozone is affected by the initial concentration ratio of nonmethane hydrocarbons to nitrogen oxides when the composition of nonmethane hydrocarbons is equal. Fig. 3 shows the relations between the maximum concentration of ozone and the initial concentrations of nonmethane hydrocarbons and nitrogen oxides. In this connection, it is known that the formation of ozone will be also affected by the intensity of light irradiation. the irradiation time, temperature, hymidity, sulfur dioxide, etc. As is clearly shown by Fig. 3, the maximum concentration of ozone will become higher when the concentration ratio of

nonmethane hydrocarbons and nitrogen oxides remains within a certain range.

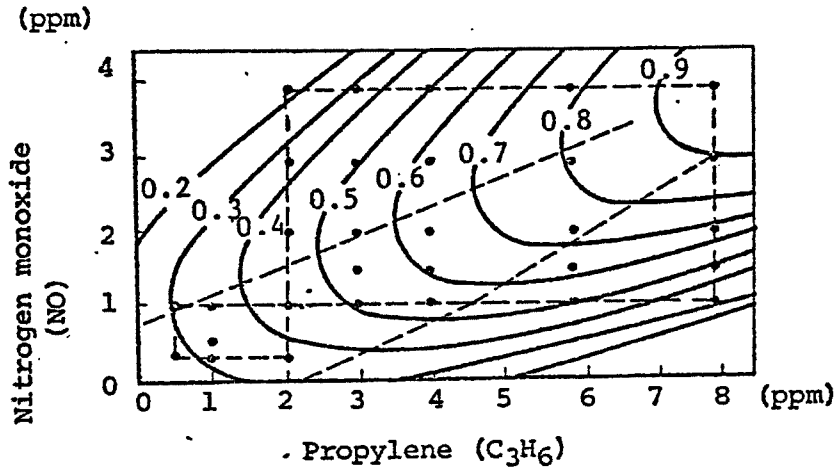


Fig. 3. Relations between the concentrations of propylene and nitrogen monoxide and the maximum concentration of ozone (ppm)-- (concentration lines for ozone, etc. have been obtained by a regressive formula and a coefficient of correlation is 0.84) the mark o represents the experimental value (source: Romanovski, 1967)

Furthermore, when the initial concentration ratio is fixed on the same level as the above (the ratio of hydrocarbons and nitrogen oxides which activates to a considerable extent the formation of ozone), the experiment using automotive exhaust gas also shows that the maximum concentration of ozone will increase in proportion to the initial concentration. (Fig. 4)

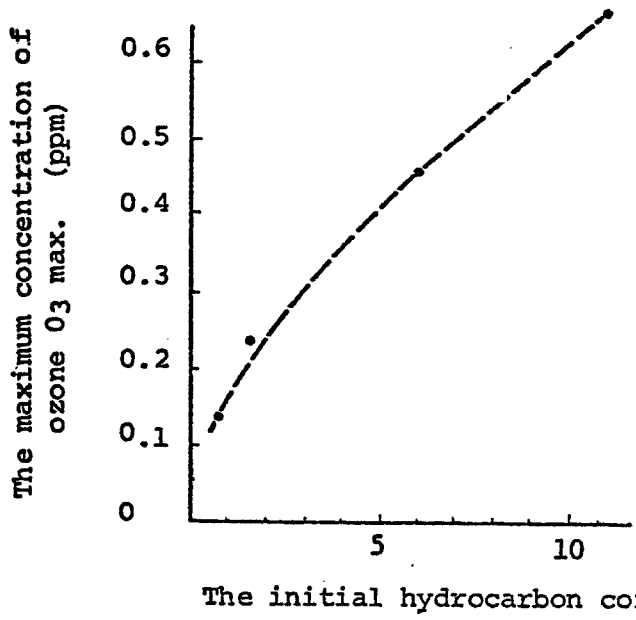


Fig. 4 The maximum concentration of ozone arising from automotive exhaust gas when the ratio of hydrocarbons and nitrogen oxides is almost steadily fixed
(HC/NO_x = 7-10; ppmC/ppm)
(source: Yanagihara ....., 1975)

Also it is reported from another experiment using automotive exhaust gas that, when the initial concentration ratio of hydrocarbons and nitrogen oxides is less than 2.5--hydrocarbons (ppmC)/nitric oxides (ppm)--, the formation of ozone is extremely slow and the ozone concentration will never exceed 0.1 ppm, regardless of the initial concentrations of hydrocarbons and nitrogen oxides, even after 5-6 hours of irradiation of light almost equal to sun light.

In Japan Yanagihara has concluded that protochemical oxidants will not exceed 0.1 ppm if in particular nonmethane hydrocarbons is below 0.4-0.5 ppmC.

In this manner, numerous results of the smog chamber

experiments have been reported from the past. These results are generally highly reliable: for example, the above experiment using automotive exhaust gas shown in Fig. 5 has been made under such conditions that hydrocarbons and nitrogen oxides were fixed at more than 0.1 ppmC and 0.08 ppm respectively. However, since a smog chamber experiment under the condition of low concentrations will face many difficulties such as the loss of reactants and substanced produced within a chamber, and other significant effects which cannot be neglected, reliable results have not been reported so far under such conditions that the initial concentrations of hydrocarbons and nitrogen oxides are fixed at less than 0.1 ppmC and 0.05 ppm respectively.

1.3 Outline of the Results of Photochemical Reaction Experiments Made by a Mobile Smog Chamber

The Environment Agency has been yearly carrying out irradiation experiments with a mobile smog chamber taking environmental atmospheres with different composition of reactant concentrations as air samples since the summer of 1972. Figs. 6 and 7 show the results of these experiments. These experiments may not be completely reliable beceause they include somewhat inaccurate measurements of nonmethane hydrocarbons and nitrogen oxides and very few attempts have been made to carry out adequate measurements to cover the

total scope of nonmethane hydrocarbon as well as nitric oxide concentrations. Yet, very roughly speaking, we may safely draw the following conclusions:

a) There is a tendency that as the concentration of nonmethane hydrocarbons will become higher, the maximum concentration of ozone will increase;

b) The maximum concentration of ozone will not exceed 0.1 ppm, with one exception, when nonmethane hydrocarbon concentrations are approximately less than 0.4 ppmC or the concentration of nitric oxides is approximately less than 0.04 ppm;

c) It is difficult to show an equal concentration line for the maximum concentration of ozone as the function of nonmethane hydrocarbons and nitric oxides.

2. Problems

Laboratory studies such as smog-chamber experiments and numerical computations using photochemical reaction models provide us with useful findings on the mechanism of photochemical reaction and relationships between reactants and products. Various problems arise, however, when attempts are made to draw on these results to establish measures against oxidant formation on the assumption that these results represent actual atmospheric phenomena.

There are, in the first place, problems in the smog-chamber experiments as such. Normally reactants are not replenished after ultra-violet irradiation in smog-chamber experiments. In other words, the most important substances in oxidant formation such as NO_x and NMHC are only consumed, and results can never be identified with phenomena in the actual atmosphere. The use of numerical simulation may enable the establishment of a reaction system which takes into account reactions at very low concentrations, replenishment and diffusion of substances, etc. This is a task that we must come to grips with in the future.

Secondly there are problems of fluctuation of NO_x and NMHC concentrations in the ambient atmosphere. In the real ambient atmosphere NO_x and NMHC fluctuate greatly over time and between places. Therefore even if certain O_x or O_3 isopleth were obtained in the smog chamber, in actual application an isopleth at maximum oxidant concentration must be considered

taking into account the fluctuation of its initial value.

In the third place, oxidants or ozones are only one of several indices of photochemical air pollution, and the reduction of these alone will not prevent photochemical air pollution. Health effects of photochemical air pollution are in the main irritation of the mucous membranes of the eye, throat, etc. According to a study by Romanovski, the irritation of the eye corresponds relatively well to the HC concentration. It is deemed that such irritation is caused by the occurrence of peroxy radical of HC as an intermediate of the oxidant formation process, or by the formation of aldehydes and organic nitrates such PAN and PBzN. In addition, inorganic nitrates are formed from oxides of nitrogen by photooxidation. It is often pointed out that all these products cause health effects such as irritation of mucous membranes. Consideration of nothing but oxidants therefore would be inadequate in countering photochemical air pollution.

3. Approach to O_x Control on the Basis of Present Scientific Findings

We would like to consider ways and means to achieve the environmental standard for oxidants by drawing on the results of smog-chamber experiments and NO_x and NMHC concentration measurements in early morning with due attention to the abovementioned aspects. Not many measurements of NMHC have been conducted in Japan so far.

According to a measurement of air pollution in the urban center of Tokyo, HC, NO_x and HC/NO_x fall within the following ranges of concentration as shown in Table 1.

Table 1. Air Pollutions: Early Morning Concentrations in the center of Tokyo

		NMHC *	NO_x *	$NMHC/NO_x$
1974 June–Sept.	Max	1.30 ppmc	0.15 ppm	21
	Min	0.25	0.03	2
	Mean	0.667	0.073	7
	S.D.	0.191	0.044	-
1975 May–Sept.	Max	1.40	0.12	35
	Min	0.10	0.01	2
	Mean	-	-	8
	S.D.	-	-	-

* 6-9 a.m. average a concentrations.

Oxides of nitrogen are major reactants along with NMHC in the formation of photochemical oxidants, and it is said furthermore that the amount of O_x produced is greatly affected by the ratio of centrations of these two precursors. In other words, ozone, the major component of O_x, is scavenged by NMHC when NMHC is in excess, and by NO when NO_x is rich. The role of hydrocarbons is to promote oxidation of NO into NO_2. Ozone is formed when NO_2 dissociates by photolysis into NO, and both HC and NO become scavengers of O_3. Isopleths are drawn Figs 5~6) when expressing the relationships of the concentrations of these three.

The concentration of air pollution in Japan is substantially lower than that in California U.S.A., and the estimate that the HC/NO_x ratio is unfavorable for O_x formation cannot be denied. Yet the theory that O_x concentration should be reduced by manipulating the ratio cannot be applied to Japan in reality.

Looking at the present situation in Japan, reduction of either precursor will lower O_x concentration.

In Japan where NO_x reduction has been implemented on NO_2 as a precursor of O_x formation and for its health effects, a realistic approach would be to reduce hydrocarbons simultaneously.

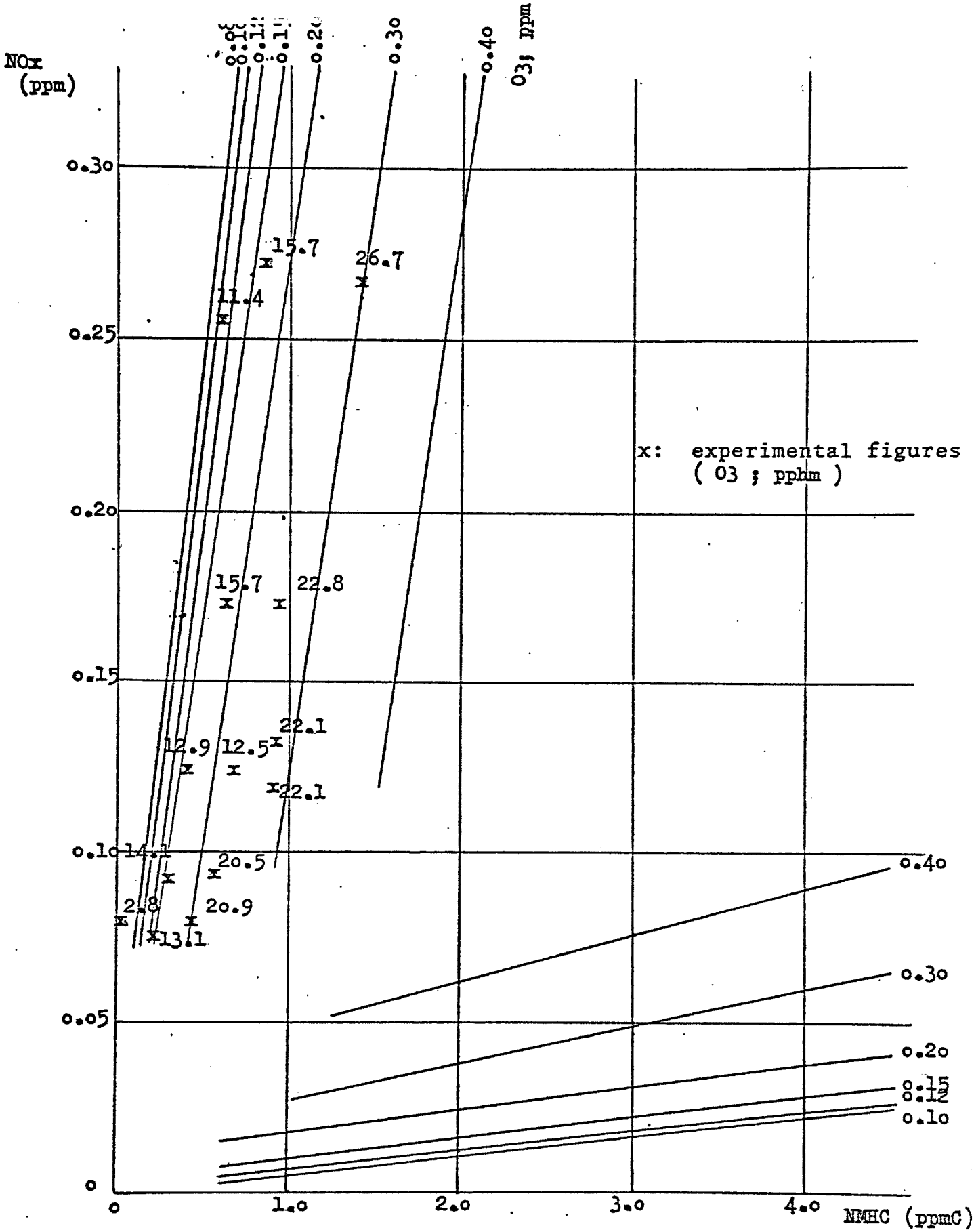


Fig. 5 O_x isopleths (by Demitriades)

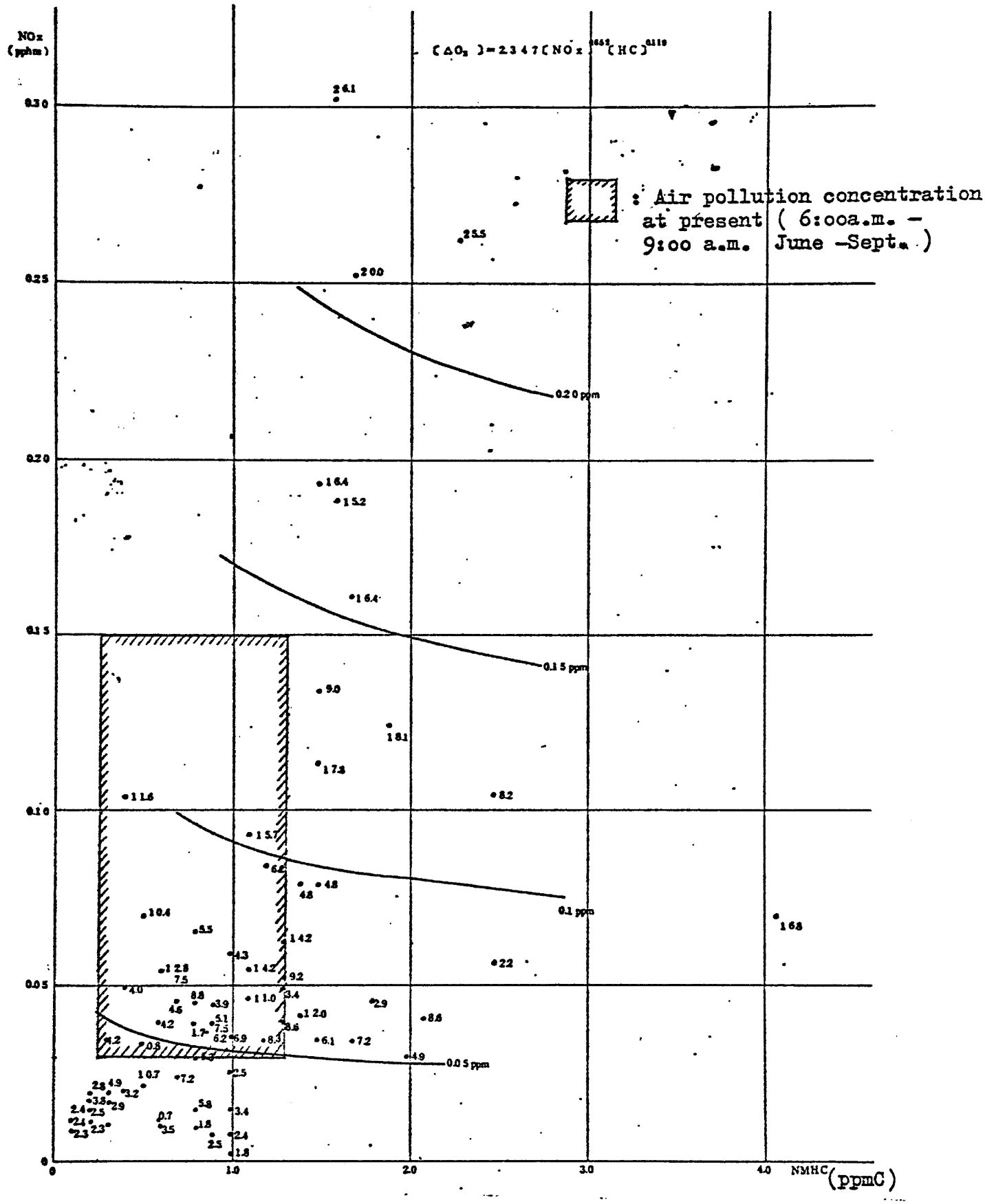


Fig. 6 Results of mobile smog-chamber experiments

Nitrogen Oxides Control Measures in Japan

(Environment Agency)
Japanese Delegation

1. Introduction

Nitrogen oxides are one of the pollutants that require the greatest attention because they not only have a deleterious effect on human health but also are one of the precursors of photochemical air pollution — so much so that the nitrogen oxides control measures have been progressively replacing in importance the sulphur oxides control measures.

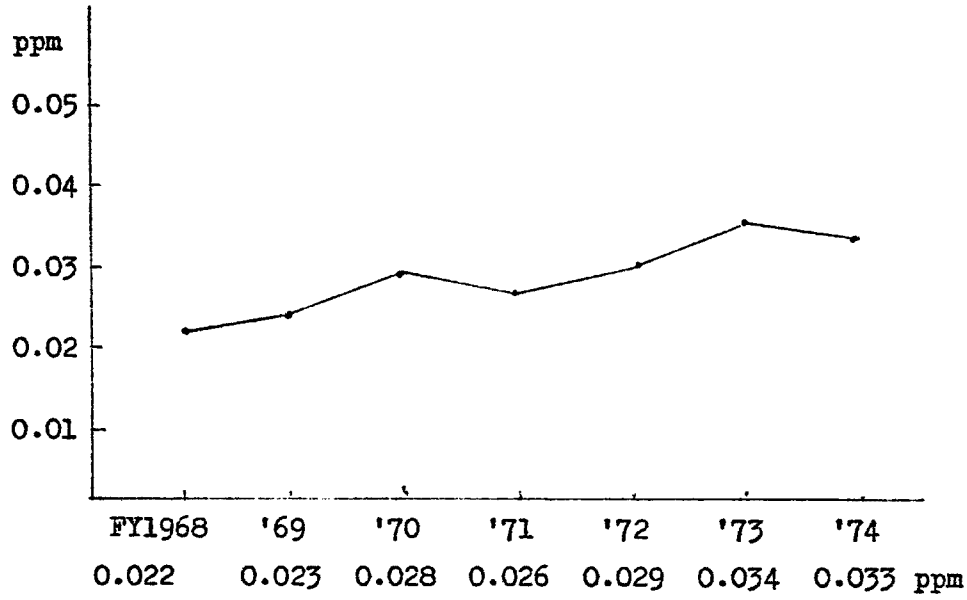
Since early in 1965, the rapid progress of air pollution by nitrogen oxides has been attracting increasing attention. Since the sensational "photochemical smog incident" that occurred in July 1970 at the Rissho Senior High School in Tokyo where many students complained of photochemical smog symptoms, there has been rapidly increasing social interest in nitrogen oxides, along with hydrocarbons, as the precursors of photochemical smog.

Nitrogen oxides are air pollutants that are produced inevitably in the course of combustion at high temperatures and their chief sources are factories and motor vehicles but there are many and diverse smaller sources that cannot be ignored such as domestic heating. The contamination of nitrogen oxides in ambient air is closely related to the expansion of economic activities and the improvement of our standards of living.

The progress of regional development, increased income and mortorization proceeding from the rapid economic growth achieved

since the 1960's have brought about such rises in the concentrations of nitrogen oxides in ambient air as shown in Fig. 1.

Fig. 1 Change in annual mean NO_2 concentration (Average of 6 monitoring stations)



Note: Saltzman coefficient : 0.72

Fig. 1 shows the change in nitrogen dioxide concentration, measured continuously since 1968 at six state-operated air pollution monitoring stations.

Fig. 1 shows that this average leveled off from FY1973 to FY 1974. However, the yearly average increased by 0.011 ppm during the six years from FY 1969 to FY1974. (Japan's GNP increased from ¥63,000,000 million to ¥136,000,000 million during the same period.)

By way of studying the geographical distribution of nitrogen oxides pollution in Japan, the NO_2 and NOx distributions in FY1974

in the southern part of the Kanto Region where Japan's industrial and administrative nerve centers are concentrated were as shown in Figs. 2 and 3. The air pollution by these pollutants is spreading from the industrial zones along the Bay of Tokyo to the widespread inland areas.

Taking a look at the annual mean NO_2 concentration at 245 monitoring stations which measured the concentration continuously during the two years' period of FY1973 and FY1974, it is seen that the NO_2 concentration lowered at 28% of the monitoring stations, levelled off at 67% and rose at 5% during the two years, suggesting the gorwing signs of improvement of air quality due to the increasing energy saving because of economic recession and the effects of the anti-pollution regulations that have been enforced since 1973.

2. Ambient air quality standards for Nitrogen dioxide

(1) Nitrogen oxides not only reach easily into the depth of lungs by respiration and produce by itself harmful effects -- even more harmful than sulphur oxides -- in lungs and other organs, but synergistic effects with sulphur oxides and suspended particulate matter are observed. They also are precursors of photochemical oxidants. Particularly, in the urban and industrial areas where a large population and industrial plants are heavily concentrated, establishment of ambient air quality standards that serve as a basis for evaluating the level of ambient air concentrations and implementing emission control

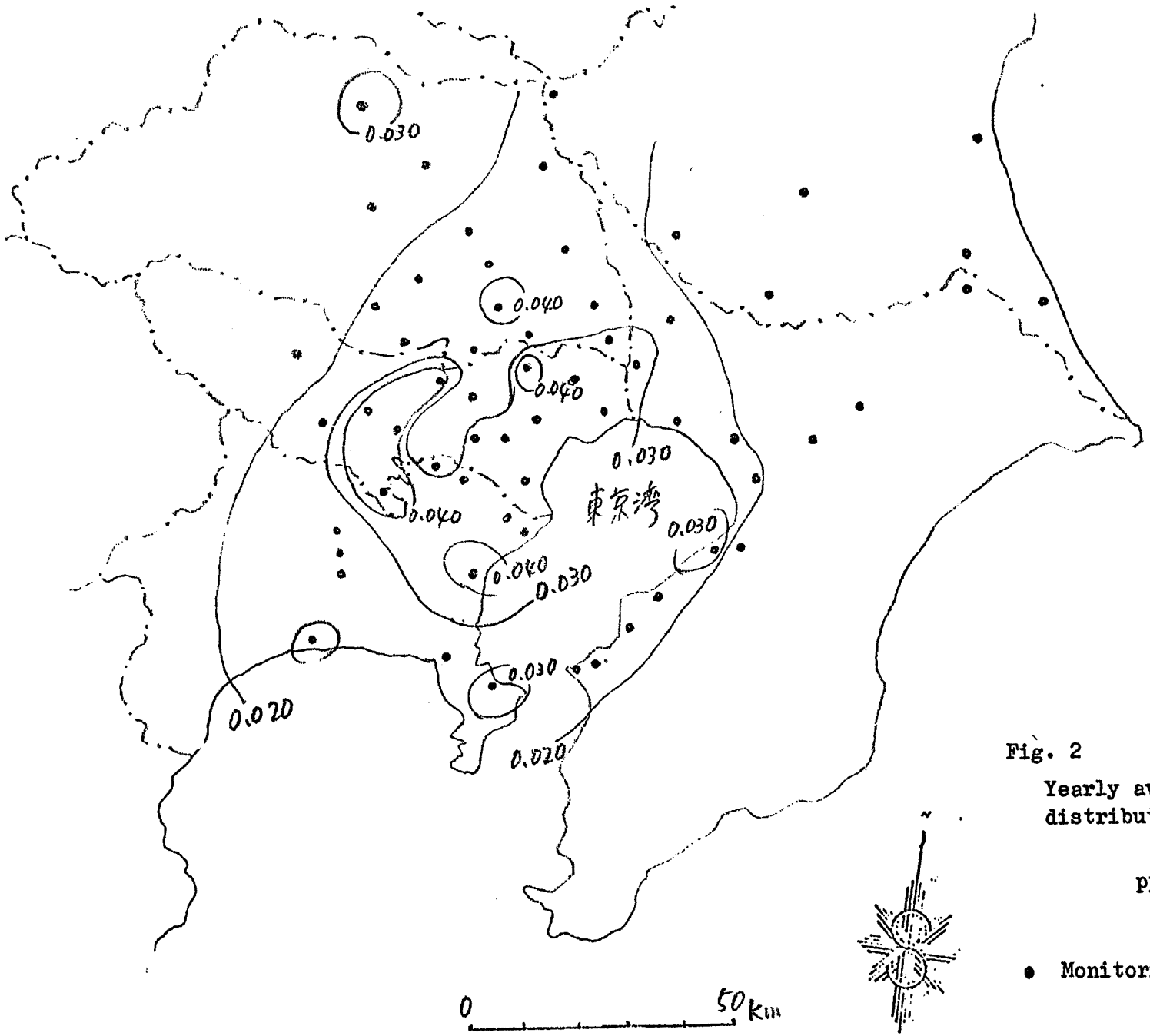


Fig. 2

Yearly average NO_2 value distribution

- 1974 -

ppm

● Monitoring Station

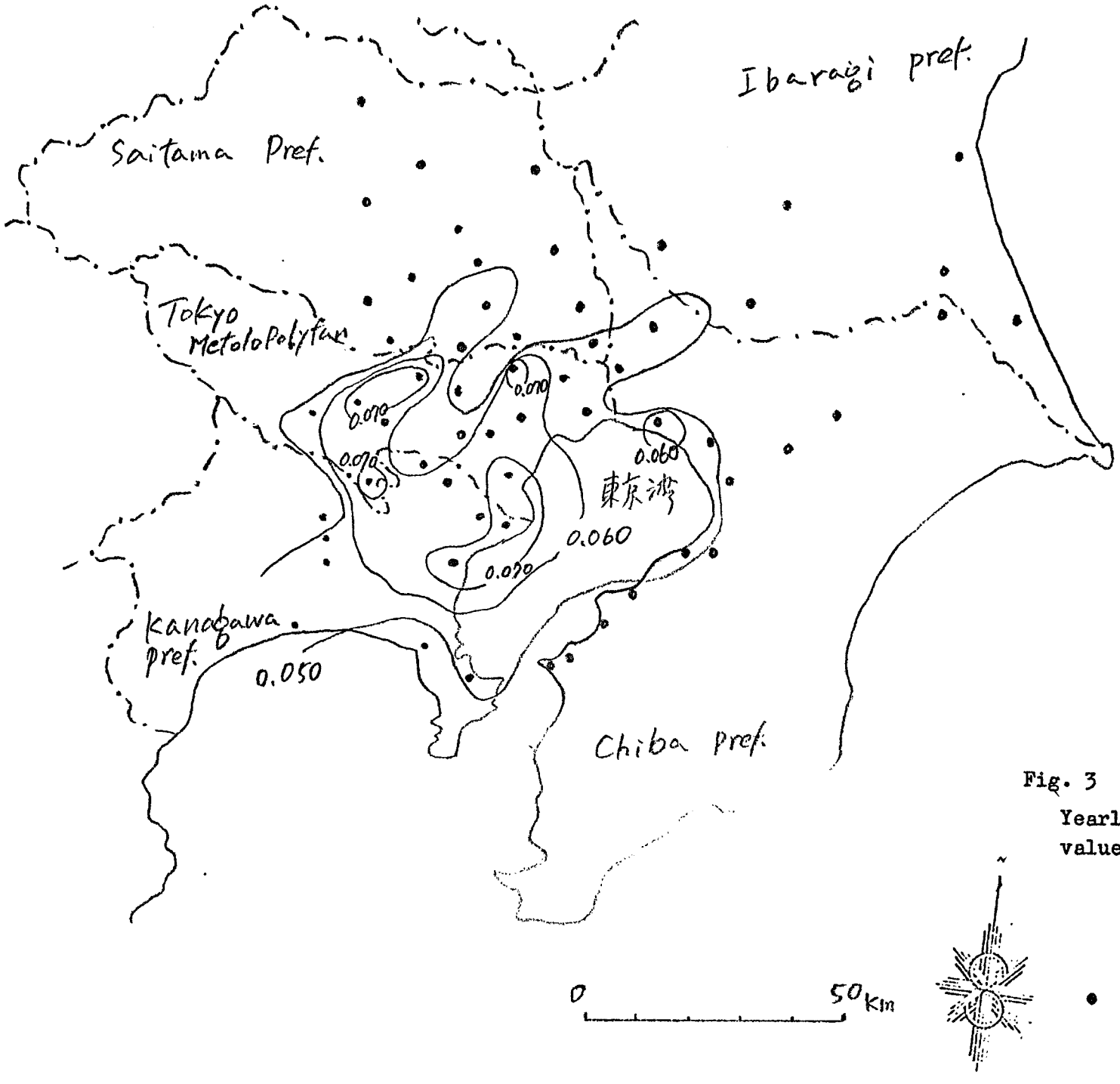


Fig. 3

Yearly average ($NO + NO_2$) value distribution

- 1974 -

ppm

● Monitoring Station

measures was an urgent necessity in order to protect human health in such areas.

Under such circumstances, the ambient air quality standard for nitrogen dioxide were established in May, 1973. The Experts Committee for the ambient air quality standards for nitrogen oxides under the Central Council for the Control of Environmental Pollution stressed in its report the further necessity of establishing an ambient air quality standard for nitrogen monoxide along with that of nitrogen dioxide. The standard provides that "daily average value of hourly values shall not exceed 0.02 ppm." The period for the attainment of the standard was also decided as follows: unless otherwide required, the standard shall be met as soon as possible within five years, although in areas where the industrial activities and the population are extremely concentrated with consequent high concentrations of nitrogen dioxide and the attainment of the newly established standard is difficult because of the lack of effective control technique available, the standard shall be met within eight years.

The ambient air quality standards for nitrogen dioxide was not decided on account of its relationship to photochemical oxidsnts but was established on account of the toxic effects of nitrogen dioxide itself, taking into consideration the combined effects of sulfur dioxide and dust.

(2) The ambient air quality standards for nitrogen dioxide were established on the basis of the results of medical examinations conducted in Japan and abroad before June 1972. Unlike in the case of sulphur oxides, the epidemiologic al data concerning the long-lasting effects of serious nitrogen dioxide pollution on human health had not been sufficiently accumulated and the available data were limited. However, the data obtained by experiments with animals had been fairly well accumulated in Japan and other countries. On the other hand the measurements of air pollution by nitorgen dioxide were rather new compared with the measurements of sulphur oxides both in Japan and abroad and the methods of measurement and analysis were liable to errors to some extent at relatively low levels of nitrogen dioxide in the air.

The air pollution by nitrogen oxides tended to gradually increase year after year to the extent that it could not be ignored from the viewpoint of its effects on human health and the ambient air quality standards for nitrogen dioxide were established in May 1973.

The scientific basis on which the ambient air quality standards for nitrogen dioxide has been much discussed since last year, because nitrogen oxides have a higher degree of indeterminancy than sulphur oxides and yet the nitrogen dioxide control measures to be taken are expected to have serious social and economic effects. Unlike in the case of sulphur oxides,

where control measures were taken only after many serious cases of damage caused to human health such as the abnormally high incidence of respiratory disease in the vicinity of the large industrial complex in Yokkaichi and the very serious cases of smog hazards in London, the air quality standards for nitrogen dioxide have been set up as a target for the long range administrative efforts to be achieved and maintained by long-range administrative efforts to protect human health by preventing the serious danger of air pollution by nitrogen oxides.

The Basic Law for Pollution Control provides that the environmental standards should be constantly subjected to proper scientific judgement and necessary amendment. However, as far as the existing ambient air quality standards for nitrogen dioxide is concerned, there have hitherto been obtained no new scientific findings sufficient to make any amendments to the standards.

The Environmental Agency is presently making a comprehensive analysis of the data obtained from the five-year survey on health damage caused complex air pollution and is tabulating the results of the survey on the health hazards of air pollution along National Highway No. 43 and Tokyo-Nagoya Expressway. A conference of experts on the criteria for the measurement of nitrogen dioxide air pollution and its effects is now held under the sponsorship of the World Health Organization (WHO) in Tokyo during later in August 23 to September 4.

The Environmental Agency is planning to reappraise the existing air quality standards for nitrogen dioxide on the basis of all such findings.

As for the social and economic effects caused by the environmental pollution control policy, the Organization for economic Cooperation and Development (OECD) is planning to undertake the Review of the Environmental Policy of Japan in Tokyo in the autumn of 1976 and thus obtained results will also be of great value for us in carrying on our nitrogen dioxide air pollution control measures in the future.

The ambient air quality standards of Japan are sometimes discussed in comparison with those in other countries. All those countries use the same term "ambient air quality standards" but their statutory charactor, method of application, the proceeds and scientific basis for such standards and method of evaluation vary from country to country and therefore it would be not appropriate to compare the standards of different countries simply by using the standard values employed in those countries.

3. Nitrogen oxides control measures

Remarkable technical advances have been made in the control of nitrogen oxides contents in motor vehicle exhaust emissions partly due to the promulgation of the ambient air quality standards for nitrogen dioxide in May 1973. All the automobile manufacturers are making vigorous efforts to achieve the initial target value of 0.25 g/km. (explained in this chapter)
Strenuous efforts are also being made for the development of techniques for controlling the emission of nitrogen oxides from stationary sources with a view to achieving the ambient air quality standards. Speaking about denitrating technology, it has been made technically possible if the emission gases are clean containing no sulphur oxides and no dust or only in very small quantities, and it is highly probable that the dirty exhaust gases which contain sulphur oxides and dust will be controlled effectively within one or two years to come. Such are the results of the efforts so strenuous as unparalleled anywhere else in the world and the incentive effects of the very strict ambient air quality standards on technological developments.

It is necessary for the nitrogen oxides emission control measures to be carried on steadily on the basis of such technological advances achieved in this field. It is also evident that the programs for achieving the standards must be put into practice, taking into consideration the social and economic effects of the enforcement of such control measures.

It may be said that the most important task left for use to

tackle in the future is to set the nitrogen oxides control measures oriented to the prevention of health hazards on the right and solid track, humbly reflecting on the fact that the anti-pollution measures were not taken quickly enough to cope with the actual situation in many cases in the past.

(1) Measures presently in force for the control of nitrogen oxides emissions

1) Measures for the control of stationary sources

With a view to attaining and maintaining the ambient air quality standard for nitrogen dioxide, the emission standards for nitrogen dioxide were established in August 1973 pursuant to the Air Pollution Control Law and were revised in December 1975.

The revised emission standards are applicable to about 3,000 nitrogen oxides-emitting installations, thereby to control about 60% of the nitrogen oxides emitted by all sooth and smoke emitting installations. As a result of these standards the total nitrogen oxides emissions are estimated to be reduced by about 25%.

Nitrogen oxides are generated by a variety of facilities ranging from boilers and various kinds of manufacturing furnaces to nitric acid manufacturing facilities and of facilities with varying scales. Initially, priorities were given to controlling the operation of those facilities which generated large quantities of nitrogen oxides or in heavy concentrations.

Under this approach, emission control was directed toward improving combustion of fuels by applying technologies designed to reduce the formation of nitrogen oxides available in 1975 (see Table 3). Kinds of facilities which are subject to control at present include boilers, oil heating furnaces, metal heating furnaces, nitric acid manufacturing facilities and coke ovens. In terms of scales, only those boilers, metal heating furnaces and oil heating furnaces having a capacity of 10,000 Nm^3/h or more and those cement kilns and coke ovens which are newly installed and have a capacity of 100,000 Nm^3/h or more are subject to control, while all nitric acid manufacturing facilities are subject to control regardless of their scales.

Table 3 Emission standards relating to nitrogen oxides

Facilities		Standard values for	
Description	Scale (Nm^3/h)	Newly installed facilities	Existing facilities
		(ppm)	
Boiler			
(1) Gas	100,000 or more	100	130
	40,000 - 100,000	130	130
	10,000 - 40,000	130	150
(2) Solid fuel	10,000 or more	480	600
(3) of which low grade coals	10,000 or more		750

Table 3 : (cont'd)

Facilities		Standard values for	
Description	Scale (Nm^3/h)	Newly installed facilities	Existing facilities
		(ppm)	
(4) Liquid fuel	100,000 or more		230
	40,000 - 100,000	150	190 (1)
	10,000 - 40,000		-
(5) of which crude tar	10,000 or more		280
Metal heating furnaces	100,000 or more	100	220 (2)
	40,000 - 100,000	150 (2)	220 (2)
	10,000 - 40,000	150 (2)	200 (2)
Oil heating furnaces	40,000 or more	100	210 (3)
	10,000 - 40,000	150	180 (3)
Cement kilns	100,000 or more	250	-
Coke ovens	100,000 or more	200	-
Nitric acid manufacturing facilities	all facilities	200	200

(Note) (1) excludes those equipped with stack-gas desulphurization equipment.
(2) excludes heating furances used for the manufacture of forge-welded steel pipes.
(3) excludes cracking furnaces used for the manufacture of ethylene, independent super-heating furnaces used for the manufacture of ethylene, reforming furnaces used for the manufacture of methanol and reforming furnaces used for the manufacture of ammonia.

These emission standards are immediately applicable to newly installed facilities, while they will become applicable in two years to the existing boilers and heating furnaces and in three years (the time needed to install high-performance denitrification equipment) to existing nitric acid manufacturing facilities.

However, the emission standards presently in force are applicable to limited scales and kinds of facilities. Furthermore, the values of their standards, are inadequate to attain the prescribed ambient air quality standards. Therefore, their coverage must be expanded gradually and their control values strengthened. At present hearings are being held to gather information on the development of nitrogen oxides control techniques from manufacturers and users for the purpose of enforcing the third regulation of nitrogen oxide emissions. Such control of nitrogen oxides emission may be useful in reducing the overall national average of nitrogen dioxide concentration but it alone is not adequate to effectively reduce the concentration of nitrogen dioxide to the level of its quality standards in individual localities. To remedy such shortcomings, the government decided to introduce the system of total mass emission control pursuant to the Air Pollution Control Law and it is presently conducting researches and studies on the air pollution forecasting method and others.

Measures designed to help the operators of these facilities

emitting nitrogen oxides were primarily concerned with improving the combustion techniques applied in boilers and heating furnaces, such as the adoption of new burner with low NOx formation, low-oxygen operation, two-stage combustion system and exhaust gas recycling system. In the future, however, not only advanced combustion techniques but also stack-gas denitrification technologies will have to be developed as a means of effective reduction on the one hand, together with the measures for switch-over of fuels to gas or distilled oil on the other.

At this point of time, technology for stack-gas denitrification is feasible provided that the stacksmoke does not contain sulphur oxides and dust (commonly referred to as "clean exhaust gas"), and technologies based on large-capacity equipment for denitrificating "dirty" exhaust gas have reached a demonstration stage. The next question will be a rational combination of these measures to bring about the maximum reduction of nitrogen oxides from stacksmoke.

As a rule, the concentrations of nitrogen oxides in stacksmoke must be measured once every two months (or twice a year in the case of facilities having the capacity of emitting exhaust gas less than 40,000 Nm^3/h) in accordance with PDS method, and the competent officials of prefectural governments are empowered to enter the premises of nitrogen oxides emitting facilities for inspection, issue an order for improvement and/or impose penalties for violations.

2) Measures for the control of mobiles sources

i) Control of passenger-car exhaust emissions

In Japan the control on the automobile exhaust emissions was first enforced to cover the new models produced in and after September 1966 in order to reduce the emission of carbon monoxide. In addition to the controls applied hitherto, new permissible limits on the emission of nitrogen oxides (reduced by about 30%) were established in December 1972 for enforcement in and after FY1973 to the ordinary small motor vehicles and light motor vehicles which run on gasoline or liquified petroleum gas.

As a rule, these permissible limits are based on the mass of pollutants emitted. This is a system designed to regulate the mass of pollutants emitted per one kilometer driven by each vehicle as measured by methods under ten mode driving cycle developed on the basis of the findings obtained from analysis of the way motor vehicles are operated in Japanese cities.

As a measure to cope with the frequent occurrence of photochemical smog, models produced to FY1973 were mandated in May 1973 to install an exhaust gas reducing device designed to curtail the emission of nitrogen oxides and hydrocarbons.
In October 1972 the Central Council for Control of Environmental Pollution submitted its interim report under the title of "Methods for long-range setting of Permissible Automotive Exhaust limits" with the result that the average emission value of

0.25 g/kg was established for the target control value to be achieved at FY1976. In January 1974, were established the permissible limits of the various pollutants emitted from passenger-cars for enforcement on models produced in and after April 1975, which were designed to reduce the average emission less than 1.2 g/km for nitrogen oxides.

The control standards enforceable in and after 1976 were announced in February 1975, taking into consideration the state of technological development for reducing nitrogen oxides.

As shown in Table 4, the 1976 control standards have the permissible limits of nitrogen oxides lower than those given by the 1975 control standards. Under the 1976 control standards, the average emission quantity is set at 0.6 g/km for passenger-cars of an equivalent inertial weight (the vehicular weight plus 110kg as the weight of two persons) of 1,000 kg of less and 0.85 g/km for those of an inertial weight exceeding 1,000kg. These standards are applicable to new models in and after April 1976, to the models now in production in and after March 1977, and to the imported cars in and after March 1978.

The intial target value (0.25 g/km in average emission quantity) is required to be attained in FY1978.

With regard to the development of nitrogen oxides emission reducing technology, the engine modification system, thermal reactor system, oxidation catalytic system, prechamber stratified-charge engine system, and rotary engine system have been put to

Table 2 1975-76 Automotive Exhaust Gas Control Standards

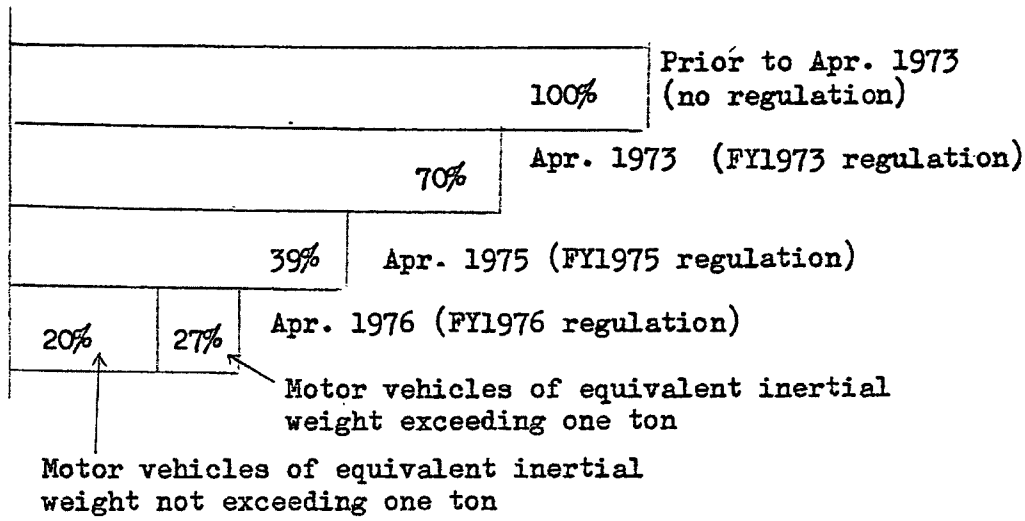
Type of vehicle				Measuring method	Permissible limit					
					1976 regulation			1975 regulati		
					CO	HC	NOx	CO	HC	
New model	Standard-size cars, compact cars, light cars (passenger-cars with a 10-seat capacity or less), gasoline- or LPG-fueld	Cars with engine other than two-cycle engine	Cars of equivalent inertial weight not exceeding 1,000 kg (excluding light cars equipped with a 4-cycle engine)	10 modes	2.7 (2.1)	0.39 (0.25)	0.84 (0.6)	2.7 (2.1)	0.39 (0.25)	(
				11 modes	85 (60)	9.5 (7.0)	8.0 (6.0)	85 (60)	9.5 (7.0)	(9.
			Cars of equivalent inertial weight exceeding 1,000kg (including light cars equipped a 4-cycle engine)	10 modes	2.7 (2.1)	0.39 (0.25)	1.2 (0.85)	2.7 (2.1)	0.39 (0.25)	1. (1.
				11 modes	85 (60)	9.5 (7.0)	9.0 (7.0)	85 (60)	9.5 (7.0)	11 (9.
		Light cars with a 2-cycle engine		10 modes	2.7 (2.1)	5.6 (4.5)	0.5 (0.3)	2.7 (2.1)	5.6 (4.5)	0. (0.
				11 modes	85 (60)	33 (25)	4.0 (2.5)	85 (60)	33 (25)	4. (2.

Type of vehicle			Measuring method	Permissible limit					
				1976 regulation			1975 regulation		
				CO	HC	NOx	CO	HC	NO
New model	Standard-size cars, compact cars, light cars (buses with a 11-seat capacity or more, total vehicular weight not exceeding 2,500 kg; trucks of vehicular weight not exceeding 2,500 kg), gasoline- or LPG-fueld	Cars other than light cars with a 2-cycle engine	10 modes	17 (13)	2.7 (2.1)	2.3 (1.8)	17 (13)	2.7 (2.1)	2.3 (1.8)
			11 modes	130 (100)	17 (13)	20 (15)	130 (100)	17 (13)	20 (15)
		Light cars with a 2-cycle engine	10 modes	17 (13)	15 (12)	0.5 (0.3)	17 (13)	15 (12)	0.5 (0.3)
			11 modes	130 (100)	70 (50)	4.0 (2.5)	130 (100)	70 (50)	4.0 (2.5)

(Note) 1. The units used in making measurements were g/kg for the 10-mode measurement and g/test for the 11-mode measurement.

2. Figures in brackets indicate the average control values.

Fig. 4 Effects of Automotive exhaust gas emission control (passenger-cars)



(Note) Equivalent inertial weight = Vehicular weight + Weight of two persons

practical use to meet the 1976 regulation requirements. Following the 1976 regulation, the Japanese automotive manufactures are now making research and development efforts to attain the initial target value of average emission quality of 0.25 g/km by FY1978.

Environment Agency has set up the "Group for the Study of Motor Vehicle Nitrogen Oxides Emission Control Technology" formed with four experts to make assessment of the progress now being made in technological developments by the automotive manufacturers. This Group has so far published its reports twice, in December 1975 and in May 1976. In August 1976 the Group had the final hearings from Japanese and foreign manufacturers to cope with

the FY1978 regulation scheduled to be established in the autumn of 1976.

The Japanese automotive manufacturers seem to have passed through the trial production stage and entered the mass trial production stage by now, suggesting good prospects for the initial target value to be attained successfully.

ii) Control of truck and diesel-engine vehicle exhaust emissions

Since July 1972, the black smoke emitted by new diesel engine-driven vehicles has been subject to control. In view of the growing contribution of the exhaust gases from diesel-engine vehicles to air pollution, the permissible limits on such exhaust gases, which were established with special emphasis on nitrogen oxides, have been in force since September 1974.

The measurements were made on the basis of the six-mode driving conditions for application to diesel-engine vehicles and the permissible limits on nitrogen oxides are set at 590ppm (1,000ppm for the direct injection type of diesel engines). By virture of the enforcement of the regulation, the quantity of nitrogen oxides emitted by diesel-engine vehicles has been reduced 20% as compared with those which were produced before the enforcement of the regulation.

The exhaust emission control on gasoline- or liquefied petroleum gas-fueld heavy trucks and buses has been enforced since FY1973. The measurements were made on the basis of the six-mode driving conditions and the permissible limits on

nitrogen oxides were 2,200ppm both for gasoline-fueld vehicles and for LPG-fueld vehicles.

Exhaust emission control standards similar to those for passenger-cars had been applied to light-duty trucks and buses until FY1974 and the standards were tightened in FY1975 to reduce the nitrogen oxide content in the exhaust missions by 17%. The exhaust emission control standards presently enforced on trucks and diesel-engine vehicles are slightly less strict than those for passenger-cars. However, their contribution to air pollution is too great to be overlooked and a technical study is now under way about the advisability of further tightening the exhaust emission control on these types of motor vehicles.

iii) Effects of control of motor vehicle exhaust emissions on air pollution

As seen from Table 3 showing the measurements made at state-operated automotive exhaust emission monitoring stations in Tokyo, the levels of air pollutants emitted by automotive exhaust gas have been lowering steadily. At the Kasumigaseki monitoring station, for example, the concentrations of nitrogen oxides lowered from 14.2pphm in 1970 to 8.2pphm in 1975.
On the other hand, the vehicular traffic volume only slightly lowered from 1,198 vehicles per hour to 1,074 vehicles per hour, practically remaining on the same level, during the corresponding period of five years. From this finding, it can be assumed that the marked decline in the air pollution level was ascribable to

the effects of automotive exhaust emission control.

Table 3 Yearly changes in nitrogen oxide concentrations measured at the state-operated automotive emission monitoring stations in Tokyo

(Unit: pphm)

Location \ Classification \ Year		1964	'65	'66	'67	'68	'69	'70	'71	'72	'73	'74	'75
Kasumigaseki	NO	3.2	3.3	2.6	2.5	4.2	9.3	9.7	8.5	8.1	7.6	6.0	5.5
	NO_2	1.3	1.8	2.1	1.8	2.2	4.3	4.5	4.1	4.1	4.6	3.7	2.8
Itabashi	NO	1.5	1.6	2.0	2.0	3.9	4.9	7.0	9.7	9.7	10.6	8.2	6.8
	NO_2	1.4	1.7*	1.7	1.8	1.5	2.0	2.7	3.6	4.9	6.6	4.7	3.4
Shinjuku	NO									4.6**	4.7	4.1	4.3
	NO_2									3.4**	3.7	3.4	3.3

(Note) 1. * September - December ** July - December
2. Saltzman coefficient: 0.72

iv) (Other measures for the control of automotive exhaust emission)

As we have seen in the preceding paragraphs, the source exhaust gas control measures, as the major means of controlling automotive air pollution, should be promoted. However, in the urban areas, the volume of automotive traffic is such that the source exhaust gas control alone proved to be inadequate to control the air pollution. In cities and regions where the air pollution has intensified with the increase in the volume of automotive traffic, it has become necessary to regulate the

traffic volume and to strengthen measures designed to improve the environment relating to automotive traffic from the long-term point of view.

In the area of regulating the flow of automotive traffic, the Public Safety Commission has been pursuing compenhensive measures; including the establishment of bus lanes and no-parking areas and the enlargement of sidewalks, which are designed to optimize the flow of automotive traffic on city streets, rational distribution of road spaces and to curtail the overall automotive traffic volume by about 10%.
In residential areas, in particular, efforts are being made to separate the local traffic from through traffic by closing streets and by regulating the speed of automobiles, and the like.

On the other hand, the Public Safety Commission is empowered to regulate, upon request from the governor of the prefecture concerned, automotive traffic in such protions of the nation's highways and the areas adjacent to them, in case the air pollution caused by automotive exhaust gas reaches a certain critical level of concentration.

Also, when the construction or rebuilding of a main road running through areas which require the conservation of wholesome environment is proposed, the builders of such road are required to establish buffer zones, green belts and improve the structural design of such road. Efforts are also being made to reduce the level of exhaust gas concentration by building multi-level crossings or by improving the traffic flow at intersections.

4. Monitoring

Table 4 Increases in the number of nitrogen oxide air pollution stations in Japan

	Ambient air pollution monitoring station			Automotive exhaust emission monitoring station		
	State-operated	Prefecture-operated	Total	State-operated	Prefecture-operated	Total
1965	3	0	3	2	-	-
'66	5	0	5	2	-	-
'67	7	0	7	2	-	-
'68	9	0	9	2	-	-
'69	11	6	17	2	-	-
'70	13	26	39	2	-	-
'71	15	53	68	2	33	35
'72	15	161	176	3	75	78
'73	15	314	329	3	122	125
'74	15	567	582	3	164	167

(Note) " - " in the above table indicates that the exact number of the stations is unknown.

At the present time there have been established nitrogen oxide air pollution monitoring stations and automotive exhaust emission monitoring stations in Japan as shown in Table 4. Apart from the above, measurements of smokestack emissions at 608 factories are telemetrically recorded at the prefectural monitoring centers for air pollution (as of the end of FY1976).

The control of NOx emissions is new compared with that of SOx and the establishment of the monitoring stations on the nationwide basis was started only recently. However, the

importance of nitrogen oxide control measures are recognized so much that the network of monitoring stations is being rapidly expanded.

In Japan, measurements of NOx concentrations in the air are made by the adsorption photometry, using Saltsman reagen standardized by the JIS (Japanese Industrial Standards), because it was necessary to develop a nationwide network of monitoring stations while there any other reliable measuring method than the Saltzman method had not yet been developed and the measuring instruments to be used required an ease of maintenance suited for the efficient operation of such a high-density network of monitoring stations that about 1,370 monitoring stations are to be established throughout the country.

The Saltzman method now in use in Japan employs the batch system instead of the spiral tube system and therefore it is less affected by the effects of obstructive substances. The state-operated monitoring stations are making investigations on the errors of measurement by this method. The chemiluminescence method is not used in Japan because automatic calibration is difficult at the present time.

Environment Agency is now making research and investigation for further improvement of the measuring method so that measurements can be made with greater accuracy.

5. NOx control strategy for the future

In view of the present progress in the technological development for controlling nitrogen oxides, it seems difficult to completely attain in all areas the target set up by a government notification, that is, "as a rule endeavors shall be made to attain the target in five years (eight years in special areas such as extremely densely populated areas). Anyway, the measures for controlling nitrogen oxides emitted by industrial installations and motor vehicles will be carried on as follow in the immediately future.

First, efforts will be made to grasp the progress in technological development for the control of emission of nitrogen oxides from stationary sources (industrial and business installations) and mobile sources (motor vehicles) and the control on such sources will be tightned as much as possible by March 1977. Taking such trends of NOx control, we are planning to clarify the relationship between the quantities of emissions from the various sources and NOx concentrations in the ambient air by March 1977 and then proceed to the formulation of NOx curtailment plan, taking into account the results of the national discussion on the control measures to be taken. (Table 5)

The Industrial Structural Council, an advisory assembly attached to the Ministry of International Trade and Industry, is discussing the way the NOx control measures should be carried on and thus obtained results will be used as a part of the national discussion in the study of the proposed NOx curtailment plan.

In order to provide useful informational material, Environment Agency is now endeavoring to establish simulation models, to make assessment of NOx control techniques and the costs and effects of the various measures to be taken. Under thus formulated NOx curtailment plan, the application schedule for the control standards, including the regulation of total mass emission, on the basis of which the measures will be carried on toward the attainment of the ambient air quality standards for nitrogen dioxide.

Table 5 The tentative schedule for the emission control of nitrogen oxides

	Apr. '73 (FY1973)	Apr. '74 (FY1974)	Apr. '75 (FY1975)
Those relating to environmental quality standards	- Ambient air quality standards for nitrogen dioxide established (May '73)		- Review of the results obtained from the survey for the health effects of compound air pollution (particularly those of smoke and soot) compiled
Others			
Those relating to controls			
Stationary sources	- Emission standards established (first round) (Aug. '73)	- Survey for the development of techniques for predicting ground level concentrations of nitrogen oxides (Himeji)	- Survey for the development of techniques for predicting ground level concentrations of nitrogen oxides (Kyoto and Kitakyushu) - Nitrogen oxide emission standards revised and strengthened (second round) (Dec. '75)
Mobile sources			
Passenger cars	- 1973 exhaust control standards - 1973 regulation standards for used cars (May '73)		- 1975 exhaust control standards (Apr. '75) - Public hearing on exhaust control, Aug. - Oct.

Apr. '76 (FY1976)	Apr. '77 (After FY1977)
- WHO Task Group Meeting on Nitrogen Oxides held in Tokyo (autumn, 1976)	- Deadline for the attainment of the prescribed ambient air quality standard for nitrogen dioxide for the areas of attaining within 5 years (FY1978) - Deadline for the attainment of the interim target of the prescribed ambient air quality standard for nitrogen dioxide for the areas of attaining within 8 years (FY1978)
- OECD reveiw of environmental policy of Japan (Nov. '76)	- Policy review for the formulation of the most appropriate nitrogen oxide control measures
- Survey for the development of denitrification technologies - Review of measuring methods - Finalization of techniques for forecasting ground level concentrations of nitrogen oxide - Drawing-up of a model plan for total emission reduction - Upward revision of nitrogen oxide emission standards (third round)	- Enforcement of total mass emission control standards (planned)

	Apr. '73 (FY1973)	Apr. '74 (FY1974)	Apr. '75 (FY1975)
Buses and trucks (gasolin-powered)	- 1973 exhaust control standards (Apr. '73)		- 1975 exhaust control standards (Apr. '75)
Diesel engine vehicles		- 1974 exhaust control standards (Oct. '74)	- Review of exhaust control standards by the Experts Committee on Automotive Air Pollution to establish new targets for control

Apr. '76 (FY1976)	Apr. '77 (After FY1977)
- 1976 exhaust control standards - Survey for the development of technologies for reducing nitrogen oxides emission - Announcement of 1978 exhaust control standards (planned)	- 1978 exhaust control (planned)
- Establishment of targets for exhaust control	

Measures Being Taken in Japan to Reduce NO_2 and Photochemical Oxidant in the Air

(Air Quality Bureau, Environment Agency)
Japanese Delegation

The paper will report, from the administrative standpoint, various problems related to photochemical oxidant, measures having been taken to reduce NO_2 and photochemical oxidant, and the future direction in the control of such air pollutants in Japan.

1. Episode

It was relatively in recent years that the problems of photochemical smog started to be considered matters of primary concern among various problems of air pollution in Japan. In the past, the air pollution was divided into two typical types, one being London-type smog and the other Los Angeles-type smog, and it is widely known that the Los Angeles-type smog is a photochemical smog.

The air pollution in metropolitan and industrial cities in Japan was considered an intermediate type between them judging from the conditions of the pollution and in the beginning, sulphur oxides, suspended particulates matters and carbon monoxide which is the main element of automotive exhaust gas were considered as typical air pollutants. Therefore, the measures were centered on reduction of them. When the Tokyo

Rissho High School incident occurred in July of 1970, the control of monoxide gas was just started as a countermeasure against automotive exhaust gas and no measure had not been taken before that time in Japan taking into consideration photochemical smog. It was found that the incident was caused by photochemical smog and since then the problem of photochemical smog has been arousing the general public to show a serious interest in it. On July 18, 1970, the incident occurred at the Tokyo Rissho High School in Suginami, Tokyo. While 43 girl students were playing on the ground, many students started to complain of irritation in the eyes, and pain in the throats. A few of them complained of breathing difficulty and convulsion in the limbs. Altogether 14 students were hospitalized for treatment. It was suspected that the incident may have been caused by photochemical smog. Since then, similar incidents of irritating symptoms in the eyes and throats have been reported in Tokyo and neighboring districts. By the fall of 1970, the number of victims reported reached 17,887 in Tokyo, Chiba and Saitama. Then in Summer of 1971, similar cases were reported not only in the Tokyo area but also the Osaka and Nagoya areas and the number of victims reported reached 48,118.

2. Tentative Measures

The Environment Agency was established on July 1 of 1971 and faced with the problem of photochemical smog as its first important task. Then the occurrence mechanism and effect of

photochemical smog were not known quantitatively and there were so many unknown factors to take the best step to prevent it. However, on the basis of the understanding that hydrocarbon and nitrogen oxides may be causing photochemical smog, the following tentative measures were taken.

Tentative Measures to Prevent Occurrence of Photochemical Smog

(Notice No.92 dated June 1, 1972
sent to Prefectural governors from
Air Quality Bureau, Environment Agency)

The air pollution by photochemical reaction (hereinafter referred to as photochemical smog) has become a serious social problem since the so-called photochemical smog incident occurred at the Tokyo Rissho High School, Suginami, Tokyo, in the last Summer. The review of the frequency of warnings issued in relation to oxidant and the number of victims reported shows clearly as seen in the attached table that the photochemical smog has been occurring more frequently and in wider region.

As countermeasures, the regulations for standards measures to be taken at an emergency caused by oxidant or NO_2 were established and the regulations for automotive exhaust gas were expanded under Air Pollution Control Law In additions, the work to establish environmental standards for nitrogen oxides and oxidant, the study of drastic measure to reduce automotive exhaust gas and nitrogen oxides from stationary sources, and the investigation into the occurrence mechanism and effect on the human health of photochemical smog are under way.

Today, the occurrence mechanism and effect of photochemical smog are fairly well understood, but there are still many unknown

aspects. Thus, a further research is required to understand those unknown aspects in order to establish countermeasures against photochemical smog.

However, in view of recent occurrences of photochemical smog, the following tentative measures should be taken in metropolitan and industrial cities and their surrounding areas from June to September in order to prevent the occurrence of photochemical smog and health hazard.

As the measures are strongly related to the administrative policies of local governments, a sufficient information should be supplied to the local governments concerned and a system of close communication and cooperation should be established among the agencies concerned.

The same letter has been sent to the Police Agency, the Ministry of Education, the Ministry of Health & Welfare, the Ministry of International Trade & Industry, the Ministry of Transport and the Ministry of Labor.

1. Measures against Stationary Sources

(1) Measures against nitrogen oxides

At present, the only effective way available to control the exhaustion of nitrogen oxides from stationary sources is to reduce consumption of fuels. Therefore, when the weather condition is very likely to cause photochemical smog, it should be appealed to general households, factories and plants to reduce

the consumption of fuels and stop burning waste products if it is not urgent.

(2) Measures against hydrocarbon

(a) As evaporated hydrocarbon is exhausted into the air when oil is supplied into oil storing tank at gas station or gas storage or due to change in the atmospheric change, the owners of such oil storing facilities should be instructed to install a device to prevent exhaustion of hydrocarbon or adopt a system of returning evaporated hydrocarbon into tanker or tank wagon.

(b) Hydrocarbon is often exhausted into the air from workshops using organic solvent or products containing organic solvent. Factories and plants using them should be requested to control the exhaustion of hydrocarbon.

(c) If the weather condition is very likely to cause photochemical smog, the general public should be asked to cooperate to postpone any action which is likely to exhaust hydrocarbon into the air.

2. Measure against automotive

(1) An automobile exhausts photochemical smog producing substances such as hydrocarbon and nitrogen oxides when it is operated. At present, there is no effective technology to reduce the exhaustion of gas from automobile. Therefore, if the weather condition is likely to cause photochemical smog, the owners and drivers of automobiles should be advised not to drive automobiles unless it is urgently necessary to do so, in cooperation with the agencies

concerned. In addition, the local authorities of the districts where there have been a large number of victims of photochemical smog should consult with the local public safety commission concerned on the effective and appropriate measures to be taken to prevent the occurrence of victims of photochemical smog, such as reduction of automotive traffic which produces polluting substances, in anticipation of the occurrence of photochemical smog of emergency level.

(2) Periodical inspection and servicing of automobile

Insufficient servicing of engine system considerably increases the density of automotive exhaust gas. The users of automobiles, therefore, should be instructed to carry out periodical inspection and servicing of automobile required under the Road Transportation Vehicle Act, in cooperation with the agencies concerned.

(3) Recommendation to attach a device to prevent exhaustion of gas from automobile

The work to develop such a device is under way. With the catalytic preventing device, there are still unsolved problems of purification efficiency, durability and occurrence of related pollutions, but as it is considered fairly effective for a shorter use under a strict control, the attachment of the device should be recommended to the users of automobiles, especially during periods of frequent occurrences of photochemical smog, in view of the recent frequent occurrences of photochemical smog.

(4) Supervision of mixing of olefin hydrocarbons and aromatic hydrocarbons

As for olefin and aromatic hydrocarbons contained in gasoline, the plan for non-leaded gasoline is being carried out to reduce the amount of those compounds while keeping the level of octane value necessary for normal operation of automobile. It is requested to investigate the actual conditions of mixing of such compounds at the stage of distribution. If it is necessary, any one who is in violation of the law should be warned and it should be reported to the agency.

3. Establishment of Warning System

As it is necessary to forecast photochemical smog for effective implementation of the measures against photochemical smog, a close communication should be maintained with the weather forecasting agency to gather informations on weather. A system of forecasting photochemical smog should be established. Under such a system, an appropriate forecast of photochemical smog will be made taking into consideration weather conditions and change in the density of oxidant at the point where the air pollution will be observed.

According to the past investigations, the density of oxidant considered an indicator of photochemical smog tends to get higher under the following weather conditions, though there are some exceptional cases due to other factors;

a. The inclination of atmospheric pressure is gentle and a weak wind remains.

b. There is a sunshine.

c. The atmosphere is stable and there is an inversion layer of front or sinking nature.

c. The temperature is over 20°C in general and the humidity is less than 75 percent.

4. Health Measures

(1) Strengthening of supervising system and information network

As for health measures against health damages due to photochemical smog, it is necessary to disseminate informations to the general public on photochemical smog and take appropriate measures promptly if any health damage is caused by photochemical smog in addition to the strengthening of general health measures. In order to do so, it is required to establish a strong system of health measure implementation through utilization of the facilities of public health centers and cooperation with the agencies concerned so that consultation, exhcnage of informations and finding of actual conditions of health damages may be smoothly carried out.

(2) Thorough dissemination of informations

With respect to health measures against photochemical smog, it is most important to get the cooperation of the general residents through deepening their understanding of photochemical smog. Thus, mass media, educational organizations, doctors' associations,

womens' organizations, and local groups should be asded to cooperate for thorough dissemination of informations.

(3) Measures to be taken when a health damage occurs

a. Prior measure

Among the recent victims of photochemical smog in Japan, the cases with serious symptoms such as breathing difficulty, numbness in the four limbs and convulsion in the four limbs, requiring hospitalization for treatment, were reported. In anticipation of possibility of occurrence of these types of health damages, it is necessary to establish a system in advance so that proper emergency measures can be taken with cooperation of medical institutions.

b. Measures to be taken when health damages actually occur

Efforts are wanted to conduct the following investigations, if necessary, to ascertain the actual conditions of health damages that occurred and to probe into their causes.

A. Survey of health damages

(a) Survey of occurrences of health damages

Survey of the number of victims, main symptoms and onset conditions of symptoms in the region where serious cases have occurred and its surrounding areas

(b) Health examination of victims, and clinical and medical examination

If it is found that a victim requires a medical treatment as a result of health examination, the clinical record of the victim should be studied as much as possible and kept.

(c) Survey of group of victims

Survey of special circumstances (even or lecture) of the group of victims, conditions of health management and meals before occurrence.

(d) Others

B. Survey of environmental conditions

(a) Survey of weather factors

Survey of weather factors including temperature, humidity, wind direction and wind velocity before and after occurrence,

(b) Survey of air pollutants

Survey of the density of major pollutants including sulphur oxides, nitrogen oxides and suspended particulate matters as well as oxidant, in addition, survey of the density of other air pollutants such as aldehyde compounds and sulfuric acid mist

(c) Survey of stationary sources

Survey of smoke producing facilities, burning of waste products, and facilities and actions which may produce irritating substances

(d) Survey of mobile pollution producing sources

Survey of road traffic

(e) Other necessary surveys

Survey of the topography (ups and downs, degree of openness), things (buildings), arragements of trees and damaged plants.

c. Measures to be taken after survey

It is considered that the density and life of various pollutants as well as factors of individual body such as sex, age and health condition including both mental and physical aspects are related to

health damages. In evaluating and making a judgement of the results of the survey, such factors should be carefully taken into consideration and at the same time, necessary measures such as disclosing of the results of the survey should be taken.

5. Report of issues of emergency warnings

If forecast warning or causion concerning oxidant is issued or if there is any report of damage appearing to have been caused by oxidant, such reports and warnings should be summarized each week (from Sunday to Saturday) using the Form 1 and the summary should be reported by the following Saturday latest. In so doing, it is requested to report the damages caused by photochemical smog, using the Form 2, if it is possible.

In addition, when there is any serious symptom such as convulsion in the four limbs or breathing difficulty, it should be promptly reported by telephone and the progress thereafter.

If a warning is issued for the first time or a case of damage is reported for the first time, it should be immediately reported by telephone.

3. Photochemical Smog Control Promotion Conference

On June 19 of 1972, the Government established "Photochemical Smog Control Promotion Conference" in order to facilitate a close communication among the administrative agencies concerned with the measures against photochemical smog and promote the execution of comprehensive and effective countermeasures, in view of the importance and urgency of the problem of photochemical smog and the necessity of comprehensive countermeasures against photochemical smog. The conference is composed of the members as shown in Table 3-1.

Table 3-1 Members of Photochemical Smog Control Promotion Conference

Environment Agency	Director of Planning and Coordination Bureau
	Director of Air Quality Bureau
Prime Minister's Office	Director of Traffic Safety Measure Bureau
National Police Agency	Director of Traffic Bureau
Science and Technology Agency	Director of Research Coordination Bureau
Ministry of Education	Director of Physical Education Bureau
Ministry of Health and Welfare	Secretariat Councilor
Ministry of Agriculture and Forestry	Secretariat Technical Councilor
Ministry of International Trade and Industry	Director of Industrial Location and Environmental Protection Bureau
	Director of Machinery and Information Industaies Bureau
Ministry of Transport	Secretariat Councilor
Ministry of Labor	Derector of Labor Standards Bureau
Ministry of Construction	Director of City Bureau
Ministry of Home Affairs	Assistant Director of Fire Defense Agency

4. Environmental Standards for Nitrogen Oxides etc.

Meanwhile, the Central Pollution Control Council established "Special Committee on Environmental Standards for Nitrogen Dioxide etc." in the Air Division in view of the fact that the condition of air pollution by nitrogen dioxide and photochemical oxidant has been getting worse year after year and the stage has been reached where such air pollution cannot be overlooked any longer from the standpoint of its effect on human health, and prepared a report of the special committee on the environmental standards for nitrogen dioxide after studying the effects and the proceduces to measure nitrogen dioxide and photochemical oxidant in the air.

As for nitrogen dioxide, the environmental standards were established not from the standpoint of controlling formation of photochemical oxidant, but from the standpoint of its effect on human health. The Central Pollution Control Council recommended the maximum value of 0.02 ppm per hour as an average value of a day with respect to nitrogen dioxide and that of 0.06 ppm with respect to photochemical oxidant as the environmental standards. At the same time, the target period of five years with respect to nitrogen dioxide (eight years in some districts) and that of shortest time with respect to photochemical oxidant were determined. In addition, the Council recommended to carry out the following measures both in the comprehensive and positive manners in order to achieve the target of the environmental standards.

"On Problems Accompanying the Establishment of the Environmental Standards for NO_2"

In order to achieve and maintain the target of the environmental standards, it is necessary to implement the following measures both comprehensively and positively.

1. Development of control technology as a national project

As for a technology to control production of nitrogen oxides in the stationary sources, it is planned to develop a denitration technology and a burning technology to be put into practical use within five years, and necessary assistances in terms of finance and taxation should be provided to facilitate technological development and introduction of technologies developed in the private sector, in view of the urgent necessity of technological development.

In addition, the same things should be done with development of control technology necessary for tightening control of automotive exhaust gas, dramatic new energy source which does not cause any environmental pollution and its production technology.

2. Enforcement of the regulations for pollutants producing sources

In order to reduce the total amount of exhaustion of nitrogen oxide into the air, the following measures should be taken and at the same time, the introduction of a control system based on the total allowable amount of exhaustion of pollutants

in the area should be examined.

(1) A rational control of exhaustion from stationary sources should be enforced through improvement of burning system and burning conversion which are presently possible. In the future, when a control technology such as a denitration technology has been developed for practical use, the control of exhaustion should be immediately tightened.

(2) The control with tougher long-term target for automotive exhaust gas should be enforced with respect to new automobiles. With respect to used cars, the necessary control should be done.

3. Planning and execution of pollution control program

In order to achieve and maintain the level of the environmental standards, a pollution control program should be planned and executed under the Basic Law for Environmental Pollution Control.

4. Execution and promotion of environmental assessment

An environmental assess-ment technique should be developed, effective and proper for city and industrial developments, and thorough execution of such environmental assessment, and the rationalization of land utilization should be achieved for effective control of air pollution by nitrogen oxides.

5. Improvement of transportation system

In order to make a contribution for effective control of air pollution by automobile traffic, the study of the metropolitan public transportation system should be facilitated and at the

same time, the quantity of pollution causing nitrogen oxides in the metropolitan areas should be reduced through absorption of increasing demand for transportation into the public transportation system.

6. Effective use of energies

The quantity of pollution causing nitrogen oxides should be reduced through effective use of energies by means of regional air-conditioning work and improvement of burning system.

Also, as it is known that heating devices, too, cause pollution by nitrogen oxides, improvement and development of heating systems and equipment should be carried out.

7. Establishment of system of monitoring and measuring

For accurate measurement and evaluation of conditions of air pollution by nitrogen oxides and making a contribution for execution of proper control countermeasures and evaluation of effectiveness of such countermeasures, it is urgently required to facilitate the establishment of a system of monitoring and measuring and at the same time, an effort should be made to manage and maintain the system in a proper form.

8. Promotion of investigation and research

Together with promotion of execution of the various measures mentioned above, investigation into and research on the effect of nitrogen oxides and measuring procedure should be carried out.

"On problems accompanying establishment of the environmental standards for Ox"

In order to achieve and maintain the level of the environmental standards, it is necessary to positively promote the execution of the following measures in addition to the measures to maintain and achieve the level of the environmental standards for nitrogen oxides, in view of the fact that the main substances which cause photochemical oxidant are nitrogen oxides and hydrocarbon.

1. Promotion of investigation and research

It cannot be necessarily said that the actual conditions and effects of air pollution by photochemical reaction are sufficiently understood in Japan. It is necessary, therefore, to carry out a comprehensive and detailed study in order to understand them, taking into consideration special weather conditions in city areas.

In addition, the mechanism of production of air pollutant by photochemical reaction of ozone, PAN or formaldehyde, effect on human health, damage of visibility, effect on living environment such as damage of plants and method of measurement should be studied.

In addition, the relationship between production and use of products containing gasoline, organic solvent or hydrocarbon and air pollution by photochemical reaction should be studied, too.

2. Control of Pollution producing sources

In order to control air pollution by photochemical oxidant, it is necessary to effectively control pollution producing sources in accordance with the progress of the studies mentioned above. In view of urgent necessity of countermeasures against photochemical oxidant, the following measures should be taken for a time being.

(1) A necessary controlling measure should be taken according to the actual conditions of exhaustion, leakage and evaporation of pollutants in the process of production, storage and use of gasoline and organic solvent in industrial plants and business establishments.

(2) Exhaustion of hydrocarbon with automotive exhaust gas should be more tightly controlled. In addition, a system of inspecting and servicing engines should be improved.

3. Execution and promotion of environmental assessment

Effective and proper technique of environmental assessment for city development and industrial development should be developed and an environmental assessment should be executed in order to control air pollution by photochemical oxidant, in view of formation mechanism of photochemical oxidant.

4. Development of control technology

In view of urgent necessity of developing technology to prevent leakage, exhaustion and evaporation of hydrocarbon from stationary sources and mobile sources, the development of the technology should be facilitated.

5. Establishment of system of monitoring and measuring

For accurate measurement and evaluation of condition of air pollution by photochemical oxidant, and execution and judgement of effect of preventive measure, it is urgently required to establish a system of monitoring and measuring. In addition, a similar system should be established for hydrocarbon and ozone.

"Special Committee Report on Environmental Standards for Nitrogen Oxides etc."

June 20, 1972.

Environmental Standerds for nitrogen oxides etc.

Committee of the Air Division, the Central Pollution Control Council.

The special committee on "environmental standards for nitrogen oxides etc. reports to the Central Pollution Control Council Air Division as follows. It should be noticed here that the committee took over the work of the Special Committee on Environmental Standards for Nitrogen Oxides of the Living Environment Council Pollution Division of the Ministry of Health and Welfare with respect to this report.

1. Introduction

Nitrogen oxides etc in this report include NOx, photochemical oxidant, ozone and so on.

Among nitrogen oxides, nitrogen monoxide and nitrogen dioxide are especially important in terms of their effects on living environment. Nitrogen oxides are also produced as a result of natural phenomena such as metabolism of microorganism in the soil. It is known that the background concentration of nitrogen dioxide in the air is less than 0.003 ppm. Ozone falls down from the stratosphere and its concentration on the surface of the earth is less than 0.05 ppm.

Nitrogen monoxide (NO) is produced and exhausted into the atmosphere when the air is heated by stationary sources such as thermoelectric power station and furnace and mobile producing sources such as automobile. Then, it is oxidized in the air to become nitrogen dioxide (NO_2). Nitrogen oxides are also produced by the chemical processes such as nitrification process and discharged directly into the air. The nitrogen oxides produced as mentioned above cause regional and local air pollution. In Japan, the air pollution by nitrogen oxides rapidly became worse in the past ten years.

If nitrogen dioxide and hydrocarbon, especially non-saturated hydrocarbon, exist together and are exposed to sunlight, secondary air pollutants are produced. If there is any sulfur dioxide, it is oxidized to become sulfuric acid mist. In this case, the air pollution by photochemical reaction is even worse.

In general, today, nitrogen monoxide and nitrogen dioxide are together called nitrogen oxides. They have an effect on human health, cause damage of visibility and color the air.

Our present knowledge about its effect is mostly about nitrogen dioxide, and we do not know much about the effect of nitrogen monoxide. Therefore, the environmental standards only for nitrogen dioxide will be recommended in this paper. As for nitrogen monoxide, it is expected that necessary data for establishment of environmental standards for it will be

obtained with the progress of research.

Among the substances produced by photochemical reaction when nitrogen dioxide and hydrocarbon coexist in the air, the following substances are especially noticed. They are ozone (O_3), nitrogen dioxide, PAN and its homologous compounds, oxidized substances such as peroxide, reductive compounds such as formaldehyde and acrolein, aerosol and highly active free radical whose effect is not known, but which should be noticed. The total effect of those substances is generally called the effect of photochemical oxidant.

Mucous membrane irritating symptom, severe effect on respiratory organs and other internal organs, effect on tissues, cracking of rubber, bad effect on plants, damage on agricultural products and fading of clothes are some of effects known as the effects of photochemical oxidant.

Here, we call oxidized products, excluding nitrogen dioxide, produced by photochemical reaction photochemical oxidant. It is measured by a method using neutral potassium iodide solvent. It is known that the measured value is mostly due to ozone. Therefore, with the understanding that photochemical oxidant is mostly ozone, we recommend the environmental standards for photochemical oxidant which is an indicator of pollutants produced by photochemical reaction.

2. Method of measurement

Both in the case of regional air pollution and local air pollution, the measurement of pollution by nitrogen oxides must be done at places so that pollution and trend of pollution will be well understood, and judgement of effects, establishment of preventive measures against pollution, and evaluation of effect of the measures can be effectively carried out.

A sample air should be collected at the level of human mouth. As a rule, it should be collected at a height between 1.5 m and 10 m above the ground.

The measured value of photochemical oxidant requires correction with respect to nitrogen oxides. Therefore, it is necessary to measure nitrogen oxides at the same place where photochemical oxidant is measured.

2-2-1 Measurement of nitrogen oxides

2-2-1.1) General matters

It is better to continuously measure nitrogen dioxide, and in totalizing the results of measurement, the data should be totalized for each hour. The unit of measurement is determined according to the concentration of nitrogen dioxide in the air. Generally speaking, the device should be able to measure from several ppb up to 2 ppm.

In order to find out the condition of pollution by nitrogen oxides, it is desirable to measure not only nitrogen dioxide but also nitrogen monoxide.

2-2-1.2) Standard method

The method of measurement based on the absorptiometry using Salzurann reagent is a standard method for measurement of density of nitrogen oxides. However, other méthod can also be used if it shows the same result.

2-2-2 Measurement of photochemical oxidant

2-2-2.1) General matters

In general, oxidant is a general name of oxidized substances which free iodine from neutral potassium iodine solvent. Using this reaction, photochemical oxidant is measured. It is desirable to continuously measure photochemical oxidant and in totalizing the results of measurement, the data should be totalized for each hour.

The device should be capable of measuring from several ppb to 1 ppm.

2-2-2.2) Standard method

The method of measurement based on the absorptiometry using neutral potassium iodine is a standard method for measurement of photochemical oxidant. Other methods such as coulometric method can be used, too, if the same result can be obtained.

With the standard method, the measured value of photochemical oxidant should be corrected with respect to the density of nitrogen dioxide. Also, as there is an effect of reductive substances such as sulfur oxide, a paper containing chromium trioxide is used to eliminate such effect. In this case, it is necessary.

to make a correction with respect to the density of nitrogen monoxide as nitrogen monoxide in the air is oxidized to nitrogen dioxide, which causes some effect on the measured value of oxidant.

The density of oxidant with correction as to the density of nitrogen oxides is mostly due to ozone.

2-2-3 Measurement of ozone

As mentioned above, if photochemical oxidant is measured by a standard method, most of the value is due to ozone and it is very clear, therefore, that it is more desirable to measure ozone directly. Today, there is a chemiluminescence method utilizing a reaction with ethylene as a usable method of measurement of ozone. With this method, ozone can be selectively measured without any effect of sulfuric dioxide or nitrogen dioxide. This method is being improved for practical use and it is hoped that it will be adopted as a standard method in the future.

2-3 Additional remark

As it is necessary to collect data from future researches and studies in order to make a judgement on the condition of air pollution by nitrogen oxides and its effect, it is strongly desired that these methods of measurement will be utilized together with the standard methods mentioned above, in view of the present situation that the method of selectively measuring ozone will soon be put into practical use.

In addition, it is strongly desired that the measurement of hydrocarbon will soon be done as a daily work, in view of the occurrence mechanism of photochemical oxidant.

3. Effect on human body

3-1 Effect of nitrogen oxide

The effect of nitrogen monoxide is not sufficiently known yet, partly due to difficulty of experiment. If an animal is exposed to extremely dense nitrogen monoxide, it develops paralysis and convulsion which are due to damage in the central nerve system. It has a strong affinity to blood cells. According to the test tube experiment, its affinity is several hundred stronger than carbon monoxide. In the animal experiment using an extremely high dense nitrogen monoxide, the formation of nitrogen monoxide blood cells and methemoglobin has been observed. At present, its effect on human body is not known much. Future study may show that nitrogen monoxide should be more seriously considered than nitrogen dioxide.

Nitrogen dioxide possesses a characteristic of easily reaching the deep part of respiratory organ regardless of existence of suspended particulate matters. It has been noticed in the human experiment that nitrogen dioxide and suspended particulate matters possess a mutually additive effect if they coexist.

Therefore, it was known from early time that nitrogen dioxide has an effect of irritating respiratory organs and its

poisoning has been noticed as an occupational disease.

The cause of death by acute poisoning of high dense nitrogen dioxide is an edema of the lungs in the animal experiment and the occupational disease. As for chronic effect, it is concerned that it may cause chronic bronchitis and emphysema of the lungs.

We are able to smell nitrogen dioxide with the concentration of 0.12 ppm. This value is lower if sulfuric dioxide exists together. A significant increase in air resistance in the human air-passages may occur within 10 minutes if the density of nitrogen dioxide is 16.9 ppm. From the reaction against increase in air pressure, it can be seen that sulfuric dioxide and nitrogen dioxide possess a mutually additive effect.

In the animal experiment, an effect on the lung cells is seen with the exposure of the subject to the nitrogen dioxide of 0.5 ppm for four hours. If an animal is exposed to nitrogen dioxide of 0.5 ppm for a several month, it may develop bronchitis and emphysema of the lungs.

It has been pointed out that an animal becomes sensitive to influenza virus and bacteria pneumoiae, its life gets shorter and its bacteria eliminating power is weakened if it is exposed to nitrogen dioxide. For example, if an animal is exposed to the nitrogen dioxide of 0.5 ppm for 12 months and infected with bacteria pneumoniae, fatal ratio will increase and its bacteria eliminating power will be weakened.

If an animal is exposed to the nitrogen dioxide of 10 ppm

for two hours a day and infected with influenza virus, it will develop intestitial pneumonia, and its pathologival symptom will get worse with the increase in days of exposure. With six-month exposure to the nitrogen dioxide of 0.5 ppm, a reactive multiplication of epithelial cells of peripheral bronchus and minor emphysema of the lungs will be seen. If the subject is infected with influenza virus, its symptom of pneumonia will be more clear and the adenoma-like multiplication of epithelial cells of peripheral bronchus will be observed.

This adenoma-like multiplication should be carefully noticed. The possibility of nitrogen dioxide causing bronchial asthma has been demonstrated in the animal experiment. It has also been shown that the production of carbon monoxide bloodcell increases if carbon monoxide coexists with nitrogen dioxide.

It has not been much studied how extensively the residents are being affected acutely or chronically at the present density level.

In America, and it has been reported that the frequency of infection to influenza and absence among school children in the region with pollution by nitrogen dioxide and nitrate and with no sulfuric dioxide pollution had increased. According to the report, the concentration of nitrogen monodixe was 0.062 to 0.109 ppm and that of nitrate 3,8 ug/m^3 or higher. In Czechoslovak, the survey of the school children in the region polluted both by sulfuric dioxide and nitrogen dioxide has been

carried out.

As mentioned above, it should be noticed that nitrogen dioxide has a mutually additive effect with sulfuric diowide. In Japan, the pollution only by nitrogen dioxide is exceptional occurring only locally. As nitrogen dioxide and sulfuric dioxide coexist in many cases, in examining the environmental standards for nitrogen dioxide, the existence of sulfuric dioxide should not be ignored.

Epidemiological survey of frequency of chronic bronchitis has been carried out in several occassions in Japan. In the report, it should be first noticed that the frequency of chronic bronchitis among the adult over 40 years old is 3 percent in the region with no air pollution. On the other hand, the frequency of simple chronic bronchitis with cough and sputum is higher than 5 percent among the male workers of local authorities in Tokyo with the yearly average concentration of 0.05 ppm per hour or below of sulfuric dioxide during 1968 and 1971. In this case, the yearly average concentration of nitrogen dioxide was higher than 0.042 ppm per hour.

The epidimiological survey of frequency of housewives with cough and sputum of continuous nature carried out in six districts nationwide in the winter of 1970 - 1971 demonstrated a high correlation between the frequency and the density of nitrogen dioxide. In this survey, the density of nitrogen dioxide was measured for 8 to 72 hours a month during three months covering

the month in which the survey was done. The average concentrations of nitrogen dioxide during the period mentioned above was 0.029 ppm in the district with the frequency of higher than 4 percent. It is well known that the frequency of adult women with the symptom is lower than that of adult men.

3-2 Effect of photochemical oxidant

The effect of photochemical oxidant is similar to that of nitrogen oxides. It should be noticed that the effect of photochemical oxidant is far stronger than that of nitrogen oxides.

Photochemical oxidant is mostly ozone and the effect of ozone is as follows:

According to the animal experiment, the absorption of ozone in the upper air-passages is limited and ozone reaches the deep part of the respiratory organs fairly easily. With four-hour exposure to ozone of the density of 1 ppm, a slight pulmonary oedema developed 20 hours after exposure. With long-period exposure, bronchitis, bronchiolitis, pulmonary emphsema, pulmonary fibrosis and adenoncus developed. With three-hour exposure to ozone of 0.25 to 0.5 ppm, an increase in the resistance of air flow was observed. With one-hour exposure to ozone of 1 ppm, a symptom which led one to suspect a change in the proteins composing lung cells was recognized. The toxicity of ozone gets stronger if an animal is subjected to exercise.

The increase of sensitivity to bacteria due to ozone is similar to that due to nitrogen dioxide. An increase was noticed

already with three-hour exposure to ozone of 0.08 ppm. It has been confirmed in the animal experiment that the possibility of ozone causing bronchial asthma is higher than that of nitrogen dioxide.

While it is known that animals develop tolerance to acute exposure, it is not known if they do so to chronic exposure.

In the human experiment, no definite effect was observed up to one-hour exposure to ozone of 0.1 ppm. With one to two-hour exposure to ozone of 0.5 to 1.0 ppm, the increase in the resistance in the air-passages, the weakening of the capacity of the lungs dispersing carbon monoxide and the reduction of the lung breathing capacity were observed. In addition, the symptoms were worse when the subjects had an exercise. The above were average reactions and there were individual differences. Therefore, it has been pointed out that a special attention should be paid to those with high sensitivity.

With a long-period exposure, no definite effect was observed among the factory workers when the density of ozone was less than 0.2 ppm. With the density of 0.3 ppm, irritation in the nose and throat was observed. With three-hour exposure per day for 12 six-day weeks, the weakening of lung breathing capacity was observed.

We smell ozone at the density of 0.02 ppm.

The above is the result of the experimental study. The effect of photochemical oxidant in the actual situation on the residents

is as follows.

According to the study in America, a damage of plants was observed with four-hour exposure to ozone of 0.05 ppm. With a short-term exposure to that of higher than 0.1 ppm, an irritating symptom in the eyes developed. The frequency of fit of asthma patients increased with the peak density of 0.13 ppm, which is equivalent to hourly average of 0.05 to 0.06 ppm. The aggravation of chronic respiratory disease occurred with the hourly average concentration of 0.2 to 0.7 ppm. But it was also reported that it did not occur with the hourly average concentration of 0.06 ppm. The athletes of cross country showed a statistically significant increase in the time when they were exposed to ozone of the hourly average density of 0.03 to 0.30 ppm before start.

The effect of photochemical oxidant on the residents has not been sufficiently studied in Japan. There have been complaints of damages of agricultural products and plants, and irritating symptom in the eyes by the residents, with the photochemical oxidant of 0.10 ppm. The effect of ozone during exercise cannot be ignored as observed in the animal experiment, and there have been reports of school children having suffered while exercising. In 1971, an incident occurred when a photochemical smog developed in the southern part of Osaka. The students developed irrtating symptom in the eyes and respiratory organs while exercising.

In this case, the hourly concentration of ozone was higher than

0.2 ppm, that of sulfaric dioxide higher than 0.05 ppm, that of sulphur acid mist 6 - 10 $\mu g/m^3$ and that of nitrogen dioxide 0.05 ppm.

3-3 Additional remarks

It is necessary to notice that the effects of nitrogen dioxide, ozone and photochemical dioxide on human living environment are cracking of rubber and damages of plants besides uncomfortableness, smell and disturbance of visibility.

The effects of nitrogen oxides, ozone and photochemical oxidant are mainly on the respiratory organs, especially lungs. The paper, therefore, paid a special attention to this aspect. It should be pointed out that these pollutants may have some effect on blood, cerebreum, heart, kidney and liver, and may be carcinogenic depending on density and the period of exposure.

4. Summary

We propose the environmental standards to be maintained throughout the year for nitrogen dioxide and photochemical oxidant on the basis of the methods of measurement and the data of the effects on human health mentioned above as follows:

(1) As for nitrogen dioxide, especially its chronic effects are concerned. Also, as it has a mutually additive effect with sulfuric dioxide, the daily average of hourly value should be less than 0.02 ppm.

(2) As for photochemical oxidant, the hourly average value of less

than 0.06 ppm should be maintained in order to prevent the effect of short-period exposure.

The report is the result of examination of the data obtained so far and proposed the conditions of judgement of nitrogen dioxide and photochemical oxidant.

It is necessary to make further efforts for progress in the study of method of measurement and effect, especially the effect and that of combined pollution of nitrogen monoxide, hydrocarbon and ozone, and method of measuring density in the environment.

As studies progress on effect of such substances on human health and environment, the environmental standards should be periodically reexamined and revised if necessary.

Members of the Special Committee on the Environmental Standards for Nitrogen Oxides

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Eiji Yokoyama	Director, Occupational Disease, Labor Hygene, National Institute of Public Health
Hiroshi Watanabe	Director, Hyogo Institute of Pollution

Following the recommendation, the Environment Agency proclaimed the environmental standards for air pollution as follows:

Environmental Standards for Air Pollution

(May 8, 1973)

The environmental standards for air pollution will be notified as follows under the provision of Article 9 of the Basic Law for Environmental Pollution Control (Law No. 132, 1967) and "Environmental Standards for Suspended Particulate Matter" will be repealed.

The standards desirable to protect human health with respect to the environmental conditions of air pollution stipulated in provision 1 of Article 9 of the Basic Law for Environmental Pollution Control (hereinafter called environmental standards) and the time to be achieved will be as follows.

I. Environmental Standards

(1) The environmental standards for each substance should be as mentioned in the table below.

(2) The environmental standards in 1 for each substance mentioned in the table should be based on the value measured at a place where it is possible to accurately judge the condition of air pollution by the said substance, by the method mentioned in the table.

(3) The environmental standards in 1 will not be applied in areas such as industrial areas, vehicle roads, and any other places where the general public usually do not spend their daily life.

II. Time to be Achieved

(1) The environmental standards for carbon monoxide, suspended particulate matters and photochemical oxidant should be maintained or achieved as early as possible.

(2) The environmental standards for sulfuric dioxide should be maintained or achieved within 5 years as a rule.

(3) The environmental standards for nitrogen dioxide should be maintained or achieved as early as possible within 5 years. However, in regions of high population density or large-scale industrial areas, the interim target mentioned below should be achieved within 5 years if it is difficult to achieve the final target even with comprehensive measures and the environmental standards should be achieved within 8 years through development of denitration technology and other control technology.

Interim target ..... The number of days with less than daily average of 0.02 ppm per hour of nitrogen dioxide should be more than 60 percent of the total days throughout the year.

Table

Substance	Sulfuric Dioxide	Carbon Monoxide	Suspended particulate matter	Nitrogen Dioxide	Photochemical Oxidant
Environmental Standards	The density should be less than 0.04 ppm in daily average per hour and less than 1 ppm per hour	The density should be less than 10 ppm in daily average per hour and less than 20 ppm in 8-hour average per hour	The density should be less than 0.10 mg/m^3 in daily average per hour and less than 0.20 mg/cm^3 per hour	The density should be less than 0.02 ppm in daily average per hour	The density sh be less than 0 ppm per hour
Method of Measurement	Conductometric analysis	Method to use non-dispersive infrared analyzer	Weight concentration measuring method by filter collection or light scattering method	Absorptiometry	Absorptionetry using neutral potassium iodide or conlometric method

Remarks

1. Suspended particulate matters are particulate matters floating in the air of less than 10 micron in diameter.
2. Photochemical oxidants are oxidized matters produced by photochemical reaction such as ozone, PAN and so on, excluding nitrogen dioxide (only those which free iodine from neutral potassium iodine solvent are included)

5. Emission Control of Air Pollutants from Automobiles and Stationary Sources

5.1 Emission Control of Automotive Exhaust Gas

As mentioned in the preceding section, it has been found through a number of studies and surveys by the Special Committee that both photochemical oxidant and nitrogen oxides have various effects on human health and photochemical oxidant is produced from nitrogen oxides and hydrocarbon. Moreover, cases of health damages due to, it seem, photochemical smog are still prevalent in Tokyo and other large cities, creating serious social problems. Therefore, the following controls have been carried out.

(10 Emission Control of Automotive Exhaust Gas

The emission control of automotive exhaust gas started with the control of carbon monoxide exhausted from new cars in September, 1966. Later, hydrocarbon and nitrogen oxides have been added for control to gradually tighten the emission control. In October of 1972, the Central Pollution Control Council presented an interim report on Methods for Long-Ranged Setting of Permissible Automative Exhaust Limits. The report concludes that the emission standard similar to the automotive emission control of 1975 and 76 under "the U.S. Clean Air Act Amendments" of 1970 should be enforced in Japan, in view of serious air pollution in Japan, particularly in big cities.

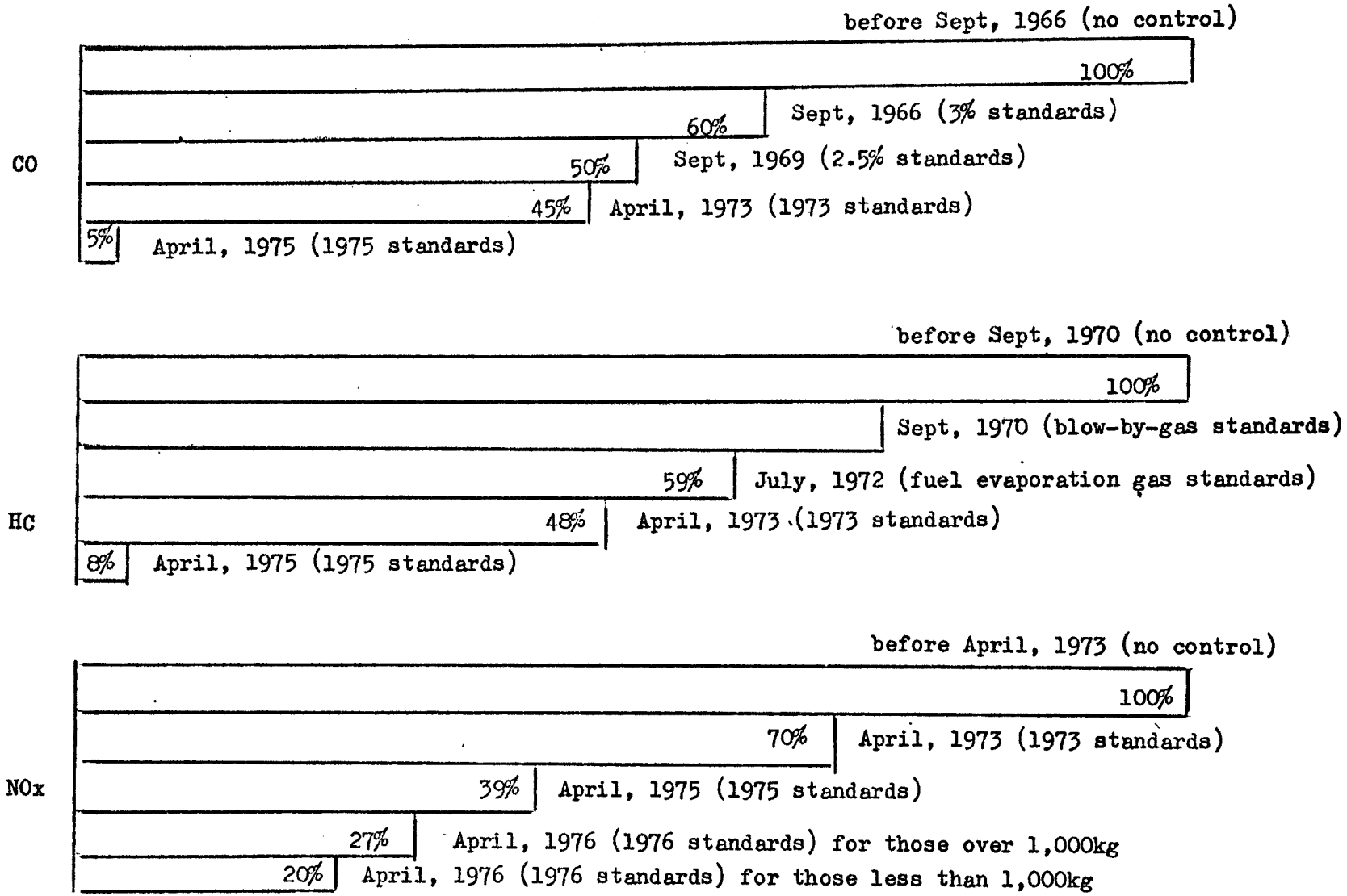
Following the recommendation, the 1970 standards for

maximum allowable emission from a passenger car were set at 2.1 g/kg of carbon monoxide, 0.25 g/kg of hydrocarbon and 1.2 g/kg of nitrogen oxides on the average emission, and enforced from April of the same year.

The 1976 standards for nitrogen oxides were to be even tighter. In the recommendation mentioned above, the target of maximum allowable amount was to be 0.25 g/km on average for those passenger cars produced after April of 1976. As a result of technical evaluation, however, the recommendation presented in December of 1974 by the Central Council for Control of Environmental Pollution set the target year to achieve the above mentioned standards as 1978. The revised standards are 0.6 g/km for passenger cars of less than 1,000 kg in equivalent inertial weight, and 0.85 g/km for passenger cars of over 1,000 kg on average exhaust. It was decided to enforce the standards from April of 1976 for new cars, from March of 1977 for cars of older models and from March of 1978 for imported cars (refer to Table 5-1-1 for comparison between the 1975 standards and the 1976 standards).

Exhaust gas reduction effect of the standards is shown in Fig. 5-1-1. As shown in the figure, the amount of carbon monoxide, hydrocarbon and nitrogen oxides was reduced by 95%, 92% and 61%, respectively as the result of enforcement of the 1975 standards and the 1976 standards had an effect of reducing the amount of emission of nitrogen oxides by 80% from passenger cars of less than 1,000 kg in equivalent inertial weight and by 73% from those of over 1,000 kg.

Fig. 5-1-1 Effect of Emission Standards for Automotive Exhaust Gas (passenger cars)



by Environment Agency

Table 5-1-1 Allowable Limit in the 1976 Control & Reduction Rate in Comparison to the 1976 Control

1. Nitrogen Oxides for Passenger Cars (New)

Type of Automobile			Method of measurement	1976 Control		1975 Control		Reduction Rate
				Allowable Limit	Average (A)	Allowable Limit	Average (B)	$\frac{B-A}{B} \times 100$
Passenger cars with the capacity of less than 10 passengers running on gasoline or LPG	Engines other than 2-cycle	Cars with less than 1,000 kg in equivalent inertial weight (excluding small 4-cycle-engine cars)	10-mode g/kg	0.84	0.6	1.6	1.2	50 %
		Cars with more than 1,000 kg in equivalent inertial weight (including small 4-chcle engine cars)		1.2	0.85	1.6	1.2	29 %
	2-cycle engine			0 0.5	0.3	0.5	0.3	0

2. Hydrocarbon for Trucks (in use)

Type of Automobile	Method of Measurement	Type of Engine	Allowable Limit
Trucks running on gasoline or LPG	Idling	2-chcle engines	7,800 ppm
		Special engines	3,300 ppm
		Others	1,200 ppm

Special engines refer to engines with special bulb, caburetter and conbustion room.

With respect to smaller cars with two-cycle engine, the standards for carbon monoxide and hydrocarbon similar to those for passenger cars with four-cycle engine were applied and the standard for nitrogen oxides was set at 0.3 g/kg on average emission in the 1975 standards.

However, as it is very difficult to reduce the emission of hydrocarbon due to the structure in the case of two-cycle engine, the target date has been postponed to September 30 of 1977. Meanwhile, an interim standards were set at 10-mode 5.6 g/kg and 11-mode 33 g/test in Decmeber, 1975.

(2) Tightening of Emission Control of Nitrogen Oxides

In the report of December, 1974, the Central Pollution Control Council pointed out the necessity of facilitating technological development, taking some measures in taxation, and controlling automobile traffic, and the Automotive Exhaust Gas Control Cabinet Council was established to study the matter in January, 1975. As for tightening emission control of nitrogen oxides from passenger cars, "Technical Discussion Group for Reduction of Nitrogen Oxides from Cars" was established in order to achieve the original target of standards. The group is proceeding with technical evaluation and an interim report was presented in December of 1975.

The report summarizes the results of the survey of the state of technical development of the passenger car manufacturers as of September, 1975. It explains about basic technologies to

reduce emission of gas and summarizes the systems to be adopted under the 1976 standards and the state of technological development of the manufacturers with respect to the target standards for nitrogen oxides under the 1978 standards.

According to the report, thirty-four models of four companies satisfied the 1976 standards as of the end of November and the other companies were to begin production from 1976.

The systems under the 1976 standards are:

(1) engine modification system: control of fuel supply system and burning

(2) thermal reactor system: combination of engine modification system, exhaust gas re-circulation device and thermal reactor,

(3) oxidation-catalyzing system: combination of engine modification system, exhaust gas re-circulation system and oxidation-catalyzing system,

(4) stratification air supply burning system with subroom: a subroom is attached to the combustion room of the engine for stratification air supply combustion, and

(5) rotary engine system: combination of rotary engine, thermal reactor and emission re-circulation system.

As for measure against exhaust gas after 1976, especially measure to reduce emission of nitrogen oxides, the above system are being improved, but all of the system still have problems in durability, safety and reliability. The report says that it is still too early to judge with which system the target can be

achieved. The manufacturers have been continuing the developmental work and a considerable progress is recognizable. Therefore, as each manufacturer makes progress in its developmental work, a technical evaluation of such progress will be made.

In addition, the interim report mentions about economy of fuel. According to the report, there has been a general tendency of increasing fuel consumption due to the reduction of thermal efficiency as a result of control of exhaust gas. Although the comparison of the cars under the 1973 standards and those under the 1975 standards disclosed an aggravation in the economy of fuel, most of the cars under the 1976 standards showed an improvement in the economy of fuel due to technological improvement, in spite of the tighter control.

(3) Comparison with American Regulation of Exhaust Gas

In America, an epoch-making regulation of exhaust gas was presented under the Federal Air Quality Act of 1970, and the regulation has been revised due to the state of technological development and the condition of energy resources since then.

Table 5-1-2 shows the comparison of present Japanese and American standards for passenger cars. As there are some differences in the method of measurement and enforcement, a direct comparison is not necessarily appropriate. However, the Japanese standards are tighter compared even with the California standards, most tight in U.S.A., and considered to

be most tough in the world.

Table 5-1-2 Comparison of Japanese and American Standards for Automotive Exhaust Gas (passenger cars)

(g/km)

Pollutant	Country	1973	1974	1975	1976
CO	U.S.A.	24.2	24.2	9.3	9.3
	California	24.2	24.2	5.6	5.6
	Japan	18.4	18.4	2.1	2.1
HC	U.S.A.	2.11	2.11	0.93	0.93
	California	1.99	1.99	0.56	0.56
	Japan	2.94	2.94	0.25	0.25
NOx	U.S.A.	1.86	1.86	1.93	1.93
	California	1.86	1.24	1.24	1.24
	Japan	2.18	2.18	1.2	0.85 *0.6

(Remarks)
1. by Environment Agency
2. fiscal year for Japan and calendar year for U.S.A.
3. Figures are average
4. *. The upper figure is for cars of more than 1,000 kg in equivalent inertial weight and the lower figure for cars of less than 1,000 kg
5. The method of measurement is 10-mode method of measurement is 10-mode method of measurement in Japan and LA-4C in 1973 and 1974 and LA-4CH after 1975 in U.S.A.

(4) Regulation of Exhaust Gas for Trucks and Buses

The regulation of exhaust gas for heavy-duty trucks and buses using gasoline or liquefied oil gas started with the regulation of carbon monoxide in 1966, was gradually tightened and the emission of hydrocarbon and nitrogen oxides was also placed

under control in 1973.

As or light-duty trucks and buses, the standards similar to those for passenger cars were applied until 1974. In the 1975 standards, however, the control was tightened as shown in Table 5-1-1 and the emission of carbon monoxide, hydrocarbon and nitrogen oxides was reduced by 68%, 44% and 41%, respectively, in comparison to that before the enforcement of the control.

As for new diesel cars running on light oil, the regulation of black smoke was started in July, 1972. From September of 1974, the emphasis was centered on nitrogen oxides and the emission of carbon monoxide and hydrocarbon was placed under control. In January of 1975, the regulation of black smoke for cars under use, too, was started.

As for tightening control after 1976, the report of the Central Pollution Control Council presented in December of 1974 recommends to promote the tightening of regulation of exhaust gas for diesel-engine cars and small trucks excluded from the 1975 and 76 controls, and the special committee on automotive pollution of the Central Pollution Control Council is studying the matter now.

5.2 Control of Stationary Sources

As for establishment of standards for emission of nitrogen oxides under the Air Pollution Control Law, an ordinance (Ordinance No. 223, 1973) which revised part of the Enforcement

Ordinance of the Air Pollution Control Law, with the establishment of emission standards for nitrogen oxides as its main content, and a Prime Minister's Office ordinance which partly revised the Enforcement Regulations of the Air Pollution Control Law were enacted and proclaimed on August 2, 1973, and enforced on August 10 of the same year.

Nitrogen oxides are harmful by themselves only and moreover substances from which photochemical oxidant is produced. The control of nitorgen oxides is considered very urgent in order to solve today's serious air pollution problem. Therefore, the environmental standards for nitrogen dioxide were established as the first step in May 1973.

As for nitrogen oxides emitted from stationary sources the environmental standards were established mainly for large boilers from the standpoint of reducing emission of nitrogen oxides as much as possible through utilization of available technology to prevent emission of nitrogen oxides.

This enforcement of the emission control is the first step to reduce the emission of nitorgen oxides from factories and plants in order to achieve and maintain the environmental standards. The philosophy in establishing the emission standards, the main contents and the points requiring special attentions of the ordinance and the Prime Minister's Office ordinance are as follows:

1) On control system

As for establishment of emission standards for nitrogen oxides emitted as a result of burning under the Air Pollution Control Law, it was originally planned to establish emission standards considering nitrogen oxides as specific harmful substances under Provision 4 of Article 3 of the Law because there was almost no technology to control production of nitrogen oxides when nitrogen oxides were classified as harmful substances in June, 1971. Since then, the technology to control production of nitrogen oxides has been developed for practical use partly through the improvement of burning system of large boilers. And as it was judged that it would be more appropriate to adopt the system of regulating emission concentration for controlling the emission of nitrogen oxides produced in the process of burning under Provision 3 of Sub-Section 2 of Section 3 of the Law, that the condition of emission of nitrogen oxides widely differs depending on each facility and that it is necessary to set standards suitable for each type of facility taking into consideration the characteristic of the facility, it was determined to set emission standards accordingly.

In adopting the system of controlling emission concentration, it was decided to calculate the density of nitrogen oxides from the amount of oxygen left in the exhaust gas in order to prevent the malpractice of diluting the exhaust gas to satisfy the emission standards.

2) On facilities to be controlled

Facilities which emit nitrogen oxides are boilers, various industrial furnaces, nitrate production facilities and so on. It is urgently required to enforce an emission control, especially for (i) those which emit a large amout of nitrogen oxides and (ii) those which emit nitrogen oxides of high density among the above facilities. This time it was decided, however, to establish the emission standards for boilers and nitrate production facilities for which the control technologies were already available and heating furnaces to which the control technologies of boilers could be applied. As for boilers and heating furnaces, only large facilities were included for control in view of the available control technologies.

3) On emission standards

It was decided to take into consideration that the present density of emission can be reduced by 30 to 40 percent by adopting the two-stage combustion system, exhaust gas recirculation system or improving burner with respect to boiler and that some degree of improvement can be expected through adoption of those technologies with respect to heating furnaces, in establishing emission standards. In addition, it was decided to establish separate emission standards for facilities in use due to difficulty of remodeling.

As for boilers, the fact that the condition of emission widely differs depending on type of fuel used was taken into

consideration.

As for nitrate production facilities, it was decided to establish emission standards on the assumption that the smoke eliminating efficiency of smoke eliminating device is about 90 percent.

In addition, an ordinance (Ordinance No. 349, 1975) which partly revised the Enforcement Ordinance of the Air Pollution Control Law and a Prime Minister's Office ordinance (Prime Minister's Office Ordinance No. 75, 1975) which partly revised the Enforcement Regulations of the Air Pollution Control Law were enacted and proclained on Decmeber 9, 1975 and enforced on December 10 of the same year.

Although the emission standards for nitrogen oxides were established in August, 1973, the application of the standards has been extended and the emission standards have been made toughter later, in view of technological development since then. The purpose of revision was to facilitate a further reduction of emission of nitrogen oxides from factories and plants in order to achieve and maintain the environmental standards for nitrogen dioxide. The philosophy, the main contents and points requiring special attensions of the ordinance and the Prime Minister's Office ordinance are as mentioned below.

1) Background for tightening of control

As for nitrogen oxides, it has been decided to achieve the environmental standards in the regions with five-year allowance

and the interim target in the regions with eight-year allowance by May, 1978. The review of the condition of air pollution in 1974 showed, however, that it would be fairly difficult to achieve the targets and it is, therefore, strongly desired to make positive progress in the control of air pollution by nitrogen oxides.

As for measures to reduce emission of nitrogen oxides from stationary sources, improvement of stack gas denitration technique and combustion system and switch of fuel can be mentioned. At present, the stack gas denitration technique is available for practical use for exhaust gases like LNG which contain neither sulfuric oxides nor soot and dust. As for exhaust gases from heavy oil, too, a large stack gas denitration facility is being used in some cases, and it seems that such facility will be developed for practical use within one year or so. However, the stage has not been reached yet to establish standards equally applicable nationwide. As for switch of fuel, there is a limitation as to supply of fuels because there is no plan to supply fuels with less nitrogen. It was decided, therefore, to concentrate the tightening of control on improvement of combustion system and partial switch of fuels.

2) On facilities to be controlled

As facilities which emit nitrogen oxides, there are boilers already under control, metal heating furnaces, oil heating furnaces and nitrate production facilities as well as cement incinerators, coke ovens, sintering furnaces, and glass melting furnaces.

In tightening the emission standards, it was decided to newly include cement incinerators and coke ovens (only new ones) for control. As it was recognized that the emission of nitrogen oxides can be reduced with both types of facilities if specific types of furnaces are used, it was decided to include them for control.

As for sintering furnaces and glass melting furnaces, the stack gas denitration technique will be, it seems, mainly used as a measure to reduce emission of nitrogen oxides. In this revision, it was decided not to include them for control, because it is still not certain when such technique can be developed for practical use.

Additionally, in view of the progress in the technology to reduce emission of nitrogen oxides after the establishment of the emission standards for nitrogen oxides in August of 1973, it was decided to extend its application to boilers, metal heating furnaces and oil heating furnaces of up to 10,000 Nm^3/h of exhaust gas.

3) On emission standards

In tightening the emission standards, improvement of burning system and partial switch of fuels were considered as prerequisite conditions. As for metal heating furnaces and oil heating furnaces, the emission standards were established on the assumption that some of them may require stack gas denitration. As for facilities already built, separate emission standards were established because it will be difficult to remodel them.

6. Future direction of measures against photochemical smog

The Promotion Conference prepared a following recommendation as to the future direction of measures against photochemical smog and agreed that the recommendation should be utilized when the agencies and ministries concerned plan or execute various measures.

Photochemical smog is occurring frequently in the large cities and their surrounding areas mainly in Summer, creating serious social problems. The Government established "the Photo-Chemical Smog Control Promotion Conference" in July of 1972 to promote a close communication among the administrative agencies concerned with countermeasures against photochemical smog, and comprehensive and effective measures, and has been carrying out various studies and measures following "On promotion of measures against photochemical smog" decided by the Conference on July 15, 1972.

The occurrence mechanism and effect of photochemical smog have been partly discovered both qualitatively and quantitatively through the three-year comprehensive study started in 1972 and carried out in Tokyo Bay and Osaka Bay areas and various basic studies by the research institutions, but still further studies on the effects on living things of photochemical smog are urgently required. Together with promotion of basic studies, comprehensive and strong measures against stationary and mobile sources should be promoted in order to achieve the environmental standards for nitrogen dioxide and photochemical oxidant and those for hydrocarbon

to be established soon within the target date for thorough prevention of photochemical smog.

As a measure against nitrogen oxides from stationary sources, an emission control was started as to large boilers in 1973. A further effort should be made for development of technology to control emission of nitrogen oxides and the application of the emission standards should be extended to other types of facilities.

At the same time, a calculating technique for maximum allowable emission in a region should be examined for early introduction of a control of total amount.

As measures against hydrocarbon from stationary sources, various measures such as a guidance to adopt the floating roof system, already in use, in building large tanks for crude oil should be taken and at the same time it is necessary to develop detailed and effective measures, paying attentions to diversification of sources.

As for measures against hydrocarbon and nitrogen oxides from mobile sources, the control of new cars running on gasoline or liquefied oil gas was drastically tightened both in 1974 and 1975. In addition, the 1976 control of nitrogen oxides was determined. However, the pollution due to concentration of automobiles in the large cities cannot be overlooked and it is necessary to tighten the control of automobiles including small trucks and diesel-engine cars. In addition, the improvement of

roads and urban structure should be studied as a part of long-range plan, and for a time being, a measure to reduce automobile traffic should be promoted as a part of the comprehensive traffice control in the large cities.

As health measures, informations on photochemical smog should be thoroughly disseminated to schools and the general public. Especially in the regions where there is a high possibility of photochemical smog occurring, measures such as instruction in emergency measures should be taken to keep damages at minimum.

In addition, the accuracy of forecast in the preceding day should be improved in order to make emergency measures more effective. Also, photochemical-smog should be prevented through effective control of sources such as voluntary control of use of automobile.

In order to prevent photochemical smog, the measures mentioned above and a comprehensive measure based on the execution plan described in the following should be promoted. By so doing, healthy and cultural living environment for the people will be secured.

Execution Plan

I. Preventive Measures

1. Establishment of environmental standards

Environmental standards for hydrocarbon which causes photochemical oxidant should be immediately established, taking into consideration the occurrence mechanism of photochemical oxidant.

2. Measures against stationary sources

1) Measures against nitrogen oxides

(1) Together with extension of the emission control of nitrogen oxides and tightening of the emission standards, the development of technologies to control emission of nitrogen oxides from stationary sources and those such as a stack gas denitration technique to eliminate them should be facilitated.

(2) As for nitrogen oxides, studies and research works including development of air pollution forecasting technique should be carried out for early introduction of the control of total emission.

2) Measures against hydrocarbon

(1) As for hydrocarbon from stationary sources, comprehensive and rational measures should be examined such as switch of raw materials and measures against secondary pollution, taking into consideration safety and efficiency, and measures which can be carried out should be gradually executed only with respect to large-scale hydrocarbon emitting facilities and organic solvents which are photochemically highly reactive and also being used in large quantities, in view of the fact that it is difficult to enforce a standard control due to diversity of hydrocarbon emitting sources.

(2) In order to prevent leakage of hydrocarbon in the process of oil refinery, distribution and selling, studies on the development of hydrocarbon processing system and surveys of

emission of hydrocarbon from various devices should be carried out.

(3) A hydrocarbon eliminating device of high efficiency should be developed.

3) Emergency measures

In order to establish emergency measures against photochemical oxidant, techniques to forecast high density pollution by photochemical oxidant and rational preventive measures should be developed.

3. Measures against mobile sources

1) Measures against automotive exhaust gas

(1) As the contribution of small trucks and diesel-engine cars to air pollution is not small, the control of exhaust gas from these types of automobiles should be tightened as early as possible.

(2) The control of exhaust hydrocarbon for trucks should be newly enforced among automobiles running on gasoline or liquefied oil gas in use.

(3) As for automobiles of 1975 models, the control of automotive exhaust gas should be considerably tightened and at the same time, the development of preventive technology should be speeded up in order to enforce the control of emission of nitrogen oxides with respect to 1976 models.

(4) Together with tightening of the control of exhaust gas, measures should be taken to make sure through inspection and

servicing of automotive exhaust gas cleaning device and other devices. At the same time, automobiles poorly serviced should be strictly controlled.

(5) Works to develop automotive exhaust gas controlling techniques should be assisted and promoted.

2) Measures against automobile traffic

(1) For reduction of automobile traffic in the large cities, optimum control of flow of traffic and rational allocation of available road space, various measures such as expansion of road for pedestrians, non-parking area and road exclusively for buses, construction of road exclusively for bicycles and improvement of automatic traffic control system should be carried out.

(2) The transportation capacity and passenger service of public transportation facilities such as bus, subway and railway should be improved and the use of such facilities should be promoted and arrangement of mono-rail or other new traffic system should be studied. At the same time, reorganization of bus routes, adoption of mini-bus, introduction of bus location system and traffic control system giving priority to buses should be facilitated.

(3) For efficient freight transportation in the cities, establishment of common distribution system and truck terminals should be promoted.

(4) Studies on the control to prevent emergency and the method of guidance at emergency should be carried out. A traffic

control system and the way to execute such control should be studied.

3) Measures with respect to composition of gasoline

(1) An administrative guidance should be continued in order to prevent increase of hydrocarbon in gasoline which is photochemically highly reactive.

(2) A study on the correlation between the composition of gasoline and photochemical reaction should be continued.

4. Rationalization of urban structures

1) Execution of surveys of air pollutions of urban type

In order to develop effective preventive measures against urban type air pollution, a comprehensive survey should be executed to find out the relationship between various activities and air pollution in the large cities. At the same time, measures to induce activities desirable from the Standpoint of preventing air pollution in the large cities should be examined.

2) Measures with respect to roads

(1) For efficient use of roads and smooth flow of road traffic, improvement of urban structures such as improvement of sub-urban center and distribution system should be carried out. At the same time, bypass roads should be constructed in order to reduce traffic passing through the central part of the city.

(2) For smooth flow of traffic and prevention of air pollution

due to traffic congestion in the central part of the city, the existing roads should be improved through such measures as expansion of roads and construction of flyover roadways.

(3) Together with rationalization of traffic, and maintenance and promotion of urban functions, establishment of new traffic system should be examined in order to reduce traffic congestion.

II Surveys and Studies

1. Surveys and studies

1) Survey of actual conditions with respect to photochemical smog

With respect to photochemical smog, a comprehensive survey covering a wide area with air pollution due to photochemical reaction was carried out in the Osaka Bay area in 1974. In addition, a correlation between environmental conditions and health damages was studied both in the Osaka Bay and Tokyo Bay areas.

As the result of the past surveys, the conditions of air pollution, flowing of pollutants, photochemical reaction characteristic of substances causing photochemical smog and the occurrence mechanism of photochemical smog are understood better now. On the basis of the results of the past surveys, it has become possible to develop a technique to forecast photochemical smog.

2) Future surveys of actual conditions of photochemical smog

(1) In 1975, special regular weather observations will be done

for issuing emergency warnings of high accuracy and data thus obtained will be supplied to the local authorities to help them in issuing emergency warnings. At the same time, together with development of photochemical smog forecasting technique in order to make possible establishing an effective controlling measure a day earlier, a way should be found to improve the efficiency of emergency measures.

(2) On the basis of the results of the comprehensive surveys of actual conditions of air pollution due to photochemical reaction, measures against air pollution in a wider area should be developed through statistical analysis of the data.

(3) Humid air pollution including the phenomenon of acid rain which is considered to be produced through a complex mechanism somewhat similar to that which produces photochemical smog should be investigated.

(4) The relationship between the symptoms and the environmental conditions such as concentration of oxidant should be investigated and analyzed with respect to the cases suffered from photochemical smog in the Tokyo Bay, Osaka Bay and Setonaikai areas.

(5) As for nitrogen oxides and hydrocarbon which cause photochemical smog, the relationship between the quantity of emission and fuel, burning condition or burning facility should be investigated.

(6) As s part of the system of monitoring air pollution due to photochemical reaction, standards for selection of indicator

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plants and judgement of effect should be established and at the same time, the effect on plants should be investigated in order to obtain basic information concerning the necessity of establishing living environmental standards for air pollutants.

2. Experimental studies

In order to find out the mechanism of photochemical reaction and the effects of pollutants on plants, the following experimental studies should be carried with the national research institutes taking the initiative.

1) Studies concerning air pollution measuring techniques

In order to define and evaluate the occurrence, dispersion and effect on living things of photochemical smog, a technique of microanalysis for harmful gases and a quick physico-chemical measuring technique for photochemical aerosol should be developed and improved. At the same time, studies necessary for standardization of correction method should be carried out with respect to measuring technique for harmful gases and suspended particulate matters.

In addition, in order to quickly find out weather factors contributing to development of photochemical smog, a remote measuring technique for atmospheric physical phenomenon should be developed.

2) Investigation into mechanism of photochemical reaction

In order to define the occurrence mechanism of air pollution

due to photochemical reaction, a survey of condition of emission of hydrocarbon and acid particulate matters in the photochemical aerosol should be done and physico-chemical analysis of those substance should be done. Also, the production mechanism of secondary pollutants produced by photochemical reaction should be investigated.

3) Investigation into effect on living things

In order to find out about chronic and combined effects among various effects of photochemical smog on living things, the effects of ozone and nitrogen oxides on living things (animals) should be studied.

As for effects on plants, sensitivity and tolerance limit of agricultural products and trees to pollutants should be clearly defined and evaluation of indication characteristic and mechanism of damaging should be carried out.

III Establishment of Forecasting, Monitoring and Measuring System

1. Establishment of forecasting system

1) In order to strengthen the system of forecasting air pollution, an air pollution weather center should be established and weather informations should be supplied to local authorities to assist them in carrying out measures against air pollution. In 1975, an air pollution weather center will be established in Takamatsu.

2) For prompt supply of weather informations, an information supply system will be established.

2. Establishment of monitoring and measuring system

The national air measuring network will be improved and at the same time, an assistance will be extended to local authorities in providing recorders for automatic measurement of nitrogen oxides, oxidant and hydrocarbon, telemeter systems and monitoring telemeter system.

3. Standardization of method of measurement

Following establishment of the environmental standards for hydrocarbon, the method of measuring hydrocarbon in the air will be standardized. In addition, the method of measuring photochemical oxidant and nitrogen oxides will be examined for improvement.

IV. Health measures

1. Investigation into the relationship between health damages and environmental conditions

In order to find out about the details of the reports of health damages due to, it appears, photochemical smog and define the relationship between environmental conditions such as the density of oxidant and health damages, surveys of actual conditions will be carried out in the Tokyo Bay, Osaka Bay, and Setonaikai areas.

2. Promotion of health measures at medical institutions

Under a close cooperation with public health centers, national hospitals, medical institutions and doctors' associations, the actual conditions of damages should be found and treatment

and recuperation should be thoroughly managed.

3. School health measures

1) Informations on photochemical smog should be disseminated at schools and a guidance should be given for emergency procedures.

2) As for the special project to improve health, mobile classes will be continued. At the same time, educational environment for improvement of health of school children should be provided, together with expansion of special health examination and school environment greening works should be carried out.

3) Double windows and air cleaning equipment should be provided at schools for which such necessity has been recognized due to air pollution.

4. Measures for general public

Informations on photochemical smog should be thoroughly disseminated. An instruction on emergency measures should be given and efforts should be made to find out the actual conditions of health damages.

5. Health measures at working places

Actual conditions of health damages of workers should be found out. Necessary administrative guidance as to provision of eye washing facility for emergency and close cooperation with medical institutions should be given.

V. International Cooperation

1. The Air Management Sector Group of OECD has set up a special committee at the proposal of Japan and the committee has been discussing the problems of photochemical air pollution. Japan has been actively participating in the study and should promote a further international cooperation.

2. Japan should promote exchange of informations with America which has much experience in the study of photochemical smog, and dispatch delegations to America to promote cooperation in research works between two countries.

EXPERIMENTAL RESULTS OF MOBILE SMOG CHAMBER

(Air Quality Bureau-Environment Agency)
Japanese Delegation

1. Construction of Mobile Smog Chamber

1.1 Object of Construction

To promote the countermeasures against air pollution caused by photochemical reaction, the mecahnism of generation of the pollution should be clarified. Hence, in addition to the basic laboratory study the field investigation should be carried out also.

The Environment Agency has a mobile smog chamber constructed in 1971 with reserve funds, ¥95,037,000, to start this investigation in the field in the photochemical smog season of 1972.

The mobile smog chamber comprises a photochemical smog chamber vehicle loaded with the photochemical reactor (smog chamber and ultra-violet irradiation apparatus), and a chemical analysis vehicle loaded with various instruments that measure precursor and secondary products generated by the photochemical reaction. The mobile smog chamber was manufactured by the Shimazu Manufacturing CO., Ltd.

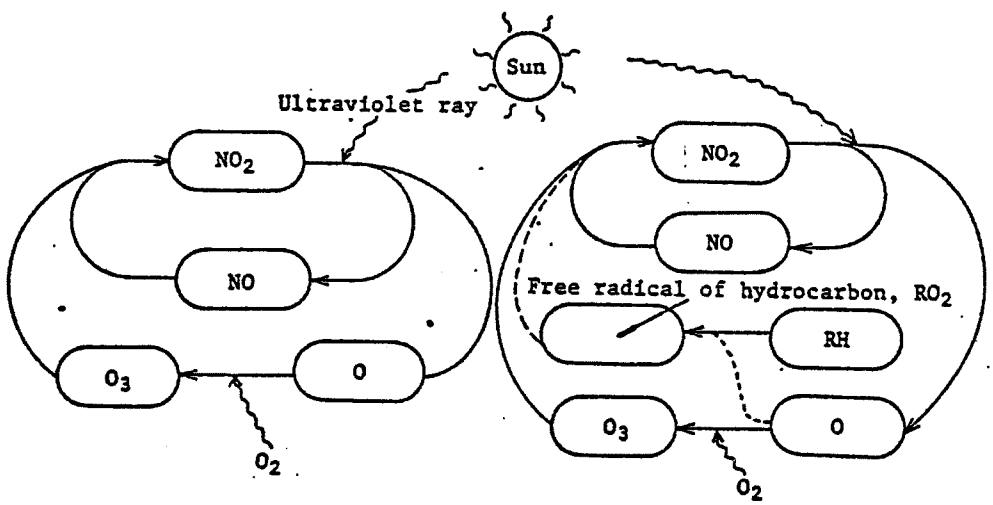
This mobile smog chamber will be sent to various places, introducing ambient air into the chamber, irradiating the air by ultra-violet light to generate photochemical reaction, and investigating in detail the conditions of pollutants before and after the reaction to facilitate the establishment of real counter-measures against photochemical air pollution.

1.2 Basic Principles of the Chamber Experiment.

It was assumed that the photochemical air pollution occurring in Japn is similar to that observed in Los Angeles, that is, oxides of nitrogen, hydrocarbons, etc., discharged from stationary and mobile sources induce photochemical reactions by the energy of ultra-violet light in the solar radiation to generate the secondary products represented by oxidants. The outline of this emission mechanism may be simply illustrated as shown in Fig. 1.2.1.

The experimental system is constructed to measure first the concentration of pollutants in the air sampled into the smog chamber in the field, then irradiated by use of ultra-violet lamps instead of sunlight to produce photochemical reaction, and then to measure the concentration of reaction products by various instruments mounted on the analysis vehicle.

Fig. 1.2.2 is a flow diagram showing the process of the introduction of ambient air for the production of photochemical reaction and the measurement of the secondary products.



(1) Dissociation cycle of NO_2 (2) Interaction of hydrocarbon and NO_2 ad photo-dissociation

Fig. 1-2-1 Forming reaction of O_x

1.3 Photochemical Smog Chamber Vehicle

1.3.1 Construction

The photochemical smog chamber vehicle (hereinafter referred to as "chamber vehicle") is equipped with apparatus that samples ambient air into the smog chamber, and applies the irradiation of ultra-violet light to produce photochemical reaction. The sample gas within the smog chamber is sent to the photochemical reaction analyzing vehicle, through a docking device, for analysis.

The chamber vehicle is constituted from the components (1) to (10):

(1) Vehicle

This is a large-sized bus modified to load various instruments and apparatus. Its dimensions are as follows:

length: 8.73 m; width: 2.43 m; hieght: 3.35 m.

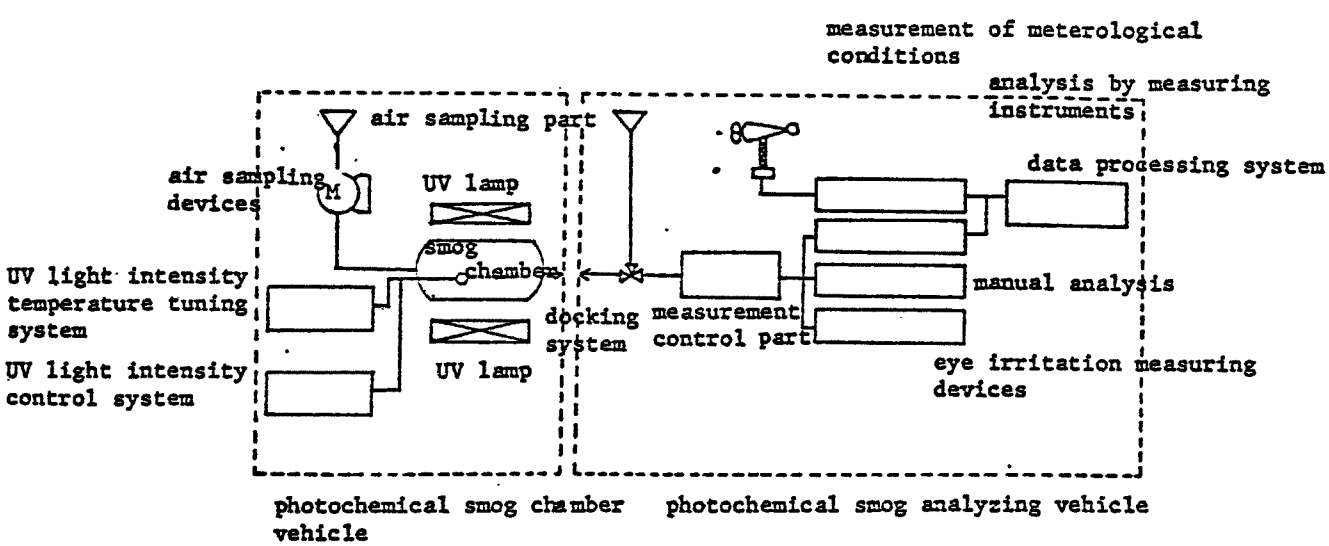


Fig. 1.2.2 Flow Sheet

(2) Air sampling apparatus

This is to sample ambient air into the smog chamber comprising an air sampling pipe and an air sampling blower of at least 0.5 m^3/min flow rate. The air sampling pipe is an aluminum pipe with the inner wall coated with Teflon and it is variable in length from 1 to 10 m above the ground.

(3) Smog chamber

This is a cylindrical chamber made of pyrex glass that adsorbs little pollutants. 2 m^3 of the ambient air is sampled into this chamber to be subject to the irradiation of ultra-violet light in order to induce the photochemical reaction within the chamber. This smog chamber is hung from a frame so as to withstand the oscillation and shock of automobile during travelling. It can be drawn from the irradiation room on rails (with the frame), and may be removed from the frame.

The upper portion of the smog chamber is provided with two holes, through which two glass shafts extend respectively to agitate the interior of the

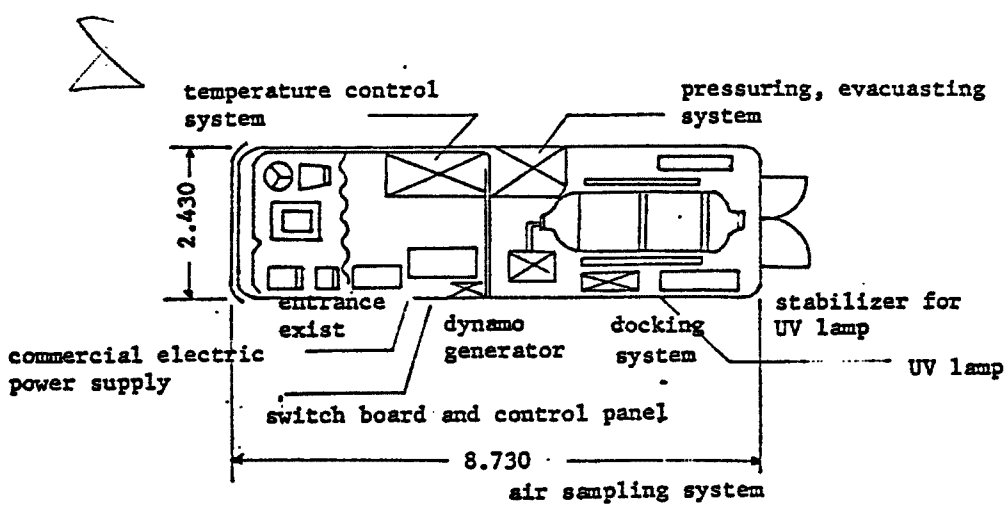


Fig. 1.3.1 Arrengements of appartuses in the chamber vehicle

chamber with glass propeller fan mounted on the end of the shaft. Further, to permit experiments under vacuum of less than about 8 mm Hg. and pressurized conditions of 0.1 kg/cm^2 the smog chamber is air tight. Packing and the like surfaces in contact with sample gas within the chamber are all made of Teflon or Teflon coated materials except for Pyrex glass.

(4) Ultra-violet irradiation apparatus and measuring and recording apparatus.

The rear portion of the vehicle is provided with an ultra-violet irradiation room which is kept warm with insulating materials. The smog chamber is installed at the center of the room and surrrounded by 96 ultra-violet lamps. An alumium electropolished reflector is mounted on the back of each lamp to provide high reflection.

The intensity of ultra-violet lamps may be controlled and its spectrum may be adjusted by a combination of the following three types of lamps:

FL40SB-A (with output peak approximately at 420 nm)
FLR40SBL-A (with output peak approximately at 365 nm)
FLR40SE-A (with output peak approximately at 310 nm)

The energy of ultra-violet light irradiated into the smog chamber is usually measured near the outer wall of the smog chamber so as to keep its intensity constant during the irradiation against the temperature change in the irradiation room and voltage variation. If the intensity of the irradiation if further varied, a manual regulator is provided to maintain constant intensity.

(5) Temperature control

Since the photochemical reaction scheme and reaction speed are affected by temperature, the temperature within the smog chamber should be controlled.

Such control is accomplished by insulating the whole irradiation room and is insured through use of temperature sensors spaced throughout the irradiation room. Temperature control is effected by manual heating and manual and/or automatic cooling.

(6) Pressure regulator

The sample gas within the smog chamber is continuously or intermittently sent through the docking device to the analyzing vehicle to measure its constituents. The volume of the sample gas within the smog chamber is then reduced.

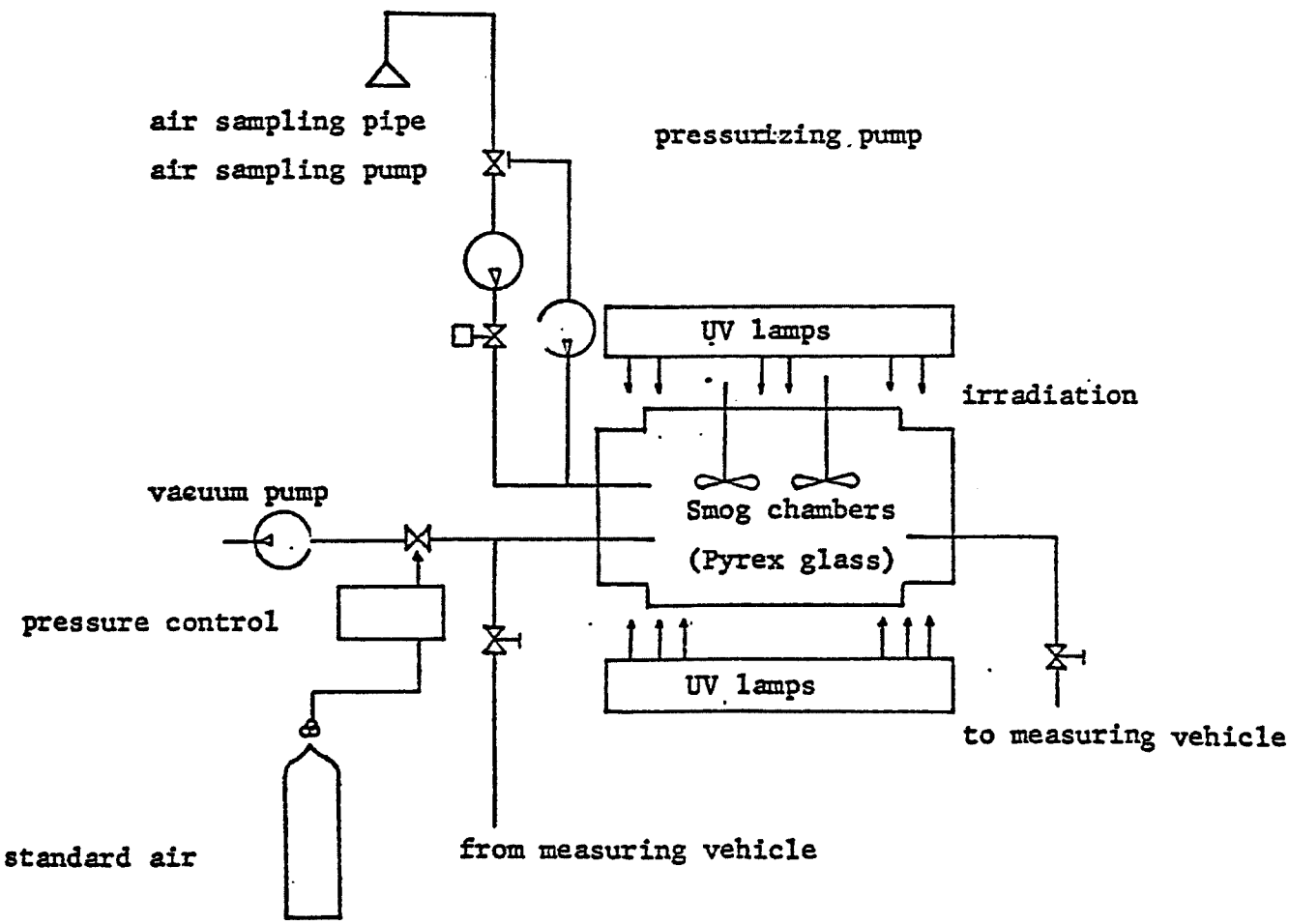


Fig. 1.3.2 Flow of the chamber vehicle

Hence this regulator is provided to supplement from a cylinder the same amount of purified air as that of gas sent to the analyzing vehicle. The reference gas is supplemented through a valve that is automatically opened upon the reduction of gas pressure to -6mm H_2O within the smog chamber because of the supply of the sample gas.

(7) Booster

Ambient air is generally sampled into the chamber by a sampling blower. Otherwise air can be sampled by evacuating the smog chamber to open valve. Further, a pressure-sensitive device is provided to raise the pressure within the smog chamber to 0.1 kg/cm^2 after air sampling. A pressure-reducing device is constructed from a mechanical booster and a conventional vacuum pump to be used for sampling under vacuum and, in addition, mainly for vacuum cleaning of the inner wall of the smog chamber before and after each experiment.

(8) Docking device

This is a connecting pipe to transfer sample gas from the smog chamber to the instruments on the analyzing vehicle or to return the gas to the chamber, the pipe being made of teflon coated with heat insulator.

(9) Self-power supply

In the experiment a commercial power supply (200V, 3 phase, 50 cycle and 50A) is mainly used, while an engine generator (200V, 3 phase, 50 cycle and 10.4 kW) is carried as self-power supply.

(10). Others

A control panel is provided to gather into one section the various instruments and controls for controlling the irradiation intensity and temperature during measurement.

1.4 Photochemical smog analyzing vehicle

1.4.1 Constitution

The photochemical smog analyzing vehicle (hereinafter referred to as the analyzing vehicle) is loaded with instruments to analyze the sample gas supplied from the smog chamber, and apparatus to observe meteorological factors.

The analyzing vehicle is constituted from the following items (1) to (7):

Location of each apparatus within the analyzing vehicle, flow diagram, etc. are shown in Figs. 1.4.1 and 1.4.2 and Table 1.4.1.

(1) Vehicle

The vehicle is a modification of a large-size bus to load various instruments, etc. Its dimensions are as follows; length; 11.40 m, width; 2.49 m, height; 3.42 m,

(2) Air sampling device

While the analyzing vehicle generally analyzes the sample gas from the chamber vehicle it may travel alone as an air pollution analyzing vehicle to measure ambient air with the air sampling device. The air sampling device comprises a stainless steel pipe with the inner wall coated with Teflon and is variable in height to extend from 3.5 to 10 m above the ground.

(3) Instruments and recorders

The instruments listed in Table 3.4.1 were selected after due consider to the requirements that (1) they shall be prevented from any damages and errors caused by oscillation. (2) they shall have high performance to sense small concentration changes caused by photochemical reaction, (3) they shall have

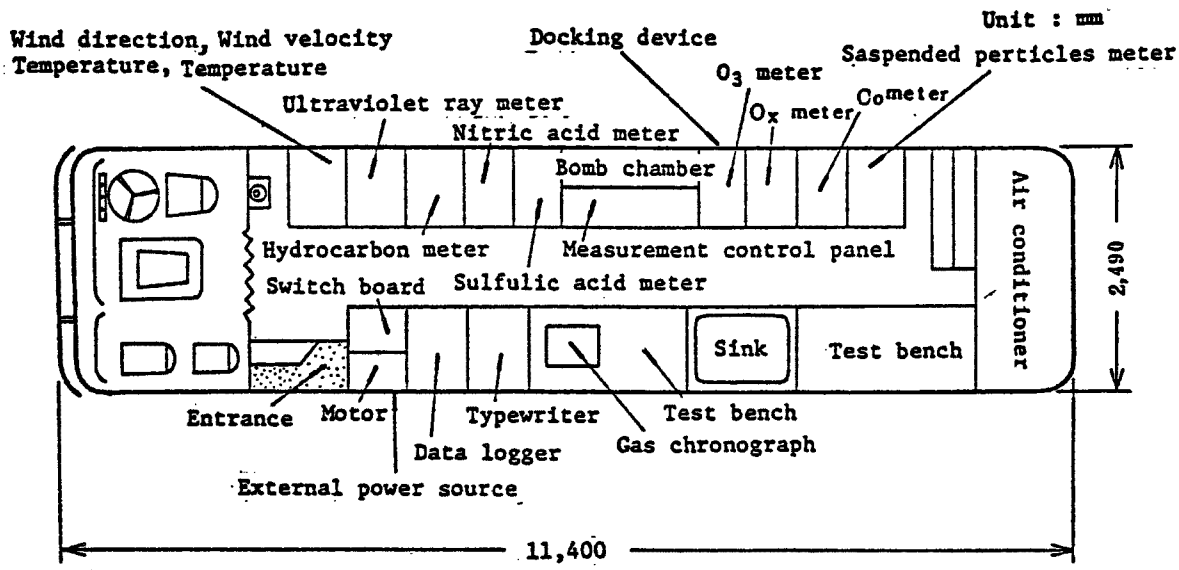


Fig. 1-4-1 Arrengements of apparatuses in the Analysis Car

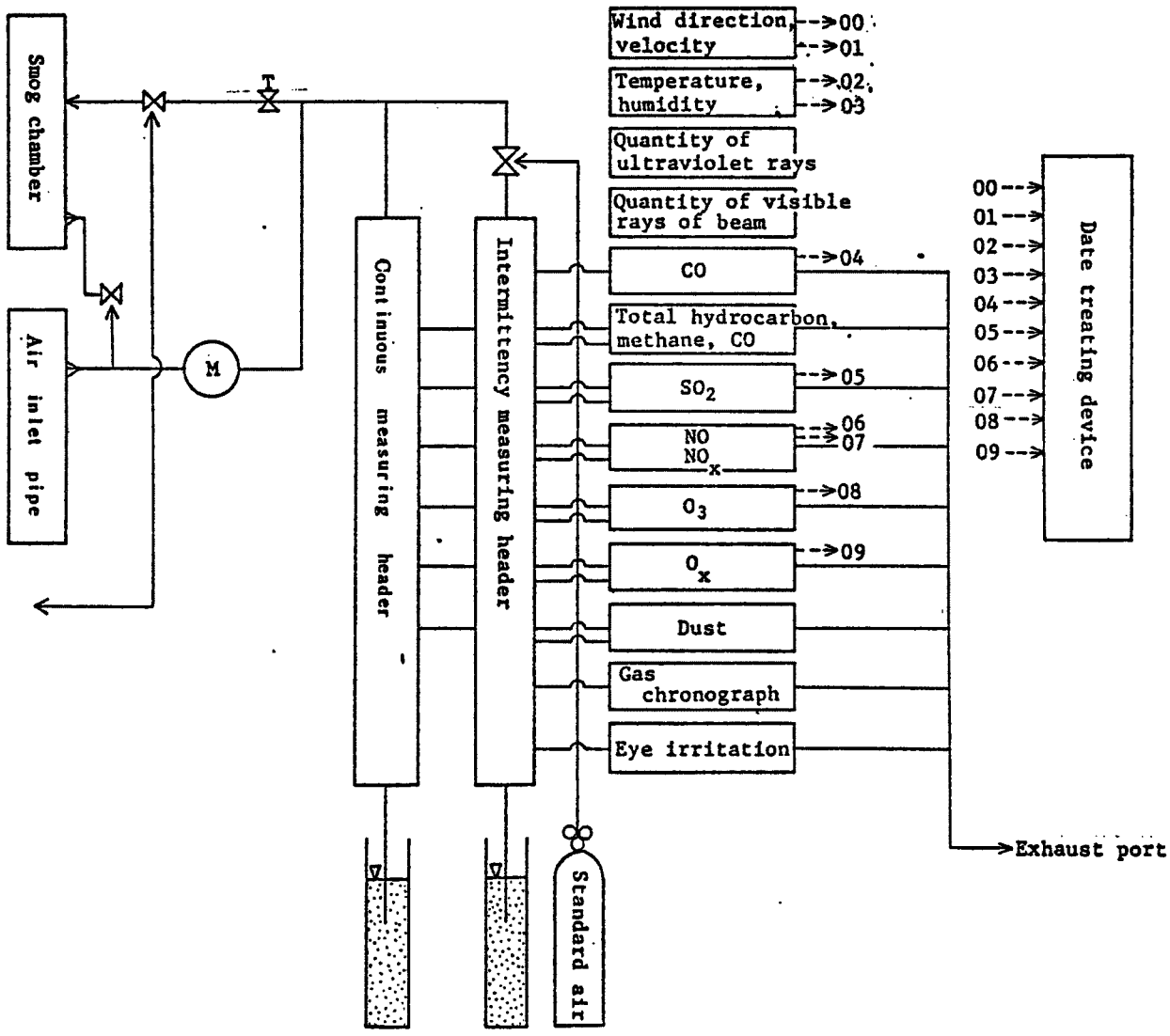


Fig. 1-4-2 Flow sheet for photochemical smog analysis car

rapid response speed to permit intermittent measurement, (4) the consumption of sample gas shall be small.

Major instruments can continuously and intermittently measure the constituents and others can intermittently measure the costituents by automatic switch-over apparatus.

(4) Data processing system

This system types out the data measured by each instrument with a required interval of time.

(5) Eye irritation monitoring device

This is a device to expose eyes to the sample gas to observe the eye irritation symptoms as the effect of secondary products formed by photochemcial reaction.

(6) Self-power supply

In the investigation, commercial power supply (200V, single phase, 50 cycle and 50A) is mainly used, while an engine generator (100V, single phase, 50 cycle and 10.4 kW) is loaded as self-power supply. Further, the voltage of the commercial power supply is changed from 200 to 100V by a transformer provided in the vehicle to operate each apparatus.

(7) Others

A cooler and a heater are loaded to reduce the errors of measured data due to the abrupt change of temperature and improve the temperature condition within the vehicle.

Also work tables, sink, etc. are provided to permit manual analysis and measurement within the vehicle.

Table 1.4.1 Instruments in the Photochemical Smog Measuring Vehicle

Measuring Item	Manufacturer	Instrument	Catalog No.	Method	Measuring Range
CO	Shimazu Seisakujo Co., Ltd.		URA-2S	NDIR method	0-50, 100 ppm
Hydrocarbon (THC, CH_4)	Beckman-Toshiba Co., Ltd.	Photochemical Air Pollution Continuous Monitor	6800	FID-GC	THC 0-10 ppm C CH_4 0-10 ppm C
NO and NO_x	Shimazu Seisakujo Co., Ltd.	Chemiluminescene nitrogen oxides monitor	CLM-201	Chemiluminescence method	0 - 0.5, 1.25, 10, 25, 100 ppm
O_x	Suga Shikenki Co., Ltd.	Oxidant recorder	OXR-1	Coulometry	0 - 0.5 pp,
O_3	Kimoto Electric Co., Ltd.	Ozone monitor	803A	Chemiluminescence method	0 - 0.5 ppm
SO_2	Shimazu Seisakujo Co., Ltd.	S monitor	SFM-1A	FPD	0 - 0.1 ppm
Suspended Particulates	Shibata Kagaku Co., Ltd.	Digital dustmeter	A-703	Light scattering method	
Wind Direction Wind Velosity	Ota Keiki Co., Ltd.			Electric generating method	0 - 540°C, 0 - 20 m/min.
Temperature, Humidity	Ota Keiki Co., Ltd.				0 - 40°C, 20 - 100%

Table 1.4.1 Instruments in the Photochemical Smog Measuring Vehicle (Cont'd.)

Measuring Item	Manufacturer	Instrument	Catalog No.	Method	Measuring Range
Light Intensity (total)	Suga Shikenki Co., Ltd.	Integrater irradiance Recorder	PH-11P2		UV 300-400 nm Visible 400-700 nm
UV light Intensity (spectral distribution)	Japan Spectroscopic Co., Ltd.	UV spectrograph	UV-55		300-500 nm 10 nm interval
Hydrocarbon (component)	Shimazu Seisakujo Co., Ltd.	Gas chromatograph	GC-4BMPFE		
NO and NO_2	Denki Kagaku Keiki Co., Ltd.	Nitrogen Oxides Automatic monitor	GP-5	Saltzman method	0 - 0.25, 0.5, 1 ppm

2. Performance Test of Smog Chamber

2.1 Outline

One of the essential points in the use of the chamber is to make the condition within the chamber approach the atmospheric one as close as possible. Accordingly, it is necessary to know whether or not the condition of the chamber to be used is close to that of the atmosphere. To this end, the rate of loss of NO_x and O_3, and the time required to homogenize air within the chamber were investigated.

2.2 Rate of loss of NO, NO_2 and O_3 in the chamber

The inside volume and surface area of this smog chamber are 2.1 m^3 and 10 m^2 respectively. The ratio S/N (surface area/volume) is 5 m^{-1}. That ratio of the smog chamber is much smaller than that of the existing immobile chambers. To investigate surface effects upon the relatively reactive NO, NO_2 and O_3, the rate-of-loss measurements were carried out with and without light and with and without agitation, and rate of decrease (hereinfater referred to as R.D.) of each component was determined.

Further, in the supplement of clean air for analysis into the chamber, the relationship between the dilution and gas concentration change within the chamber is expressed as follows:

$$\int_{o}^{t} \frac{-V}{Vo} \, dt = \int_{Co}^{C} \frac{dc}{C-C'} \qquad (2.21)$$

where C : gas concentration (ppm) after t hours

Co : initial gas concentration (ppm)

C' : gas concentration (ppm) in diluted air

Vo : volume of chamber (2.1 m^3)

V : amount of air to be supplemented per unit time (ℓ/hr)

The correction for dilution was made by the above equation.

(1) Loss of NO

After the chamber was filled with clean nitrogen, 0.6ℓ of a 1670-ppm-NO-in-N_2 mixture was introduced directly into the chamber through the regulator with flow meter, and left for 2.5 hours with the initial concentration of NO_x of 0.567 ppm, and NO of 0.502 ppm as measured by chemiluminescence NO_x meter without irradiation and agitation.

Also similar experiment was carried out in which NO sample was left for 2 hours with agitation and without irradiation.

In both experiments, it was found that R.D. of NO is low in the order of less than 1.1%/hr. while there is little oxidation to NO_2, so that th loss of NO was found to be negligible if no irradiation was conducted.

(2) Loss of NO_2

In the same way as the above-mentioned adsorption experiment of NO, about 1 liter of a 906-ppm-NO_2-in-N_2 mixture was introduced into the chamber, and maintained with the initial concentration of NO_x, 0.625 ppm, and NO, 0.155 ppm, without agitation and irradiation.

The R.D. of NO_2 in the order of 2.3%/hr. Also similar experiment was carried out in which NO_2 sample was left for 2.5 hours darkness with agitation.

It is presumed for the present from these results of the experiments that the loss of NO_2 on the surface of the chamber is scarce. However, since this measurement of NO_2 was carried out by chemiluminescence system its concentration was represented by NO_x-NO.

(3) Loss of O_3

The chamber was filled with clean air and the air was charged with O_3 from O_3 generator, then the O_3 was left for 2.5 hours with its initial concentration of 0.697 ppm under darkness weith agitation.

R.D. in tis case seemed to be rather high in the order of 8.8%/hr. Also similar experiment was carried out without agitation. The latter was in the order of 6.6%/hr, being slightly lower than that with agitation. It is noted that both experiments showed relatively high R.D. in the order of over 6.6%/hr.

Further, when the loss of O_3 was examined under irradiation (initial cncentrations of O_3; 0.215 ppm in air), R.D. was found to be 21%/hr. THe change and loss of O_3 is considered very large even if the effect of purities in the balance air was taken into consideration.

The above-mentioned results are shown in Table 2.1.1.

The examination of the surface effect of the chamber, i.e., one of the basic characteristics of the smog chamber, resulted in a presumption that R.D. of both NO and NO_2 were negligible under no matter whether agitation is employed or not.

Referring to O_3, 6.6%/hr. of R.D.was shown even under dark without agitation. Further 8.8%/hr and 21%/hr of increased R.D. were noted respectively with agitation and under irradiation with agitation. This showed that the O_3 in the chamber has some problems.

Table 2.1.2 R.D. of NO, NO_2 and O_3

			NO	NO_2	O_3
in N_2	dark	with agitation	-1.1%/hr	-4.6%/hr	%/hr
		without agitation	-1.0	-1.6	
in air	dark	with agitation	-1.5	-2.3	-8.8
		without agitation	-0.7	-0.7	-6.6
	irradi-ation	with agitation			-21.0

Experimental Condtions:

Temperature: 20 ∿ 25°C
Humidity: less than 30%
Intensity of ultra-violet light: 9.5 mW/CM^2

2.3 Measurement of ultra-violet irradiation intensity

2.3.1 Method based on photodissociation speed of NO_2 (K_1 value)

(1) Outline

It is impossible because of the complexity of the shape, reflection factor, transmission factor, effective light path, etc. of the chamber to accurately measure the quantity of light contributing to the photochemical reaction in the chamber by means of conventional actinometer. As a method that overcomes these difficulties, there is frequently used the method of estimating the intensity of light by the use of photodissociation reaction of NO_2 in N_2.

The primary quantum yield in the photodissociation of NO_2 is close to 1 within the spectrum range associated with photochemical air pollution. Low concentration NO_2 is photodissociated in the absence of O_2. The reduction rate of NO_2 then is represented by the following equation:

$$-\frac{d(NO_2)}{dt} = k_1 (NO_2)$$

where $K_1 = I_0 \Sigma \phi$, ϕ is the primary quantum yield and I_0 is light absorptivity. The intensity of light measured by this method is represented by the value of Kd. It corresponds to the primary rate of NO_2 photodissociation reaction and has the unit of min^{-1}.

This method of measuring the intensity of light has some feasiblity depending upon the requirements for the measurement, and is effective experimentlaly since it comprises the equipment parameters such as shape, light spectrum, effective light path length, etc.

(2) Experimental method

After vacuum cleaning of the Tedlar bag the bag was filled with high purity N_2 gas and then evacuated again. Again it was filled with high purity N_2 gas. After the amount of remaining oxygen was confirmed to be less than 0.1% by the oxygen meter manufactured by Koritsu Kiki, the predetermined amount of the

reference gas of NO_2 (960 ppm/N_2 balance) was introduced and irradiated for 1 minute in the chamber. The changes of NO_x and NO were measured by chemiluminescent recorders.

In this situation, the experiment was carried out with initial NO_2 concentration of 4.25 and 0.805 ppm, 1 minute of irradiation time and 9.5 mW/cm^2 of light source intensity. As a result, a k_1 value of 0.3 min^{-1} was obtained, compared with the aimed value of 0.3 to 0.4 min^{-1}.

Also the K_1 value for natural light was measured by the same method as that of the chamber experiment using tedlar bag. As the result, 0.27 to 0.67 min^{-1} of k_1 were shown on fine day in summer.

Therefore when K_1 in the chamber was about 1/2 to 1 of that of natural light in summer.

2.3.2 K_1 obtained from photochemical reaction of propylene-NO-air system.

(1) Outline

Glasson et al reproted the linear correlation between NO photoxidation rate and NO_2 photodissociation speed in the photochemical reaction experiment of propylene-NO system, where NO photo-oxidation rate (R) is repreented by

$$R = \frac{(NO)_o}{2T_{1/2}} \qquad (2.3.1)$$

where

(NO)o: initial concentration of NO(ppm)
t1/2 : half-life of NO (min)

TABLE 2.3.1 (1) K_1 by static method in chamber

Irradiation Time	Residual O_2 conc.	Initial conc. (ppm)		Conc. after irradiation (ppm)		K_1 (min^{-1})		Temp.	U.V.
min.	%	NO_x	NO	NOx	NO	Measured value	Corrected value	°C	mW/cm^2
1	0.1	4.35	0.10	4.50	1.15	0.276	0.362	33°	9.0
1	0.1	0.835	0.03	0.83	0.18	0.206	0.270	30°	9.0

TABLE 2.3.1 (2) K_1 by static method in urban

Irradiation Time	Weather	Initial conc. (ppm)		Conc. after irradiation (ppm)		K_1 (min^{-1})	
		NO_x	NO	NO_x	NO	Measured Value	Corrected Value*
Summer 12:30 ∿ 1 min	Fine	1.140	0.400	1.180	0.670	0.432	0.567
Summer 13:10 ∿ 1 min	Fine	0.730	0.218	0.730	0.428	0.512	0.672
Summer 14:40 ∿ 1 min	Fine	0.260	0.003	0.260	0.051	0.206	0.270

* Correction Coefficient 0.762

Table 2.3.2 Experiment of propylene-NO-air system

a) Conditions set in the chamber

	UNIT	MEAS. VALUE
Temp.	°C	30±2
Humid.	%	30
U.V. int.	mW/cm^2 (300-600nm)	9.5
D.A.F	L/hr	134

b) Measured pollutants *

	Unite	Initial	1	2	3	4	5
SO_2	pphm	1.0					
THC	ppmC	1.85	1.71	1.59	1.45	1.03	0.96
NMHC	ppmC	1.75	1.60	1.48	1.33	0.90	0.83
CO	ppm	1					
NO_x	ppm	0.500	0.476	0.426	0.380	0.340	0.294
NO	ppm	0.460	0.224	0.046	0.000	0.000	0.000
NO_x-NO	ppm	0.040	0.252	0.380	0.380	0.340	0.294
O_3	ppm	0.000	0.005	0.028	0.178	0.329	0.431

* Value corrected for dilution

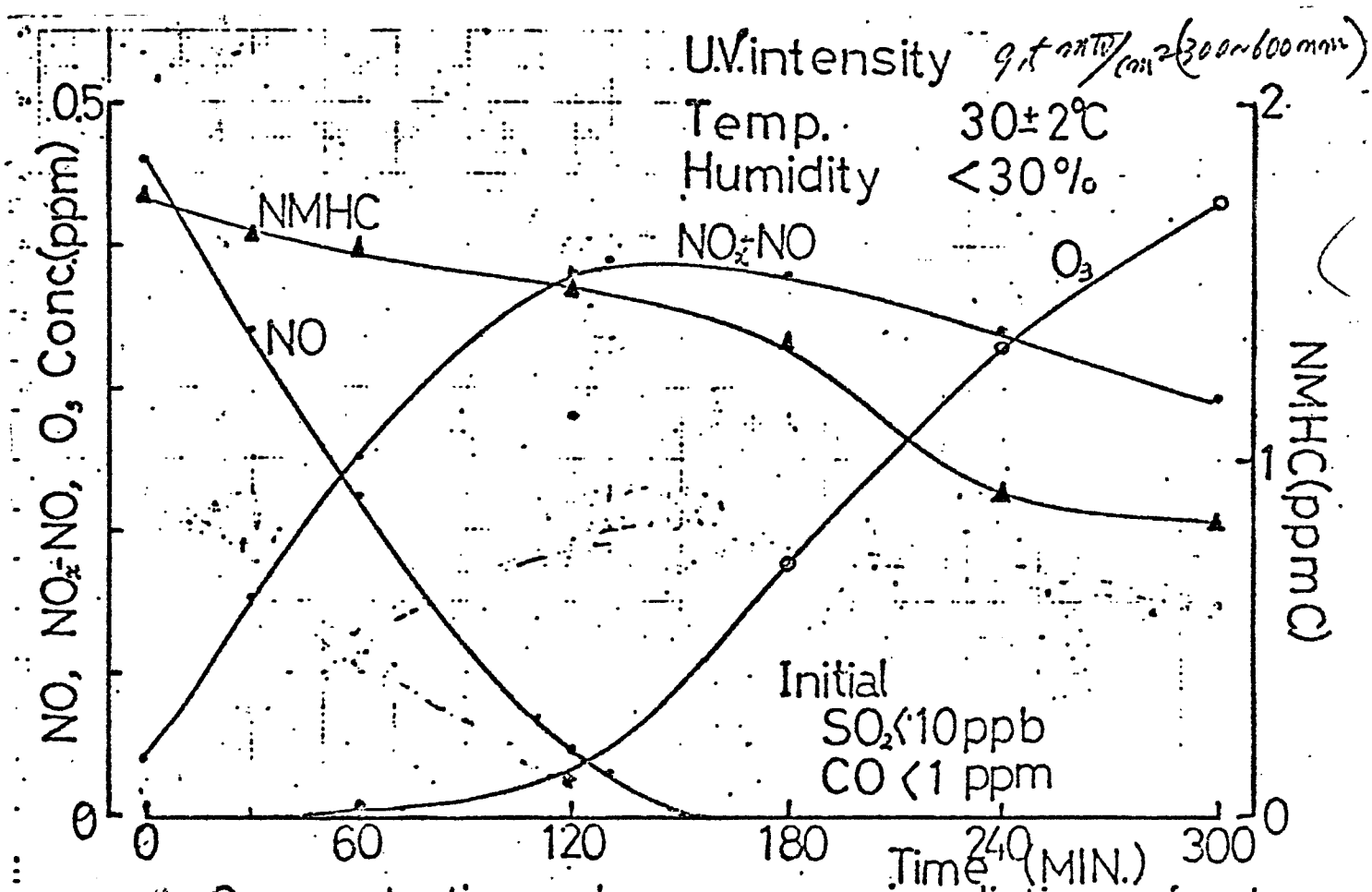
TABLE 2.3.2 Propylene + NO + Air Wet Test

a) Test Conditions in the Chamber

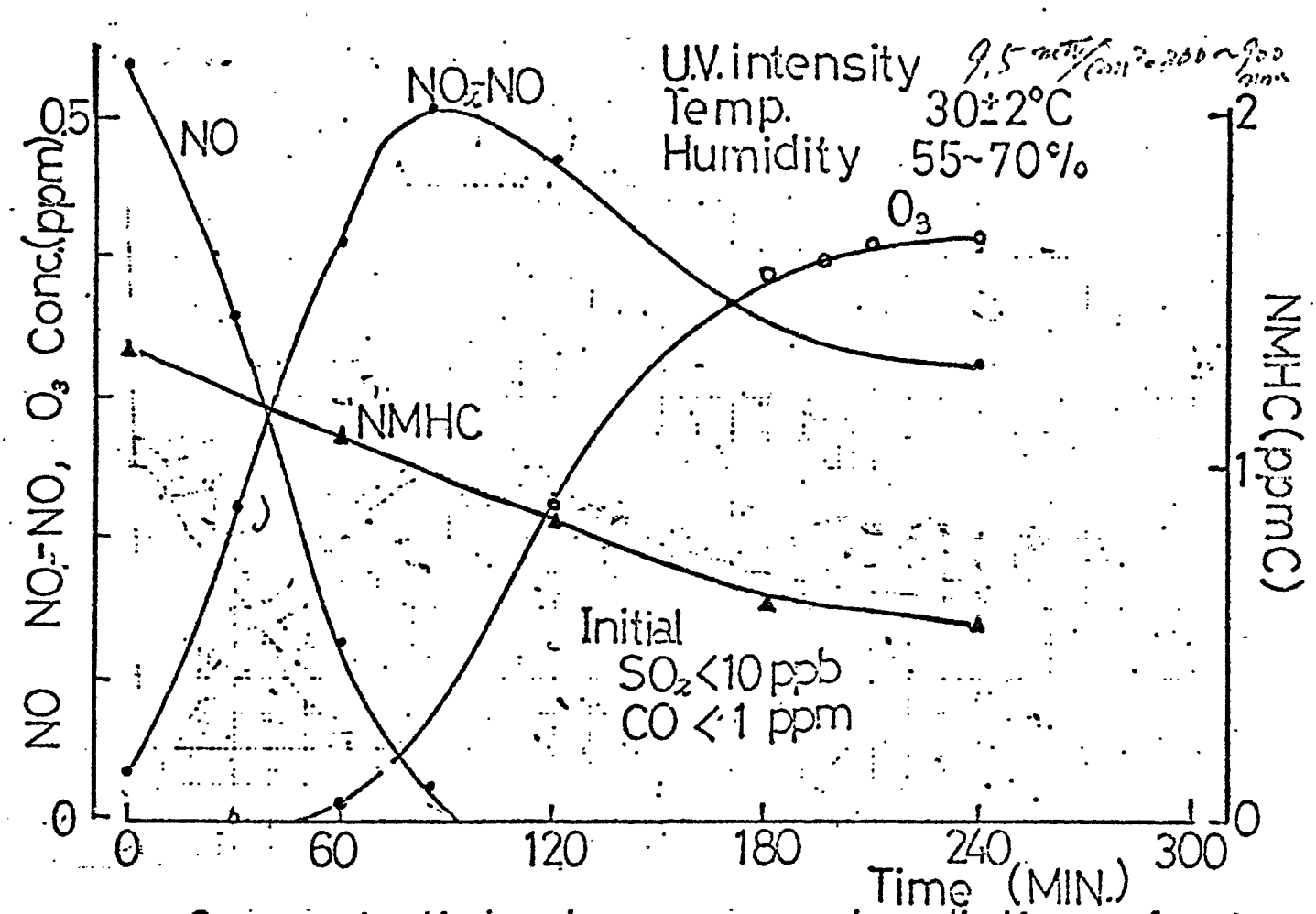
	UNITE	MEAS. VALUE
Temp.	°C	30±2
Humid.	%	55 ∿ 70
U.V.int.	MW/cm (300∿600nm)	9.5
D.A.F.	L/hr	218

b) Polutants Measured

Polutants*		Irradiation time (hr)					
	Unite	Initial	1	2	3	4	5
SO_2	pphm	< 1.0					
THC	ppmC	1.45	1.20	0.98	0.75	0.71	
NMHC	ppmC	1.35	1.09	0.86	0.61	0.56	
CO	ppm	< 1					
NO_x	ppm	0.570	0.536	0.468	0.368	0.324	
NO	ppm	0.536	0.126	0.000	0.000	0.000	
NO_x-NO	ppm	0.034	0.410	0.468	0.368	0.324	
O_3	ppm	0.000	0.011	0.222	0.389	0.417	



Concentration changes on irradiation of mixture of Propylene + NO + Air



Concentration changes on irradiation of mixture of Propylene + NO + Air

(3) Results of Experiment and Consideration

The photochemical reaction result under the conditions of this experiment were compared with those of the Machinery Technical Laboratory at the tests by Glasson et al with a result as shown in the following Table

TABLE 2.3.4 Results of Photochemical Reaction Experiment of Mixture of Propylene + NO + Air

Experiments	Initial Condition		Humidity R.H (%)	~~Minutes~~ elapsed Time until rapid O_x idant concentration rise (min) occurs	kd Value (min)
	Propylene (ppmC)	NO (ppm)			
Present experiment	1.75	0.460	below 30% <None>	approx. ~~abt.~~ 52	0.30 ~~0.10 *~~
	1.35	0.536	55 ∿ 70%	~~abt.~~ 40	0.30 ~~0.10 *~~
Experiment by Machinery Technical Laboratory	4.0	0.5	below 30% None	~~abt.~~ 30	0.35 ∿ 0.40 **
	2.0	0.5	"	~~abt.~~ 45	
Experiment by W.A. Glasson et al	1	0.5	"	~~abt.~~ 71	0.29
	2 (")	0.5	"	~~abt.~~ 40	

* Refer to 4-2-1.

** Estimated value at the Machinery Technical Laboratory

TABLE 2.3.5 Comparison of NO Photo-oxidation Speed

Experiments	Initial Condition		Humidity R.H (%)	NO photo-oxidation speed (rough value) ($ppm \cdot min^{1-1}$)	Rough value of NO photo-dissociation speed per 1 ppm propylene ($ppm \cdot min^{-1}$)	kd Value (min^{-1})
	Propylene (ppm)	NO (ppm)	less than			
Experiment by W.A. Glasson et al	1	0.5	30 % ~~None~~	3.5×10^{-3}	3.5×10^{-3}	0.29
	2	0.5	~~None~~	6.3×10^{-3}	3.2×10^{-3}	
Present experiment	0.69*	0.460	~~None~~	4.4×10^{-3}	6.3×10^{-3}	~~0.10~~ 0.30
	0.87*	0.536	55 ∿ 70	6.7×10^{-3}	7.7×10^{-3}	

* Propylene Value obtained by SP. HC meter.

TABLE 2.3.4 Comparison of NO Photo-oxidation Speed

NO photo-oxidation speed (rough value) ($ppm \cdot min^{1-1}$)	Rough value of NO photo-dissociation speed per 1 ppm propylene ($ppm \cdot min^{-1}$)
3.5×10^{-3}	3.5×10^{-3}
6.3×10^{-3}	3.2×10^{-3}
4.4×10^{-3}	6.3×10^{-3}
6.7×10^{-3}	7.7×10^{-3}
2.7×10^{-2}	1.8×10^{-2}

This measuring method of the intensity of light is affected by the initial concentration of NO so that attention should be paid especially to the initial concentration.

(2) Operation and reaction process of photochemical reaction experiment was to be carried out by setting the initial concentration of proylene and NO to 1 ppm C_3 and 0.5 ppm respectively. However, due to excessive dilution, the experiment was performed with initial concentrations shown in Table 2.3.2 and Fig. 2.3.1.

Further under the same initial conditions, experiment was carried out with added moisture (55 to 70%R.H.) (see Table 2.3.3).

The experimental result of Glasson et al can not be generally compared with the above result since the initial concentrations of propylene differ. However the relative comparison between both results in NO photoxidation rate per 1 ppm of corrected propylene concentration shows that the rate of the present experiment can be assumed to be about two times faster than that of Glasson et al.

Also Glasson et al showed the linear relationship between the NO photoxidation rate and NO_2 photodissociation rate so that K_1 value in this experiment can be also presumed to be higher than that of Glasson's.

2.3 Photochemical reaction experiment of hydrocarbon-NO-air system

2.4.1 Background reactivity

The high purity and high pressure air in cylinder used for this experiment contains various gases such as CO_2, CO, methane, non-methane HC, and NO_x. Even with low concentration of the gases, their effects on the photochemical reaction may not be negligible. For this reason, we carried out the experiment by carefully removing HC component from the purified air through molecular sieve 5A and active carbon trap under ice refrigerant.

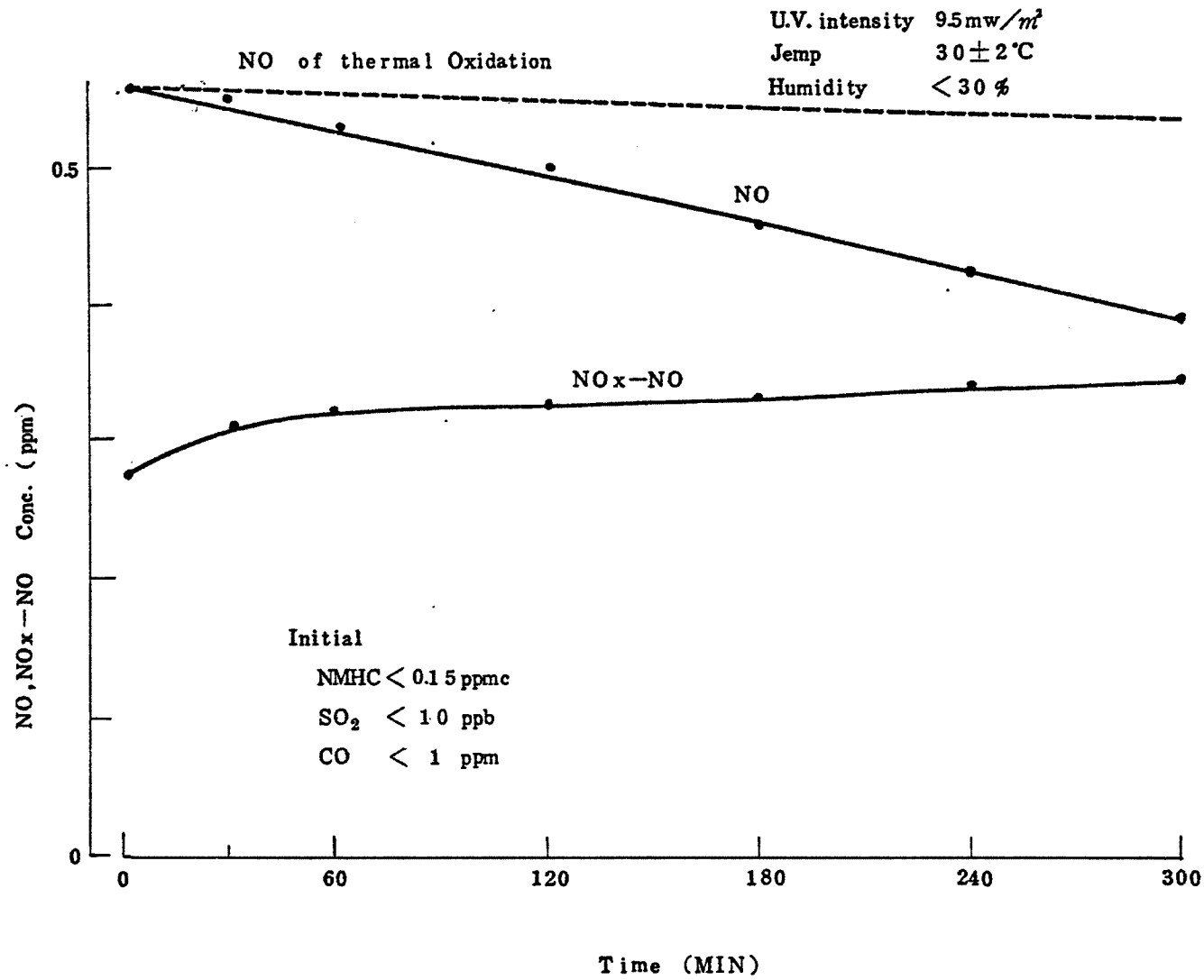


Fig 2.4.1 Concentration changes on irradiation of mixture of NO + NOx − NO + Air

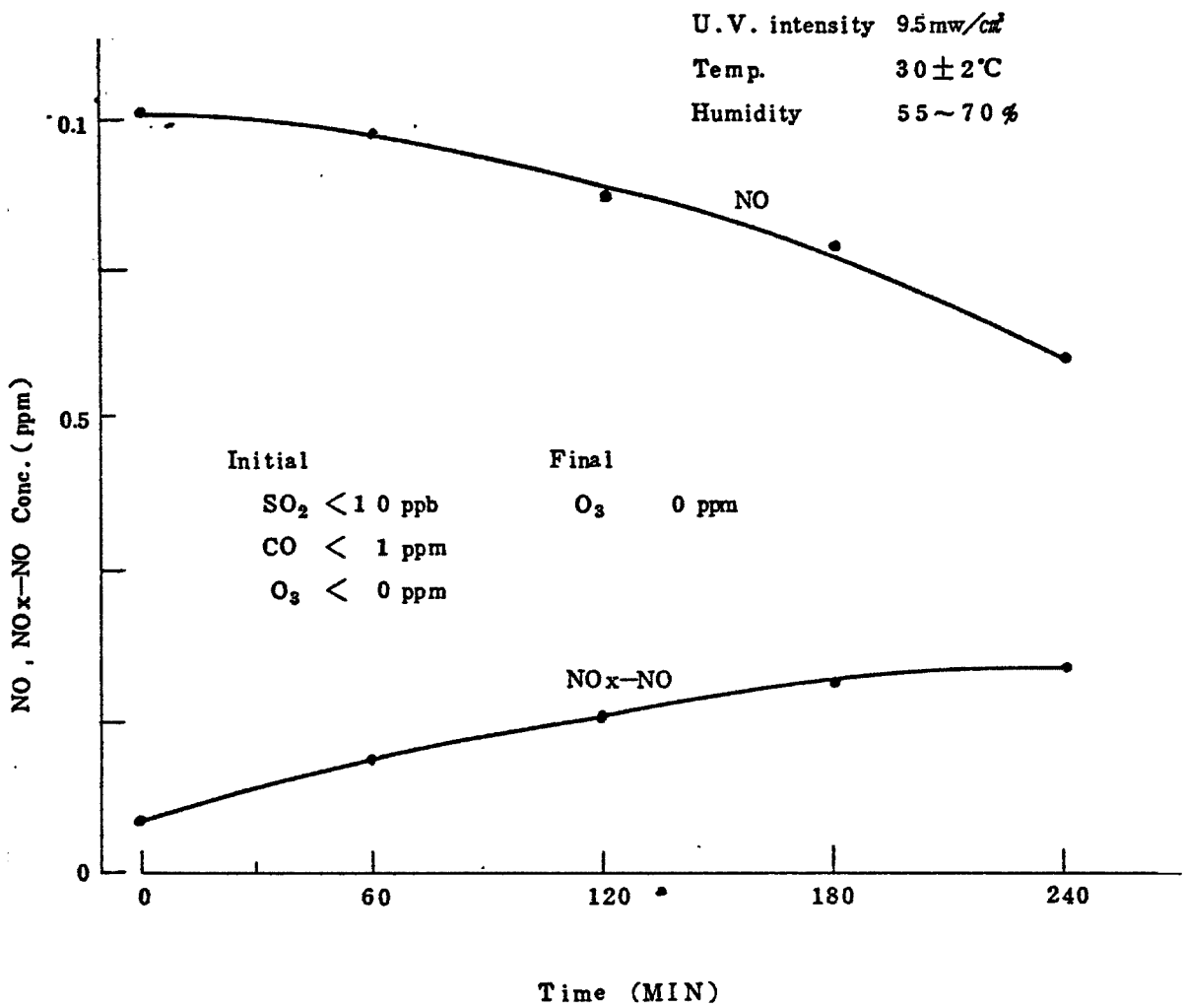


Fig 2.4.2 Concentration changes on irradiation of mixture of NO+NOx−NO+Air

The concentration of each component then was as follows:

Total HC; less than 0.20 ppmC, methane; less than 0.1 ppm, CO; less than 1 ppm, SO_2; less than 10 ppb, NO_x; less than 5.5 ppb.

When the irradiation experiment was carried out for such background air the concentration of O_3 increased to 0.038 ppm after 4 hours of irradiation. It is to be noted that this is the reactivity of background air in the smog chamber.

2.4.2 Reaction experiment of NO-air system

Further, we carried out an irradiation experiment in which NO and NO_2 was introduced into this background air.

The result of the experiment is shown in Figs. 2.4.1 and 2.4.2.

When the conversion NO to NO_2 proceedsthrough thermal reaction, it can be obtained from the folowing oxidation equation:

$$2NO + O_2 \xrightarrow{K'} 2NO_2$$

$$\Delta[NO] = K'[NO]^2 [O_2] \cdot \Delta t$$

where $K' = (1.955 - 0.0232t) \times 10^{-9}$ (ppm^2 min) (t; temperature °C). When the data shown in Fig. 2.4.1 is substituted into this equaiton, 0.08 ppb/min of NO thermal oxidation rate is obtained. It is found to be about one half of the 0.19 ppb/min NO oxidation rate during irradiaiton.

Similarly, we carried out an irradiation experiment with added moisture (55 to 70% R.H.) shown in Fig. 2.4.2, wherein 0.26 ppb/min of thermal oxidation rate was obtained that was about 1/3 of 0.88 ppb/min of NO photo-oxidation rate. In view of the above results, in the irradiation experiment with very low HC, the

TABLE 2.4.1 Photochemical Reactivities of Materials

Exp. No.	Material	NO		NO_x-NO		O_3			Hydrocarbon (D.R.)				HCHO	T-CHO	NO_x	NO_x	NO	NO
		D. R.	Max	t-Max	F.R.	Max	t-Max	F.R.	THC (%)		sp, HC (%)		ppm	ppm	5h Dec.			Non-methan
		ppb/min	ppm	min	ppb/min	ppm	min	ppb/min	3h	5h	3h	5h	5h	5h	ppm			ppmC
1	Propylene	6.4	0.92	146	6.6	0.90	300	2.2	26.3	58.5	-	-	-	11.3	0.47	1.055	1.035	4.00
2	Propylene	4.1	0.39	140	4.2	0.43	300	1.1	23.3	51.2	57.7	93.7	0.34	0.53	0.21	0.500	0.460	1.75
3	Propylene	1.6	0.56	300	3.9	0.06	300	0.11	13.9	33.3	39.7	65.7	-	0.06	0.06	0.665	0.505	1.45
4	Propylene	1.9	0.39	240	3.2	0.12	300	0.24	18.2	36.4	43.6	66.7	0.21	0.69	0.14	0.520	0.500	1.35
5	Propylene	6.3	0.50	85	6.8	0.42	240	1.8	54.5	59.1*	-	-	0.48*	0.68*	0.25*	0.570	0.536	1.35
6	Toluene	1.4	0.45	300	1.8	0	-	-	13.0	19.0	13.6	22.5	0.03	0.04	0.19	1.000	1.000	5.03
7	Toluene	1.4	0.30	240	1.3	0.10	270	0.21	12.5	25.0	17.3	59.2	-	0.08	0.16	0.400	0.400	4.80

Exp. No.	Material	NO_x		Pro.	NO_x
		Non-methan	Fumidified or not	Test target	
		ppmC		ppm	
1	Propylene	3.8	x	2	1
2	Propylene	3.5	x	1	0.5
3	Propylene	2.2	x	1	0.5
4	Propylene	2.6	x	1	0.5
5	Propylene	2.4	55~70%R.H	1	1
6	Toluene	5.0	x	1	0.5
7	Toluene	12.0	x		

D.R.: Depletion Rate, F.R.: Formation Rate,
sp.HC: measured with CC, O_3 data are in 5th,
*: 4h value, - : not measured

rate of NO thermal oxidation should be taken into consideration. FInally it should be noted that the results of these experiments are not corrected for the reactivity of the background air.

2.4.3 Photochemical reaction experiment of propylene or toluene-NO-air system

The summary of the irradiation experimental results of propylene or toluene-NO air system is shown on Table 2.4.1. The rate of decrease (D.R.) of NO was measured by chemiluminescence method. The rate of formation (F.R.) of O_3 was calculated from the following equation:

$$O_3 F.R. = (O_3 \text{ max} - O_3 \text{ initial})/2 \times t_{1/2}$$

where O_3 max is maximum of O_3 in the course of irradiation, O_3 initial is the initial concentration of O_3, and $t_{1/2}$ is the time (minute) taken for O_3 to reach a half of its maximum concentration. Also the rate of decrease of NO and the rate of formation of (NO_x - NO) were calculated according to this equation.

The decrease of NO_x concentration is shown by its change during 5 hour irradiation. This value, measured by a chemiluminescence NO_x recorder differs from that of (NO + NO_2) and is considered to contain all components that can be reduced to NO by a catalyzer of the NO_x recorder. The decrease of NO_x indicates the loss caused by the oxidation of most of initial NO_x to NO_2 and includes the conversion of NO to components that cannot be reduced by the catalyzer into NO. When the maximum values of NO_x -NO, O_3, etc. were not obtained during irradiation, the irradiation time (up to 300 minutes) is shown as the time for reaching the maximum concentration.

3. Investigation Method

3.1 Outline of Investigation

The chamber carried on the photochemical smog chamber vehicle, as mentioned in the previous section 1.3, has the inner volume of 2 m^3 which is usually smaller than that of other fixed chambers. THus, the continous running of measuring all instruments is difficult during irradiation. Hence, as shown below, the investigation was carried out by opeating some instruments intermittently or omitting the measurement of some pollutants that seemed not directly related to such reaction.

3.1.3 Method of this investigation

The experimental procedures of this investigation are as follows;

1) The inside of the chamber is vacuum cleaned the day before the investigation.

2) The temperature in the chamber is in principle set to 4°C higher than ambient temperature in order to prevent the formation of dew within the chamber during sampling.

3) After setting the pressure in the chamber to atmospheric pressure by manual air sampling valve, ambient air is sampled by air sampling blower.

4) Air is sampled until the inside of the chamber is filled with the ambient sample air.

5) By using analytical instruments, carried on the analyzing vehicle, the concentration of each component within the chamber is quickly measured (hereinafter referred to "initial concentration").

6) After the measurement of the initial concentration, ultra-violet irradiation is started. The temperature in the chamber is then maintained constant to maintain the intensity of UV radiation.

Table 3.1.2 Analytical method

Measurement Items	Chemical formula or abreviation	Analytical method
Pollutants		
1 Total aldehyde (aliphatic)	-	absorbed light intensity method·according to M.B.T.H method
2 Formaldehyde	HCHO	pararosanilen method
Ambient air measurement		
1 Wind direction·Wind velocity		anemoscope·anemometer
2 Temperature·humidity		Themometer, Hygrometer
3 U.V ray intensity		Integrated irradiation recorder
4 Visible ray intensity		"
5 U.V ray intensity by wave length		UV spectrophotometer
Irradiation condition		
1 Temperature in chamber		Dew cell method
2 Humidity in chamber		"
3 UV ray intensity		UV spectrodetector

* CO meter on Table 1.4.1 was not used for certain reasons.

7) After the irradiation, digital air flowmeter is read at a certain time interval (about 1 hour) to calculate the dilution rate of sample in the chamber. The irradiation is continued until the dilution reaches at least 30%.

8) The inside of the chamber is vacuum cleaned after the completion of the irradiation.

3.2 Pattern of photochemical reaction

3.2.1 Outline

The pattern of the photochemical reaction generally becomes as follows. When the irradiation of light is started, initial oxidation of NO to NO_2 is promoted rapidly to decrease hydrocarbon and increase aldehydes.

The accumulation of O_3 is started from the period when NO concentration is considerably decreased. The increase of O_3 becomes remarkable when NO_2 concentration passes over the maximum value and then decreases. The decrease of hydrocarbon and increase of aldehydes tend to continue until the concentration of O_3 increases to its maximum concentration and begins to decrease.

Such general trend is noted not only in the irradiation experiment of artificial mixture but also in that of actual ambient air sample. However distinct trend was not sometimes discerned since the initial concentrations of consittents varied and some gas analysis was still unsatisfactory.

The reaction pattern of the irradiation experiment will be analyzed principally with respect to the trend of O_3 formation.

The O_3 formation is much affected by the initial concentrtaions of hydrocarbon and NO_x When the concentrations of both substances are high the maximum concentration of O_3 reaches to high value. It is clarified that in particular the initial concentration of hydrocarbons apparently has close relation to the maximum concentration of O_3.

3.2.2 Method of Measurement

In the irradiation experiment the entire sample is charged in the chamber at the beginning. Since there is no subsequent sample injection the irradiation time is also the reaction time. The irradiation was continued by artificial light sourch shown in section 1.4 for 3 to 6 hours. During this irradiation, continuous or intermittent measurement of concentration of components in the chamber, i.e., NO_x, NO, O_2, total hydrocarbon and methane, nonmethane hydrocarbon, CO, etc. (see Item 3.1.1) was carried out.

In order to avoid the pressure reduction caused by the consumption of sample for analysis in the reaction chamber, purified air contained in cylinder was automatically introduced to keep the pressure balance.

The intensity of irradiation was set to the maximum limit of intensity measured in order of about 13 mW/CM^2 within the range of the allowance of light source capacity.

The absolute value of the irradiation intensity, however, encounters problems such as correction of incident angle of light onto detector and others so that it may not be compared with other measured intensity.

The temperature in the reaction chamber was controlled, but due to the effect of the ambient temperature it was slightly higher than the preselected level.

The measurements of NO, NO_x and hdyrocarbon concentrations were carried out continuously and other constitutents by intermittent measurement. In the early investigation, some analzers had malfunctions. Also in the measurement of NO and NO_x by chemilimunescence method, the concentration of NO_2 tends to be uncertain. There was an experiment in which the measurement of NO_2 and NO_x was carried out by Saltzman method, though it was not simultaneoulsy conducted with the chemluminescent method.

The measurement of aldehyde and other constituents was also carried out. However it will be described in another paragraph.

4. Results of Investigation

4.1 Arrangement of experimental data

In the photochemical reaction investigation by the mobile smog chamber, about 110 experiments were carried out in the areas around the Tokyo Bay and Osaka Bay from 1972 to 1975.

In 102 cases of these experiments, ambient air was sampled in the morning.

Measured and analyzed results somewhat differed with regard to the investigated areas and years. Results included those from automatic measurements of NO_x (NO, NO_2), HC (THC, CH_4), SO_2, CO, O_3, OX, and temperature, humidity and intensity of ultra-violet irradiation in the chamber, as well as those from manual measurements of hydrocarbon composition, PAN, aldehydes, aerosol, etc. In addition, the dilution of air within the chamber, the meteorological conditions during air sampling, etc. were measured.

The present statistical analysis attempted to explore relationships between the increase of O_3, and the composition of non-methane hydrocarbon, initial concentration of NO_x, and ultra-violet light irradiations.

The experimental data used for this analysis are shown in table 1 and the classification of hydrocarbon composition in Table 2.

28 cases among 102 examples were excluded since the dilution rate and the concentrations of CH_4 and O_3 were uncertain, and the remaining 74 examples were analyzed.

The items in the tables are as follows:

1) List of Experimental results shown in Table 1

(1) Initial Value

Value of non-methane hydrocarbon, NO_x, HC/NO_x (ppmC/pphm) ratio, and O_3 concentration before ultra-violet irradiation.

(2) Uncorrected value

The increase (ΔO_3) of O_3, i.e., the maximum concentration of O_3 (O_3 max) after ultra violet irradiation minus the initial concentration of O_3, provided it is not corrected for dilution.

(3) Time for O_3 maximum to be attained

Time from the beginning of ultra-violet irradiation to the appearance of the maximum O_3 concentration. It was described as 5 hours when O_3 was still in the incerasing at the completion of experiment in 5 hours.

Further the time was encircled with mark 0 when the experiment was completed within 5 hours.

(4) Corrected value

The maximum concentration of O_3 (O_3 max) corrected for the dilution effect of sample air, and corrected increase of O_3 concentration (O_3) that is O_3 concentration max minus the initial concentrations.

All of these value were used for the analysis.

The following equation was used for the correction;

$$C = Co\ e^{Vt/Vo}$$

Where C : Corrected concentration after t hours
Co : concentration measured after t hours
Vo : volume of chamber
V : volume of air supplemented in unit time
t : time

(5) Ultra-violet light

Intensity of ultra-violet irradiation, irradiation time until the maximum concentration of O_3 appears and Dose (intensity of irradiation X irradiation time)

2) Content of table 2 of hydrocarbon composition

(1) The composition was classified for 72 cases, in which the composition of hydrocarbon was analyzed out of 74 experiments shown in table 1.

(2) The composition was classified, according to the group classification of hydrocarbon in table 3, into 3 dividions, i.e., parrafins, oleffins and aromatics. The ppb concentration was converted to ppbC by being multiplied by carbon number.

(3) The initial concentration is the concentration before the ultraviolet irradiation and the final concentration is the concentration after the ultra-violet irradiation. Also the ratio of the final concentration to the initial concentration (rate of decrease) was represented by %.

(4) The initial composition was the percentage of the initial concentration of Paraffins, olefins and aromatics.

TABLE 4.1.1 Results of Experiment

	Initial value			Value not corrected			H_2 until O_3 max. value obtained	Corrected value		Ultraviolet ray			Year	Season	
	NO. Non-methan	NO_x	Non-methan/NO_x	O_3	(O_3 max)	(ΔO_3)		O_3 max	ΔO_3	Strength	Hrs.	Sosℓ			
Ex.	ppmC	pphm	ppmC/pphm	pphm	pphm	pphm	hr	pphm	pphm	max/cm^2	hr	MW/cm^2·hr	Syowa		
1.	1.3	5.3	0.25	2.2	8.8	6.6	5	11.4	9.2	13.4	5	67	47	S	Suginami
2.	1.4	4.2	0.33	0.8	8.5	7.7	5	12.8	12.0	13.1	5	66			
3.	1.3	4.0	0.33	1.5	7.5	6.0	5	10.1	8.6	13.1	5	66			
4.	4.1	7.0	0.59	0.0	14.7	14.7	2	16.8	16.8	12.1	2	24			Shinjuku
5.	1.1	4.7	0.23	1.7	10.6	8.9	4	12.7	11.0	12.1	4	48			
6.	0.9	4.0	0.23	4.7	9.5	4.8	5	12.2	7.5	12.1	5	61			
7.	7.4	8.0	0.93	0.0	17.5	17.5	2	18.6	18.6	12.9	2	26			Kawasaki
8.	1.5	12.4	0.12	1.2	16.7	15.5	3	19.0	17.8	12.6	3	38			
9.	5.7	7.9	0.72	1.5	20.0	18.5	3	22.6	21.1	12.3	3	37			Kamata
10.	1.1	9.4	0.12	0.0	12.0	12.0	5	15.7	15.7	12.1	5	61			
11.	0.5	7.1	0.07	0.0	8.7	8.7	5	10.4	10.4	12.1	5	61			
12.	1.9	12.5	0.15	0.0	13.7	13.7	5	18.1	18.1	7.3	5	37	47	W	Kamata
13.	2.3	26.5	0.09	0.0	18.5	18.5	5	25.5	25.5	7.3	5	37			
14.	1.7	16.2	0.10	0.0	13.7	13.7	3	16.4	16.4	7.3	3	22			
15.	1.7	25.5	0.07	0.0	15.0	15.0	5	20.0	20.0	7.5	5	38			
16.	1.6	31.0	0.05	0.0	19.5	19.5	5	26.1	26.1	7.3	5	37			
17.	0.4	10.5	0.04	0.0	8.5	8.5	5	11.6	11.6	7.3	5	37			
18.	1.5	8.0	0.19	4.0	8.2	4.2	2	8.8	4.8	12.5	2	25	48	S	Kawasaki
19.	1.5	13.5	0.11	1.2	9.0	7.8	3	10.2	9.0	12.5	3	38			
20.	0.9	4.5	0.20	1.0	4.3	3.3	5	4.9	3.9	12.0	5	60			
21.	1.6	19.0	0.08	0.5	13.4	12.9	4	15.7	15.2	12.0	4	48			
22.	2.5	10.5	0.24	8.0	14.6	6.6	3	16.2	8.2	12.5	3	38			
23.	1.5	19.0	0.08	0.0	14.9	14.9	(4)	16.4	16.4	12.5	4	50			
24.	1.0	3.6	0.28	3.0	8.2	5.2	5	9.9	6.9	12.5	5	63			Urawa
25.	1.0	6.0	0.17	3.0	6.8	3.8	(3)	7.3	4.3	11.1	3	33			
26.	0.9	4.0	0.23	0.5	4.5	4.0	5	5.6	5.1	12.5	5	63			
27.	0.4	5.0	0.08	0.5	3.6	3.1	5	4.5	4.0	12.5	5	63			
28.	2.0	3.0	0.67	0.5	4.5	4.0	(4)	5.4	4.9	13.0	4	52			
29.	0.8	4.5	0.18	0.0	7.5	7.5	4	8.8	8.8	6.6	4	26	48	W	Kawasaki
30.	1.1	5.5	0.20	0.0	11.0	11.0	5	14.2	14.2	7.1	5	36			
31.	0.5	2.2	0.23	0.0	7.5	7.5	5	10.7	10.7	7.0	5	35			
32.	0.8	4.1	0.20	0.0	10.5	10.5	5	14.1	14.1	7.0	5	35			
33.	0.6	5.5	0.11	0.0	9.5	9.5	5	12.8	12.8	6.9	5	35			
34.	1.3	6.3	0.21	0.0	11.3	11.3	5	14.2	14.2	7.0	5	35			
35.	0.6	3.5	0.17	0.0	3.0	3.0	(4)	4.2	4.2	12.5	4	50	49	S	Sumiyoshi
36.	1.3	5.0	0.26	0.0	2.5	2.5	(4)	3.4	3.4	12.5	4	50			
37.	1.5	3.5	0.43	0.0	3.5	3.5	5	5.1	5.1	12.6	5	63			
38.	0.7	2.5	0.29	0.0	5.5	5.5	4	7.2	7.2	13.5	4	54			
39.	1.7	3.5	0.49	0.0	5.5	5.5	5	7.2	7.2	13.5	5	68			
40.	1.2	3.5	0.34	0.0	6.5	6.5	(4)	8.3	8.3	13.5	4	54			
41.	0.9	1.6	0.56	1.2	3.0	1.8	(3)	3.7	2.5	13.5	3	41	49	S	Sumiyoshi
42.	0.8	3.0	0.27	0.0	5.0	5.0	5	5.8	5.8	13.5	5	68			Fujiidera
43.	1.0	1.6	0.63	2.0	3.5	1.5	3	4.4	2.4	13.5	3	41			
44.	0.8	1.0	0.80	3.0	4.0	1.0	5	4.8	1.8	13.5	5	68			
45.	1.0	1.5	0.67	1.0	3.5	2.5	(4)	4.4	3.4	13.5	4	54			
46.	1.0	2.5	0.40	1.3	3.1	1.8	(4)	3.8	2.5	6.0	4	24			Ohyamazaki
47.	2.1	4.1	0.51	0.0	6.9	6.9	5	8.6	8.6	6.0	5	30			
48.	1.0	0.5	7.00	4.0	4.5	0.5	5	5.8	1.8	5.9	5	30			
49.	1.2	8.5	0.14	0.0	5.0	5.0	5	6.2	6.2	5.1	5	26			Ichikawa
50.	0.8	3.0	0.27	0.8	4.6	3.8	5	6.1	5.3	5.0	5	25			
51.	0.2	2.0	0.10	1.0	2.5	1.5	(4)	3.8	2.8	5.0	4	20			
52.	0.6	1.0	0.60	(0.0)	2.5	2.5	(4)	3.5	3.5	4.9	4	20			
53.	0.2	1.5	0.13	1.5	3.0	1.5	5	4.0	2.5	5.0	5	25			
54.	0.9	4.0	0.23	0.0	4.6	4.6	5	6.2	6.2	4.9	5	25			
55.	0.3	1.1	0.27	1.0	2.4	1.4	4	2.9	1.9	7.2	4	29	49	W	Chiba
56.	0.8	6.6	0.12	0.0	4.5	4.5	5	5.5	5.5	7.8	5	39			
57.	0.6	4.0	0.15	0.0	3.3	3.3	5	4.2	4.2	7.5	5	38			
58.	0.3	2.0	0.15	0.4	4.5	4.1	5	5.3	4.9	7.2	5	36			
59.	0.3	3.5	0.09	0.0	4.0	4.0	4	4.6	4.6	7.5	4	30			
60.	0.6	5.5	0.11	0.0	6.5	6.5	5	7.5	7.5	7.8	5	39			
61.	1.8	4.6	0.39	0.0	2.1	2.1	4	2.9	2.9	6.7	4	27	50	S	Ohyamazaki
62.	2.5	5.7	0.44	0.0	2.0	2.0	1	2.2	2.2	6.2	1	6			
63.	0.5	3.4	0.15	0.0	0.7	0.7	1	0.8	0.8	6.2	1	6			
64.	0.8	4.0	0.20	0.0	1.4	1.4	3	1.7	1.7	6.7	3	20			
65.	1.4	8.0	0.18	0.0	4.1	4.1	3	4.8	4.8	9.0	3	27			
66.	0.7	4.6	0.15	0.0	3.7	3.7	3	4.6	4.6	9.0	3	27			
67.	0.6	1.1	0.55	0.0	0.6	0.6	(4)	0.7	0.7	9.1	4	36			Chiba
68.	0.2	1.8	0.11	0.3	3.4	3.1	3	4.1	3.8	9.1	3	27			
69.	0.2	1.2	0.17	0.0	1.7	1.7	5	2.3	2.3	8.2	5	41			Tochigi
70.	0.3	1.9	0.16	0.0	2.2	2.2	5	2.9	2.9	8.2	5	41			
71.	0.4	2.1	0.19	0.0	2.5	2.5	5	3.2	3.2	8.5	5	43			
72.	0.1	0.9	0.11	0.0	2.0	2.0	5	2.4	2.4	8.2	5	41			
73.	0.1	1.2	0.08	0.2	2.0	1.8	5	2.6	2.4	7.9	5	40			
74.	0.1	0.9	0.11	0.3	2.2	1.9	5	2.6	2.3	7.9	5	40			

Note: O mark in Hr. Column indicates the suspension of measurement at the time Initial O_3 value in ( ) shows the lock of measured value. Accordingly, the initial value in assumed to be zero.

	Initial Value					Value not corrected				Corrected value				
No.	NO_x	Non-methan	A + O	Benzene	A + O - Benzene	O_3	O_3 max	ΔO_3	H_2 until O_3 max. value obtained pphm	O_3 max	ΔO_3	Year	Season	
Ex.	pphm	ppmC	ppmC	ppmC	ppmC	pphm	pphm	pphm		pphm	pphm	Syowa		
12.	12.5	1.9	0.469	0.059	0.410	0.0	13.7	13.7	5	18.1	18.1	47	W	Kamata
14.	16.2	1.7	0.532	0.010	0.522	0.0	13.7	13.7	3	16.4	16.4			
15.	25.5	1.7	0.917	0.012	0.905	0.0	15.0	15.0	5	20.0	20.0			
16.	31.0	1.6	0.816	0.009	0.807	0.0	19.5	19.5	5	26.1	26.1			
35.	3.5	0.6	0.382	-	0.382	0.0	3.0	3.0	(4)	4.2	4.2	49	S	Sumiyoshiku
36.	5.0	1.3	0.465	0.090	0.375	0.0	2.5	2.5	(4)	3.4	3.4			
37.	3.5	1.5	0.562	0.072	0.490	0.0	3.5	3.5	5	5.1	5.1			
38.	2.5	0.7	0.399	0.038	0.361	0.0	5.5	5.5	4	7.2	7.2			
39.	3.5	1.7	0.648	0.014	0.634	0.0	5.5	5.5	5	7.2	7.2			
40.	3.5	1.2	0.352	0.084	0.268	0.0	6.5	6.5	(4)	8.3	8.3			
41.	1.6	0.9	0.385	-	0.385	1.2	3.0	1.8	(3)	3.7	2.5			
42.	3.0	0.8	0.224	-	0.224	0.0	5.0	5.0	5	5.8	5.8			Fujiidera
43.	1.6	1.0	0.440	0.180	0.260	2.0	3.5	1.5	3	4.4	2.4			
45.	1.5	1.0	0.322	0.120	0.202	1.0	3.5	2.5	(4)	4.4	3.4			
46.	2.5	1.0	0.791	-	0.791	1.3	3.1	1.8	(4)	3.8	2.5			Ohyamazaki
47.	4.1	2.1	0.606	-	0.606	0.0	6.9	6.9	5	8.6	8.6			
48.	0.5	1.0	0.673	-	0.673	4.0	4.5	0.5	5	5.8	1.8			
61.	4.6	1.8	0.606	0.037	0.569	0.0	2.1	2.1	4	2.9	2.9	50	S	Ohyamazaki
62.	5.7	2.5	0.429	0.042	0.387	0.0	2.0	2.0	1	2.2	2.2			
63.	3.4	0.5	0.080	0.007	0.073	0.0	0.7	0.7	1	0.8	0.8			
64.	4.0	0.8	0.197	0.013	0.184	0.0	1.4	1.4	3	1.7	1.7			
65.	8.0	1.4	0.295	0.022	0.273	0.0	4.1	4.1	3	4.8	4.8			
66.	4.6	0.7	0.277	0.017	0.260	0.0	3.7	3.7	3	4.6	4.6			
67.	1.1	0.6	0.073	0.005	0.068	0.0	0.6	0.6	(4)	0.7	0.7			Chiba
68.	1.8	0.2	0.080	0.006	0.074	0.3	3.4	3.1	3	4.1	3.8			
69.	1.2	0.2	0.075	0.008	0.067	0.0	1.7	1.7	5	2.3	2.3			Tochigi
70.	1.8	0.3	0.132	0.015	0.127	0.0	2.2	2.2	5	2.9	2.9			
71.	2.1	0.4	0.173	0.021	0.152	0.0	2.5	2.5	5	3.2	3.2			
72.	0.9	0.1	0.039	0.005	0.034	0.0	2.0	2.0	5	2.4	2.4			
73.	1.2	0.1	0.043	0.005	0.038	0.2	2.0	1.8	5	2.6	2.4			
74.	0.9	0.1	0.029	0.003	0.026	0.3	2.2	1.9	5	2.6	2.3			

Notes : No. 12 ∿ 17 : Ethan, ethylen inseparable and excluded from calculation.
No. 35 ∿ 45 : Ethan, ethylene, propane and propylene.
Aromatics was measured up to m.p-xylene.

TABLE 4.1.2 Composition of Hydrocarbon

No.	Paraffins Initial	Paraffins Final	Paraffins Final/Initial	Olefins Initial	Olefins Final	Olefins Final/Initial	Aromatics Initial	Aromatics Final	Aromatics Final/Initial	Initial composition ratio P : D : A	A/P	Remarks
Ex.	ppb. c	ppb. c	%	ppb. c	ppb. c	%	ppb. c	ppb. c	%	%		
1.												
2.												
3.												
4.												
5.												
6.												
7.												
8.												
9.												
10.												
11.												
12.	355	279	79	70	41	59	399			43, 8, 48	1.1	Ini.30m, Fin.4h
13.												
14.	439	468	107	67	26	39	465	409	88	45, 7, 48	1.1	
15.	555	217	39	85	24	28	832	575	69	38, 6, 57	1.5	
16.	579	317	55	76	28	37	740	664	90	42, 5, 53	1.3	
17.	135	121	90	24	16	67	507	1,121	221	20, 4, 76	3.8	Ini.30m
18.	452						381				0.8	
19.	381	513	135				862	167	19		2.3	
20.	267	174	65				162	84	52		0.6	
21.	529	332	63				174	121	70		0.3	
22.	1,940	680	35				1,361	399	29			
23.	2,653	294	11				179	420	235			
24.	228	230	101				151	129	85			Ini.30m,Fin.4h
25.	364	207	57				386	144	37			Fin.4h
26.	390	164	42				519	126	24			
27.	248	74	30				479	196	41			
28.	925	366	40				639	235	37		0.7	Fin.4.5h
29.	9	17	189				68	79	116		7.6	
30.	24						276					
31.	39	29	74				103	108	105		2.6	
32.	35	16	46				204	407	200		5.8	
33.	16	401	2,506				507	629	124		31.7	
34.	9	8	89				109	72	66		12.1	
35.	214	127	59	5			377	147	39	36, 1, 63		
36.	362	294	81	25			440	51	12	44, 3, 53	1.2	
37.	187	182	97	29			533	310	58	25, 4, 71		
38.	260	98	38	40			359	241	67	42, 1, 58		
39.	209			8			640			48, 2, 50	3.1	
40.	154	123	80	8	6	75	344	180	52	30, 2, 68	2.2	
41.	147			3			382			28, 1, 72	2.6	
42.	158	135	85	10	4	40	214	366	171	41, 3, 56		
43.	94	90	96	4	4	100	436	324	74	18, 1, 82	4.6	
44.	222	117	53	4	4	100	1,070	278	26	17, 0, 83	4.8	Ini. 1h
45.	112	63	56	5	4	80	317	271	85	26, 1, 73	2.8	
46.	173	89	51	16	34	213	775	551	71	18, 2, 80		
47.	301	173	57	48	16	33	558	499	89	33, 5, 68		
48.	129	76	59	34	13	38	639	448	70	16, 4, 80		
49.	65	41	63				408	124	30		6.3	Fin.4h
50.	45	55	122				247	128	52		5.5	
51.	21	16	76				89	108	121		4.2	Fin.4h
52.	18	12	67				79	108	137		4.4	
53.	9	16	178				73	84	115		8.1	
54.	31	31	100				128	140	109		4.1	
55.	9						11	21	191		1.2	
56.	64	66	103				116	64	55		1.8	
57.	34	8	24				61	72	118		1.8	
58.							59	49	83			
59.	35	7	20				88	52	59		2.5	
60.	81	74	91				106	70	66		1.3	Fin.4h
61.	357	255	71	63	42	67	543	370	68	37, 7, 56	1.5	Fin.4h
62.	155	75	48	29	23	79	400	219	55	27, 5, 68		Fin.4h
63.	52	32	62	17	17	100	63	64	102	40, 13, 48	1.2	Fin.4h
64.	81	42	52	17	11	65	180	135	75	29, 6, 65		
65.	173	96	55	35	15	43	260	128	49	37, 7, 56	1.5	
66.	138	103	75	11	16	145	266	149	56	33, 3, 64	1.9	
67.	59	66	112	10	4	40	63	50	79	45, 7, 48	1.1	Fin.4.5h
68.	40	51	128	25	12	48	55	65	118	33, 21, 46	1.4	
69.	81	53	65	13	4	31	62	38	61	52, 9, 40	0.8	
70.	141	85	60	14	4	29	118	50	42	52, 5, 43	0.8	
71.	121	160	132	17	10	59	156	72	46	41, 6, 53	1.3	
72.	39	32	82	4	3	75	35	27	77	50, 5, 45	0.9	
73.	28	35	125	7	2	29	36	27	75	40, 10, 51	1.3	
74.	21	29	138	5	1	20	24	19	79	41, 10, 49	1.1	

Notes: The final concentration values are not corrected

No. 12 ∿ 17, No. 35 ∿ 48 : Ethan, Ethylene inseparable and excluded from calculation.
No. 18 ∿ 48 : Ethan, Ethylene, propane and propylene.

Table 4.1.3 Table of hydrocarbon classified by group

Paraffins saturated hydrocarbon		Oleffins unsaturated hydrocarbon		Aromatics aromatic hydrocarbon	
ethane	2	ethylene	2	benzene	6
propane	3	propylene	3	toruene	7
iso-butan	4	1-butene	4	ethyl benzene	8
n-butan	4	iso-butene	4	m-p-xylene	8
iso-pentane	5	trans-2-butene	4	m-p-xylene	8
n-pentane	5	cis-2-butene	4	iso-propyl benzene	9
2-methyl pentane	6	1·3·butadiene	4	m-p·ethyl toruene	9
3-methyl pentane	6	2-methyl butene	4		
n-hexane	6				
2-4 dimethyl cyclopentan	7				
methyl cyclopentane	7				
2-methyl hexane	7				
1·3 dimethylcyclopentane	7				
n-heptane	7				
2-methyl heptane	8				
3 methyl heptane	8				
n-octane	8				
2-2 dimethyl butane	7				
2·2 dimethyl butane	6				
2·3 dimethyl butane	6				

The last number is carbon number.

Further aromatics/parraffins (A/P) was shown only for the experiment in which aromatics was measured up to o-xylene.

(5) In addition, the sume of oleffins and aromatics as active hydrocarbon minus benzene, (A + O - benzene), was calculated. But it was not listed in the table.

(6) Further, the final concentration of hydrocarbon is the one uncorrected for the dilution.

4.2 Range of initial concentration

Since the experiments by the mobile smog chamber were carried out in selected areas having different air polltuion levels and areal conditions, the initial concentration of NO_x and HC covering the wide range of concentration from low to relatively high concentration was obtained.

Table 4.2.1 shows the distribution of initial concentration

Non-methane hydrocarbon (hereinafter briefly referred to NMHC) exceeded 2.0 ppmC in 8 examples in which the maximum concentrtion was 7.4 ppmC.

The range of most frequent HC concentration as shown in Table 4.2.1, was 0.8 - 1.0 ppmC and the average concentration was 1.2 ppmC.

Also only 7 cases of the measurements had a range (2 - 4 ppmC) of considerably high concentration of NMHC.

NO_x concentration was the sum of NO concentration measured by chemiluminscence method and NO_2 by Saltzman's method. Its maximum concentration was 31.0 pphm, the minimum 0.9 pphm and the most frequent one covered the range from 3.1 to 4.0 pphm, the average being 6.0 pphm.

TABLE 4.2.1 Distribution of Initial Values

HC		NO_x		HC/NO_x	
Class	Num. of example	Class	Num. of example	Class	Num. of example
ppm.c		pphm		ppmc/pphm	
under 0.0 ∿ 0.2	3	0.0 ∿ 1.0	5	0.00 ∿ 0.10	12
0.2 ∿ 0.4	8	1.1 ∿ 2.0	12	0.11 ∿ 0.20	28
0.4 ∿ 0.6	6	2.1 ∿ 3.0	7	0.21 ∿ 0.30	14
0.6 ∿ 0.8	8	3.1 ∿ 4.0	13	0.31 ∿ 0.40	5
0.8 ∿ 1.0	12	4.1 ∿ 5.0	10	0.41 ∿ 0.50	3
1.0 ∿ 1.2	9	5.1 ∿ 6.0	6	0.51 ∿ 0.60	5
1.2 ∿ 1.4	6	6.1 ∿ 7.0	3	0.61 ∿ 0.70	3
1.4 ∿ 1.6	7	7.1 ∿ 8.0	5	0.71 ∿ 0.80	2
1.6 ∿ 1.8	5	8.1 ∿ 9.0	1	0.81 ∿ 0.90	
1.8 ∿ 2.0	2	9.1 ∿ 10.0	1	0.91 ∿	2
2.0 ∿	8	10.0 ∿ 15.0	5		
		15.1	6		
Total	74	Total	74	Total	74

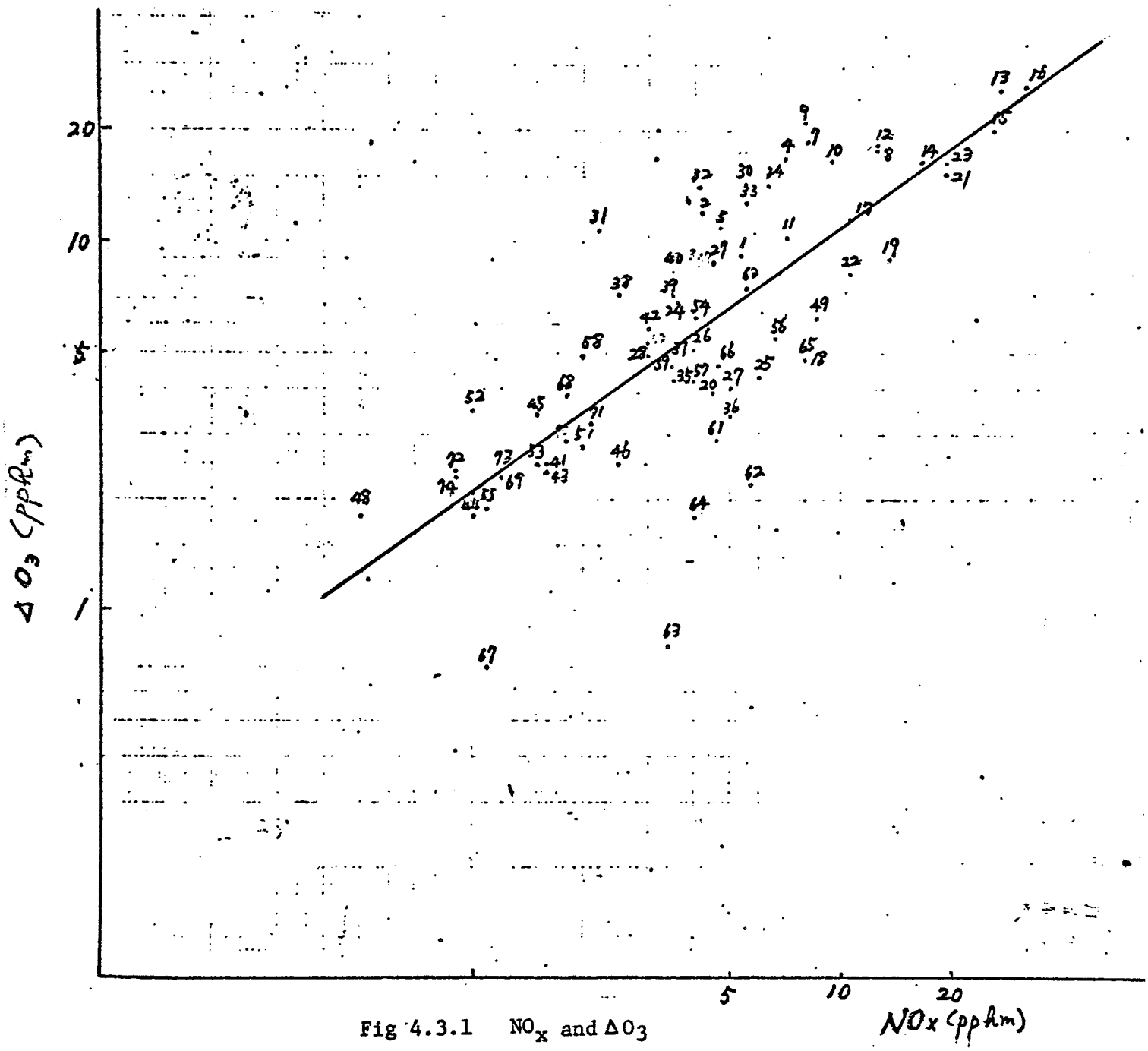


Fig 4.3.1 NO_x and ΔO_3

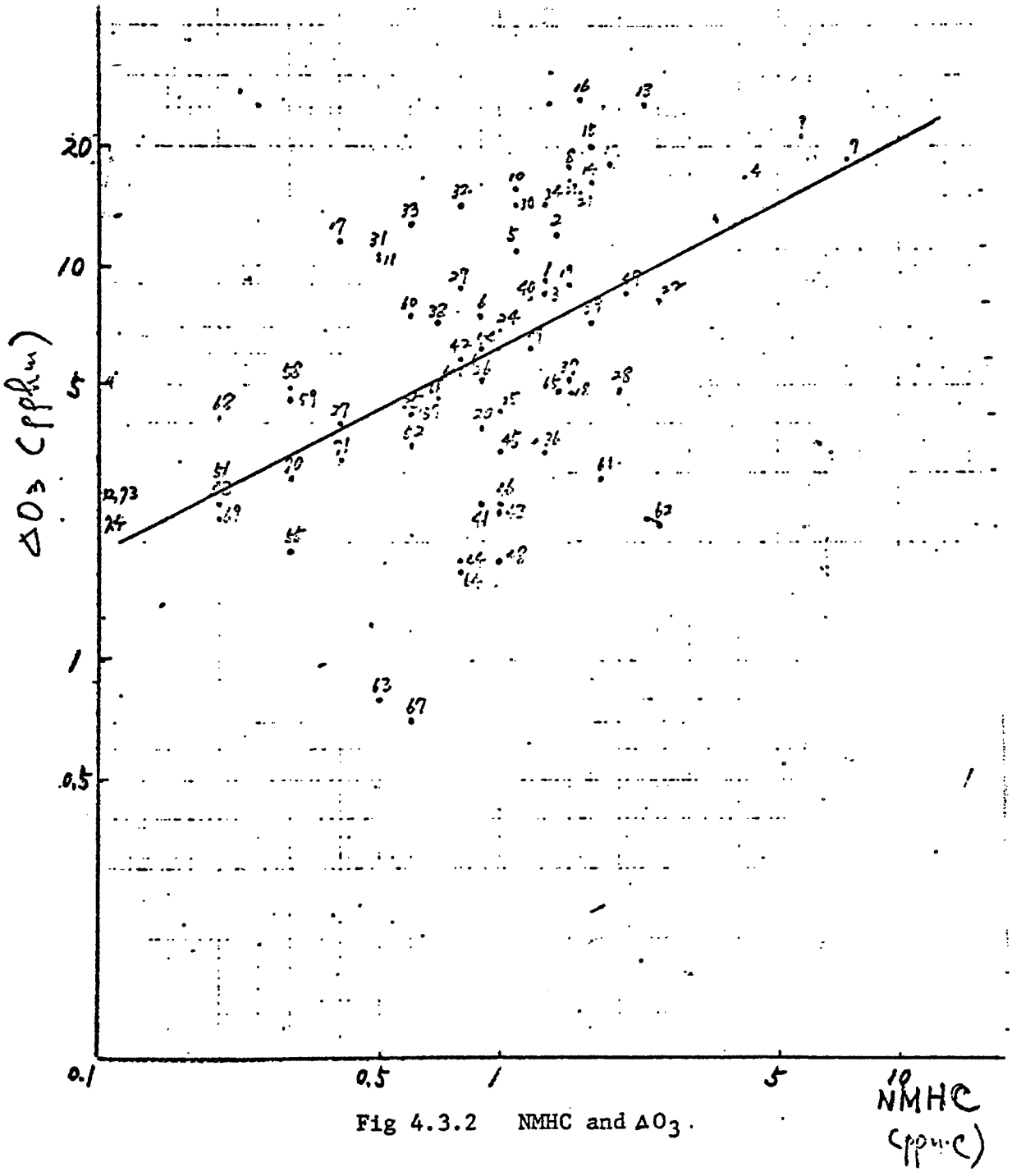


Fig 4.3.2 NMHC and ΔO_3.

0.11 - 0.20 of HC/NO_x (ppmC/pphm) were the most frequent values. The maximum was 2.00 and the minimum 0.007. 5 examples exceeded HC/NO_x of 0.63 for which no high O_3 concentration was observed. Since no case was less than 0.025 of the ratio no through consideration could be made in this range.

4.3 Single Correlation Analysis

4.3.1 Study of results by correlation diagram

To grasp first generally the relationships between ΔO_3 and NO_x and between ΔO_3 and HC all data were plotted on logarithmic graph. The results are shown in Fig. 4.3.1 and 4.3.2. The respective single logarithmic regressing equations are obtained as follows;

$$\text{Log } [\Delta O_3] = 0.723 \log [NO_x] + 0.319 \ (r = 0.768) \quad (4.3.1)$$

$$\text{Log } [\Delta O_3] = 0.522 \log [HC] + 0.799 \ (r = 0.545) \quad (4.3.2)$$

It will be understood from these equations that ΔO_3 is more significantly affected by NO_x than by HC.

4.3.2 Relationship between NO_x and O_3

Thus the initial concentration of NMHC was divided into 5 divisions (NMHC, 0-0.4, 0.5-0.9, 1.0-1.4, 1.5-1.9 and >2.0 ppmC) to show the relationship between, NO_x and ΔO_3, i.e. ΔO_3 corresponding to the initial concentration of NMHC.

The results are shown in Fig. 4.2.3 (1) - (5).

TABLE 4.3.1 Correlation between Initial NO_x and ΔO_3 in NMHC Class

Initial NMHC Class	Logarithmic one-dimension regression formula	Correlation	Number of data
ppmC			
0 ∿ 0.4	$\log [\Delta O_3] = 0.645 \log [NO_x] + 0.320$	0.912**	14
0.5 ∿ 0.9	$\log [\Delta O_2] = 0.757 \log [NO_x] + 0.276$	0.535**	23
1.0 ∿ 1.4	$\log [\Delta O_3] = 0.638 \log [NO_x] + 0.416$	0.689**	17
1.5 ∿ 1.9	$\log [\Delta O_3] = 0.793 \log [NO_x] + 0.206$	0.851**	12
2.0 ∿	$\log [\Delta O_3] = 0.776 \log [NO_x] + 0.341$	0.604**	8

** Level of significance 1%.

* Level of significance 5%.

TABLE 4.3.2 Correlation between Initial NMHC and ΔO_3 in NO_x Class

Initial NO_x Class	Logarithmic one-dimension regression formula	Correlation	Number of data
pphm			
0 ∿ 1.9	$\log [\Delta O_3] = -0.070 \log [HC] + 0.329$	-0.157	15
2.0 ∿ 4.9	$\log [\Delta O_3] = 0.350 \log [HC] + 0.750$	0.326*	30
5.0 ∿ 9.9	$\log [\Delta O_3] = 0.296 \log [HC] + 0.868$	0.352	18
10.0 ∿	$\log [\Delta O_3] = 0.164 \log [HC] + 1.167$	0.208	11

TABLE 4.3.3 Correlation between Initial NO_x and O_3 in HC/NO Class

Initial HC/NO_x Class	Logarithmic one-dimension regression formula	Correlation	Number of data
0 ∿ 10	$\log [\Delta O_3] = 0.771 \log [NO_x] + 0.245$	0.979**	11
11 ∿ 18	$\log [\Delta O_3] = 0.684 \log [NO_x] + 0.299$	0.761**	23
19 ∿ 28	$\log [\Delta O_3] = 0.503 \log [NO_x] + 0.491$	0.407	20
29 ∿	$\log [\Delta O_3] = 0.898 \log [NO_x] + 0.276$	0.276	20

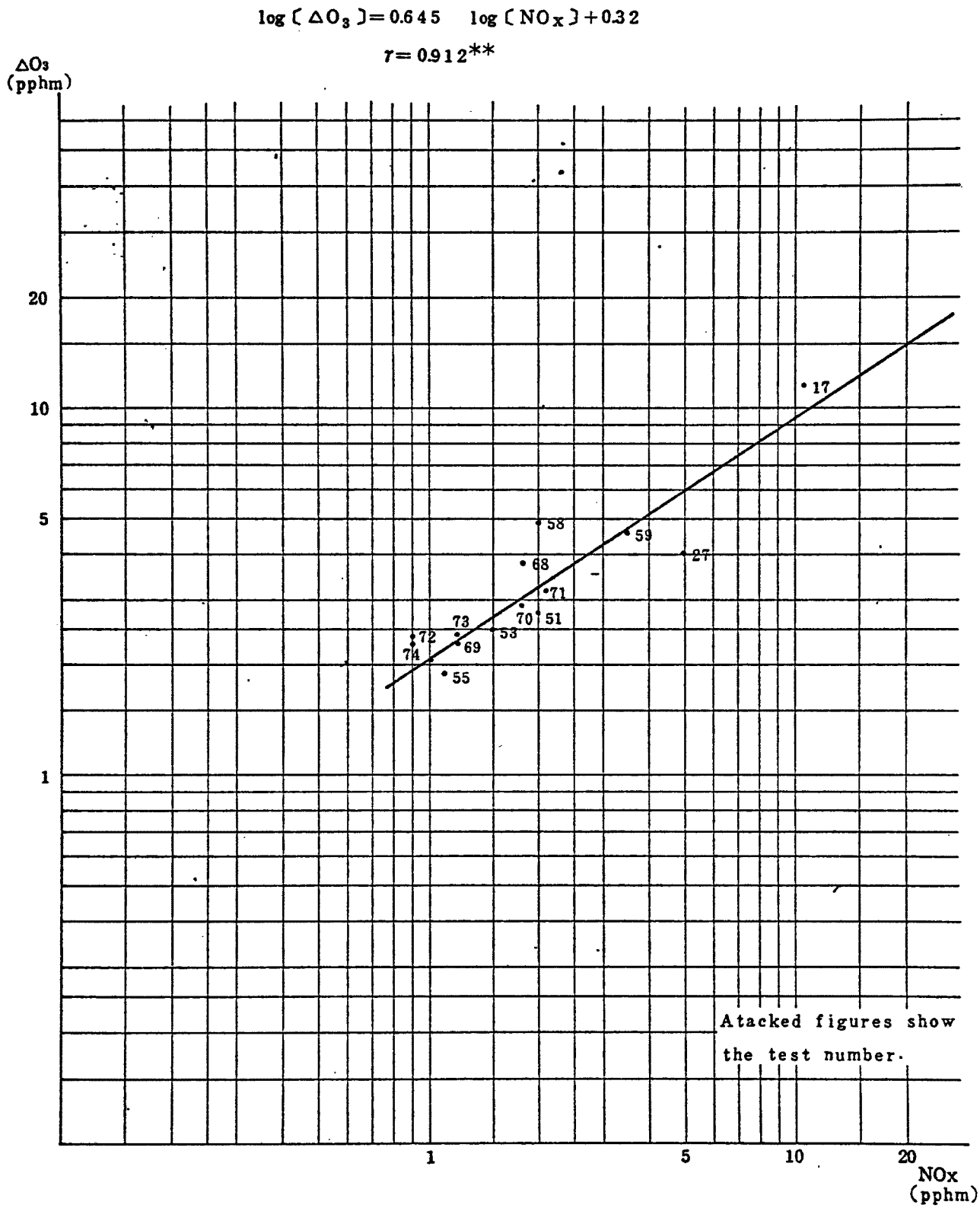


Fig 4.3.3(1) Correlation between NO_3 and ΔO_3 (NMHC 0～0.4 ppmC)

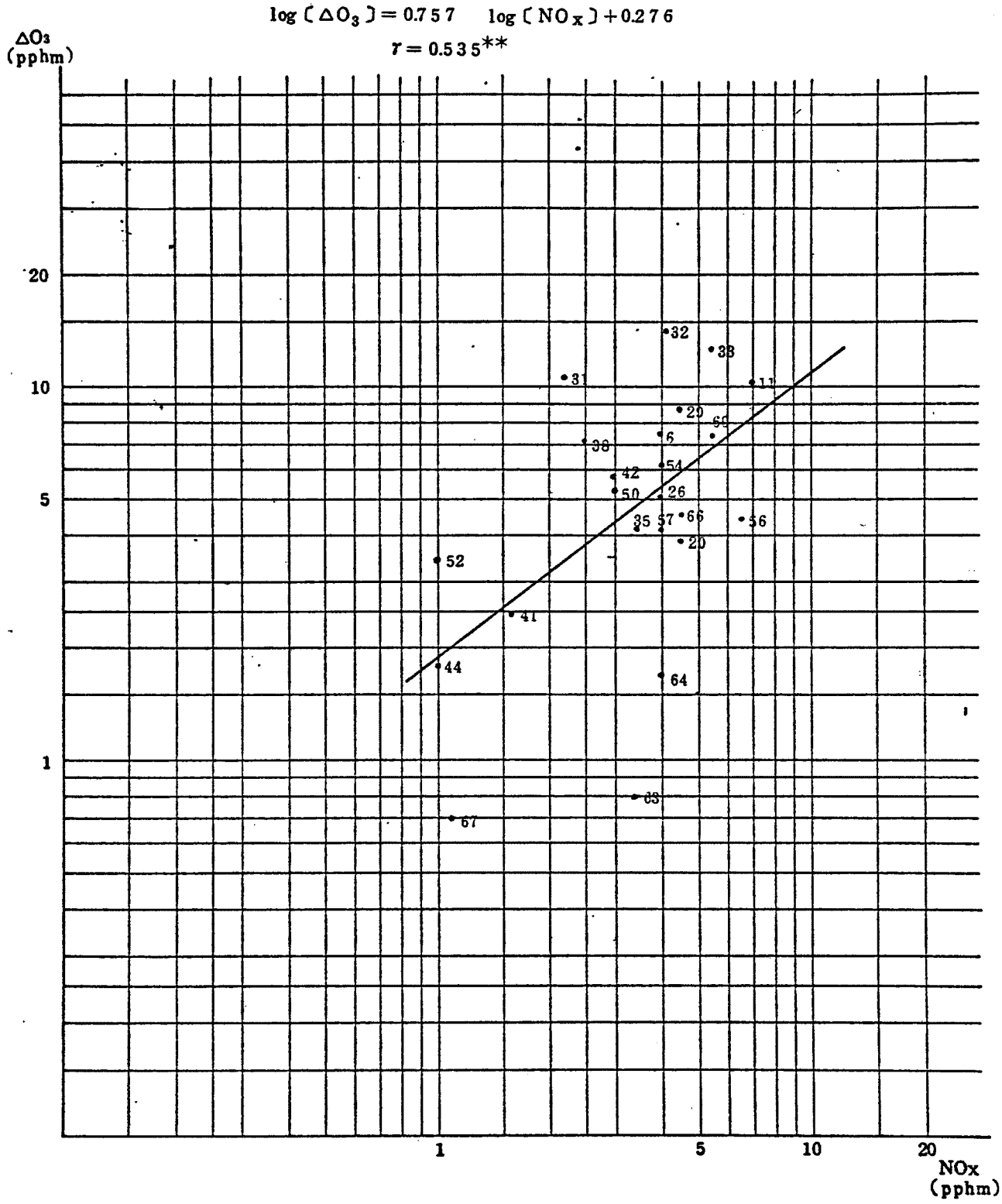


Fig 4. 3. 3 (2) Correlation between NO_X and ΔO_3 (NMHC 0.5～0.9 ppm C)

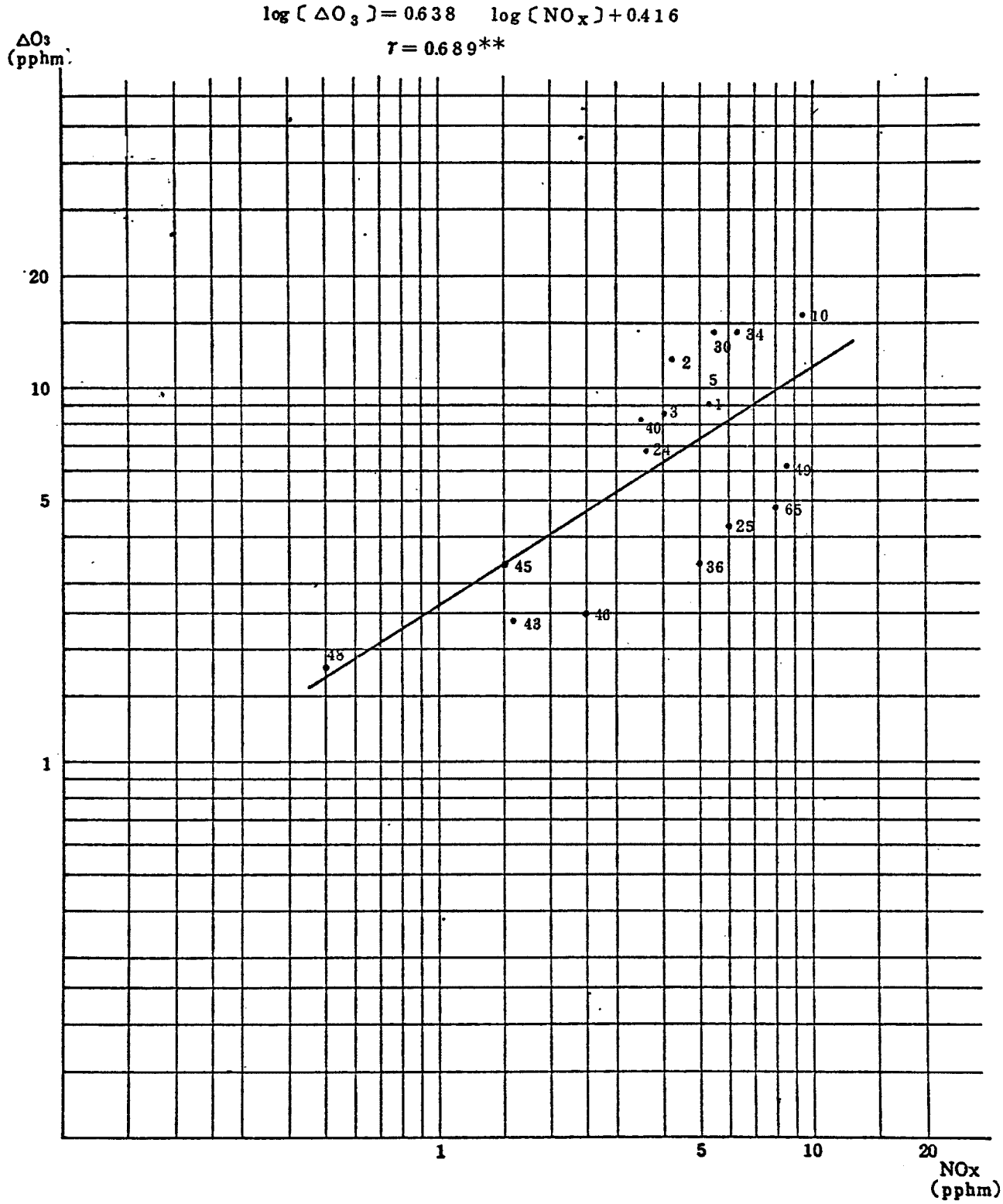


Fig 4.3.3(3) Correlation between NOx and ΔO_3 (NMHC 1.0 ~ 1.4 ppm C)

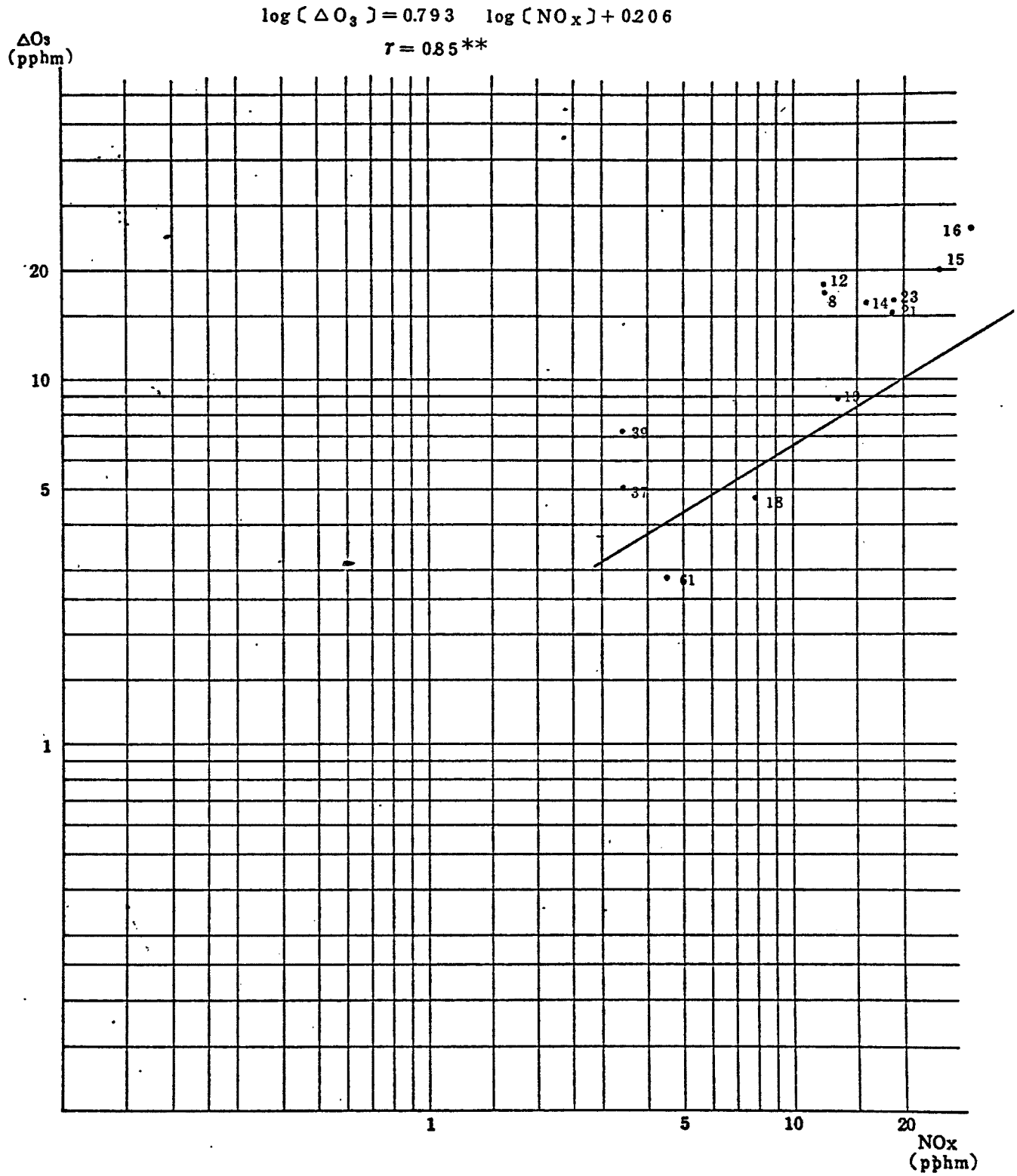


Fig 4.3.3(4) Correlation between NO_x and ΔO_3 (NMHC 1.5~1.9 ppmC)

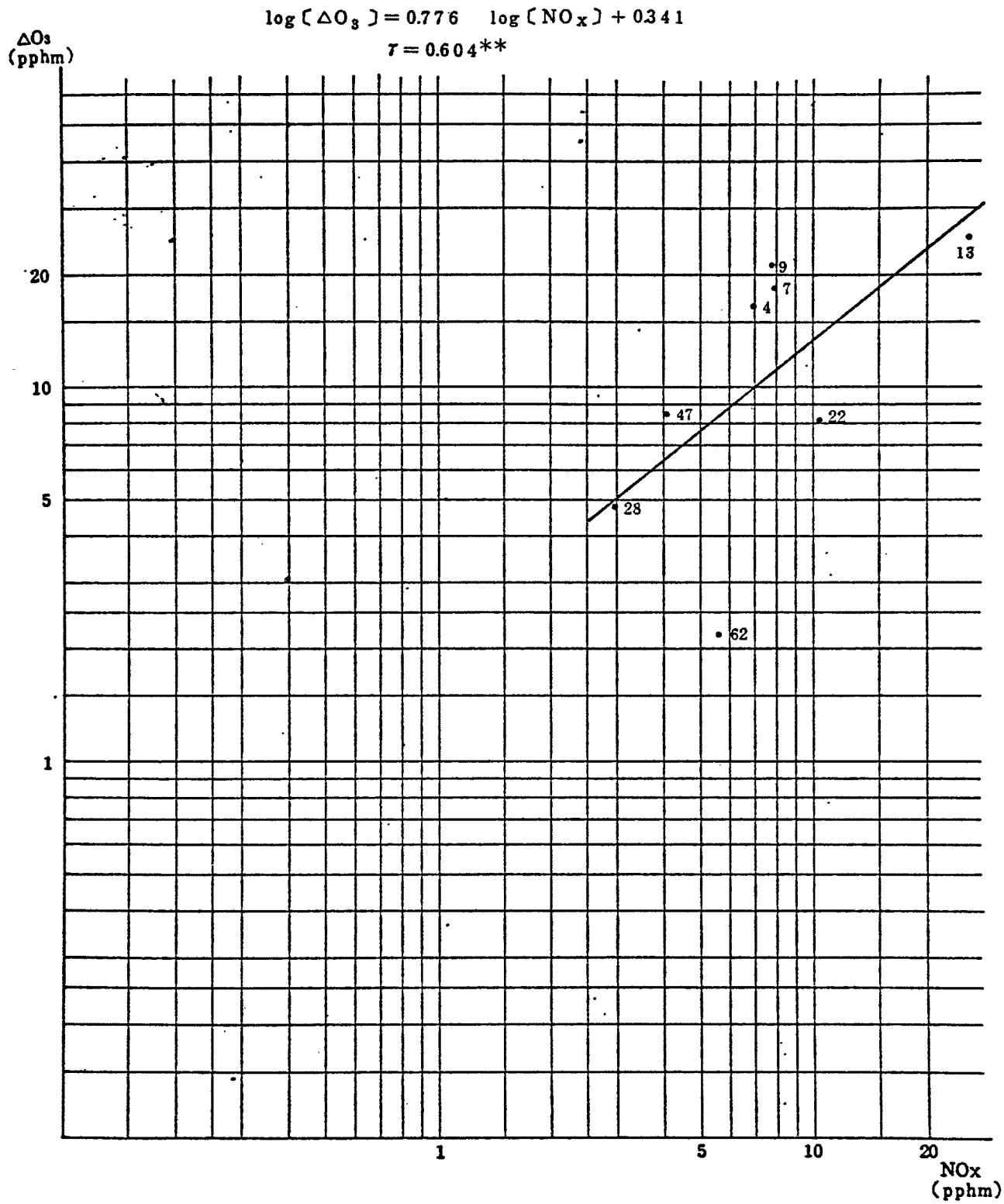


Fig 4.3.3 (5) Correlation between NO_x and ΔO_3 (NMHC 2.0 ppm C～)

According to this result, the relationship between NO_x and ΔO_3 was approximately linear on logarithmic paper except when the initial concentration of NMHC wer 0.5 - 0.9 ppmC.

From this confirmed relationship, single correlation model was assumed wherein the relationship between NO_x and O_3 was made exponential for each division of the initial concentration of NMHC., i.e.,

$$[\Delta O_3] = a\ [NO_x]^b \qquad (4.3.3)$$

Taking common logrighm of both sides, we obtained

$$\log [\Delta O_3] = \log a + b \log [NO_x] \qquad (4.3.4)$$

to determine factors log a and b by the method of least square.

This result is shown in Table 4.31. If was found that considerably close correlation existed in all cases.

4.3.3 Relationship between NMHC and ΔO_3

Next the initial concentration of NO_x was divided into 4 classes (NO_x 0 - 1.9, 2.0 - 4.9, 5.0 - 9.9 and > 10.0 pphm) to show the relationship between NMHC and ΔO_3 corresponding to the initial concentration of NMHC.

The results are shown in Fig. 4.3.4, (1) - (4).

In view of these results, the relationship between NMHC and ΔO_3 is considerably meager. Particularly in the small range of NO_x concentration points were distributed in the horizontal or ellipse-like shape. In the same way as that in the case of NO_x, regression equation was obtained from these points as shown in Table 4.3.2. Significant correlation was not obtained except for when the initial concentration NO_x was 2.0 - 4.9 pphm.

4.3.4 Relationship between NO_x or NMHC and ΔO_3 according to the division of HC/NO_x ratio and others.

Furhter, HC/NO_x ratio was divided into 4 divisions ($NMHC/NO_x$ = 0 - 10, 11 - 18, 19 - 28 and >29 ppmC/ppm) to show the relationship between NO_x or NMHC and ΔO_3, i.e., ΔO_3 corresponding to the initial concentration of NO_x.

The results are shown in Fig. 4.3.5 (1) (4).

In view of the results, the relationship between NO_x and ΔO_3 in any divisions showed approximately rightward-ascending one. In the same way as before, regression equation was obtained with respect to this relationship. It is shown in Table 4.3.3. It was found that there was considerably close correlation in all cases.

In addition, the relationship between UV Dose or UV intensity and ΔO_3 was also contemplated.

Though UV Dose was considered to be an important factor for ΔO_3, there was found no distinct relationship between them. This was possibly because the formation of ozone was affected mainly by the initial concentrations of NO_x and NMHC so that the time taken for the concentration of ozone to be maximized varied remarkably. Accordingly when the ultra-violet light was considered as a factor, it seemed suitable to use the intensity of ultra-violet light. This will be described later.

4.4 Multiple Correlation Analysis

In the previous section, the single correlation analysis of NO_x and O_3, etc. was carried out. In this section, we attempted to obtain multiple correlation as the product of NO_x , HC, UV intensity and concentration of olefins = aromatics in HC.

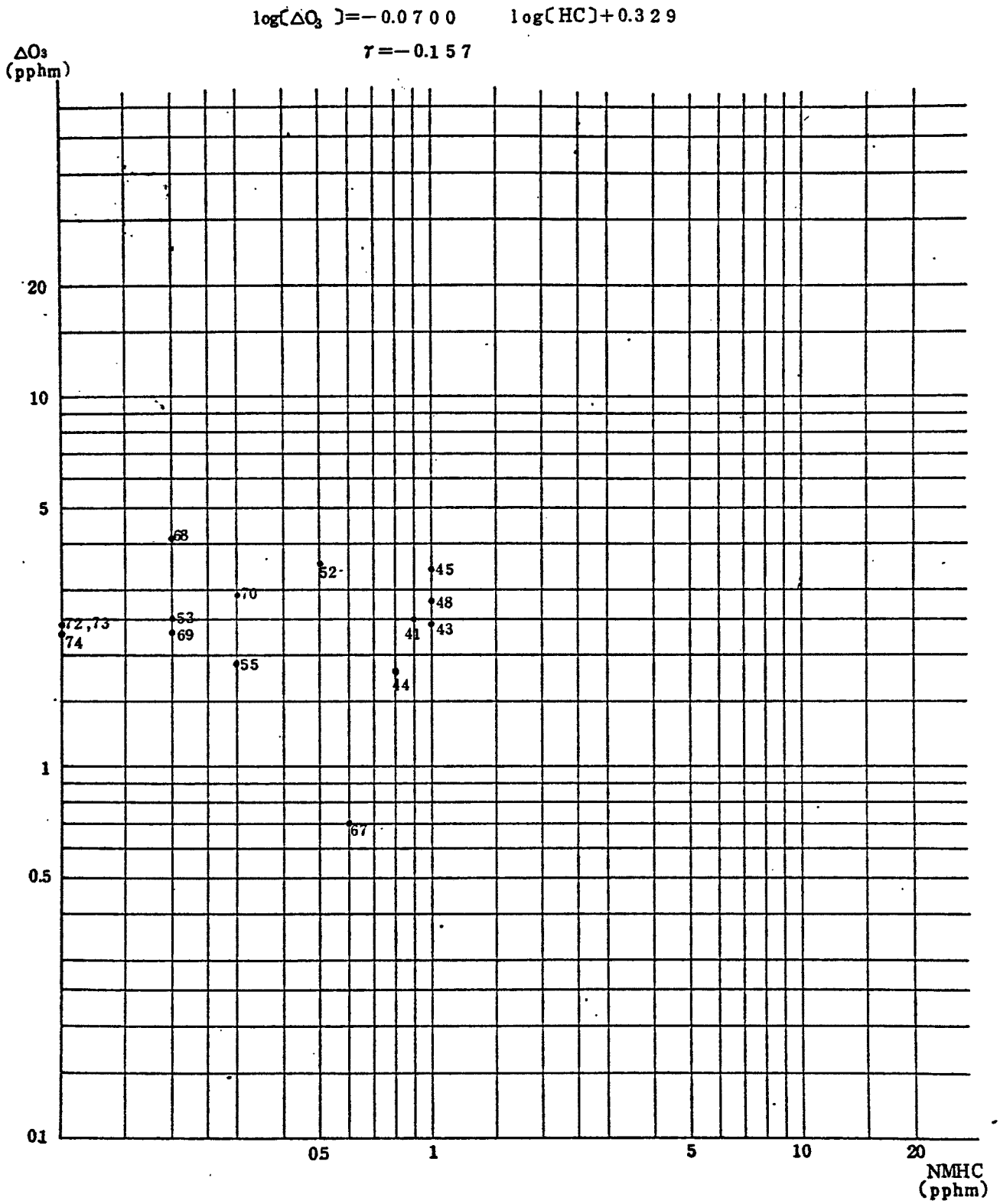


Fig 4.3.4 (1) Correlation between NMHC and ΔO_3 (NO×0～0.9 pphm)

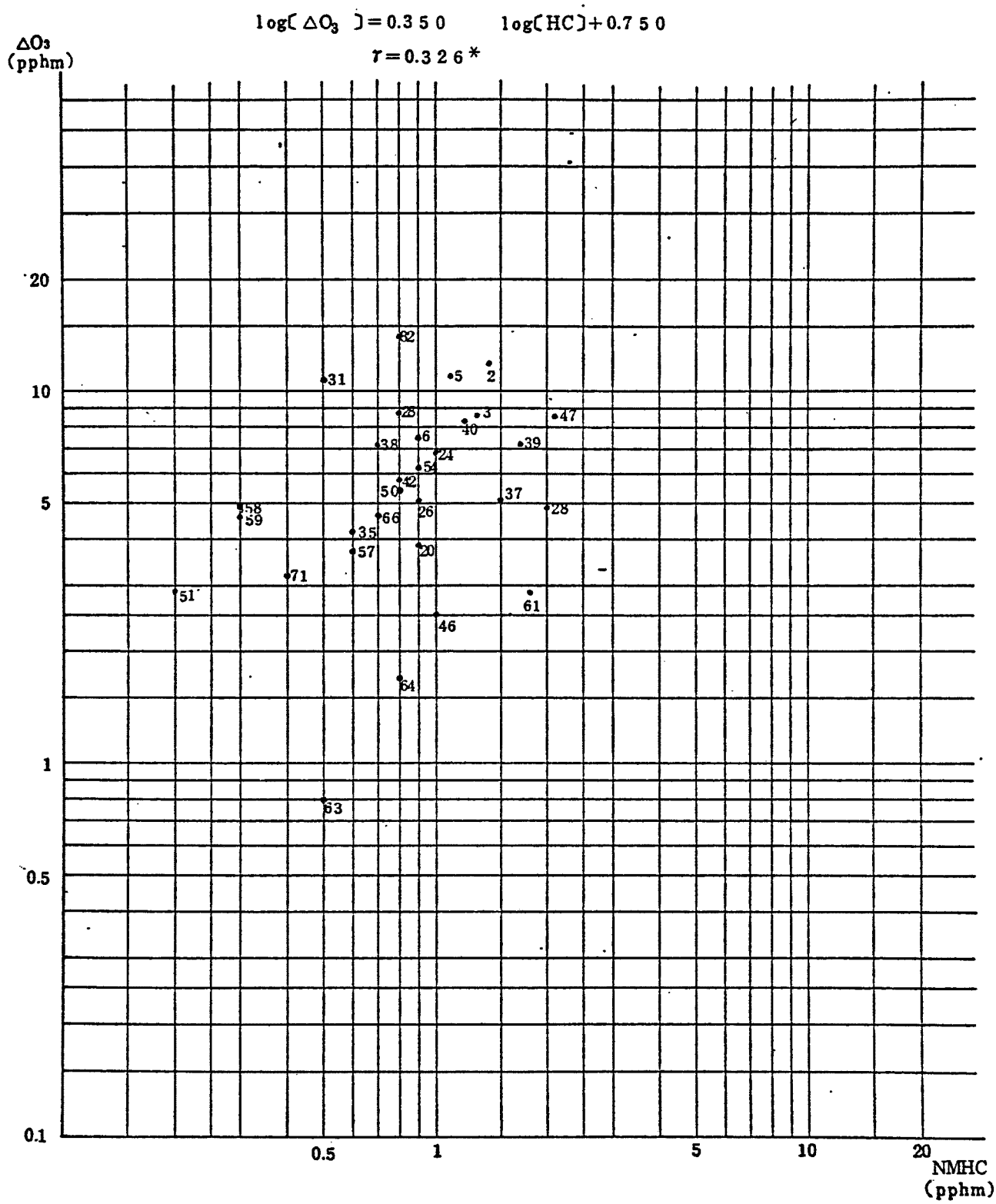


Fig 4.3.4 (2) Correlation between NMHC and △O3 (NOx 2.0～4.9 pphm)

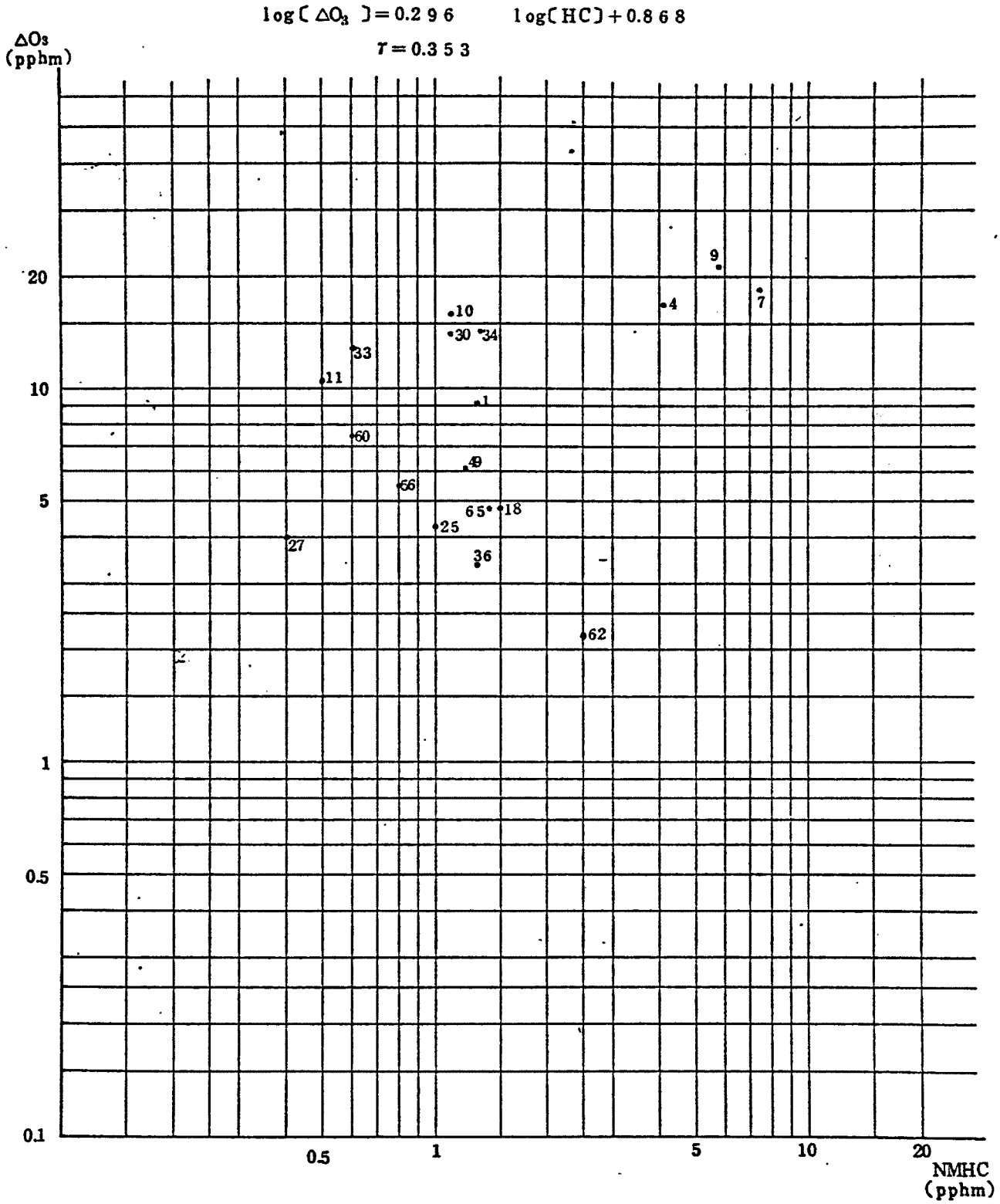


Fig 4. 3. 4 (3) Correlation · between NMHC and ΔO_3 (NOx 5.0~9.9 pphm)

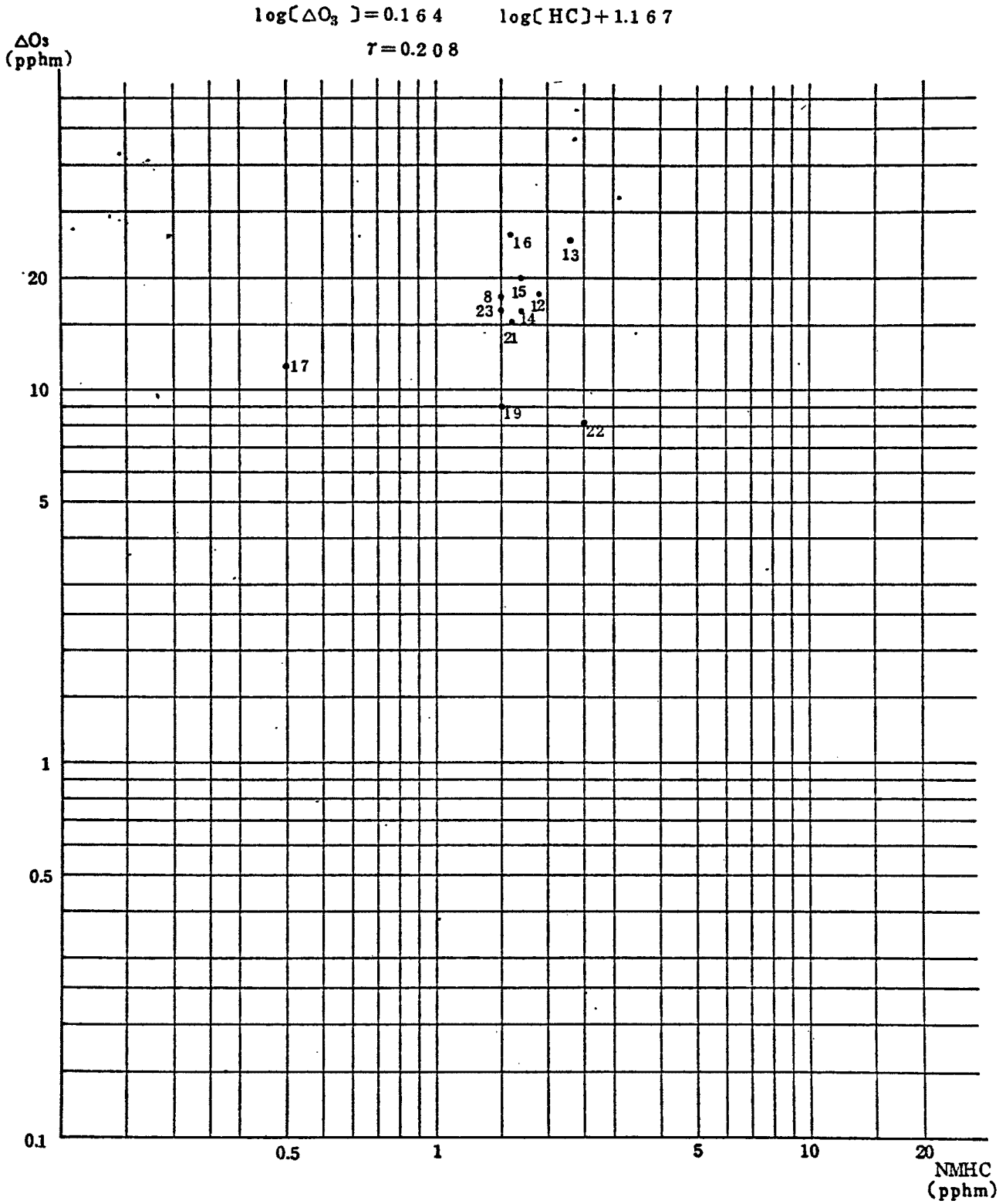


Fig 4.3.4 (4) Correlation between NMHC and ΔO_3 (NOx 10.0 pphm)

$$\log[\Delta O_3] = 0.771 \quad \log[NOx] + 0.245 \qquad (1)$$

$$r = 0.979^{**}$$

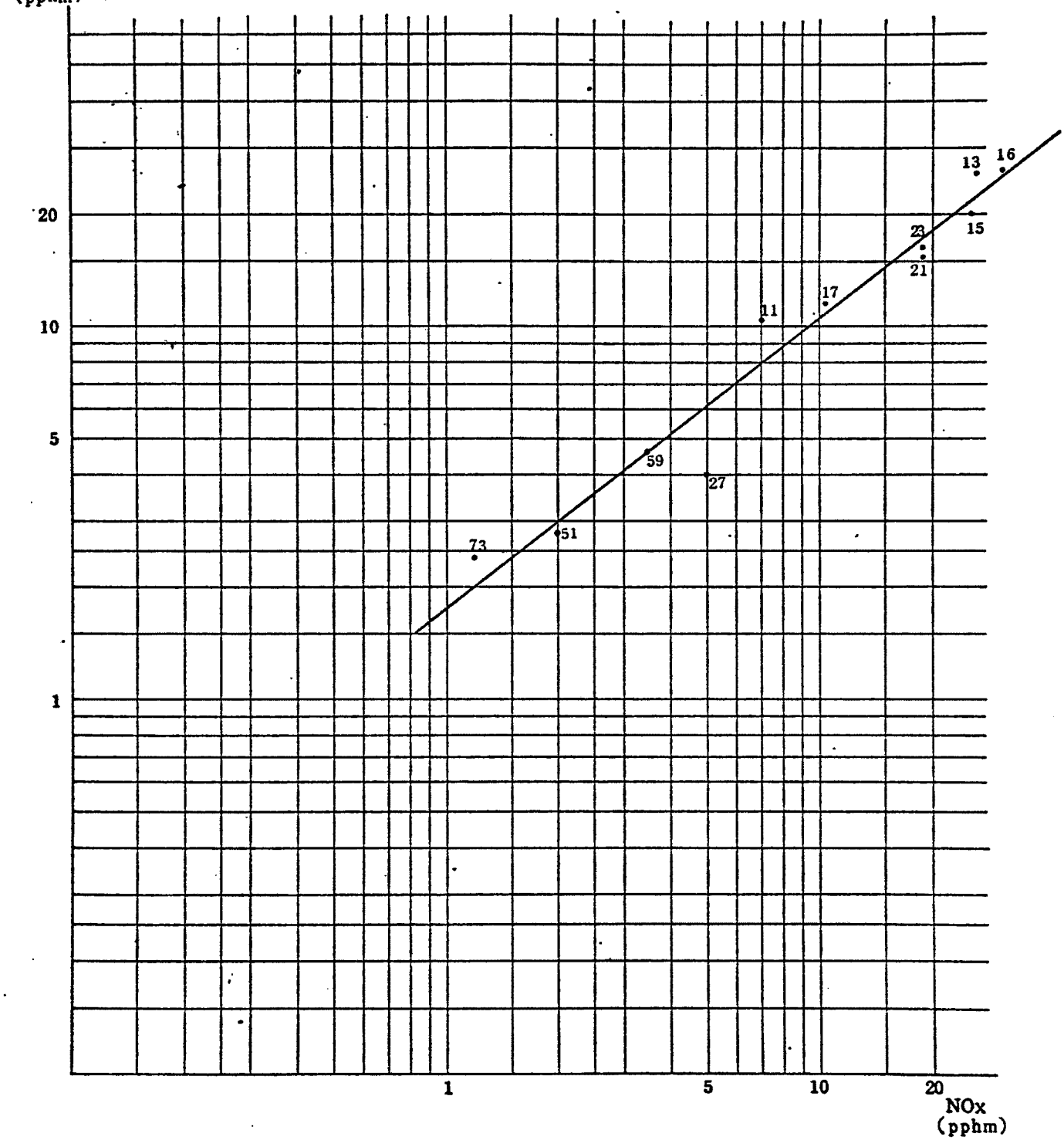


Fig 4 3.5 (1) Correlation between NOx and ΔO_3 (HC/NOx 0~10)

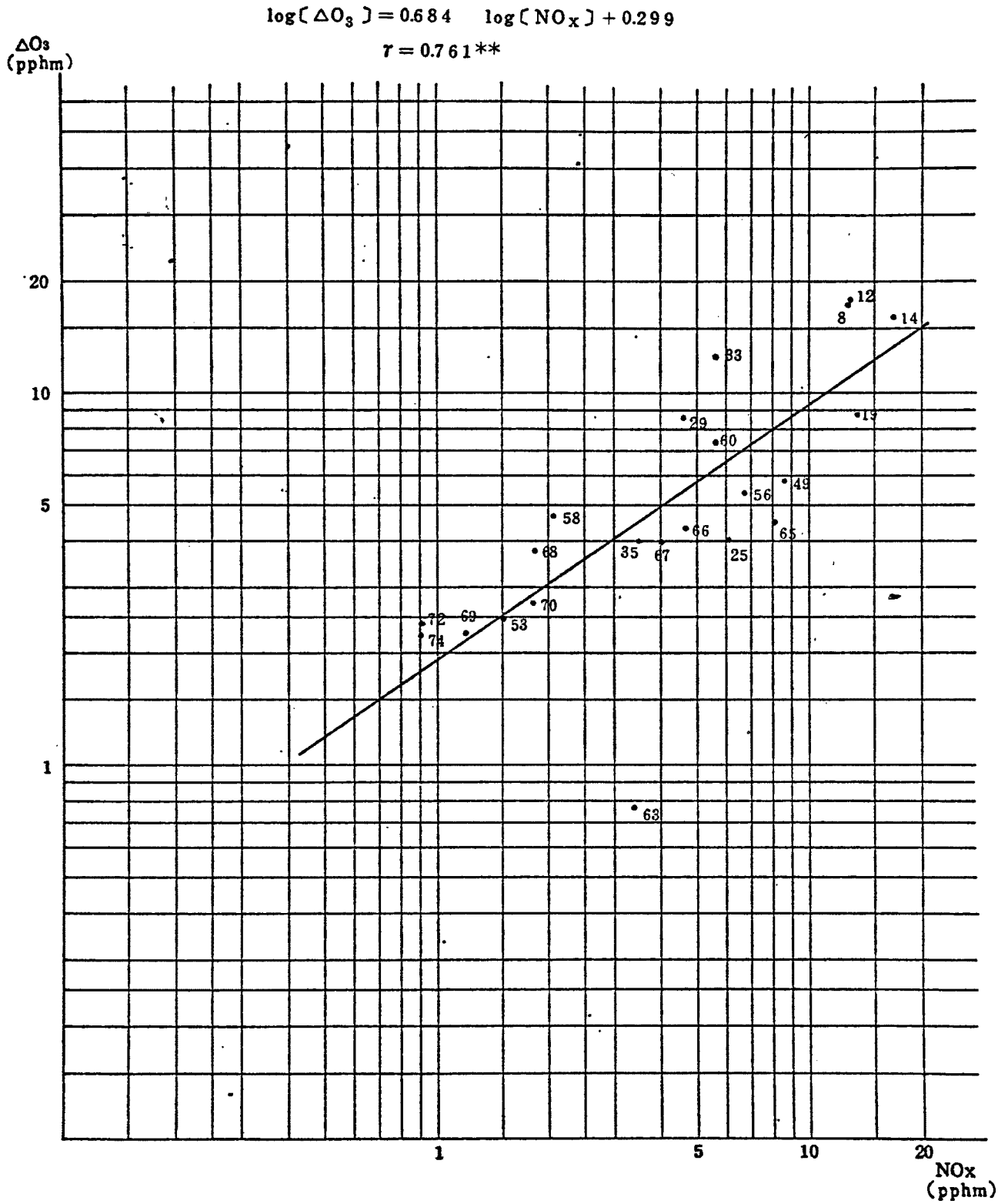


Fig 4.3.5(2) Correlation between NOx and ΔO_3 (HC/NOx 11~18)

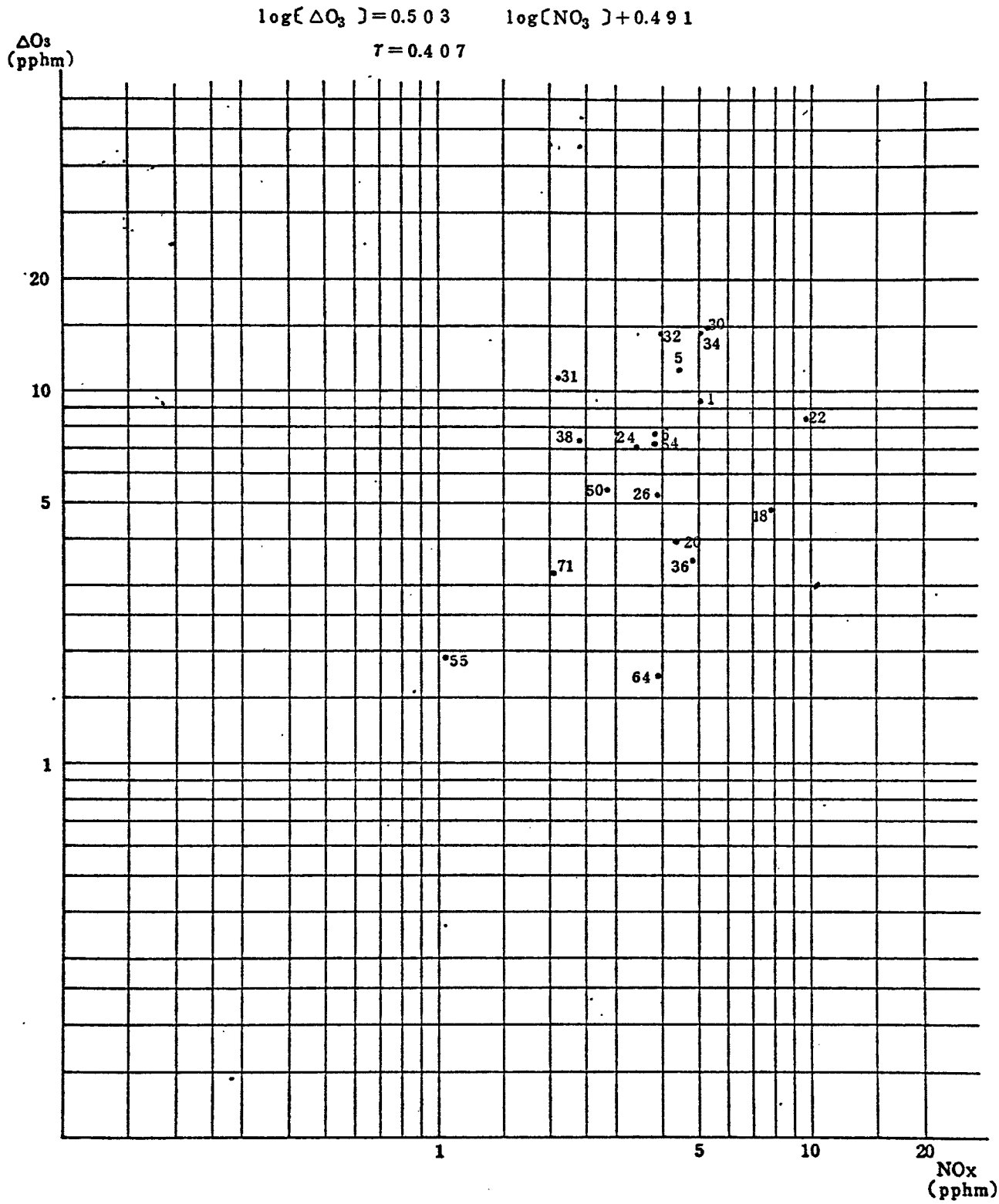


Fig 4.3.5(3) Correlation between NOx and ΔO_3 (HC/NOx 19~28)

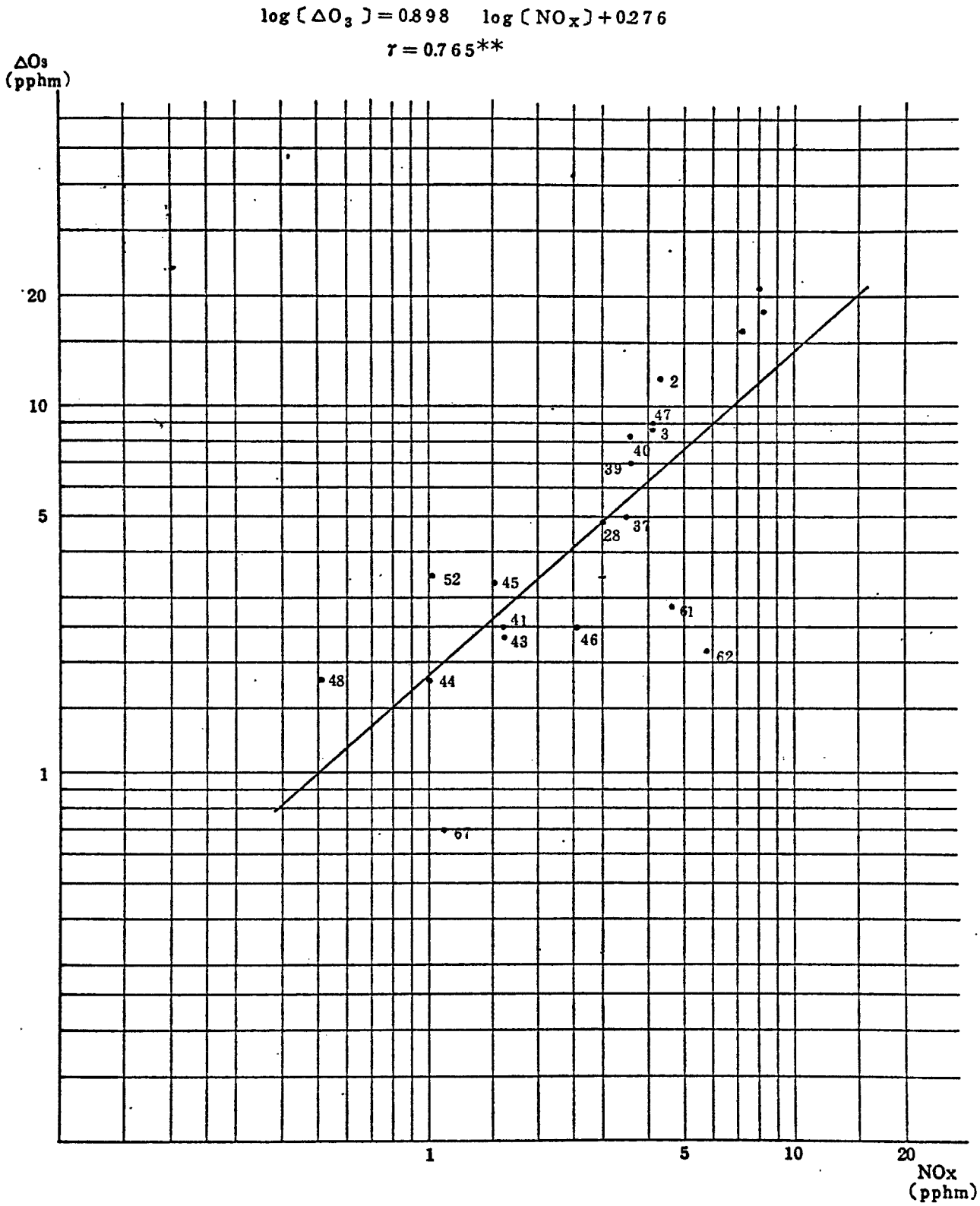


Fig 4.3.5(4) Correlation between NOx and ΔO_3 (HC/NOx 29~)

In this case multiple regression equation was assumed to exist, so that the following multiple regression equation model was employed to carry out multiple regression analysis:

$$[\Delta O_3] = \alpha[NO_x]^{\beta} \cdot [HC]^{\gamma}$$

Taking common logarithm of both sides, we obtained

$$\log [\Delta O_3] = \log \alpha + \beta \log [NO_x] + \gamma \log [HC]$$

to calculate α, β, and γ by method of least square.

The value of ΔO_3 corresponding to NO_x and HC in all experiments was plotted as shown in Fig. 4.4.1.

Making NO_x and HC variables, we can obtain the following multiple regression equation with respect to ΔO_3;

$$[\Delta O_3] = 2.347\ [NO_x]^{0.652}\ [HC]^{0.119},\ (r = 0.774) \qquad (4.4.1)$$

Unit of ΔO_3; pphm
Unit of NO_x; pphm
Unit of HC; ppmC

Further we obtained the correlation between the actually measured value of ΔO_3 and UV Dose (UV intensity x irradiation time) and UV intensity that were assumed to be correlated with the ratio of measured ΔO_3 to ΔO_3 calculated by the above equation. The caluclation showed that UV intensity had closer correlation than UV Dose. Thus adding the UV intensity as the next factor, we obtained the follwoing multiple regression equation. However it did not show a satisfactory multiple correlation factor.

$$[\Delta O_3] = 1.671\ [NO_x]^{0.687}\ [HC]^{0.0971}\ [UV]^{0.149}\ (\ = 0.777) \qquad (4.4.2)$$

Unit of ΔO_3; pphm
Unit of NO_x: pphm
Unit of HC : ppmC
Unit of UV : mW/cm^2

Thus we substituted the initial value of NO_x and NMHC into equation (4.4.1) to calculate ΔO_3. The ratio of that calculated value to actually measured one is shown in Fig. 4.4.2 Also we substituted the initial value of NO_x and NMHC and the UV intensity into equation (4.4.2) to calculate ΔO_3, the comparison of the calculated value to measured value being shown in Fig. 4.4.3.

When the measured value of ozone to the calculated one in these two figures is compared with each other, the equation (4.4.2) shows better correlation in the range of low concentation.

Next we summed the olefinic and aromatic hydrocarbon components that were believed to be reactive, and used this sum in lieu of total hydrocarbon in the multiple correlation analysis.

The resultant regression becomes as follows:

$$[\Delta O_3] = 2.599\ [NO_x]^{0.573}\ [A + O]^{0.180}\ (r = 0.769) \qquad (4.4.3)$$

Also the use of aromatic hydrocarbon, except benzene, as a factor gives the following equaiton:

$$[\Delta O_3] = 2.634\ [NO_x]^{0.571}\ [A + O - B]^{0.175}\ (\ \ 0.768) \qquad (4.4.4)$$

Referring to the equations (4.4.3) and (4.4.4) the comparison of the calculated value to the measured one was obtained by the same way as the previous one. They are shown in Figs. 4.4.4 and 4.4.5.

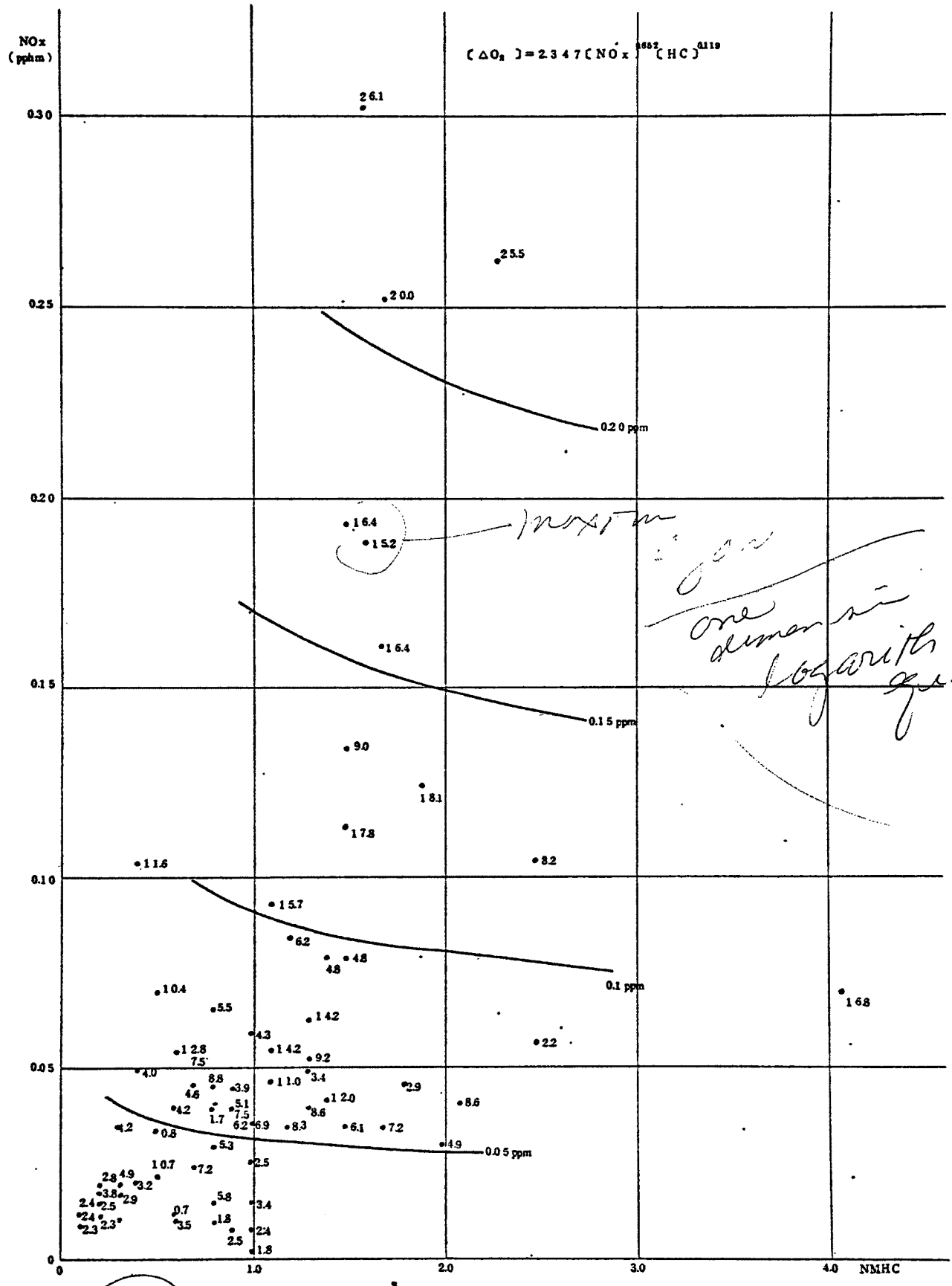


Fig 4 4 1 Curve showing correlation between NOx, HC and ΔO_3

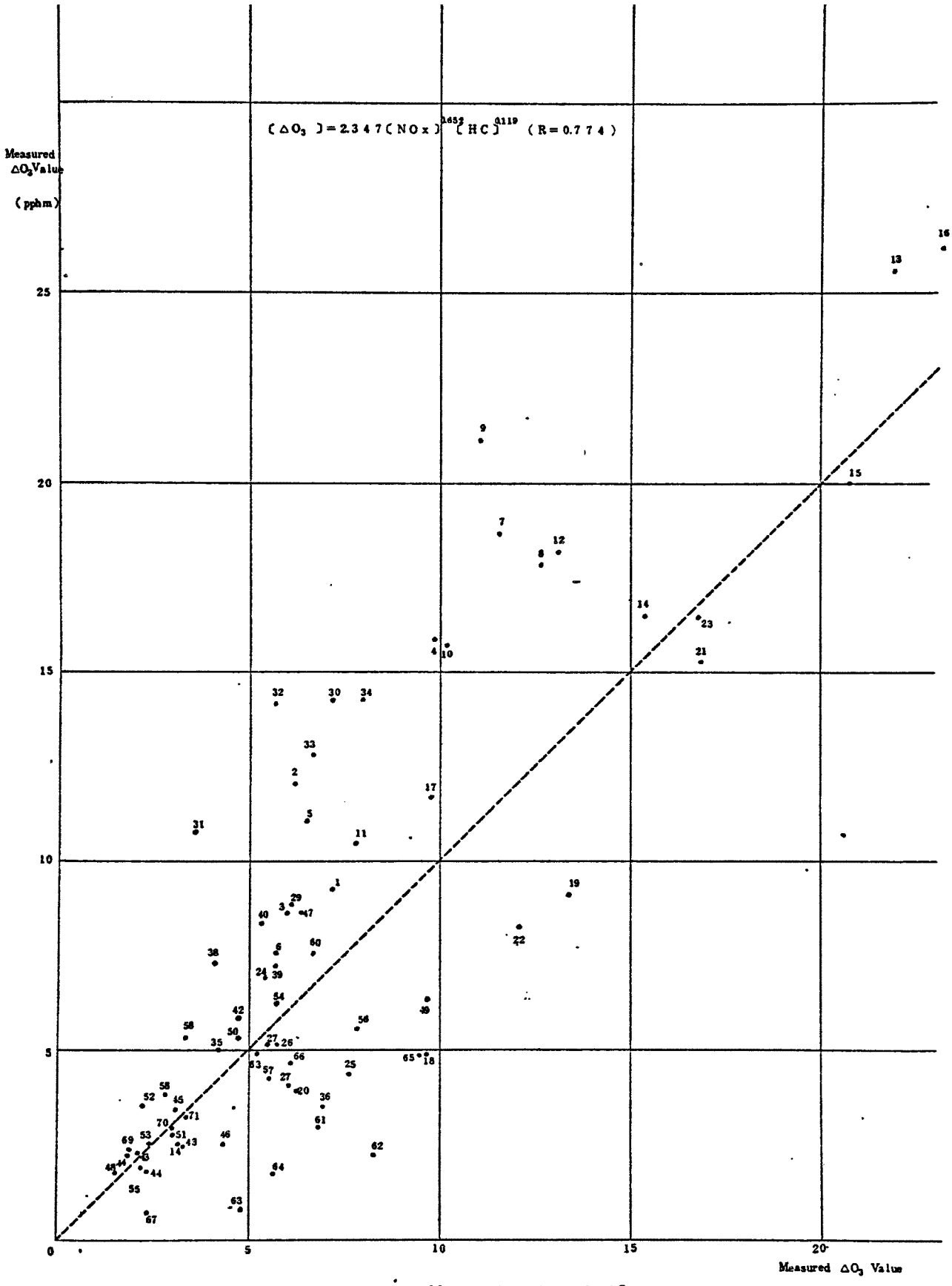


Fig 4 4 2 Calculated value and Measured value of ΔO_3

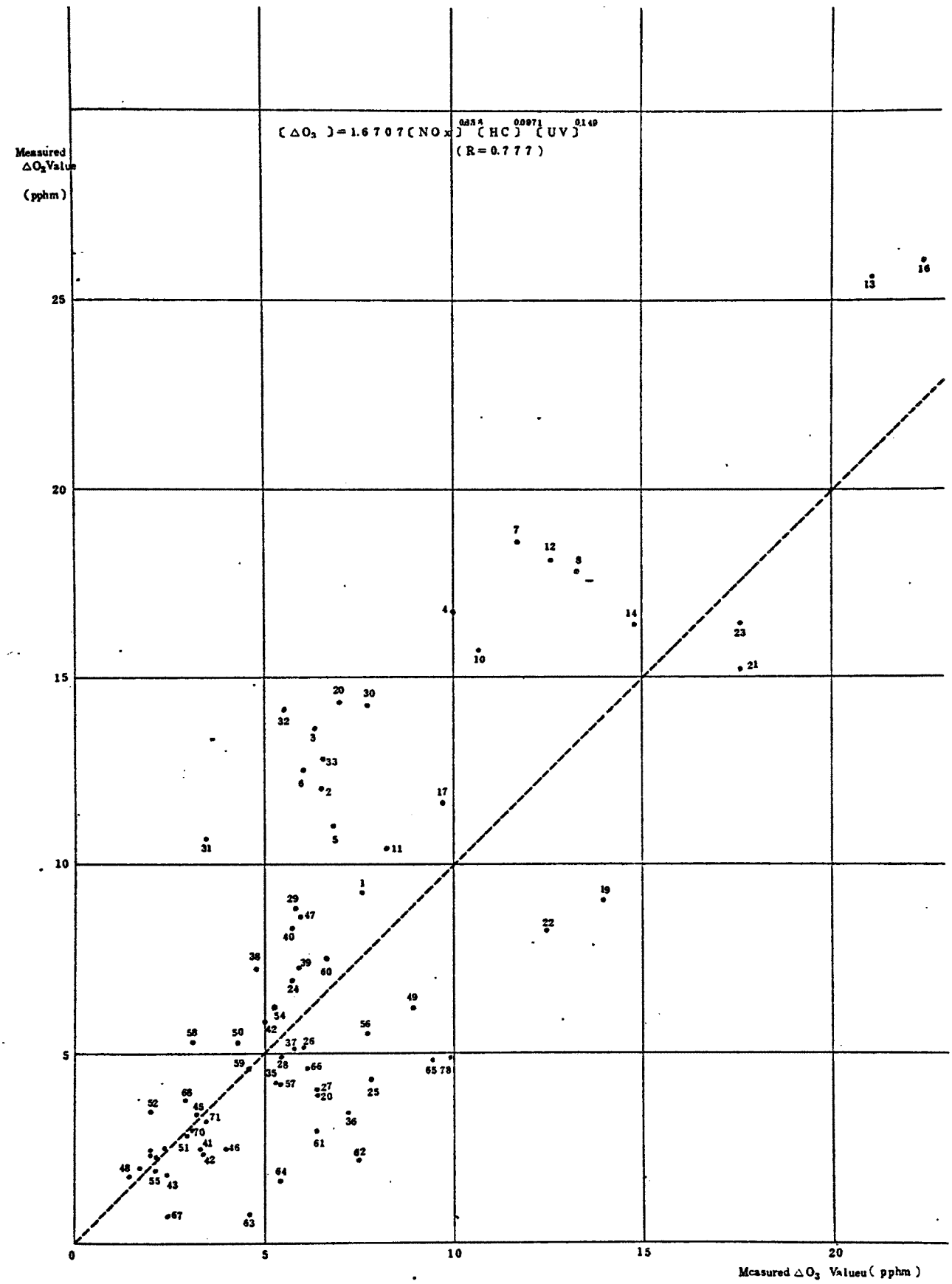


Fig 4 4 3 Calculated value and Measured value of ΔO_3

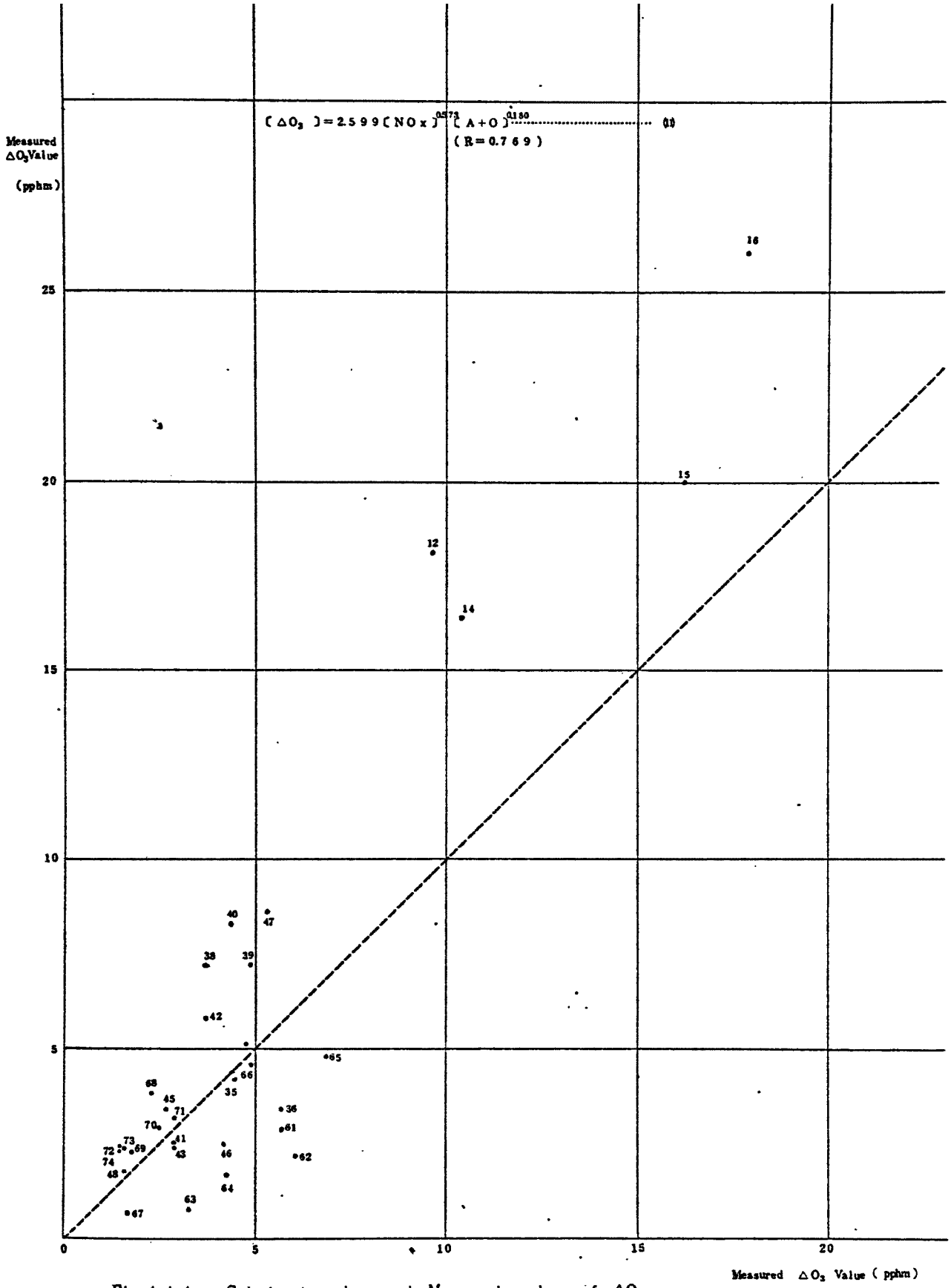


Fig 4 4 4 Calculated value and Measured value of ΔO_3

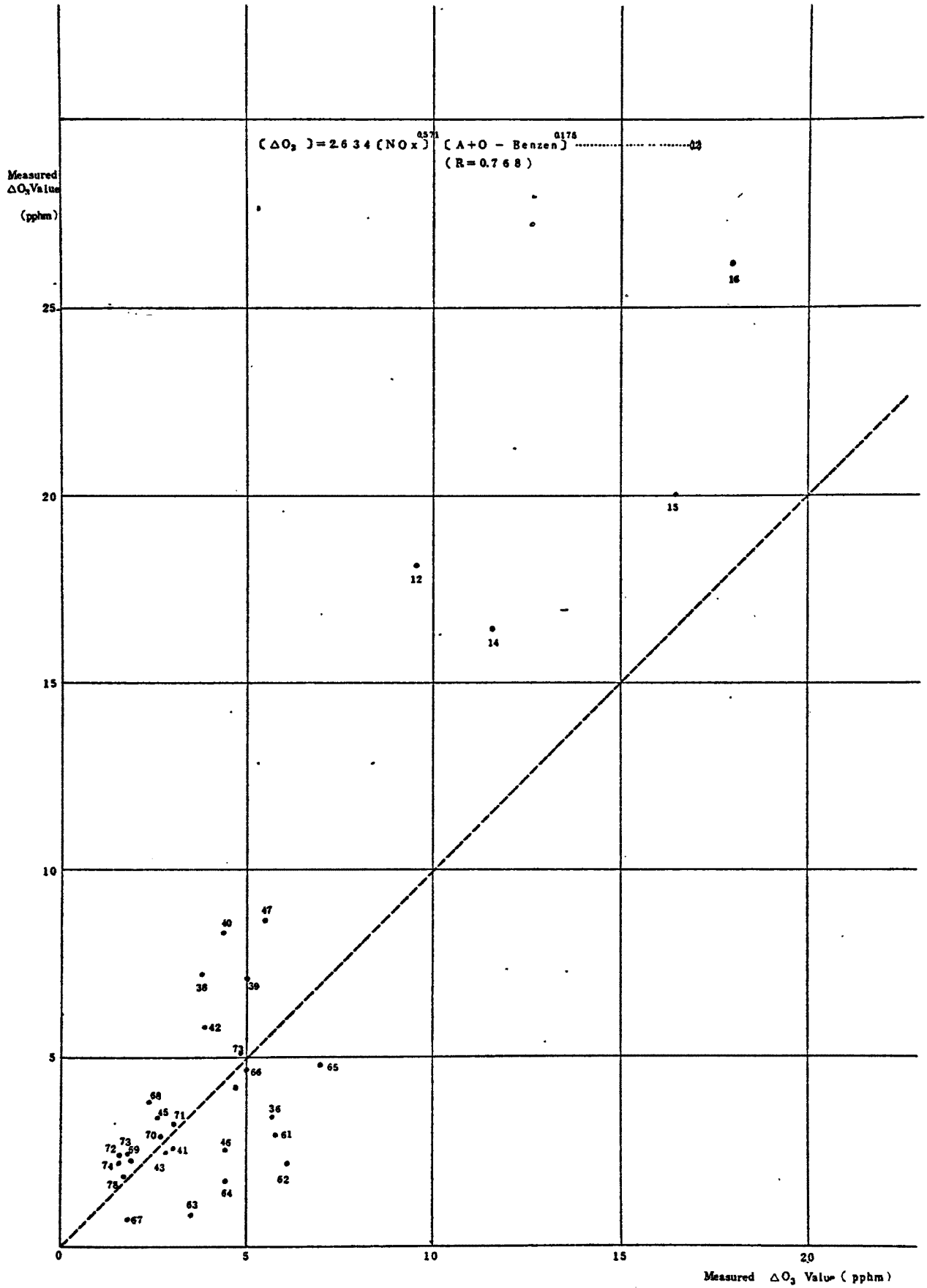


Fig 4 4 5 Calculated value ,and Measured value of ΔO_3

The comparison between these figures and the two previous ones shows that the ratio of the measured concentration of ozone to the calculated one becomes better in the low concentration ragne.

The comparison between equations (4.4.3) and (4.4.4) and equations (4.4.1) and (4.4.1) and (4.4.2) shows that the multiple correlation coefficient hardly changes so that the correlation can not be said to be improved, but equations (4.4.3) and 4.4.4) have higher exponent with respect to HC so that the quantities of high activity olefins and aromatics in NMHC should be still taken into consideration when HC is assuemd to be a factor for ΔO_3. As shown in Fig 4.4.2, Kawasaki (in winter 1973) and Kamata areas provided more experiments in which the ratio of the measured value to the calculated one of ΔO_3 was at least 1.5, and Kawasaki (in summer 1973) and Oymazaki areas provided more experiments in which the ratio was less than 0.75. These were considered to be caused by the difference between local air pollutants, in particular, the difference between hydrocarbon compositions or experimental conditions, especially the variation of ultra-violet light intensity. However we are not sure of these causes.

5. Summary

By representing ΔO_3 as the function of NO_x, HC, UV intensity, A + O, A + O-benzene, etc. we attempted to establish the basis for quantitative decision and obtained a tentative result from the above-mentioned statistical analysis.

As a result, NO_x was found to be the most important factor as a substance related to the formation of ozone according to single correlation analysis. However the formation of ozone could not be sufficiently explained only by NO_x. Thus, according to multiple correlation analysis reactive olefins and aromatics, except benzene, was found to be the 2nd factor. Also we carried out the multiple correlation analysis, adding UV intensity that, however, was insignificant factor. This seemed to be caused by uncertain data (value measured by a ultra-violet light sensor provided in the chamber)

Also in view of experiments in which the difference between the measured value and the calculated one of O_3 was large, the causes of this difference should be examined by future investigation.

At last, the following should be performed:

(1) to carry out many experimental and analytical experiments in one area,

(2) the same method should be employed,

(3) to improve the accuracy of HC composition analysis,

(4) to carry out experiments in aras having large and small HC/NO_x

(5) to establish and standardize the method of measuring ultra-violet light.

Also referring to the statistical analysis, it is believed that there is room for further examination to be applied to the classification of data, the selection and combination of factors, other multiple regression models, etc.

Health Hazards of Photochemical Air Pollution

(The results of a survey on health hazards of photochemical air pollution in 1975) -- Japanese Delegation

March 1976

Air Quality Bureau,

Environment Agency

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I. Preface

In Japan the photochemical air pollution has become a serious social problem since the incidents that occurred in the western coastal areas of Chiba Prefecture in June 1970 and at the Rissho Senior High School in July of the same year. Since then, various surveys and investigations have been made on photochemical smog hazards. Since 1972, the Photochemical Air Pollution Investigation Committee of the Environment Agency has been conducting a comprehensive research and investigation on the conditions for causing photochemical smog, the incidence of the particular air pollution, and its effects on human health. As for the effects on human health, the subcommittee for health survey of the above-mentioned committee has been conducting various surveys.

The 1975 survey on the effects of photochemical air pollution on human health was carried out to investigate the effects of photochemical air pollution on human health, thereby to make further advances in this country's public health preservation measures on the basis of the results of all the surveys conducted previously. This report gives the results of an analytical study of the reports submitted to the above sub-committee from seven prefectures where surveys were carried out.

II. Overall Analysis

1. Introduction

This chapter is a summary of the results of the analytical study

the working groups set up in the photochemical air pollution health hazards investigation subcommittees in seven prefectures had made a study of the following points on the basis of the reports submitted to those subcommittees.

a) To make a study on the contents of the received reports on damage to health by photochemical air pollution, particularly the points common with all of them, thereby to make clear the effects of photochemical air pollution on human health.

b) To make a case study to investigate the condition of the victims and the environmental conditions on the day a mass incidence of photochemical air pollution symptoms was reported (on such days as June 6 and July 18 in Kanagawa Prefecture and July 15 and July 16 in Saitama Prefecture, for instance).

c) The previously made studies revealed that the constitutional factors of individuals must be taken into consideration when making a study on the effects of photochemical air pollution on human health. As a pilot study, the results of surveys conducted in Osaka and Hyogo Prefectures will be studied.

d) To make a clinical study on the serious cases (victims hospitalized) which occurred on July 18 in Kanagawa Prefecture.

e) To study the relationship between environmental considitions and incidence of sufferings from photochemical air pollution on different days, that is, the day when the "photochemical

smog alert" is not issued (oxidant concentration in the air< 0.15ppm), the day when the alert is issued (oxidant concentration > 0.15ppm), and the day when the "alarm" is issued (oxidant concentration > 0.30ppm in Kanagawa Prefecture and > 0.25ppm in Saitama Prefecture).

f) In order that the results of the 1975 survey on the health hazards of photochemical air pollution may be duly reflected in the public health preservation measures to be taken in the future, a careful study will be made from the standpoint of experts and of the prefectural governments which undertook the survey and the Environment Agency and further efforts will be made to clarify the problems to be dealt with in the future.

2. The state of photochemical air pollution in Japan in 1975

This section is devoted to the study on the environmental conditions and the reported cases of sufferings from photochemical air pollution throughout Japan, thereby to make clear the positions of the abovementioned seven prefectures in the nationwide situation of photochemical air pollution.

The numbers of oxidant warnings issuances and photochemical smog victims are summarized in Tables 2-2-1 through 2-2-4.

From these data, it may be said that the photochemical air pollution during 1975 had the following characteristics.

a) About 58% of the total reported cases of sufferings from photochemical smog occurred on the days when the oxidant alarms were issued (June 6, July 15 and 18, August 13).

Particularly, in Saitama Prefecture, as many reported cases as 84% occurred on July 15 alone and about 98% on June 6 and July 15 in Kanagawa Prefecture. However, there was a case in which the number of reported victims was very small even on the day when the photochemical smog alarm was issued as it occurred in Saitama Prefecture (August 13). It was presnmably due partly to the fact schools were closed on August 13 because of summer vacation. There might have been some other unknown reason for such a singularly small number of reported photochemical smog victims on that particularly day and a further study is necessary to solve this problem.

b) Looking at the numbers of reported photochemical smog victims, the number of reported victims was issued was greater in the eastern part of Japan than in the western part, that is, 98% of the total reported victims (42,839) was issued in Japan east of Mie Prefecture while the corresponding figures were very small in the Kansai region and the areas along the shore of the Inland Sea. Investigations were made on the causes of this phenomenon, including the meteorological conditions, but nothing is not known for sure. It is notable that the frequency distribution of oxidant alert and alarm issuances agree with the distribution of the numbers of reported victims in Table 2-2-1.

c) A photochemical oxidant level as high as 0.39ppm was detected

in Isogo of Yokohama on July 18, the highest concentration of oxidant in the air ever recorded in Japan.

From the above nationwide characteristics of photochemical air pollution, it is possible to have a general idea of the situation in the prefectures where the present survey was conducted as follows.

In Saitama and Kanagawa Prefectures, very high percentages of reported cases of photochemical smog victims occurred on the days when the alarms were issued (over 0.25ppm in Saitama Prefecture and over 0.30ppm in Kanagawa Prefecture). In Mie Prefecture, the number of reported cases of sufferings photochemical smog was greater than in the preceding year in spite that no "alert" was issued. (In Mie Prefecture the photochemical smog alert is issued only when the oxidant levels are found exceeding 0.15ppm when measured at two photochemical oxidant monitoring stations in the area concerned while the alert is issued when the oxidant level exceeds 0.15ppm at a single monitoring station in other prefectures.) In Osaka, Hyogo and Okayama Prefectures, the "alerts" were issued but the number of reported victims greatly decreased from the preceding year. There was no reported case of suffering from photochemical smog is Hiroshima.

Table 2-2-1 Oxidant alerts issued in 1970 - 1975

( ) Bracketed are "alarms"

Prefecture \ Year		1970	1971	1972	1973	1974	1975
Tohoku Region	Miyagi				3		
	Fukushima						3
Kanto Region	Ibaraki			16	21	14	17
	Tochigi				10	10	6
	Gumma				1	4	11
	Saitama		23	15	45	29	44(2)
	Chiba		19	21	28	26(1)	33
	Tokyo	7	33	33	45	26(1)	41(1)
	Kanagawa		11	31	30	26	27(2)
Chubu Region	Shizuoka				8	15	16
	Aichi		1	5	8	2	6
	Mie			4	6	7	
Kinki Region	Shiga				4	4	4
	Kyoto			7	17	17	11
	Osaka		4	18	26(1)	27	23
	Hyogo		7	19	23	19	11
	Nara			1	6	3	9
	Wakayama			1	1	1	
Inland Sea districts	Okayama			3	14	16	5
	Hiroshima				9	18	4
	Yamaguchi					5	1
	Tokushima					2	2
	Kagawa				1	4	1
	Ehime				22	13	1
Total		7	98	176	328(1)	288(2)	266(5)

Table 2-2-2 Oxidant alerts issued in 1975

Prefecture	Month	Apr.	May	June	July	Aug.	Sept.	Oct.	Total
Tohoku Region	Miyagi								0
	Fukushima				1	1	1		3
Kanto Region	Ibaragi		1	1	6	5	4		17
	Tochigi		1		3	1	1		6
	Gumma				3	6	2		11
	Saitama		2	8	13(1)	13(1)	8		44(2)
	Chiba		3	4	7	11	7	1	33
	Tokyo	2	3	7	6(1)	11	11	1	41(1)
	Kanagawa		3	5(1)	3(1)	8	6	2	27(2)
Chubu Region	Shizuoka		2		2	2			6
	Aichi			1	4		1		6
	Mie								0
Kinki Region	Shiga				2		2		4
	Kyoto			5	4		1	1	11
	Osaka		2	8	7	2	4		23
	Hyogo			3	3	3	2		11
	Nara		1	1	5	5	2		9
	Wakayama								0
Inland Sea districts	Okayama		1	2			1		5
	Hiroshima			1	2	1	1		4
	Yamaguchi						1		1
	Tokushima			1		1			2
	Kagawa					1			1
	Ehime				1				1
Total		2	19	47(1)	72(3)	68(1)	53	5	266(5)

(Note) Bracketed are "alarms".
June 6: Kawasaki, Kanagawa Pref. (0.32ppm)
July 15: Shakujii, Tokyo (0.31ppm) Fujimi, Saitama Pref. (0.33ppm)
July 18: Yokohama, Kanagawa Pref. (0.39ppm)
Aug. 13: Fujimi, Saitama Pref.

Table 2-2-3 Reported victims in 1970 - 1975

Prefecture	Year	1970	1971	1972	1973	1974	1975
Tohoku Region	Miyagi						
	Fukushima						31
Kanto Region	Ibaragi			728	207	17	31
	Tochigi				776	38	23
	Gumma						1,959
	Saitama	1,262	3,663	5,726	6,774	1,498	16,624
	Chiba	5,923	1,169	561	155	237	277
	Tokyo	10,064	28,223	8,439	4,035	2,711	5,210
	Kanagawa	638	13,183	1,383	2,526	941	8,255
Chubu Region	Shizuoka				8,278	162	6,345
	Aichi		277	716	330	151	1,787
	Mie			231	1,148	630	1,786
Kinki Region	Shiga				16		1
	Kyoto			13	599	1	79
	Osaka		1,600	1,640	3,122	774	290
	Hyogo		3	430	989	4,373	62
	Nara			150	27		
	Wakayama			136	102	7	4
Inland Sea districts	Okayama				2,470	523	75
	Hiroshima			1,167	367	2,660	
	Yamaguchi						
	Tokushima						
	Kagawa				4		
	Ehime					2	
Total		17,887	48,118	21,320	31,936	14,725	42,839

Table 2-2-4

Prefecture	Month	Apr.	May	June	July	Aug.	Sept.	Oct.	Total
Tohoku Region	Miyagi								0
	Fukushima				1		30		31
Kanto Region	Ibaragi				18		13		31
	Tochigi				23				23
	Gumma				1,857	102			1,959
	Saitama		38	1,926	14,485	101	74		16,624
	Chiba		69	25	183				277
	Tokyo	1	1,208	1,132	2,652	49	167	1	5,210
	Kanagawa			4,931	3,253	35	2	34	8,255
Chubu Region	Shizuoka				6,345				6,345
	Aichi		33	14	1,728	4	8		1,787
	Mie			38	269		1,479		1,786
Kinki Region	Shiga				1				1
	Kyoto				48		3	28	79
	Osaka		5	67	212		6		290
	Hyogo			50	11	1			62
	Nara								0
	Wakayama			4					4
Inland Sea districts	Okayama	18	56	1					75
	Hiroshima								0
	Yamaguchi								0
	Tokushima								0
	Kagawa								0
	Ehime								0
Total		19	1,409	8,188	31,086	292	1,782	63	42,839

(Note) Reported victims on the days the "alarms". were issued.
June 6 Kanagawa Pref. (4,853)
July 15 Tokyo (2,557) Saitama Pref. (14,032)
July 18 Kanagawa Pref. (3,227)
Aug. 13 Saitama Pref. (17)

3. Method of Surveying

2-3-1 The method employed in the present survey

The basis method of surveying was described in Chapter 1. The concrete method differed with the prefectures where the survey was conducted, for those prefectures had so far been undertaking their own surveys on the health hazards of photochemical air pollution.

The methods of surveying employed by the respective prefectures are summarized in Table 2-3-1. In studying the survey results, such differences in the surveying methods used by different prefectures were taken into consideration and the common and characteristics points were summarized.

2-3-2 Brief description of the effects on human health

The survey results reported from the prefectures concerned were tabulated and their common points and differences were reviewed.

a) The numbers of people on whom the survey was conducted and the numbers of reported victims broken by sex are given in Table 2-3-2. There was no reported victim in Okayama and Hiroshima Prefectures, therefore, omitted from the following analytical review.

From this table, the following points can be confirmed.

* There was little difference in number between male and female reported victims, except for Osaka Prefecture where male victims accounted for 61.7% of the total.

It was previously said that the number of reported cases of females suffering from photochemical smog was larger than that of males but this tendency was not confirmed by the results of the present survey..

* Junior high school students accounted for the largest proportion of the reported victims. In Saitama Prefecture, 52.1% of the junior high school students under survey reported on their sufferings. About two-thirds of the reported victims were junior high school students in Kanagawa Prefecture.

b) Places where the reported cases occurred

The numbers of reported cases which occurred indoors and outdoors is shown on Table 2-2-3. It was previously said that there was a larger number of reported cases of sufferings occurring out of doors and the school students were told to remain indoors when the photochemical smog alarm was issued. The results of the present survey revealed that there was considerable numbers of people suffering from photochemical smog even when they were staying indoors. Particularly, in Kanagawa Prefecture more than two-thirds of the total reported cases complained of sufferings from photochemical smog. Therefore, it may be said that there is practically no difference between the inside and outside of houses in the summer when the doors are usually kept open.

Table 2-3-1 Methods of surveying employed in the seven prefectures

Prefecture	Schools designated for surveying	Response to questionnaire	Time of filling out the questionnaire	Remarks
Saitama	4 elementary schools (Over third-year students) 4 junior high schools 2 senior high schools	The students filled out the questionnaire themselves	Filled out not later than the day after the occurrence of damage.	Questionnaire A was filled in by the students themselves. As for the students who complained of physical disroders and were taken into the rest-room, nurse-teachers and school doctors made clinical examinations, checking their symptoms and medical history in compliance with Questionnaire B.
Kanagawa	No designated school	The students filled out the questionnaire themselves.	Same as above	Questionnaire was conducted on the schools where more than 10 students complained of physical disorders on June 6 and July 18 when the "photochemical smog alert" was issued. However, the schools went into summer vacation on July 18 and therefore it was impossible to collect all the answers to the questionnaire. June 6: 5 elementary schools, 8 junior high schools, 4 senior high schools July 18: 1 elementary school, 5 junior high schools, 2 senior high schools
Mie	3 elementary schools 2 junior high schools and Daian Junior High School	Surveyors interviewed students to fill in the questionnaire (except Daian Junior High School).	Same as above	At Daian Elementary School, a method different from other schools was used, that is, questions were asked to the students and they answered by raising their hands.

Osaka	All public elementary and junior high schools in Osaka Prefecture (excluding those in the cities of Osaka and Sakai)	Surveyors interviewed students to fill in the questionnaire.	(Unknown)	The first survey was conducted, using the ordinary questionnaire. After October, the secondary survey was conducted on orthostatic disorders and blood pressure to make investigations on the constitutional disposition of the affected students.
Hyogo	Public elementary schools (over fourth-year students) and junior high schools in the designated areas.	Same as above	(Unknown)	The number of the reported cases was so small during 1975 that health survey was conducted on the reported victims of 1975 and 1974 to make investigations on the personal dispositions of the reported victims.
Okayama	15 elementary schools, 7 junior high schools and 2 senior high schools	Same as above	-	There was no reported victims at these disignated schools.
Hiroshima	8 junior high schools	Students filled in the questionnaire themselves	Filled in on the day of occurrence of damage	Same as above.

Table 2-3-2 The numbers of people under survey and the numbers of reported victims, classified by sex

	Prefecture	Saitama			Kanagawa			Mie			Osaka			Hyogo			Okayama			Hiroshima		
		Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total
Numbers of people under survey	Elementary school students	897	812	1,709	-	-	-	1,250	1,172	2,422	-	-	-	-	-	-	-	-	9,913			
	Junior High school students	1,944	1,911	3,855	-	-	-	830 (1,091)	836 (1,101)	1,666 (2,192)	-	-	-	-	-	-	-	-	4,302	-	-	-
	Senior High school students	1,035	841	1,876	-	-	-										-	-	1,425			
	Adult people							2,080	2,008	4,088												
	Total	3,876	3,564	7,440	-	-	-	(2,341)	(2,273)	(4,614)	-	-	-	-	-	-	-	-	15,640	-	-	-
Numbers of reported victims	Elementary school students	103	95	198	473	461	934	124	68	192	40	21	61	-	-	50	0	0	0			
	Junior High school students	941	1,069	2,010	1,702	1,686	3,388	76 (206)	70 (160)	146 (366)	10	10	20	-	-	3	0	0	0	0	0	0
	Senior High school students	67	63	130	288	31	322							-	-	0	0	0	0			
	Adult people							200	138	338				-	-	9						
	Total	1,111	1,227	2,338	2,463	2,181	4,644	(330)	(228)	(558)	50	31	81	-	-	62	0	0	0	0	0	0
Reported victims classified by sex (%)		47.5	52.5	100.0	53.2	46.8	100.0	59.2 (59.1)	40.8 (40.9)	100.0 (100.0)	71.7	38.3	100.0	48.4	51.6	100.0						
Ratio of reported victims to the total (%)	Elementary school students	11.5	11.7	11.6	-	-	-	9.9	5.8	7.9	-	-	-	-	-	-	-	-	0.0			
	Junior High school students	48.4	55.9	52.1	-	-	-	9.2 (18.9)	16.5 (14.5)	8.8 (16.7)	-	-	-	-	-	-	-	-	0.0	-	-	0.0
	Senior High school students	6.5	7.5	6.9	-	-	-										-	-	0.0			
	Adult people							9.6	6.9	8.3												
	Total	28.7	34.4	31.4	-	-	-	(14.1)	(10.0)	(12.1)	-	-	-	-	-	-	-	-	0.0	-	-	0.0
	Remarks				The results of questionnaire were tabulated only for June 6. Schools were closed on July 18 and therefore it was impossible to collect the relies.			Figures in brackets represent the percentages when the students of Daian Junior High School are included.									There was no reported victim at the designated schools			There was no reported victim throughout the prefecture		

Note) 1) - indicates "unknown" because no report was received from the prefectures concerned.

2) Okayama and Hiroshima Prefectures had no reported victim and therefore not included in the tables to follow.

Table 2-3-3 Places where the reported cases occurred

	Prefecture	Saitama	Kanagawa	Mie	Osaka	Hyogo
Numbers of reported cases which occurred incoors	Elementary school students	67	528	72	-	-
	Junior High school students	862	2,479	59 (299)	-	-
	Senior High school students	71	217			-
	Total	1,000	3,224	131	52	44
Numbers of reported cases which occurred outdoors	Elementary school students	131	409	116	-	-
	Junior High school students	1,148	938	62 (62)	-	-
	Senior High school students	59	114			-
	Total	1,338	1,461	178 (178)	26	18
Unknown Total		0	110	9	0	0

Note) According to the survey conducted in Saitama Prefecture, most of the reported cases of indoor victims (elementary school students 98%, junior high school students 92.6% and senior high school students 97.1%) occurred when the windows were kept open. It was presumably the same with the reported cases of indoor victims in other prefectures. Bracketed are the figures including the students of Daian Junior High School in the case of Mie Prefecture.

Table 2-3-4 Physical exercises and photochemical smog damage

	Prefecture	Kanagawa	Osaka
Physical exercise (+)	Elementary school students	553	-
	Junior high school students	1,273	-
	Senior high school students	108	
	Total	1,934	22
Physical exercise (-)	Elementary school students	377	-
	Junior high school students	2,069	-
	Senior high school students	211	
	Total	2,657	52
Unknown		53	4

Note) The questionnairing results not tabulated for Saitama, Mie and Hyogo Prefectures.

c) Physical excercises and photochemical smog damage

The numbers of reported victims occurring when they were taking some forms of physical exercise or not engaged in any form of physical activity is shown in Table 2-3-4.

The tabulation of the questionnairing results have been completed only in Kanagawa and Osaka Prefectures. Thus obtained results show that there occurred many cases of victims among the students not engaged in physical exercises. However, considering the fact that when one is taking a physical exercise one breathes in more air and consequently more air pollutants than when not engaged in a physical exercise, it is considered necessary to make a more detailed study on this question in relation to the degree of intensity of physical movement in such exercises and the subjective symptoms of the photochemical smog victims.

d) Subjective symptoms (Table 2-3-5)

Table 2-3-5 shows the percentage proportions of the total symptoms reported by the photochemical smog victims.

The most common subjective symptoms due to photochemical smog are the eye, nose and throad mucous membrane irritations, which account for about 50% of the total. Apart from the above, there are respiratory, circulatory and general symptoms (including neurotic symptoms). The reported cases of general symptosm (including neurotic symptoms) were nearly equal in number to the mucous membrane irritation symptoms.

e) The ratios of subjective symptom complaints to the reported

victims of photochemical smog (Table 2-3-6)

Table 2-3-6 shows the ratios of subjective symptom complaints to reported victims in the various categories of symptoms. About 50 to 90% of the reported victims complained of eye, nose and throat symptoms in other prefectures than Osaka. In Kanagawa Prefecture 87.9% of the reported victims complained of eye symptom. Further details of the respective symptoms in the case of Kanagawa Prefecture are given in Table 2-3-7. The complaints of general symptom were so many as 62.9%, 40.7%, 49% in Kanagawa, Mie and Osaka Prefectures, respectively, suggesting the necessity for further investigations in the future.

f) Health preservation measures taken for the photochemical smog victims (Table 2-3-8)

The questionnaire results have been tabulated only in Saitama and Mie Prefectures. According to the tabulated relies to this particular questions, most of the victims "washed their eyes and gargled their throats" or "did nothing". There was no one who "received medical treatment from a doctor" or "was hospitalized" in either of the two prefectures. Although not given in this table, there were hospitalized cases in Kanagawa Prefecture on July 18.

In Mie Prefecture the students who "left school earlier" accounted for 16.6%.

Such a high percentage was ascribable to the fact that all of the 220 reported victims at the Daian Junior High School left school early.

g) The time required for the victims to recover (Table 2-3-9)

As in the case of the above f), the tabulation has been completed only in Saitama and Mie Prefectures. According to those tabulated questionnaire results, the majority of the victims recovered at schools or in their homes within the same day. However, the victims who "went to school although not completely recovered on the following day" and who "were absent from school on the following day" accounted for about 6% and slightly less than 1%, respectively. This fact is notable in relation to the serious damage caused to health by photochemical air pollution and it is a subject which requires further investigations in the future.

2-3-3 Places where photochemical smog victims occure and the effects of physical exercises

To make clear the effects of photochemical smog according to the places where the victims occure and whether they are engaged in physical exercises is important in working out effective protective measures against the hazardous air pollution.

It was notable that the results of the present survey showed that the percentage of the victims remaining indoors (windows were kept open in most cases) was fairly high. The simple tabulation of the questionnaire results showed no distinct difference in number between indoor and outdoor victims and between the exercising and not exercising victims.

In order to study the effects of such factors on the incidence

of sufferings from photochemical smog, it is not suffice simply to make clear the percentage proportions of indoor and outdoor victims and the exercising and not exercising victims. It is necessary to make a more detailed study, including the ratios to the populations of the respective groups of victims and the time factors (relationship to the level of contamination) to be discussed later.

A survey conducted on the students of the Mihashi Junior High School in Saitama Prefecture on July 15 showed little disparities in the ratio of reported victims, difference between male and female and symptoms according to the school years. However, as seen from Fig. 2-3-1, there were obvious time disparities for the students to complain of physical disorders, that is, many third-year students complained of photochemical smog symptoms earlier when the Ox level was still not very high. In this district the photochemical smog alert was issued at 11:00 and the alarm at 12:15 and the Ox concentration in the air reached its peak at 13:00 when measured at the municipal office of Omiya situated near the junior high school. On the other hand, about one-third of the first- and second-year students were taking gymnastic lessons in the gymnasium and the rest were taking lessons in their classrooms. This particular case is considered suggestive of the fact that physical damage caused by photochemical smog varies according to whether the victims are within or out of doors or whether they are engaged in physical exercises.

A further detailed study is necessary to be made on the effects

of such factors on the occurrence of photochemical smog damage to human health.

Table 2-3-5 Reported subjective symptoms (%)

Symptom \ Prefecture		Saitama	Kanagawa	Mie	Osaka	Hyogo
Eye symptom	1)	24.4	35.6	38.0 (36.3)	24.9	55.4
Nose and throat symptom	2)	20.7	28.3	24.9 (28.0)	14.4	20.3
Respiratory symptom	3)	28.5		11.0 (16.0)	17.7	
Circulatory symptom	4)		3.1			
General symptom (Including ~~neurotic~~ nerve system symptom)	5)	25.7	33.0	26.1 (19.7)	33.4	24.3
Others		0.7	0.0	0.0 (0.0)	9.8	
Remark Total number of reported symptoms			11,476	599 (1,166)	153	

Bracketed figure include the victims at Daian Junior High School

Note) Detailed description of symptoms complained by the photochemical smog victims

1) Feel pain in the eyes, eyes are irritated and smart and tears flow.
2) Noses are irritated, run, voice becoms hoarse, throats are irritated, noses sting, sneeze, noses feel itchy, noses bleed.
3) Cough, feel opressed in the chest, feel choky, chests pain, cough up phlegm.
4) Hearts pound, feel the sense of constriction in the chest.
5) Feel the numbness of the extremities, feel foggy, feel dizzy, have headache, feel nausea, feel pain in the extremities, feel languid, feel feverish, feel sick.

Table 2-3-6 Ratio of reported subjective symptoms to the reported victims

Prefecture	Kanagawa	Mie	Osaka
Eye symptom	87.9%	67.5% (75.8%)	38%
Nose and throat symptom	69.9%	44.1% (58.6%)	27%
Respiratory symptom		19.5% (33.5%)	33%
Circulatory symptom	7.8%	-	-
General symptom (Including neurotic symptom)	81.5%	46.2% (41.3%)	63%
Others	-		19%
Remarks		Brocked figures include the victims at Daian Junior High School	

Table 2-3-7 Detailed description of reported subjective symptoms

(From the survey on photochemical smog damage in Kanagawa Prefecture on June 6)

Eye symptoms	87.9%
Irritated	43.0
Pain	31.4
Smart	28.9
Tearing	24.9
Respiratory symptoms	69.9
Throat irritation	43.0
Coughing	29.1
Feel thirsty	27.1
Feel choky	24.5
Feel pain in the chest	16.2
Circulatory symptoms	7.8
Thumping of the heart	5.1
Feel opressed in the chest	3.5
General symptoms	62.9
Feel languid	48.0
Headache	42.6
Feel feverish	2.8
Neurotic symptoms	18.6
Feel foggy	16.5
Numbness in the extremities	2.5
Convulsions	1.4

Table 2-3-8 Protective measures taken for the photochemical smog victims

	Saitama Pref.	Mie Pref.
o Washed eyes and gargled	69.6%	19.4% (42.7%)
o Remained quiet in the classrooms	12.3	-
o Kept quiet in the rest-room	1.1	1.9 (1.0)
o Received medical care from doctor	0.0	0.0 (0.0)
o Left school early	0.1	0.3 (16.6%)
o Taken into the hospital	0.0	0.0 (4.0)
o Others	17.1	78.4 (39.7)

Note) "Other" include "Did nothing".

Table 2-3-9 The time required for the victims to recover

	Saitama Pref.	Mie Pref.
o Recovered at the school	24.4%	93.8% (85.4%)
o Recovered after coming home	68.1	
o Went to school although not recovered until the next day	6.5	5.9 (14.2)
o Did not go to school on the next day	0.7	0.3 (0.4)

Note) Report from other prefectures.

The bracketed figures for Mie Pref. include the cases at the Dian Junior High School.

2-3-4 A pilot study on the constitutional disposition o reported victims of photochemical smog

It has been found that the majority of the serious v themselves and the members of their families previously s such allergic dieseases as drug rash, nettle rash, contra dermatitis, allergic nasitis and asthma. The survey cond 1974 has revealed that the group of students suffering fr disorders (O.D.) showed different patterns of subjective other ordinary students both at the time of photochemical the normal time.

Surveys were conducted, paying attention to the const of the victims were conducted in Osaka and Hyogo Prefectu results of those surveys will be summarized below.

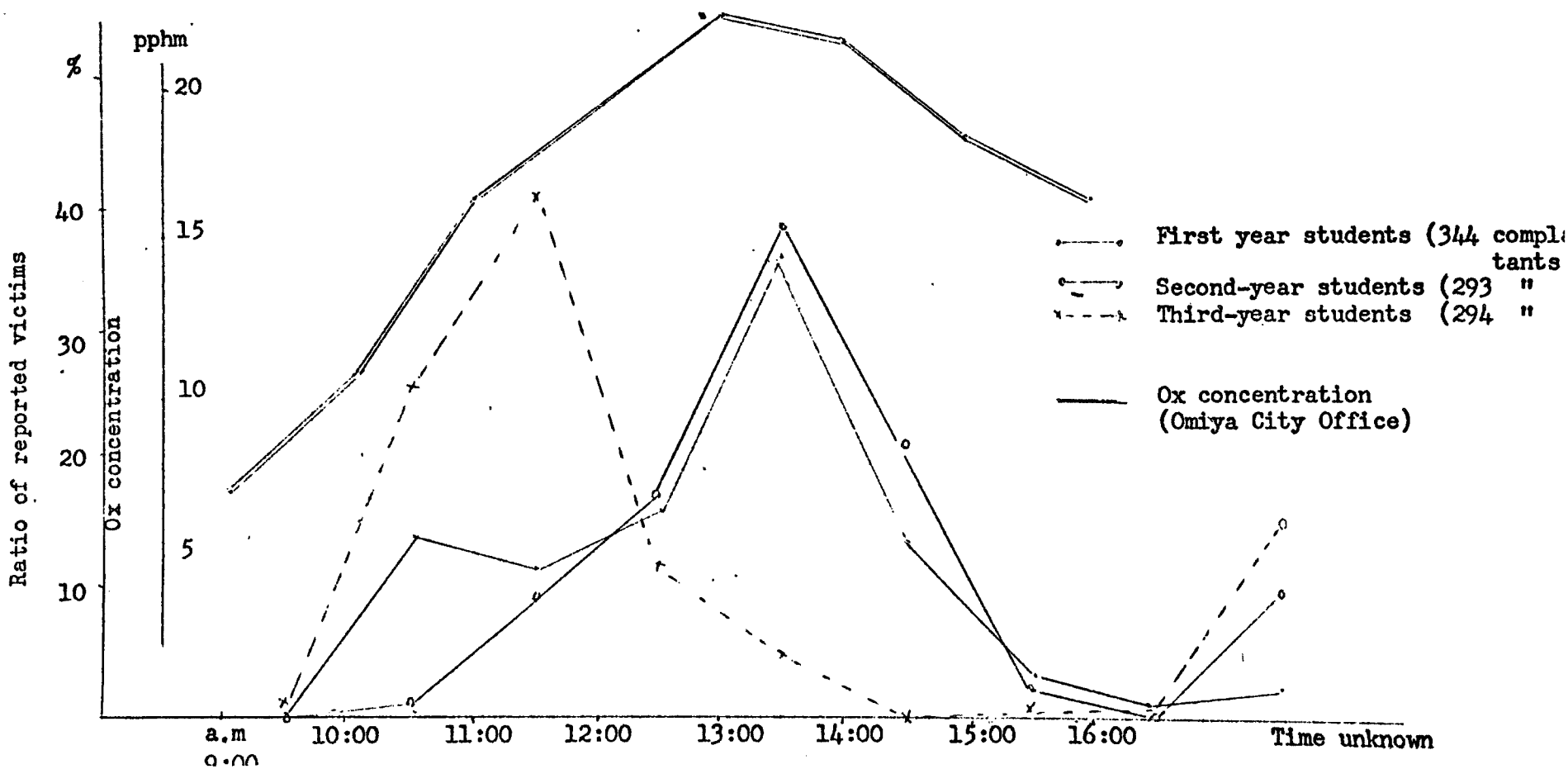
As for the group of students of alergic disposition, Prefectural Association of Medical Practitioners made a cc study of those who complained of photochemical smog symptc those who made no such complaints and reached the conclusi there was difference between them. However, it must be no the highest oxidant level measured in Hyogo Prefecture was in the town of Taishi in the two years of 1974 and 1975 an ocidant level was relatively low in other parts of the pre And the number of reported cases of photochemical smog dam relative small and therefore it was impossible to make a t review on the relationship between the constitutional disp and photochemical smog hazards.

Surveys on the relationship between orthostatic diso
(O.D.) and reported photochemical smog symptoms were cond
in Osaka and Hyogo Prefectures. In Osaka Prefecture the s
was conducted only on those who complained of photochemica
symptoms. In Hyogo Prefecture a comparison was made of ne
the same numbers of complaitants and non-complaitants. In
Prefecture the O.D. group showed higher percentages of suc
complaints as "coughing" and "opressive feeling in the che
than the non-O.D. group. In Hyogo Prefecture the complain
12.9% of positive O.D. reaction and the complaintants 6.8%
suggesting that there is a close relationship between O.D.
photochemical smog symptoms.

With regard to the surveys on photochemical smog haza
human health in relation to the constitutional disposition
be necessary to make further reappraisals of the surveying
and to make a comprehensive analytical study including the
and the degrees of seriousness of symptoms and also to cons
relationship to the environmental conditions as a viewpoint
taken in making an analytical review.

The above-mentioned surveys conducted in Osaka and Hyo
Prefectures must be further developed with various improven
to be made to the surveying methods but they played a valu
as a pilot study.

Fig. 2-3-1 The times when the students of different school years first complained of photochemical smog symptoı ıoı at the Mihashi Junior High School on July 15



重傷例

2-3-5 Serious cases of photochemical symptoms

a) Subjects of survey

About 140 students of the Asahi Elementary School (with 1,510 students in total) in Tsurumi Ward complained of obviously photochemical smog symptoms in the afternoon of July 18 (Friday). The measurements made at a nearby monitoring station showed 0.253ppm of Ox, 0.042ppm of SOx and 0.018ppm of NO_2 when a south-southeasterly wind was blowing at 3.6m per second. About 100 of the victims were in the classrooms and about 40 were out of doors, cleaning the swimming pool. There were 28 serious cases and 11 of them complained of choky feeling and numbness in the extremities and immediately taken by an ambulance to a nearby hospital, where they were given emergency medical treatments such as oxygen inhalation and instillation. As their conditions improved, four of them were allowed to go home in the evening but the other seven students were slightly feverish and stayed at the hospital overnight. On the next morning, they all felt good again are allowed to go home at 10 a.m. We visited five of the seven students at their home to make medical examination and blood test.

b) Results of medical examination

(1) Subjective symptoms: Eye irritation, throat irriation, feeling of a foreign matter present in the throat, chocky feeling, numbness in the extremities, feeling of fatigue and feverish feeling were observed in almost all of the five cases. There was a case in

which the victim complained of severe throat irritation and a cough productive of blood-streaked sputum several times.

(2) Objective symptoms: When hospitalized, all of the five victims were found slightly feverish (26.1° to 27.6°), had a an increased frequency of respiration (31 to 42), reddened throatsflushed faces but almost completely restored their normal condition on the next day.

(3) Past history of alergic diseases and family history (Table 2-3-9): All of the five victims had a past history of alergic diseases and four of them had their family members with a past history of alergic symptoms, skin inflamation in most cases.

(4) Examination results: The serum was separated within three hours after the blood samples were taken and measurements were made of the values of direct and indirect bilirubin, GOT, GPT, alkali phosphatase and serum haptoglobin. As for the serum haptoglobin, the separated serum was kept in frozen storage at -25°C and the first and second measurements were made at the same time. Blood tests were made on the day following the occurrence of the photochemical smog symptoms and one week later. The test results all showed normal values. The first and second tests showed almost the same values of alkali phosphatase, which were higher than in the case of adults and this was presumably related to the development of bones.

c) Summary

The five hospitalized victims of photochemical smog complained

of mucous membrane irritation symptom, difficulty in breathing, general symptoms and neurotic symptoms and showed such objective symptoms as reddened throats, flushed faces and the rise of body temperature. These cases showed close resemblance to the symptoms of the serious hospitalized cases of photochemical smog victims occurring in Japan since 1970 and the oxidant concentration was so high as 0.253ppm on the day in question. In view of such facts, these five cases belonged to the same category as the previously reported serious cases. The rise of body temperature and reddened faces were also observed in the above-mentioned five cases and they are worth of note as the characteristic symptoms of the serious cases in Japan. Blood-streaked sputum was observed in a case in which the throat was seriously reddened.

It has been reported that the alergic people are more susceptible to photochemical smog hazards and the seriously affected victims are often found to have an alergic constitutional disposition. In the case of the survey conducted on the students of the Asahi Elementary School (oxidant concentration: 0.253ppm), the minute investigations of the past medical history of the serious affected victims and their family members showed that they were found to have considerably strong allergic symptoms and hypersensibility, suggesting a relationship between the serious photochemical smog symptoms and hypersensitive constitutional disposition.

The test results showed no previously reported phenomena such as the increase in indirect bilirubin.

アレルギー既往歴

Table 2-3-9 Past medical history and family history

	Past medical history of the victim	Family history
O.T	Urticaria, eczema, drug allergy, food allergy, allergic rhinitis	Father: Urticaria by eating cuttlefish and ham. Mother: Rash caused by astringent juice of Japanese chestnut, taro, and Yam and cold drugs. Brother: Rash caused by drugs
Y.H	Urticaria causeded by cheese, milk allergy, exanthema caused by cold rugs	Mother: Urticaria caused by cider (?)
T.K	Used to wheeze when catching a cold in childhood	(-)
K.O	A rash appeared throughout the face when yam juice came into contact with the nose. Used to wheeze when catching a cold in the childhood.	Father: Suffering occassionally from urticaria since a few years before
Y.A	A rash came out when eating half-broiled rainbow trout when one year old and three years old. A rash appeared all over the body when a cold drug was taken 2 months before.	Sister: Suffers frequently from urticaria

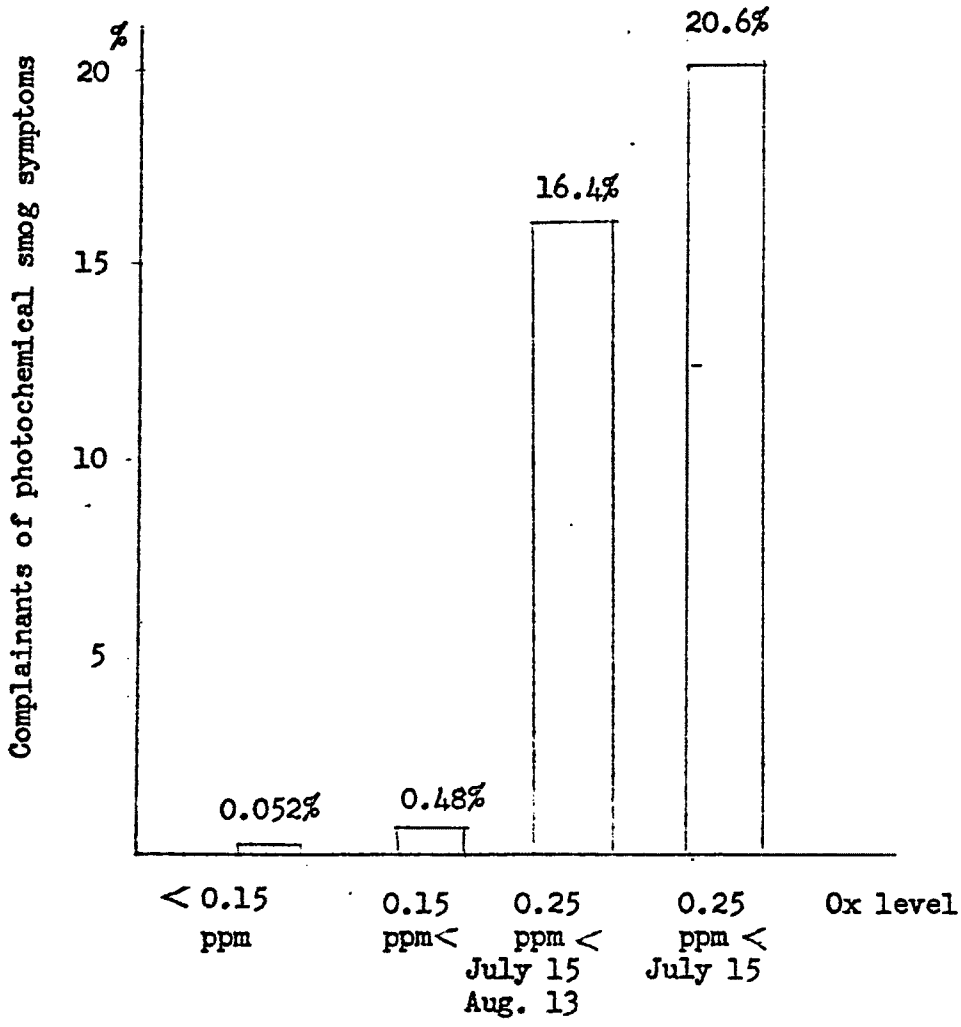
2-3-6 Correspondence between environmental conditions and reported cases of photochemical smog victims

No sufficient analysis has been made with regard to the correspondence between environmental conditions and the number of reported cases of photochemical smog victims. However, the surveys made this year have clarified some noteworthy points as described below.

a) Three levels of oxidant concentration and the number of reported victims

Fig. 2-3-2 shows the correspondence between the oxidant concentrations in the air and the percentage proportions of photochemical smog victims, according to the results of survey conducted on 7,440 students of 10 schools in Saitama Prefecture. As seen from this figure, only one out of 2,000 students complained of photochemical smog symptoms on a day when the maximum oxidant level was below 0.15ppm but on a day when the oxidant level exceeded 0.15ppm one out of 200 students complained of their physical disorders, that is, the reported victims increased tenfold. One out of five to six students were affected on a day when the oxidant level exceeded 0.25ppm. The results of this particular survey have revealed that the number of complaints of photochemical smog symptoms sharply increases when the oxidant level exceeds 0.25ppm. A similar survey was conducted in Kanagawa Prefecture and it produced similar results, although no difinite percentage proportions of the reported cases were known because no specific shools had been designated for the survey.

Fig. 2-3-2 Oxidant concentrations and percentage proportions of complainants of photochemical smog symptoms



b) The times when the victims first complained of photochemical smog symptoms and the oxidant concentration in the air

In the case study on the days when many reported victims occurred, it is seen that there are cases in which the peaks of the numbers of reported victims agree with the peaks of oxidant levels in the air and also many cases in which considerable numbers of reports had already begun to be made when the oxidant level began to rise sharply. The oxidant alerts and alarms are issued when the oxidant concentration has exceeded 0.15ppm and it is reported to the schools after a certain delay and therefore it is obvious that the initial reports of victims were not biased by the alerts. Such reports indicate the presence of the people who are constitutionally susceptible to photochemical smog hazards and these who are particularly sensitive to such air pollutions and they are worthy of further attention and investigations in relation to varions factors such as physical exercises and the concentrations of other pollutants in the air.

c) Other air pollutions, temperature and humidity

As for the concentrations of other pollutants and the air temperature and humidity, the present survey has not produced such results as to enable use to draw a definite conclusion. The reports received from the prefectures contained some information suffestively pointing out the fact that there occurred many reported victims of photochemical smog victims on the days when

the dust level was high during the morning or the discomfort index was high but no accurate analysis was made, leaving this problem to be solved in the future.

d) Differences according to the conditions of location

There were many cases in which one of the two closely located schools produced many reported cases of photochemical smog victims but the other school had not victims even when the students of both schools were out of school buildings on the same day, suggesting the presence of the factors related to the microclimatic conditions in urban areas such as sunk places, elevated places, inlets and flat places, airy or airless places. These are the problem remaining to be solved in the future. There is an increased necessity for the on-the-spot investigations at the schools where many victims of photochemical smog occur. It is also essential to carry out surveys and checks on the sources of primary pollution in the neighborhoods of the schools. This type of survey was conducted to some extent in Saitama Prefecture to find that there is no source of such pollution near any schools. However, there is such a case as the Daian Junior High School, in which the existence of such pollution sources cannot be denied. It may be necessary to make a check as to the sources of air pollution located near the schools.

e) Social and psychological factors

It must be recognized as an inevitable phenomenon that a collective psychological bias is given to the number of complaints

of photochemical smog damage. However, we would like to point out that it would be mistaken if the variations in the number of complaints are explained by this factor alone. This is condirmed by the fact that complaints were reported before the photochemical smog alarms were issued and also from the results of the careful observations made by the surveyors. However, it can be said that the social, historical and psychological biases are inevitably given to the complaints as far as the complaints are made voluntarily on the basis of the subjective symptoms of the victims.

We would like to add that the development of subjective index of the effects of photochemical smog on human health, the physiological and biochemical indexes or parameters is one of the important subjects of study to be made in the future.

4. Conclusion

Owing to the cooperation of the prefectural authorities concerned, many advances were made in this year's survey on photochemical air pollution hazards to human health as summarized below.

In a word the numbers of reported victims of photochemical smog in 1975 tended to be larger in the eastern part than in the western part of Japan and the survey results showed clearly there was a parallel relationship between the numbers of reported victims and oxidant concentrations in the air and that the percentage proportions of reported victims varied according to the oxidant levels.

This year's survey has found some cases in Saitama and Kanagawa Prefecture where the reported victims began to occur before the "alert " were issued when the oxidant level rose sharply. In this respect there are various noteworthy questions to be solved in the future such as the relationship of photochemical smog and other pollutants and the exposure differences (outdoor excercises and the like) and sensitivity differences due to constitutional disposition of the individual.

As for the photochemical smog symptoms, the surveys conducted in the various prefectures showed that the mucous membrane irritation and also general symptoms showed fairly large percentages. In some places there occurred serious cases where the victims were taken to hospital. A further study must be made on such serious cases of photochemical smog symptoms. This year's survey has revealed the fact the cases where the victims had to rest in the rest-room and the cases where the victims complained of the symptoms remaining on the following day accounted for 0.2% to 3% and 7% to 8%, respectively. These cases may be considered as transitional to the serious cases and require further analysis and survey in the future.

No differences were observed between male and female students with regard to the number of complaints in all prefectures concerned.

As for the differences according to whether the students were taking excercises out of doors or staying indoors, it was

noteworthy that there was observed an obvious relationship between the reported complaints and outdoor exercises at the Mihashi Junior High School in Saitama Prefecture. Generally speaking, however, it has been found that there occurred fairly large numbers of reported victims whether the students were taking exercises out of doors or remaining in the classrooms, suggesting that when the photochemical air pollution has exceeded a certain level there occur the victims when exposed to the pollutants wherever they are.

The effects of the health condition and predisposition of the individual students on the damage by photochemical smog had been suspect. In this respect, this year's survey can be said to have successfully play its role as a pilot study, although it is still premature to draw any definite conclusion. Further developments in this area of study are desired.

This year's survey has revealed the fact that the reported victims began to occur before the "alert" and "alarm" were issued in the respective areas. This fact indicates the urgent need for further improvements of the system of warning issuance and delivery and for the observations on the spot and a study on the relationship of the warnings and the occurrence of victims so that thus obtained information may be effectively used in the health care at school.

Reviewing the results of the present survey, we felt keenly that it would be impossible to prevent the photochemical air pollution hazards unless further advances are made in the control

of pollutants at the sources of pollution. Adding a few more words, the reported victims in this report are those who voluntarily complained of their subjective symptoms.

Photochemical Oxidants Control Measures in Japan

(Environment Agency)
Japanese Delegation

1. Introduction

In Japan, since the summer of 1970, there have occurred each summer the cases of health damage with such typical symptoms as eye irritation, throat sore and chest oppressed feeling, which are considered attributable to photochemical smog. Apart from the above light cases, relatively serious cases such as general symptoms and nervous disorders also have been reported. It is generally considered, although there are some different opinions in regard to such relatively serious cases, that these are caused by the effects of the pollutants which are secondarily produced as a results of photochemical reaction of nitrogen oxides and hydrocarbons. It is now urgently needed that a clear explanation and solution of this problem was obtained for the sake of the preservation of ambient air quality.

2. Basic conception for abating photochemical oxidants

Photochemical oxidants were adopted as an index for photochemical air pollution and there was established the ambient air quality standard for photochemical oxidants from a viewpoint of the protection of human health in May 1973.

On the basis of the Central Council for Control of Environmental Pollution's proposal that the hourly value of photochemical oxidants should preferably be held down to less than 0.06 ppm for the protection

of human health paying attention to the protection of the effects of a short-term exposure to photochemical oxidants, the Government officially announced that the same value for photochemical oxidant concentrations in the air as the environmental standard for ambient air pollution as given in Article 9 of the Basic Law for Environmental Pollution prevention. And this value was required to be achieved at the earliest possible time.

At the same time when above standard was determined the ambient air quality standard for nitrogen dioxides was established, paying attention to its own effects on human health.

In Japan various measures have been taken to achieve the requirements of the ambient air quality standard for photochemical oxidants. As for nitrogen dioxides, one of the precursors of photochemical oxidants, the ambient air quality standard for nitrogen dioxides has been established and NOx prevention measures have been taken. In addition to that, measures are also taken for decreasing hydrocarbons, another precursor of photochemical oxidants.

The quantitative relationship between the concentration of hydrocarbons and the production of photochemical oxidants was searched for and a comprehensive study was made by the Central Council for Control of Environmental Pollution and it proposed in August 1976 a guideline for the hydrocarbon concentrations in the air (hourly values of 0.20 to 0.31 ppm during 6 to 9 in the morning) so that adequate measures would be taken in the fugure.

As we have just seen, the Japanese are endeavoring to prevent

the production of photochemical oxidants by reducing both nitrogen dioxides and hydrocarbons, thereby to decrease the total quantity of photochemical reaction.

3. Control strategy and various measures

In order to promote the systematic and efficient execution of the photochemical air pollution control measures, the Japanese Government in June 1972 established the "Photochemical Smog Control Promotion Conference" composed of the bureau chiefs of the administrative organs concerned and in April 1975 the Conference decided on the basic policy to be taken for the promotion of the photochemical smog control measured to be taken in the future. That is to say, the Conference decided that increased efforts should be made to reduce the concentrations of nitrogen oxides and hydrocarbons in the air in an attempt to prevent photochemical air pollution and that further research and investigations should be made to have a better knowledge of the mechanism of air pollution, and that increased efforts should be made to improve further the photochemical smog warning and monitoring systems, health protecting measures and international cooperation in this field.

We will make our atmost to carry on our anti-pollution measures in accordance with the above basic policy. The following are the measures which are being taken now and the future trends.

(1) Precursors control measures

a. Hydrocarbons

As for the mobile sources of hydrocarbons, the emission standards enforceable in and after FY1970 require passenger-cars to reduce the average quantity of exhaust gases by 92% from when no such standards were enforced. From now one, regulations will be enforced to control the emission of hydrocarbons from stationary sources such as oil tanks (now control measures are already taken in the form of administrative guidances for some industrial installations) and also from trucks and diesel motor vehicles. As for organic solvents, we are planning to enforce proper emission standards on the basis of the results of technological assessment. (See Fig. 1)

b. Nitrogen oxides

For this, reference should be made to "Nitrogen Oxides Control Measures in Japan".

(2) Emergency Measures

In addition to the precursors control measures which are taken at normal times, emergency measures are taken when photochemical oxidant levels are higher than normal and likely to continue in view of the existing weather conditions.

In such a state of emergency the 23 prefectural governments issue warnings as given in Table 1 to ask or order precursors emitting industrial installations to curtail the

Fig. 1 Flow Chart of Hydrocarbons Control Measures in Japan

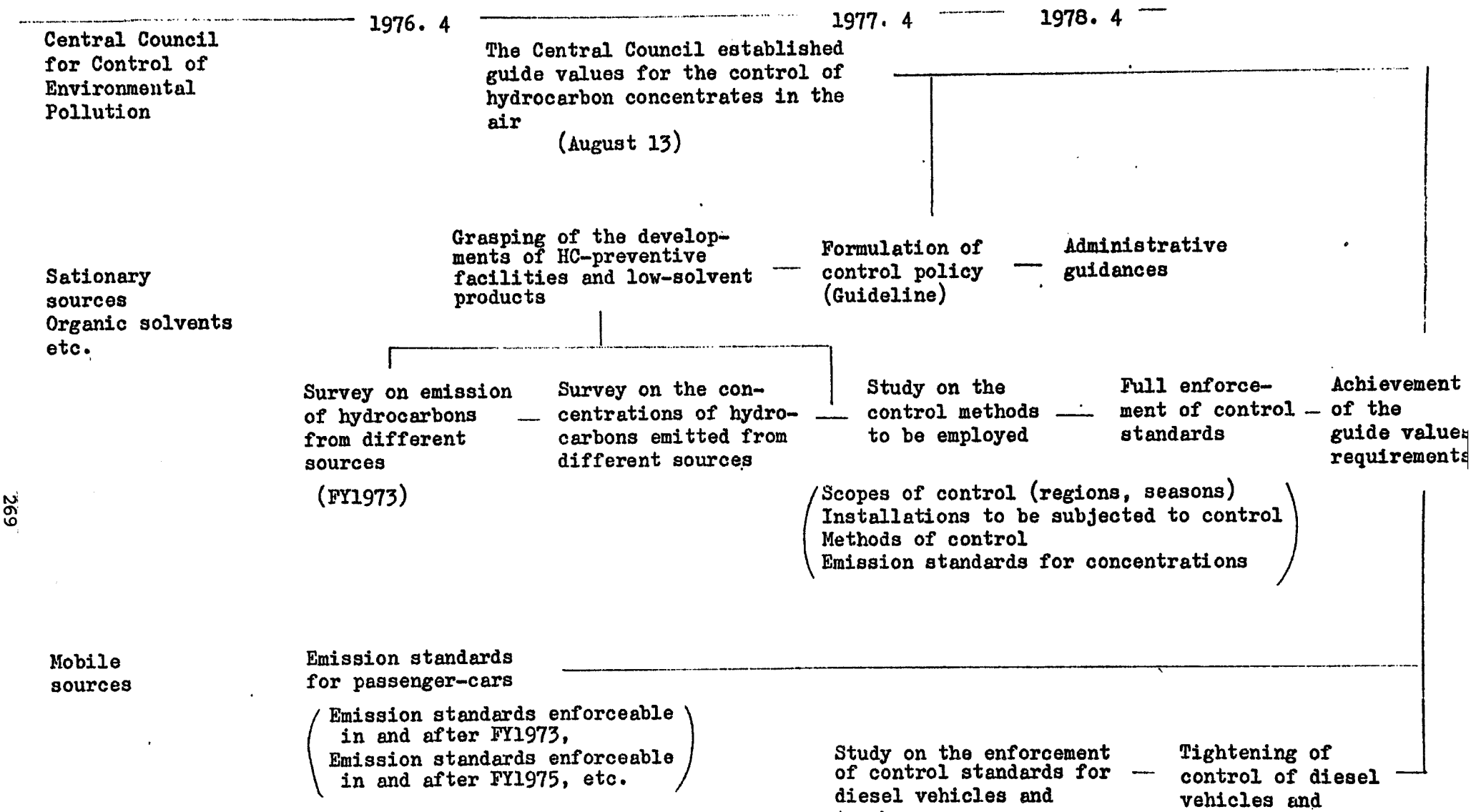


Table 1 Photochemical smog warning issuance standards and percentage reductions of fuels consumption

Item	Forecast		Alert
Prefecture	Warning issuance standard (Concentration ppm)	Percentage reduction * (%)	Warning issuance standard (Concentration ppm)
Miyagi	When predictable from weather conditions	Preparatory measures	0.15
Fukushima	-	-	0.15
Ibaraki	When predictable from weather conditions	Preparatory measures	0.15
Tochigi	"	"	0.15
Gunma	"	Voluntary cooperation	0.15
Saitama	"	"	0.15
Chiba	"	20	0.15
Tokyo	"	Voluntary cooperation	0.15
Kanagawa	"	"	0.15
Shizuoka	-	-	0.15
Aichi	0.1	Voluntary cooperation	0.15
Mie	0.1	Preparatory measures	0.15
Shiga	-	-	0.15
Kyoto	-	-	0.15
Osaka	0.1	Preparatory measures	0.15
Hyogo	0.1	20	0.15
Nara	0.1	-	0.15
Kakayama	0.1	-	0.15
Okayama	When predictable from weather conditions	30	Weather conditions etc
Hiroshima	0.1 (Information) 0.12 (Special information)	- 20	0.15
Yamaguchi	0.1 (Information) 0.15 (Special information)	- 20	0.15
Tokushima	-	-	0.15
Ehime	When predictable from weather conditions	Voluntary cooperation	0.15

(Note) *: The "percentage reduction" is the rate of reduction of fuel to that at normal times

(As of Apr., 1975)

	Alarm		Emergency alarm	
Percentage reduction (%)	Warning issuance standard (Concentration ppm)	Percentage reduction (%)	Warning issuance standard (Concentration ppm)	Percentage reduction (%)
20	0.3	40	0.5	40
20	-	-	0.5	40
20	0.3	40	0.5	40
20	0.3	40	0.5	40
20	0.25	40	0.5	40
20	0.25	40	0.5	40
20	0.3	40	0.5	40
20	0.3	40	0.5	40
20	0.3	25	0.5	40
20	0.3	40	0.5	40
20	0.3	30	0.5	40
20	0.3	30	0.5	40
-	0.3	-	0.5	-
20	0.3	40	0.5	40
20	0.3	40	0.5	40
20	0.3	20	0.5	40
-	0.3	-	0.5	-
20	0.3	40	0.5	40
40	Weather conditions etc.	40	Weather conditions etc.	40
20	-	-	0.5	40
20	-	-	0.5	40
20	0.3	30	0.5	40
40	0.3	40	0.5	40

(Remarks) Based on the results of surveys made by the Environment Agency

amounts of fuels they use and also call on the general public to use their motor vehicles less frequently and to refrain from taking vigorous physical exercises.

(3) Health protection measures

For the purpose of health protection, measures such as disseminating the knowledge of photochemical smog widely among the general public and giving guidances in the emergency actions to be taken when photochemical warnings are issued.

(4) Promotion of surveys and researches

The surveys and researches concerning photochemical air pollution have been promoted, paying special attention to the following points.

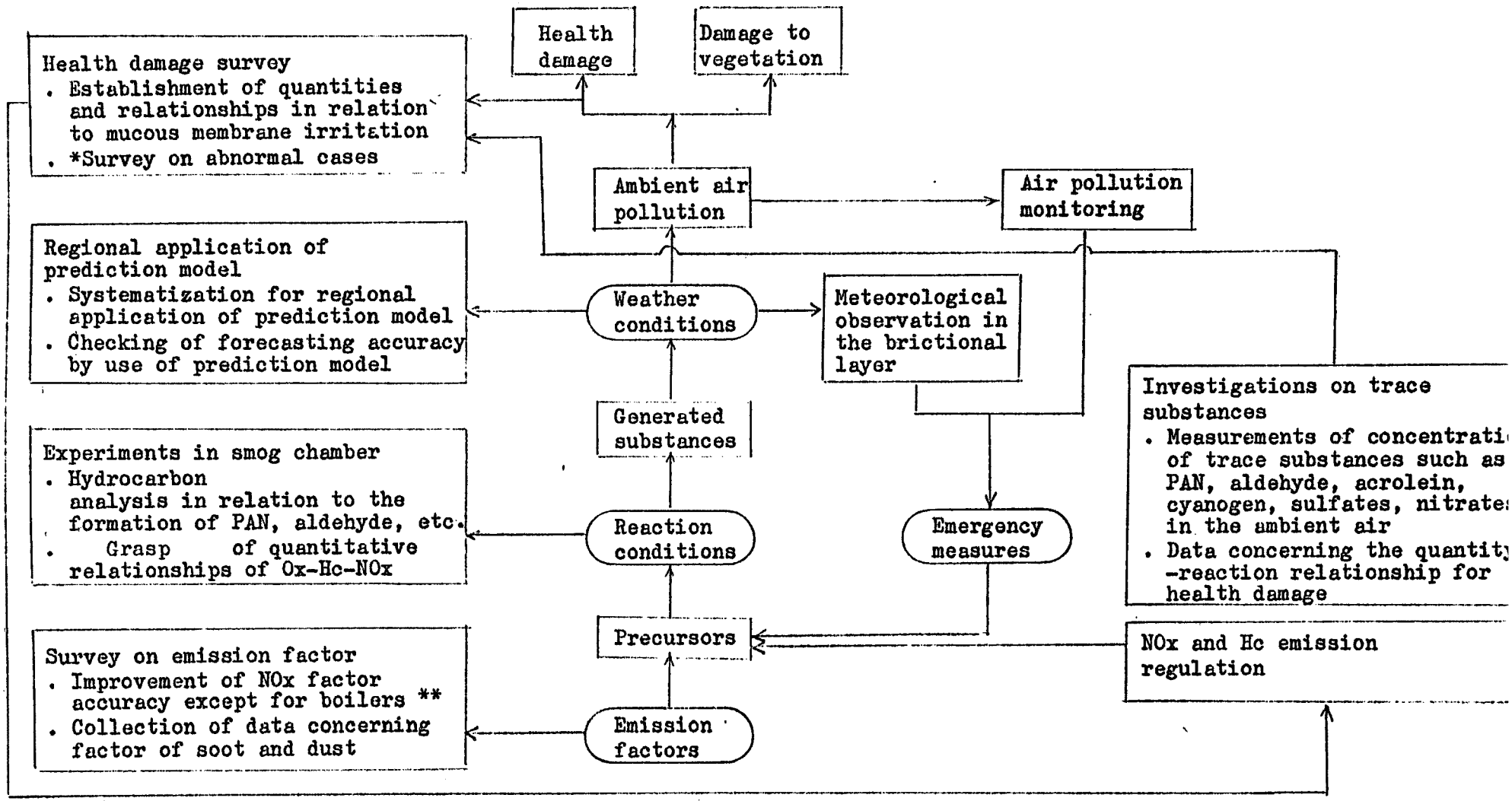
a. To clarify the mechanism of photochemical reaction. (Experiments in smog chambers)

b. To clarify the effects of photochemical air pollution on human health and vegetation

c. To clarify the weather conditions contributing to photochemical reaction and to develop a reliable prediction model.

The subjects of those surveys and researches and their relations to the countermeasures are shown in Fig. 2.

Fig. 2 Photochemical air pollution survey and research system



* Since not much is still unknown about such relatively serious cases as general symptoms and nervous disorders, investigations are now under way about their relationships to photochemical air pollution.

** Emission factor have been grasped with a considerably high accuracy for boilers.

4. Monitoring system and photochemical air pollution in recent years

(1) Since 1968 when photochemical oxidant monitoring stations were first set up in Japan, the number of them have yearly increased and there were 519 stations located in 282 cities throughout the country in FY1974.

Table 2 Increases of oxidant monitoring stations and the number of the days when alerts were issued *

Item \ FY	1968	'69	'70	'71	'72	'73	'74	'75
Number of cities	2	2	4	38	110	209	282	...
Number of monitoring stations	2	2	10	68	175	349	519	...
Number of days alerts were issued			7	98	176	328	288	266

* A total number of days when prefectural governments issued photochemical smog alerts.

As for the measurement method of the photochemical oxidant levels in the air, colorimetry or coulometry using neutral buffer potassium iodine solution is used. These methods are used because oxidants which are measurable by those methods, are a suitable index for photochemical air pollution, the monitoring stations using these methods are easy to operate and

maintain and suited for the monitoring on a nationwide basis.

Apart from these monitoring system, the Environmental Agency undertake observations of low-layer ambient air to provide useful information to local autonomous bodies so that they can take effective emergency measures when needed. In order to carry out the analysis of weather conditions tending to cause photochemical air pollution and to strengthen the forecasting system, the atmospheric pollution meteorological centers are established at six local meterological observatories.

(2) Photochemical air pollution in recent years

Table 3 shows the numbers of days when oxidant concentration in the air exceeded 0.15 ppm at which oxidant alerts are to be issued. The measurements of oxidants were made at the monitoring stations where oxidants have been measured continuously since 1970. There were several days when the oxidant level exceeded 0.3 ppm in a year but there was no day when it exceeded 0.5 ppm.

Table 4 shows the numbers of days when alerts or forecasts were issued in Tokyo. As seen from this table, the ratio of days when alerts or forecasts were issued to the days when photochemical-causing weather conditions occurred has been decreasing since 1973.

Table 3 Numbers of days when the hourly value for oxidants exceeded 0.15 ppm in 1970 to 1974 years

City	Monitoring station	1970	1971	1972	1973	1974
Tokyo	In front of Tokyo Metropolitan Government Office	0	4	7	25	2
"	State-operated Tokyo Photochemical Oxidants Monitoring Station	28	15	7	28	4
"	Setagaya	1	20	10	22	9
Osaka	State-operated Osaka Photochemical Oxidants Monitoring Station		0	9	7	5
Sakai	Hamadera		1	4	16	14
Takarazuka	Old People Welfare Center		1	11	14	5

Table 4 Comparison of oxidant forecast and alert issuances and the days when there occurred weather conditions for causing photochemical smog, in Tokyo *

Month, Year \ Item		Number of days Ox alerts were issued		Number od days Ox forecast or alert were issued		Number of days when there were photochemical smog-causing weather conditions occurred
		A	(A / C %)	B	(B / C %)	C
1973	June	4	(50 %)	7	(88 %)	8
	July	16	(80 ")	18	(90 ")	20
	Aug.	13	(72 ")	15	(83 ")	18
	Total	33	(72 ")	40	(87 ")	46
1974	June	6	(46 %)	6	(46 %)	13
	July	2	(50 ")	3	(75 ")	4
	Aug.	9	(69 ")	12	(92 ")	13
	Total	17	(57 ")	21	(70 ")	30
1975	June	7	(64 %)	9	(82 %)	11
	July	6	(43 ")	9	(64 ")	14
	Aug.	11	(52 ")	11	(52 ")	21
	Total	24	(52 ")	29	(63 ")	46
1976	June	1	(17 %)	2	(33 %)	6
	July	3	(25 ")	4	(33 ")	12
	Aug.					
	Total					

* Weather conditions

Atmospheric temperature:	Over 20°C (daytime)
Wind velocity:	Less than 5m/sec (9:00, 12:00 and 15:00 average)
Solar radiation:	40 cal/cm^2/h over 3 hours (9:00 to 15:00)

(Tokyo District Meteorological Observatory statistics)