A Critique of the 1975-1976 Federal Automobile Emission Standard for Hydrocarbons and Oxides of Nitrogen (1973)

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A CRITIQUE OF THE 1975-76 FEDERAL AUTOMOBILE EMISSION STANDARDS FOR HYDROCARBONS AND OXIDES OF NITROGEN

Prepared by the Panel on Emission Standards
and the Panel on Atmospheric Chemistry

for the
COMMITTEE ON MOTOR VEHICLE EMISSIONS
NATIONAL ACADEMY OF SCIENCE

May 22, 1973

NOTICE

The Committee on Motor Vehicle Emissions has evaluated the technological feasibility of meeting the light-duty motor vehicle emissions standards as prescribed by the Clean Air Amendments of 1970. This study was performed under the sponsorship of the National Academy of Sciences and with the express approval of the Governing Board of the National Research Council.

The Committee obtained much of its information from eight panels of consultants, each panel dealing with a particular subject area of importance in the Committee deliberations. Panel members were selected by the Committee on the basis of recognized competence in specific areas.

The panel reports are reports of the panels to the Committee. Before publication, each panel report was reviewed by appointed members of the Committee. The views represented by the panels are one of the sources of information provided to the Committee and were used as a partial basis for the Committee judgments.

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PREFACE

In legislating the Clean Air Amendments of 1970, the Congress asked the Environmental Protection Agency to contract with the National Academy of Sciences to conduct a comprehensive study and investigation of the technological feasibility of meeting the motor vehicle emissions standards prescribed in accordance with the law. In responding to this request, pursuant to a contract with the Environmental Protection Agency, the Academy established a Committee on Motor Vehicle Emissions and charged it with the conduct of this study. The Committee published the results of its work in a report to the Environmental Protection Agency dated February 12, 1973.

As means of providing itself with authoritative information and expertise in the various critical aspects of the problem it undertook to study, the Committee appointed specialist panels to undertake investigations and report their findings. The following report, A Critique of the 1975-76 Federal Automobile Emission Standards for Hydrocarbons and Oxides of Nitrogen, was prepared jointly by the Panel on Emission Standards and the Panel on Atmospheric Chemistry.

Taken together, the special panel reports, of which this is one, constitute a very substantial accumulation of data and analysis brought together by many specialists in many investigations in a very fast-moving area of technological development. In its published report, the Committee on Motor Vehicle Emissions has, of course, brought together that part of all this information and analysis required to fulfill its stated obligation to the Environmental Protection Agency. The separate reports of the specialist panels are published for the public record and to complete the documentary record.

The members of the Panel on Emission Standards are:

Professor Arthur C. Stern, Panel Chairman
University of North Carolina
Chapel Hill, North Carolina

Professor Leslie A. Chambers
University of Texas
Houston, Texas

Mr. James Fitzpatrick
Environmental Analysts, Inc.
Garden City, New York

Mr. John A. Maga
Air Resources Board
Sacramento, California

The members of the Panel on Emission Standards acknowledge the efforts of its technical Assistant, Richard Kamens, in the preparation of this report. He, in turn, was assisted by Drs. Guiseppe Fumarola, University of Genoa, Italy, Yuji Horie and John Overton of the EPA-supported research project #1 R01 AP01130-01 "Critique of Air Quality Management Standards" at the University of North Carolina at Chapel Hill.

The members of the Panel on Atmospheric Chemistry are:

Dr. Lowell Wayne
Pacific Environmental Services, Inc.
Los Angeles, California

Dr. Edgar Stephens
Air Pollution Research Center
University of California
Riverside, California

A member of the Committee on Motor Vehicle Emissions, Harold S. Johnston, has prepared an independent statement in which he identifies and comments upon matters he feels should have been included in the report, and without which he considers the report to be incomplete. Professor Johnston's statement is presented following the joint Panel report.

Contents

1. Introduction

Even if oxides of nitrogen (NO_x) did not participate in the smog reaction with non-methane hydrocarbons (NMHC) to produce undesirably high levels of oxidant (O_x) and other photochemical reaction products it would still be necessary to control NO_x emissions to prevent atmospheric NO_2 concentrations from reaching levels unsafe for health (1). This report examines the air quality standard for oxidant (2); the atmospheric concentrations of NMHC (3) required to achieve this oxidant standard and the atmospheric concentrations of NO_x required to achieve the air quality standard for NO_2; and the automotive emissions of hydrocarbons (HC) and NO_x necessary to achieve these air quality standards.

2. Oxidant

Background Concentration of Oxidant

If there were no background ozone or other oxidant in the air, it would be expected that when both HC and NO_x were zero, oxidant would also be zero. However, in the ambient atmosphere there is a background value of from 0.01 to 0.05 ppm; a reasonable typical value may be 0.02 ppm (4).

Choice of Oxidant Standard

The Federal standard for oxidant is 0.08 ppm. The California standard is 0.1 ppm. Both are 1-hour averages. The difference between these standards is equal to the typical background value of 0.02 ppm. These two values can be considered as if they were essentially the same standard. The models that relate oxidant to HC and NO_x are not refined enough at this time to distinguish between these two standards.

Oxidant Production in the Atmosphere

Most of the oxidant is ozone. Although ozone is produced in a large quantity in the upper atmosphere, only a relatively small quantity reaches ground level. Photochemical reactions in nonurban air also produce ozone. Some of this ozone is in the background air that may reach urban areas. However, these sources of ozone are small compared to the ozone generated in urban air by photochemical reaction among hydrocarbons, nitrogen oxides, and oxygen (5-6).

Average hourly values of ozone, hydrocarbons, aldehydes for 1953-54 are compared in Figure 1 to average values of nitric oxide and nitrogen dioxide for 1958 on days of eye irritation in Los Angeles. This typical pattern is cited by Leighton (7) from Los Angeles County data. Ambient air monitoring records such as this reflect the effects of vertical

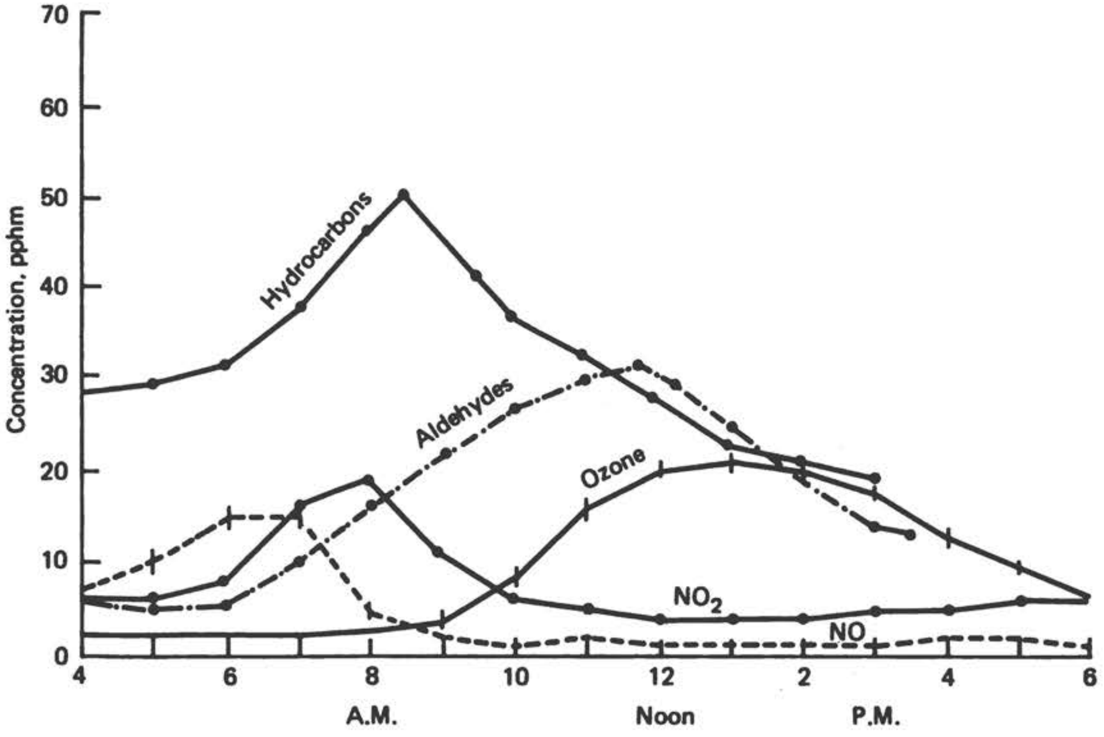

FIGURE 1 Average concentrations during days of eye irritation in downtown Los Angeles. Hydrocarbons, aldehydes, and ozone for 1953 - 54. Nitric oxide and nitrogen dioxide for 1958. From data of the Los Angeles County Air Pollution Control District. (From Leighton, Ref. 7)

dilution, photochemistry, advection, and continued contamination of the atmosphere. It is very difficult to disentangle these various influences. Trapping of pollutants is often best in the early morning hours when radiation inversions are strongly developed. Maximum concentrations of primary pollutants are found at this time. During the course of the day, sunlight not only causes photochemical reactions, it also causes increased mixing of the pollution and it generates a sea breeze that causes advection of pollutants from upwind areas. Most of the nitrogen oxide emitted by automobiles and other combustion sources is in the form of nitric oxide. It is well recognized that nitric oxide reacts extremely rapidly with ozone. It is paradoxical that automobiles and other sources emit hundreds of tons of nitric oxide into the atmosphere, but that nitric oxide is capable of scavenging the ozone in the atmosphere at an extremely rapid rate. In other words, auto exhaust destroys photochemical smog or at least the principal index of photochemical smog, namely ozone. Time and irradiation are required to generate ozone in dilute auto exhaust. This accounts for the observation that very high oxidant levels are being reported increasingly from remote areas, such as the San Bernardino Mountains, the San Jacinto Mountains, Palm Springs, Indio and Banning and Beaumont in the San Gorgonio pass. Recent aircraft surveys have revealed much higher levels of oxidant aloft than at ground level (8). Oxidant has also been found in remote locations well after dark. All of these observations show the importance of irradiation of the polluted air for a significant period of time away from the source of pollution, namely, dense concentration of automobiles.

The fast reaction between ozone and nitric oxide results in a delay of the actual appearance of ozone when dilute auto exhaust is irradiated. Many laboratories have found that during this interval NO is converted more or less rapidly to NO_2. Significantly, not only is ozone appearance delayed, but appearance of PAN and aerosol are also delayed. Since these products cause several of the most important smog symptoms, these are also delayed until the conversion of NO to NO_2 is complete.

In Appendix A, 15 diagrams drawn from reports of laboratories around the country using a variety of experimental methods are discussed, showing various aspects of the inhibition of the smog reaction by NO. These results are synthesized into one diagram in Figure 2, which is schematic and somewhat idealized. The upper left quadrant describes the present situation in which conversion of NO to NO_2 is rapid and is followed by the appearance of ozone, peroxyacylnitrate (PAN) and aerosol. Many laboratory studies have shown that reactive hydrocarbon is necessary for this conversion, and reduction in the amount of hydrocarbon or its reactivity slows down this reaction. So, partial control of hydrocarbon, either of the quantity or the reactivity, is shown in the lower left quadrant. In this case, symptoms of ozone, PAN and aerosol would be delayed, would develop later in the day, and would be observed farther downwind. The increasing levels of oxidant in Riverside and in desert areas of Southern California support this premise. However, the lower left quadrant also shows a high NO_2 level at long radiation times, and this is not acceptable. Control of NO is shown by the quadrant at the lower right. Since there is less NO to be converted to NO_2, less time is required; and the ozone, PAN, and aerosol appear sooner.

No one experimental investigation shows all three of these products so clearly as they are shown in Figure 2. But collectively, the data in Appendix A support this diagram. To provide a basis for control strategy, experiments with actual auto exhaust, with realistic irradiation times, and at realistic concentrations should be consulted. At present, the best reference for this purpose is the work (cited in No. 15 of Appendix A) performed at the Bureau of Mines in Bartlesville, Oklahoma, and reported by Basil Dimitriades. Auto exhaust at realistic concentration levels was irradiated for 6 hours. At the highest levels of nitric oxide, acceptable oxidant levels were obtained even though the NO_2 standard was exceeded. Reduction of nitric oxide actually

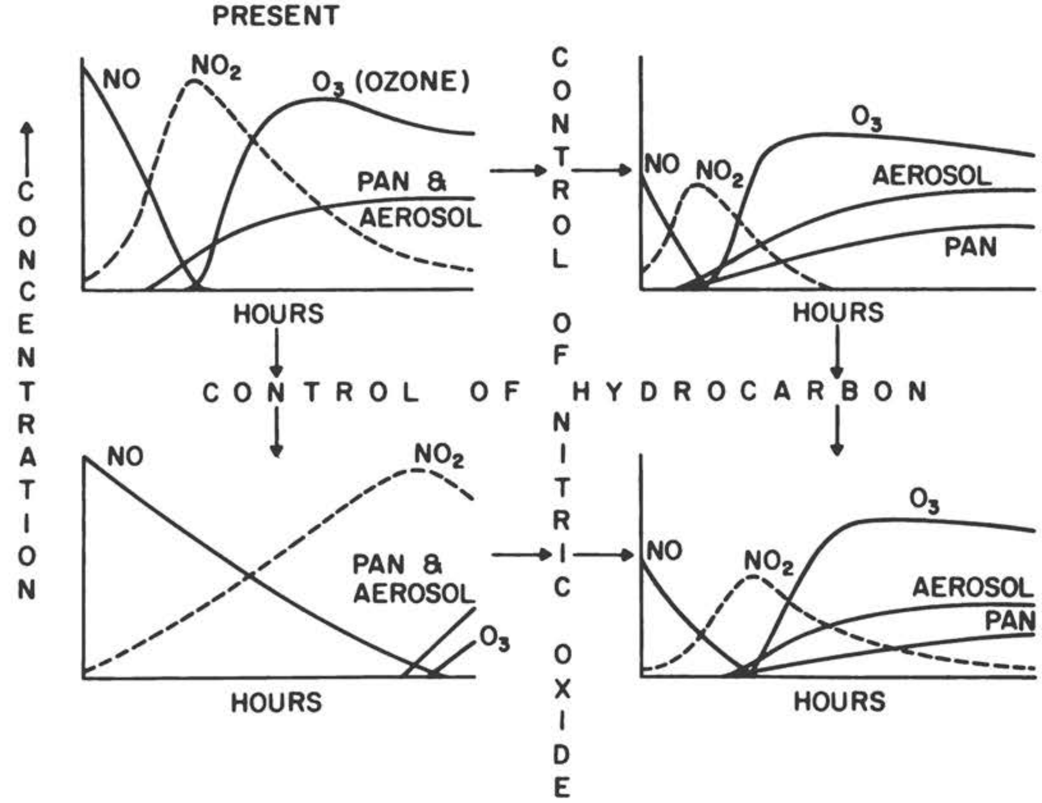

FIGURE 2 Idealized schematic representation of NO, NO_2, O_3, aerosol and PAN (peroxyacylnitrate) interaction. The coordinates of concentration and time are deliberately left unnumbered because quantitative knowledge is still lacking.

caused the oxidant standard to be exceeded. In the next section, the Bureau of Mines Study is used to estimate the control of HC and NO_x needed to attain acceptable air quality.

The National Air Quality Standard for HC is based on a 6-9 a.m. average concentration (measured as non-methane hydrocarbon to exclude nonreactive methane), because this time period is when the highest atmospheric concentrations at central urban locations are usually found, and it is followed by the sunlight needed to drive the photochemical reaction.

3. Hydrocarbon and Nitrogen Oxide Concentration Required To Meet Oxidant Standard

General

The results from recent reaction chamber experiments by Dimitriades (9), in which known concentrations of HC and NO_x were added to initially oxidant-free air, are shown in Figure 3. The sloping lines of Figure 3 correspond to the National Air Quality Standard for oxidant - 0.08 ppm (1-hour average). The chart shows that values of HC and NO_x to the left of line a-b and below b-c yield less than 0.08 ppm oxidant after 6 hours of irradiation equivalent to Los Angeles sunlight. Line a-b is dotted near the origin, and line b-c does not reach the origin because it is recognized that when both HC and $NO_x = 0$, there is no photochemical oxidant production. The author of Figure 3 has included line d-f to represent his estimate of the average NO_x concentration equivalent to the National Air Quality Standard for NO_2, expressed as an annual average, and he has cross-hatched the areas in which neither this NO_x concentration nor the 0.08-ppm oxidant concentration are exceeded. Although this estimate of the equivalent 3-hour average NO_x value (i.e., line d-f) differs from the value derived later in this report, this difference affects only the locus of line d-f, not its meaning. Figure 3 characterizes the atmospheric oxidant-producing system in an experimental chamber and is readily interpretable. This is in contrast to atmospheric data, which often show much scatter and produce ill-defined oxidant curves.

Figure 4, which follows the form of Figure 3, graphically illustrates what must be accomplished to control atmospheric oxidant. Line d-f represents the atmospheric concentration of NO_x equivalent to the air quality standard for NO_2. Curve a-c represents the air quality standard for oxidant according to Figure 3. Stephens (10) states, in part: "The upper boundary of Figure 4 reflects the inhibiting power of NO. . .

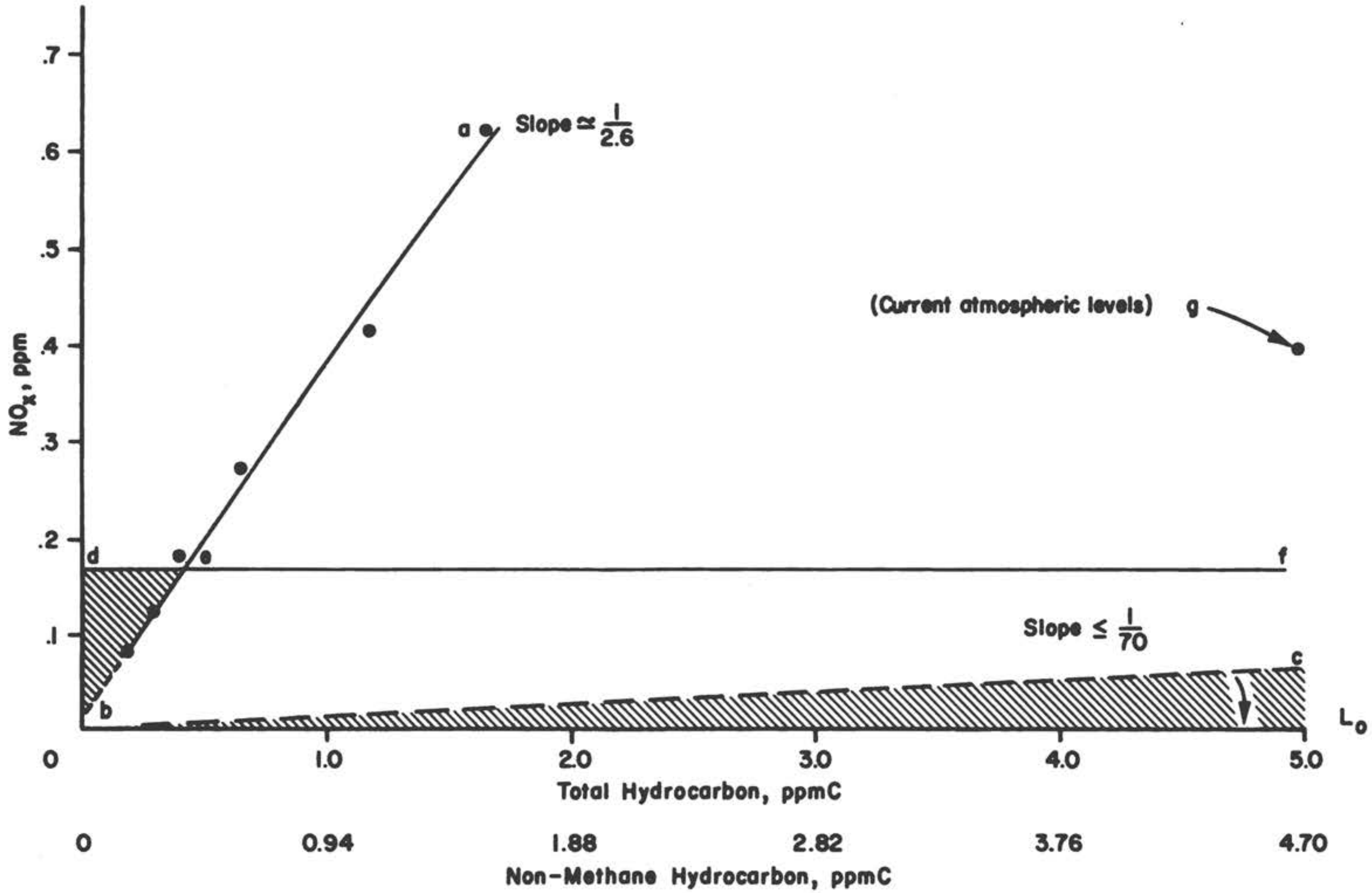

FIGURE 3 Equal response lines representing combinations of total hydrocarbon and NO_x corresponding to oxidant and NO_2 yields equal to current national standards. Exhaust data. (From Dimitriades, Ref. 9)

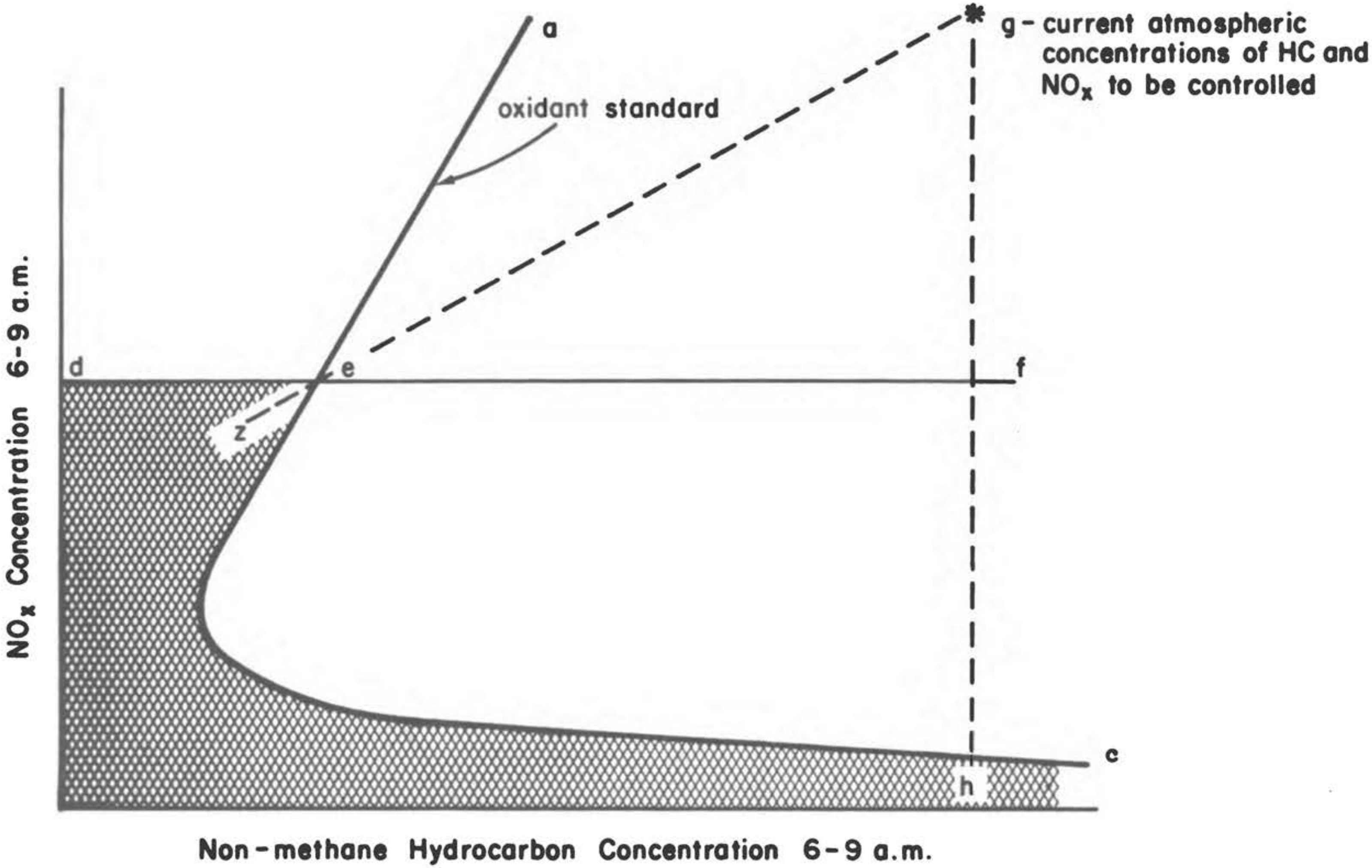

FIGURE 4 General oxidant control diagram.

If the other boundary slopes. . . [away from the hydrocarbon axis] it would indicate inhibition by hydrocarbon. I question if this has ever been shown. . . A far more reasonable boundary would slope toward the hydrocarbon axis. The two boundaries would then meet somewhere near the origin of the plot." Point g represents present air quality. The area between curve a-c and the chart axes represent allowable concentrations of HC and NO_x at which the oxidant standard will be achieved. The area below d-f represents allowable combinations at which the NO_2 standard based on health is met. The area below d-e-c will allow both the oxidant and NO_2 standards to be met. It is possible to get from point g to area d-e-c by following line g-z, in which case both HC and NO_x are reduced or by following line g-h without decreasing HC. In considering the feasibility of going to point h by only controlling NO_x, note must be taken (a) of the fact that point h is located in terra incognita and its location is completely speculative; (b) of the background concentration of NO_x, which is of the order of 0.006 ppm (11); and (c) of the large contribution to NO_x from stationary sources of combustion in urban areas. No point h, achievable by reducing automobile exhaust NO_x emission, will exist, since the combination of the urban stationary source contribution plus the nonurban background of NO_x (12) will in most cases exceed NO_x values along the right arm of curve d-e-c. This leaves path g-z as the only feasible path.

Air Quality Standard for Nitrogen Oxides

The National air quality standard for NO_2 is 0.05 ppm, annual average. If it is assumed that NO_2 data are log-normally distributed, and that the equivalency procedure of Larsen (13) is used, an annual average NO_2 of 0.05 ppm is equivalent to a 1-hour average NO_2 concentration of the order of 0.35 ppm.* The California NO_2 standard of

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*For a discussion of this equivalency procedure, see Appendix B-2.

0.25 ppm, 1-hour average, is somewhat more restrictive (Figure 5).

In Figures 3 and 4, line d-f is the NO_x equivalent of a 3-hour average NO_2 standard. Using the same equivalency procedure as the previous paragraph, the 3-hour average NO_2 value comparable to the 0.25 ppm, 1-hour average, California standard, is approximately 0.19 ppm. However, NO_x varies from about 16 to 92 percent NO_2, so that the NO_x values equivalent to 0.19 ppm NO_2 range from 0.21 to 1.2 ppm.* For purposes of computing emission limits on automobiles, it must be recognized that there are nonautomotive sources of NO_x. Therefore a value of 0.3 ppm NO_x, 3-hour average, has been used in these computations. This value appears to be conservative, since it is at the low end of the above range.

Air Quality Standard for Non-Methane Hydrocarbon

The hydrocarbon standard is based solely on oxidant production, since at the atmospheric concentrations of oxidant production in concern, there are no health or vegetation damage effects of HC or NMHC. If we use an oxidant standard of 0.08 ppm (1-hour average) and the above-noted NO_x standard of 0.30 ppm (3-hour average), a 3-hour average non-methane hydrocarbon standard of 0.75 would follow from Figure 3. (See Appendix C for further discussion.)

Some concentrations of NO_x and non-methane hydrocarbons that proponents believe will achieve the oxidant standard are

	NO_x (ppm)	HC (ppm, 3-hr)
Federal Standards	(0.05 ppm NO_2) (annual av.)	0.24
Merz *et al.*(12)	0.25 (3-hr)	0.5
Dimitriades	0.17 (3-hr) 0.33 (3-hr)	0.4 0.8
This report	0.3 (3-hr)	0.75

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*The NO_2 referred to is the daily 3-hour maximum. The NO_x is the 6-9 a.m. value for the same station.

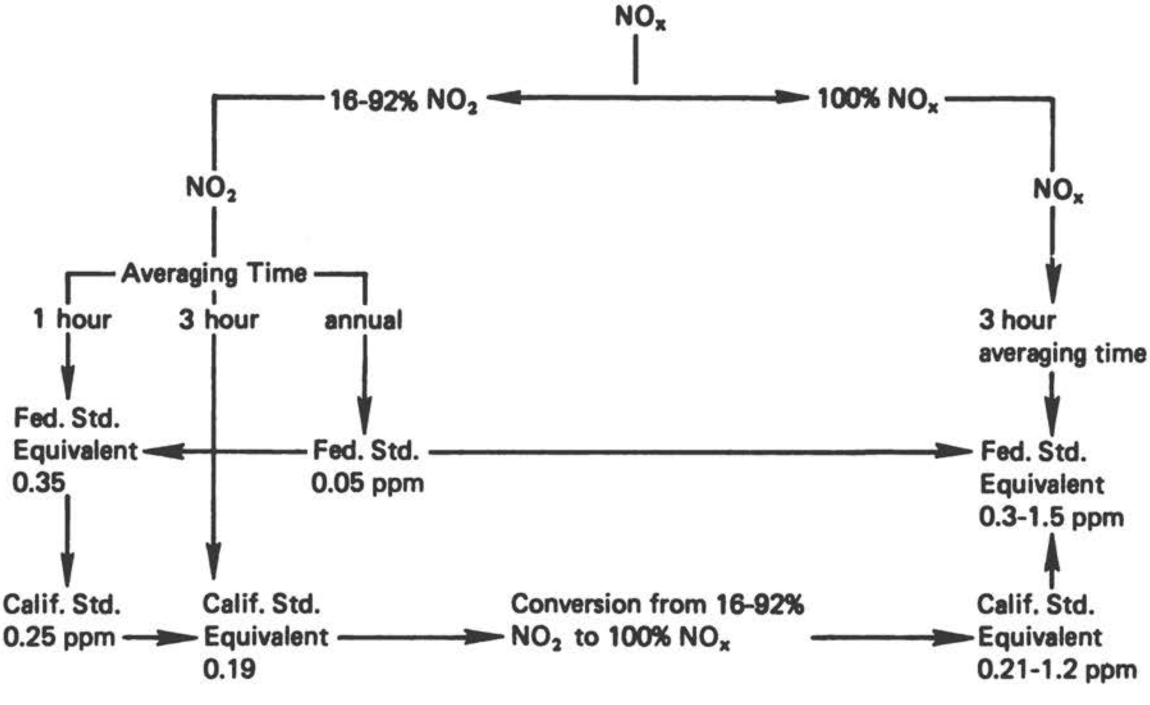

FIGURE 5 From NO_2 standard to equivalent NO_x. Value used in computations -- 0.3 ppm.

4. Computing Emission Standards

The Proportional or Rollback Model

The proportional model assumes that local emissions and air quality are linearly related to one another and that growth in emission will produce a linear growth in atmospheric pollutant concentrations. By this reasoning a reduction in emissions will result in a corresponding reduction in atmospheric pollutant concentrations.

The general form of the rollback model as derived by Larsen (14, 15) and used by Barth (16) to compute 1980 automotive emission goals is

$$R = \frac{g\ (P) - D}{g\ (P) - B} \times 100, \qquad \text{Eq. 1}$$

where:
R = % reduction in all sources necessary to meet air quality standards
D = air quality standards or goals in ppm or $\mu g/m^3$
P = present air quality in ppm or $\mu g/m^3$
g = growth factor
B = background concentration in ppm or $\mu g/m^3$

The term g(P), growth times present air quality, is equal to the future concentration of the pollutant if no controls are instituted. From the reduction percentage, R, the permissible automotive emissions can then be calculated, R applied to all sources.

$$E = A(1 - \frac{R}{100}) \qquad \text{Eq. 2}$$

where:
E = permissible automotove emissions which will achieve the air quality standards
A = present automobile emissions
R = reduction percentage from Eq. 1

The automotive industry has offered another form of Eq. 1, which computes the term $(1 - \frac{R}{100})$ directly:

$$1 - \frac{R}{100} = \frac{(D-B)}{g(P-B)}. \qquad \text{Eq. 3}$$

Equations 1 and 3 are essentially the same and give almost the same results when used to solve for E in Equation 2.

The use of a proportional-type model to develop emission standards is a simplistic approach to a very complex atmospheric system. Its use can be better justified for the development of carbon monoxide emission standards, since carbon monoxide is mainly emitted from automobiles and is neither rapidly consumed nor produced to any great extent by atmospheric reactions. Applying the proportional model to hydrocarbons and NO_x somewhat strains the assumptions on which the model is based. Both NO and NO_2 are consumed and generated in the photochemical process. In addition, stationary sources contribute more significantly to total emissions of HC and NO_x than to total emissions of CO (Table 1) (17). For these reasons, there are much wider limits of uncertainty associated with the use of the rollback procedure to compute HC and NO_x automotive emission limits than to compute CO automotive-emission limits. Finally, although the use of the rollback model assumes the same percentage reduction of all sources, mobile and stationary, this report does not address itself to stationary source reduction. This does not negate the purpose for computing these standards in this manner. We have no better present alternative. The magnitude of uncertainty in the resulting emission standards is a function not only of basic limitations of the rollback technique but also of the actual numbers used in the computation. However, it should be recognized that desired air quality will not be achieved unless stationary source emissions are decreased by at least the same factor as is proposed for the reduction of automotive sources.

Present Automobile Emissions (A in Equation 2)

As previously stated, the proportional rollback technique assumes that emissions and air quality are linearly related and that reduction in emissions will result in a linear improvement in air quality.

Table 1 Emission Inventory for CO, HC, and NO_x

		CO		HC		NO_x	
		Mobile	Stationary	Mobile	Stationary	Mobile	Stationary
National Totals (10^6 Tons)		98	53	17	20	9	15
National (%)		65	35	46	54	38	62
By Regions	Study Year	% Mobile	% Stationary	% Mobile	% Stationary	% Mobile	% Stationary
Chicago	1967	94	6	81	19	35	65
Denver	1967	93	7	78	22	48	52
Los Angeles	1966	95	5	72	28	73	27
New York	1965	96	4	84	16	38	62
Philadelphia	1967	70	30	47	53	27	73
Washington, D.C.	1966	96	4	86	14	44	56
Dallas	1967	97	3	93	7	80	20
Phoenix-Tucson	1967	94	6	87	13	71	29
Portland, Oregon	1968	72	28	64	36	79	21
Cincinnati	1967	85	15	83	17	34	66
Louisville	1967	75	25	83	17	35	65
Miami	1968	90	10	7	93	60	40
Atlanta	1968	89	11	86	14	71	29
Houston	1967	75	25	58	42	43	57
New Orleans	1968	47	53	49	51	56	44
Oklahoma City	1968	98	2	49	51	69	31
Pittsburgh	1967	80	20	70	30	29	71
St. Louis	1967	77	23	80	20	48	52
Charlotte	1968	92	8	86	14	28	72
Hartford	1967	95	5	82	18	52	48
Indianapolis	1967	85	15	86	14	52	48
Providence	1967	95	5	88	12	56	44

Thus, if we use 1970 air quality to compute an emission reduction, this reduction should be applied to 1970 emissions.

The 1970 emission baseline, as used here, means the average emissions for all cars driven during that year, not just the emissions from 1970 model-year cars. This is because in 1970, 1970 model cars accounted for only 15 percent of the total miles driven. Thus, the 1970 emission baseline to be reduced must be the weighted emission from all cars. The baseline computed in this manner and converted to the currently required constant volume sample, Hot/Cold start (CVS-H/C) test procedure is 6.14 g/mi for NO_x emissions and 13.2 g/mi for HC emissions. The computations on which these baseline values are based are not included in this report. However they are similar to computations for CO baseline emissions that appear in our parallel report on CO emission standards (18), and the reader is referred to that report. The HC baseline values include methane. The significance of such inclusion has been discussed elsewhere (19).

5. Present Air Quality

General

In general, high oxidant and NO_2 concentrations occur during the summer and fall months. Therefore, NO_x and non-methane hydrocarbon control is most critical during these times of the year, when there is the greatest potential of producing high oxidant. Even though it may be possible to find high concentrations of NO_x and HC during the night or during the winter months, these are not the critical concentrations, for they do not result in the highest oxidant and NO_2 concentrations.

Present Air Quality for Non-Methane Hydrocarbons (P in Equation 1)

The air quality standard for hydrocarbons states, "0.24 ppm - maximum 3-hour concentration (6-9 a.m.) not to be exceeded more than once per year." This means one 6-9 a.m. period out of 365 such periods, or the 99.7th percentile value, $P_{99.7}$. Non-methane hydrocarbon concentrations as high as 5.3 ppm (3-hour average) have been reported in Los Angeles in 1967. The maximum 3-hour average non-methane hydrocarbon concentration in Los Angeles in 1970 was 4.7 ppm. If only the months July-October (1970) are considered, the highest 6-9 a.m. non-methane concentration at the downtown station in Los Angeles was 4.0 ppm. Therefore, in these computations, the non-methane hydrocarbon concentration to be rolled back is 4.0 ppm. This is a good estimate for the $P_{99.7}$ value for NMHC, considering the existence of a maximum value of 4.7 ppm.

The foregoing values were developed by examining data on the 6-9 a.m. concentration of non-methane hydrocarbons on days of high photochemical air pollution. Data for 1-hour maximum total hydrocarbons from California showed values at some stations that were higher than similar measurements for Los Angeles. However, these values were not always associated with periods of high oxidant or with the 6-9 a.m.

time interval. Also, the total hydrocarbon data would have had to be corrected to establish non-methane hydrocarbons. This correction factor varies with the concentration of hydrocarbons, time of day, and other factors. Had it been feasible for the total hydrocarbon data to have been resolved in terms of 6-9 a.m. non-methane hydrocarbon, a value above 4.7 ppm may have been located. The panel did not find it feasible to do this. However, after reviewing the data available, the panel concluded that a value of 4.7 ppm non-methane hydrocarbons is a reasonable concentration to use.

Present Air Quality for Nitrogen Oxides (P in Equation 1)

The two highest NO_2 hourly values from the downtown Los Angeles Station in 1970 were 0.71 and 0.66 ppm (July 2, 9-10 a.m. and May 15, 8-9 a.m.) (Table 2). The 6-9 a.m. NO_x concentrations associated with these two highest hourly NO_2 concentrations were 0.60 ppm and 0.91 ppm respectively; there were a few 6-9 a.m. NO_x concentrations higher than 0.91 ppm in 1970, but these were associated with relatively low 1-hour NO_2 values.

Background Concentrations (B in Equation 1)

The background concentration used in the rollback calculation, for non-methane hydrocarbons (3-hour average) is 0.1 ppm. The average annual background concentrations for NO_2 and NO_x are of the order of 0.004 and 0.006 ppm (11) respectively. This translates into a maximum 1-hour average background for NO_2 of 0.028 ppm, and a maximum 3-hour NO_x average background concentration of about 0.03 ppm.

Table 2 High NO_2 and NO_x, Downtown Los Angeles Station (1970)[a]

Day	Max. 1-hr NO_2 (ppm)	6-9 a.m. NO_x (ppm)
May 15	.66	.91
June 2	.40	.50
June 25	.32	.47
July 2	.71	.60
Aug 7	.45	.91
Sept 30	.23	.76
Oct 2	.40	.92
Oct 27	.25	1.20
Oct 30	.36	.87
Nov 13	.25	1.04
Nov 14	.23	.85
Nov 17	.45	.86
Nov 18	.31	.98

[a] Data collected by Air Pollution Control District, County of Los Angeles, and analyzed at University of North Carolina.

6. Growth Factor (g in Equation 1)

There seems to be no reason to use different growth factors in the rollback computations for HC and NO_x than those used in the rollback computations for carbon monoxide. In our companion report, "A Critique of the 1975 Federal Automobile Emission Standards for Carbon Monoxide" (18), we concluded: "The original EPA recommendation for growth factor was for a time interval different from that enacted into the Clean Air Act of 1970. After adjustment of time interval to conform to that enacted, the value of g recommended by EPA is 1.92. Barth and Romanovsky (20) have indicated that this could reasonably be relaxed to a value of 1.54. The automobile manufacturers argue for a value of 1.0. The discussion of growth factors earlier in this report indicates the reasonableness of values ranging from 1.34 to the above-noted 1.54. The value of 1.92 is at the high end of the range of values. The value of 1.54 is more nearly the median of the set of numbers.

In the computations that conclude this report, values of g of 1.9, 1.5, 1.3, and 1.0 have been used to show the range of values of R, percent reduction, resulting, recognizing that values of the growth factor are not accurate to the third significant figure."

For a more detailed discussion of growth factor, the reader is referred to the companion report (18).

7. Rollback Computations

Calculation of Reduction Percentage (R in Equations 1 and 2)

Having converted previously discussed NMHC and NO_x values of D (desired air quality), P (present air quality), and B (background air quality) into 3-hour average values, these values are used in computations for R, percentage reduction required in Tables 3 and 4. Since the California Air Quality Standard (D) for NO_2 is based on 1-hour average values, corresponding 1-hour average values of P and B have been used in similar computations in Table 5. The values of R from these tables indicate that reduction of HC of the order of 90 percent and of NO_x (or NO_2) of the order of 75 percent are adequate.

Calculation of Emission Standard (E in Equation 2)

The values of R, percentage reduction required, and the emission baselines discussed in Chapter 4 have been used in Equation 2 to yield the values of E in Tables 3, 4, and 5. Values of HC emission of the order of 1.3 g/mi (CVS-H/C start basis) and NO_x of the order of 1.5 g/mi (CVS-H/C start basis) seem to be adequate. Present Federal emission requirements of 0.41 g/mi (HC) and 0.4 g/mi (NO_x) seem more restrictive than need be by a factor of about 3. Based on the state of knowledge now available, the California 1975-76 standards of 1.0 g/mi (HC) and 1.5 g/mi (NO_x) seem more nearly what is required.

Table 3 **Calculation of Percent Reduction Required (R) and Emission Standard (E) on Constant Volume Sample - Hot/Cold Start Basis (g/mi) for HC Using 1970 Emission Baseline and 1970 Air Quality Data**

	National Air Quality Standard for HC used for D				Value for Desired HC developed in this report used for D			
Desired air quality, D, ppm	0.24	0.24	0.24	0.24	0.75	0.75	0.75	0.75
Present air quality, P, ppm	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Background, B, ppm	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Growth factor, g (1970-1988)	1.9	1.5	1.3	1.0	1.9	1.5	1.3	1.0
% Reduction required, R	98.1	97.6	97.3	96.4	91.3	89.0	87.3	83.3
Reduced emissions[a] for 1975 CVS - CH, E 1970 baseline - 13.2 g/mi	0.25	0.31	0.36	0.47	1.14	1.45	1.68	2.20

[a] Federal standard is 0.41 g/mi.

Table 4 **Calculation of Percent Reduction Required (R) and Emission Standard (E) on Constant Volume Sample - Hot/Cold Start basis g/mi for NO_x using 1970 Emission Baseline, 1970 3-Hour Average Air Quality Data and 3-Hour Average Equivalent NO_x Value for Federal Annual Average NO_2 Air Quality Standard**

Desired air quality, D, ppm	0.3	0.3	0.3	0.3
Present air quality, P, ppm	0.91	0.91	0.91	0.91
Background concentration, ppm, B	0.03	0.03	0.03	0.03
Growth factor, g (1970-1988)	1.9	1.5	1.3	1.0
% reduction required, R	84.1	79.8	76.6	69.3
Reduced 1976 emissions in g/mi,[a] CVS - CH, E 1970 baseline - 6.14 g/mi	0.98	1.24	1.44	1.88

[a] Federal standard is 0.4 g/mi.

Table 5 Calculation of Percent Reduction Required (R) and Emission Standard (E) on Constant Volume Sample - Hot/Cold Start Basis (g/mi) for NO_x Using 1970 Emission Baseline, 1970 1-hour Average Air Quality Data and California NO_2 Air Quality Standard

Desired air quality, D, ppm	0.25	0.25	0.25	0.25
Present air quality, P, ppm	0.66	0.66	0.66	0.66
Background concentration, B, ppm	0.028	0.028	0.028	0.028
Growth factor, g (1970-1988)	1.9	1.5	1.3	1.0
Percent reduction required, R	81.9	76.9	73.3	64.9
Reduced 1976 emissions in g/mi,[a] CVS - CH, E 1970 baseline - 6.14 g/mi	1.11	1.42	1.64	2.16

[a] Federal standard is 0.4 g/mi.

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Statement by H. S. Johnston*

A Review of the CMVE Panel Report

"A Critique of the 1975-76 Federal Automobile Emission Standards for Hydrocarbons and Oxides of Nitrogen"

The Committee on Motor Vehicle Emissions of the National Academy of Sciences formed a series of Panels to make detailed studies of various components of the overall problem. These included the Panel on Standards and the Panel on Photochemical Reactions. The Panel on Standards prepared "A Critique of the 1975-76 Federal Automobile Emission Standard for Carbon Monoxide," and later both panels worked together to produce "A Critique of the 1975-76 Federal Automobile Emission Standards for Hydrocarbons and Oxides of Nitrogen." This joint project was judged by the Environmental Protection Agency not to be within the scope of Committee on Motor Vehicle Emissions, and support of the work of both panels was stopped. The final report of the panels is incomplete in several important respects, and this review points out some instances wherein it is incomplete.

Inhibition of Smog by Oxides of Nitrogen

Although there is abundant evidence (1) of "inhibition of smog" at early stages in smog chambers, there is also evidence (2) that the inhibition is but a delay. For long-time irradiations in smog chambers, one may draw opposite conclusions from those based on short-time irradiations. The Panel on Atmospheric Chemistry was requested to investigate the extent to which long-term results differed from short-term results, but the study was not completed. The final report of the Panel in Appendix A discusses the well-known effect of nitric oxide as an inhibitor of the early stages of the smog reaction, and it presents 15 figures related to this subject.

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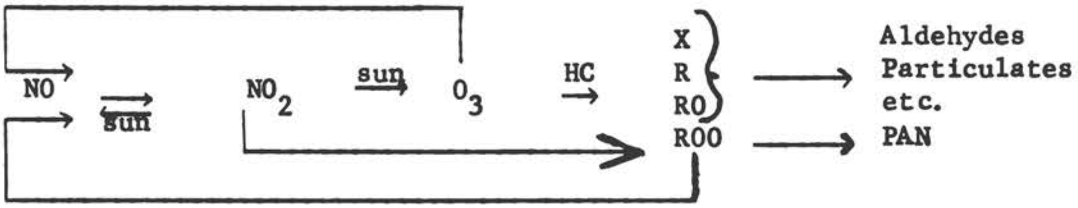
*Member of Committee on Motor Vehicle Emissions, National Academy of Sciences.

In this supplement to the Panel on Atmospheric Chemistry report, an important distinction is made between the roles of NO and NO_2 with respect to ozone on the one hand and photochemically produced free radicals on the other hand, and several figures are given illustrating the difference between short-term and long-term irradiations insofar as the oxides of nitrogen are concerned.

The diagram below shows some of the essential relationships in the photochemical smog reactions



Nitric oxide (NO) is the primary product of combustion. Nitric oxide is slowly converted by oxygen to nitrogen dioxide, and it is rapidly converted to nitrogen dioxide by ozone and by peroxyl-free radicals. Nitrogen dioxide is rapidly dissociated by sunlight to form ozone and nitric oxide. In the absence of hydrocarbons, there is a rapid cycle of reactions of NO, NO_2, O_2, and O_3, which gives a very small steady ozone concentration. In the presence of certain hydrocarbons, ozone reacts with the hydrocarbons to produce a series of reactive intermediates, including free radicals. The highly oxygenated free radicals rapidly convert NO to NO_2 to O_3 in a branching chain process. The net effect of loss of one ozone by reaction with certain hydrocarbons is to produce two or three or more ozones from the chain reaction of the free radicals with nitric oxide (3). On the other hand, when the free radicals react with nitrogen dioxide, the free radicals are neutralized to form PAN (peroxyacylnitrate), nitric acid, and other nitrates.

In this mechanism of smog reactions, the ozone concentration is promoted by NO_2 and inhibited by NO

$$\text{Ozone} \propto [NO_2]^{1} \; [NO]^{-1}$$

The attack of ozone on certain hydrocarbons is required to set off the "breeder reaction" that makes additional ozone. The free radicals (ROO and RO), which are an essential part of the chain reaction, are not changed in number by reaction with nitric oxide

$$RO\cdot + NO \rightarrow RONO \xrightarrow{sun} \dot{R}O + NO.$$

$$ROO + NO \longrightarrow RO + NO_2.$$

However, these chain-carrying free radicals are eliminated by reaction with nitrogen dioxide

$$RO + NO_2 \rightarrow \text{nitrates, nitric acid,}$$

$$ROO + NO_2 \rightarrow PAN.$$

Thus the free radicals are related to the oxides of nitrogen as

$$\text{Radicals} \propto [NO_2]^{-1}[NO]^0$$

There is a long induction period during which the free radicals and ozone build up to such a point that virtually all NO is converted to NO_2. Then there follows a rapid buildup of ozone to a very high value, and PAN accumulates at a fast rate. At a given concentration of hydrocarbon, the induction period tends to lengthen as nitric oxide increases. This phenomenon is well documented in Appendix A of the panel report. On the other hand, if the irradiation is continued long enough, large initial concentrations of NO_x lead to higher rates than small initial values. These effects are illustrated in the next four figures.

Figure 1-J represents a set of three runs at the same temperature and light intensity in a smog chamber (4). The initial hydrocarbon was 3 ppm of propylene in each case. In one run the initial nitric oxide was 0.5 ppm, in another 1.5 ppm; and in another 3.0 ppm.

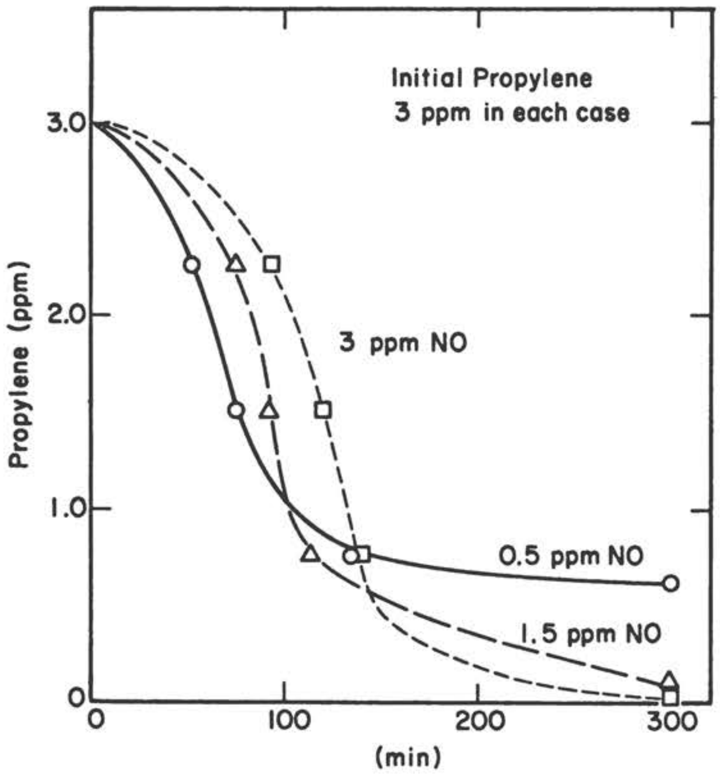


FIGURE 1-J Consumption of hydrocarbons by the photochemical smog reaction for 3 ppm propylene and for 3, 1.5, and 0.5 ppm initial NO_x. Static reaction in a smog chamber (data from Ref. 4). Note the fast initial rate with low NO_x and the slow long-term rate with low NO_x.

During the first hour the fastest destruction of propylene occurred with the least NO_x (0.5 ppm), and the slowest rate of destruction of hydrocarbon occurred in the case of most NO_x (3.0 ppm). After about 2 hours the reaction rate with 0.5 ppm NO_x slowed down and leveled off with about 20 percent of the hydrocarbon unreacted after 5 hours. After about 2 hours the rate with 3 ppm NO_x increased, and at the end of 5 hours the residual hydrocarbon was essentially zero.

The usual diagrams illustrating "inhibition by NO_x" show how some rate parameter at constant initial hydrocarbon varies with initial NO_x. Figure 2-J gives the same data as Figure 1-J, replotted to show the total propylene consumed between 0 to 1 hour, between 0 to 2 hours, and between 0 to 3 hours. The amount of reaction from 0 to 1 hour shows the classic "inhibition" pattern. The maximum effect is shown by 0.5 ppm NO_x and the degree of reaction is less for 1.5 ppm NO_x and least for 3.0 ppm NO_x. However, the amount consumed between 0 and 3 hours is exactly opposite. The least amount of hydrocarbon consumed is associated with 0.5 ppm NO_x, 1.5 ppm is the mid-case, and the maximum degree of reaction is shown by 3.0 ppm NO_x.

Another set of experiments (3) is given by Figures 3-J and 4-J. In Figure 3-J a series of runs is given, each with 2 ppm propylene and various amounts of initial NO_x. The oxidant concentration at 2 hours and at 6 hours is plotted against initial NO_x. For 2 hours of irradiation time, the data show the usual "inhibition" function. The oxidant increases with NO_x up to 1 ppm and then falls almost to zero for 2 or 3 ppm. For 6 hours of irradiation time the plot of oxidant against initial NO_x has the same general shape as for 2 hours of irradiation time, but the curve is shifted to higher oxidant values and to larger NO_x values. For 6 hours, the maximum occurs at 2 ppm NO_x, and it decreases sharply at 3 and 4 ppm. Figure 4-J shows the same features as Figure 3-J, except that the measure of smog is the concentration of peroxyacylnitrate (PAN). Although both 2-hour and 6-hour irradiations show inhibition by NO_x, the maximum PAN is 0.3 ppm at 0.8 ppm NO_x for 2-hour irradiation, and it is 0.6 ppm at 1.8 ppm NO_x for 6-hour irradiation. Presumably these curves would be shifted

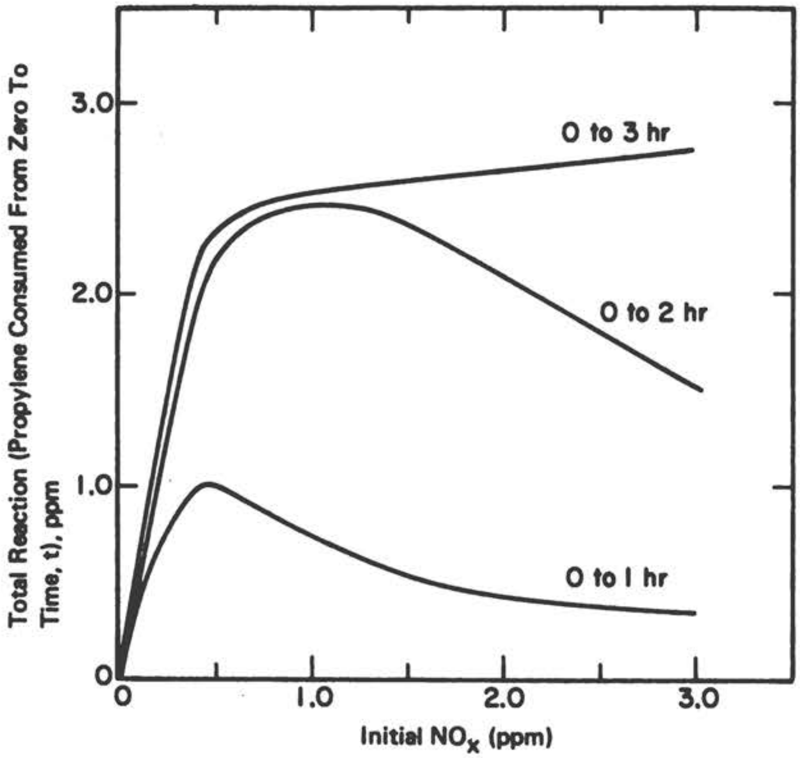


FIGURE 2-J The "inhibition of smog by NO$_x$" using the data from Figure 1-J. For short-term irradiation, the propylene consumed decreases with increasing NO$_x$ above 0.5 ppm. For long-term irradiation, the propylene consumed increases with increasing NO$_x$.

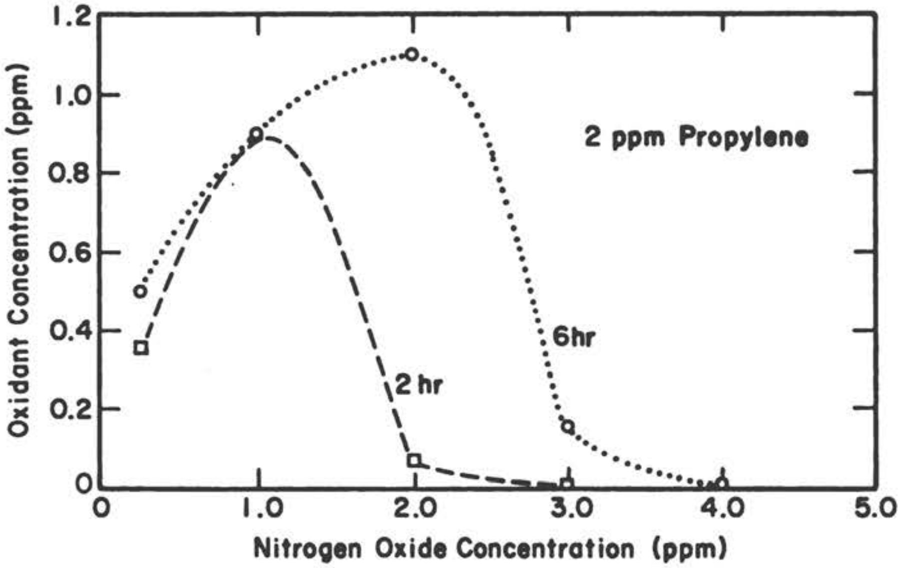


FIGURE 3-J Oxidant concentrations produced as a function of initial nitrogen oxide concentrations for smog-chamber studies with 2 ppm propylene (data from Ref. 3). For a 2-hour irradiation the maximum oxidant occurs with 1 ppm NO_x; for a 6-hour irradiation the maximum oxidant occurs with 2 ppm NO_x.

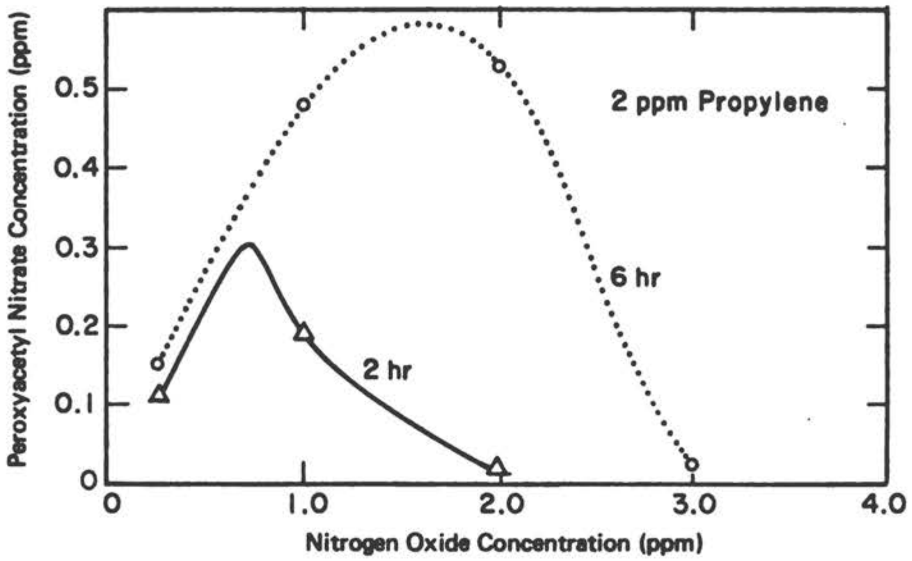


FIGURE 4-J Peroxyacetylnitrate concentrations produced as a function of initial nitrogen oxide concentration (same experiments as in Figure 3-J). Although each curve shows an "inhibition by NO_x", the maximum PAN is much higher for the 6-hour exposure than for the 2-hour exposure and occurs at a higher initial value of NO_x. A comparison of the two curves shows that the "inhibition" of smog by NO_x is but a delay. For large initial concentration of NO_x (2 ppm, for example) there is almost no PAN after 2 hours but a very large amount develops between 2 and 6 hours. High NO_x tends to lead to long-lasting smog, covering a wide area.

both higher and to the right with irradiation time longer than 6 hours.

Translated to the atmosphere, these analyses indicate that a control strategy that attempted to decrease smog by allowing NO_x to increase might achieve this goal in a downtown area but the duration and geographical extent of smog would increase in suburban and outlying areas. It might improve the situation in downtown Los Angeles but make it worse in Pasadena, Azusa, and Riverside, for example.

Although it is well recognized that many aspects of smog are "inhibited" by nitric oxide, there is at least one case where one measure of smog is inhibited by hydrocarbons. Figure 5-J shows the NO_2 dosage as a function of initial hydrocarbon in (6-hour) irradiated automobile exhaust (5). Figure 5-J shows the classic shape of inhibition, except that in this case the inhibition is correlated with hydrocarbons.

Recalculated Emission Standards for Hydrocarbons and Oxides of Nitrogen

At ambient concentrations, hydrocarbons are innocuous in themselves. They are harmful only by virtue of the chemical reactions that they undergo and the products that they form when irradiated in the presence of the oxides of nitrogen. In the preceding section and in Appendix A of this report, the complicated, highly nonlinear nature of this process was indicated. In Chapter 4 of this report, it is clearly stated that the linear, rollback formula is particularly inappropriate for hydrocarbons and oxides of nitrogen.

However, the authors state that there is no better alternative for computing these standards than the present unsatisfactory method. In the limited time available to the Panels, this may have been true. However, when the Panels carried through the rollback calculations, their report inherited the weaknesses of the method. Instead of a well-aimed attack on an inappropriate method, the report is an in-

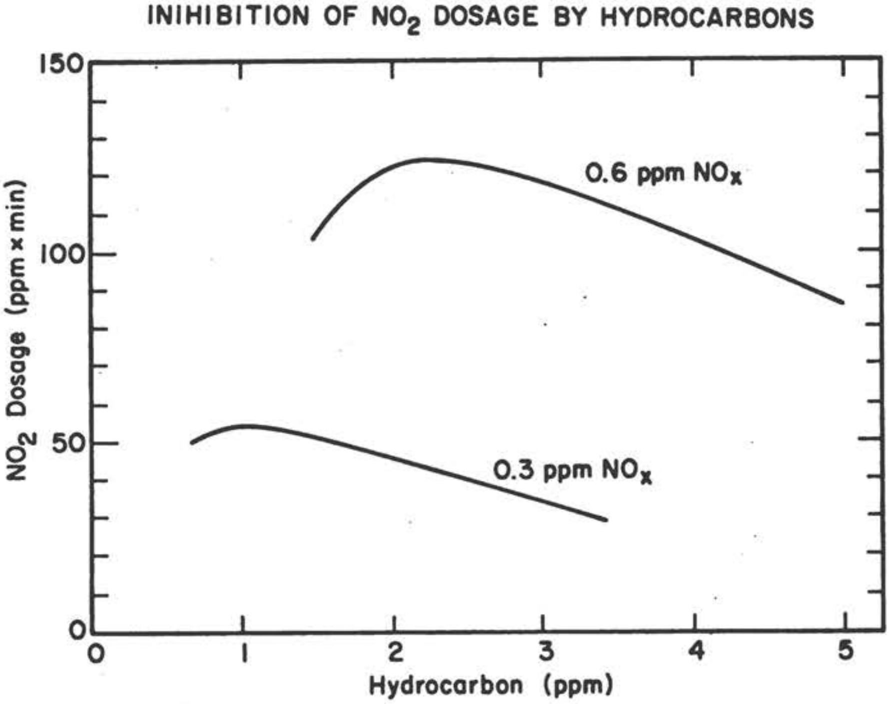


FIGURE 5-J "Inhibition" of nitrogen dioxide dosage by hydrocarbons (data from Ref. 5). In the highly nonlinear smog reactions, it is possible to find this measure of smog that is "inhibited" by hydrocarbons. This "inhibition" by NO_x, is a deceptively oversimplified picture of the true nature of the photochemical smog reactions.

complete application of the inappropriate method.

One aspect of incompleteness is the "present air quality" for non-methane hydrocarbons. The present air quality was based on 6 to 9 a.m. 3-hour averages "at the downtown station in Los Angeles." The highest figure for 1970 and the value used in the computation was 4.0 ppm of non-methane hydrocarbon. From Figure C-2 this value of non-methane hydrocarbon corresponds to 9.5 ppm of total hydrocarbon. According to Appendix B, a 3-hour average would be 1.3 times less than a 1-hour average. Thus the maximum 3-hour total hydrocarbon concentration of 1970 upon which the calculations are based corresponds (roughly) to a 1-hour maximum average of 12 ppm <u>at downtown Los Angeles</u>.

To be sure, Los Angeles has the reputation of being the major locus of smog. It does not follow, however, that the station at downtown Los Angeles would represent the worst case. As can be seen from Table 1, the 1-hour maximum hydrocarbon concentration for a 8-month period of 1969 was higher at eight stations in the San Francisco Bay area, at four stations in the central valley of California, and at San Diego. In some cases the maximum hydrocarbon figure is far greater than that at downtown Los Angeles. These high hydrocarbon figures require considerable detailed analysis to ascertain which is the effective worst case so far as oxidant formation is concerned. Given more time, presumably the Panel on Standards would have examined a wider range of data than those of downtown Los Angeles.

The calculated standards in the hydrocarbon-NO_x report depend very heavily on the results of one smog-chamber study (5). There are other carefully done studies in smog chambers, and some of these indicate features somewhat different. Also, the calculated standards depend very heavily on use of downtown Los Angeles as the reference point for hydrocarbons, whereas several other stations report much higher values for peak hydrocarbon concentrations. The nonlinear relationships between smog effects and the initial concentrations of hydrocarbons and oxides of nitrogen (in particular, the reversal of roles of low and high values of oxides of nitrogen at short and at long times) make it very difficult to justify the use of linear rollback formulas for hydrocarbon and NO_x standards.

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APPENDIX A - PHOTOCHEMICAL REACTIONS

It is probably unfortunate that NO and NO_2 are so frequently lumped together as NO_x, for their properties and their roles in the smog reaction are quite different. It would be scientifically sound to set separate standards for each of them, both atmospheric air quality standards and emission standards. There is ample reason to regard NO as a reactant in the smog reaction and NO_2 as an intermediate or a product. Almost all of the NO_x entering the atmosphere from all major sources is in the form of NO rather than NO_2.

But the most important distinction between NO and NO_2 is that NO acts as an inhibitor while NO_2 is a promoter or initiator. Since NO is converted to NO_2 when hydrocarbon and sunlight are present, the inhibitor is consumed. This is entirely in accord with the usual behavior of inhibitors; they retard some reaction or postpone some effect but are consumed in the process and, therefore, are effective only for a limited time. The inhibitor is not merely destroyed; it is converted into a photo-initiator, nitrogen dioxide. A truly remarkable behavior! This takes time, therefore time is a real not an artificial factor, and the inhibition by nitric oxide is a real and important factor. This inhibition has been known for almost as long as the photochemical nature of the reaction has been recognized.

The inhibition of the smog reaction by nitric oxide extends to almost all of those smog products responsible for symptoms. These symptoms are the following:

1. Oxidant: This is mainly caused by ozone, which is one of the most serious if not the most dangerous health hazard in smog.

2. Plant damage: The two principal plant toxicants associated with photochemical smog are ozone and peroxyacylnitrates (PAN's).

3. Eye irritation: Although several potent eye irritants have been identified in photochemical smog mixtures, it is still not established which one (or ones) is most important in real polluted air. Recognized irritants are acrolein, formaldehyde, and the peroxyacylnitrates. By far the most potent of these on a ppm basis is peroxybenzoylnitrate.

4. Aerosol: Two mechanisms of photochemical aerosol formation are now under study, one involving hydrocarbons and nitrogen oxides and the other including sulfur dioxide. Evidence is mounting that aerosol generated photochemically is the principal cause of visibility loss.

5. Rubber cracking: This smog effect is no doubt caused by ozone.

6. Odor: Ozone may well be the major cause of the typical smog odor.

7. Color: Under some conditions photochemical smog appears red, yellow, or reddish brown. This could be due to either scattering from aerosol or absorption by NO_2.

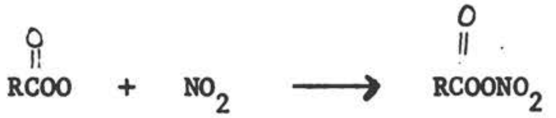
The formation of almost all of the chemical species responsible for these smog effects is inhibited to a significant degree by nitric oxide. Formation of ozone, peroxyacylnitrates, and sulfuric acid aerosol are all delayed until the first stage of the photochemical reaction (conversion of NO to NO_2) is complete. These three products are surely responsible for much of the most deleterious smog effects. The attached diagrams (A-1 - A-15) were selected from the work of ten laboratories to demonstrate the inhibition of the formation of these products by NO. In this collection the inhibition of ozone formation by NO is evident in the data from six laboratories; inhibition of PAN's formation by NO from three laboratories, and inhibition of aerosol formation from four laboratories. Theoretical insight into the mechanism and reasons for the inhibiting effect of NO is not really essential since the observations can stand on their own merits. Nevertheless, understanding of the mechanism is valuable in interpreting these observations in terms of the real atmosphere. The clearest understanding is available for the inhibition of ozone formation because the extremely rapid reaction between NO and O_3 is well documented:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad \text{Eq. A-1}$$

This reaction is so rapid that appreciable NO and O_3 cannot coexist in the same atmosphere. This rapid reaction has recently been made the basis for a chemiluminescent method for measurement of ozone and NO. Inhibition of the formation of the PAN's can be ascribed to the reaction of NO with peroxyacyl radicals.

$$R\cdot \overset{\overset{O}{\|}}{C}OO + NO \longrightarrow R\overset{\overset{O}{\|}}{C}O + NO_2 \qquad \text{Eq. A-2}$$

The peroxyacyl radicals are the precursors of PAN's and are scavenged by reaction (Diagram A-2) so that PAN's are only formed by reaction (A-3) after the conversion of NO to NO_2 is nearly complete.



$$R\overset{\overset{O}{\|}}{C}OO + NO_2 \longrightarrow R\overset{\overset{O}{\|}}{C}OONO_2 \quad \text{(PAN's).} \qquad \text{Eq. A-3}$$

The reasons for the inhibition of aerosol formation are not so easily determined. Oxidation of sulfur dioxide to sulfuric acid surely occurs in these photochemical systems, but is is not due to direct reaction of SO_2 with either ozone or PAN's since these reactions have been shown to be slow under realistic conditions.

It has been suggested that peroxy radicals are responsible for reaction:

$$R\cdot \overset{\overset{O}{\|}}{C}OO + SO_2 \longrightarrow R\cdot \overset{\overset{O}{\|}}{C}O + SO_3\,. \qquad \text{Eq. A-4}$$

Scavenging of these peroxy radicals by NO could then inhibit this reaction. Another possibility is the reaction with NO_3:

$NO_3 + SO_2 \longrightarrow NO_2 + SO_3$. Eq. A-5

The NO_3 would be formed by reaction of O_3 with NO_2:

$NO_2 + O_3 \longrightarrow NO_3 + O_2$. Eq. A-6

And NO_3 is also scavenged by NO:

$NO_3 + NO \longrightarrow 2NO_2$. Eq. A-7

Which of these two mechanisms (if either of them) is responsible for SO_2 oxidation remains to be proven. The reality of SO_2 oxidation in the photochemical system after the conversion of NO to NO_2 is well demonstrated experimentally, however.

The importance of hydrocarbon in promoting the NO conversion is well established. The rate of the conversion is dependent on both the amount of hydrocarbon and on its structure. The rate of the conversion of NO roughly parallels the rate of the oxidation of the hydrocarbon. There cannot be much doubt that reduction in either the amount or the reactivity of the hydrocarbon will retard the conversion of NO and thereby delay the appearance of ozone, PAN's, and sulfuric acid aerosol. It is the quantitative aspects of the conversion that are hard to evaluate. How much reduction in hydrocarbon will be required to significantly delay the completion of NO conversion and therefore delay the appearance of ozone, PAN's, and sulfuric acid aerosol? Time for reaction is not unlimited. If the reaction could be slowed sufficiently by hydrocarbon reduction, it is reasonable to believe that formation of these three products could be delayed beyond the limited time available. This could lead to excessive concentrations of NO_2 that could only be controlled by reducing emissions of NO as shown in Figure 2.

How much time is actually available for reaction? This is not readily determined but studies of the relative amounts of reactive and unreactive hydrocarbons suggest that it may be about 8 hours to 1 day.

Trapping of photochemically reactive pollutants occurs in the marine layer of air over coastal areas such as the South Coast Basin of California. Such a polluted air mass is only temporarily stable. It is vulnerable to heating by the ground below. As it flows inland it absorbs heat and is ultimately warmed enough to mix with the air above. This is especially true where the polluted marine air encounters mountain slopes that are heated by solar radiation. These form thermal chimneys that ventilate the polluted air into the upper atmosphere.

What then can be expected to happen if hydrocarbons are reduced without NO reduction? The laboratory data indicate that the appearance of ozone, PAN, and sulfuric acid aerosol would be delayed and, with sufficient reduction in hydrocarbon, might be nearly eliminated. This is shown in Figure 2 in which the upper left diagram represents the present situation, while the lower left shows the qualitative changes to be expected for a major reduction of hydrocarbon. The reduction in ozone, PAN, and aerosol is accompanied by a higher level of NO_2 (presuming that at the reduced hydrocarbon level just sufficient time is available to convert all the NO to NO_2). If, having reached this state, the amount of NO being emitted is reduced to control the formation of NO_2, then less time is required for the NO conversion to go to completion (lower right diagram, Figure 2). Then ozone, PAN, and aerosol will be increased even though NO_2 is decreased. Therefore, control of NO is a course of action having advantages and disadvantages.

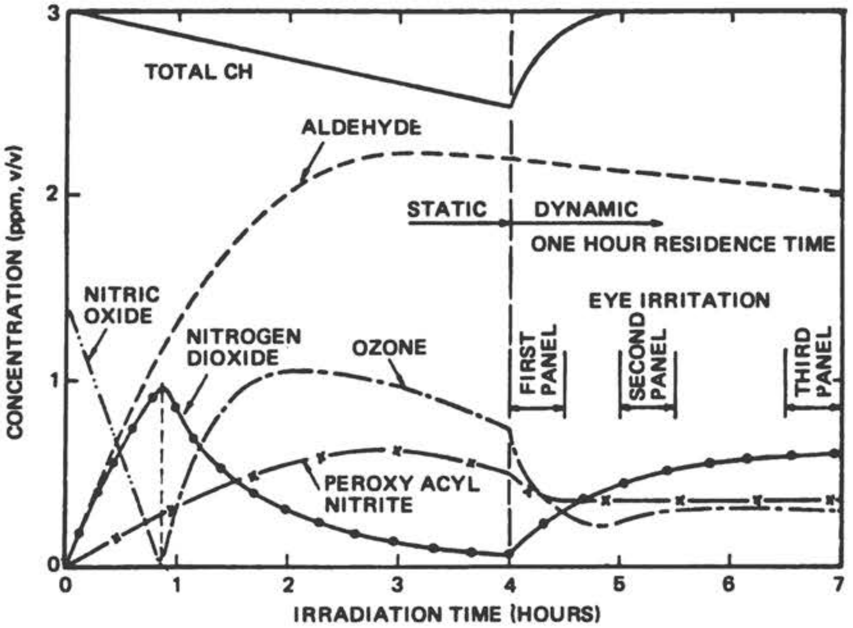
The coordinates of concentration and time in Figure 2 are deliberately left unnumbered because quantitative knowledge is still lacking. The emission levels of hydrocarbons and NO that must be reached to achieve any given reduction in the products cannot at this time be accurately estimated. Neither the theoretical nor the experimental approach has solved this problem. Atmospheric monitoring data indicate that NO conversion is complete within a few hours of sunrise, certainly by noon, with present emission levels. This suggests that very substantial reductions in hydrocarbon will be required to avoid complete NO conversion and ozone-formation. Theoretical models of air chemistry are not well enough advanced to permit confident calculation of the degree of control necessary, nor are smog chamber research techniques sufficiently well advanced to experimentally determine this reduction. This, however, is exactly the problem to be solved in setting emission standards. At this time the Bureau of Mines chamber study (Dimitriades) probably provides the best set of experimental guidance.

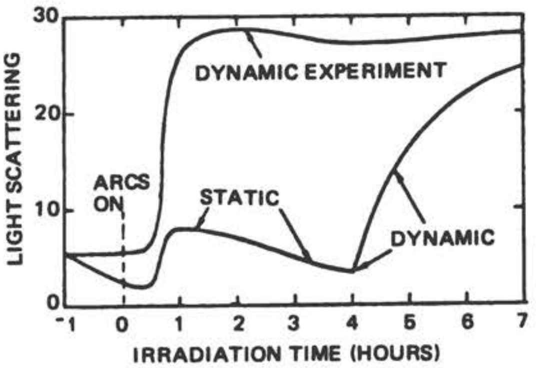
Laboratory: Stanford Research Institute, The Franklin Institute

Reference: Stephens, E. R., and Schuck, E. A., Chem. Eng. Prog., vol. 54, No. 11, p.75, Nov. 1958.

See also Schuck, E. A., Ford, H. W., and Stephens, E. R., Air Pollution Foundation, Report No. 26, Oct. 1958.

Comment: Ozone formation is delayed until NO conversion is complete (upper figure). Aerosol formation is also delayed (lower figure).

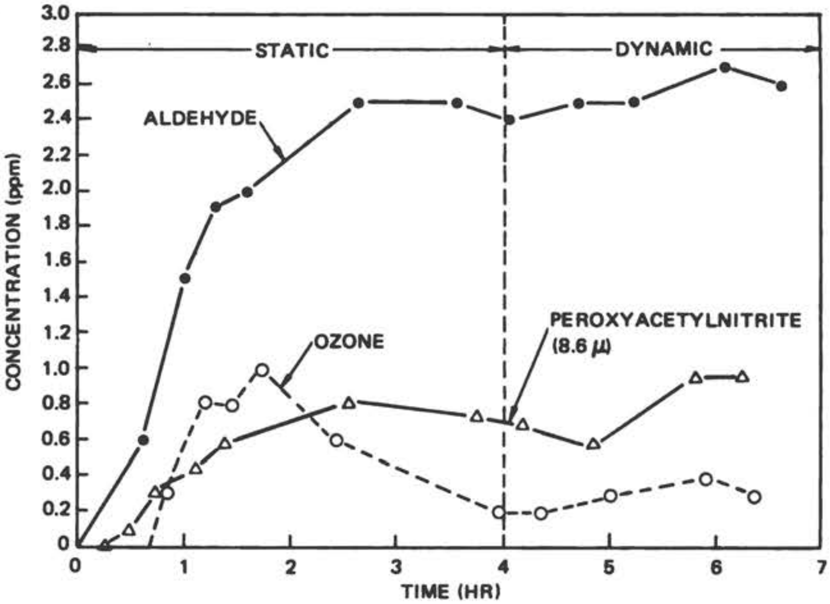




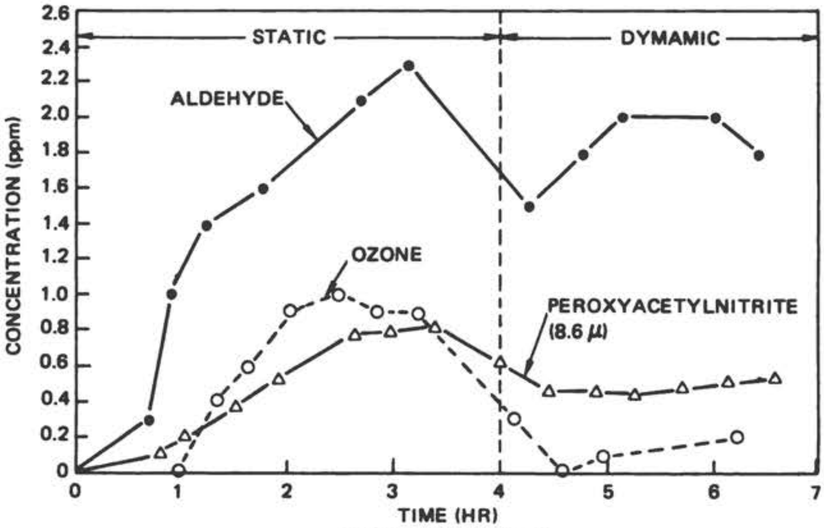
Laboratory: Stanford Research Institute, The Franklin Institute

Reference: Schuck, E. A., Ford, H. W., and Stephens, E. R., Air Pollution Foundation, Report No. 26, Oct. 1958.

Comment: Ozone formation is delayed as long as nitric oxide is present. The experiment A was done with diluted auto exhaust using "basin mix" fuel, a blend of the then-used commercial gasoline. There is a suggestion that PAN (here called peroxyacetylnitrite) is also delayed.



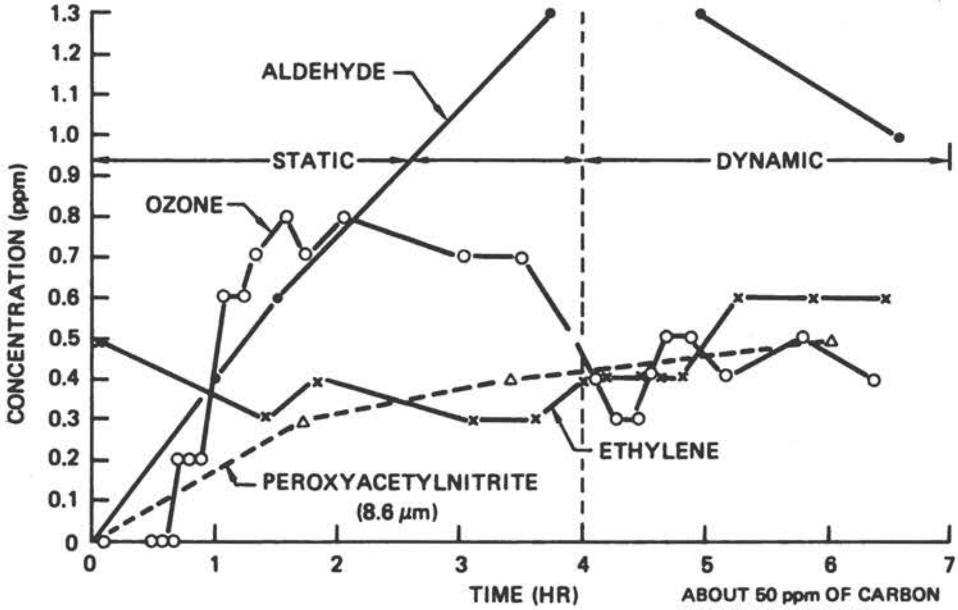
(A) BASIN MIX FUEL



(B) AROMATIC FUEL

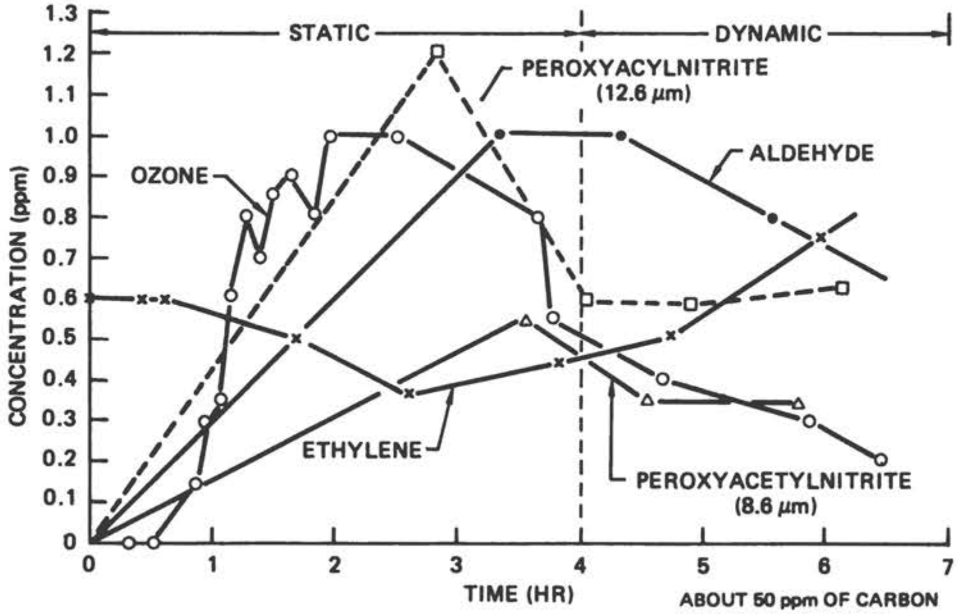
Diagram A-3

Laboratory:	Stanford Research Institute, The Franklin Institute
Reference:	Schuck, E. A., Ford, H. W., and Stephens, E. R., Air Pollution Foundation, Report No. 26, Oct. 1958.
Comment:	Ozone formation is delayed as long as nitric oxide is present. The experiment A was done with diluted auto exhaust using "basin mix" fuel, a blend of the then-used commercial gasoline. There is a suggestion that PAN (here called peroxyacetylnitrite) is also delayed.



ABOUT 50 ppm OF CARBON MONOXIDE PRESENT THROUGHOUT EXPERIMENT

(A) BASIN MIX FUEL



ABOUT 50 ppm OF CARBON MONOXIDE PRESENT THROUGHOUT EXPERIMENT

(B) AROMATIC FUEL

Diagram A-4

Laboratory: The Franklin Institute, Philadelphia, Pa.

Reference: Prager, M. J., Stephens, E. R., and Scott, W. E., Ind. & Eng. Chem., vol 52, p. 521, June 1960.

Comment: Aerosol formation is delayed about 15 minutes when pentene-2 is photolyzed with NO and SO_2, but it is not delayed when NO_2 is used. Nitric oxide is an inhibitor, but nitrogen dioxide is not.

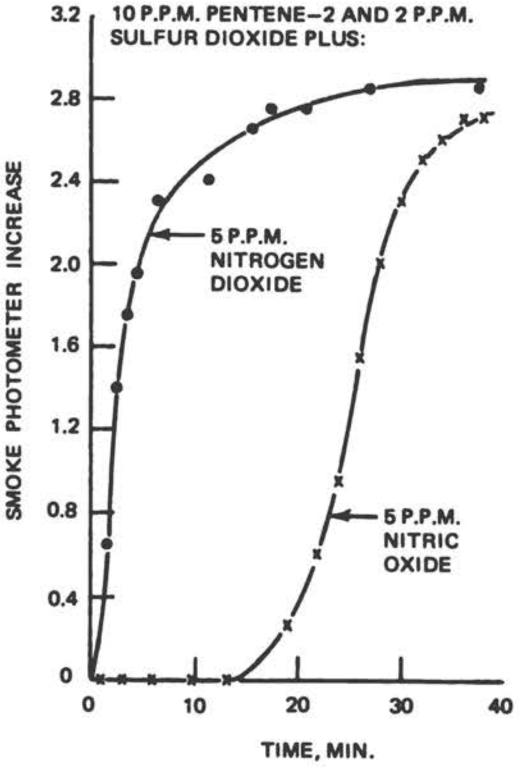


Diagram A-5

Laboratory: Scott Research Laboratories and University of California, Riverside.

Reference: Stephens, E. R., Chemical Reactions in the Lower and Upper Atmosphere, ed. R.D. Cadle, Chapter 3, p. 51, Interscience, New York, 1961.

Comment: Formation of peroxyacylnitrates (in this case peroxypropionylnitrate, PPN) is delayed when NO is used as a starting material, but not when NO_2 is the starting material.

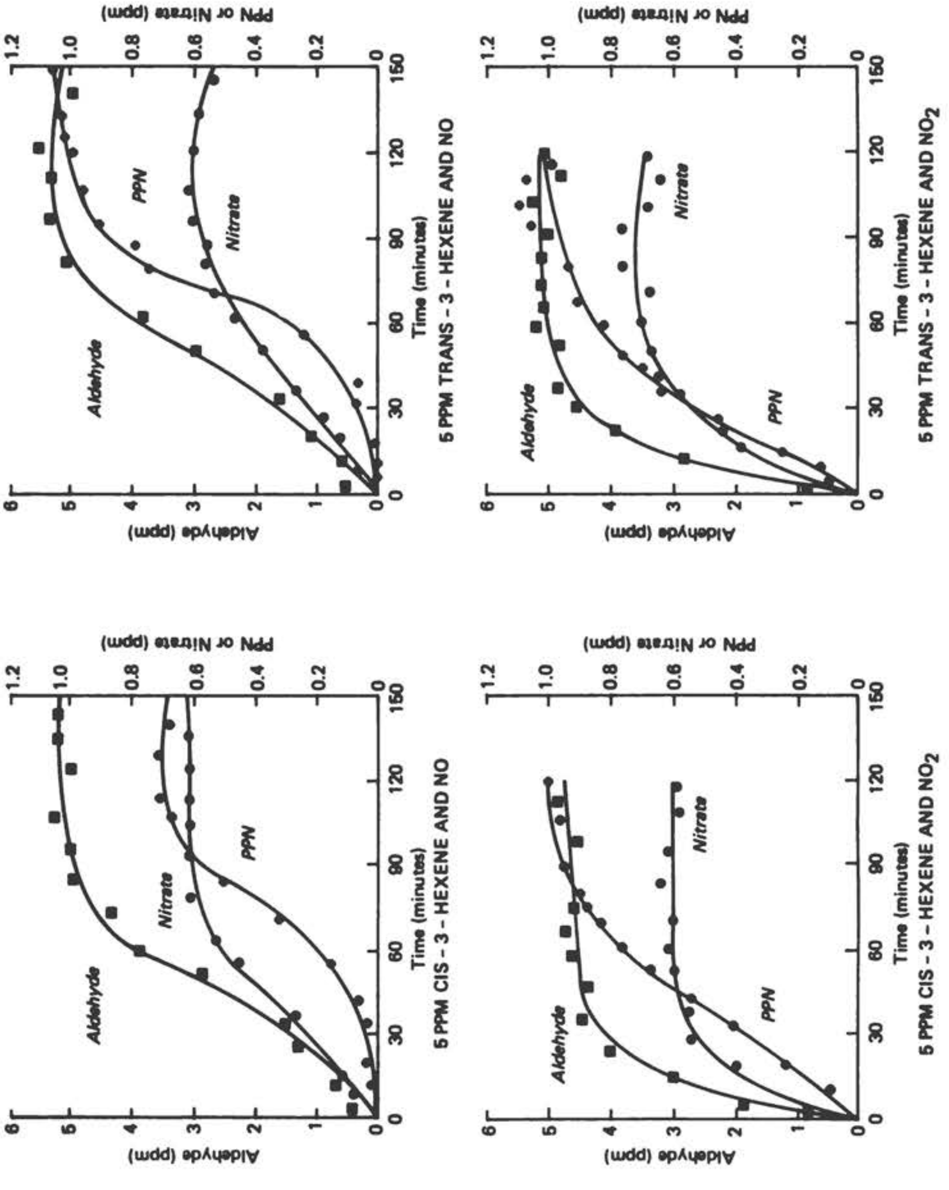


Diagram A-6

Laboratory: General Motors Research

Reference: Tuesday, C. S., Chemical Reactions in the Lower and Upper Atmosphere, ed., R. D. Cadle, Chapter 2, p. 15, Interscience, New York, 1961.

Comment: PAN (here called compound X) is not formed appreciably until NO conversion is complete.

PHOTOOXIDATION OF *trans*-BUTENE-2 AND NITRIC OXIDE

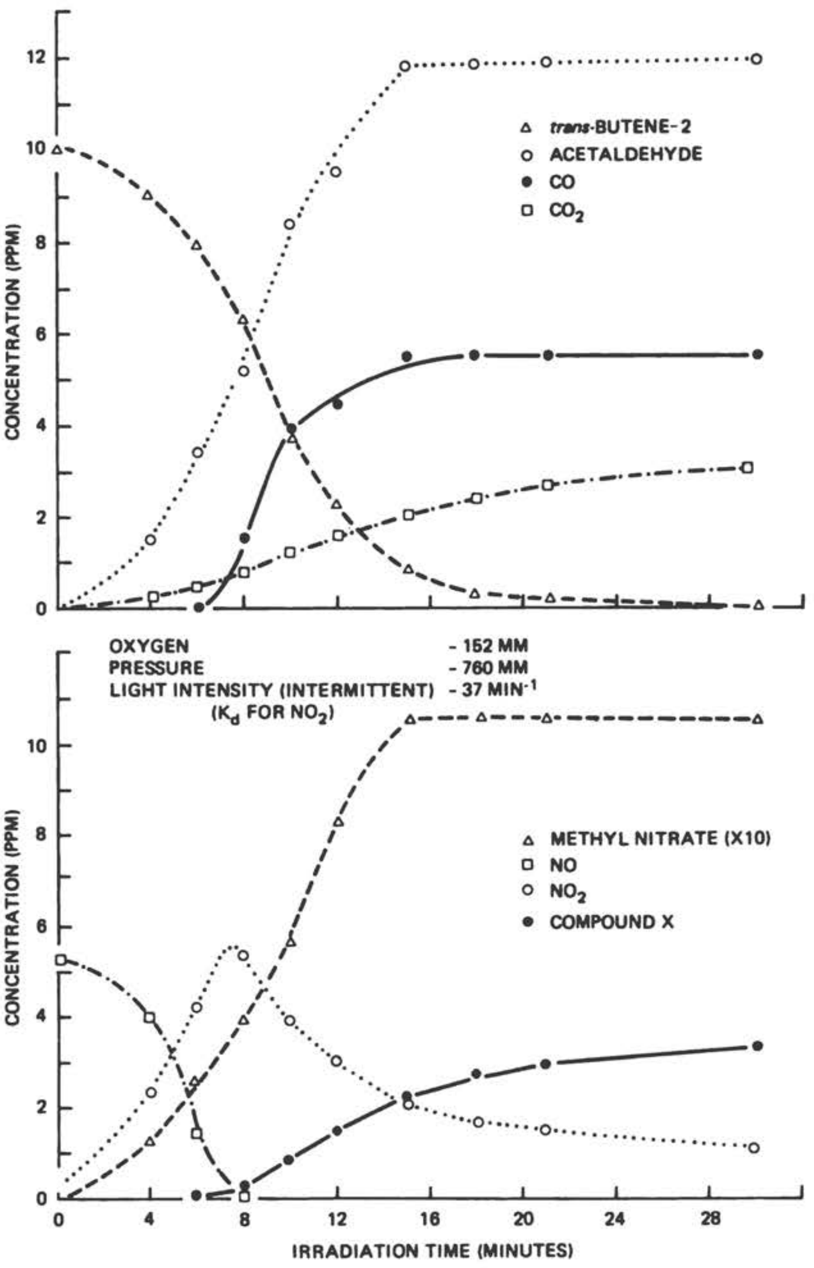


Diagram A-7

Laboratory: General Motors Research

Reference: Heuss, J. M., and Glasson, W. A., Environ. Sci. & Tech., vol. 2, No. 12, p. 1109, Dec. 1968.

Comment: Formation of eye irritant (presumably peroxybenzoylnitrate (PBzN) is delayed until NO conversion to NO_2 is complete (NO_2 peak).

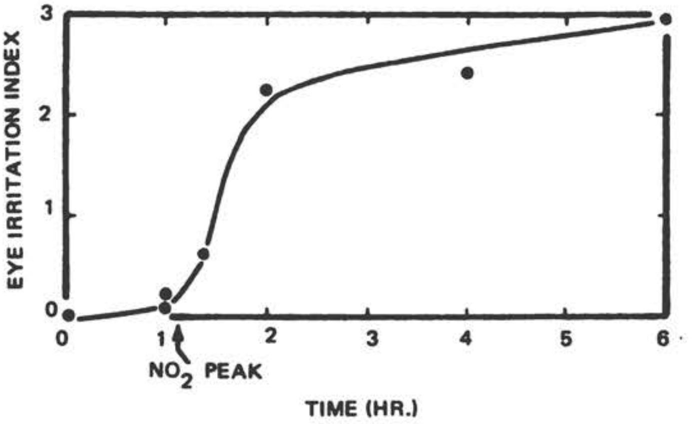


Diagram A-8

Laboratory: General Motors Research

Reference: Groblicki, P. J., and Nebel, G. J., "Chemical Reactions in Urban Atmospheres, " G. M. Technical Center, Oct. 1969. American Elsevier Publ., 1971, ed., C. S. Tuesday.

Comment: Both ozone and aerosol (smokemeter) are delayed until conversion of NO to NO_2 is nearly complete.

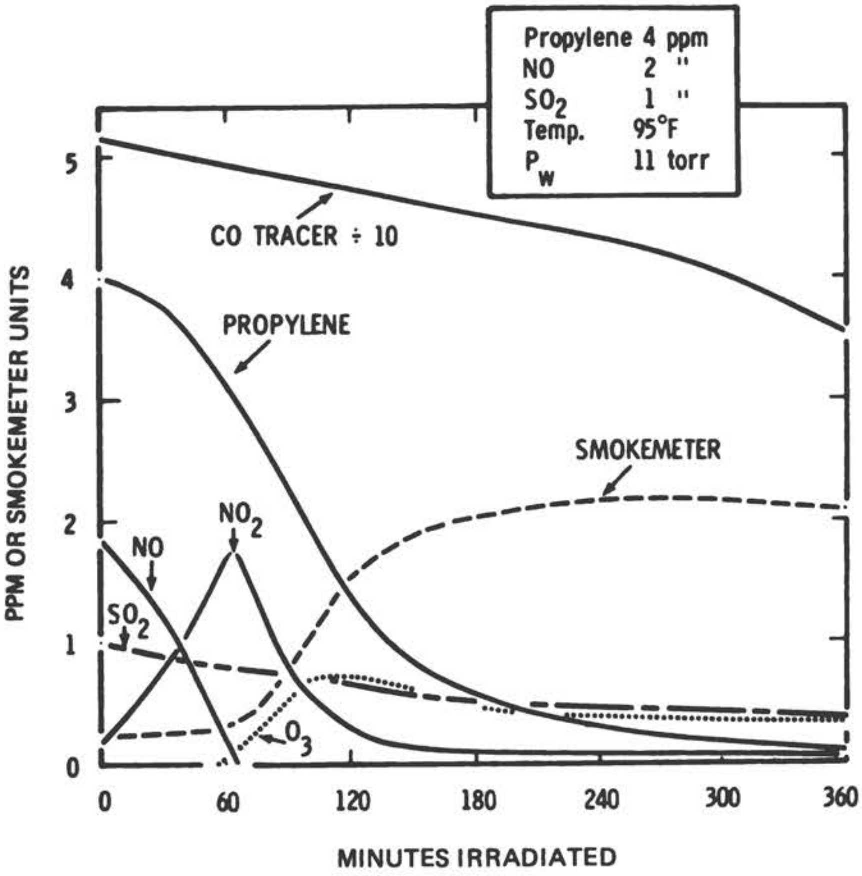


Diagram A-9

Laboratory: Battelle Memorial Institute, Columbus Labs.

Reference: Wilson, W.E., and Levy, A., American Petroleum Institute Project S-11, August 1, 1968.

Comment: Ozone (O_3) and aerosol formation are delayed until NO conversion is complete. These plots also show butene consumption and aldehyde formation accelerating as NO is converted to NO_2.

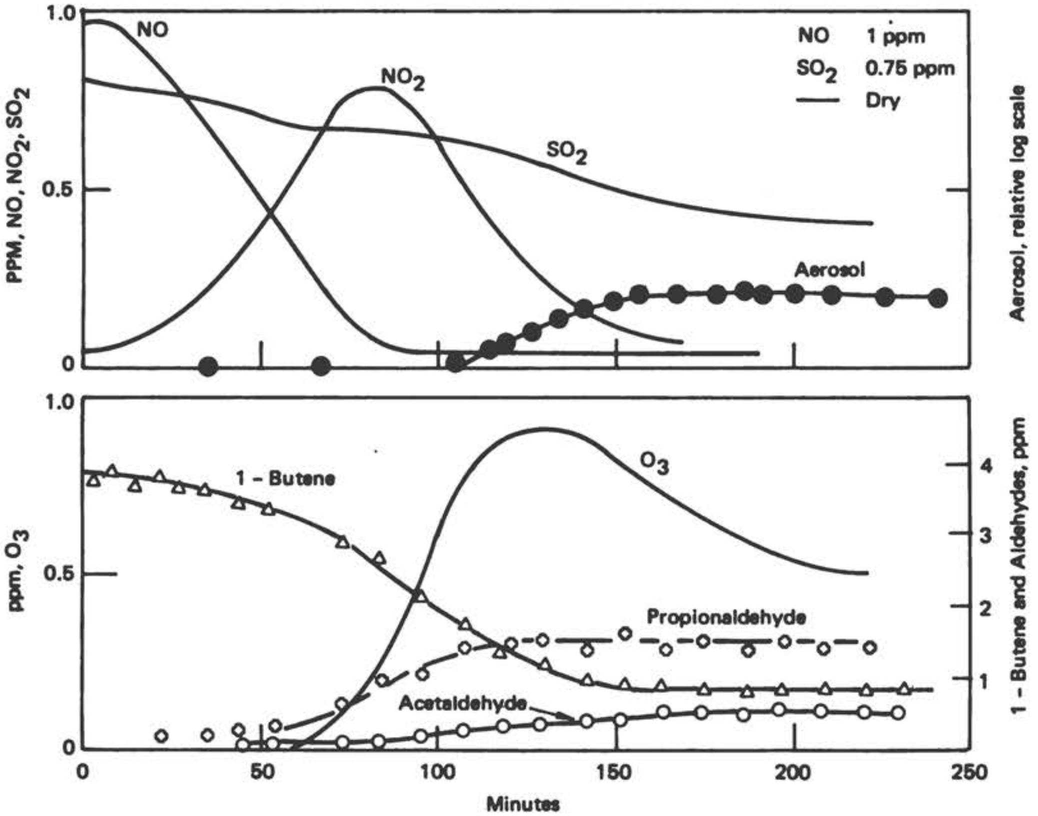


Diagram A-10

Laboratory: California Institute of Technology
Los Angeles County Air Pollution Control District

Reference: Haagen-Smit, A. J., and Fox, M. M., Paper No. 421, Society of Automotive Engineers, January 1955, Reprinted in "Vehicle Emissions," SAE, 1964.

Comment: This classic plot shows ozone formation (measured by rubber cracking) apparently inhibited by high levels of NO_2 (~ 6 to 600 ppm). It is thought that at these high levels NO_2 is converted to NO at a significant rate by the reaction: $NO_2 + O \longrightarrow NO + O_2$. This competes with the conversion of NO to NO_2 promoted by hydrocarbon. When hydrocarbon is high (10,000 ppm 3-methyl heptane) higher levels of NO_2 (600 ppm) are needed to accomplish this reverse conversion. Conversion of NO_2 to NO at high levels of NO_2 and low HC levels has been demonstrated. Thus, in this case NO (not NO_2) is the inhibitor.

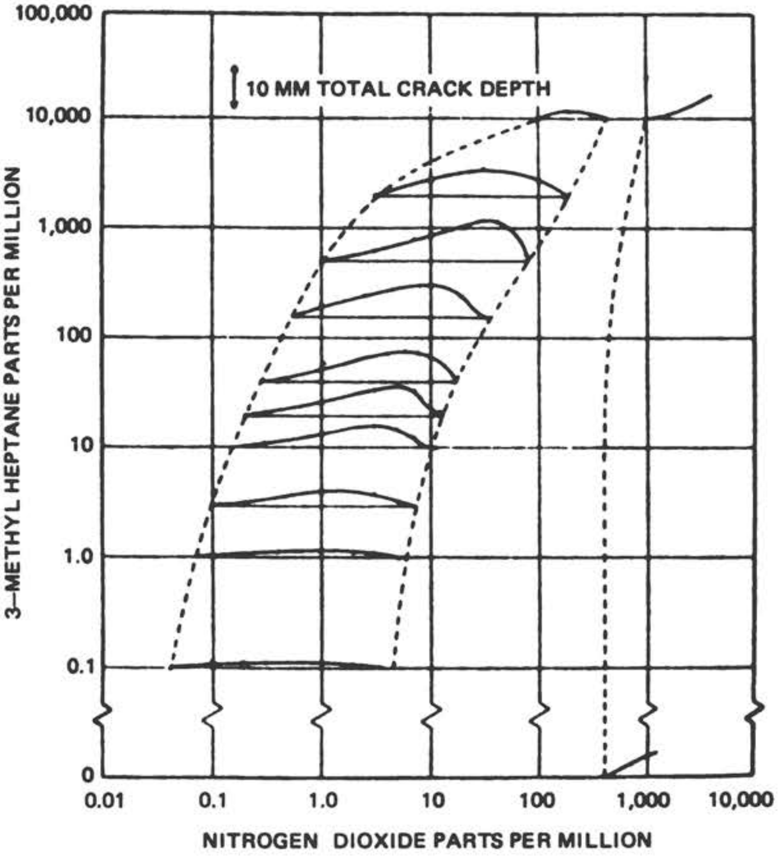
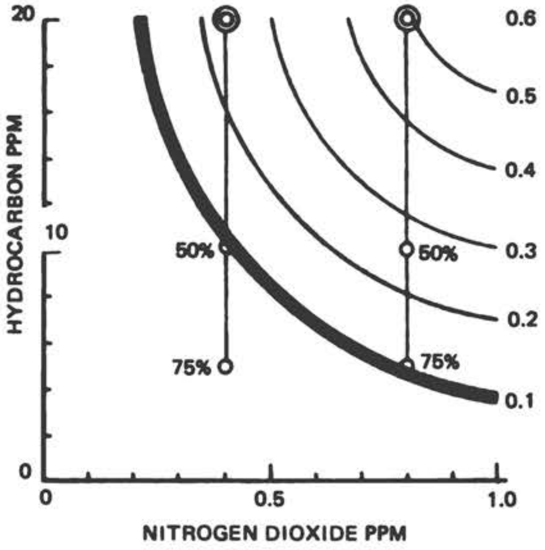


Diagram A-11

Laboratory: California Institute of Technology
Los Angeles County Air Pollution Control District

Reference: Haagen-Smit, A. J., and Fox, M. M., Paper No. 421, Society of Automotive Engineers, January 1955. Reprinted in "Vehicle Emissions, "SAE, 1964.

Comment: This plot is from the same paper as Diagram A-10. It shows no inhibition by NO_2. It has been used to justify equal emphasis on nitrogen oxides and hydrocarbon control. But this figure shows only that NO_2 is <u>not</u> an <u>inhibitor</u>. It does not apply to NO since NO was not used. Furthermore, the rubber cracking method used to detect ozone was used after 4 hours and could not reveal a delay in ozone formation even if one had occurred.



Laboratory: U.S. Department of Health, Education, and Welfare

Reference: Korth, M. W., Rose, A. H., Jr., and Stahman, R. C., JAPCA, vol. 14, No. 5, p. 168, May 1964.

Comment: This set of experiments shows not only the delay in oxidant (ozone) formation but also shows that the delay is increased by increasing nitric oxide concentration or by decreasing hydrocarbon concentration. At the highest NO concentrations no oxidant at all was formed in these experiments with diluted auto exhaust.

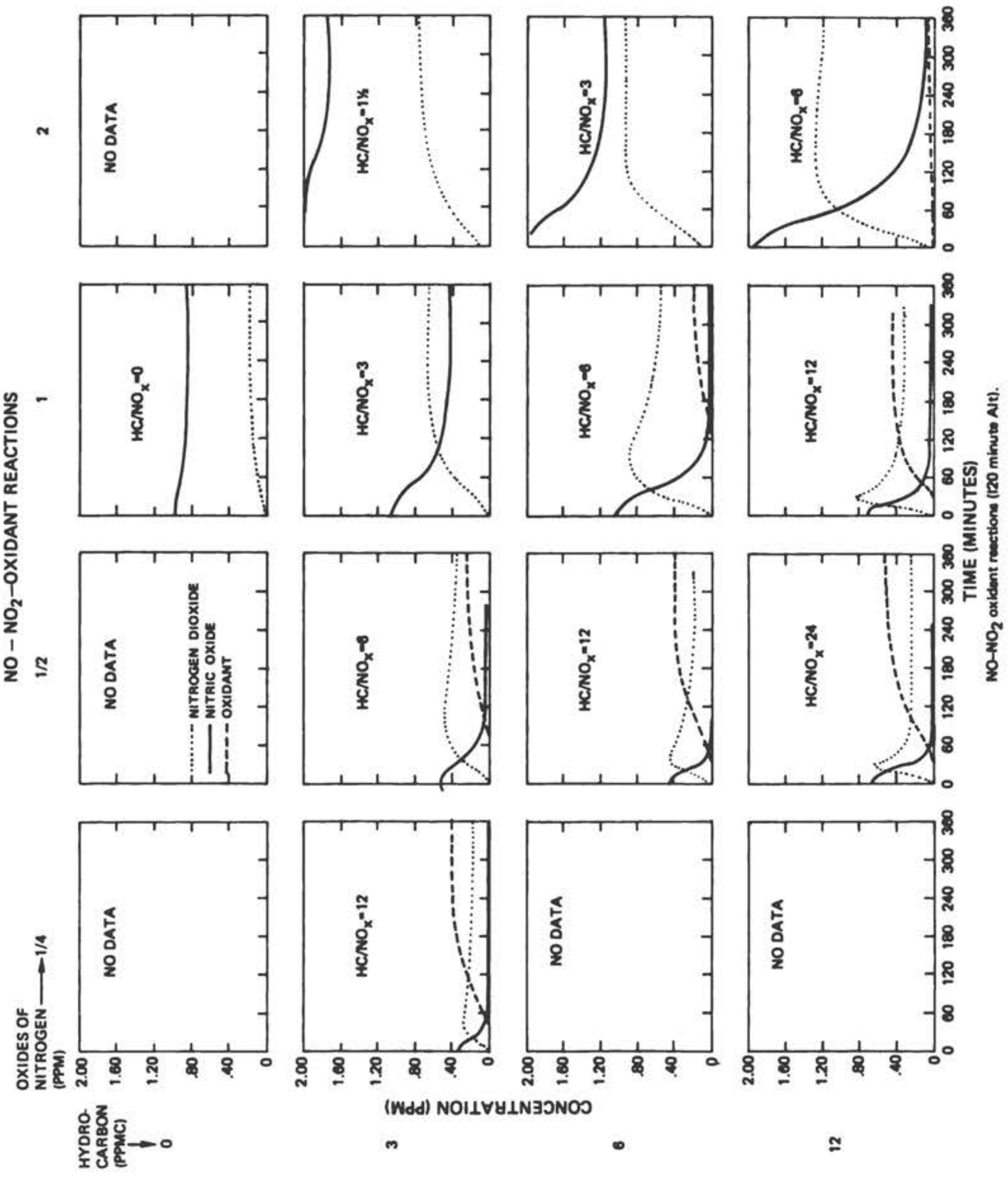


Diagram A-13

Laboratory: U.S. Department of Health, Education, and Welfare

Reference: Korth, M. W., Rose, A. H., Jr., and Stahman, R. C., JAPCA, vol. 14, No. 5, p. 168, May 1964.

Comment: This diagram of equilibrium oxidant is in striking contrast to the Haagen-Smit diagram of Diagram A-11 because it shows oxidant increasing with decreasing nitric oxide concentration and with increasing hydrocarbon concentration. It clearly reflects the role of nitric oxide as inhibitor of ozone (corrected oxidant) formation and the role of hydrocarbon in destroying this inhibitor. Although the average irradiation time of 120 minutes used in these experiments may be too short, the use of a longer irradiation time would do no more than displace this contour.

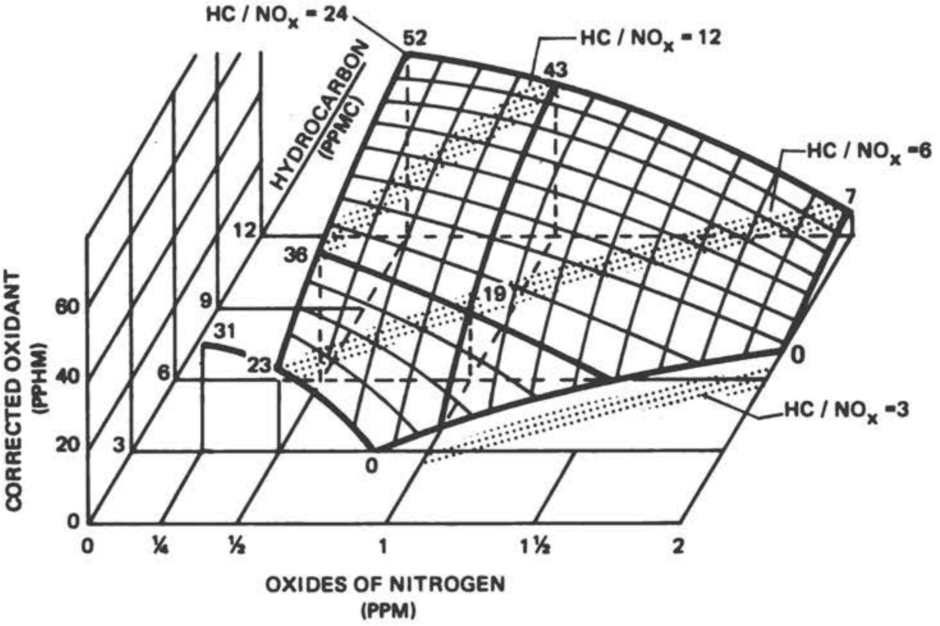


Diagram A-14

Laboratory: Los Angeles County Air Pollution Control District

Reference: Hamming, W. J., MacBeth, W. G., and Chass, R. L., Arch. Env. Health, vol. 14, p. 137, Jan. 1967.

Comment: Ozone formation and eye irritation are both delayed until the conversion of NO to NO_2 is complete.

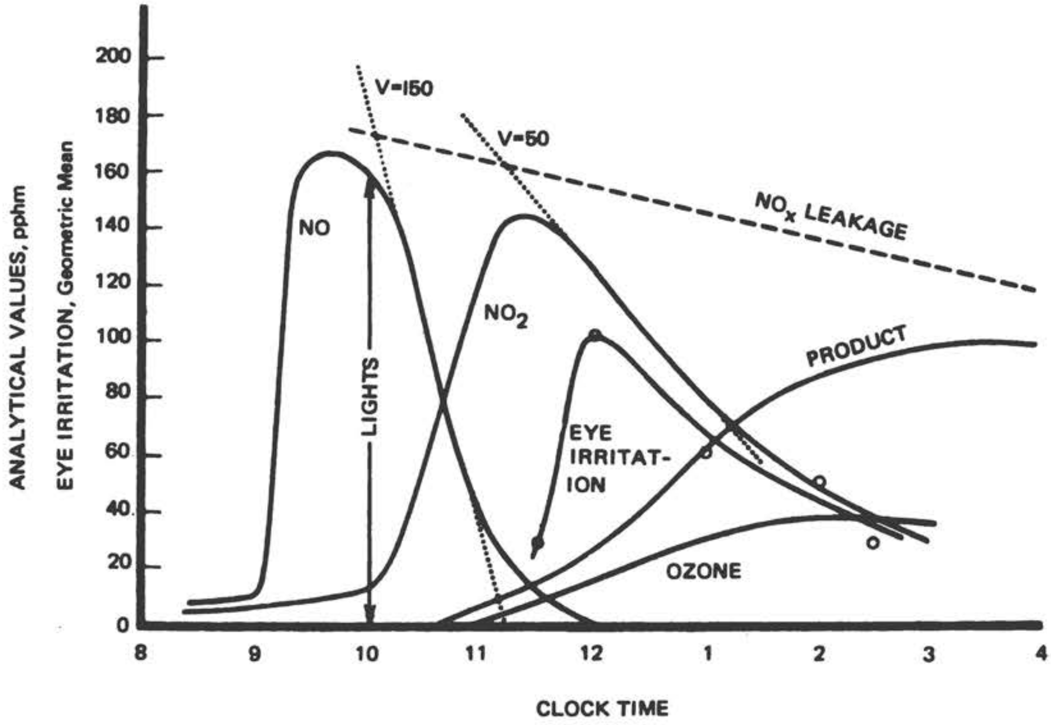
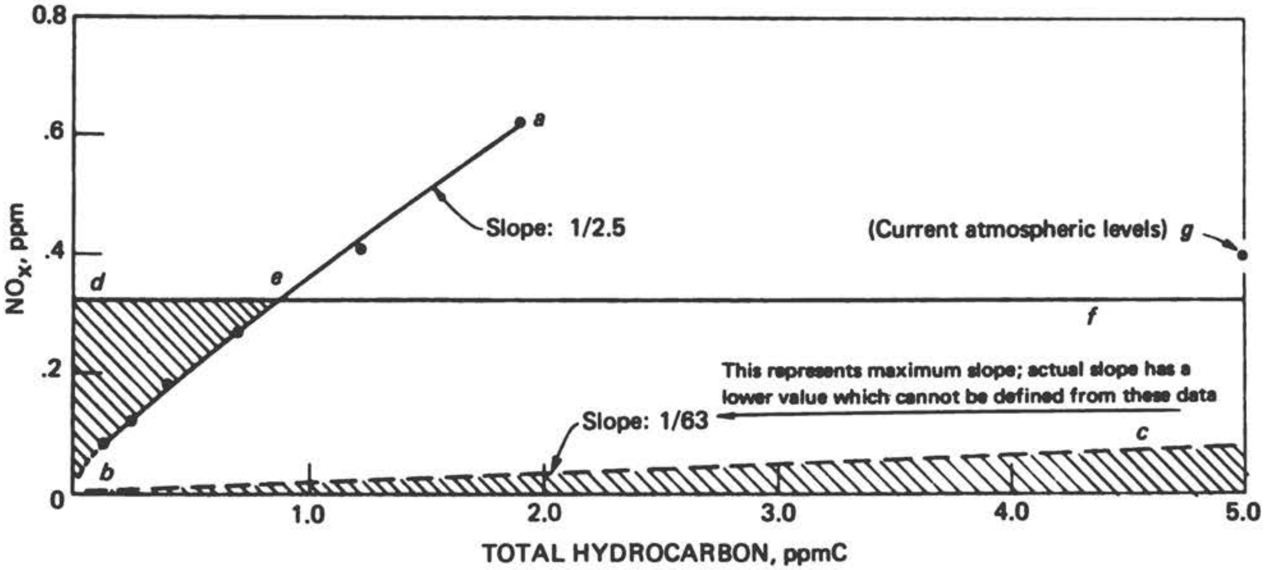


Diagram A-15

Laboratory: Bureau of Mines, Bartlesville, Oklahoma

Reference: Dimitriades, Basil, Report of Investigations 7433; also Env. Sci. Tech., vol. 6, No. 3, p. 253, March 1972.

Comment: This line of slope 1/2.5 separates the area above which (at higher NO concentrations) oxidant is less than the California standard. The other boundary (shown with a slope of 1/63) could not be defined because data were not obtained below 0.08 ppm of NO_x.



APPENDIX B

Equivalency between Different Averaging Times

The relationships between concentration of nitrogen oxides and the averaging time used to measure them are shown graphically in the arrowhead chart (Figure B-1). The slopes of the lines on the chart are determined by the standard geometric deviation (SGD) of the air quality data. For the Continuous Air Monitoring Program (CAMP) Stations of the Environmental Protection Agency with more than 2 years of data, the SGD's for nitrogen dioxide 1-hour data are

Chicago	1.65 (1962-68)
Cincinnati	1.67 (1962-68)
Denver	1.76 (1965-68)
Philadelphia	1.80 (1962-68)
St. Louis	1.77 (1964-68)
San Francisco	1.85 (1962-64)
Washington, D.C.	1.67 (1962-68)
Average	1.74

Using the method of Larsen (13), the ratio of 1-hour average concentration to annual average concentration for a SGD of 1.74 is 7.08. This means that the 1-hour average concentration is approximately seven times the annual average value. Thus the 1-hour average equivalent to an annual average of 0.05 ppm is 0.35 ppm.

For data with an SGD of 1.74 for 1-hour average, the corresponding ratio of 3-hour average maximum value to annual mean value is 5.47, and the resultant ratio of maximum 3-hour average value to maximum 1-hour average value is 0.77. Thus the 3-hour average value equivalent to the California 1-hour standard of 0.25 ppm is 0.19 ppm.

Conversion between NO_2 and NO_x Values

Three means have been used to establish the range of values to convert NO_2 to NO_x values. The first one involves converting from 1-hour

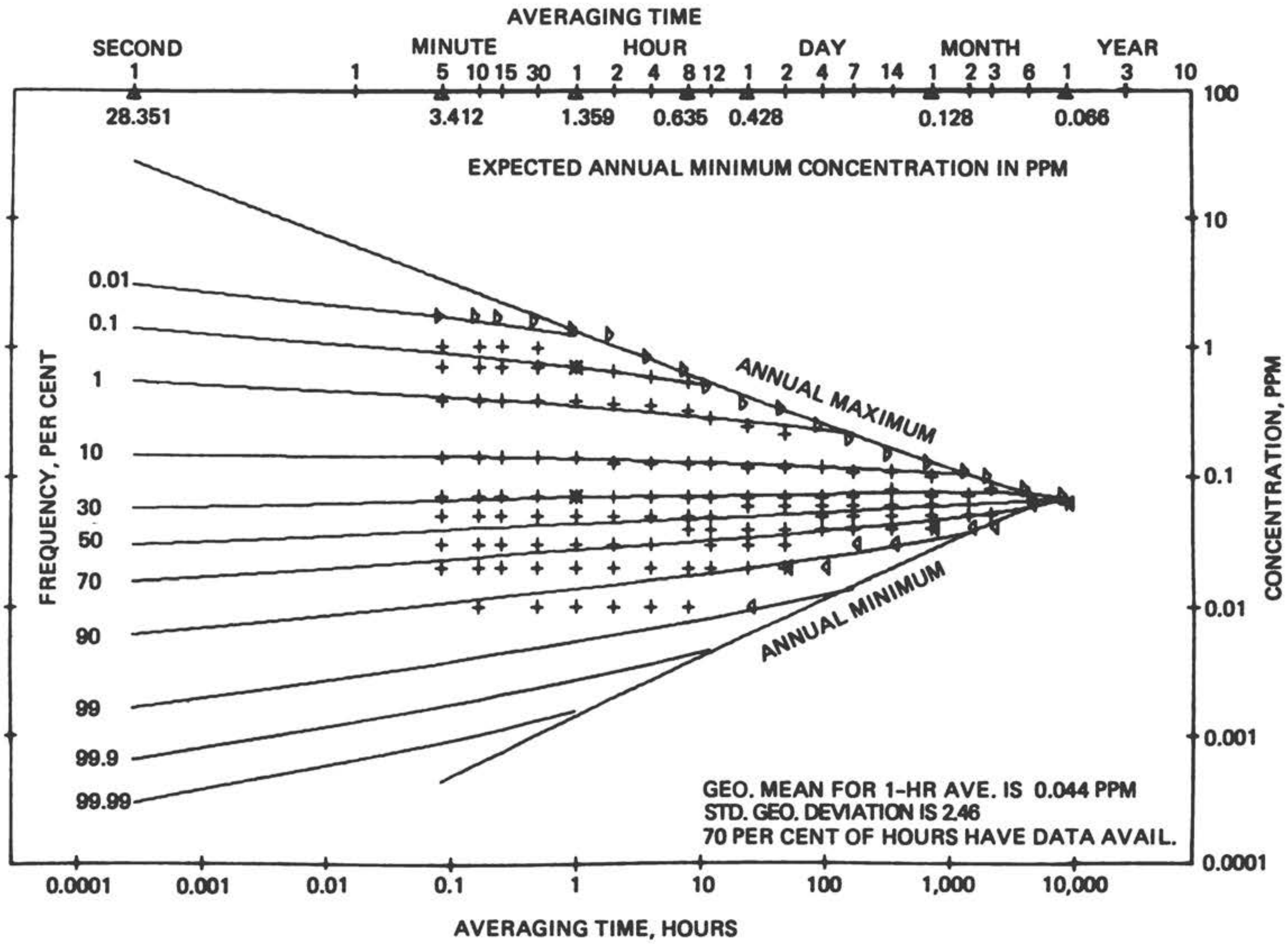


FIGURE B-1 Arrowhead chart (produced by computer) for concentration versus averaging time and frequency for nitrogen oxides in Washington, D.C. -- December 1, 1961, to December 1, 1964.

to 3-hour average the maximum 1-hour NO_2 values in Table 2 of the main portion of this report by multiplying by 0.77, as noted above, and then finding their percentage of the corresponding 6-9 a.m. NO_x values. The resulting percentages are

May 15--56%
June 2--60%
June 25--54%
July 2--92%
Aug. 7--38%
Sept. 30--24%
Oct. 27--16%
Oct. 30--33%
Nov. 13--18%
Nov. 14--21%
Nov. 17--41%
Nov. 18--25%

These data show a range of from 16 to 92 percent.

The second approach involves computing the same percentage from the 3-hour average annual maximum and 50 percentile values for the seven CAMP stations for which there are more than 2 years of data (see above). These are:

	3 hour Average	
Percent NO_2 value is of NO_x value	Annual Maximum	50 Percentile
Chicago (1962-68)	31	31
Cincinnati (1962-68)	22	60
Denver (1965-68)	33	50
Philadelphia (1962-68)	17	57
St. Louis (1964-68)	34	55
San Francisco (1962-64)	43	38
Washington (1962-68)	18	60

These latter data show a range of from 17 to 60 percent. The overall range shown by these two approaches is 16 to 92 percent. By applying these percentages to the 3-hour equivalent of the California 1-hour NO_2 standard, the 3-hour average NO_x equivalent ranges from 0.21 to 1.2 ppm. Transposing this to the Federal Standard equivalent by multiplying by the ratio (0.35/0.25) yields a Federal Standard

Equivalent range of 0.3-1.5 ppm.

The lowest three-hour NO_x value equivalent to the Federal Standard for NO_2 is 0.3 ppm. Because it is the lowest value, it is, in our opinion, conservative and contains a reasonable factor of safety. We therefore have used this value in our computations.

A third way to estimate the 3-hour morning NO_x concentration that would result in a one hour NO_2 concentration of .25 ppm can be estimated from some of the data in Dimitriades' smog chamber experiment (Figure B-2). A maximum 1-hour NO_2 concentration of .25 ppm would occur if the initial NO_x in the chamber was of the order of 0.37 ppm. Since the total NO_x did not significantly change during the first few hours of the experiment, we can assume that this initial injection of NO_x is a reasonable and good estimate of 6-9 a.m. period NO_x average. Hence in this chamber experiment, 0.37 ppm NO_x (3-hour average) is the equivalent of the 0.25 ppm California NO_2 standard and 0.48 ppm NO_x (3-hour average) is the equivalent of 0.35 ppm NO_2 1-hour average (the Federal Standard equivalent).

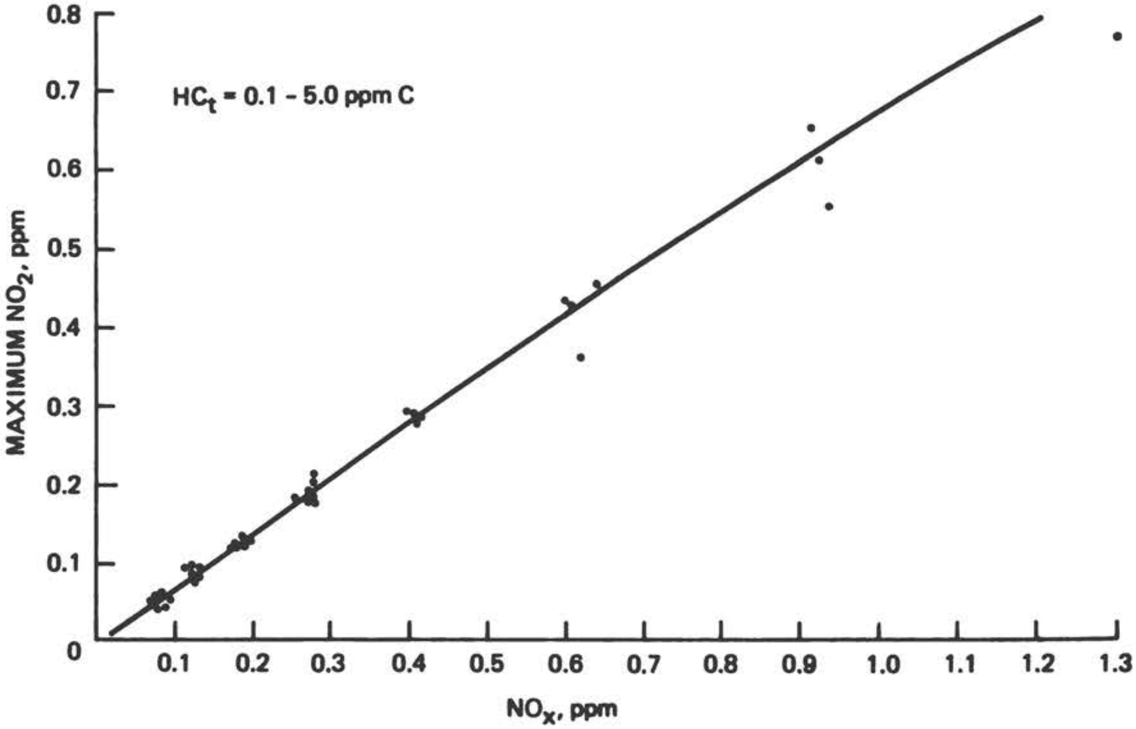


FIGURE B-2 Dependence of maximum 1-hour average NO_2 on HC and NO_x. Exhaust data.

APPENDIX C

Quantification of NMHC and NO_x

Los Angeles Air Quality data supplied by Hamming (21) can help quantify the NMHC and NO_x axes of Figure 4. NO_x and total HC (6-9 a.m.) values from the downtown Los Angeles station are compared for low oxidant, 0.1 ppm, readings in the San Gabriel Valley (Azusa and Pasadena) in Figure C-1. This permits one to see the oxidant-producing potential of oxidant precursors in the downtown Los Angeles air mass as it moves downwind to the San Gabriel Valley. The total HC concentration corresponding to 0.3 ppm NO_x, for oxidant 0.1 ppm, ranges from approximately 5 ppm C in 1962 and 1963-65 data to approximately 4 ppm C in 1970-71 data. By use of the relationship shown in Figure C-2 (22) it will be seen that 4 ppm C total HC in Los Angeles is equivalent to 1.5 ppm NMHC. This suggests that there is a factor of safety of about 2 in the value of 0.75 ppm NMHC proposed in Chapter 3 of this report, and that the final oxidant concentration achieved by 0.3 ppm NO and 0.75 ppm NMHC would result in point z in Figure 4 being well within the shaded area of that figure and represents values below both the NO_2 and oxidant air quality standards.

These data must be viewed with the following reservations: They show that the morning hydrocarbon readings at downtown Los Angeles were occasionally as high as 6 ppm C for total hydrocarbons, with NO_x simultaneously around 0.3 ppm on days when the maximum oxidant at Azusa and Pasadena remained less than 0.1 ppm. This implies that oxidant will not exceed 0.1 ppm if the concentration of the precursors are kept as low as 6 ppm C and 0.3 ppm, respectively. The fallacy here is in leaving the weather out of account. Since these were days on which the weather was not conducive to smog, there is no guarantee as to what oxidant concentration might have been found if the morning precursor concentration had been 6 ppm C and 0.3 ppm NO_x on a day when the weather was such as to promote oxidant formation.

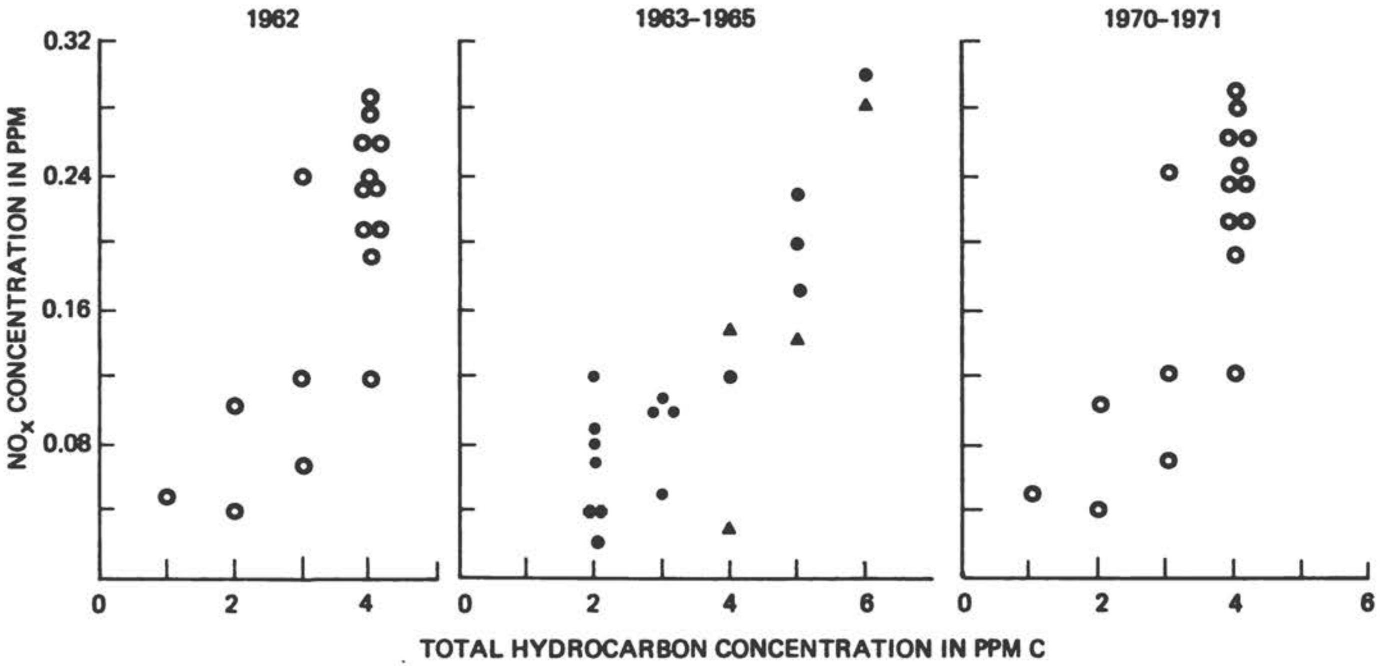


FIGURE C-1 Hydrocarbon and oxides of nitrogen data provided by Hamming for oxidant less than 0.1 ppm in Los Angeles.

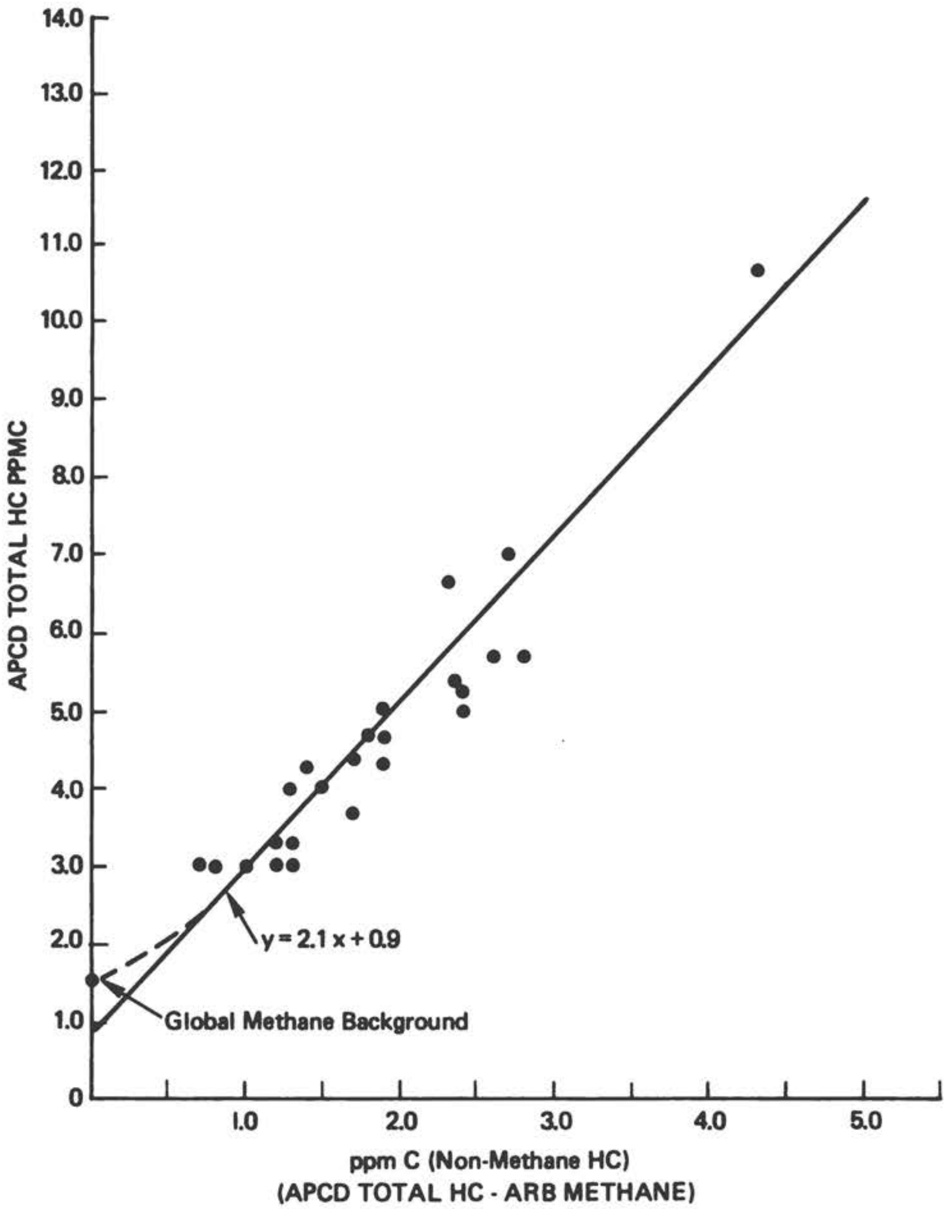

14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
APCD TOTAL HC PPMC
y = 2.1 x + 0.9
Global Methane Background
1.0
2.0
3.0
4.0
5.0
ppm C (Non-Methane HC)
(APCD TOTAL HC - ARB METHANE)

FIGURE C-2