REPORT

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Report No. 12

SECOND TECHNICAL PROGRESS REPORT

Volume 1
Number 12

AIR POLLUTION FOUNDATION
Los Angeles, California

"Dedicated to the solution of the smog problem"

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W. M. Keck Engineering Laboratories
California Institute of Technology

THE AIR POLLUTION FOUNDATION BELIEVES

That the answers to the smog problem will be found; that eye irritation and air pollution can be conquered; that it will take time.

That the evaluation of existing research and the conduct of new research projects will make possible the control of smog and shorten the time required for its elimination.

That impartial fact-finding, without fear or favor, is now, and will continue to be, the object of our Scientific Team.

The Foundation's Scientific Team

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SECOND TECHNICAL PROGRESS REPORT

Prepared by the

Scientific Staff of the

AIR POLLUTION FOUNDATION

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November 1, 1955

FOREWORD

In the Air Pollution Foundation's First Technical Progress Report presented one year ago we could report largely only what we were doing; in this second report we point out what we have done. The significance of our results can only be brought into proper focus by concurrent consideration of the work of many other agencies dedicated to the solution of the air pollution problem; accordingly, we have reviewed the progress of others in this report and evaluated the Foundation's results in the light of these other findings. Both the progress attained in the last year and the questions remaining to be answered are presented under four headings:

WHAT IS SMOG?

HOW IS SMOG FORMED?

WHAT ARE THE SOURCES?

HOW MAY SMOG BE CONTROLLED?

No final or complete answers are given. The entire report is really a summary of our knowledge at the present time. Those who want only a brief summary are referred to the first section in Chapter I.

Much more knowledge will be required before clean air returns to our cities. Undoubtedly, the greatest headway will be made in the future, so we also present the lines of attack which we believe will yield positive advances in this war against smog. If the report does nothing more than stimulate others into joining battle with us along orderly scientific lines, we will be well repaid.

We would be remiss if we did not acknowledge the help and encouragement of our trustees and contributors, the advice and technical contributions of scientists throughout the world, and the patience of a long-suffering public. For this support we are grateful.

W. L. Faith

November 1, 1955

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I. WHAT IS SMOG?

A. STATUS OF THE SMOG PROBLEM

The Los Angeles smog problem is a direct consequence of air pollutants arising from man's activities. Operation of factories, motor vehicles, and rubbish burners, to name three principal categories, contribute a great variety of pollutants in gas, liquid, or solid form. Some of these are visible at the point of origin, and some are not. None of these pollutants at the point of origin possess the characteristics of smog, which we will define shortly.

While our smog problem is a direct consequence of man-made pollution, meteorological and topographical influences contribute to the undesirable effects, although they do not of themselves cause these effects. Los Angeles did not have a smog problem of any moment prior to around 1940, yet the meteorology and topography of this area have undergone no significant change as far back as there is any record. The quantity and variety of pollutants, being a direct consequence of man's activities increase, with the number of factories, motor vehicles, tonnage of refuse burned, etc.

About the beginning of World War II man's activities in the Los Angeles Basin resulted in a daily production of pollution which began to exceed the natural dissipating capacity of the environment, particularly on those days when the inversion was low and winds were low. Man's activities had always produced pollution, but up until then, while we had had the same cycles of low inversions and low winds, objectionable concentrations did not arise because the emissions were not excessive. The same opportunities for escape of pollution exist today as existed then, no worse or no better, but the daily production of pollutants has increased enormously so that their concentrations attain higher values than they used to.

Methods of Attack

Two obvious approaches to the problem have received a vast amount of speculative consideration by both scientists and laymen. The first approach is to find some way of changing our meteorological or topographical features. The second is to reduce our pollutants at their points of origin. Another way is neutralization, treatment or dilution of the atmosphere.

Profound studies by properly qualified meteorologists and physicists have failed thus far to reveal any likelihood that man can economically change either meteorological or topographical features sufficiently to have any significant effect on our air pollution problem. The quantities of energy associated with these natural influences appear to be far beyond any resources of man of which we have knowledge at present.

The second approach, to reduce pollutants at their sources, is the only approach which has resulted in any progress in abating air pollution here or elsewhere. Beginning about eight years ago, various control devices were installed. These controls include, for example, sulfur recovery systems, electrostatic precipitators, bag filters and other devices for collecting some of the dusts, floating roofs on gasoline storage tanks, closed recovery systems in oil refineries, and many others. These installations have been made either voluntarily by the parties concerned or as a direct consequence of regulations of the Air Pollution Control District, which estimates that in total these devices are keeping out of our air today about 1,000 tons per day of pollutants.

In metropolitan areas with better natural ventilation, this achievement would undoubtedly have been far more significant. One can only speculate on what our smog problem here would be like today if the above progress had not been made. That it is inadequate is due to the tremendous continuing growth here in man's activities, a growth unequalled elsewhere in this country. The continuation of severe smog attacks shows that either the pollutants which have been controlled are not the ones which contribute substantially to our smog effects, or if they are, that they have not been reduced sufficiently.

Are Some Pollutants More Harmful?

This brings up a third approach to a solution of our smog problem, which is really a special case under the second method of reducing pollutants at their points of origin. In this third approach it is assumed that some pollutants are much worse than others. By the same token it is assumed that there are some pollutants which are relatively innocuous. This, of course, has been the traditional approach to development of our sanitary water supplies, which contain innocuous contaminants, but in which the harmful agents are controlled to levels which have been carefully determined to be tolerable.

This third approach has in its favor the possibility that the control of only harmful air pollutants would be considerably less expensive to the community; for to attempt to solve our problem by reducing all pollutants to, let us say, 1940 levels would require the development and installation of a vastly greater amount of equipment, hence take more time and money. The third approach assumes that the harmful pollutants can be identified, and that devices can be developed and installed specifically for these pollutants in less time and at less expense.

There is evidence that some of our numerous pollutants here are more harmful than others. On the other hand, no one knows yet what the health effects are of long-time continued exposure to heavily polluted air, although there is mounting suspicion that the effects are adverse. Corrosion, soiling, plant damage, and other adverse air pollution effects, apart from health effects, are for the most part conceded to be very substantial. Pittsburgh, for example, places the economic value of its partial smoke abatement at about $26,000,000 per year. The definition of "harmfulness" in a pollutant is not one easily arrived at in our present state of ignorance. This is one very important and basic aspect of man's modern air pollution problem which demands a great deal more investigation.

Returning to our third approach based on the concept of "harmful" pollutants, it becomes apparent upon brief reflection that we must have some yardstick of harmfulness. We know of no single pollutant entering our atmosphere which is known to be harmful to man at the highest concentrations here. Ozone, which has come to be the index of our smog intensity, does not originate in any of man's activities but forms in our atmosphere as a consequence of complex photochemical reactions involving certain of our pollutants. Neither has anyone been able to find among our myriad pollution sources any compounds which, as emitted, produce the specific forms of eye irritation or plant damage characteristic of Los Angeles smog in the concentrations measured in the atmosphere. Again, therefore, these agents are formed in our atmosphere subsequent to the point of escape.

Pursuing this third approach then, one wishes to know which pollutants take part in the reactions which produce the harmful or undesirable effects.

Let us at this point offer a definition of Los Angeles smog: it is an atmospheric condition which can be defined so far only in terms of its identifiable effects. These are (1) eye irritation; (2) reduced visibility; (3) oxidant formation, including ozone; and (4) plant damage. This is admittedly a loose and arbitrary definition, but we know of no better one at present. It distinguishes between gross air pollution on the one hand and the condition which develops objectionable effects. It is useful only to the extent that it provides some basis for selecting harmful or undesirable pollutants from the great variety we have. To put it another way, if by removing certain pollutants we could prevent the above-named effects, we would say that we had found the smog formers.

Principal Pollutants

In pursuing the third approach, it seems logical to begin with an inventory of our atmosphere. An inventory of pollutants at their points of origin is also pertinent. Both inventories are germane in taking either the second or third approach. Much work has been done in an effort to develop these data. While much more remains to be done, estimates of the composition and quantities of sources, reinforced by extensive air sampling, indicate that our principal initial pollutants arising from man's activities include these:

- Carbon monoxide
- Organic Compounds
    - Hydrocarbons
    - Partially oxidized hydrocarbons
    - Miscellaneous organics from partial combustion of rubbish
    - Miscellaneous solvents (dry cleaning, paint thinners)
- Oxides of nitrogen
- Oxides of sulfur
- Particulate matter
    - Carbon (soot)
    - Dust (silicates, carbonates, sulfates, etc.)
    - Ash (great variety of metallic oxides)
    - High molecular weight organic polymers, tars, finely divided particles from the abrasion of tires, etc.
- Water vapor
- Carbon dioxide

In some of these categories there are a great variety of compounds.

Water and carbon dioxide are considered to be innocuous. Carbon monoxide is not found in our atmosphere at concentrations remotely approaching toxic levels published by public health authorities, nor has it been shown yet to take part in atmospheric reactions. Accordingly, it is set aside tentatively as harmless under presently known conditions prevailing here.

Particulate Matter

Particulate matter is suspect not only because of its more obvious role in forming aerosols and reducing visibility, but because of the growing evidence that submicron particles may collect gaseous and liquid pollutants existing at nontoxic levels, concentrate them, and transport them into the deeper portions of the respiratory system. Some metallic oxides existing normally in our particulate matter are also capable of catalyzing oxidation reactions, including the conversion of SO_2 to SO_3.

Analyses of our particulate matter by the U.S. Public Health Service, as reported by Chambers (Ref. 1), are preliminary but indicate that the sulfate and nitrate content here is higher than in any of 30 other American cities sampled. Because of the obvious contribution to grime and smoke, let alone the unproven but suspected effects, it is generally conceded that particulate matter should be the object of more complete control. Despite the efforts of the Air Pollution Control District (APCD) and others, one important source of particulate matter, namely the burning of rubbish, remains largely uncontrolled mainly because of political factors. APCD regulations exist, the purpose of which is to limit the rate at which the particulate matter may be emitted as defined either by grains per cubic foot of stack gases or by opacity as estimated by the Ringelmann chart. Burning of refuse has been estimated by APCD to account for as much as 65 per cent of the "smoke" in Los Angeles.

The control of particulate matter is subject to the same approach as air pollution in general, in that one may strive to control all particulate matter at the source, or to identify harmful particulates and seek to control these selectively. Again, we are in need of much more information. Except for the reduction of visibility, there is no evidence so far that particulate matter contributes to smog as defined above by its manifestations.

Sulfur

Sulfur dioxide itself is found in our atmosphere normally at lower levels than found in some other large cities. If we really do have a high content of sulfates, then one might assume that we produce unusually high quantities of SO_3, or that under our conditions SO_2 is rapidly converted to SO_3, in either case the anhydride rapidly reacting with water vapor to form sulfuric acid to react in turn with metal salts or oxides to form sulfates. Recent work by Johnstone (Ref. 2) indicates that the photochemical oxidation of SO_2 at low concentrations proceeds very slowly. (He has no published reports on the possible accelerating effects of oxidation catalysts present in our particulate matter.) In the absence of such catalytic effects, Johnstone concludes that oxidation of SO_2 could account for little, if any, reduction in visibility. Plant damage due to smog is definitely distinguishable from that due to oxides of sulfur and sulfuric acid. Data on the concentration of SO_3 and sulfuric acid in our atmosphere are virtually nonexistent. There is no evidence that SO_2 in the maximum concentrations ever reported here causes any eye irritation. There is no evidence that oxides of sulfur or sulfuric acid contribute to measurements of oxidants or ozone. Cholak reports that SO_2 reduces the oxidant reading by potassium iodide. In short, at the concentrations found in our atmosphere in Los Angeles, there is no evidence that sulfur dioxide exerts any harmful effects, despite the popular impression that "sulfur is a culprit," a view traceable to incidents in other cities where at times SO_2 or H_2S have been found at higher concentrations and associated with acute air pollution effects. The extent to which SO_2 in the Los Angeles atmosphere is a harmful pollutant is yet to be established.

Organic Compounds

Among the so-called principal pollutants listed above, there remain organic compounds and oxides of nitrogen. These include all the hydrocarbons found in natural gas, and petroleum and petroleum products, beginning with methane. Such compounds enter our atmosphere from gas distribution systems; from the production, refining, and marketing of petroleum products; and from the incomplete combustion of these products; also, from the vaporization and/or atomization of heavier products such as lubricating oils; and by evaporation from carburetors and motor vehicle fuel tanks. Depending upon air-fuel ratios and upon normal operating temperatures and design characteristics of the great multitude of combustion devices which man operates today, both unburned and partially oxidized fuel escapes to the atmosphere. Partially oxidized fuel exists as assorted aldehydes, ketones, and organic acids. In addition there are pyrolysis products, including carbon, hydrogen, ethylene, acetylene, etc.

In addition to the galaxy of hydrocarbons and hydrocarbon derivatives connected with the production and use of commercial fuels, there are organic compounds resulting from the incomplete combustion of miscellaneous refuse. While but a few of these organic compounds have been identified, it is known that they include phenols, acetone, methanol, organic acids and tars, somewhat analogous to the products of wood distillation.

The consumption of miscellaneous solvents, as in dry cleaning or in paint thinners in the Los Angeles area, must closely approximate the input of these compounds to our atmosphere. Among such solvents would be found carbon tetrachloride, trichloroethylene, tetrachlorethylene, benzene, monochloro benzene, solvent naphthas, turpentine, etc. Weaver (Ref. 3), seeking to interpret Shepherd's mass spectrographic data, has found preliminary indications that both lubricating oil and halogenated hydrocarbons, while having low absolute concentrations, show relatively greater values than other pollutants at times of heavy smog.

Haagen-Smit (Ref. 4) has produced oxidant and/or ozone by irradiating mixtures of single organic compounds with NO_2 and O_2, in which the organic compound has been any one of a number of different saturated hydrocarbons, olefins, diolefins, straight chain or branched molecules, aldehydes, alcohols, ketones, and complex mixtures of organic compounds such as commercial gasoline as well as auto exhaust. The capacity for oxidant or ozone formation may vary widely from one organic molecule to another. The amount of oxidant and/or ozone formed is also dependent upon the starting concentration of NO_2 and upon the intensity and time of radiation.

Reduction of Selected Organic Compounds

In the light of these experiments and others carried out along similar lines, observed oxidant and ozone values in the Los Angeles atmosphere can be accounted for qualitatively in terms of observed concentrations of organic compounds and NO_2, even though we do not yet understand the complex reaction mechanisms. We can say that organic compounds and NO_2 in the presence of radiation and oxygen produce ozone. However, we cannot yet say that the reduction or the elimination of certain classes of organic compounds, such as gasoline hydrocarbons, would cause a proportionate, or any, reduction in ozone, because it is entirely possible in our present state of knowledge that the remaining organic matter plus the unchanged NO_2 would still produce as much ozone as before. Conceivably, reduction of nitrogen oxides might have a more significant effect in reducing smog than reduction of organic compounds, particularly if the latter reduction were confined to certain classes of compounds.

So far we have been discussing one smog effect, namely oxidant-ozone. The experimental production of eye irritation, plant damage, and reduced visibility by irradiation of organic compounds and NO_2, presumably at experienced concentrations, is far less extensively reported in the literature.

There are indications that auto exhaust blended from all four operating cycles, and hydrocarbons at concentrations close to those estimated for the Los Angeles atmosphere during heavy smog periods when irradiated, will produce both eye irritation and plant damage. There are indications that the same may be true with gasoline vapors themselves. We do not know what the compounds are which irritate eyes or damage plants, nor do we know from which hydrocarbons or other organic compounds they are formed. Ozonated olefins produce typical smog damage to plants in controlled laboratory tests. Consequently, we cannot say that reducing the hydrocarbon content of auto exhaust by 50 per cent or any other fraction will or will not reduce eye irritation and plant damage. If what might be termed "gasoline economizer" devices are developed, which would reduce the hydrocarbon content in auto exhaust on an over-all average by 50 per cent for example, at the present time we can only say that this would effect fuel savings of about 3 per cent, based on the total fuel consumption of the average motor vehicle. Based on an average consumption of two gallons per day, this should represent a saving of about 20 gallons per car per year, or about $6. If a device were to cost $10, some people feel that such a cost would be justified by fuel economy alone. Multiplied by over two million vehicles, this would amount to keeping out of our air something like 500 tons of gasoline vapors per day. With respect to smog effects, however, without control of oxides of nitrogen at the same time and without control of the very substantial remainder of the organic compounds, we can see little basis at present for the conclusion that a significant reduction in smog is to be expected by the use of a device which will reduce hydrocarbons from automobile exhaust by 50 per cent.

This statement will doubtless seem unreasonable to some people and disappointing to a great many. It is a statement based on lack of data rather than on the basis of facts in hand. This is why we feel that "chamber" experiments are urgently needed in order that the smog-forming potential of actual sources, singly and in combination, may be tested, as well as the effects of proposed control devices for these sources. Experimentation in this way could forestall the premature adoption of devices which might cost the community many millions of dollars without commensurate gains.

Other Data Needed

We believe that additional information is essential as to the variation of various pollutants with respect to both time and place. We have no data showing the concentrations of organic compounds and oxides of nitrogen, for example, in the immediate proximity of heavy traffic arteries. Our data so far are limited to a few scattered monitoring stations where in all likelihood we have measured residual values, after both chemical reaction and dispersion have taken place. Similar comments may be made with respect to composition and concentrations of other pollution sources, such as industrial stacks. Considerable progress has been made in developing methods of analysis, particularly in the direction which will permit continuous automatic recording for monitoring purposes. Much, however, remains to be done. Without sufficiently accurate and dependable methods of analysis and monitoring, we cannot know with what we have to contend.

Reactions at Higher Concentrations

We know that pollutants exist in much higher concentrations at their points of origin than they do after dispersion over the metropolitan area. It is quite possible that important photochemical reactions take place a short time period after the pollutants leave their points of origin.

It seems reasonable to assume that during this initial reaction and dispersion period, reactants exist at higher average concentrations than subsequently observed at relatively remote sampling stations. What we have called experienced or realistic concentrations for so long may come much closer to being residual concentrations. Difficulty in reproducing eye irritation from synthetic mixtures at these lower levels might be explained on the basis that the eye irritants actually form at higher concentrations in what is called above the "initial dispersion period."

The many uncertainties on what seem to us crucial questions indicated throughout the foregoing discussion are the basis of the numerous research projects we propose. Any practical estimate of the cost of such research now in sight far exceeds our own financial resources. We hope that other agencies will recognize the importance of these research projects so that more rapid progress may be made.

B. BACKGROUND

One of the difficulties in establishing the severity of smog at any point in time is the lack of continuous data dating back to the 1930's. One exception to this is the fact that visibility data obtained in the downtown Los Angeles area are available from the U. S. Weather Bureau.

Trend in Visibility

To examine the effects of air pollution on visibility a study of the trend of visibility in downtown Los Angeles was undertaken by the Foundation. A preliminary report on this study was presented in the First Technical Progress Report (Ref. 5), and the complete results were published as Report No. 11 of the Foundation (Ref. 6). The following brief summary gives the essence of the procedures and results.

Visibility observations at the Los Angeles city office of the Weather Bureau were tabulated according to the frequency by months with which the visibility exceeded certain values. To eliminate partially the variation due to other meteorological factors, the data were sorted according to wind direction and relative humidity, and the visibility trend for particular wind direction and relative humidity groups was studied.

The data, both treated as a whole and when separated into wind direction and relative humidity groups, show lower visibility in the 1940's than in the 1930's, with lowest values around 1944-1947 and some indication of improvement since then. As an example of the results, Table I shows the frequency in percentage of observations with visibility greater than the stated values by groups of years for the entire year. It will be seen that the frequency with which the visibility exceeded 12 miles at noon decreased from 30 per cent in the period 1932 - 1937 to 18 per cent in the period 1944 - 1949, and then increased to 23 per cent in the period 1950 - 1954. Similar trends are shown for the other visibility limits and the other times of day. Table II shows that these results hold for various combinations of relative humidity and wind direction. This table gives the frequencies with which the visibility exceeded stated values at midday during various seasons for the three most frequent wind-humidity groups for three four-month periods by groups of years. For instance, in the 1930's the visibility in the months from July to October exceeded 12 miles more than 40 per cent of the time, when the wind was in the southwesterly quadrant and the relative humidity was less than 40 per cent, but in the period 1944 - 1947 this frequency was down to 13 per cent.

CHAPTER I - TABLE I

FREQUENCY (PER CENT) OF OBSERVATIONS WITH VISIBILITY GREATER THAN STATED VALUES FOR GROUPS OF YEARS

	A.M. (0500)				Noon				P.M. (1700)			
	2½	6	12	35	2½	6	12	35	2½	6	12	35
	Miles				Miles				Miles			
Entire Year												
1932-37	81	63	47	24	79	49	30	14	94	76	54	27
1938-43	86	68	46	11	82	54	29	8	96	79	51	12
°1944-49	77	57	34	6	72	40	18	3	93	71	40	5
1950-54					79	45	23	4	95	80	48	11
All years	81	62	42	14	78	47	25	7	95	77	48	14

From these statistics it was deduced that the effect of air pollution on visibility was greatest around 1947 and that approximately one-fourth of the deterioration from the 1930's to that date has been recovered, presumably as a result of the control measures put into force subsequent to 1947. Since population and industrial activity have increased in the meantime, the success of the measures taken to control the visibility-reducing contaminants may be considered higher than indicated by the 25 per cent recovery.

CHAPTER I - TABLE II

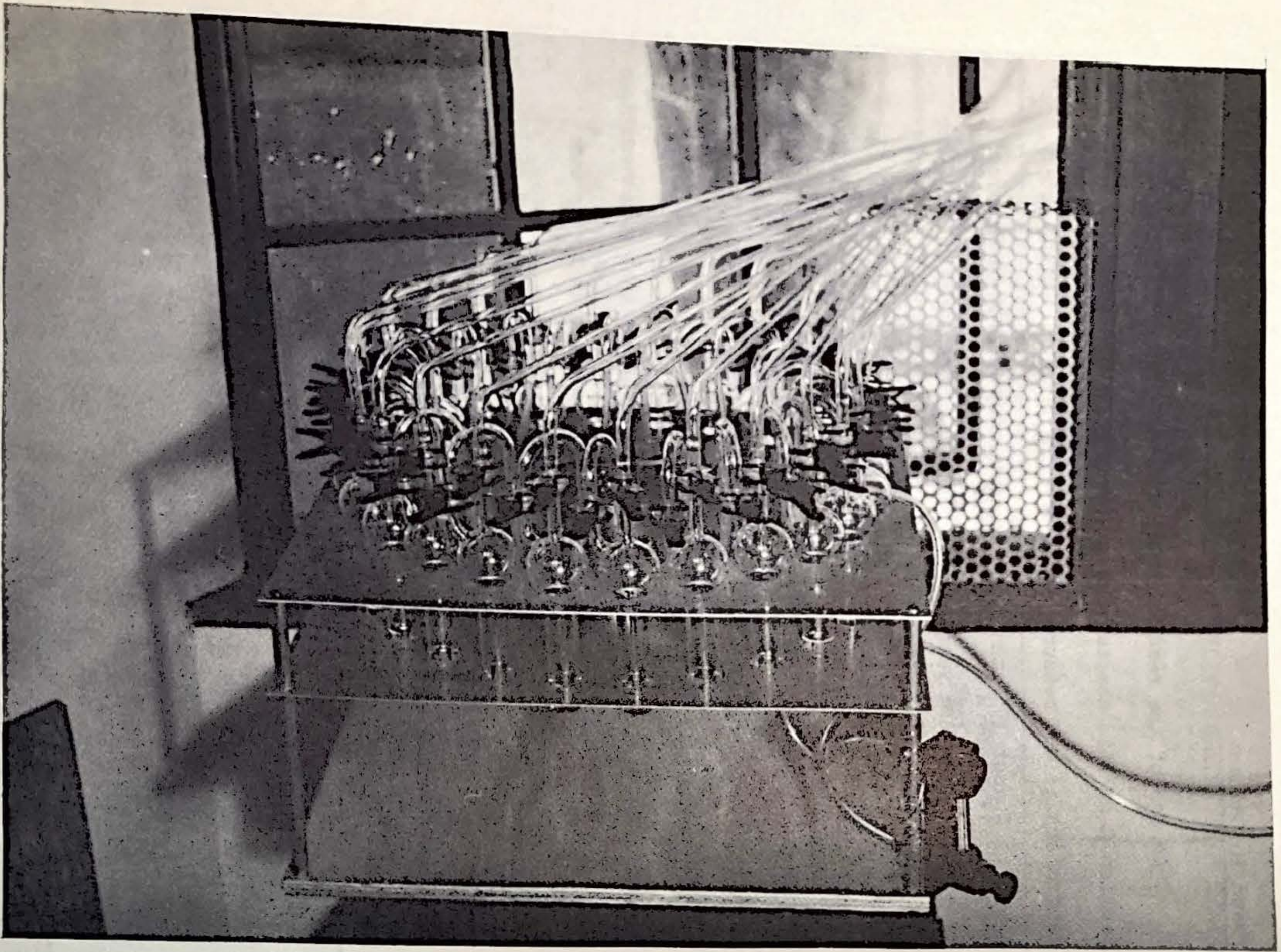
FREQUENCY (PER CENT) OF OBSERVATIONS WITH VISIBILITY GREATER THAN STATED VALUES FOR THE THREE MOST FREQUENT WIND-HUMIDITY GROUPS EACH SEASON BY GROUPS OF YEARS

MIDDAY												
Year Group	March-June				July-October				November-February			
	2½mi	6 mi	12mi	35mi	2½mi	6 mi	12mi	35mi	2½mi	6 mi	12mi	35mi
	RH 1%-40% Wind ESE-S				RH 1%-40% Wind SSW-W				RH 1%-40% Wind NNE-E			
1933-35	97	76	50	18	91	66	48	18	100	96	84	65
1936-39	96	77	42	11	90	73	43	12	92	84	67	36
1940-43	89	60	26	6	84	56	25	4	98	86	74	21
1944-47	91	60	32	2	80	44	13	0	96	75	43	2
1948-51	94	52	19	3	84	42	19	0	90	74	50	8
1952-54	88	69	41	3	87	43	11	0	100	91	67	9
	RH 41%-70% Wind ESE-S				RH 41%-70% Wind ESE-S				RH 1%-40% Wind ESE-S			
1933-35	76	41	18	4	57	23	11	1	93	68	58	30
1936-39	74	38	14	5	78	32	11	2	90	63	32	10
1940-43	72	43	20	1	61	29	10	1	88	72	46	5
1944-47	63	32	10	0	35	10	2	0	83	44	19	3
1948-51	75	33	13	1	64	20	4	0	87	63	32	5
1952-54	75	47	21	1	51	13	3	0	98	77	41	9
	RH 41%-70% Wind SSW-W				RH 41%-70% Wind SSW-W				RH 41%-70% Wind ESE-S			
1933-35	87	54	35	13	73	29	8	0	64	38	21	9
1936-39	89	53	29	10	85	53	12	1	76	50	24	2
1940-43	80	51	22	1	69	29	9	1	74	58	30	3
1944-47	78	42	18	1	57	18	7	0	78	41	12	0
1948-51	83	50	22	4	72	20	5	0	70	48	23	1
1952-54	80	47	22	2	64	18	1	0	79	46	20	0

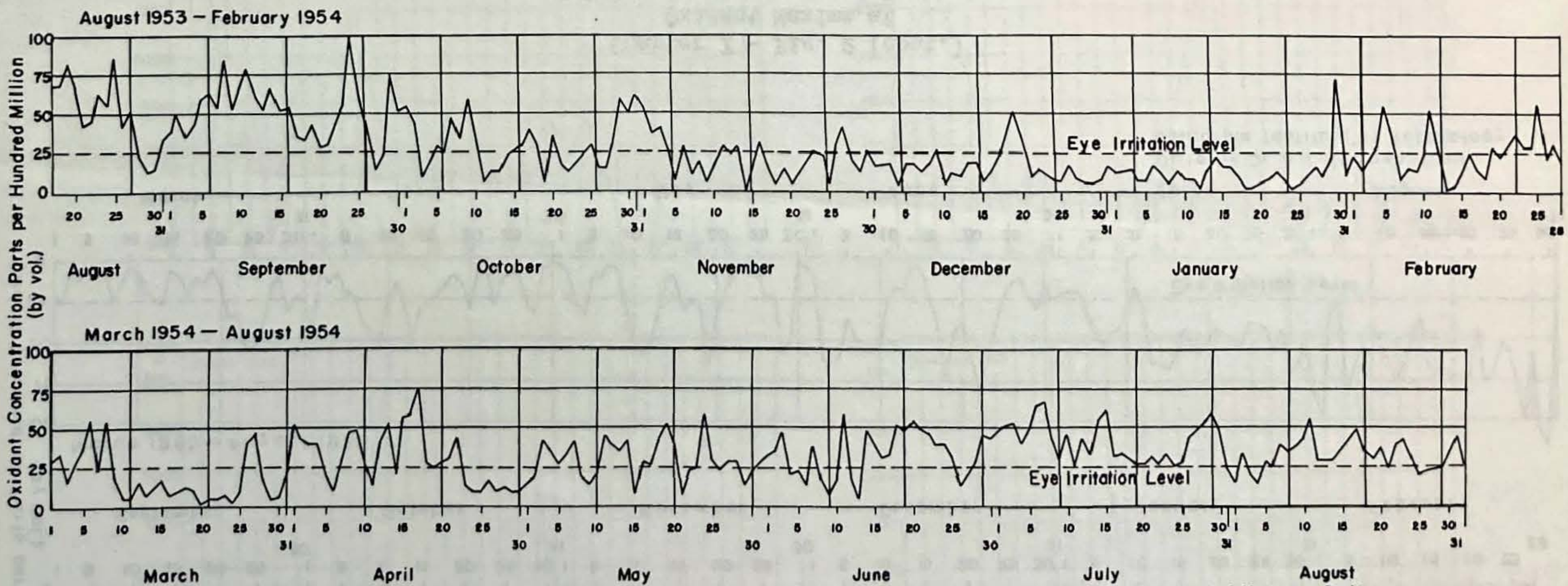
Trend in Oxidant

As one of the results of the 1954 aerometric survey (see Section C of this chapter) it was established that oxidant concentration is one measure of the severity of smog. Unfortunately, prior to August 1954 there are no continuous records on the trend of oxidant over the years except for the data obtained by Professor A.J. Haagen-Smit at his laboratory at the California Institute of Technology in Pasadena. He has monitored the atmosphere for oxidant continuously since August 1953. Figure 1 shows his apparatus, which uses the phenolphthalin procedure[1/] for the determination of oxidant concentration. Figure 2 shows the daily maxima for the period August 1953 to August 1955. It is quite apparent that smog conditions were worse during July and August 1955 when compared to the same period in 1954. It can be assumed that some of this is due to the effect of lower inversion layers (see Figure 3) and the rest to increased pollution. Also there are insufficient data for this period in 1953, so that it will not be possible to establish a definite yearly trend until all the data have been obtained for 1955.

[1/] This procedure is described in a paper to be published in the Journal of the Air Pollution Control Association.

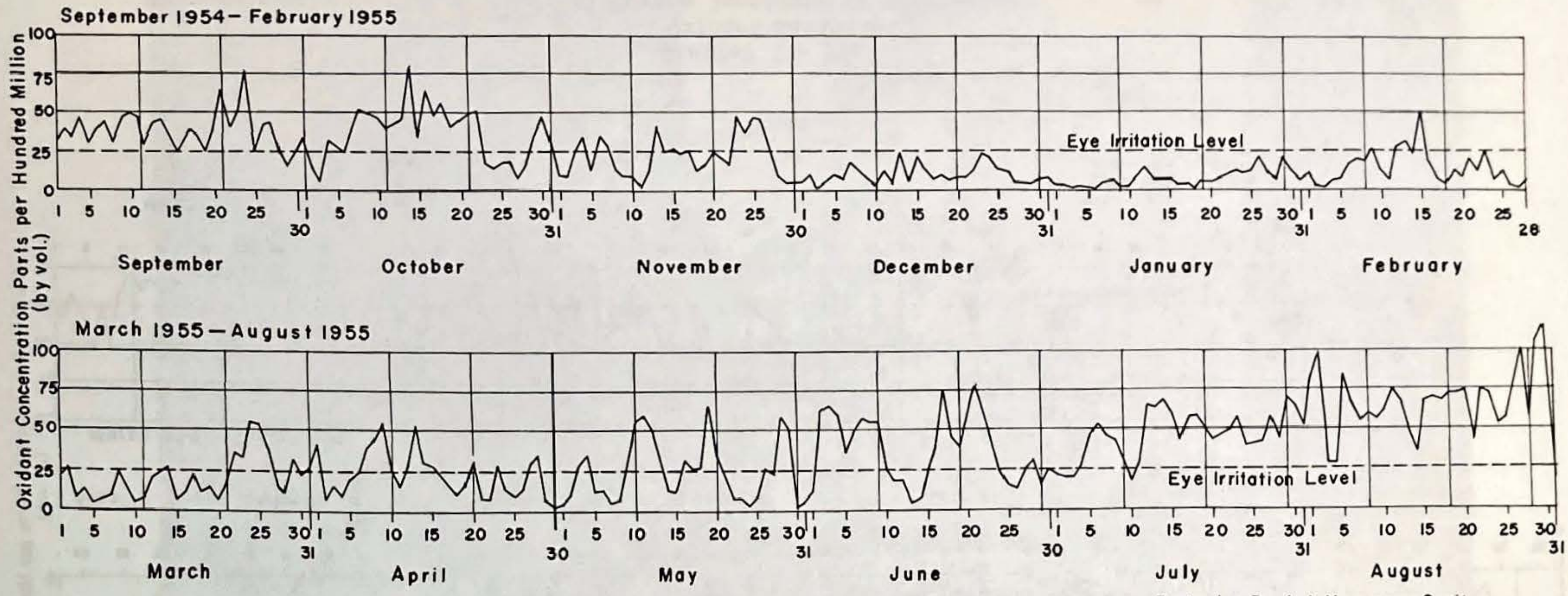


Chapter I - Fig. 1
Phenolphthalin Oxidant Apparatus



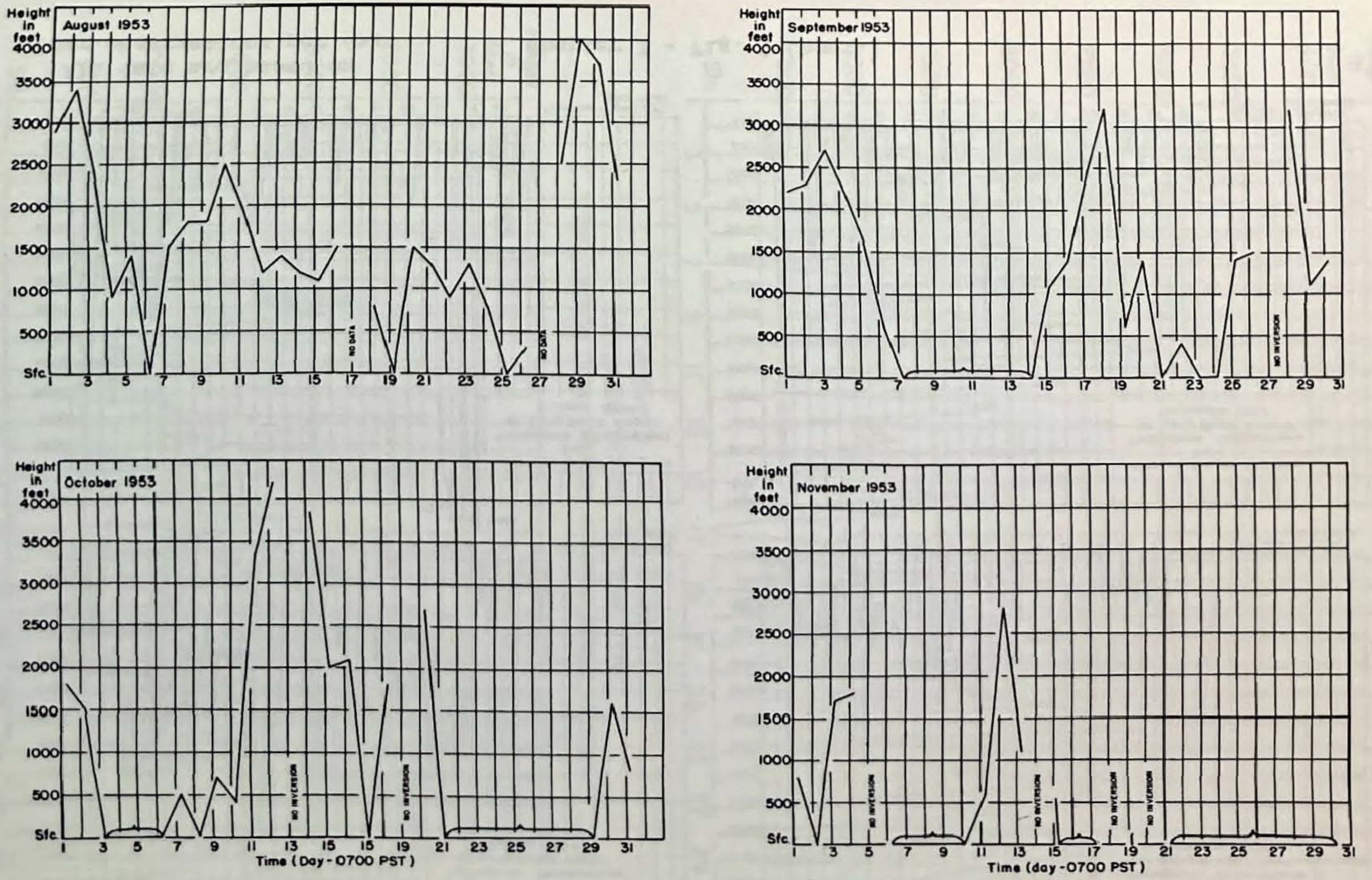
Data by Dr. A. J. Haagen-Smit
California Institute of Technology

Chapter I - Fig. 2
Oxidant Maxima at
California Institute of Technology
August 1953 - August 1954



Data by Dr. A.J. Haagen-Smit
California Institute of Technology

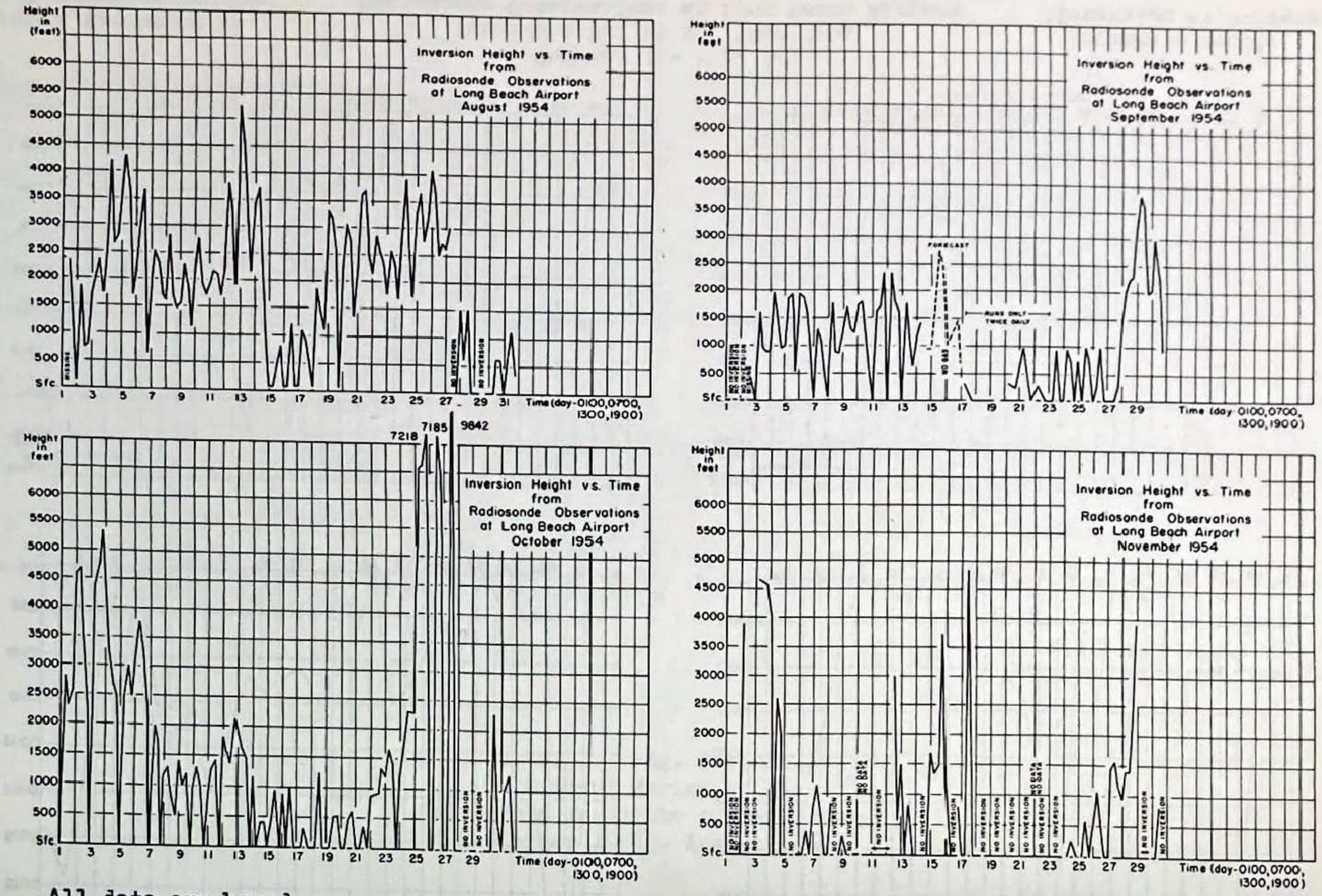
Chapter I - Fig. 2 (cont.)
Oxidant Maxima at
California Institute of Technology
September 1954 - August 1955



Chapter I - Fig. 3
Inversion Height vs. Time from
Radiosonde Observations at Long Beach Airport

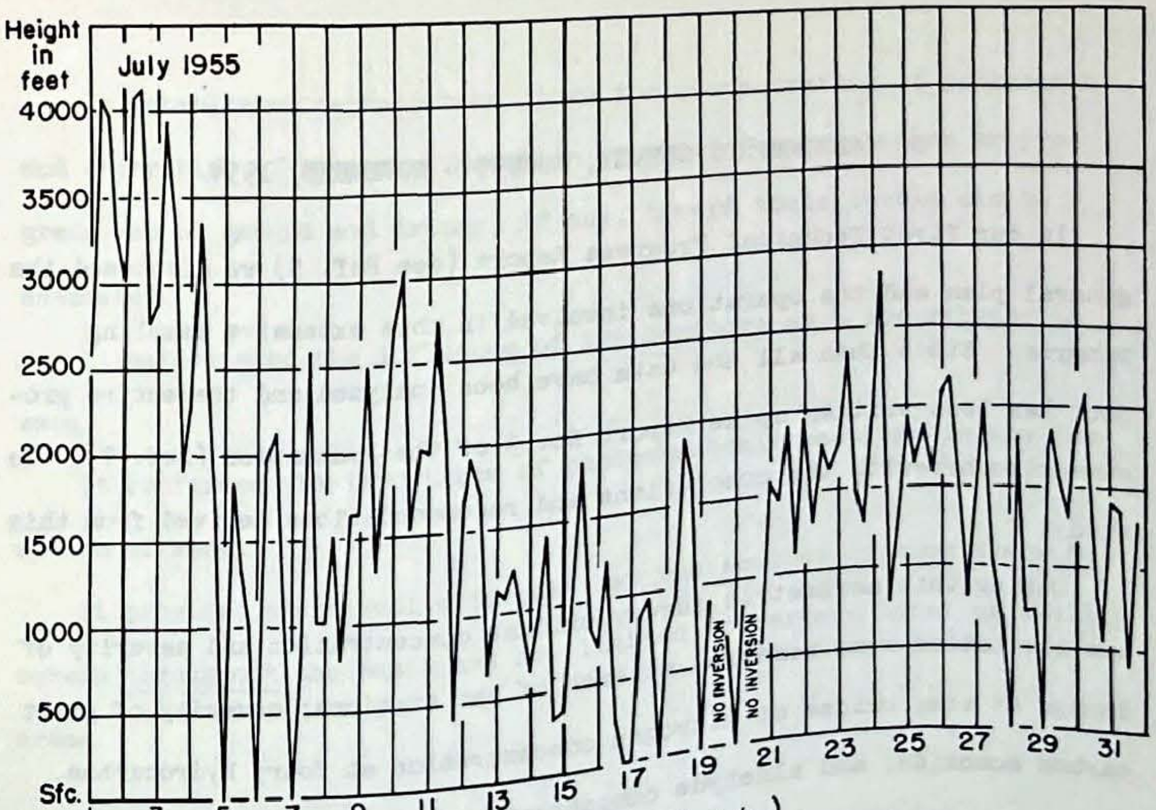
All data are based on
one observation per day

Brackets denote
'Inversion at Surface'

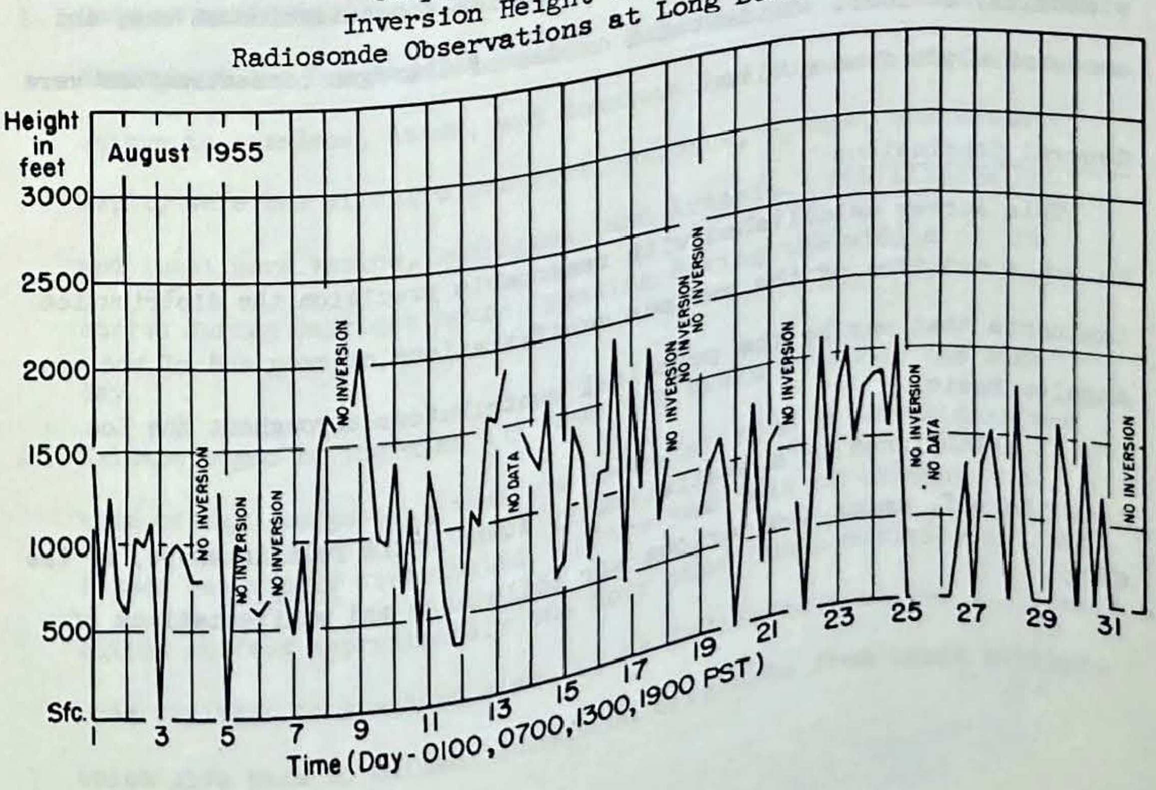


All data are based on
four observations per day

Chapter I - Fig. 3 (cont.)



Chapter I - Fig. 3 (cont.)
Inversion Height vs. Time from
Radiosonde Observations at Long Beach Airport



All data are based on
four observations per day

C. AEROMETRIC SURVEY, AUGUST - NOVEMBER, 1954

In our First Technical Progress Report (see Ref. 5) we discussed the general plan and the operations involved in this extensive sampling program. Since then all the data have been analyzed and the entire project has been written up as Report No. 9 of the Foundation (Ref. 7). We summarize herewith the conclusions and recommendations derived from this study.

During this aerometric survey oxidant concentration and severity of eye irritation were measured at each of ten stations; severity of plant damage at six; oxides of nitrogen concentration at four; hydrocarbon, carbon monoxide, and aldehyde concentrations at two; concentration of various particulates at two; sulfur dioxide concentration at one; and visibility at four. Oxidant and oxides of nitrogen concentrations were measured aloft from a blimp.

General Conclusions

This survey established with reasonable precision the distribution in space and time of the various manifestations of smog and of the contaminants that may be the principal contributors throughout the Los Angeles Basin.

It established on a statistically sound basis relationships, or the lack thereof, among the various air pollutants and manifestations of smog.

It established certain base lines for concentration of pollutants and severities of smog manifestation by which future changes or progress can be gauged and trends, if any, toward toxic levels can be estimated.

It established the influence of incinerators as a contributor to smog.

It confirmed the importance of photochemical reactions in the formation of smog.

It provided additional evidence that the sources of smog are widespread throughout the basin and not limited to certain local or small areas.

Specific Conclusions

1. Smog as manifested by high average oxidant concentration occurred throughout the Los Angeles Basin. Attacks were consistently most severe in Pasadena, Azusa, and downtown Los Angeles; next in severity were the Wilshire district, Burbank, Rivera, and Bassett; and least were Venice, Dominguez, and Artesia. The attacks occurred during daylight hours, peaking during the middle of the day.
2. Oxidant began to increase all over the basin at about the same time of day, suggesting that the material from which oxidant was formed was widely distributed. Since the peak of oxidant formation shifted approximately one hour when human activity shifted from daylight to standard time, it is indicated that the pollutants which give rise to oxidant formation originate from human activity.

3. The highest oxidant values on any one day may occur anywhere in the basin, although preferentially in the north and east.
4. The measurement of oxidant concentration constitutes the best available objective indicator of the severity of smog.
5. Smog as manifested by human eye irritation occurred throughout the Los Angeles Basin, with the maxima in Burbank and Pasadena. Appreciable eye irritation throughout the basin was experienced on 69 per cent of the days sampled (29 days). Severity of eye irritation increased as oxidant increased for values of the latter above 10 pphm. Severity of eye irritation increased as hourly values of concentration of particulate matter increased.
6. Lines of equal oxidant and eye irritation values look like contour lines on a topographic map. Typical air streams crossing these contours from the ocean to the foothills go from low to high values, apparently corresponding to the length of time the air has spent over source areas, the number and strength of pollutant sources encountered on the way, and the amount of insolation the air has experienced. These indications are broadly consistent with the laboratory findings of earlier investigators of photochemical oxidative reactions.
7. Smog as manifested by damage to plants occurred throughout the basin. The damage regularly observed was similar to that produced by oxidized hydrocarbons. It occurred on 80 to 88 per cent of the days of this survey when normal experimental conditions existed. The correlation between the injury index, or quantitative estimate of damage,

and oxidant is below the level of significance. However, the per cent of plants damaged, or the qualitative estimate of injury, is significantly correlated with oxidant. The test plants did not show ozone damage, even though the oxidant values were high enough to have produced typical ozone damage, distinct from smog damage, if the oxidant is mainly ozone.

8. The correlations among oxidant, aldehydes, hydrocarbons, and oxides of nitrogen are broadly consistent with the postulate proposed previously on the basis of laboratory experiments, which have demonstrated that the oxidants and aldehydes are produced by photochemical reactions between hydrocarbons and oxides of nitrogen under the influence of sunlight.
9. The correlations confirm that concentrations of contaminants increase as the inversion height decreases. This is consistent with the smaller dispersion volume available.
10. Particulate matter collected from large volumes of air showed large fluctuations in concentrations of total particulates, lead, organic matter (by benzene extraction), sulfates, and nitrates. Of these, the most striking differences were the considerably higher concentrations of sulfates, nitrates, and, to a lesser extent, the organic component in Los Angeles in comparison with those of other American cities (Ref. 1). Furthermore, a higher concentration of the phenol component of the particulates was obtained at Pasadena than at downtown Los Angeles.

11. Oxidant and oxides of nitrogen concentrations tend to increase with altitude up to the base of the inversion and to decrease upwards through the inversion layer. These data suggest that gaseous pollutants are largely confined to the volume of atmosphere under the inversion layer.
12. Smog tends to reduce the solar radiation in downtown Los Angeles some 10 per cent below the amount that would occur in the absence of pollution.
13. Solar radiation may be a limiting factor for the formation of oxidant for days with less than 500 langleys per day.

Recommendations

1. In order to monitor the distribution and trend of pollution in the Los Angeles Basin and to maintain a check on the possibility of development of dangerous concentrations, a minimum of fourteen stations should be established in the Los Angeles Basin.
2. Automatic recording equipment should be installed to provide more complete monitoring of the important variables.
3. In the interests of efficiency and economy the information thus recorded at the monitoring stations should be telemetered to a central office and transferred automatically to punched cards.
4. More complete meteorological measurements should be obtained with respect to the distribution of the inversion and the winds aloft over the basin. Also, the surface wind observations should be improved by calibration of wind instruments presently used, by filling gaps in the

network, and by replacement of insensitive instruments with more sensitive ones.

5. Plant damage should be given more extensive laboratory and field study since it does not appear so far to be related quantitatively to any of the measured contaminants or other smog manifestations. Furthermore, an explanation should be sought of the apparent anomaly that no ozone damage was found at concentrations of oxidant which, if largely ozone, would have produced ozone damage in the laboratory.
6. The mechanism of formation and composition of aerosols in smog should be investigated. Questions to be answered as a result of this survey are: (1) What is the significance of the higher phenol concentrations found in Pasadena as against Los Angeles? (2) Why are the sulfate and nitrate concentrations in the particulate loading in smog higher in Los Angeles than in other cities?
7. More data should be obtained on the vertical variation of the concentration of various pollutants, particularly carbon monoxide and aerosols, up through the inversion layer.

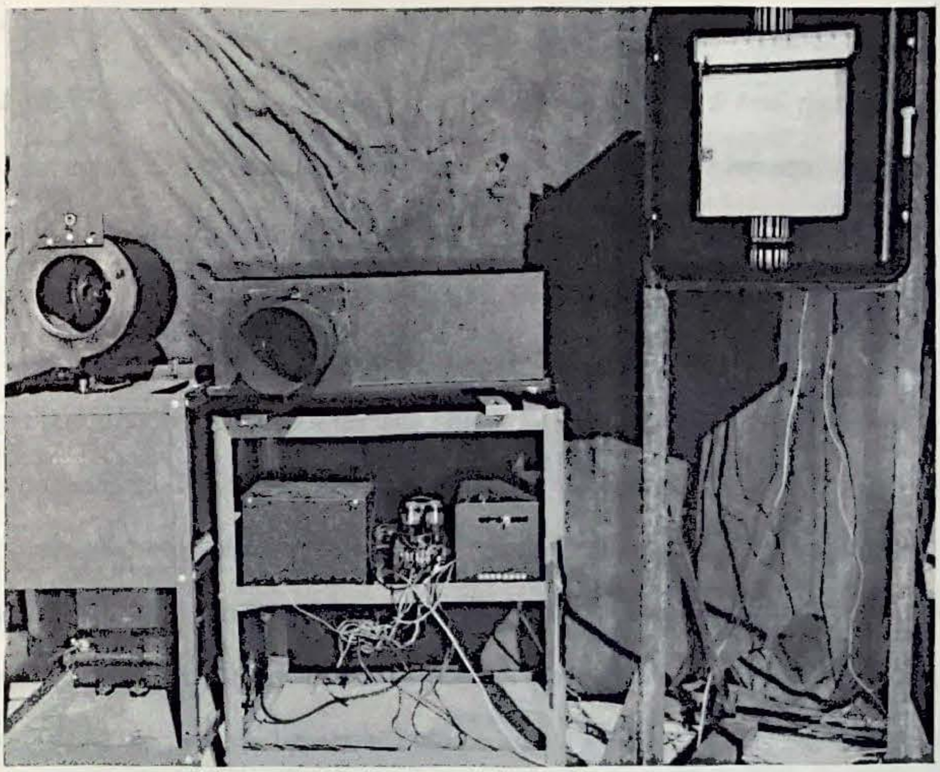
D. AIR MONITORING INSTRUMENTS

Ozone Radiometer

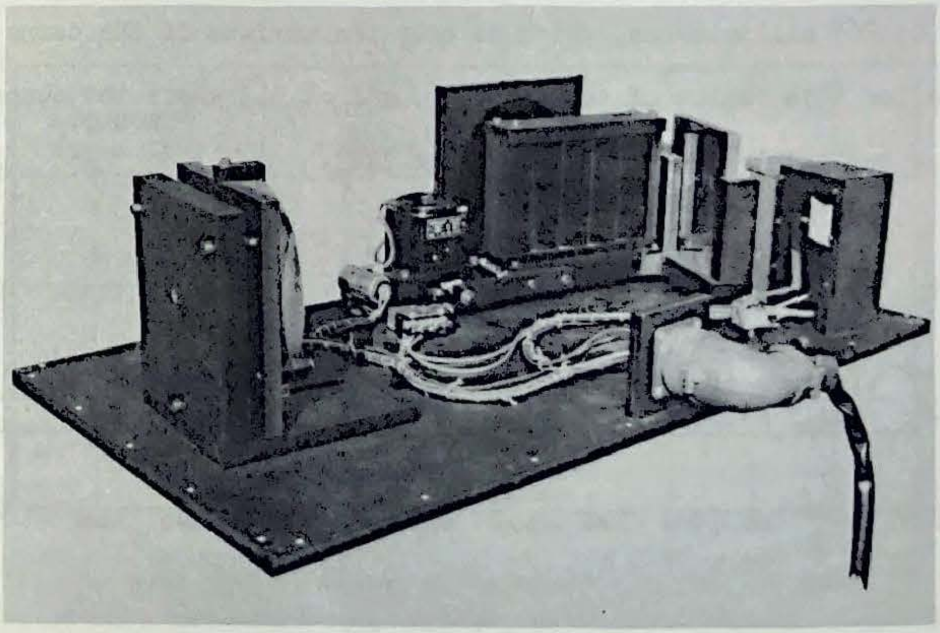
In our First Technical Progress Report we indicated the need for specific and quantitative measurements of ozone concentration in smog. To meet this objective, we undertook the development, at the Borman Engineering Company in North Hollywood, of an ultraviolet spectrometer which would operate continuously and automatically for extended periods.

Description of Equipment. Figures 4 and 5 show the essential components of this instrument. The light projector uses a type CH3 85-watt high pressure mercury lamp and has a 6-inch aperture. Due to the pressure the lines are broad and the spectrum is well filled. The radiation is pulsed at 120 times a second. The receiver consists of a prism radiometer having an exit collimator $5\frac{1}{2}$ inches in diameter and 20 inches focal length. The prism is a Fresnel type assembly of four 60° fused quartz prism elements. Synchronous motors drive the wave-length and programming cams. The radiation is measured by means of a photomultiplier tube, modified by transmission through similar Corning glass filters (No. 9863) and recorded on a Leeds and Northrup recorder. The instrument traverses the spectrum between 254 and 365 millimicrons in 45 seconds. Two such traverses are made for each determination of ozone and repeated at 15-minute intervals continuously and automatically throughout the 24-hour period.

Operations. During the initial field trials conducted on the roof of the Borman Engineering Company, the projector and receiver were set alongside each other using a folded path of 302 feet with a remote plane



Chapter I - Fig. 4
Borman Ozone Radiometer
Light Projector, Receiver, Recorder



Chapter I - Fig. 5
Borman Ozone Radiometer
Optical System

mirror 151 feet away. These trials demonstrated the adequacy of the experimental setup and behavior of the instrument. However, the remote mirror presented operational problems, since it became dirty from exposure to the atmosphere and required constant cleaning. In July the instrument was removed to the roof of the Biology Building at the California Institute of Technology with the projector 269 feet away from, and looking directly at, the receiver without the use of the remote mirror. After some experience at this location, for which 169 feet of the optical path lay directly above roof surface (3 feet), it was decided to vary this latter condition because of the troubles with atmospheric boiling and other sources of local turbulence. The new setup, with projector on one building and receiver on another, avoids some of these difficulties.

Method of Ozone Determinations. The present technique for obtaining concentrations from the attenuated radiation readings is as follows: the intensity at 265 millimicrons, which is near the maximum of the ozone absorption for this region of the spectrum, and at 313 where the absorption by ozone is negligible, is noted (see Table III).

CHAPTER I - TABLE III*

OZONE ABSORPTION DATA

λ (wave length in millimicrons)	O_3 (decadic absorption coeff. in km^{-1} times pphm)
313	0.00087
302	0.0038
280	0.0543
265	0.123

---

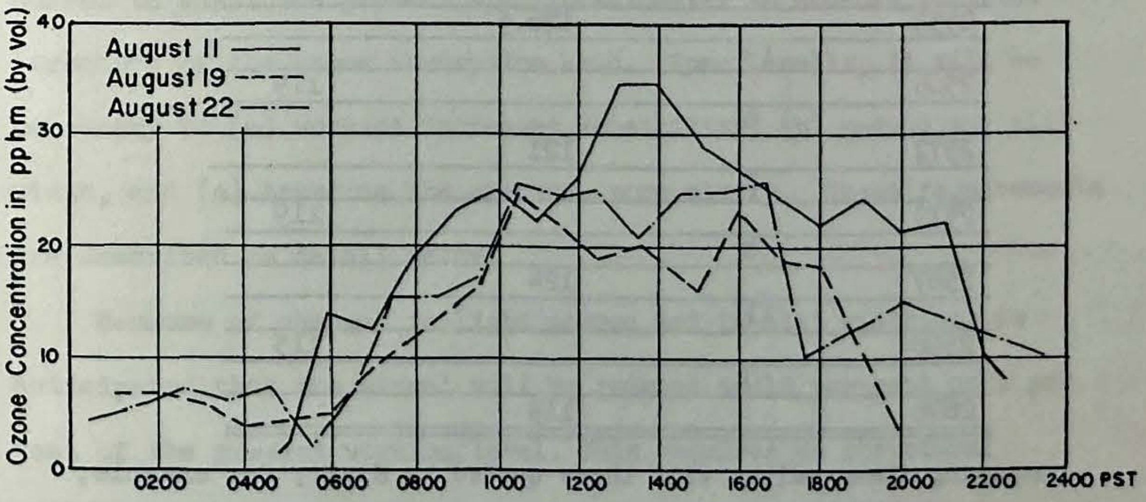
* See Ref. 8

The ratio of these intensities is related to the concentration by the following formula:

$$C_{O_3} = \frac{\log \frac{I_{265}}{I_{313}} \text{ times } \frac{I^{o}_{313}}{I^{o}_{265}}}{269\ (0.123 - 0.00087)} \text{ plus } C^{o}_{O_3} ,$$

where the zero superscripts refer to the intensities measured at night when ozone is known to be absent or in very small concentration ($C^{o}_{O_3}$).

Preliminary Results. We have run the instrument continuously at Pasadena from July 15 through August 31, 1955, and will continue to do so until November. Figure 6 shows some graphs of data for days selected at random. In Section E of this chapter we shall display additional data in connection with the comparative study of oxidants in the atmosphere.



Chapter I - Fig. 6
Diurnal Variation of Ozone Concentration
(by ultraviolet spectrometry)
Pasadena, California Institute of Technology

Future Plans. We have designed an additional experiment to identify the observed attenuation with this instrument as that due uniquely to ozone. This experiment will attempt to measure the fine structure of the ozone absorption band in the region 250 - 260 millimicrons.

CHARACTERISTICS OF OZONE SPECTRUM - The absorption coefficients of ozone have been measured and reported by M. Ernest Vigroux (Ref. 9). The following values are typical of the band structure at maximum absorption:

λ	Δλ	α maximum	α minimum
2500		121	
	8		
2508			119
	11		
2519		125	
	10		
2529			121
	10		
2539		125	
	7		
2546			121
	7		
2553		126.5	
	13		
2566			119
	6		
2572		121	
	7		
2579			119
	8		
2587		124	
	11		
2598			115
	8		
2606		119	

Comparing these values with those quoted by Stair, for example, indicates that the Vigroux data are expressed in optical density units so that multiplication by 10^{-3} serves to express the coefficient in km^{-1} and pphm. This means that if the ozone concentration is 10 pphm, the spread of transmission over the strongest band (2553 - 2566 A.) is 0.747 - 0.760. It is evident that if the resolution is adequate, it will show as a measurable ripple on the chart record. The data in the $\Delta\lambda$ column indicate that a resolution of about 5 A. should be provided.

CHARACTERISTICS OF LIGHT SOURCE - Obviously we cannot use the present mercury lamp with its discontinuous radiation spectrum; we therefore propose to use a commercially available hydrogen tube and power supply. We will mount this at the focus of a suitable quartz lens in a simple tube assembly. The source will be pulsed at a peak value of about 140 watts. The existing projector can be used as an auxiliary source for wave-length calibration. Manifestly the intensity will be less than that presently available, but we believe it will be adequate.

MODIFICATIONS TO SPECTRORADIOMETER - Only minor changes will be required to adapt the present spectroradiometer to measure the fine structure of the ozone absorption band. Specifically, it will be necessary to (a) work at increased sensitivity, (b) reduce the slit width, and (c) traverse the spectrum more slowly. These requirements are described in detail below.

Because of changes in light source and in slit width, it is anticipated that the signal will be reduced to 10 per cent or 1 per cent of the present working level. This requires no structural alterations because an even greater range of sensitivity can be covered by adjustment of the present amplifier controls. In the existing spectroradiometer we employ a fixed slit 0.030 inches wide.

It will be necessary to fabricate and substitute a slit 0.005 inches wide to achieve the required spectra resolution.

Since the new requirements relate to a very narrow spectral range, 245 - 320 millimicrons, it will be necessary to substitute a new wave-length cam and drive motor. This will produce a spectrum about 10 inches long on the chart with the fine structure of the absorption band well displayed.

SETUP AND OPERATION - In harmony with the above exposition we propose to use a completely separate hydrogen source projector rather than modify the existing mercury source projector. With this arrangement the two projectors can be mounted side by side, and continuous-type and line-type spectral energy can be delivered to the receiver in any desired proportion.

The modified receiver will yield the absorption band details desired; and with no further structural changes it can be returned to its present mode of operation for ozone measurements with the mercury spectrum.

Our present experience indicates that considerable data must be obtained and analyzed to distinguish between the fine structure of the O_3 band and irregularities in the atmosphere and in the equipment. We plan to obtain data which will simultaneously identify the band structure and also determine the gross variation in absorption at the center and edge of the band. It is anticipated that the information obtained will be helpful in differentiating between ozone and nonspecific attenuants.

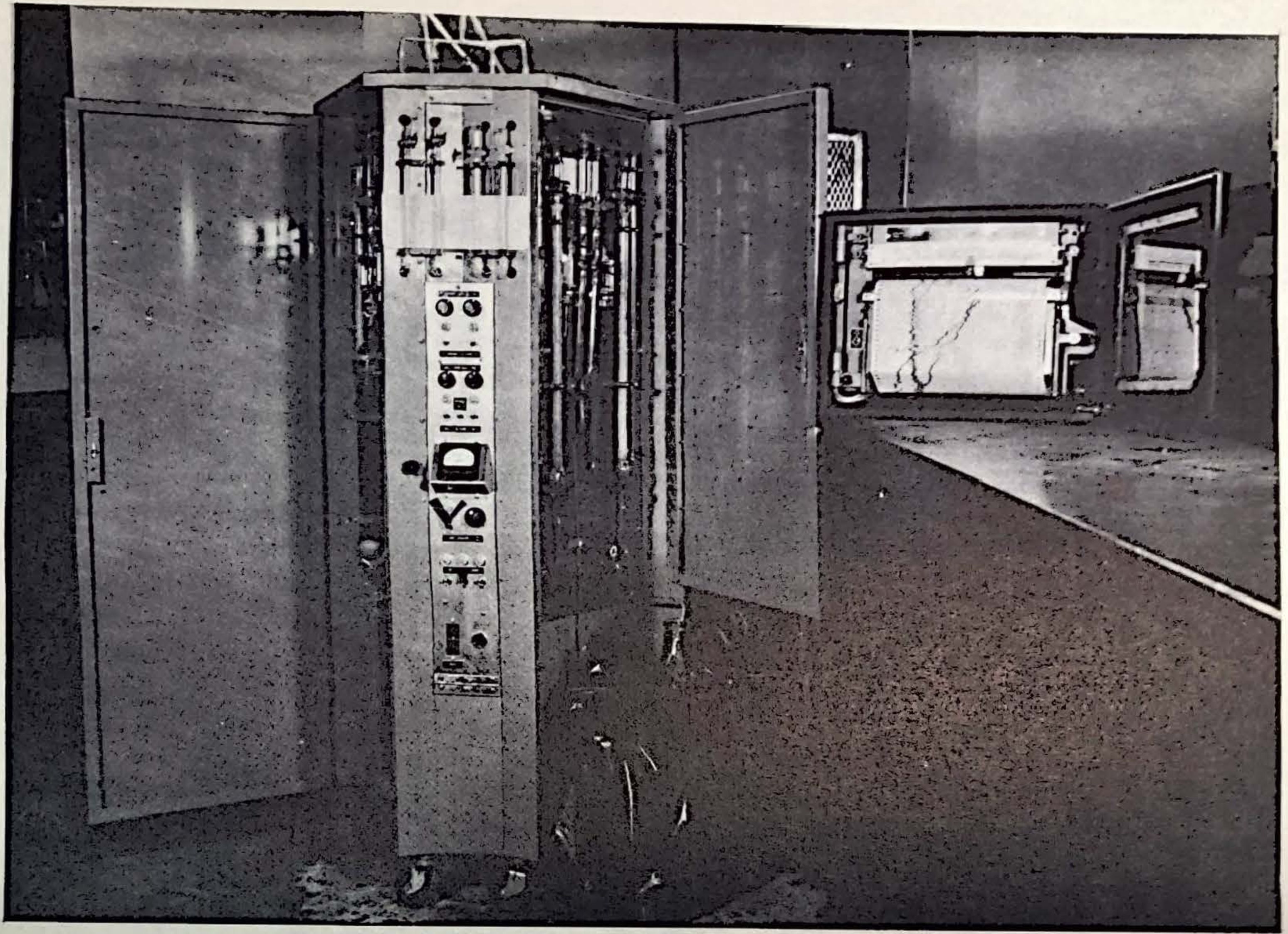
Four-in-One Analyzer Recorder

Several studies have shown that nitrogen dioxide and nitric oxide play an important role in smog reactions. Results from the 1954 aerometric survey (Ref. 7) showed the need for better methods to measure these nitrogen oxides. Continuous recording of the measured value is also desirable.

Stanford Research Institute, under contract with the Air Pollution Foundation, has developed an instrument for this purpose. The prototype was built to record four atmospheric variables on a single "four point" strip chart recorder. The four variables are nitrogen dioxide, nitric oxide, oxidant, and oxidant precursor. This instrument is at present being operated by the Air Pollution Foundation at a station in Pasadena to determine its operating characteristics. It is illustrated in Figure 7.

Nitrogen Dioxide. The initial problem was to find a suitable absorbing medium and contacting device for nitrogen dioxide. After extensive testing of various solutions, Saltzman's reagent was chosen (Ref. 10). Detection of the nitrogen dioxide absorbed is accomplished colorimetrically. Bubblers of various types, packed columns, and coils were tested. Analysis showed that a column, 20 mm. in diameter by 60 cm. long, packed with glass helices, was the most efficient contacting device.

The nitrogen dioxide recorder consists of an absorber, a colorimeter, and a recorder. The absorbent (Saltzman reagent) passes through a reference colorimeter cell, countercurrent to the air sample, and



Chapter I - Fig. 7
Four-in-One Analyzer Recorder

from there through a column packed with glass helices. The liquid coming from the bottom of the column passes into a second colorimeter cell. The color intensity, due to the formation of an azo dye, is proportional to the nitrogen dioxide concentration. The difference in signals between the reference and test cells is received in the circuit of a Brown amplifier, which records the resultant value on a chart. Since continuous comparison is made between reacted and unreacted solutions, zeroing of the instrument is unnecessary.

Comparisons were made between the results obtained with this instrument and with other methods by a cooperative testing program between the Los Angeles County Air Pollution Control District, the Chaney Laboratories, and Stanford Research Institute. Each laboratory used a different absorbing solution and method of sampling. Three groups of air samples were taken simultaneously and then analyzed by each of the three organizations. The results may be summarized as follows: when known amounts of nitrogen dioxide and carbon-filtered air mixtures were used, approximately the same results were obtained by all three laboratories. Several outside air samples were taken and analyzed by all three laboratories. When the "grab" samples were analyzed within a few hours after being taken, agreement with the recorder values was satisfactory. When 19 hours elapsed between collection of samples and analysis, the agreement was poor. Much more work is needed on this type of comparison.

A number of interfering substances were tested. Of these, alkyl nitrites showed positive interference in the recorder. If alkyl nitrites were present in the atmosphere, they would induce a response in the analyzer and be recorded as nitrogen dioxide, but the interference was not quantitative.

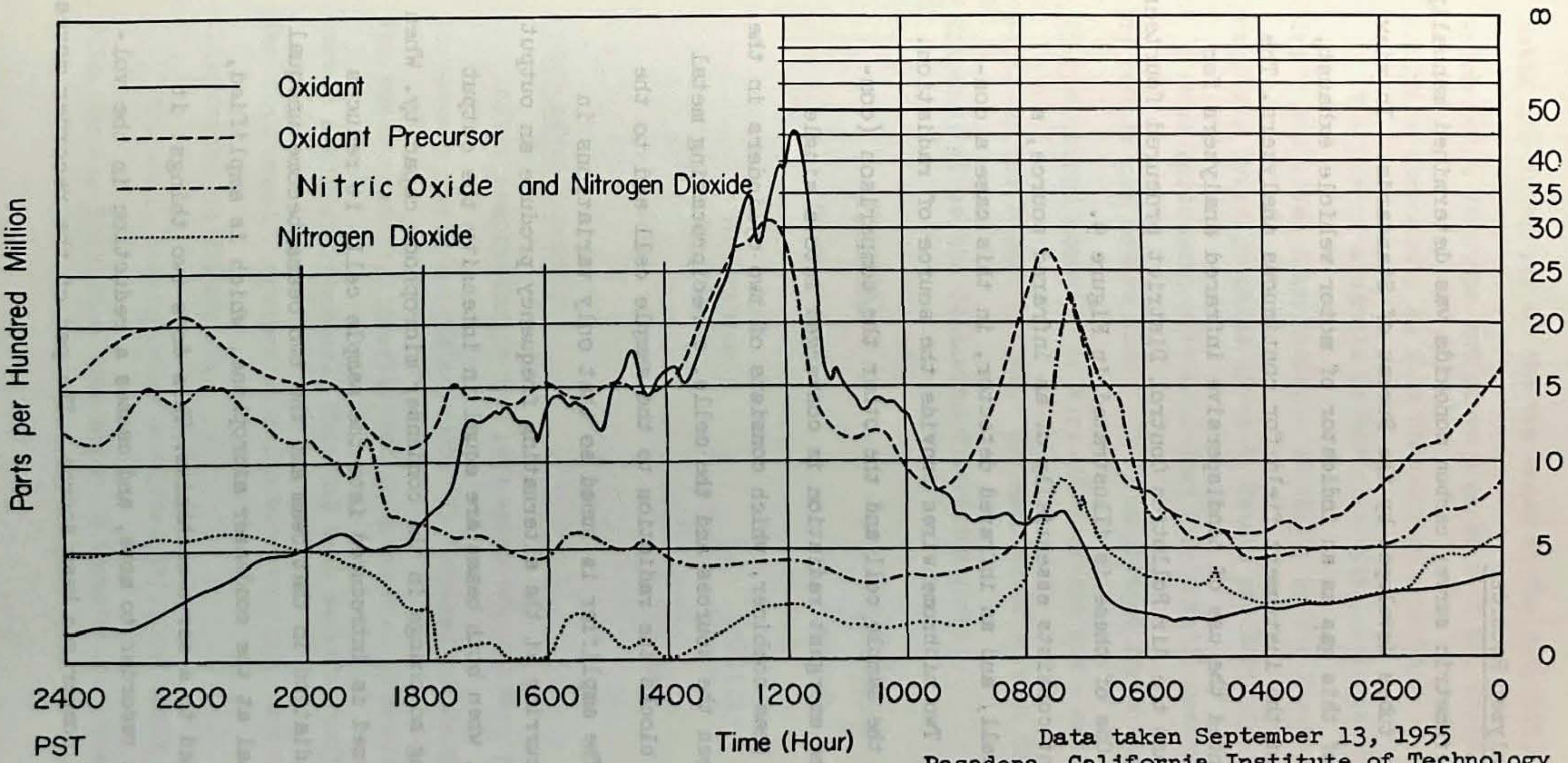
Nitric oxide is oxidized to nitrogen dioxide with ozone in a separate air stream. An ozonizer was installed in the instrument for this purpose. The ozone concentration is controlled by the lamp current at a level of approximately 1 ppm. The resulting nitrogen dioxide, which includes any nitrogen dioxide in the original air sample, is absorbed and read in the same manner in a different absorbing column.

A seven-cell colorimeter electronic system was devised for use with this four-component recorder. Four of these cells carry the respective absorbants from the absorbing columns, the other three cells being used as reference.

Oxidant is measured by the same system used in the oxidant recorder (Ref. 11) with a solution of neutral buffered potassium iodide.

Oxidant Precursor is measured by passing another sample of air through a 50-liter flask exposed to artificial irradiation using four mercury arcs, and then absorbing the oxidants in potassium iodide solution.

An example of the type of record produced by this four-point recorder is given in Figure 8.



Data taken September 13, 1955
Pasadena, California Institute of Technology

Chapter I - Fig. 8
Sample Record for
Four-in-One Analyzer Recorder

Carbon Monoxide Analyzer Recorder

In the 1954 aerometric survey carbon monoxide was determined manually using the indicator tubes developed by the Bureau of Standards. In view of the importance of this gas as an indicator of motor vehicle exhaust, a survey was made of the instrument field for continuous analyzers. The Foundation recommended the use of nondispersive infrared analyzers for this measurement, and the Air Pollution Control District procured fourteen such instruments. One of these is illustrated in Figure 9.

This instrument consists essentially of an infrared source, a sample and filter cell, and an infrared detector, in this case a condenser microphone. Two nichrome wires provide the source of radiation. One beam traverses the sample cell and the other the comparison (compensator) cell. The emergent radiation is converged into a single detector cell by a beam combiner, which consists of two cylinders in the form of a V. Between the sources and the cells, a reciprocating metal slider alternately blocks the radiation to the sample cell and to the comparison cell. The amplifier is tuned so that only variations in light intensity occurring at the alternating frequency produce an output signal. Therefore, when both beams are equal in intensity the output is zero, there being no change in the condenser microphone capacity. When the gas to be analyzed is introduced into the sample cell, it reduces the intensity of radiation in that beam and the two beams become unequal. This sets up a signal at the condenser microphone, which is amplified, rectified, and passed to a servo-mechanism. This does two things: it causes the pen of a recorder to move, and causes a reduction in the voltage applied to the comparison beam source. The pen of the recorder moves until the intensity of the two beams at the detector are the same, at which point it stops and gives a measure of the concentration of the analysis component, in this case carbon monoxide.

The use of a single detector in this instrument minimizes zero drift and gives high internal stability in the instrument. A more complete description is given by Waters and Hartz (Ref. 12).

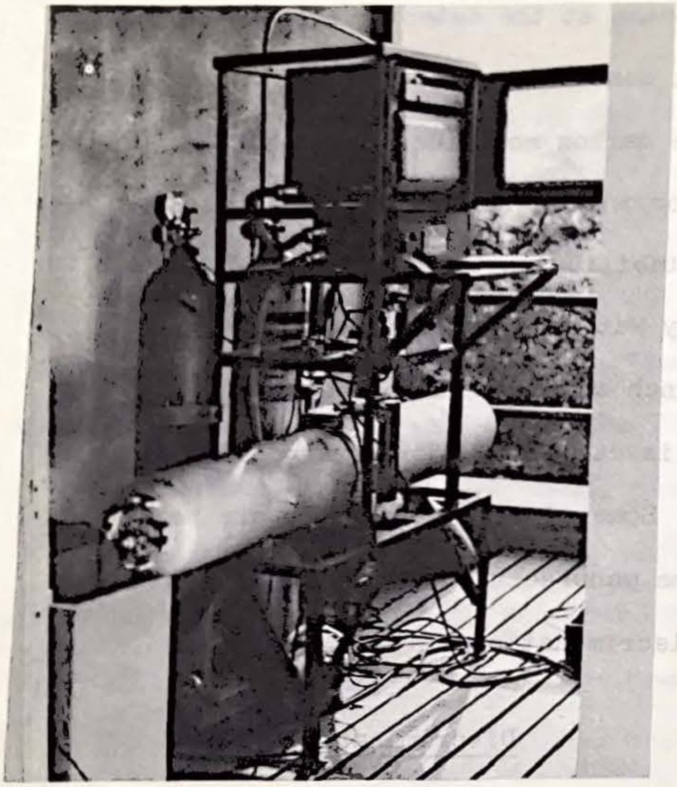
The instrument uses a 40-inch sample cell, pressurized to 45 pounds per square inch. It is calibrated for a range of 0 to 25 ppm carbon monoxide in air. Some of the instruments are being modified for higher ranges. The manufacturer, Mine Safety Appliances Company, gives the following discriminations:

Material	Discrimination
Carbon dioxide	5000/1
Light hydrocarbons	
A. Methane	5000/1
B. Ethane	500/1
Water vapor	4000/1

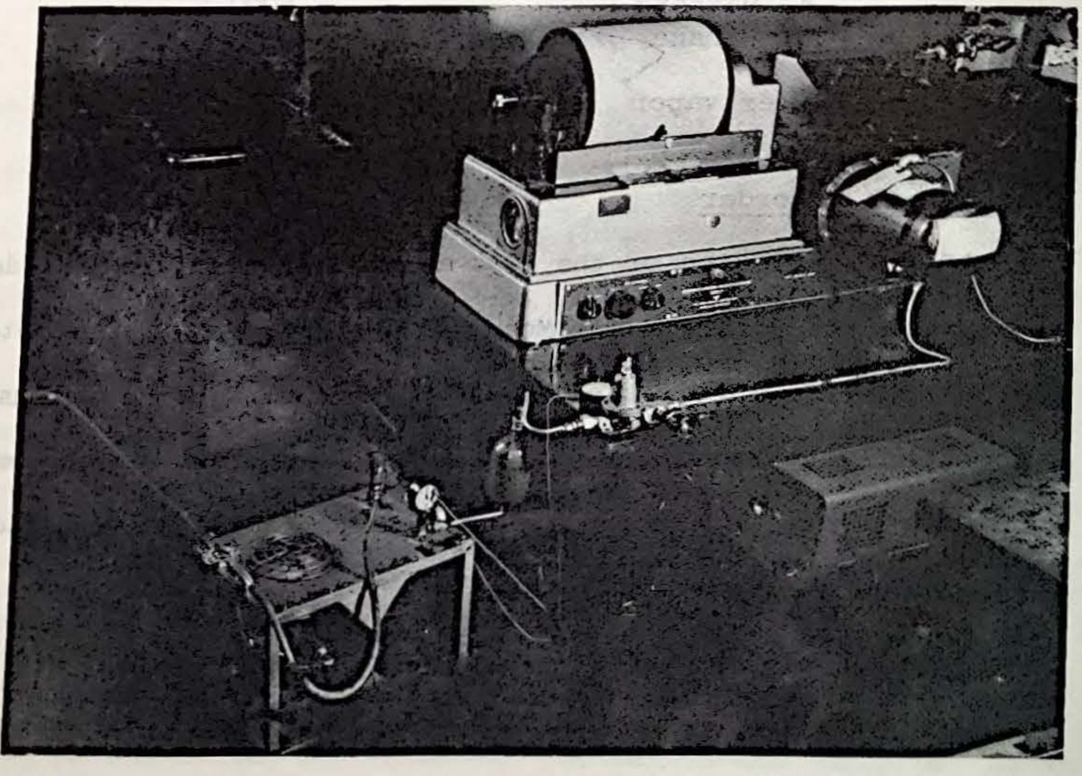
Hydrocarbon Recorder

After completion of the 1954 aerometric survey, it was decided to convert the Perkin-Elmer Model 21 infrared spectrophotometer with its pressurized multireflection 10-meter cell to a continuous hydrocarbon analyzer recorder. This has been satisfactorily accomplished. The instrument, together with its accessory pump and regulators, is illustrated in Figure 10.

Truesdail Laboratories developed this instrument under contract with the Air Pollution Foundation. A three-stage Cornelius compressor,



Chapter I - Fig. 9
Carbon Monoxide Analyzer Recorder



Chapter I
Fig. 10
Hydrocarbon
Recorder

capable of delivering air at 2500 pounds per square inch was purchased. This compressor was modified by reducing its speed to one-tenth of the original speed and by substituting Dow Corning Silicone 550 as a lubricant. This was done to avoid contamination of the air sample with hydrocarbons when a hydrocarbon lubricant was used.

The air sample must be dried before admission to the pressure cell. Several drying agents were tested for retention of low concentrations of hydrocarbons in the presence of water vapor, and Drierite was found to be satisfactory.

The spectrometer, although not designed originally as a continuous recorder at a fixed wave length, was adapted for recording at 3.45 microns. With a cell pressure of 140 pounds per square inch, a hydrocarbon concentration of 0.10 ppm can be estimated. A constant flow is obtained by allowing about 3 liters of air per minute to bleed out of the gas cell. Under these conditions an average turnover time of about 15 minutes is obtained. A small surge vessel was introduced into the line between the compressor outlet and intake of the pressure cell to smooth out small pressure irregularities. The spectrometer was modified by substituting a 20 per cent wedge in place of the 100 per cent unit. Full-scale deflection is equivalent to approximately 2 ppm of hydrocarbon in the air sample.

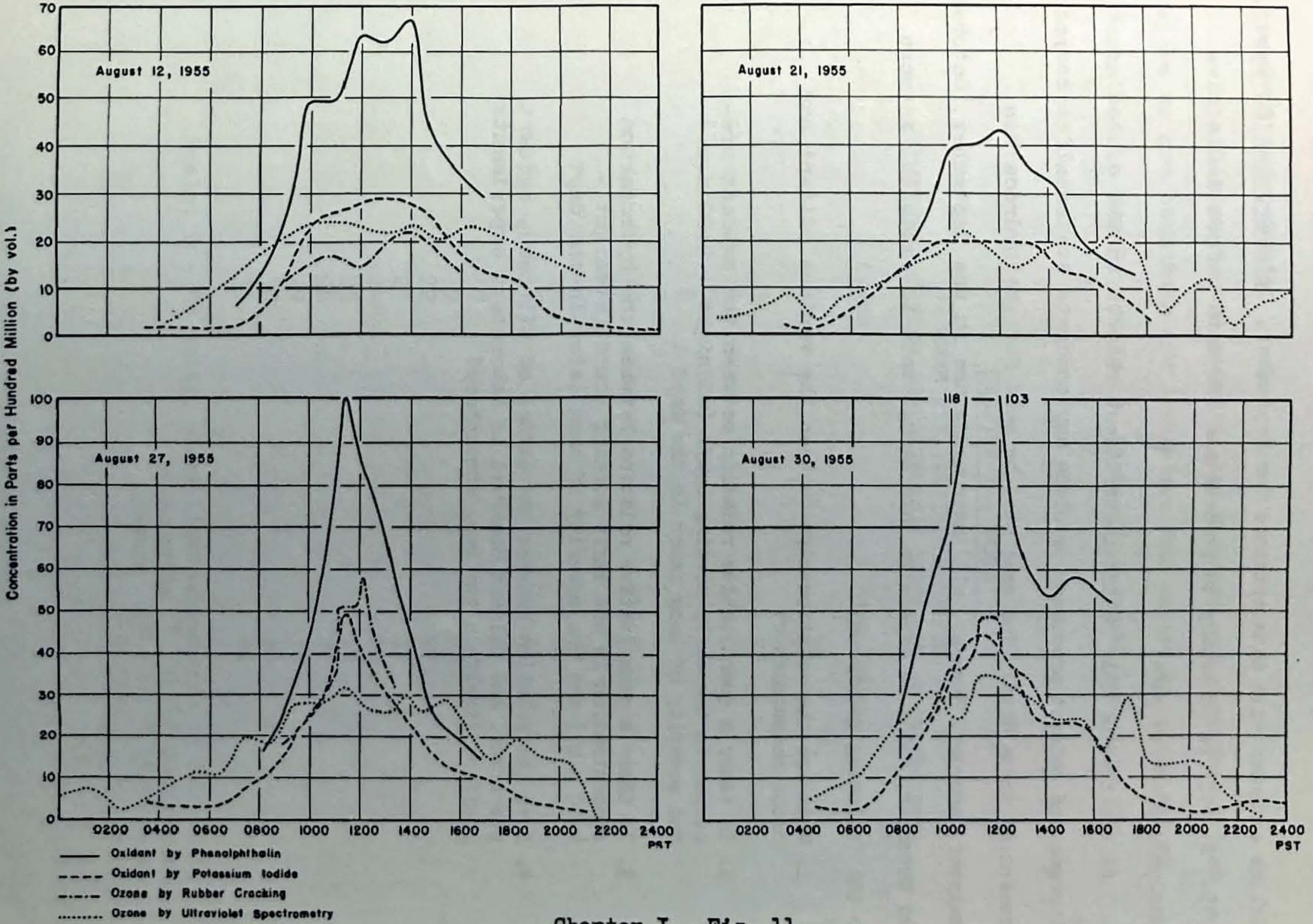
This unit is presently being operated by the Foundation at the Pasadena station to determine its operating characteristics.

The present unit demonstrates the feasibility of this approach to the problem of reading hydrocarbons in the air continuously in the range of 0 to 2 ppm. For air monitoring, a more economical unit should be designed, using an infrared stream analyzer, either of the dispersion or nondispersion type.

E. AIR MONITORING STUDY IN PASADENA — JULY - NOVEMBER 1955

Comparative Study of Oxidant and Ozone

In connection with the development of the various instruments discussed in the previous section, we are obtaining considerable data on concentrations of oxidant, ozone, and oxides of nitrogen in the atmosphere. In particular, in cooperation with the Air Pollution Control District and Dr. A.J. Haagen-Smit of the California Institute of Technology, we are able to make an extensive comparative study of oxidants with special reference to ozone. The District has kindly made available to us their data on oxidant by potassium iodide and ozone by rubber cracking; Dr. Haagen-Smit has made available to this study his determinations of oxidant by phenolphthalin. Figure 11 shows plots of the oxidant and ozone values obtained by the various techniques. It had previously been known that the phenolphthalin method shows a greater response to total oxidants in smog, being responsive not only to ozone but also to peroxides and nitrogen dioxide. This pattern is consistently reproduced over the forty days of data obtained. A second characteristic of these data is the relatively close agreement between oxidant by potassium iodide and ozone by rubber cracking (Ref. 13) for much of the time. However, there are some departures from this behavior (see Figure 11). As a third characteristic of these data, ozone concentrations by ultraviolet spectrometry are consistently below all other measurements, although there are isolated cases of agreement with either oxidant by potassium iodide (Figure 11) or ozone by rubber cracking. Furthermore, the differences become greater for the larger values. These studies



Chapter I - Fig. 11
Diurnal Variation of Oxidants and Ozone Measured at Pasadena
California Institute of Technology

will be extended with data obtained for September, October, and November, 1955. It will be necessary to process all the data before definitive conclusions can be made.

At the time of this report insufficient records on the oxides of nitrogen and oxidant precursor preclude any concrete statement to be made concerning these data. The same must be said for the hydrocarbon analyzer recorder. However, all instruments are in use September, October, and November, 1955. We expect to have enough data to establish answers to the following questions:

1. What are the relationships between the various oxidant and ozone measurements?
2. Is there a quantitative relation between the oxidant precursor in the early morning hours (midnight - 4:00 a.m.) and severity of smog later in the day?
3. Is there a quantitative relation between the hydrocarbon concentration in the early morning hours (midnight - 4:00 a.m.) and the severity of smog later in the day?
4. Does the relation between the oxides of nitrogen, oxidant precursor, and oxidant observed in laboratory experiments manifest itself in the smog atmosphere?

Eye Irritation Study

In addition to the chemical and physical measurements outlined above we are obtaining eye irritation data according to the method described in our Report No. 4. Table IV presents these data for August 1955.

CHAPTER I - TABLE IV

MEAN EYE IRRITATION VALUES
SAMPLING STATION AT CALIFORNIA INSTITUTE OF TECHNOLOGY

August	Mean Value
1	24
2	28
3	23
4	24
5	24
8	20
9	19
10	24
11	24
12	26
15	14
16	17
17	20
18	19
19	20
22	22
23	23
24	20
25	19
26	27
29	36
30	36
31	22

Scale: 0 - 55 units, where Light corresponds to 0-20 units
Moderate " " 20-35 units
Severe " " 35-55 units

F. EXPLORATORY STUDIES

Ultraviolet and Infrared Spectrometry

Early in our review of the needs for detecting and identifying the many components of smog, we developed the point of view that spectroscopic methods had not been sufficiently exploited for this problem. Accordingly, we undertook a spectroscopic study of smog using readily available prism spectrometers to investigate the spectrum from the ultraviolet to the infrared. We also simplified the experiment by using a readily available powerful light source, the sun. The work was done in two parts: 290 millimicrons to 2 microns using a spectrometer with quartz optics during October 1954, and 1.0 to 15 microns using a spectrometer with rock salt and lithium fluoride optics during November 1954. The results were reported at the Third National Air Pollution Symposium in Pasadena, California, and published in the proceedings of that meeting.[1/] Briefly, they are as follows:

A pollutant, or pollutants, responsible for high optical absorption within the spectral region of 340 to 400 millimicrons was also responsible for the incidence of high oxidant as measured by potassium iodide. Nitrogen dioxide could be this pollutant.

Attenuation in the region of 290 to 320 millimicrons, which could be ascribed to ozone, was detected. However, it is not possible to make a quantitative determination of ozone thereby.

[1/] "Proceedings of the Third National Air Pollution Symposium," sponsored by Stanford Research Institute, April 18-20, 1955.

In the infrared, there were indications of increased absorption in the 3.4 micron hydrocarbon band and of a new unidentified absorption at 3.36 microns. In order to adequately resolve these data it appears necessary to go to the use of a grating instrument with a land-based powerful source of infrared energy.

Mass Spectrometry - Carbon Isotope Study

INTRODUCTION - A study of carbon isotopes in the Los Angeles atmosphere is being performed by Professor S. Epstein at the California Institute of Technology under a research grant from the Air Pollution Foundation.

Previous studies of the isotope ratio C^{13}/C^{12} of carbon in coal, petroleum, wood, and atmospheric carbon dioxide showed a variability which reflected both natural and man-made activities. In addition, the isotope ratio O^{18}/O^{16} of oxygen, found in carbon dioxide equilibrated with the ocean, is different from that found in the normal atmosphere. Therefore, a study of these ratios in carbon dioxide found in the Los Angeles atmosphere seems pertinent to an understanding of the processes taking place therein.

For example, the C^{13}/C^{12} ratio of carbon in coal and oil is different from that in atmospheric CO_2. Therefore, burned carbonaceous material may be expected to affect this ratio as well as that of oxygen O^{18}/O^{16} in CO_2. In particular, the C^{13}/C^{12} ratio in carbon dioxide equilibrated with the ocean would be about 2 per cent greater than in carbon dioxide from combustion of coal and petroleum derivatives. Similarly, the O^{18}/O^{16} oxygen ratio in carbon dioxide equilibrated with the ocean would be 1.5 per cent greater than this ratio in normal atmospheric oxygen.

During this reporting period, work on this project has been limited to a study of carbon (C^{13}/C^{12}) and oxygen (O^{18}/O^{16}) isotopes in atmospheric carbon dioxide. A series of samples were taken to determine the diurnal effect as well as the geographical distribution over the Los Angeles Basin.

EXPERIMENTAL PROCEDURE - Five-liter flasks are evacuated and taken to the sampling sites. For each flask, a stopcock is opened to admit the sample at the time desired. The flasks are returned to the laboratory where in turn each is connected to the gas-handling glass system. The sample of air is slowly pumped through a liquid nitrogen trap in order to condense the carbon dioxide and other condensable material. Purification is accomplished by distillation. In this manner, about 1½ cubic centimeter of pure carbon dioxide is obtained and measured in a monometer, and this sample is introduced into a specially designed mass spectrometer in order to obtain the C^{13}/C^{12} and O^{18}/O^{16} ratios.

VARIATION IN CARBON DIOXIDE CONCENTRATION IN PASADENA AIR - Between April 4 and April 22, 1955, forty-nine samples of air taken at the California Institute of Technology were analyzed. The concentration data suggest that two factors operate nearly independently to produce variations in the concentration of carbon dioxide at a level of 15 meters above ground.

A diurnal variation with highest values in the early morning near sunrise and lowest values near midday is attributed to gas exchange with plants and soil. This variation was almost completely suppressed during a gentle rain during the night of April 21-22, 1955. A smaller variation, which can be expressed by a fluctuation in the midday concentration, correlates with features of local weather: clear, windy days - lowest, stagnant smoggy days - highest in concentration. A comparison of midday values with the concentration of oxidant in the air at the same time (taken as a measure of smog) shows roughly parallel behavior with major inflections in midday concentration curves occurring twice on identical days, once on successive days. A weather cycle with a period of about six days can be noted in the data, the highest minima and oxidant concentrations occurring during the fourth to sixth days of a period which begins with a front passage and strong winds aloft (see Table V). A few nighttime values are quoted in Table VI. The C^{13}/C^{12} ratios vary systematically with the concentration (see Figure 12). O^{18}/O^{16} ratios fluctuate between zero and -1.1 per cent but show no trends with any of the other quantities measured.

ISOTOPE RATIOS OF CARBON DIOXIDE IN AIR OF THE LOS ANGELES AREA - On June 22, while Pasadena experienced a smog attack, air samples were taken across the smog gradient between the California Institute of Technology and the ocean at Corona del Mar. A direct relationship was found between carbon dioxide concentration and isotope composition, suggesting the addition to normal air of industrial carbon dioxide with an isotopic composition $\delta_c = -35$ per cent. The O^{18}/O^{16} ratio was close to the ratio for atmospheric oxygen (Epstein, private communication), and combustion in air of very light (negative C^{13}/C^{12}) carbon was indicated. The fluctuations observed at California Institute of Technology during April give, by similar calculation, $\delta_c = -30\%$.

CHAPTER I--TABLE V *

CONCENTRATION AND C^{13}/C^{12} RATIOS OF CARBON DIOXIDE COMPARED WITH OXIDANT CONCENTRATION IN MIDDAY AIR AT CALIFORNIA INSTITUTE OF TECHNOLOGY

Date	CO_2 Conc. (ppm)	δ_c	Oxidant Conc. (pphm)	Approx. Day of Cycle
1955				
April 4	324	-7.1	10	1st (mP)
" 5	322	-6.9	10	2nd
" 6	328	-7.6	30	3rd
" 7	327	-7.7	40	4th
" 8	338	-8.2	40	5th
" 9	338	-8.5	60	6th
" 10	328	-7.8	30	1st (mP)
" 11	missing	--	20	2nd
" 12	324	-7.3	30	3rd
" 13	342	-8.8	60	4th
" 14	338	-8.7	30	5th
" 15	337	-8.5	30	6th
" 16	329	-7.4	20	1st (mP)
" 17	missing	--	10	2nd
" 18	324	-7.1	10	3rd
" 19	326	-7.3	10	4th
" 20	330	-7.6	30	5th
" 21	323	-7.4	10	6th (rain)
" 22	327	-7.8	10	1st (mP)

---

* Samples were taken between 1100 and 1600 PST

Oxidant as determined by Dr. Haagen-Smit at California Institute of Technology

δ_c = ([C^{13}/C^{12} divided by C^{13}/C^{12} of standard gas] minus one) x 1000

mP = maritime polar air aloft

CHAPTER I--TABLE VI

CONCENTRATION AND C^{13}/C^{12} RATIO OF CARBON DIOXIDE IN NIGHT AIR AT CALIFORNIA INSTITUTE OF TECHNOLOGY

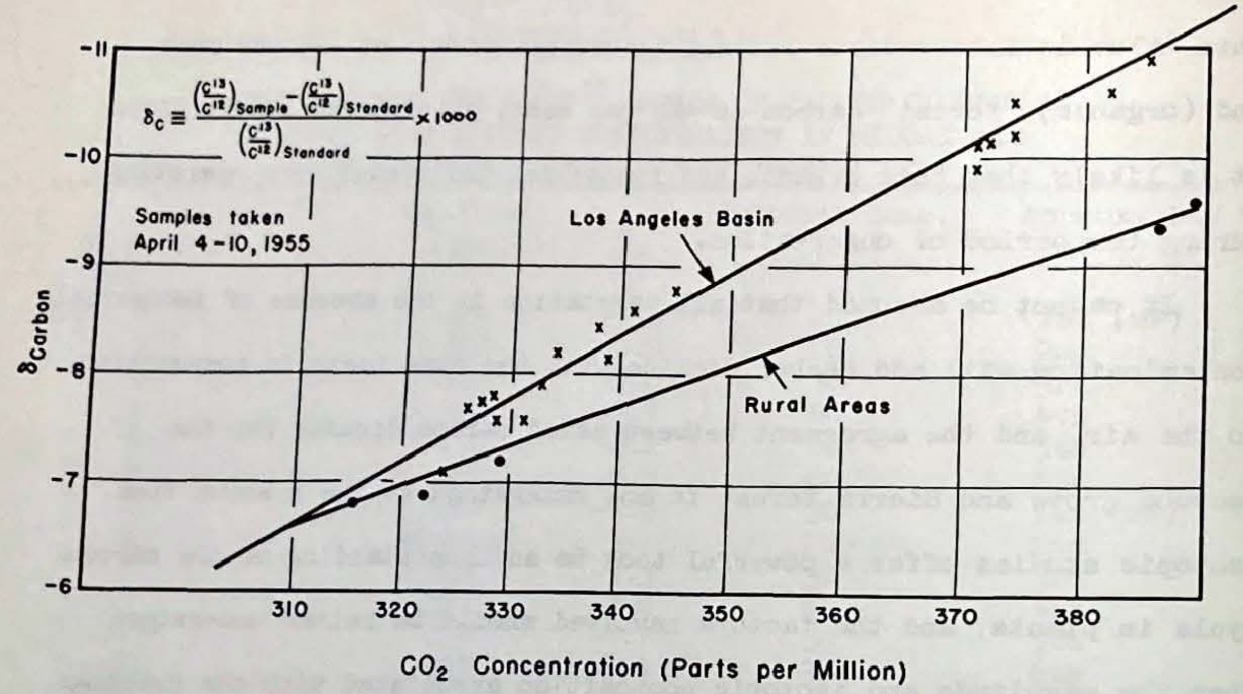
Date	Time	CO_2 Concentration (ppm)	δ_c
1955			
April 5	0200	370	-10.2
" 6	0630	372	-10.2
" 7	0100	371	- 9.9
" 8	0040	374	-10.1
" 9	0000	385	-10.9
" 10	0040	382	-10.6

This value is intermediate between industrial carbon at -35 per cent and (organic) "forest" carbon at -22 per cent, an expected result since it is likely that both organic and industrial influences were operating during the period of observation.

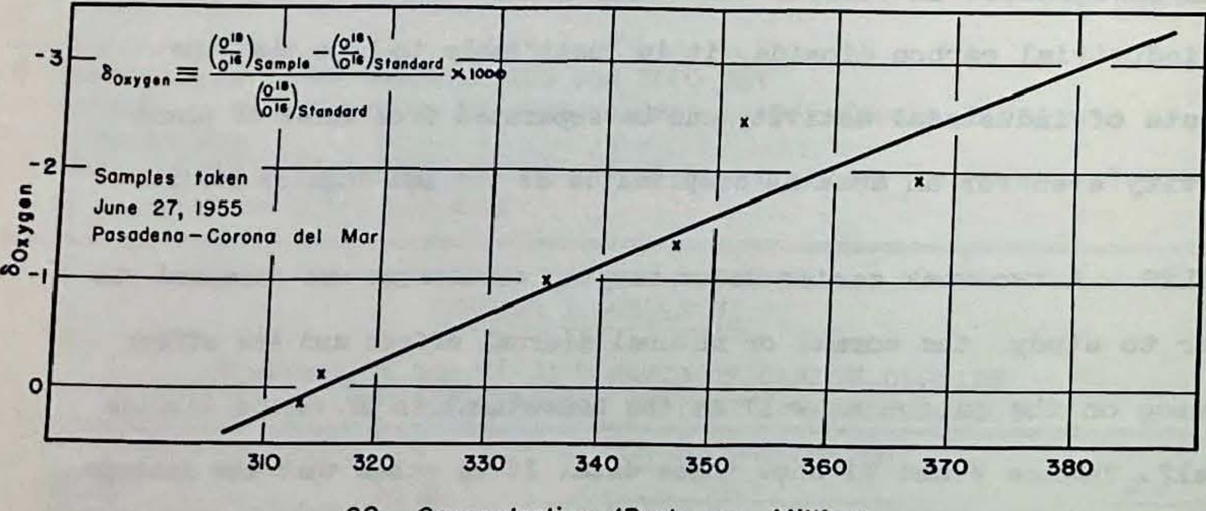
It cannot be assumed that all vegetation in the absence of industrial contamination will add carbon dioxide with the same isotopic composition to the air, and the agreement between added carbon dioxide for the redwood grove and Sierra forest is not understood at the present time. Isotopic studies offer a powerful took to an understanding of the carbon cycle in plants, and the factors involved should be better understood when the magnitude and isotopic composition associated with the exchange have been measured at a sufficient number of locations to allow generalizations to be made with respect to plant species, climate, and local influences. In view of the very negative C^{13}/C^{12} ratios observed for industrial carbon dioxide, it is justifiable to hope that the effects of industrial activity can be separated from those of plant activity even for an area as complicated as the Los Angeles Basin.

RESULTS - A two-week series under varying conditions was obtained in order to study the normal or natural diurnal effect and the effect of smog on the ratios as well as the concentration of carbon dioxide itself. Tables V and VI show these data. It is noted that the isotope ratio is proportional to the concentration of carbon dioxide.

A second series was collected in remote rural areas free from industrial contamination. Nighttime concentrations reached values comparable to those in industrial areas, but the C^{13}/C^{12} ratio does not go as low in the rural areas as it does in industrial areas for



Chapter I - Fig. 12
Variation of Carbon Isotope Ratio C^{13}/C^{12} in
Carbon Dioxide with Concentration of Carbon Dioxide



Chapter I - Fig. 13
Variation of Oxygen Isotope Ratio O^{18}/O^{16} in
Carbon Dioxide with Concentration of Carbon Dioxide

equivalent concentrations.

A third series was collected during a smoggy day over a period of one and one-half hours. Samples were taken at ground level across a traverse from Pasadena (foothills) to Corona del Mar (ocean). The concentration of carbon dioxide was highest in Pasadena and decreased toward Corona del Mar. Figure 12 shows the data. Again a direct relationship between the isotopic ratios and the concentration is noted. In this case, there is also a relationship between the O^{18}/O^{16} ratio and the concentration of carbon dioxide (see Figure 13). In fact, the isotopic composition of the oxygen in the carbon dioxide samples cannot be distinguished from the free oxygen (O_2) in the normal atmosphere. Thus, it appears that the oxygen ratio can serve as an indicator of carbon dioxide derived from oxidation of organic material.

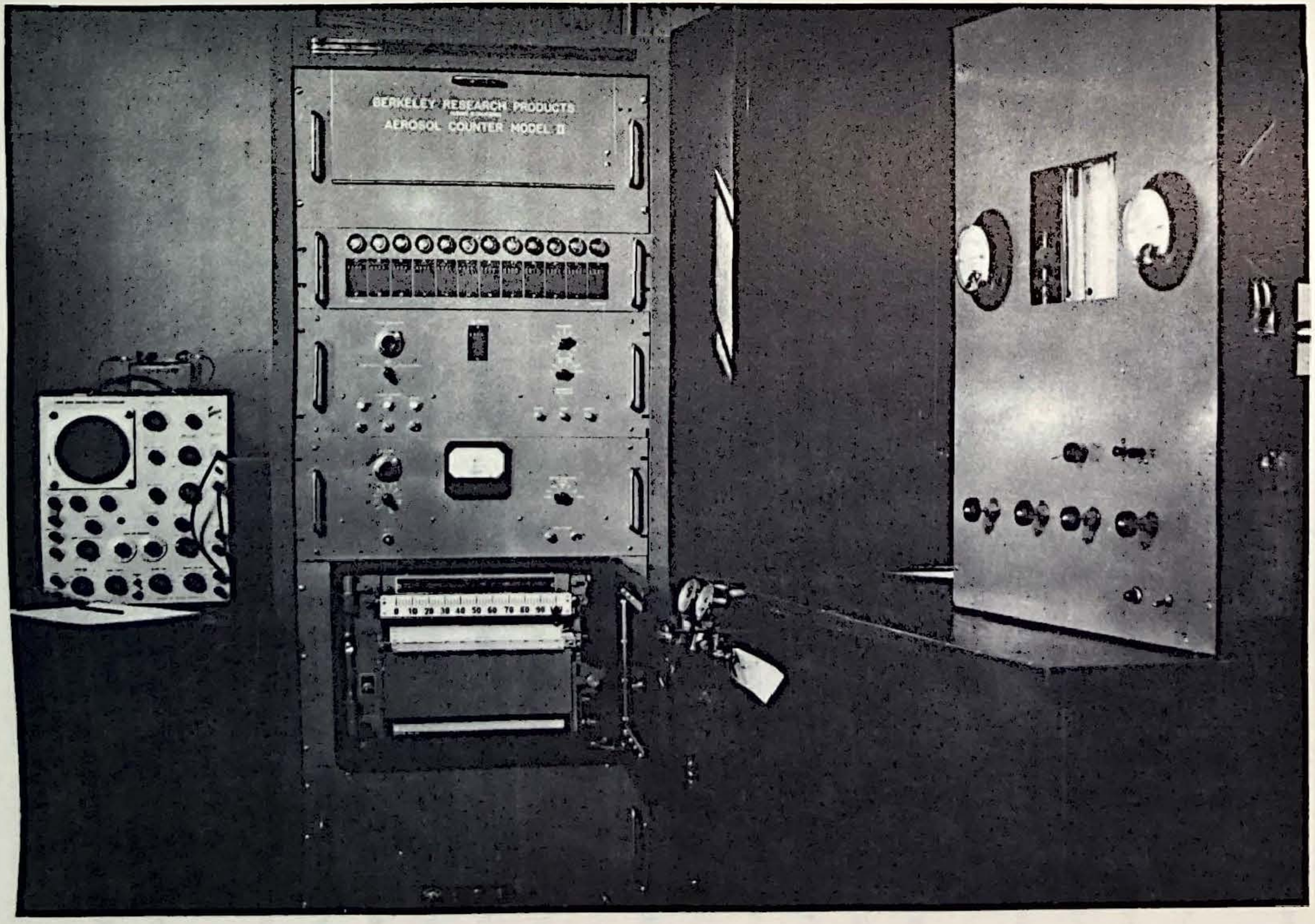
Since it is expected that the C^{13}/C^{12} ratio of photosynthesized material should be affected by the C^{13}/C^{12} ratio of the atmospheric carbon dioxide, a series of tree rings from trees on the campus of California Institute of Technology was obtained and dated by Dr. Schulman of the University of Arizona; then these were run for the C^{13}/C^{12} ratios. In one case the C^{13} concentration increased with age. However, further work is necessary to ascertain whether this effect is correct and what other factors play important roles in carrying the C^{13}/C^{12} ratios in wood.

FUTURE WORK - We expect to sample the smog atmosphere for carbon dioxide at various altitudes in the Los Angeles Basin. Thereby we hope to get more data on the effect of smog on the oxygen isotope ratio to substantiate the preliminary results obtained so far.

Aerosol Studies

The word aerosol is a convenient name for particulate matter, whether liquid or solid, which is dispersed in air. In order to remain dispersed for a long period of time, the particles must be very small (less than 5 microns) in size. These small particles are responsible for the reduction of visibility and also may play a role in the other objectionable aspects of smog by providing surfaces where reaction can take place and on which reactants can be adsorbed, concentrated, and transported to sensitive tissues. Some knowledge of the chemical composition of the particulate component of smog was obtained by high volume sampling during the aerometric survey. In order to find out more about the size distribution of the aerosol component, to determine the chemical composition of the particles in various size ranges, and ultimately to learn the source of the aerosol component and the mechanism of its formation, the Foundation has established a project in which the several aspects of the aerosol problem will be correlated.

As a first step in the organization of this project a conference on aerosols was conducted on April 20 and 21, 1955 under the auspices of the Foundation. At this conference thirty of the leading experts on the subject of measurement and analysis of particulates in the atmosphere exchanged their views. Reports were presented on the natural and industrial aerosols which had been measured elsewhere in the world, the present knowledge of the aerosol component in Los Angeles smog, and the merits of various types of instruments and methods of analysis of the particle size distribution, the gross chemical composition, and the composition by size groups of individual particles. The discussion showed that there was general agreement



Chapter I - Fig. 14
Aerosol Counter

that additional information was needed concerning the aerosol component.

For the determination of size distribution of aerosols, the Air Pollution Foundation has procured an aerosol counter manufactured to its order by Berkeley Research Products, Albany, California. This instrument follows the design by O'Konski and Doyle (Ref. 14). It is based on the fact that the intensity of light scattered by a particle at right angles to the incident beam, when averaged over angle and wave length, varies monotonically and linearly with the area intercepted by the particle. Strictly speaking this result applies only to spherical particles of a given refractive index. Thus the counter results will be interpreted as giving the distribution of sizes of spherical water droplets, for instance, which would have the same distribution of scattering intensities as the observed aerosol. The counter has ten channels so that it will give the size distribution in ten intervals as well as the total number of particles and the number of particles larger than the largest falling into a presented channel. In order to avoid having more than one particle in the scattering beam at a time, it is necessary that the ambient air be diluted before passing through the counter. For this purpose a dilution system has been designed and built. Figure 14 shows the aerosol counter and the dilution system.

At the time of this writing the aerosol counter and dilution system are still undergoing tests and adjustments before being put into operation.

Microwave Spectrometry

As indicated previously, the Department of Engineering at the University of California at Los Angeles is actively investigating the usefulness of the microwave region of the spectrum for the analysis of smog components. As indicated in their report (Ref. 15), work is proceeding in three directions:

1. Propagation studies over a long path in smog;
2. Laboratory absorption studies of smog samples;
3. Paramagnetic resonance studies for such components as NO, NO_2, and free radicals.

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II. HOW IS SMOG FORMED?

A. INTRODUCTION

There is now ample evidence that much of the eye-irritating, plant-damaging, visibility-reducing and oxidant-forming mixture which exists in the Los Angeles atmosphere is the result of various photochemical reactions. The mechanism is not completely understood and there is still uncertainty as to the exact chemical equations. However, much progress has been made in recent months. To give a more complete account of this progress, the discussion in this chapter is not limited to projects sponsored by the Foundation but includes summaries of recent work by Haagen-Smit of the California Institute of Technology and Margaret Fox of the Air Pollution Control District (Ref. 1) and by Stephens, Hanst, Doerr, and Scott (Ref. 2) of the Franklin Institute, under sponsorship of the American Petroleum Institute.

B. RECENT WORK BY HAAGEN-SMIT AND FOX

Experiments were made on the formation of ozone, using various concentrations of hydrocarbons or their derivatives and nitrogen dioxide. Bent rubber strips were suspended in 5-liter flasks and exposed to blue fluorescent lights for 10 hours. The depth of rubber cracking was used as a measure of ozone concentration.

A maximum of rubber cracking was found with 3 ppm 3-methylheptane and about 1 ppm to 3 ppm of nitrogen dioxide. With the same concentration of hydrocarbons and 5 ppm to 10 ppm of nitrogen dioxide, no rubber cracking was observed. In other experiments the hydrocarbon concentration was varied from 0.1 ppm to 10,000 ppm. Results indicated that the formation of ozone was limited to definite relative proportions of hydrocarbons and nitrogen dioxide. Furthermore, it was shown that ozone formation was not limited to hydrocarbons but was also due to their oxidation products, including acids, aldehydes, ketones, and alcohols.

The general shape of the curves obtained was attributed to at least two simultaneous reactions: (1) the formation of ozone, and (2) the removal of ozone by nitrogen dioxide and the hydrocarbon oxidation products. The average rate of ozone formation during the first 10 hours' irradiation of 3 ppm 3-methylheptane and 1 ppm nitrogen dioxide was about 0.8 ppm per hour.

It was observed that as the length of the carbon chain in the straight chain paraffins increased from C_4 to C_9, the ozone-forming capacity became greater. Methane, ethane, and propane were found to be inactive.

With olefins, ozone formation was greater than with the corresponding saturated paraffins. The optimum ozone formation was found with olefins of four to six carbon atoms.

Pronounced rubber cracking was observed with the alcohols and aldehydes with one to four carbon atoms. The effect of substitution of the hydrogen by different functional groups was studied in the case of ethane. The following partial list is arranged in ascending order of ozone-forming ability, with ethane itself having no activity: ethane, ethyl nitrate, ethyl amine, ethyl alcohol, and ethyl nitrite.

In summary, these workers have shown that ozone can be formed by photolyzing suitable mixtures of many organic compounds and nitrogen dioxide. Hydrocarbons and their derivatives, including gasoline as well as automobile exhaust, in the presence of certain definite proportions of nitrogen dioxide will give this reaction.

C. RECENT WORK BY STEPHENS, HANST, DOERR, AND SCOTT AT FRANKLIN INSTITUTE (SPONSORED BY AMERICAN PETROLEUM INSTITUTE)

A photolysis system consisting of a large multiple reflection infrared cell equipped with a water-cooled high-pressure mercury arc was used to study the reactions of various hydrocarbons and organic compounds with nitrogen dioxide. Direct infrared evidence of the formation of ozone was found.

When nitrogen dioxide (5ppm) and 3-methylheptane (10 ppm) in oxygen were irradiated, the products observed were alkyl nitrate, alkyl nitrite, formic acid, and ozone. The rate of formation of ozone from 3-methylheptane and nitrogen dioxide was studied over a range of concentrations of both reactants. The results agree quite well qualitatively with those reported by Haagen-Smit and Fox.

The photochemical reaction of nitrogen dioxide with a series of organic compounds representative of various types was also reported. Butyraldehyde, biacetyl, methyl-ethyl ketone, 1-pentene and 2-pentene, all formed ozone when irradiated with nitrogen dioxide in oxygen. Butyl alcohol produced a small amount while benzene and butyric acid gave none. Both the rate of formation of ozone and the rate of disappearance of nitrogen dioxide were most rapid with the olefins.

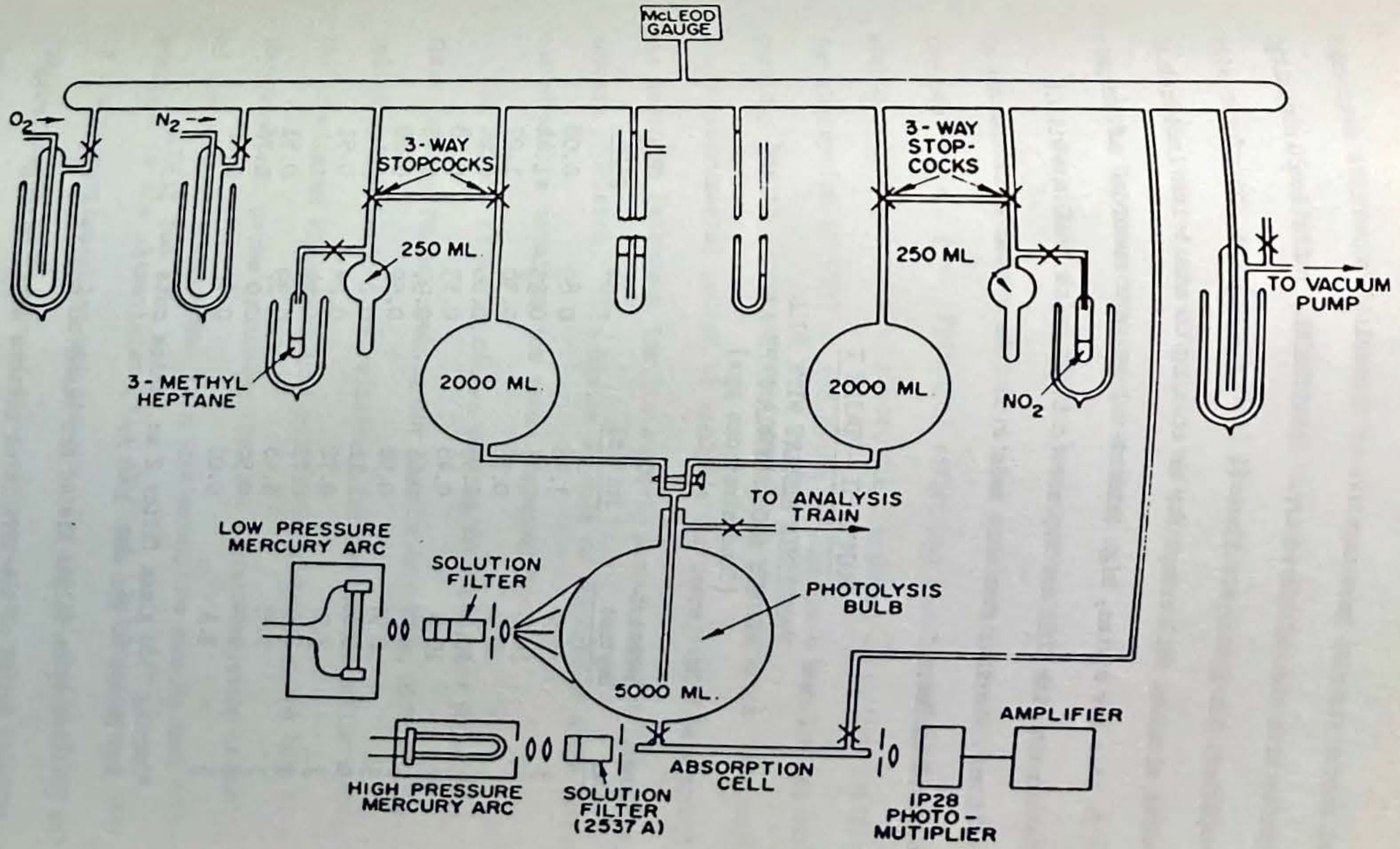
It was found that irradiation of nitrogen dioxide alone in oxygen will rapidly produce a transitory concentration of ozone. This was interpreted in terms of the build-up in nitric oxide concentration which reacts rapidly with any ozone formed. The data obtained thus far were not sufficient to determine unambiguously the detailed mechanism of ozone formation.

D. ARMOUR RESEARCH FOUNDATION PROJECT (SPONSORED BY AIR POLLUTION FOUNDATION)

In the Foundation's "First Technical Progress Report," issued March, 1955, reference was made to this project as being in the construction phase.

The objective of this program is to determine the conditions for photochemical reaction of selected trace materials in air to form ozone or other strong oxidants commonly associated with Los Angeles smog. Nitrogen dioxide and 3-methylheptane as a typical hydrocarbon have been selected for primary study.

The photolysis system shown in Figure 1 provides for irradiation through a lens system and chemical filters for isolation of selected spectral regions. With a mercury arc source (Hanovia Type A - 600 watts)



PHOTOLYSIS SYSTEM

Chapter II - Fig. 1
Photolysis System at Armour Research Foundation

initial photolysis runs gave negative or inconclusive results even on irradiation with the unfiltered arc. Insufficient radiation intensity was suspected; the photolysis flask (2 liter-Vycor) was therefore wrapped in aluminum foil except for an opening to admit the incident beam. In this new system, high oxidant values were recorded after irradiation with the full mercury arc (cut off below 3000 A. with a pyrex filter). Several runs were made with this system with the results listed in Table I.

CHAPTER II - TABLE I

PHOTOLYSIS RESULTS WITH FULL
MERCURY ARC (HANOVIA TYPE A)
(Concentrations ppm)

Time Hour	3-Methyl-heptane	NO_2 Initial	O_3	NO_2 Final
3	13.2	1.36	0.89	0.08
1	14.7	1.47	0.33	1.44
1	8.9	0.76	0.38	1.07
3	20.4	0.93	0.86	0.24
17	10.0	0.48	0.53	0.18
3	3.5	0.65	0.97	0.05
3	0.97	0.50	0.59	0.20
5	0.00	1.11	0.0	1.47
3	3.9	0.72	0.2*	0.51
3	2.3	0.72	0.44	-
3	1.35	0.48	0.39	0.51
3	0.04	0.50	0.0	0.76
3	3.3	0.00	0.0	0.00

*Corning 7380 glass filter 2 mm. thick cuts out 3130 A. but passes 60 per cent 3660 A.

The positive ozone values listed are based on analysis by the phenolphthalin method of the irradiated mixture after passage through traps packed with glass beads and cooled in liquid oxygen. Control tests of the procedure showed that ozone passed through the traps and nitrogen dioxide was efficiently trapped. Possible oxidants less volatile than nitrogen dioxide would presumably be trapped also. The oxidant results are, therefore, listed as ozone values based on evidence comparable to that of previous workers.

An independent instrumental method of analysis for ozone adapted to this photolysis system has not yet obtained sufficient sensitivity for use below 1 ppm. Principal effort has been concentrated on the adaptation of ultraviolet absorption. Apparent extinction coefficients for absorption of 2537 A. radiation by ozone have been low and variable, possibly due to decomposition of ozone by the radiation. Adaptation of a new instrumental method of analysis for ozone, under development for the American Petroleum Institute by the Armour Research Foundation, appears promising. This device depends on response of a thermistor coated with a catalyst for ozone decomposition.

The effect of a reflective coating around a Vycor photolysis flask, except for an opening for the incident beam, diffuses the radiation and leads to a relatively uniform radiation flux within the irradiated mixture. Analysis of the system with the help of a photoelectric probe indicates that the average radiation intensity of the present arrangement is approximately the same as that of noon sunlight in the ultraviolet (3000 to 3250A.), but considerably less in the near ultraviolet and visible. The initial design of the system was for isolation of selected wave-length regions rather than duplication of sunlight. A 900-watt DC Xenon arc will be used in future runs for a closer approach to the intensity and spectral distribution of sunlight.

For quantitative comparison of the photolysis results at different concentrations it is essential to have more data on the time variation of ozone concentration during a run. However, the present results show that irradiation of traces of nitrogen dioxide and 3-methylheptane results in a photochemical process producing ozone. The data also suggest that nitrogen dioxide is converted in the course of the reaction to a low vapor pressure product not recovered from the analysis trap after warming to room temperature. Analysis of nitrogen dioxide by the Saltzman reagent normally gives high results, but a pattern of low recovery in runs with high ozone is evident.

E. LITERATURE AND EVALUATION PROJECT, PHILIP A. LEIGHTON AND WILLIAM A. PERKINS, STANFORD UNIVERSITY (SPONSORED BY AIR POLLUTION FOUNDATION)

In the Foundation's "First Technical Progress Report" this project was mentioned as being in its initial stages.

The rates of photochemical primary processes within the polluted layer have been calculated for a number of substances for which absorption coefficients are available. These calculations were based on the equation

$$I_a = \Sigma\, 2.303\, \alpha\lambda\, c(I_{d\lambda} \sec Z + 2I_{s\lambda})$$

where $\alpha\lambda$ is the absorption coefficient at wave length λ and c the concentration of the substance in question, $I_{d\lambda}$ and $I_{s\lambda}$ are respectively the direct and diffuse solar irradiance per unit horizontal area over interval $\Delta\lambda$ centered on wave length λ, and Z is the solar zenith angle. Calculations are made for intervals of $\Delta\lambda$ = 100A. The rate of absorption I_a is the summation of these values over the entire absorption range.

CHAPTER II - TABLE II

RATE OF PHOTOCHEMICAL PRIMARY PROCESSES

Absorber	Wave Length Region, A.	Probable Primary Process	Rate in pphm/hour
NO_2	2900-3850	$NO_2 + h\nu \rightarrow NO + O$	150
NO_2	3850-6500	$NO_2 + h\nu \rightarrow NO_2$	800
Ethyl Nitrite	2900-4100	$RONO + h\nu \rightarrow RON + O$ $\searrow RO + NO$?	40
Oxygen	6800-7700	$O_2 + h\nu \rightarrow O_2' \; ({}^{1}\Sigma \quad g)$	14
Ozone	2900-3500	$O_3 + h\nu \rightarrow O_2' \; ({}^{1}\Sigma \quad g) \; O$	1.3
Ozone	4500-7000	$O_3 + h\nu \rightarrow O_2 + O$	7.2
Butylene Ozonide	2900-3300	?	(0.3)
Acetaldehyde	2900-3500	$RCHO + h\nu \rightarrow R + CHO$	0.2
Nitric Acid	2900-3200	$HNO_3 + h\nu \rightarrow OH + NO_2$?	(0.0)
Diethyl Peroxide	2900-3200	$ROOR + h\nu \rightarrow 2RO$?	(0.02)
Allyl hydroperoxide	2900-3200	$ROOH + h\nu \rightarrow RO + OH$?	(0.01)

The results given in Table II are for a solar zenith angle of 60°, corresponding to 7:20 a.m. PST in Los Angeles on June 21, 8:15 a.m. PST on September 21, and 10:40 a.m. PST on December 21. In all cases except oxygen they are for concentrations of 10 pphm.

Uncertainty in the primary process is indicated by a question mark, and uncertainty in the rate due to uncertainty in absorption coefficients is indicated by brackets. The list is by no means complete, and values for other substances are in process of calculation.

The observed rates of increase in oxidant concentration at zenith angles of 60° on the mornings of smoggy days in Los Angeles are for the most part between 1 pphm and 15 pphm/hour. Occasional very sharp increases may be due to changes in wind trajectory. The average rate of increase in oxidant concentration at ten stations in the Los Angeles Basin for the period August through November 1954 was 1.8 pphm/hour at $Z = 60^\circ$. The rate of increase at $Z = 60^\circ$ on the day of greatest oxidant value at each station during this period averaged 7.6 pphm/hour (Ref. 3). The latter figure is compared in Table III with the rates of production of the primary products listed in Table II. It is assumed that the rates of absorption of the organic compounds in Table II are representative of their classes.

CHAPTER II - TABLE III

RATE OF PRODUCTION OF PRIMARY PRODUCTS COMPARED WITH OBSERVED RATE OF INCREASE IN OXIDANT.

Primary Product	Ratio of rate of production at absorber concs. of 10 pphm, to av. max. rate of increase in oxidant conc. (7.6 pphm/hr)
Excited NO_2 molecules	105
O Atoms	22-26
NO molecules	20-25
Excited O_2 molecules $(^1\Sigma^+_g)$	2
Organic free radicals from alkyl nitrites	5
Organic free radicals, all other primary sources	0.07
OH radicals	0.009

The figures in Tables II and III lead to several interesting conclusions. In the first place, in order to produce oxidant without a secondary chain reaction, the rate of production of primary products must be equal to or greater than the observed rate of increase in oxidant concentration. That is, the ratio in Table III must be equal to or greater than unity. The only absorbers which would appear to qualify on this basis are nitrogen dioxide, organic nitrites, oxygen, and possibly ozone; and the only primary products formed at sufficient rates are oxygen atoms, excited NO_2 molecules, NO, excited O_2 molecules, and free radicals from organic nitrites. The primary products from absorption by aldehydes, ozonides, peroxides, hydroperoxides, and nitric acid will require secondary chain reactions in order to lead to oxidant production at the observed rates.

In making this comparison several points should be kept in mind. First, the calculated rates are for concentrations (except O_2) of 10 pphm. For other concentrations the rates are proportional. Second, highly absorbing substances not in the table, such as acrolein or biacetyl, might produce primary radicals at the required rate, provided they exist in the air at sufficient concentrations. Third, the almost symmetrical shapes of the curves showing oxidant concentrations vs. time, with afternoon decreases in concentration matching the morning increases (Ref. 4), suggest a stationary concentration, with the possibility that the actual rate of oxidant production may be much greater than the observed rate of increase in its stationary concentration.

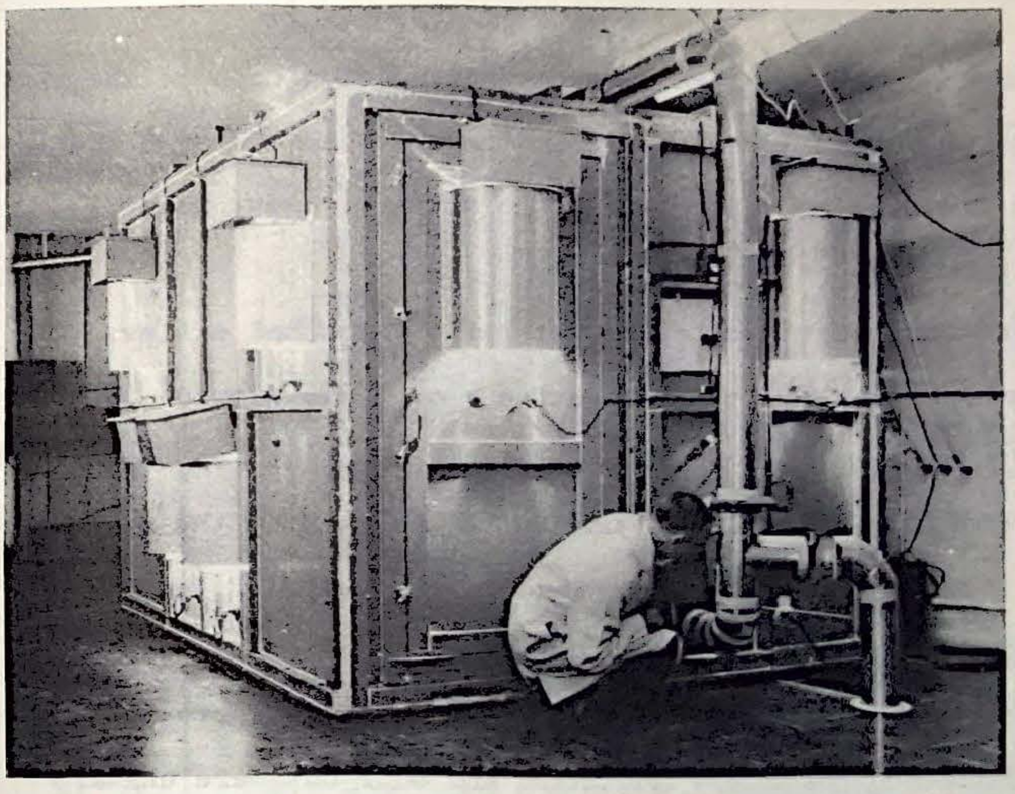
The above information on primary rates is now being applied to secondary reactions.

F. SMOG-FORMING REACTIONS AT STANFORD RESEARCH INSTITUTE, PASADENA, CALIFORNIA (SPONSORED BY THE AIR POLLUTION FOUNDATION)

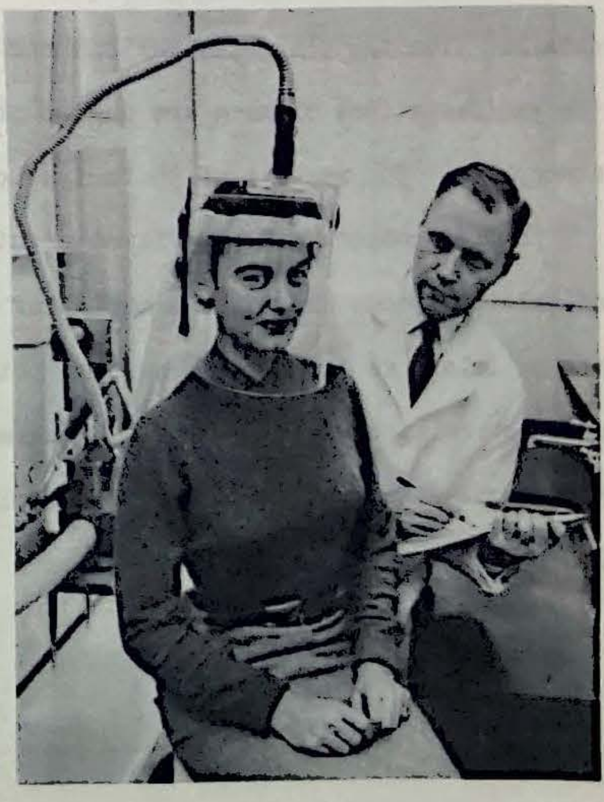
In the Foundation's "First Technical Progress Report," March, 1955, some early results from this project were given.

A chamber was constructed in which the average light intensity (between 3200 and 4000 A.) was made to approximate midday sun by means of mercury arcs. The chamber was about 500 cubic feet in volume and was so constructed that the residence time for a parcel of air passing through it could be varied from a few minutes to two hours. (See Fig. 2). This chamber with two smaller auxiliary plant fumigation chambers formed the basic equipment used in this study.

Night air was irradiated in the chamber and passed into a smaller fumigation chamber in which a number of plants of several species were placed. Phytotoxic substances were produced in the night air by irradiation, as proved by the subsequent markings obtained on the plants. In addition, these marking were identical to those observed in the field after a natural smog attack. Among the plant species used, romaine lettuce gave very reliable markings and poa annua and pinto beans typical smog damage, whereas spinach exhibited no characteristic damage. These results with irradiated night air gave confirmation to the premise that smog had been formed by the irradiation of night air.



Chapter II - Fig. 2
Five Hundred Cubic Foot Irradiation Chamber, Stanford Research Institute



Chapter II - Fig. 3
Plastic Mask Used for Eye Irritation Studies
Stanford Research Institute

An attempt was made to generate smog by adding compounds to the existing atmosphere and irradiating the mixtures. When adding 5 ppm of gasoline to night air and irradiating the mixture, heavy plant damage was obtained.

A special transparent plastic mask was built which had a sieve-type duct at forehead height through which air at 1 cfm flowed over the face of a human subject. Night air, irradiated night air, or carbon-filtered night air could be admitted to the mask by the experimenter in any desired sequence without the knowledge of the subject. (See Fig. 3). Eye irritation tests were conducted during several of the irradiated night air fumigations. The subjects recorded their observations on eye irritation and odor but were unaware of the type of air being tested. The results showed definite irritation from irradiated night air. These results correlate with those obtained from the plant fumigations and give additional evidence that the manifestations of smog are due to photochemical reactions in the atmosphere. The results of 39 fumigations are summarized in Table IV.

In the studies with irradiated night air there was a higher level of oxidizing compounds at the outlet of the irradiation chamber than at the inlet, as measured by neutral potassium iodide. This finding again correlates with the results generally obtained with natural smogs. With romaine lettuce the threshold of plant damage was shown to be about 150 pphm of oxidant multiplied by hours of irradiation.

CHAPTER II - TABLE IV

SUMMARY OF PLANT FUMIGATIONS AND EYE IRRITATION STUDIES

Condition	Number of Fumigations	Measurements	Results
Irradiated night air (12 hour fumigation)	26	a. Oxidant b. 20,000 plant leaves on 4 species c. Eye irritants on 33 subjects; total 132 exposures to (1) Carbon filtered air (2) Night air (3) Irradiated night air	When total dosage of oxidant 150 pphm-hour, definite and characteristic smog damage on plants. Under same condition 50% of subjects tested experienced eye irritation. When dosage was < 150 pphm-hour, plant damage was erratic and eye irritation dropped to 10 - 20% of subjects tested.
Night air plus auto exhaust at 1,000 ppm plus irradiation (12 hours).(Idling exhaust at 1,000 rpm 30 minute residence time)	3	a. Oxidant b. 800 leaves examined on 4 species c. Eye irritants on 1 subject	Irradiation caused a substantial increase in oxidant; experimenter also noted an increase in eye irritation; damage to plants extensive and similar to smog.
Carbon filtered air plus ozone mixture (2 to 12 hours). (Ozone from 15-50 pphm)	10	a. Oxidant b. 4,000 leaves examined on 4 species	When oxidant > 20 pphm, plant damage usually resulted. Damage on romaine lettuce similar to smog damage.

G. AUTOMOBILE EXHAUST STUDIES. PROJECT AT MIDWEST RESEARCH INSTITUTE (SPONSORED BY AIR POLLUTION FOUNDATION)

In the Foundation's "First Technical Progress Report," March, 1955, reference was made to a project just started at Midwest Research Institute. The objective of this project was to determine the particular fraction or fractions of hydrocarbons from automobile exhaust which in the presence of ozone would produce typical smog damage on a selected plant, the pinto bean. In the report it was stated: "Initial results indicate that considerable difficulty may be expected in using the pinto bean for more than a qualitative estimation of plant damage." Later, difficulties in obtaining significant plant damage with comparatively high concentrations of either ozone alone or with ozone and automobile exhaust were laid to the hardiness of the particular plants used as compared with the test plants developed by Middleton (Ref. 5).

After consultation with Dr. Middleton, growing conditions for the plants were revised until a very susceptible plant was developed. This new plant was damaged by ozone alone at a concentration of 8 pphm but not at 5 pphm. It was apparent, then, that much closer control of growing conditions would be required to produce plants suitable for the desired objective of the project. At this point, information from our aerometric survey became available, which indicated that the plant-damaging characteristics of smog did not correlate well with other smog manifestations.

Therefore the project was re-evaluated and it was decided that in view of the difficulties encountered it would be simpler to ascertain the effect of automobile exhaust on smog manifestations by measuring eye irritation using a panel of fifteen subjects. Preliminary experiments failed to produce eye irritation when ozone was added to automobile exhaust at concentrations several times those believed to be realistic (as high as 6 ppm for hydrocarbons). However, when experienced quantities of nitrogen dioxide were added to the exhaust in a greenhouse in the presence of sunlight, severe eye irritation was noted almost immediately (see Fig. 4). In these first experiments, the calculated hydrocarbon concentration based on the amount of exhaust added was between 5 ppm and 10 ppm. However, probably because of wall absorption, the actual concentrations in the air during the period when eye irritation was noticeable were 1 ppm to 4 ppm of hydrocarbon and 0.13 ppm to 1.5 ppm of nitrogen dioxide. The study is being continued.

H. SUMMARY AND FUTURE PLANS

Production of ozone by photochemical reaction of a few parts per million of hydrocarbon and a few parts per million of nitrogen dioxide has now been confirmed in four laboratories. Much work remains to be done on the upper and lower limits of concentration of the materials which produce this reaction, the identity of the eye irritants, phytotoxicants and other products, and on the equations for these reactions. The work at Midwest Research Institute, the data

Chapter II - Fig. 4
Greenhouse Used for Experiments Irradiating
Automobile Exhaust - Midwest Research Institute

obtained in the 1954 aerometric survey, and other evidence indicate that the mechanisms by which eye irritation, ozone and phytotoxicants are produced are due to different reactions although these may occur in sequence.

A better understanding of the reactions contributing to eye irritation and other smog effects is essential in order to establish ~~minimum~~ maximum permissible concentrations of the various reactants. With this information, reasonable goals for the controls of emissions can be safely established.

In future experiments, irradiation of mixtures of organic materials (hydrocarbons and their derivatives from automobile exhaust, incinerators, and gasoline) with nitrogen dioxide will be emphasized. Variables to be studied will include (1) concentration of reactants and products; (2) irradiation time, intensity, and wave length; (3) eye irritation; (4) oxidant, and (5) plant damage. Study of the mechanism and kinetics of the reactions will be carried forward. Both small-scale laboratory experiments with volumes of several liters as well as larger-scale chambers with volumes of several hundred cubic feet will be used. In addition, calculations on probable absorbers and mechanisms will continue.

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CHAPTER II

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III. WHAT ARE THE SOURCES?

A. BACKGROUND AND STATUS

There is general agreement that the obnoxious effects of smog in the Los Angeles Basin come from pollutants put into the air by human activities. [1] The three major effects are eye, nose, and throat irritation; plant damage; and reduced visibility. As pointed out in the preceding chapters, the consensus is that the first two of these effects are due to products of photochemical reactions involving hydrocarbons and nitrogen dioxide, while the third is due not only to the aforementioned photochemical reactions but also to particulate matter resulting from various types of combustion and industrial processing.

Hydrocarbons escape into the air during the production, refining, and distribution of petroleum products and as a result of incomplete combustion in the internal-combustion engines which power our motor vehicles. The relative contributions of these two sources are still a subject of controversy. To provide an independent and unbiased estimate of the amount of hydrocarbons entering the air from the petroleum industry, the Air Pollution Foundation engaged the Southwest

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[1] A widely publicized suggestion that they are due to natural causes was rejected by scientists to whom it was submitted by the editor of the publication in which it appeared, and by the scientific staff of the Air Pollution Foundation who examined it at the request of the Board of Supervisors of Los Angeles County.

Research Institute of San Antonio, Texas, to conduct an independent audit. The results of this audit were published in Report No. 5 of the Foundation and a brief summary is presented in Section C of this chapter. The composition of automobile exhaust and its contribution to smog effects have likewise been the subject of studies sponsored by the Foundation, as well as of work sponsored and carried out by other agencies. Burning of refuse including garden clippings, particularly in single-chamber home incinerators, also gives rise to organic compounds as well as to aerosols. The Foundation is sponsoring a project at Battelle Memorial Institute to study the composition of incinerator effluents.

Nitrogen dioxide arises as a result of all combustion processes. Estimates of total oxides of nitrogen (much of which is converted into NO_2) entering the Los Angeles atmosphere by combustion processes were reviewed in the Foundation's Report No. 2. More recent information on the nitrogen dioxide production from various sources will be discussed in the following sections.

Particulate matter dispersed in the air, or aerosols, are responsible for the restriction of visibility. Natural haze and fog occur frequently in this region; the additional particulate matter which further reduces the visibility arises from all combustion processes, including industrial and home incineration, and from industrial processing and vehicular traffic. Available information regarding the contribution of each of these sources is reviewed briefly below.

It would be desirable to have a census of the strength of the various sources distributed over the Los Angeles Basin, in order that an emission rate could be assigned to every square mile of the basin for each pollutant as a function of time. The Air Pollution Control District has some data on emission rates obtained in the course of inspections of control procedures and compliance. These data are far from adequate for the aforementioned purpose and are regarded as confidential by the District. The only data regarding the distribution of sources are the over-all locations of industrial establishments and the approximate distribution of traffic load.

Figure 1 shows the locations of the industrial plants regarded as contributors to air pollution, and the distribution of traffic expressed in percentage of total county traffic per square mile. 1/ It will be seen that the industrial plants, excepting refineries, are mostly to the southeast and south of the central business district, while traffic is heaviest in central and west-central Los Angeles.

The current consumption of gasoline in the Los Angeles Basin is estimated to be 5,000,000 gallons per day. Of this it is estimated that approximately 7 per cent, or about 1,000 tons per day, escapes through the exhaust into the atmosphere in the form of unburned hydrocarbons. (See Section C of this chapter.) Thus in Figure 1 the 0.1 traffic density line can be interpreted as representing a rate of hydrocarbon

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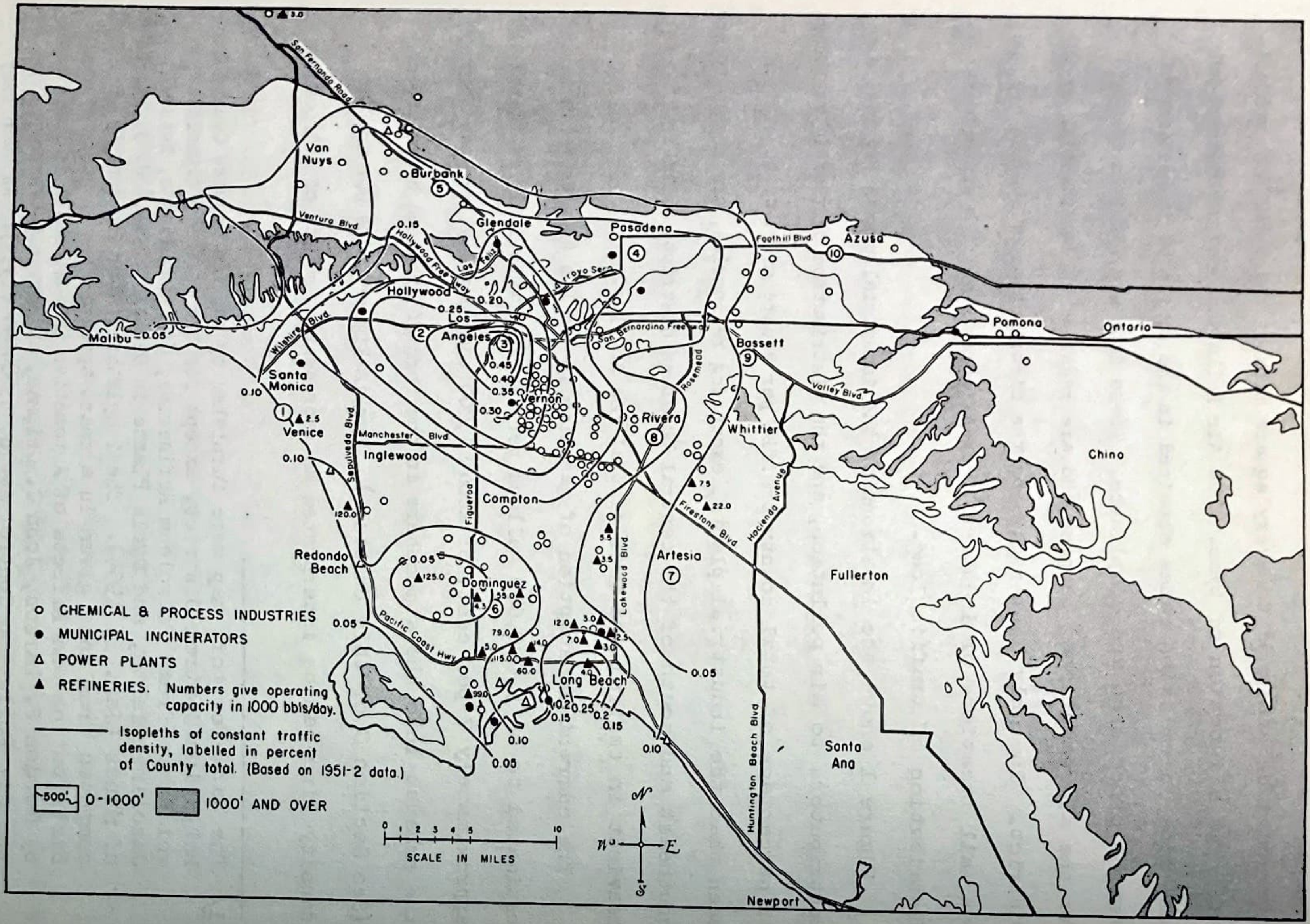
1/ The data for this map were furnished by the Los Angeles County Air Pollution Control District, except for the refinery capacities, which are from "Petroleum Refineries, Cracking Plants, Natural Gasoline Plants, and Cycle Plants in District Five," U. S. Bureau of Mines (Jan. 1, 1954). The isopleths of traffic density were computed from data given in a chart appearing in "A Study of the Distribution and Effects of Automotive Exhaust Gases in Los Angeles," by Gordon P. Larson, John C. Chipman, and Erwin K. Kauper, Jour. of the Air Pollution Control Ass'n, 5: 84-90 (1955). As such they represent the traffic distribution as of 1951.



Chapter III - Fig. 1
Map of Industrial Sources and Traffic Density in Los Angeles

loss of one ton per square mile per day, and the maximum value, 0.45 per cent per square mile, corresponds to 4½ tons per square mile per day of hydrocarbons emitted into the air. The concentration which would be attained by the rate of emission indicated by the traffic density can be computed for any given inversion height. Table I gives the cumulative concentration in parts per hundred million per day assuming an average inversion height of 1650 feet. While the actual concentration at any point in the basin will be affected by the transport by wind and by chemical reaction processes into which the hydrocarbons enter, it is interesting to compare these concentrations with those actually observed in the basin. Hydrocarbon concentrations were measured at five stations during the aerometric survey of 1954. Table II gives the average measured concentrations at these stations, together with the traffic density interpolated from Figure 1 and the corresponding cumulative concentration taken from Table I. At Stations 2, 3, and 13 the average measured concentration is approximately one-half the rate of accumulation per day from vehicle exhaust, which corresponds to the fraction of the total daily traffic which takes place during the night and morning hours of air stagnation. At Station 4, Pasadena, the average measured concentration is very little less than the cumulative concentration from local traffic in a day, but higher traffic rates are present a short distance to the windward. At Dominguez, however, the average measured concentration is almost four times the rate of accumulation per day from vehicle traffic. Thus at stations remote from the refinery area the observed concentration of hydrocarbons bears a reasonable relationship to the rate of accumulation from exhaust, so that it seems likely that the exhaust is the major source of hydrocarbons in these areas, while in the midst of the refinery area it is clear that refineries are the major source of hydrocarbons in the air. 1/

CHAPTER III--TABLE I

HYDROCARBON ACCUMULATION CORRESPONDING TO TRAFFIC DENSITY

Traffic Density (Per cent of County total per square mile)	Exhaust Hydrocarbons (Tons per square mile per day)	Cumulative Concentration* (pphm per day)
0.05	0.5	8
0.10	1.0	15
0.15	1.5	23
0.20	2.0	30
0.25	2.5	37
0.30	3.0	45
0.35	3.5	52
0.40	4.0	60
0.45	4.5	68

* Based on average inversion height of 1650 feet.

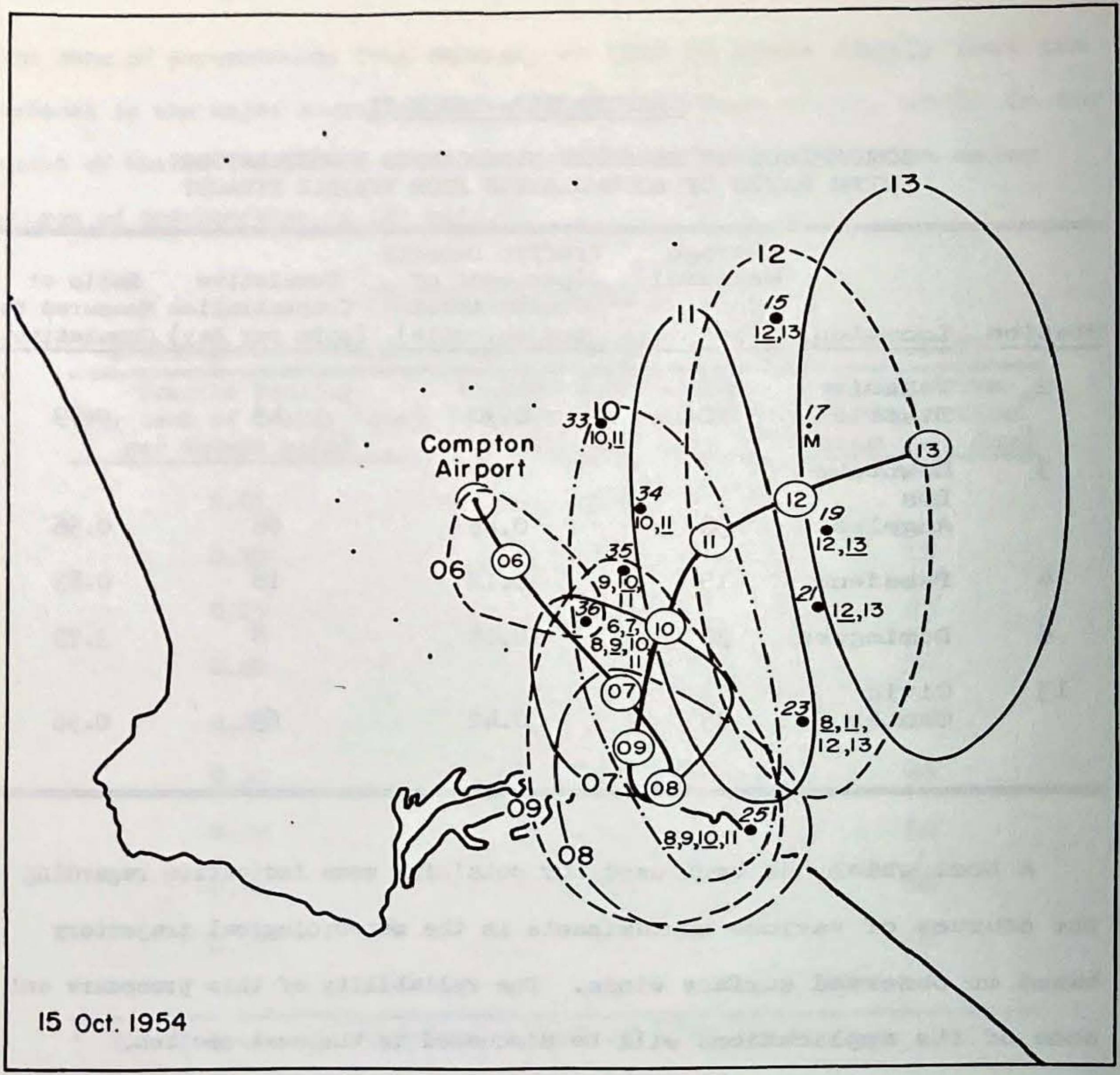
1/ Similar conclusions are contained in a report by Larson, Chipman, and Kauper, loc. cit., and in an unpublished report prepared by James R. Taylor and George I. Fisher for the Los Angeles County Air Pollution Control District in November, 1953.

CHAPTER III--TABLE II

COMPARISON OF MEASURED HYDROCARBON CONCENTRATIONS WITH RATES OF ACCUMULATION FROM VEHICLE EXHAUST

Station	Location	Average Measured Conc. (pphm)	Traffic Density (per cent of County total per sq. mile)	Cumulative Concentration (pphm per day)	Ratio of Measured to Cumulative
2	Wilshire District	22	0.30	45	0.49
3	Downtown Los Angeles	38	0.45	68	0.56
4	Pasadena	15	0.12	18	0.83
6	Dominguez	30	0.05	8	3.75
13	Civic Center	35	0.42	63	0.56

A tool which has been used for obtaining some indication regarding the sources of various contaminants is the meteorological trajectory based on observed surface winds. The reliability of this procedure and some of its applications will be discussed in the next section.



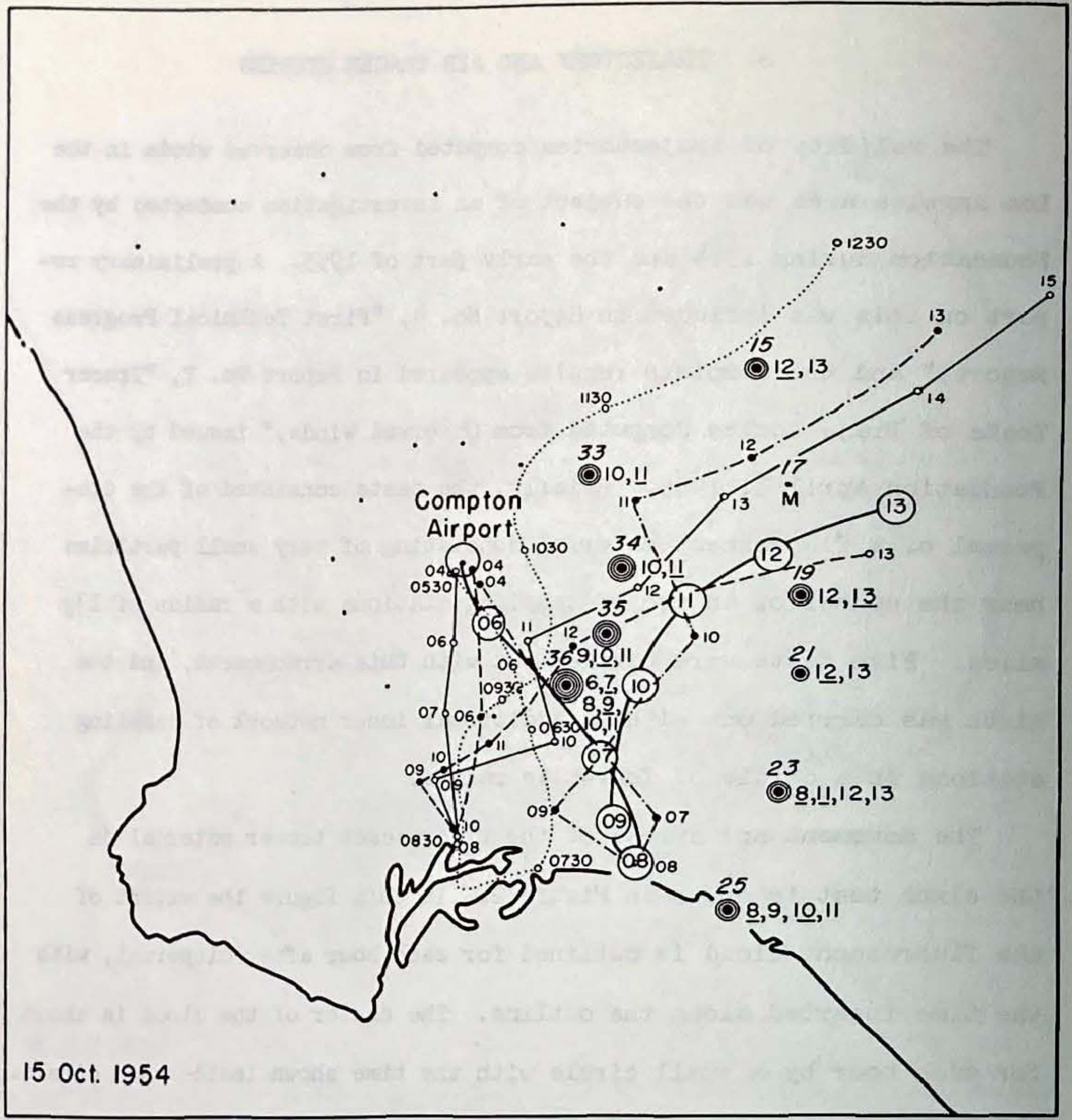
Chapter III - Fig. 2
Movement and Spreading of Fluorescent Cloud in Test 6
Deduced from Particle Counts

B. TRAJECTORY AND AIR TRACER STUDIES

The validity of trajectories computed from observed winds in the Los Angeles area was the subject of an investigation conducted by the Foundation during 1954 and the early part of 1955. A preliminary report on this was included in Report No. 4, "First Technical Progress Report," and the complete results appeared in Report No. 7, "Tracer Tests of Trajectories Computed from Observed Winds," issued by the Foundation April 1, 1955. Briefly, the tests consisted of the dispersal of a fluorescent material consisting of very small particles near the center of an arc of sampling stations with a radius of $13\frac{1}{2}$ miles. Five tests were carried out with this arrangement, and the sixth was carried out with an additional inner network of sampling stations in a circle of four-mile radius.

The movement and spread of the fluorescent tracer material in the sixth test is shown in Figure 2. In this figure the extent of the fluorescent cloud is outlined for each hour after dispersal, with the time inserted along the outline. The center of the cloud is shown for each hour by a small circle with the time shown inside each circle. The heavier line connecting the circles indicates the path of the center of the cloud.

Figure 3 shows the comparison of the movement of the centroid of the cloud of tracer material with the trajectories computed from the observed surface winds by four different meteorologists. While none of the computed trajectories is exactly coincident with the observed movement, the



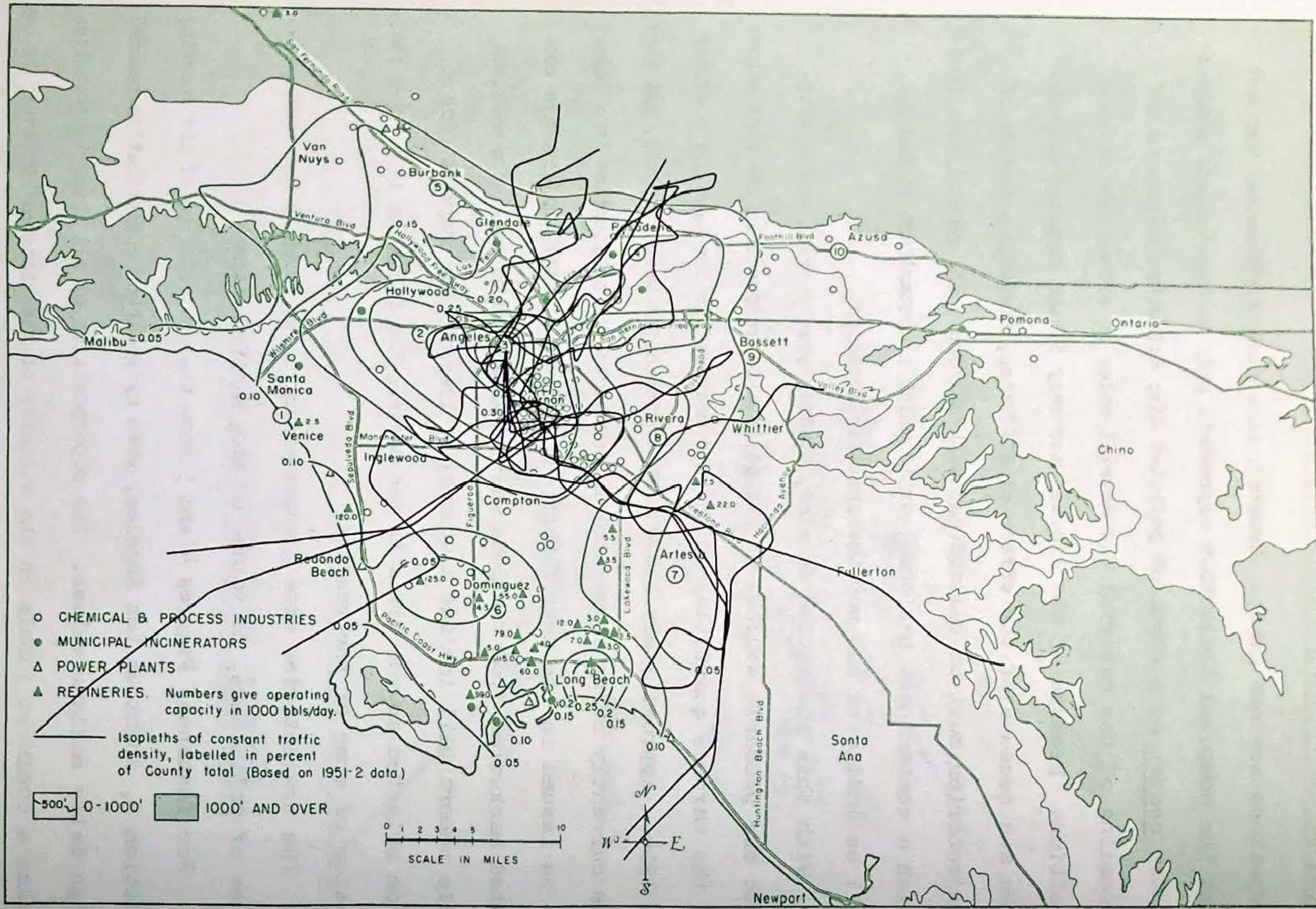
Chapter III - Fig. 3
Movement of Centroid of Fluorescent Cloud in Test 6
Compared with Trajectories Computed from Surface Winds

deviations are not great. However, this example emphasizes the fact that the computed trajectory represents only the approximate movement of the center of a cloud of polluted air; diffusion results in the spreading of the material for several miles on either side of this position. Because of the limited accuracy of the computed trajectories and because of the effect of diffusion, the interpretation of trajectories must be carried out with caution. The general area from which a contaminant has come, or to which a contaminant is carried, will be indicated but not the specific location.

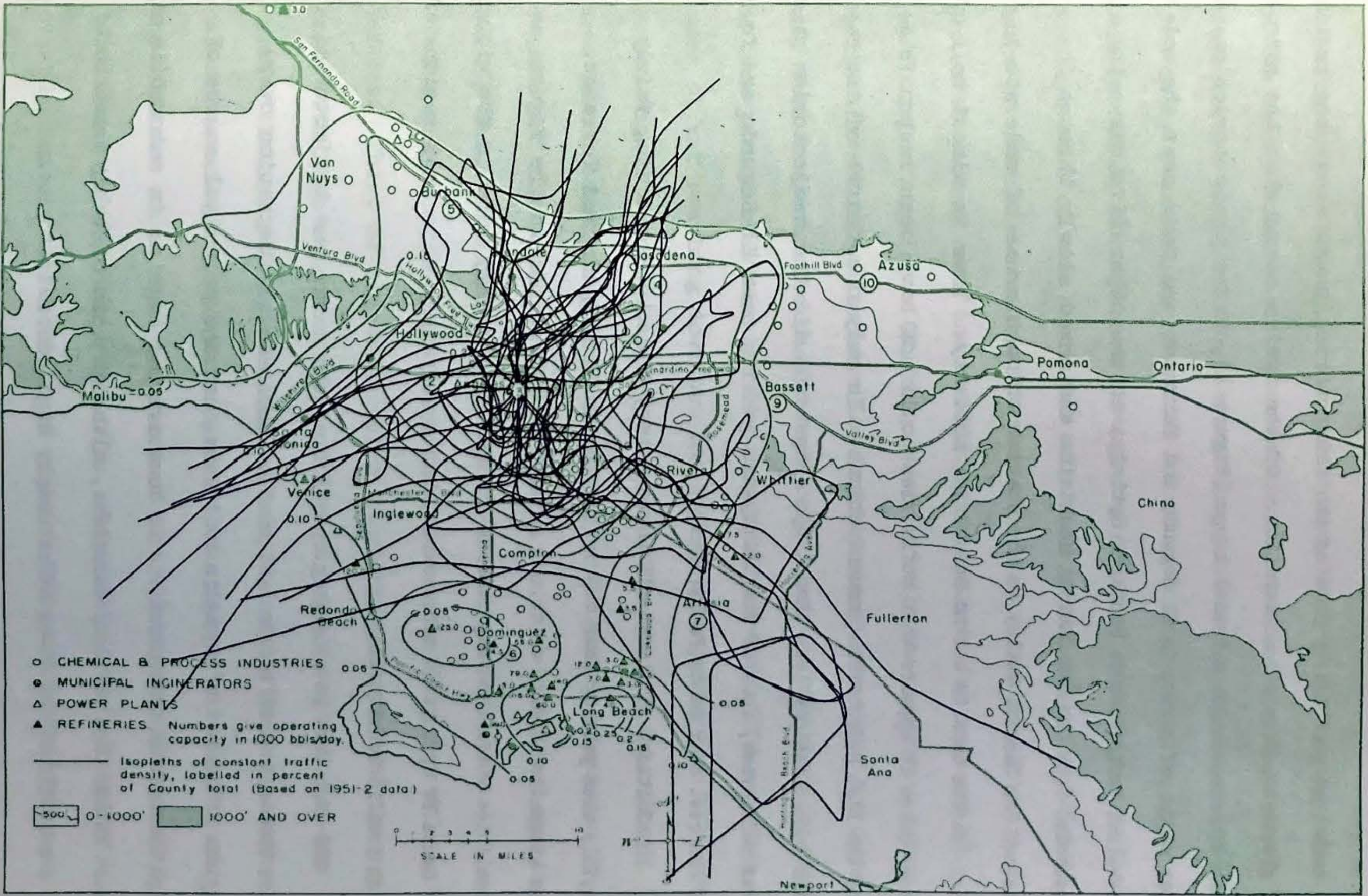
With this limitation in mind, studies were carried out to estimate the probable sources of the pollutants responsible for high values of the various quantities which were measured in the aerometric survey of 1954. Approximately 1,000 such trajectories were computed, and they are currently being summarized and prepared for publication in a report to be issued in the near future. In addition to the trajectories computed backwards from stations where high values of smog were measured, this report will include a summary of trajectories computed forward from selected source areas in the basin. The following is a brief indication of some of the results.

The trajectories were grouped according to stations and concentration of pollutants, or values of smog manifestations.

For instance, Figures 4 and 5 show the trajectories of air reaching Station 3, downtown Los Angeles, when hydrocarbon concentration reached high daily maximum values. The superposition of all these trajectories makes a confused jumble in the vicinity of the station. However, it can



Chapter III - Fig. 4
Trajectories Reaching Station 3, Downtown Los Angeles, with Hydrocarbon Concentrations Greater than 1 ppm



Chapter III - Fig. 5
Trajectories Reaching Station 3, Downtown Los Angeles, with Hydrocarbon Concentrations Less than 1 ppm

be seen that practically none of the trajectories pass near the region of greatest refinery concentration. Of the twelve cases when the hydrocarbon concentration exceeded 1 ppm (Figure 4), three trajectories passed near major refineries in El Segundo and Torrance and four near the moderate-sized refineries in Santa Fe Springs; in the other five cases the air descended from the San Gabriel Mountains and moved slowly through the western San Gabriel Valley to the station through areas of moderate to high traffic density but no industrial activity. Thus in almost half of these cases it appears that refineries could not have been responsible for the high hydrocarbon concentrations. In only one-fourth of the cases with concentrations less than 1 ppm (Figure 5) did the trajectories pass near refineries, four of the thirty-two passing near El Segundo and four of the rest near Santa Fe Springs.

In addition, in almost all these cases, the air was moving fairly rapidly when passing near the refineries in El Segundo and Torrance. The stagnation areas, which can usually be recognized in the figures as localities where the trajectories are curved sharply, were in the vicinity of Santa Fe Springs in a few cases, but mostly they were over regions of high traffic density.

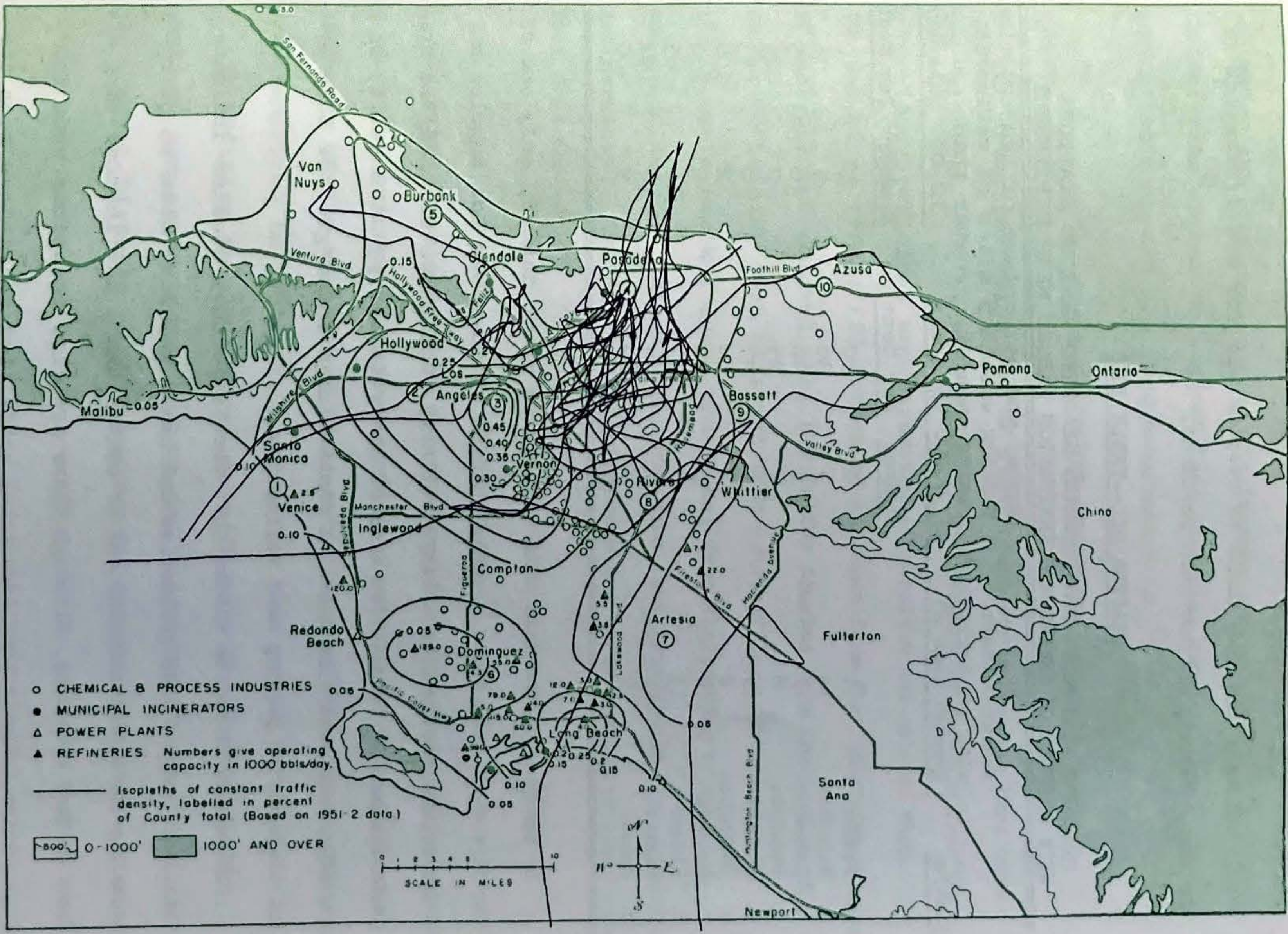
The fact that in a large proportion of the cases the trajectories were remote from refineries and most of them showed stagnation over regions of heavy traffic again indicates that the principal source of high hydrocarbon concentrations in downtown Los Angeles is automobile exhaust rather than refinery emissions, although both probably contribute to a majority of the cases of extremely high concentrations.

With respect to other air pollutants, there is also strong indication that nonindustrial sources are important. Thus, of seventeen trajectories computed for air reaching downtown Los Angeles at times when daily peak values of oxides of nitrogen in excess of 50 pphm were recorded, none passed through the principal refinery area in the southern part of the basin and only three passed within five miles of large or moderate-sized refineries elsewhere. Also, only five trajectories passed near the heavily industrialized area southeast of downtown Los Angeles. Of forty cases in which the particulate matter in the air reaching downtown Los Angeles was greater than 5 Coh units, only five trajectories passed near refineries, and only about one-third of them passed over the heavily industrialized area. Of twenty-five cases of air reaching downtown Los Angeles with greater than 10 ppm of carbon monoxide, none had trajectories which came from the refinery area in the southern part of the basin, although four passed near El Segundo and five near Santa Fe Springs; about one-half passed over the heavily industrialized area southeast of downtown Los Angeles.

The trajectories computed for other stations also gave similar results. Thus, of the trajectories reaching Pasadena six of twenty cases with high concentrations of hydrocarbons, seven of twenty-four cases with high aldehyde concentrations, two of the four cases with carbon monoxide concentrations greater than 20 ppm, and only four of the nineteen cases with densities of particulate matter greater than 5 Coh units passed near refineries. Relatively few of them passed over the heavily industrialized region. Using oxides of nitrogen as a typical example at Burbank, of nineteen trajectories reaching there with concentrations greater than 50 pphm, none passed within six miles of a major refinery and only two passed near the area of heavy industry southeast of downtown Los Angeles.

The smog reaction products and effects also appear to originate frequently in other than industrial areas. Figure 6 shows the trajectories of air reaching Pasadena with peak concentrations of oxidant greater than 30 pphm. Of the fifteen cases represented only three passed near refinery areas of consequence, six passed in the vicinity of the heavily industrialized region, and most of them appear to have stagnated principally over the traffic arteries between downtown Los Angeles and Pasadena.

Table III shows some of the results with respect to eye irritation. It shows the number and percentage of trajectories of air reaching various stations at times when moderate or severe eye irritation was reported (eye irritation index greater than 25 on scale of 0 to 55), these trajectories having passed within five miles of refineries. In only one-fourth of the cases at Pasadena and about half of the cases in downtown Los Angeles and Burbank does it appear that the eye-irritating air could have come from the vicinity of refineries. In the southern and extreme eastern part of the basin, on the other hand, the normal flow pattern does carry air from the refineries to the stations where eye irritation was observed. It must be emphasized that this does not prove that refineries are responsible for the eye irritation in the southern and extreme eastern part of the basin, but only that it is possible that they might be responsible for it in these areas; and it proves that it is



Chapter III - Fig. 6
Trajectories Reaching Station 4, Pasadena,
with Oxidant Concentrations Greater than 30 pphm

highly unlikely that they could be responsible for eye irritation in the west, central, and northern portions.

CHAPTER III--TABLE III

FREQUENCY WITH WHICH TRAJECTORIES REACHING VARIOUS STATIONS WITH MODERATE OR SEVERE EYE IRRITATION PASSED NEAR REFINERIES

Station	Number of days with eye irritation greater than 25	Number and percentage of trajectories passing within 5 miles of refineries having capacity greater than 50,000 bbls/day		10,000 bbls/day	
		Number	Per Cent	Number	Per Cent
1. Venice	1	0	0	0	0
2. Wilshire	14	5	36	5	36
3. Downtown	11	5	46	6	55
4. Pasadena	8	2	25	2	25
5. Burbank	15	7	47	8	53
6. Dominguez	2	2	100	2	100
7. Artesia	2	2	100	2	100
8. Rivera	13	9	69	11	85
9. Bassett	11	7	64	10	91
10. Azusa	9	8	89	9	100

As examples of the data with respect to plant damage, only one of the five cases with index greater than 20 at downtown Los Angeles had a trajectory passing near a large refinery, but three of them had trajectories passing through the area of heavy industry; at Bassett, on the other hand, all nine cases of plant damage index greater than 20 had trajectories passing near refineries.

In summary it may be stated that the trajectory studies indicate that other sources than refineries and heavy industry seem to be responsible for high concentrations of contaminants and intense smog effects on many occasions, although there are also occasions when the trajectories indicate that industrial activities could have been the source of the various smog manifestations observed. All in all, the trajectories appear to suggest that vehicular exhaust plays an important role in all the smog manifestations.

C. STACK GASES AND INDUSTRIAL EFFLUENTS

The principal emissions of significant air pollutants from industry fall into four categories: (1) Hydrocarbon evaporation from the production, refining, and marketing of gasoline and related fuels, and the use of solvents; (2) Oxides of nitrogen from the industrial burning of fuel oil and natural gas; (3) Sulfur dioxide from the burning of sulfur-containing fuel oils and from some refinery operations; and (4) Aerosols (smoke, dust, and fumes) from the burning of fuel oil and miscellaneous industrial operations, but principally from industrial incinerators. New data of significance and an evaluation of their accuracy follow.

Hydrocarbons

Industrial emissions of hydrocarbons arise almost entirely from the production, processing, and marketing of petroleum. Three different estimates of the amounts of these emissions have been made recently and are summarized in Table IV.

In addition to the figures shown in Table IV, losses at filling stations are estimated at 50 tons and 56 tons per day respectively by the Control District and the Western Oil and Gas Association.

CHAPTER III--TABLE IV

HYDROCARBON EMISSIONS OF THE PETROLEUM INDUSTRY (TONS PER DAY)

Source of Loss	Los Angeles Co. Air Pollution Control District July, 1955	Western Oil and Gas Ass'n March, 1955	Air Pollution Foundation Audit March, 1954
Petroleum production	50	30	28
Petroleum refining	193	102	179
Petroleum marketing	35	28	44
Total	278	160	251

Differences in figures shown in the table reflect differences in methods of estimating losses. It is known, however, that the petroleum industry has installed further controls since the time of the Air Pollution Foundation audit shown in the third column; the amount of the decrease is unknown to the Foundation. On the other hand, differences in various estimates become less significant when it is realized that automobile exhaust accounts for approximately 1000 tons to 1100 tons of hydrocarbon emissions daily.

The hydrocarbon losses from the petroleum industry thus have been reduced to less than 25 per cent of the hydrocarbon losses from automobile exhaust. However, it must be remembered that 80 per cent of the the total refinery capacity is located in an area of about 50 square miles in the southern portion of the basin. Assuming hydrocarbon loss proportional to processing capacity, the average rate of loss in this area is 4 tons per square mile per day, only slightly less than the rate of hydrocarbon loss from exhaust in the region of heaviest traffic density. This value is consistent with the fact that the average measured hydrocarbon concentration at Dominguez during the 1954 aerometric survey was 30 pphm (see Table II), very little less than that observed in downtown Los Angeles. In the Wilmington area the concentration of refinery capacity is so great that, if the loss is proportional to capacity, the hydrocarbon loss is more than 15 tons per square mile per day, over three times the highest daily rate due to traffic anywhere in the basin.

In addition to the figures shown in Table IV, the District estimates that the combined chemical, paint, and rubber industries are responsible for 50 tons of hydrocarbon emissions daily as a result of solvent use.

Sulfur Dioxide

The only new data on sulfur dioxide emissions by industry are those released by the Control District. The estimated values for 1955 are 170 tons per day - petroleum refineries; 30 tons per day - sulfur recovery plants; and 268 tons per day - burning of fuel oil (both domestic and industrial). The first two values are accepted both by the District and industry. The third value is of questionable significance because fuel oil consumption during the warmer and so-called smog months is only about half that during the winter months when smog is less prevalent.

Aerosols

The District's recent estimate of industrial aerosol emissions, other than those from incinerators, is 59 tons per day, well divided among various industrial classifications. The significance of this or any such value has been seriously questioned for the following reasons:

1. Tonnage figures may be misleading because of the great variation in size of aerosol particles. There is reason to believe that extremely fine particles difficult to control (0.05 to 2 microns) may exert an influence in direct relation to their large number and chemical composition rather than to their weight.
2. Observation of stack plumes indicates that aerosol growth and perhaps formation may take place after combustion effluents have left the top of the stack and entered the atmosphere.
3. Variations in number, analysis, and weight of aerosol particles from one stack to another, and even from one day to another, may be so great as to leave average values meaningless.

The Foundation realizes that the aerosol problem is a complex and difficult one and, accordingly, has initiated research into the size distribution and chemical composition of atmospheric aerosols. The Control District, in conjunction with the United States Public Health Service, the California Department of Health, and the Western Oil and Gas Association, is planning a concerted attack on the analysis of plumes from industrial stacks, which should throw more light on this confusing problem.

Other Industrial Emissions

The only other industrial emission presently considered significant is that of oxides of nitrogen. Every burning process, whether industrial or domestic and regardless of the type of fuel burned, fixes some atmospheric nitrogen as nitric oxide, which later may be converted in the atmosphere to higher nitrogen oxides or to nitrogen compounds. The present chaotic state of knowledge with regard to nitrogen oxide reactions and methods of analysis is such as to render estimates almost meaningless. For instance, recent work at the University of California (Ref. 1) indicates that emissions of oxides of nitrogen from a domestic water heater using natural gas for fuel were 8 pounds per ton of fuel. This compares with 2 pounds to 4 pounds per ton reported by another investigator and 14 pounds per ton by still another. Accordingly, the Foundation plans to initiate basic research in this field and to coordinate it with the University of California studies which are being continued.

D. COMPOSITION OF AUTOMOBILE EXHAUST

A great deal of work on the composition of automobile exhaust gases has been carried out during the past year. In 1954 the Coordinating Research Council (a joint venture of the Society of Automotive Engineers and the American Petroleum Institute) formed a Group on Composition of Exhaust Gases under its Coordinating Fuel and Equipment Research Committee. The Group on Composition of Exhaust Gases consists of specialists on fuels and combustion, working both in the automotive and petroleum fields. The group if further divided into a Sampling and Analysis Panel, a Variables Panel, a Literature Survey Panel, and a Field Survey Panel. As a result of the activities of these panels, the exhaust gases of hundreds of automobiles have been analyzed under a variety of conditions, particularly for hydrocarbons.

A survey of all published and some unpublished data on hydrocarbons in exhaust gases has been made by the Foundation. The most pertinent results are summarized in Table V. It should be realized that the data presented in Table V are averages and were obtained by various methods of analysis from cars of various makes and ages and in different mechanical conditions, under different operating conditions and with different fuels. It is therefore surprising that data of various investigators agree as well as they do. Furthermore, the term hydrocarbons covers thousands of molecular species of varying chain length and structure. The smog-forming potential of the various hydrocarbons is at best known only qualitatively.

To convert these data into tons of hydrocarbons emitted to the atmosphere daily involves assumptions as to average car condition and average operating cycle. Recent calculations made by the Los Angeles County Air Pollution Control District (Ref. 2) and by Stanford Research Institute (Ref. 3) are 1090 and "in excess of 1000 tons" respectively.

These figures can, however, be misleading if not considered in proper perspective. Of much greater importance is the distribution of emissions both geographically and by time of day. It is conceivable that a more even distribution of hydrocarbon emissions could cause a worse situation than at present, depending on the level of the emissions. But until more is known about the manner in which hydrocarbons contribute to various smog manifestations it must be assumed that a uniform reduction of hydrocarbon emissions to a certain percentage of present levels would be the most effective control measure. In this connection Hutchison and

CHAPTER III--TABLE V

HYDROCARBON LOSSES IN AUTOMOBILE EXHAUST
(In Percentage of Supplied Fuel)

	Laboratory							Buses		
(Number of Cars Tested)	SRI (10)	SwRI (6)	APCD (2)	GM (7-152)	Ford (2-5)	Chrysler (2)	Other (5-17)	Gasoline (3)	Propane (3)	Diesel (3)
Operating Condition:										
Idling	10.7	2.5	8.7	4.0 (152)	5.5 (4)	3.4	5.3 (17)	3.9	3.9	11.7
Acceleration	6.0	0.9	1.5			0.7	2.1 (5)	1.6	0.6	1.0
Cruising	5.7	0.7	1.4	1.5 (7)	2.0 (5)	0.9	2.5 (13)	0.4	0.7	1.2
Deceleration	19.2	28.9	23.0	12.5 (33)	20.0 (2)	15.6	24.9 (5)	39.3	34.3	37.1

Sources of Data:

Stanford Research Institute - Magill, P. L., Hutchison, D. H., and Stormes, J. H., "Hydrocarbon Constituents of Automobile Exhaust Gases," Second National Air Pollution Symposium, p. 71 (1952)

Southwest Research Institute - Calculated from data in Report No. 8, "Field Evaluation of Houdry Catalytic Exhaust Converters," Air Pollution Foundation (June, 1955)

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Chrysler Corporation - Twiss, S. B., Teague, D. M., Bozek, S. W., and Sink, M. V., "Application of Infrared Spectroscopy to Exhaust Gas Analysis," *Jour. of the Air Pollution Control Ass'n*, 5:2, pp. 75-83 (August, 1955)

Other Laboratories - From unpublished data made available to the Air Pollution Foundation.

Buses - Elliott, M. A., Nebel, G. J., and Rounds, F. G., "The Composition of Exhaust Gases from Diesel, Gasoline, and Propane Powered Motor Coaches," *Jour. of the Air Pollution Control Ass'n*, 5:2, pp. 103-8 (August, 1955)

Holden (Ref. 4) have estimated that a 60 per cent decrease in exhaust hydrocarbon emissions would return the Los Angeles atmosphere to 1945 conditions. On the other hand, Larson (Ref. 5) has suggested that we "should strive for a 90 per cent over-all removal under conditions of operation experienced in heavy traffic." There is a considerable practical difference between these two figures, and the Foundation believes it is extremely important to know definitely how much partial control of exhaust hydrocarbons will contribute to smog reduction. Only then can various devices for exhaust hydrocarbon control be effectively evaluated. Studies directed toward answering this question are currently under way.

Data on the other constituents of automobile exhaust gases, principally oxides of nitrogen and aldehydes, show that previous estimates of the amount of oxides of nitrogen emitted to the air in automobile exhaust varied from 132 (Ref. 6) to 177 (Ref. 7) tons per day. Recently the District has recalculated its estimate of oxides of nitrogen emissions from this source and reported daily emissions of 771 tons. This value is based on analysis of the exhaust effluent of a 1951 Ford "6" (Table VI).

CHAPTER III--TABLE VI

RESULTS OF A TYPICAL ANALYSIS OF AUTOMOBILE EXHAUST GASES *

Component	Idling	Acceleration	Cruising	Deceleration
Hydrocarbons (C_3-C_9) as hexane, ppm	1275	410	354	5125
Acetylenic, as acetylene, ppm	825	18	64	587
Oxides of nitrogen, as NO_2, ppm	8	4180	1606	18
Lower aldehydes, as formaldehyde, ppm	88	1369	264	193
CO percentage	3.6	0.0	0.4	1.5
CO_2 percentage	10.0	13.7	12.9	6.1
O_2 percentage	1.4	1.3	1.1	9.5

* See Ref. 5 in bibliography.

No other data as complete as these have been published. Three sets of unpublished data have been made available to the Foundation. In the following table they are compared with the District data.

CHAPTER III--TABLE VII

OXIDES OF NITROGEN (AS NO_2) CONTENT OF AUTOMOBILE EXHAUST GASES (PPM)

Operating Condition	1951 Ford "6" (APCD)	Ford V-8	1950 Ford V-8	1954 Ford V-8
Idling	8	170	275	190
Acceleration	4180	990	1100	1090
Cruising	1606	1290	1500	1480
Deceleration	18	40	50	50

The greatest discrepancy between these values is for the acceleration phase of the operating cycle. Since it is during acceleration that the exhaust gas flow rate is the highest, analytical differences are magnified considerably. Accordingly, a quantitative estimate of the amount of oxides of nitrogen emitted by automobiles must await more data. In the meantime it must be realized that the automobile is a major contributor to the oxides of nitrogen content of the Los Angeles atmosphere, although perhaps it does not contribute so much as the 70 per cent indicated by the District's estimate (771 tons out of a total of 1040 tons per day, not including a few unknown sources that might raise the total to 1100 tons per day).

Similarly, data on the aldehyde content of automobile exhaust are meager. In some cases aldehydes are reported as hydrocarbons because the analytical method does not distinguish between the two. The

District's estimate of aldehyde emissions from automobiles based on Table VI is 133 tons per day as of 1955.

E. COMPOSITION OF INCINERATOR GASES

Very little new information on the composition of incinerator gases has become available during the year. The Los Angeles County Air Pollution Control District has recalculated its estimate of incinerator effluents reaching the Los Angeles atmosphere (Ref. 2). The data are shown in the following table.

CHAPTER III--TABLE VIII

EFFLUENTS FROM INCINERATORS IN LOS ANGELES COUNTY - 1955

Type of Incinerator	Tons per Day Aerosols	Tons per Day Oxides of Nitrogen (Calc. as NO_2)	Tons per Day Organics
Domestic	41	5	Unknown
Municipal	6.4	Unknown	Unknown
Other *	93	8	Unknown
Total	140.4	13	Unknown

* From industrial incinerators and open fires.

The importance of these aerosol emissions may be gathered from the following:

1. Aerosols (140 tons per day) from incineration of refuse represent 60 per cent of the total aerosol emissions (230 tons per day) to the Los Angeles atmosphere (from Los Angeles County Air Pollution Control District's "Total Pollution Survey," see Ref. 2).

2. The 1954 aerometric survey of the Los Angeles Basin, conducted by the Foundation (Ref. 8), showed a strong correlation between particulate matter in the air and eye irritation. Definite evidence was also found that the concentration of particulate matter and aldehydes at the Pasadena station in 1954 was relatively greater when backyard incinerators were in operation than when they were not. The change in burning hours from morning to evening, beginning the first week in November, showed this effect unmistakably.

The biggest gap in our knowledge of the composition of incinerator effluents is in the organic content of the emissions. Stanford Research Institute estimated several years ago that 414 tons or organic gases reached the Los Angeles atmosphere daily from this source. To check and extend these results the Air Pollution Foundation placed a project at Battelle Memorial Institute in late 1954. Because of sampling and analysis difficulties, only preliminary results are available at this time.

Aldehydes, organic acids, phenols, methanol, acetone, ethylene, and methane have been found in the effluents. Exact quantities have not been determined, but preliminary results indicate that the total quantity of organics is of the same order of magnitude as that shown in the Stanford estimate. Organics of this nature in the amounts indicated could well undergo reactions in the atmosphere similar to those of exhaust hydrocarbons, and perhaps even at lower concentrations because they are already partially oxidized.

Contrariwise, however, oxides of nitrogen content is definitely lower.

This may be due to the nature of the fire [1] and the charge used. [2] However, considerable ammonia is produced (1 lb. to 4 lbs. per ton of refuse) and if only part of this were converted to NO_2 (by higher temperature burning), the two estimates would be in line.

With regard to aerosols, experiments at Battelle have yielded no data as yet.

A preliminary report on the number and size of particles in the effluents from both domestic and municipal incinerators has been released by the University of California (Ref. 9). In a typical experiment the burning of dry paper in a laboratory combustion chamber produced an effluent which contained 32 billion particles per cubic foot (mean particle diameter - 0.13 microns). The effluent from a similar charge containing 15 per cent moisture contained 98.6 billion particles per cubic foot, with a mean diameter of 0.11 microns.

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[1] It is extremely difficult to reproduce burning conditions from one run to another, even when great pains are taken to operate the incinerator by identical procedures. For this reason, many experiments must be made to obtain average conditions.

[2] The typical charge used in the Battelle experiments consists of newspapers - 25% by weight; cardboard - 5%; rags - 1%; wood - 2%; tree trimmings, flower cuttings, grass clippings, and hedge trimmings - 67%.

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CHAPTER III

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IV. HOW MAY SMOG BE CONTROLLED?

A. BACKGROUND AND STATUS

There is general agreement among air pollution authorities that the ultimate solution to the smog problem is control of the emissions of deleterious pollutants. Current control regulations in Los Angeles County have been directed primarily toward:

Aerosols (dust, smoke, fumes, and particulate matter) from all sources except single-chamber incinerators. Control of the latter will be accomplished by Air Pollution Control District Rule 58, effective October 1, 1957, which will ban the operation of single-chamber incinerators in Los Angeles County.

Sulfur dioxide from all sources.

Hydrocarbon emissions during the production, refining, and marketing of gasoline.

Although these regulations (with the exception of the incinerator ban, which has not yet taken effect) have undoubtedly removed many tons of pollutants from the Los Angeles atmosphere, smog still persists.

The remaining pollutants of significance are listed in Chapter III of this report, together with their estimated quantities in those cases where estimates are deemed reliable. It is apparent from the data in Chapter III that from the standpoint of tonnage of emissions the most important remaining emissions are:

Hydrocarbons from automobile operation, refining of petroleum, and petroleum marketing activities.

Sulfur dioxide from fuel oil burning, petroleum refining, and related activities.

Nitrogen oxides from automobile operation, fuel oil burning, and natural gas burning.

Aldehydes from automobile operation.

Aerosols from automobile operation and industrial stacks.

The work of the Foundation during the past year in the development of control methods has been directed toward reduction of hydrocarbons from automobile exhaust. Remedies for the automobile exhaust problem may be in either of two directions, i.e., modification of fuel in order to change the characteristics of exhaust emissions, or modification of the automotive engine to reduce the emissions from presently used fuels.

B. USE OF FUELS OTHER THAN LEADED GASOLINE

The contribution of hydrocarbons from automobile exhaust to smog manifestations is based on the classic researches of Haagen-Smit (Ref. 1). His work shows that the photochemical reaction between hydrocarbons of more than three carbon atoms per molecule and nitrogen dioxide gives rise to ozone formation and typical smog damage to vegetation and perhaps to other smog manifestations. 1/ From this work, it was postulated by others that certain alternate fuels that would not contribute to smog might be used in the Los Angeles area as stopgap methods until suitable mechanical or chemical control devices were developed.

1/ Later work by Haagen-Smit (paper presented at Minneapolis meeting of American Chemical Society) shows that most organic compounds from C_2 up produce ozone in the same manner.

Feasibility of Alternate Fuels

The Foundation believed that it was in the public interest to collect the facts and to evaluate the technical and economic feasibility of proposals for alternate fuels. Accordingly, the Foundation entered into a contract with Southwest Research Institute, San Antonio, Texas, to make this evaluation. The significant conclusions of the study 1/ are summarized in the following.

PROPOSAL NO. 1: THAT ALL AUTOMOBILES, TRUCKS, AND BUSES BE REQUIRED TO USE LIQUEFIED PETROLEUM GAS (LPG) AS FUEL IN PLACE OF GASOLINE.

Economic Feasibility

Sufficient LPG to replace the required 4,900,000 gallons per day of gasoline can be made available in the Los Angeles area under the following conditions:

Build adequate pipeline transportation facilities (could be built in about one year) - $96,000,000.

Build new storage facilities - $4 to $8 per barrel for required storage capacity.

Convert automobile fuel system - $250 to $300 per car.

Construct dispensing equipment at filling stations - $5,000 to $9,000 per station.

Possible change in location of filling stations.

Supply suitable trucks for transportation of LPG from bulk terminal to filling stations - cost undetermined.

Present gasoline production in Los Angeles would have to be disposed of elsewhere.

1/ The complete study was published by the Foundation as its Report No. 10, "Feasibility of Control Methods for Automobile Exhaust."

Probable price increase of LPG for domestic use.

Probable cost of LPG to automobile operators - about the same as present gasoline.

Technical Feasibility

LPG can be adapted to motorcar use.

Engine power is decreased eight per cent.

Maintenance costs are lower.

Fuel consumption is greater.

Whether or not smog would be reduced has not been proved.

PROPOSAL NO. 2: THAT ONLY PUBLIC SERVICE BUSES BE REQUIRED TO USE LPG AS FUEL IN PLACE OF GASOLINE.

Economic Feasibility

Sufficient LPG already available.

Conversion of gasoline buses - $1,000 each.

Replacement of diesel bus engines - $3,000 each.

Dispensing equipment and storage - $390,000.

Fuel price about the same as gasoline.

Technical Feasibility

Same as for all automobiles.

PROPOSAL NO. 3: THAT ALCOHOL OR ALCOHOL-GASOLINE BLENDS BE USED IN PLACE OF GASOLINE.

Economic Feasibility

Alcohol price - about 40 cents per gallon, not including any motor fuel tax.

Sufficient alcohol facilities could be built in about one and one-half to two years.

Technical Feasibility

Since the report was prepared, it has been found that use of alcohol-gasoline blends does not markedly reduce hydrocarbon emissions. These data are presented later in this chapter.

PROPOSAL NO. 4: THAT THE OCM CATALYTIC MUFFLER (OFTEN CALLED THE "HOUDRY WHITE GAS MUFFLER") BE INSTALLED ON ALL CARS AND THAT ALL MOTOR VEHICLES BE REQUIRED TO USE NONLEADED (WHITE) GASOLINE TO MAKE THE MUFFLER EFFECTIVE.

Economic Feasibility

Probable cost of muffler (installed) - $56 per car.

Deleading of existing automobiles - $95 to $125 per car.

Muffler maintenance - 0.4 to 1.5 cents per mile.

Area petroleum refiners could probably make sufficient 81-octane gasoline available at no extra cost, 92-octane (premium) gasoline at 1 to 2 cents more than present price of premium grade, and 100-octane gasoline (for future requirements) at 8 cents per gallon above present premium grades.

Time requirement for change-over in gasoline production - 12 months.

Potential octane ceiling for leaded gasoline marketed outside area would probably be lowered at an undetermined cost to refiners.

Present supply system at refineries and service stations would have to be deleaded.

Automobiles going outside area from time to time would have difficulty finding an adequate supply of white gasoline. Use of leaded gasoline would require replacement of the catalyst upon return to white gasoline.

Not mentioned in the report, but to be considered, is the additional cost of government inspection of all automobiles - probably every 6 months.

Technical Feasibility

Most cars would give satisfactory performance with 92-octane unleaded gasoline.

Some 1955 models might not perform well.

Whether or not or how much an assumed 80 per cent reduction in exhaust hydrocarbons would aid the smog problem has not yet been determined.

Studies on Alcohol-Gasoline Blends

A review of the literature on the composition of exhaust gases from automotive equipment using alcohol-gasoline blends as fuel failed to disclose any data on the hydrocarbon or aldehyde content of the gases. Therefore, Midwest Research Institute at Kansas City, Missouri, was asked to gather such data in conjunction with another project they were conducting. The purpose of the study was to assess the validity of the suggestion that alcohol-gasoline mixtures burn with greater efficiency than gasoline alone, thus contributing less organic compounds to the atmosphere via exhaust effluents.

Experiments were conducted using a 1952 Ford station wagon with 30,000 miles on its odometer and in good mechanical condition. The air-fuel ratio under idling conditions was adjusted to 12:1. Three fuels (gasoline alone, a 15 per cent alcohol-gasoline mixture, and a 30 per cent alcohol-gasoline mixture) were tested under both idling and decelerating conditions. The results are summarized in Table I.

The investigators conclude: "The data show that no great changes which would be of help in solving the air pollution problem may be expected from using ethanol-gasoline fuel mixtures. The trends were the same for both idling and deceleration conditions. The following changes in the exhaust content are noteworthy: (1) The total amount of aldehydes increased, while the formaldehyde decreased; (2) The hydrocarbon concentration increased; and (3) The carbon monoxide was decreased greatly."

CHAPTER IV--TABLE I

EFFECT OF ALCOHOL BLENDS ON COMPOSITION OF AUTOMOBILE EXHAUST *
(PPM BY VOLUME)

Percentage Alcohol in Blend	Hydrocarbons (As Hexane)	Carbon Monoxide Per Cent	Formaldehyde	Total Aldehydes	Oxides of Nitrogen (As NO_2)
IDLING (450 rpm)					
0	1280	5.75	38.7	82.6	11.9
15	2230	2.57	22.3	92.3	17.0
30	1810	0.79	49.1	124.7	39.9
DECELERATION (35 mph to 25 mph)					
0	1670	10.59	148.9	224.9	9.4
15	1360	5.51	177.8	383.7	---
30	2370	3.20	98.9	250.0	12.9

* Details of the tests and analytical procedures were presented at the Minneapolis, Minn., meeting of the American Chemical Society, September 11-16, 1955, in a paper entitled "The Exhaust Content of Automobiles Burning Ethanol-Gasoline Mixtures," by F. V. Morriss, _et al_. Will probably be published during 1956 in _Industrial and Engineering Chemistry_.

Other Fuel Studies

Further work on the effect of fuels on hydrocarbon emissions from exhausts was done by Elliott, Nebel, and Rounds of General Motors Corporation (Ref. 2). They published an interesting study on the composition of exhaust gases from diesel-, gasoline-, and propane-powered motor coaches. They showed that for a typical city driving pattern the carbon monoxide emission from diesel coaches was only a small fraction of that from gasoline and propane coaches, but that only small differences existed among the three types of coaches in the emissions of oxides of nitrogen, formaldehyde, and hydrocarbons.

C. DEVICES FOR THE CONTROL OF HYDROCARBONS FROM AUTOMOBILE EXHAUST

The Foundation has followed closely the work of various organizations toward the development of an adequate device for controlling hydrocarbons in exhaust gases. Proposed devices fall into two general categories: (1) prevention of emissions by effecting better combustion in the cylinder, and (2) treatment of exhaust gases to remove hydrocarbons.

Prevention of Emissions

The more promising devices in this class are throttle retarders, devices to limit the manifold vacuum, devices to cut off or reduce fuel flow during deceleration, and fuel injectors. Several automobile manufacturers are presently engaged in research and development studies along these lines.

Preliminary data on the effect of engine variables on the hydrocarbon content of exhaust and on the effectiveness of various devices were published during the year. The most extensive studies were presented by Rounds, Bennett, and Nebel of General Motors. Their preliminary findings may be summarized as follows:

1. Fuel type had little or no effect on the total hydrocarbon content in the exhaust.

2. Hydrocarbon emissions during idling increased markedly as the air-fuel ratio deviated further from "best idle" conditions toward rich mixtures. They estimated that proper idle adjustment of all cars would result in a 30 per cent reduction in the total idle hydrocarbon emission.
3. At idle, exhaust gas hydrocarbon content of compact V-8 engines was less than for the line 6's or the line 8's.
4. At "part throttle," engine load had little or no effect on hydrocarbon content of exhaust gas.
5. At "part throttle," air-fuel ratio had no significant effect on hydrocarbon content of exhaust gas; neither did engine speed, compression ratio, or coolant temperature.
6. Under decelerating conditions, simulated by coasting downhill at constant engine speed at closed throttle, hydrocarbon content was independent of manifold vacuum below 21 inches of mercury. Above 21 inches, the hydrocarbon content increased very rapidly. Cars with automatic transmissions developed lower manifold vacuum than cars with standard transmissions. Accordingly, it was estimated that cars with automatic transmissions would release less hydrocarbons to the atmosphere during deceleration.
7. Limited tests on public transit buses using gasoline, LPG, and diesel fuel indicated no significant difference in hydrocarbon emissions from the exhaust.

J. M. Chandler <u>et al</u>. (Ref. 3) of the Ford Motor Company corroborated some of the above conclusions. Their chief conclusions were:

1. Hydrocarbon emissions were about 2 per cent by weight of supplied fuel from full throttle until idling manifold vacuum was exceeded. Above 21 inches manifold vacuum, hydrocarbon losses reached 50 to 80 per cent of supplied fuel.
2. Spark advance beyond present settings on either centrifugal or full-vacuum advance distributors was found helpful and could reduce hydrocarbon emissions during deceleration by 20 to 25 per cent.
3. Forty-six cars, in good mechanical condition and properly tuned, were found to have an average air-fuel ratio of 12.2:1, and lost via their exhaust $3\frac{1}{2}$ per cent of the fuel supplied.
4. Various methods of reducing exhaust hydrocarbons during deceleration were evaluated preliminarily. Reduction in hydrocarbon content was reported as follows: medium dashpot - 10 per cent; spark advance - 22 per cent; slow dashpot - 70 per cent; idle cutoff, carburetor - 84 per cent; and idle cutoff, manual - 89 per cent.
5. A depopper carburetor (to reduce air flow during high manifold vacuum periods) actually allowed hydrocarbon emissions from exhaust to increase; a similar result was obtained with an enrichener carburetor, which adds fuel at high manifold vacuum.

Published studies of the Chrysler Corporation (Ref. 4) also dealt briefly with engine variables and possible control devices. Their results follow:

1. Under decelerating conditions, hydrocarbon losses were low until 21 to 22 inches manifold vacuum was reached, at which time hydrocarbon losses from exhaust increased rapidly.

2. Use of a throttle control unit reduced hydrocarbon losses during deceleration by 79 per cent.

Wentworth and Daniel of General Motors (Ref. 5) reported tests on two devices to limit hydrocarbon emissions during deceleration. One device, operating on the principle of fuel flow shutoff of the carburetor idle circuit, was installed on a 1947 model automobile. A reduction of 90 per cent of the normal hydrocarbon losses during deceleration was attained.

A second device, which limited the manifold vacuum during deceleration by admitting additional air-fuel mixture to the manifold when the vacuum tended to rise above 21 inches, was installed on a 1954 model car equipped with a torque converter type of transmission. This device produced a 61 per cent reduction in hydrocarbon emissions during deceleration.

The preceding summary of activities by automobile manufacturers shows quite clearly the intense program of research and development they are conducting to reduce hydrocarbon emissions from exhausts. A great deal more work (none of which has been published) on the sampling and analysis of automobile exhaust, the effect of engine variables, and the development of control devices is going on in the laboratories and on the proving grounds of all motorcar manufacturers and many oil companies. Although all the published work deals with devices which affect combustion in the engine cylinders, studies are also being conducted on exhaust converter devices. Studies sponsored by the Foundation in this latter field are presented in the following section.

Treatment of Exhaust Gases

One of the first activities of the Air Pollution Foundation after its formation was to survey the field for promising devices for treatment of exhaust gases for hydrocarbon reduction or removal. A wide variety of such equipment was studied. Among these were absorbers using various liquids; adsorbers using solids such as activated charcoal; and several air oxidation units, both catalytic and noncatalytic. None of the absorbers or adsorbers appeared to be sufficiently developed to warrant testing. On the other hand, the Houdry catalytic converter for private passenger vehicles and the Clayton afterburner for trucks and buses were sufficiently attractive to be subjected to tests.

Catalytic Mufflers

The Foundation entered into a contract with Southwest Research Institute, San Antonio, Texas, for a field evaluation of the Houdry device 1/. Seven converters or mufflers were obtained from Oxy-Catalyst, Inc., Wayne, Pennsylvania, and installed on six automobiles as follows:

Automobile	Identification Number	Muffler Type
1954 Chevrolet "6"	260	Oxy-Catalyst muffler
1954 Chevrolet "6"	261	Intermediate muffler
1953 Buick 70	262	Leaded muffler
1953 Cadillac 62	263	Two leaded mufflers (dual exhaust)
1954 DeSoto 519	264	Leaded muffler
1954 Ford Customline	265	Leaded muffler

1/ The complete report has been published by the Air Pollution Foundation as its Report No. 8, "Field Evaluation of Houdry Catalytic Exhaust Converters."

All cars were four-door sedans equipped with automatic transmissions and, with the exception of the Chevrolets, were powered by V-8 engines. All cars except the Buick had been operated previously for 20,000 to 22,000 miles. The Buick registered 33,000 miles on its odometer. Prior to the tests, each car was "tuned up" and put into good operating condition. However, the oil rings on the Buick were filed and replaced without expanders to induce high oil consumption. Two types of oil were used: one containing a calcium compound detergent was used in the DeSoto and Ford; the other containing a barium compound detergent was used in the other cars. The two Chevrolets were fueled with 76- and 78-octane number (Motor method) nonleaded gasolines; the others, with a premium gasoline containing 3 ml. TEL per gallon.

Because the two Chevrolets to be fueled with "white" gasoline had previously been operated with leaded gasoline, residual lead in the engine and fuel system had to be removed. The Chevrolet on which the Oxy-Catalyst muffler was installed was extensively deleaded by the equivalent of a "carbon-and-valve job" and the fuel system oil pan thoroughly cleaned, at a cost of approximately $100. Only the fuel system of the other Chevrolet was deleaded, but this car was operated on white gasoline for more than 50 hours to accomplish engine "deleading" prior to muffler installation.

Each car was operated for 10,000 miles over a course and under conditions believed to be roughly equivalent to the average traffic conditions of Los Angeles as determined by the Los Angeles County Air

Pollution Control District. At the end of each 1,000 miles (about every third day of operation), the exhaust gases were analyzed for hydrocarbon content on an infrared spectrophotometer. Samples were obtained during idling, acceleration (0-40 mph), cruising (50 mph), and deceleration (60-45 mph), all simulated with cars on a chassis dynamometer. A summary of the results follows.

The "Oxy-Cat" (for unleaded gasoline), similar to a commercial catalytic converter used on material-handling equipment operating in confined areas, maintained an efficiency during decelerating conditions varying between 82 per cent and 94 per cent conversion of hydrocarbons to combustion products (carbon dioxide and water). Analysis of a limited number of samples collected during other types of operation indicated conversions of 85 per cent to 88 per cent during idling, 0 to 46 per cent during acceleration, and 40 per cent to 70 per cent during cruising.

The "Intermediate White Muffler" (for unleaded gasoline), similar in outward appearance to the units supplied for use with leaded gasoline, varied in conversion efficiency under decelerating conditions from 56 per cent to 92 per cent during the first 3,000 miles, after which activity fell off so sharply that conversion was negligible during the last 5,000 miles. Analysis of a limited number of samples taken during other conditions of operation indicated conversions of 0 to 74 per cent during idling, 0 to 73 per cent during acceleration, and 0 to 62 per cent during cruising.

The "Leaded Mufflers" (summary of results of five units) varied in conversion efficiency under conditions of deceleration from 20 per cent to 90 per cent during the first 3,000 miles, and during the remainder of the program from 0 to 45 per cent. As with the "white gas" mufflers, only a limited number of samples were collected under the other phases of operation; analyses indicated that conversion varied between 0 and 95 per cent during idling, 0 and 88 per cent during deceleration, and 0 and 94 per cent during cruising.

Weighting the hydrocarbon conversion data to reflect realistic operation (with the application of the ratio of exhaust gas volumes and driving times previously reported by the Los Angeles County Air Pollution Control District), the results may be summarized as follows:

CHAPTER IV--TABLE II

HYDROCARBON CONVERSION EFFICIENCY

Muffler Type:	Oxy-Cat	Intermediate	Leaded
Miles	- - - - Per Cent Efficiency - - - -		
0	80	58	81
1,000	90	74	67
2,000	86	83	63
3,000	85	87	59
4,000	86	41	22
5,000	85	9	17
6,000	87	33	15
7,000	86	6	13
8,000	82	4	11
9,000	82	6	9
10,000	82	6	8

The failure of the leaded mufflers resulted from two factors--poisoning of the platinum catalyst by lead compounds in the exhaust, and structural failure of the muffler itself. When the mufflers were removed from the cars, they were examined by employees of Oxy-Catalyst, Inc., but not by personnel of Southwest Research Institute (because of a previous agreement with the manufacturer).

Just how the problem of poisoning may be solved has not been determined. Oxy-Catalyst has developed a method by which, it is claimed, the activity of the catalyst may be restored in place by a 30-minute treatment at any filling station, and they suggest that this treatment be made after each 3,000 miles of operation. The treating method was not evaluated at Southwest Research Institute, but the practical difficulties of enforcement are obvious.

With regard to the structural failure of some of the units, Mr. Houdry says, "Based on the condition of the structure after 10,000 miles of operation, the problems involved were minor and easy to solve. New designs were discussed and approved. A perfected prototype was built immediately and has been under test with very satisfactory results for 336 hours. We are continuing the testing at the rate of 100 hours per week." The Foundation continues to watch this development closely.

Clayton Afterburner

The other exhaust device of promise, the Clayton afterburner, is a product under development by the Clayton Manufacturing Company, El Monte, California. Several prototypes of this afterburner have been built and are currently under test on buses in public service operation in Los Angeles. The unit replaces the muffler and oxidizes the hydrocarbons in the exhaust by mixing outside air with the hot exhaust gases. Burning is initiated by sparking. One prototype has recently been tested in the automotive laboratory of the Los Angeles County Air Pollution Control

District. The main problem appears to be that of sustaining a flame under all conditions of engine operation, particularly cruising. When the flame is existent, the efficiency of hydrocarbon removal appears to be above 90 per cent. Further development work is in progress by the manufacturer.

A study of the theoretical aspects of noncatalytic afterburners was recently published by the University of California, Los Angeles (Ref. 6). The authors concluded that a reduction of unburned exhaust hydrocarbons from 600 ppm to 20 ppm can be accomplished by noncatalytic afterburning but that design of a practical device required further studies.

Critical Review of Control Devices for Hydrocarbons from Automobile Exhaust

At the request of the Air Pollution Foundation, Southwest Research Institute, San Antonio, Texas, made a study of the principles involved in the design and application of various devices for the reduction of hydrocarbons in automobile exhaust. Significant conclusions were:

1. Catalytic Exhaust Converters. When used with white gasoline, the OCM muffler would probably reduce hydrocarbon emissions at least 70 per cent. The leaded muffler is currently effective for less than 3,000 miles of operation. Costs are given in the report. Further development work is in progress.
2. Afterburners. Two models show promise for use on buses.
3. Absorption by Liquids. No suitable device known; probably not an effective approach to problem.
4. Adsorption by Solids. Same as above.

5. Condensers. Would be much too large.
6. Filters. Not effective for hydrocarbon removal.
7. Manifold Vacuum Control. Effective only during deceleration; under development by automobile industry.
8. Deceleration Fuel Cutoff. Highly effective during deceleration; presents operating problems; under development by automobile industry.
9. Throttle Dashpot. Highly effective during deceleration; cheap; under consideration by automobile industry.
10. Automatic Spark-Retarding Mechanism. No data available.
11. Improved Engine Maintenance. May reduce hydrocarbons by as much as 50 per cent and at the same time reduce operating costs.
12. Fuel Injection. More test data required; would involve major engine design changes.
13. Exhaust Gas Recycling. Not feasible for automobiles.
14. Engine Design Changes. Improvement will be slow.

The authors conclude that the only system that warrants immediate consideration is the combination of unleaded gasoline with a suitable catalytic converter, but even this is considered of marginal feasibility.

Of secondary importance, chiefly because of lack of information, is the combination of improved car maintenance and a device to limit fuel flow during deceleration. It is possible that this combination could reduce hydrocarbon emissions by as much as 80 per cent and still allow use of present leaded gasolines. The Air Pollution Foundation recommends that this approach receive further investigation promptly.

D. SUMMARY OF CONTROL DEVICE DEVELOPMENT AND FUTURE PLANS

The status of the development of air pollution control methods may be summarized as follows:

Aerosols

A wide variety of devices is available for partial control of aerosols in stack gases. Reasonable devices are still needed, however, for effective elimination of particles smaller than one micron.

Aerosols and other pollutants from domestic incinerators can best be controlled by elimination of backyard burning. Cut-and-fill methods are feasible means of refuse disposal until more efficient large-scale incinerators can be developed. If aerosols from automobile and diesel engine exhaust prove to be significant, methods of removal must be developed.

Hydrocarbons and Other Organics

Hydrocarbon evaporative losses from the production, refining, and marketing of petroleum products have been reduced, according to District figures, by more than 60 per cent. Methods and devices for further reduction are being developed by the District and the oil companies concerne

Hydrocarbons from automobile exhaust have not yet been subjected to control measures. The development of suitable devices, however, is being aggressively attacked by automobile manufacturers and other industrial and governmental organizations. If application of technical talent is any criterion, this work should bear fruit in the near future.

Sulfur Dioxide

Currently, sulfur dioxide control regulations in Los Angeles County are more severe than any similar regulations known to be in force anywhere. Further reduction of emissions could be obtained by limiting the sulfur content of fuels, but the economic burden would probably be intolerable and in our present state of knowledge of questionable value in smog reduction.

Oxides of Nitrogen

At the present time, oxides of nitrogen are not under control regulations, nor are effective methods known which are applicable to the low concentrations involved. Recent attempts by the British Ministry of Fuel and Power to reduce oxides of nitrogen in diesel exhaust by a scrubbing device were reported as unsuccessful (Ref. 7).

Data on exhaust gases from diesel engines were also published by Davis and Holtz (Ref. 8), who reported on wet-scrubbing tests (using ferrous sulfate solution) for removal of oxides of nitrogen from diesel exhaust gases. Results were erratic, varying from 0 to 40 per cent removal.

Current Problems

The development of adequate controls for the further reduction of important air pollutants is obviously a job of considerable magnitude. Accordingly, the Air Pollution Foundation finds it necessary to limit its studies in this field to the most pressing needs of the community and to those areas neglected by others. An intensive survey of current needs raises the following questions of immediate pertinence:

1. Will a 50 per cent reduction in hydrocarbon emissions from automobile exhaust markedly reduce the frequency or severity of smog attacks? If not, is 70 per cent required? 90 per cent?

This is an extremely important question for the following reason. The automobile manufacturers expect to have available by January 1, 1957 a device that may reduce hydrocarbon emissions by 50 per cent. At that time, the Los Angeles County Air Pollution Control Board will be faced with these questions: Is there enough evidence to warrant enforced application of such a device to all automobiles in Los Angeles County on the basis that smog manifestations will be reduced markedly by its use? Should they await development of a device to reduce hydrocarbons by a larger amount? How much? Or will any conceivable device be helpful?

Unfortunately, although there is considerable circumstantial evidence that exhaust hydrocarbons are the major contributors to eye irritation, the exact relationship has not been proved or demonstrated to the satisfaction of many scientific and technical authorities. The Foundation is currently trying to answer this question through its project at Midwest Research Institute, Kansas City, Missouri. The first order of business for 1956 will be intensification of the study by means of an additional project at another location. Once we are able to demonstrate quantitatively the relationship between hydrocarbons from automobile exhaust and eye irritation, the evaluation of suggested devices should be simplified.

2. Concurrently with a reduction in atmospheric hydrocarbons, will reduction of oxides of nitrogen be necessary?

There are several scientists of high repute who believe that not only will reduction of atmospheric hydrocarbons be essential to eliminate smog, but some concurrent reduction in oxides of nitrogen will also be necessary. This entire problem is complicated by lack of knowledge of many of the relationships between the various oxides of nitrogen and organic nitrogen compounds in the atmosphere, and how these oxides are formed during combustion.

The Foundation therefore believes it to be of utmost importance to study these basic relationships further, with the hope that such studies may indicate a favorable avenue of approach to a control method. Without such basic studies, development of controls will not only be an expensive undertaking but also of questionable value. A basic program is being planned for next year.

Concurrently, however, development of suitable analytical methods and a more careful analysis of the content of oxides of nitrogen in automobile and stack emissions are imperative. The Foundation is recommending that the Control District, industry in general, and the Coordinating Research Council initiate or continue work along these lines.

3. How may extremely fine aerosol emissions, presently uncontrollable, be controlled?

The opinion of medical authorities as to the probable health hazards of very fine aerosols is sufficient reason for seeking a method of control. Furthermore, the high correlation between the aerosol content of the atmosphere and eye irritation found in our aerometric survey (Ref. 9) lends support to the need for more information and, possibly, control. Further information should also be sought as to the nature and amount of aerosol emissions in automobile exhaust.

A complicating factor is some evidence that aerosols not emitted from pollution sources form in the air as the result of chemical reactions between normally gaseous compounds. Consequently, the Foundation is presently carrying out work on the formation, growth, size distribution, and chemical composition of atmospheric aerosols. This work will be continued and expanded. In cooperation with the United States Public Health Service and the California Department of Health, the Control District plans to study the composition of stack plumes with the objective of learning more about the nature of aerosol formation in the open atmosphere. This leaves the field of aerosols from automobile exhaust untouched, although currently the University of California is studying the effectiveness and economy of removing particulate matter from automobile exhaust by means of a water scrubber.

A Look at the Future

Any summary of the status of development of control devices would be incomplete without a discussion of the probable nature of ultimate controls. Although any prediction is largely conjecture, certain probabilities stand out. They are:

1. There is little likelihood that any practical changes in the meteorology or topography of the Los Angeles Basin would be effective in reducing smog. The quantities of energy required to transform or modify these natural influences appear to be far beyond any resources of man of which we have knowledge at present.

2. Control of the effluents from the domestic burning of rubbish can well be accomplished by banning this archaic practice. Cut-and-fill disposal may offer effective relief for some years, but eventually improved designs for municipal large-scale incinerators will probably have to be developed. Adequate designs await further research.

3. The control of air-borne particulate matter from industrial stacks will have to be attacked from two different standpoints. Improved efficiency of combustion could eliminate organic aerosols, but inorganic materials will have to be removed from the stack gases by physical or chemical means. Both approaches require further research.

4. If sulfur dioxide emissions are found to require further reduction, the most effective attack may well be elimination of sulfur from the fuel. Suitable methods, particularly for residual fuel oil, are currently not available.

5. Further control over hydrocarbon and solvent losses by evaporation means an extension of vapor recovery or combustion systems. More engineering research will be required to develop economic equipment for this purpose.

6. Control of the hydrocarbon emissions from the exhaust of internal-combustion engines awaits an effective method. In the case of spark-ignited engines, four areas show promise: fuel cutoff devices operating during deceleration, exhaust converters (either catalytic or noncatalytic), fuel injection, and improved maintenance. It may well be that ultimately some combination of the above may be most suitable. In the first three areas adequate devices are not yet developed, although automobiles using fuel injection could well appear in 1957. Such designs would obviate the need for a fuel cutoff device. Even so, exhaust converters would still be needed.

   The quantitative value of improved maintenance has not yet been determined. Whether governmental action in this regard will be desirable depends on the magnitude of hydrocarbon reduction that could be achieved and the nature of other control devices to be used.

   Slightly different problems are presented by the diesel engine, but these should be amenable to further research. Such work should be initiated at once.

If the gas turbine engine becomes a reality for automobiles, other problems may develop. It is assumed that the automobile manufacturers will anticipate this possibility.

7. The one area in which it is difficult to envision an effective control device is for oxides of nitrogen, whether they are emitted from automobiles, diesels, or industrial stacks. Obviously, a concerted research study is badly needed.

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STATEMENT OF POLICY OF THE AIR POLLUTION FOUNDATION

PURPOSE OF THE FOUNDATION

An independent, nonprofit corporation has been established for the following purposes:

1. To cooperate with, and to assist in coordinating the efforts of, governmental agencies, educational institutions, specialized research groups, and medical, legal, and other technologists, so that every phase of air pollution shall be the object of careful study and constructive, remedial action.
2. To provide for research on those phases of the problem not already undertaken or completed by other agencies.
3. To inform the public periodically concerning the nature and extent of air pollution, progress made in its elimination, and obstacles to such elimination.

ORGANIZATION OF THE FOUNDATION

The Board of Trustees of the Foundation is composed of business, professional, and industrial leaders with records of conspicuous public service. About one-third are representatives of industrial enterprises which are or may be contributors in some degree to air pollution. The principal reason for their membership on the Board, in addition to their recognized standing in the community, is to make certain that they will be parties to all facts and evidence brought to light on the problem, so that they and their colleagues in like enterprises can continue to devote their best efforts toward the abatement of air pollution.

As a matter of policy, not more than one representative of a given industry serves on the Board at a time. Trustees serve without compensation, nor do they contribute financially to the Foundation. Less than half of the Trustees represent companies or organizations which are providing financial support, and most of these do not contribute to air pollution.

The funds of the Foundation are donated by about 150 different enterprises, trade associations, banks, insurance companies, and industries, representing a cross section of the community. Few of the donors are or may be contributing to air pollution, and less than one-half of total funds received come from all such sources combined.

Financial contributions are unrestricted as to purpose and convey no rights to the donors other than to receive copies of reports, findings, and recommendations. Neither membership on the Board of Trustees nor donation of funds can in any way obtain privileged treatment in connection with responsibility for air pollution or its abatement. The work of the Foundation will be conducted with complete objectivity at all times and its findings are made impartially.

A Managing Director and a limited staff of experts will conduct the day-to-day activities of the Foundation under the general supervision of the Board of Trustees.

WHAT THE FOUNDATION PROPOSES TO DO

1. To assemble a competent technical staff to organize and direct a broad program of cooperation, research, and public information.
2. To determine, record, and publish what has been accomplished to date by all agencies dealing with air pollution.
3. To determine what remains to be done and to employ experts through the device of research or service contracts, who will provide information and advice for the shaping of future policies and action.
4. To collect information as to what other municipal areas have done, and are doing, under similar circumstances.
5. To maintain a library of materials pertinent to the subject of air pollution.
6. To consult with, exchange information with, and to suggest to governmental and private agencies those research activities, enforcement methods, or other matters, which have not yet been conducted or tried and which seem to offer promise of air pollution abatement, so that the efforts of all groups and individuals may be coordinated properly.
7. To hold technical conferences with experts and specialists working in this country or abroad on selected phases of the air pollution problem in order to facilitate and accelerate the process of finding solutions.
8. To publish current information by the most appropriate means on all phases of air pollution and its abatement.

WHAT THE FOUNDATION DOES *NOT* PROPOSE TO DO

1. It will not duplicate services already rendered by governmental or private agencies.
2. It will not conduct research activities directly, unless it appears clear that no existing agency can conduct them as advantageously.
3. It will not expend funds entrusted to it for the construction or equipping of Foundation laboratories that will duplicate facilities already available.
4. It will not hold public hearings for the purpose of receiving complaints, or in any way substitute for governmental agencies now charged with responsibility for certain phases of the air pollution problem.
5. It will not offer any immediate or ready solution for a very complicated, long-range problem.

HOW THE WORK OF THE FOUNDATION MAY BE ASSISTED

Those who believe that the proposed activities of this independent Foundation can be of help may assist in this work by making contributions payable to the AIR POLLUTION FOUNDATION, addressed to its headquarters at 704 South Spring Street, Los Angeles 14, California.

Contributions from governmental organizations, business or industrial enterprises, and from private citizens will be welcomed by those in charge of its program.

A WORD OF CAUTION . . . AND AN INVITATION

The smog-free skies of an earlier day in California cannot be brought back immediately by any endeavor, however resolute the attempt, or through any quick expenditure of funds; they can be restored over a reasonable time by diligent and honest fact finding, by wise and effective action.

Air pollution is now recognized as a national problem. The fundamental contributions which the Foundation is making toward the solution of urban air pollution are attracting increasing national attention.

ASSUMPTIONS MADE BY THE FOUNDATION

1. That the problem of air pollution is one of the most serious confronting urban areas in California and elsewhere; that it is worthy of the best efforts of everyone concerned; and that it calls for the expenditure of whatever funds are needed for its solution.
2. That the air pollution problem is not new and is generally increasing.
3. That geographical and meteorological features often contribute materially to the air pollution problem, especially in the Southern California area.
4. That every additional person or industrial enterprise locating in this area potentially adds to the problem.
5. That much excellent work has been done by governmental and private agencies to reduce air pollution, and by the press to keep the public informed; that the public should be informed of all significant phases of the problem.
6. That further information must be obtained and additional action taken before the air pollution problem can be brought under proper control.
7. That there is no quick or easy solution to the problem, no matter what funds should be spent immediately or what laws should be invoked. There is an understandable tendency to oversimplify this problem and to insist that its obvious seriousness and urgency somehow must expedite its solution.
8. That the control of emission of particular gases, fumes, or dusts may not alone solve the problem. (Some of these pollutants, believed to be harmless or of minor importance individually, may in combination undergo photochemical reactions in a manner not completely understood at present.)
9. That while the solution of the urban air pollution problem is long range, short-range steps should be taken to alleviate it further, as soon as reliable facts are available and policy decisions have been made.
10. That many of the findings of the Foundation, including methods of attacking the air pollution problem as well as remedies, are applicable to all metropolitan areas and should be widely disseminated.

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