A Guide to the Control of Photochemical Pollution

Occasional Paper

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A Guide to the Control of Photochemical Pollution

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FOREWORD

Current interest in urban air quality and the role of motor vehicle emissions standards has encouraged the Bureau of Transport Economics to support a series of studies aimed at improving the basic understanding of the physical processes involved and the economic implications of both problems and solutions.

The present work builds on that published previously (BTE Occasional Paper 6, Photochemical Pollution in Australian Airsheds) to develop a discussion of the basic principles and specific measures appropriate to the improvement of urban air quality. The paper discusses the physical effectiveness of alternative emission control strategies in reducing the impact of high oxidant levels in urban areas.

The paper was prepared for the Bureau by Dr N.J. Daly of the Department of Chemistry, Australian National University. The Bureau of Transport Economics does not necessarily accept or endorse the findings of the paper.

Technical liaison and editing of the paper were carried out by Mr L. Lawlor, assisted by Mr C. Sayers and Mr G. Morris, all from the Planning and Technology Branch.

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SUMMARY

Photochemical pollution is recognised as being a problem in a number of Australian cities, but is most developed in the Sydney airshed.

Photochemical smog contains a number of chemicals which are reputed to cause damage to health, materials and vegetation. It is the result of a complex sequence of chemical reactions, initiated by the action of sunlight on nitrogen dioxide and fed by non-methane hydrocarbons and air.

This paper reviews the present state of knowledge regarding the nature and effects of photochemical pollution and draws some conclusions concerning the setting of goals for oxidant concentrations and the most effective strategies for oxidant control.

The nature of photochemical pollution is explored with some emphasis on the limitations of ozone as an indicator of pollution. The conclusion reached parallels that of the United States National Academy of Science to the effect that ozone is an acceptable indicator given current knowledge, but that its use should be reviewed periodically in light of any emerging information on the synergistic effects of ozone and nitrogen oxides.

The major chemical variables in the formation of ozone are found to be:

(a) the concentrations of non-methane hydrocarbons (NMHC) and nitrogen oxides (NOx);

(b) the ratio of NMHC/NOx;

(c) the duration of the period of irradiation;

(d) the rate of dilution of the reacting mixture; and

(e) the composition of the hydrocarbon mixture.

The role of these variables is discussed in some detail; their relative importance is shown to depend on the duration of solar irradiation, which is influenced in turn by meteorological conditions within an airshed. Because of the variety of irradiation conditions possible within Australian urban airsheds including the likelihood of multi-day irradiations, it is concluded that limits need to be placed on emissions of both hydrocarbons and nitrogen oxides.

The setting of overall goals for oxidant levels is discussed and standards used throughout the world are critically examined. It is concluded that there is insufficient information on the health effects of smog mixtures to permit the setting of a final oxidant goal for Australia. The possibility is discussed of setting a goal for an interim period to enable necessary studies to be undertaken.

Options available for the control of oxidant formation are discussed. A critical analysis is made of the applicability and use of two models which have been put forward to describe the ozone-precursor relationships in the Sydney airshed. The results of the analysis show that these models have limited validation at present. Thus the models are of limited use in determining ozone concentrations in the Sydney airshed resulting from a range of concentrations of hydrocarbons and nitrogen oxides.

It is also shown that the use of these models to predict the results of control strategies based on large reductions in hydrocarbons alone requires major extrapolation into regions beyond which they are claimed to apply. Thus the models cannot be reliably used for this purpose.

Within the limits for which the models are said to be validated, the models indicate that ozone concentrations are equally sensitive to reductions in either hydrocarbons or nitrogen oxides. It is also demonstrated that strategies based on the combined control of hydrocarbons and nitrogen oxide emissions can be as effective in reducing oxidant levels as strategies involving reduction of hydrocarbons only, and would require less stringent control standards to achieve this result. These findings conflict with the contention that control of hydrocarbons only is the optimum route to oxidant control. This analysis, together with the likely role of nitrogen oxides during extended irradiations, makes it prudent to effect some controls on both hydrocarbon and nitrogen oxides emissions, and to review the situation as more evidence becomes available from chemical studies.

CHAPTER 1 - NATURE OF PHOTOCHEMICAL POLLUTION

INTRODUCTION

Air pollution has been a problem associated with cities for centuries and has its origins in the traditional practice of dumping airborne wastes into the environment and relying upon the natural dispersion forces in the airshed to remove them. Since waste production tends to grow as population grows, there comes a time when emissions exceed the environmental capacity of the airshed to disperse them. The result is air pollution.

The London smogs of the 1950s are a classic example of severe pollution episodes in which sulphur oxides and suspended matter, resulting from the burning of high sulphur solid fuels, accumulated to dangerous levels during periods of poor dispersion. In recent times such problems have been largely contained by controlling the sulphur content of domestic and industrial fuels. As often happens, however, a new type of problem has risen in its place.

During the mid-1940s a new kind of oxidising air pollution became apparent in Los Angeles. This new type had the effects of causing eye and throat irritation, vegetation and materials damage, and reduction of visibility, and came to be known as Los Angeles or Photochemical Smog. It has now been established that the pollutants of concern are formed by chemical reactions which take place in the airshed. These pollutants, which are formed by atmospheric reactions during periods of bright sunshine and poor dispersion, are termed oxidants.

The name oxidant arose because the polluted air has the property of oxidising solutions of potassium iodide, and this process formed the original basis for the classical method of analysis. In practice, the oxidising power of the polluted air is mainly (ca 90 per cent) due to the ozone component of the mixture; the major substances of concern are ozone, peroxyacetyl nitrate

(PAN), aerosols, nitrogen dioxide, and a range of secondary pollutants which have little oxidising power. A list of some of the compounds which have been observed during photochemical smogs together with a guide to typical or maximum concentrations which have occurred is given in Table 1.1.

TABLE 1.1 - COMPOUNDS OBSERVED IN PHOTOCHEMICAL SMOG

Compound	Concentrations Reported (ppm) Typical	Concentrations Reported (ppm) Maximum
Ozone	0.10	0.70
Peroxyacetyl Nitrate	0.004	0.01
Hydrogen Peroxide	-	0.18
Formaldehyde	0.04	-
Higher Aldehydes	0.04	-
Acrolein	0.007	-
Formic Acid	-	0.05

Source: US National Academy of Sciences 1977.

In recent times, advances in technology have led to the development of instruments which permit accurate and continuous measurement of ozone in the parts per hundred million range. As a result ozone is measured on a continuous basis and the concentration is used as a measure of the degree of advancement of the oxidant forming process. Thus the terms oxidant and ozone are frequently used interchangeably, and the success in controlling photochemical pollution is evaluated in terms of the concentrations of ozone.

The question of whether ozone always acts as a suitable surrogate for the effects of photochemical pollutants on health and materials has been raised and has yet to be resolved (Daly and Steele 1977). This question is also related (Daly 1975) to the controversial issue of whether rural values of ozone observed in the Northern Hemisphere are natural or anthropogenic in origin (Chatfield and Rasmussen 1977). A list of compounds that may be formed in photochemical smog is given in Table 1.2.

TABLE 1.2 - COMPOUNDS WHICH ARE LIKELY TO OCCUR IN PHOTOCHEMICAL SMOG

Peroxybenzoyl nitrate	Ozonides
Nitric acid	Ketene
Organic hydroperoxides	Nitrous acid
Organic per-acids	Pernitric acid
Organic peroxynitrates	Pernitrous acid
Sulphoxyperoxynitrate	

Source: US National Academy of Sciences 1977.

ORIGINS OF URBAN OXIDANTS

Photochemical oxidants are formed in urban airsheds by interaction between sunlight and substances emitted into the airshed during periods of poor dispersion due to atmospheric stability.

The basic nature of the oxidant forming processes was established by the pioneering work of Haagen-Smit and his co-workers who showed that irradiation by ultra-violet light of either the exhaust gases from motor vehicles or synthetic mixtures of non-methane hydrocarbons (NMHC) and nitrogen oxides (NOx) produces ozone, and products which cause eye irritation and plant damage (Haagen-Smit 1952) (Haagen-Smit, Bradley and Fox 1953). The foundations for understanding the chemical mechanism of the oxidants forming processes were laid by Leighton (Leighton 1961).

The sequence of chemical reactions which form oxidants is now well researched and reasonably well understood (Demerjian, Kerr and Calvert 1974) (Pitts and Finlayson 1975) (Graedel, Farrow and Weber 1976) The sequence of reactions can be summarised by the equation:

$$\text{NOx} + \text{NMHC} + \text{Sunlight} \longrightarrow \text{oxidants}$$

Such an equation is an extreme simplification of hundreds of chemical reactions (Leighton 1961) (Graedel, Farrow and Weber 1976) (Pitts and Finlayson 1975) but serves to identify non-methane hydrocarbons and nitrogen oxides as the controllable precursors to oxidant formation.

OXIDANTS IN AUSTRALIA

The problem of photochemical pollution has been rapidly growing in the last decade and affects major cities throughout the Western world. Ambient concentrations of ozone which are sufficiently high to cause concern for public health are now experienced in Mexico City, major cities in North America and Western Europe, the United Kingdom, and Japan (Daly 1977) (Apling et al 1977). Australia too, is greatly affected. In both Sydney and Melbourne, high levels of ozone have been observed, and incidents in which the goal of the World Health Organisation is exceeded have been recorded in all State capitals (Miller, unpublished data).

The extent of the problem in the State capitals varies, and ranges from the scale experienced in Sydney, where ozone concentrations exceeded the one-hour goal of the World Health Organisation on 129 days in 1976, to that experienced in Adelaide and Brisbane where the same goal was exceeded on 38 days and 20 days respectively in the same year (Miller, unpublished data). Comparative data are summarised for Australian State capitals in Table 1.3 and for Melbourne in Table 1.4. The occurence of such incidents may have a cost in economic and health terms.

TABLE 1.3 - NUMBER OF DAYS ON WHICH THE WHO ONE-HOUR GOAL FOR OZONE WAS EXCEEDED IN AUSTRALIAN STATE CAPITALS, 1974 TO 1976

Location	Year		
	1974	1975	1976
Lidcombe N.S.W.	52	120	129
Marrickville N.S.W.	99	78	126
Perth	7	8	na
Adelaide(a)	na	na	38
Hamilton Qld	na	na	20
Fortitude Valley Qld	na	na	11

(a) Results expressed as oxidant.

Source: Miller S., unpublished data.

TABLE 1.4 - NUMBER OF DAYS ON WHICH OZONE EXCEEDED STATED LEVELS FOR MELBOURNE AND METROPOLITAN AREA, 1974 TO 1978

Year	Ozone Concentration		
	0.06ppm	0.15ppm	0.20ppm
1973	17	3	2
1974	34	4	0
1975	45	1	1
1976	48	5	4
1977	22	0	0
1978	48	2	0

Note: The number of days each year should not be interpreted as any indication of trends as much of the monitoring equipment was placed in varied locations, and different quantities of equipment were used from year to year. The numbers should be strictly taken as the number of days recorded with the available monitoring resources at the time.

The 1977 results should be viewed in the context that during that year, monitoring was only carried out at the Museum (City), Box Hill (Jan. to Oct.) and South Caulfield (Nov. and Dec.).

Source: Data supplied by Environ. Protection Authority of Victoria.

NATIONAL AIR QUALITY GOALS AND STANDARDS

Both the Japanese and U.S. Federal Governments have set legal standards governing ambient levels of oxidants on the basis of potential damage to human health. The U.S. Federal Standard resulted from epidemiological studies which have been reviewed by the U.S. Department of Health, Education and Welfare (U.S. National Air Pollution Control Administration 1970) and took into account the relationship of oxidant levels to eye irritation (Richardson and Middleton 1957) impaired athletic performance (Wayne, Sherle and Carroll 1967) (Hasselblad, Lorimore and Nelson 1971) and the onset of asthmatic attacks (Schoetlinn and Landau 1961). The standard set is that a one-hour average concentration of ozone is not to exceed 0.08 parts per million (ppm) more than once per year.

The existence of the oxidant standard for air quality has an influence in countries in which no formal standards are set since they provide a yardstick against which to judge the air quality. The oxidants problem in the Netherlands tends to be evaluated against the one-hour average of 0.08 parts per million (Guicherit, Blokzijl and Plasse 1976) while in Australia data from each state tend to be compared with the World Health Organisation goal of 0.06 parts per million (Miller, unpublished data).

A summary of the present standards for oxidant concentrations is given in Table 1.5. Some of these standards are in the process of re-examination. The World Health Organisation for example appears likely to restate its goal in a form which notes that oxidants standards range from a concentration of 0.08 to 0.10 parts per million.

TABLE 1.5 - AIR QUALITY GOALS OR STANDARDS[(a)] FOR POLLUTANTS

Pollutant	Goal or Standard Type	Averaging Time	U.S.	Japan	Canada	WHO	California
TOTAL OXIDANTS OR OZONE	Legal Standard	1 hour	240 $\mu g/m^3$ 0.12 ppm oxidants	160 $\mu g/m^3$ 0.08 ppm oxidants	–	–	200 $\mu g/m^3$ 0.10 ppm oxidants
	Goal	8 hours				60 $\mu g/m^3$ 0.30 ppm	
		1 hour				120 $\mu g/m^3$ 0.60 ppm oxidants	
	Acceptable objective	1 hour			160 $\mu g/m^3$ 0.08 ppm ozone		
NITROGEN DIOXIDE	Legal Standard	24 hours		38 $\mu g/m^3$ 0.02 ppm			
	Legal Standard	1 year	94 $\mu g/m^3$ 0.05 ppm				
	Legal Standard	1 hour					472 $\mu g/m^3$ 0.25 ppm
NON-METHANE HYDROCARBONS	Guidelines	3 hours (6-9 am)	0.24 ppmC				

(a) Not to be exceeded more than once per year.

Source: Various national standards.

OZONE AS AN OXIDANTS STANDARD

The problems of photochemical pollution are problems associated with the operation of a large number of chemical reactions during periods of poor dispersion in the airshed. These reactions produce a range of compounds (Tables 1.1 and 1.2) which pose threats to health and welfare until they are dispersed by atmospheric processes. As examples of these real and potential threats in photochemical smog, Pitts lists threats from ambient lead, carbon monoxide, nitrogen dioxide, ozone, secondary aerosols such as sulphates and nitrates, and organics such as alkyl nitrates and the carcinogenic nitrosamines (Pitts 1976).

Daly and Steele pointed out that while the body of epidemiological studies implicates total oxidant and the products of the smog-forming reactions rather than ozone as the threat to health, the effects on humans have been correlated with the concentrations of ozone in polluted city airsheds (Daly and Steele 1975). Such a correlation assumes that the ozone concentration is a good indicator of the degree of advancement of the photochemically-initiated reaction sequence.

Recent studies of the physiological effects tend to confirm that the adverse effects on health of photochemical pollutants are due to combinations of components of the mixtures. Thus in experiments with mice Ehrlich et al (Ehrlich et al 1977) have shown that ozone and nitrogen dioxide have additive effects during single 3-hour exposures. Moreover, the workers considered that a synergistic effect operated for multiple exposures.

In experiments with humans, Mizoguchi et al showed that a range of symptoms such as cough, shortness of breath, sore throat and eye-irritation correlated well with combined pairs of pollutants such as oxidant and aldehyde, oxidant and suspended particulate matter and so on (Mizoguchi et al 1977). Results have been summarised in Table 1.6.

TABLE 1.6 - HEALTH SYMPTOMS AND PAIRS OF ENVIRONMENTAL FACTORS WITH WHICH THEY CORRELATE SIGNIFICANTLY

Symptom	Environmental Factors
Eye irritation	oxidant - sulphur dioxide, oxidant - sulphate; oxidant - aldehyde; oxidant - temperature; oxidant - suspended particulate matter (SPM); oxidant - nitrate.
Shortness of Breath	oxidant - sulphate; oxidant - aldehyde; oxidant - sulphur dioxide; oxidant - temperature; oxidant - nitrate; oxidant - SPM.
Sore Throat	oxidant - sulphate; oxidant - SPM; oxidant - sulphur dioxide; oxidant- temperature; oxidant - aldehyde; sulphur dioxide - SPM; oxidant - nitrate.
Cough	sulphur dioxide - SPM; oxidant - SPM; SPM - sulphate.
Hoarseness	sulphur dioxide - SPM; oxidant - SPM; SPM - sulphate; SPM - nitrate; SPM - aldehyde.
Phlegm	sulphur dioxide - SPM, sulphur dioxide - sulphate.

Source: Mizoguchi et al 1977.

In a recent survey on photochemical oxidants, the National Academy of Sciences of the United States accepted that at present ozone may be taken as a surrogate for the complex mixture of noxious substances although it is suggested that this role be periodically re-evaluated (U.N. National Academy of Sciences 1977).

EMISSION SOURCE INVENTORIES

In general the source inventories of non-methane hydrocarbons and nitrogen oxides for Australian cities are not well documented. That for the Sydney Basin is, however, well documented (Iverach, Mongon, Nielsen and Formby 1970) and the projections extend to the year 2000 (State Pollution Control Commission of N.S.W. 1977).

Data from Sydney show that, in terms of gross emissions, motor vehicles contribute about 56 per cent of emissions of nitrogen oxides, and about 79 per cent of non-methane hydrocarbons, the remainder coming from industrial sources. These estimates are currently being revised. Other Australian cities may have smaller contributions from industrial sources although the position needs to be quantified.

EMISSION SOURCES FOR OXIDANT EPISODES

As part of the Sydney Oxidant Study, Hawke et al have used detailed chemical and meteorological analyses to identify the sources of precursors responsible for high concentrations of ozone in the Sydney Basin (Hawke et al 1978). These procedures are illustrated by the analysis of data collected in one day of the study - 22 December 1976. Hawke et al stress that the sequence of meteorological events on this day is only one of a number of mechanisms that can produce high concentrations of ozone (Hawke et al 1978).

The detailed chemical and meteorological analyses used were:

- to 'fingerprint' a parcel of air enabling confirmation of the estimated trajectory for the period; and
- to pinpoint the source of the hydrocarbons in the air parcel by calculating a proportional contribution of motor vehicle tail-pipe emissions and a proportional contribution of gasoline vapour.

The study showed the relative contributions of motor vehicles and industrial emissions to the total hydrocarbon burden, and identified source and receptor areas for that day.

During the study high oxidant concentrations ranging up to 0.27 parts per million occurred within the sea-breeze. The proportional contributions of tail-pipe emissions to the air packet within the sea-breeze ranged from 8 per cent at Botany Bay to 20 per cent at Parramatta and Fox Hill (Hawke et al 1978). The results are summarised in Table 1.7.

TABLE 1.7 - PROPORTIONAL CONTRIBUTIONS OF TAIL-PIPE EMISSIONS WITHIN THE SEA-BREEZE, 22 DECEMBER 1976 FOR VARIOUS LOCATIONS IN SYDNEY

Botany Bay (0840 hours)	Mrs Macquaries Chair (0930 hours)	Parramatta (1045 hours)	Fox Hill (1245 hrs)
8%	10%	20%	20%

Source: Hawke et al 1978.

The combination of hydrocarbon analyses and surface air trajectories during the study identified the source and receptor areas for oxidant pollution on that day. The oxidant precursors moved north across the coastal region and were then recirculated within the Parramatta River Valley by westerly drainage flow and the easterly sea-breeze. Hawke et al point out (Hawke et al 1978) that without the detailed chemical analyses and meteorological measurements the occurrence of high concentrations of ozone could have been mistakenly attributed to emissions from the inland source area. They conclude that the relatively frequent occurrence of southerly changes during summer in the Sydney Basin may cause high concentrations of ozone (produced by the mechanism of 22 December 1976) to occur more frequently than expected.

The study shows that the precursors in an air parcel in which oxidants are formed may arise substantially from industrial sources. The implications are that three broad classes of oxidant episodes may need to be recognised:

- episodes in which the precursors arise substantially from industrial sources;
- episodes in which the precursors arise substantially from motor vehicle emissions; and
- episodes in which both industrial sources and motor vehicles make significant contributions to precursor concentrations.

The relative contributions of each of these classes has an obvious impact on the types of controls needed in an airshed, and need to be determined. For example, if one-third of the oxidants episodes in an airshed arose from industrial emissions only, one-third from motor vehicles only, and one-third from the combined emissions, controls on both types of sources would be needed to be effective.

NATURAL SOURCES OF HYDROCARBONS

Hydrocarbons are emitted into the atmosphere by various forms of vegetation and are known to cause aerosol formation and blue hazes in the atmosphere (Went 1960). The existence of such hazes during summer seems the likely origin of the name of the Blue Mountains to the west of Sydney.

In Australia many native trees and commercial plantations of conifers emit terpenes which are hydrocarbons with a high reactivity with respect to the photochemical smog forming processes (Grimsrud et al 1975) and are graded as Class V on the reactivity scale of Pitts et al (Pitts et al 1977). Rasmussen et al have estimated that on a global basis, by weight, the rate of emissions of reactive hydrocarbons from forests is about six times the rate of anthropogenic emissions (Rasmussen et al 1974).

The role of naturally emitted terpenes in generating rural ozone has been examined by Gay and Arnts (1977) who showed that although they could generate high ozone concentrations, they react with ozone. Accordingly Gay and Arnts concluded that all of the ozone would necessarily react with the excess of terpenes available.

Recently Kamiyama et al (1978) have correlated terpene concentrations in forests with meteorological conditions and showed that significantly higher values occur during cloudy days, thus raising the possibility that advection into urban areas could provide a very dilute source of very reactive hydrocarbons. Sandberg et al (1978) have examined data for the San Francisco Bay Area and have shown that summer ozone excesses over the Federal Standard are very well correlated with precipitation for the two proceeding winters. They advance the hypothesis that reactive hydrocarbon emissions from vegetative biomass affects these ozone excesses.

It is generally considered that the contribution of natural hydrocarbons to ozone in cities is relatively insignificant. However the evidence justifies the determination of the reactivity weighted rate of flux into city airsheds.

CHAPTER 2 - CHEMICAL FACTORS IN OXIDANT FORMATION

INTRODUCTION

Photochemical pollution involves the formation and accumulation of noxious substances in the airshed due to insolation of mixtures of hydrocarbons and nitrogen oxides. The problem of controlling the formation of these substances requires a knowledge of the chemical reaction sequence. Since ozone concentrations are used as the indicator of the degree of advancement of the photochemical processes, particular attention needs to be given to the chemistry of ozone formation.

The irradiation by ultra-violet light of mixtures containing low concentrations of hydrocarbons and nitrogen oxides leads to the following sequence of observations (Leighton 1961) (Pitts 1969) (Altshuller 1965) (Kerr 1972).

- non-methane hydrocarbons are oxidised and their concentrations fall;
- secondary pollutants such as aldehydes, alkyl nitrates, peroxyacyl nitrates, and heterocyclics are formed;
- nitric oxide is oxidised to nitrogen dioxide; and
- ozone concentrations increase to a maximum and then fall.

Some of these features are shown in the smog chamber data summarised (Kerr 1972) in Figure 2.1. These reaction processes are initiated by highly reactive entities known as radicals which are formed either directly or indirectly by photo-dissociations brought about by sunlight or ultraviolet light (Leighton 1961) (Kerr 1972) (Greiner 1970) (Morris 1971) (Niki 1972) (Wang and Davies 1974) (Pitts and Finlayson 1975). Essentially similar processes occur in urban airsheds. The roles of nitrogen oxides and hydrocarbons in these processes are considered in the following sections.

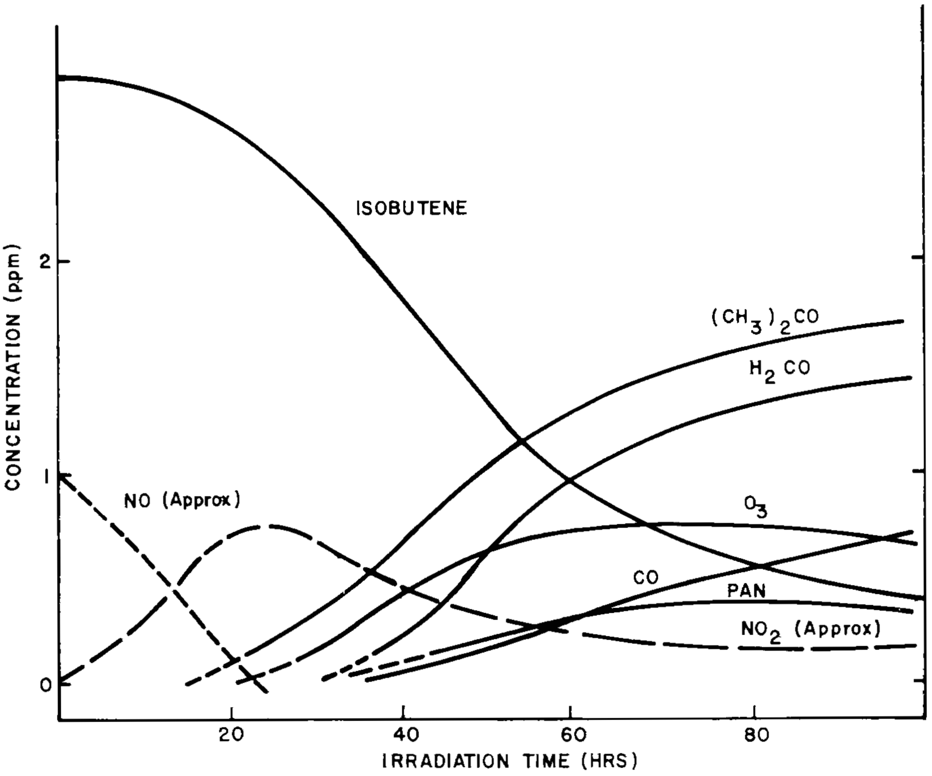

FIGURE 2.1
CONCENTRATION CHANGES UNDER IRRADIATION
CONDITIONS IN A SMOG CHAMBER

SOURCE : Kerr J.A., Calvert J.G., and Demerjian K.L.,

NITROGEN OXIDES AND THE FORMATION OF OZONE

Nitrogen oxides are an important precursor to the formation of photochemical oxidants. Two oxides are important, namely nitric oxide (NO) and nitrogen dioxide, (NO_2).

Nitric oxide is a primary pollutant for which the major source is the exhaust emissions from motor vehicles. Nitric oxide is relatively non-toxic and is readily converted to nitrogen dioxide by the oxygen in air. This conversion takes place rapidly during the early stages of dilution of the exhaust gases, and effectively ceases once nitric oxide concentrations are diluted to the parts per million range. Such dilution has normally occurred by the time the exhaust gases are a few metres from the point of emission from the tail-pipe.

A prime result of emitting nitric oxide into the airshed is to create a mixture of nitric oxide and nitrogen dioxide in that airshed. Such a mixture is collectively termed nitrogen oxides and given the symbol NOx.

Nitrogen dioxide is a primary pollutant emitted mainly from industrial sources and is also formed from nitric oxide emissions. The substance is toxic and injurious to public health above certain concentrations. Nitrogen dioxide has the important property of absorbing the ultraviolet content of sunlight (light with wavelengths between 290 and 420 nanometres) and undergoing photodissociation. This photodissociation produces atomic oxygen (O), a very reactive species. Atomic oxygen is important because it reacts with oxygen (O_2) in the air to give ozone (O_3). This reaction is the only reaction which is known to occur in urban airsheds to produce significant quantities of ozone (Pitts and Finlayson 1975) (Kerr 1972) although recent developments suggest that dissociation of peroxyacetyl nitrate (PAN) may also make a contribution (Nieboer et al 1978).

Experiments on mixtures of nitric oxide, nitrogen dioxide, and air have established that the photolytic reaction sequence is (Kerr 1972) (Leighton 1961):

- photodissociation of nitrogen dioxide to give nitric oxide and atomic oxygen;
- combination of atomic oxygen with molecular oxygen from air to give ozone; and
- combination of nitric oxide with ozone to reform nitrogen dioxide which restarts the cycle.

This reaction sequence is summarised by the chemical equations (i), (ii), (iii):

$$NO_2 + \text{Sunlight} \longrightarrow NO + O \qquad \text{(i)}$$

$$O + O_2 \longrightarrow O_3 \qquad \text{(ii)}$$

$$O_3 + NO \longrightarrow O_2 + NO_2 \qquad \text{(iii)}$$

Reaction (i) is very fast under sunny conditions. Reaction (iii) has the feature that it is considerably faster than reaction (ii) under airshed conditions. Because of this, nitric oxide exerts a controlling influence on concentrations of ozone in the airshed. During sunny conditions in a well-mixed airshed, reaction (i), (ii), and (iii) quickly reach and maintain a steady state (Leighton 1961) (Daly 1975) (Calvert 1976). The conditions of the steady state are such that ozone concentrations are given by the relationship:

$$(O_3) = Ok\ (NO_2)/(NO)$$

The terms (O_3), (NO_2) and (NO) denote the concentrations of ozone, nitrogen dioxide, and nitric oxide. Ok is a coefficient whose values are determined by the zenith angle of the sun (Leighton 1961) (Daly and Steele 1975) (Calvert 1976).

The steady state relationship shows how nitric oxide controls ozone concentrations which remain low until most of the nitric oxide in the airshed is converted to nitrogen dioxide. In smog-chamber experiments, ozone concentrations do not begin to rise until nitric oxide concentrations have been reduced to the point where the ratio $(NO_2)/(NO)$ exceeds values of about 10. This is shown by the smog chamber data of Figure 2.1.

This ability of nitric oxide emissions to control ozone levels in an airshed leads to the result that injections of fresh emissions of nitric oxide into a system can have the short-term effect of lowering ozone concentrations (Daly and Steele 1975) in the immediate vicinity of the source although it may lead to a higher ozone concentration at a later time downwind of the source.

THE ROLE OF HYDROCARBONS

The contribution of hydrocarbons to the reaction sequence is one which involves over 200 elementary reactions for each hydrocarbon (Kerr et al 1972). A typical airshed contains many hydrocarbons. More than 90 have been isolated in the Sydney Air Basin (Mulcahy et al 1976). The major types of hydrocarbons present in an airshed can be classified as alkanes, mono-alkylbenzenes, alkenes, and polyalkylbenzenes. In general alkanes and mono-alkylbenzenes are the least reactive while alkenes and polyalkylbenzenes are the most reactive.

The combination of the hydrocarbon reaction sequence with the nitrogen oxides photolysis leads to the formation of secondary pollutants such as peroxyacetyl nitrate (PAN), organic nitrocompounds, aldehydes, and oxygenated heterocyclics. In addition, the early part of the sequence contains steps which allow ozone concentrations to increase. In the later stages of the reaction sequence, alkenes consume significant quantities of the ozone which causes the concentrations to decline as the reactions proceed.

The steps which lead to an increase in the concentrations of ozone are those which modify the steady state concentration of ozone set up by the photolytic sequence of reactions (i), (ii), and (iii) involving nitrogen oxides and ozone.

The hydrocarbon reactions provide an alternative mechanism for converting nitric oxide to nitrogen dioxide without consuming ozone. These reactions compete with reaction (iii) above and modify the control it exerts on ozone. As the hydrocarbon reactions progress they consume nitric oxide to the point where its concentration becomes low enough to allow ozone concentrations to increase markedly. Thus the concentration of ozone provides an indicator of the extent to which the sequence of photochemical reactions has progressed.

Hydrocarbons of the type classified as alkenes react with ozone to give ozonides and a range of secondary pollutants (Daly and Steele 1976). The rate at which these reactions occur depends upon the concentration of ozone. Thus as ozone concentrations increase the alkene reactions become more important, and consume ozone. With extended irradiation times, the ozone concentrations reach a maximum and may decline depending on the relative balance of generation to consumption.

REACTIVITY OF HYDROCARBONS

One of the key factors which determines the extent of photochemical reactions in an airshed is the reactivity of each of the hydrocarbons present in the airshed. The reactivities of the hydrocarbons varies markedly from one chemical class to another, and, even within the one class, may show variations. The existence of this range of reactivities makes possible the use of selective controls on hydrocarbons as part of an oxidants control program. In California, Rule 66 seeks to encourage the substitution of hydrocarbons with low reactivity for those with high reactivity wherever possible (Los Angeles Air Pollution Control District).

Smog chamber data have provided the basis for the reactivity scales, and indices such as the degree of eye irritation, rate of conversion of nitric oxide to nitrogen dioxide, and maximum ozone levels have been used. To an extent the results depend upon the conditions chosen for the experiments and the criteria adopted for smog production. Altshuller and Bufalini (1971) critically reviewed the hydrocarbon reactivity data and ranked hydrocarbons on a scale 0 to 3 in order of their ability to produce ozone under standard laboratory conditions. The U.S. Environment Protection Agency adopted a scale of 0 to 7 based on the rate of consumption of hydrocarbons. In general the two scales are consistent with each other and range from alkanes with little reactivity to alkenes and alkylbenzenes which are most reactive. These scales, however, were based on short-term irradiation periods which reflected the control strategies of correlating oxidant peaks occurring around the middle of the day with the average of 0600 to 0900 hour concentrations of hydrocarbons.

Recent developments in the understanding of photochemical pollution have shown that the irradiation times of ambient mixtures of hydrocarbons and nitrogen oxides can be quite lengthy and have led to the need for a review of the reactivity scales (Pitts 1976). Two major factors that have emerged are:

- the realisation that with lengthy irradiation periods of up to 9 to 12 hours, the alkanes can generate as much ozone as alkenes and alkylbenzenes; and

- such lengthy irradiation times exist during stagnant air conditions characteristic of severe smog episodes, and can be exceeded during long-range transport of pollutants across, and recirculation in, a given air basin, or during multi-day irradiations.

The effect of increased irradiation time on the consumption of selected alkanes, alkenes, and alkylbenzenes is shown by the smog chamber data of Darnall et al (1976). These workers irradiated a mixture of hydrocarbons, made to be representative of the mixture found in ambient air in Los Angeles, for periods of up to 10 hours. Results from the study are shown in Figure 2.2.

The data in Figure 2.2 show that the alkene (propene) and the dialkylbenzene (m-xylene) undergo rapid reaction. After the traditional 6 hour irradiation period both are essentially consumed and the ozone concentration is 0.25 parts per million. As the irradiation is continued beyond the 6 hour period, the reactions of the hydrocarbons butane and toluene (the 'unreactive' mono-alkylbenzene) become important, and the ozone concentration continues to rise. After about 12 hours the ozone concentration reaches 0.50 parts per million.

These results show that reactivity scales based on short irradiation periods are weighted in favour of alkenes and polyalkylbenzenes. When longer irradiation periods occur the hydrocarbons regarded as unreactive also make significant contributions to ozone formation.

Pitts et al (1977) have proposed a reactivity scale based upon the reaction rates of hydrocarbons with hydroxyl radicals which enables the effects of extended irradiation periods to be considered. The scale is divided into 5 convenient classes and is shown in Table 2.1.

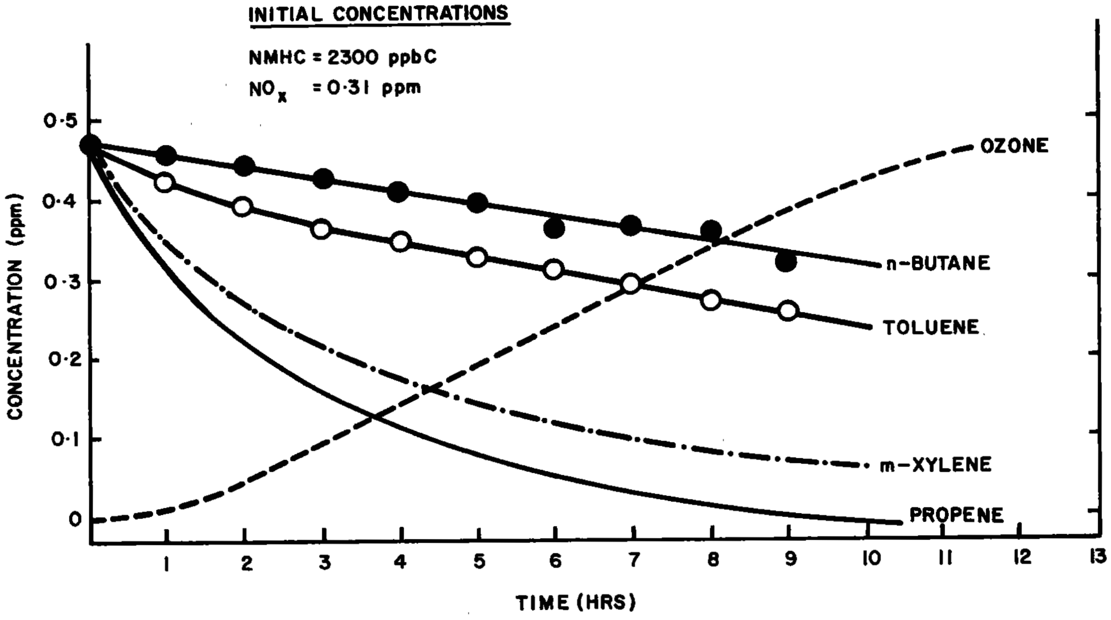

FIGURE 2.2
CONCENTRATION CHANGES OF SELECTED HYDROCARBONS
IN SMOG CHAMBER STUDIES

SOURCE : Darnall K.R., Winer A.M., and Pitts J.N.

TABLE 2.1 - REACTIVITY SCALE FOR HYDROCARBONS BASED ON REACTION RATES WITH HYDROXYL

Class	Half-Life[(a)] (Days)	Reactivity Relative to Methane
I	$\geqslant$ 10	$\leqslant$ 10
II	1-10	10-100
III	0.1-1	100-1000
IV	0.01-0.1	1000-10000
V	$\leqslant$ 0.01	$\geqslant$ 10000

(a) Half-life is the time taken for the hydrocarbon concentration to fall to half its initial value.

Source : Pitts et al 1977.

Where oxidant episodes result from an irradiation period of up to 0.1 days (2.4 hours), the substitution of Class IV and V hydrocarbons by Class I, II or III hydrocarbons would prove an effective means of abatement. Where oxidant episodes result from an irradiation period of 0.1 to 1 day, substitution of Class III, IV and V hydrocarbons by Class I and II hydrocarbons is needed to be effective. Where recirculation of the airmass, and second or multi-day irradiations occur only Class I hydrocarbons can be permitted if the oxidant problem is to be avoided.

For a particular airshed the overall effectiveness of selective controls needs to be assessed in terms of the proportion of oxidant episodes which would be mitigated by the proposed controls. Such an assessment needs to balance the costs of controlling each class of hydrocarbons against the proportion of the oxidant episodes which would be affected by the controls. The assessment requires, inter alia, a knowledge of the distribution of the irradiation times which are observed in the airshed during oxidant forming episodes.

Dimitriades and Joshi (1977) have examined the usefulness of the criterion of the reactivity of hydrocarbons in controlling oxidants and have suggested that the existing reactivity classifications be revised to consist of two classes, reactives and unreactives, defined as follows:

- unreactive organics are those which under optimum irradiation and organic-to-NOx ratio conditions in an appropriate smog chamber yield no more than 0.08 parts per million of ozone; and

- reactive organics are all organics except those found by measurement or theoretical estimation to be unreactive.

In practice such a classification appears to approximate unreactives to Class I and reactives to Class II through V. How greatly the classification of Dimitriades and Joshi differs from that of Pitts et al depends upon the distribution of irradiation times in the airshed. The classification into reactives and unreactives appears intrinsically less flexible until the distribution of irradiation times for the airshed of concern is established.

FACTORS AFFECTING OXIDANT FORMATION

Major factors which influence the concentrations of oxidants formed during solar irradiation are:

- the duration of the period of irradiation;
- the concentrations of both nitrogen oxides and hydrocarbons; and
- the composition of the mixture of hydrocarbons.

The effects of variations in these factors is considered in the following sections. Meteorological factors such as sunlight intensity and rate of dilution are also important and are discussed in Chapter 3. Throughout the discussion it is accepted that the major criterion is the maximum ozone concentration. This is in accord with general practice and fits in with the results of the health damage functions described in Chapter 4. Additionally it is accepted that ozone concentrations are the first concern in considering oxidant concentrations although concentrations of other oxidants may also need consideration.

OXIDANT DEPENDENCE ON THE PERIOD OF IRRADIATION

The concentration of ozone formed from a given mixture of hydrocarbons and nitrogen oxides depends upon the time of irradiation, and whether the irradiation of the mixture is confined to one day, or carried over to second and subsequent days.

The effect of varying the time of irradiation during the first day can be seen by examining the results obtained by Pitts et al (1976) in smog chamber studies. The studies were carried out using a mixture of hydrocarbons and nitrogen oxides said to be a surrogate for that found in the Los Angeles airshed and using conditions of steady ultra-violet irradiation. The results, summarised in Figure 2.2, show that ozone concentrations increase steadily as the length of the period of irradiation increases. Thus, were conditions such as to terminate the irradiation after a period of 5 hours an ozone maximum of about 0.18 parts per million would be observed, and this is in the main due to the reactions of the more reactive classes of hydrocarbons such as alkenes. Alternatively, if the conditions were to lead to an irradiation of 8 hours, a maximum of about 0.35 parts per million would be observed. The increase over this last three hours is substantially due to the reactions of the less reactive classes of hydrocarbons such as alkanes.

When a photochemically polluted airshed remains stagnant beyond sundown the photolytic generation of ozone ceases. The ozone present will undergo reaction with alkenes and nitric oxide in the airmass, and the concentration of ozone will decrease. The introduction of further emissions of alkenes and nitric oxide will consume ozone formed in earlier irradiations. Thus after sundown, the ozone concentrations may fall even when the airmass is not being diluted at a significant rate.

The presence in the airmass of a range of secondary pollutants undoubtedly means that the air retains some toxicity even though ozone concentrations fall to zero. For example, the consumption of ozone by alkenes leads to the formation of α-carbonyl hydroperoxides which are considered likely to be the phyto-toxicant in photochemical smogs (Pitts and Finlayson 1975).

When the airmass remains undispersed into a second sunrise the problem then becomes one of the multi-day irradiation of an aged smog.

It has been shown (Ripperton et al 1977) in smog chamber studies that irradiations of aged smogs with low concentrations of nitrogen oxides can generate high concentrations of ozone. The reasons for this become evident when the nature of the aged mixture is considered.

The most active of the hydrocarbons in generating ozone, alkenes, are those which are most reactive in consuming ozone to give, initially, ozonides. Alkenes and other reactive hydrocarbons react rapidly under irradiation conditions while the less reactive hydrocarbons are mainly preserved to react later. These less reactive hydrocarbons can generate high ozone concentrations given extended irradiations, and do not consume the ozone which they help form. The more aged the smog the more favourable the conditions for retaining the ozone it generates.

Studies of smog forming processes show that the maximum ozone concentrations formed from given concentrations of known mixtures of hydrocarbons and nitrogen oxides depend upon the length of the irradiation period for both one-day and multi-day irradiations. The observed differences between the ozone-precursor relationships for one-day and multi-day events arises from the changing chemical nature of the reaction mixture as the reactions proceed.

The influence of reaction time on the ozone-precursor relationships means that these relationships need to be evaluated for various classes of reaction times. The various classes which may need to be considered are:

- partial or one-day irradiations of fresh emissions;
- partial or one-day irradiations of 'aged' mixtures(1);
- partial or one-day irradiations of combinations of fresh emissions and aged mixtures; and
- multi-day irradiations.

Multi-day irradiations may need to be subdivided into the further categories:

- multi-day irradiations of a mixture of precursors without further additions of precursors on succeeding days; and

- multi-day irradiations of mixtures of precursors with further additions of precursors on succeeding days.

The necessity for this sub-division would have to be examined by suitable studies such as smog chamber simulations.

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(1) 'Aged' mixtures may be regarded as mixtures in which the hydrocarbons have undergone some transformation due to reactions with species such as ozone, hydroxyl radicals, and singlet and triplet oxygen atoms, to give a hydrocarbon blend with a potentially different reactivity towards photo-oxidation from the original mixture.

OXIDANT PRECURSOR RELATIONSHIPS FOR ONE-DAY IRRADIATIONS

It is well estblished that the concentrations of products formed from a complex system of simultaneously occurring reactions such as the oxidant-forming process are likely to depend upon the concentrations of the precursors in an extremely non-linear manner. Thus a given reduction in ambient concentrations of either hydrocarbons or nitrogen oxides does not ordinarily lead to the corresponding percentage reduction in the concentration of oxidant.

In addition to this complex dependence of oxidant on precursors due to the complexity of the reactions, the oxidants formed in an airshed depend upon a range of airshed variables such as:

- the period of irradiation;
- ambient temperatures at which reactions occur;
- the nature of the mixture of hydrocarbons;
- the relative amounts of nitric oxide and nitrogen dioxide in the NOx mixture; and
- the rate at which atmospheric forces dilute the reacting mixture during the course of the day.

Within these limits the use of observational relationships derived from airshed measurements and the results of smog chamber studies permit the identification of the general features of the way oxidant concentrations, as measured by ozone concentrations, depend upon those of the precursors.

The concentrations of ozone found in ambient air have been found to depend upon the ratio NMHC/NOx (Guicherit 1976). The dependence established from airshed data measured in the Netherlands is shown in Figure 2.3.

The relationship shown in Figure 2.3 has a maximum in the ozone forming potential at ratios of NMHC/NOx in the region 3 to 4. Airshed values observed in Sydney during the Sydney Oxidant

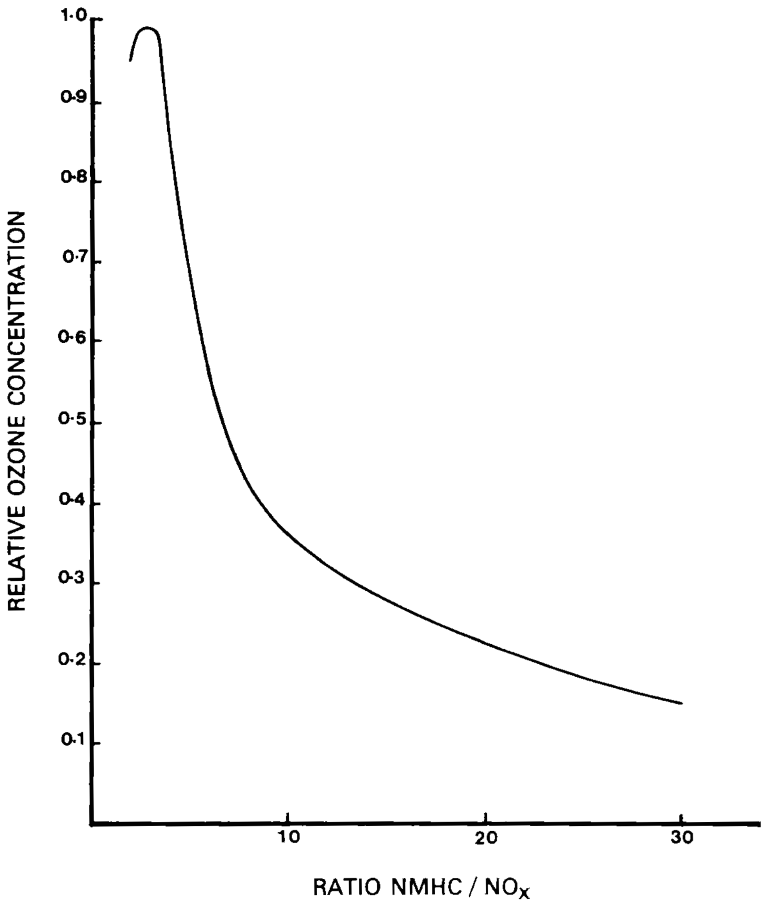


FIGURE 2.3
DEPENDENCE OF RELATIVE OZONE
ON THE RATIO NMHC/NO$_x$

SOURCE: Guicherit R.,

Study are said (Post and Bilger 1978) to fit this relationship, although there is a shortage of ozone concentrations in the important region near the maximum which appears to make this conclusion tentative.

In addition to this result studies carried out at the Statewide Air Pollution Research Centre in California show that hydrocarbon concentrations have an important influence on the ozone concentration. Thus the 6 hour irradiations in smog chambers of mixtures of hydrocarbons which duplicate the balance found in Los Angeles air (Pitts 1976) lead to the results shown in Figure 2.4.

These results show that reducing the concentration of hydrocarbons leads to lower ozone for all cases except those where nitrogen oxides are low. For example, for NOx concentrations of 0.10 parts per million or higher, reducing hydrocarbons leads to lower ozone after 6 hour irradiations. Where NOx is 0.05 parts per million, lowering of hydrocarbon concentrations from 2.6 to 2.1 or 1.3 parts per million carbon has no effect. By contrast, for some conditions, the lowering of NOx concentrations may lead to higher levels of ozone formed in the 6 hour period. For example, if a fixed concentration of hydrocarbons of 1.3 parts per million carbon is considered, a lowering of NOx levels from 0.25 to 0.10 parts per million can actually increase ozone levels. In general terms the data of Figure 2.4 show that for each hydrocarbon isopleth there is an ozone maximum. Beyond this maximum the effect of increasing NOx concentrations is to depress ozone due to the scavenging effect of nitric oxide. The chemistry is such that this scavenging is likely to lead to the formation of other oxidants and also to increase the ozone formed during longer irradiation periods.

The sets of results shown in Figures 2.3 and 2.4 have been construed as having differing requirements for the control of ozone. One is seen as requiring control of the airshed ratios

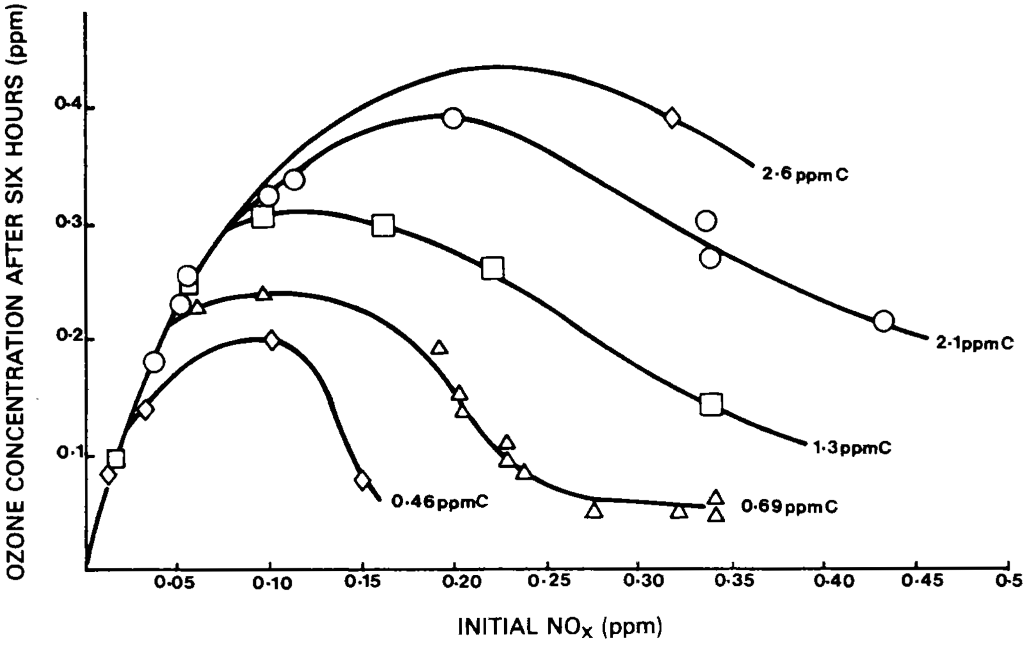


FIGURE 2.4
OZONE CONCENTRATION REACHED AFTER A 6-HOUR IRRADIATION IN SAPRC ALL GLASS SMOG CHAMBER OF HYDROCARBON-NOx MIXTURES OF VARYING INITIAL CONCENTRATIONS

SOURCE : Darnall K.J., Winer A.M., and Pitts J.N.

of NMHC/NOx which implies controls on both hydrocarbons and NOx, while the other is taken as implying controls on NMHC emissions only. A comparative analysis of the studies has shown (Daly 1977) that the smog chamber data show a dependence of ozone upon the ratio NMHC/NOx.

The smog chamber data were shown to give ozone values with a similar general form of dependence on the ratio NMHC/NOx as the relationship of Guicherit. Results obtained by the analysis are shown in Figure 2.5.

The data of Figure 2.5 were obtained as follows:

- each initial concentration of hydrocarbon was considered;
- ozone concentrations resulting from irradiations with various NOx concentrations at each hydrocarbon concentration were tabulated. The maximum ozone obtainable from each hydrocarbon concentration was also tabulated;
- each ozone concentration was expressed as a percentage of the maximum ozone attainable at the chosen hydrocarbon concentration;
- these ozone percentages were termed relative ozone potential and plotted against the ratio NMHC/NOx.

The results shown in Figure 2.5 give the relative ozone potential after a 6 hour irradiation period under smog chamber conditions and correspond well with the form of dependence observed by Guicherit for airshed data. The smog chamber data show that the maximum ozone formed for any concentration of hydrocarbons across the range 0.46 parts per million carbon to 2.60 parts per million carbon occurs in the range of NMHC/NOx from about

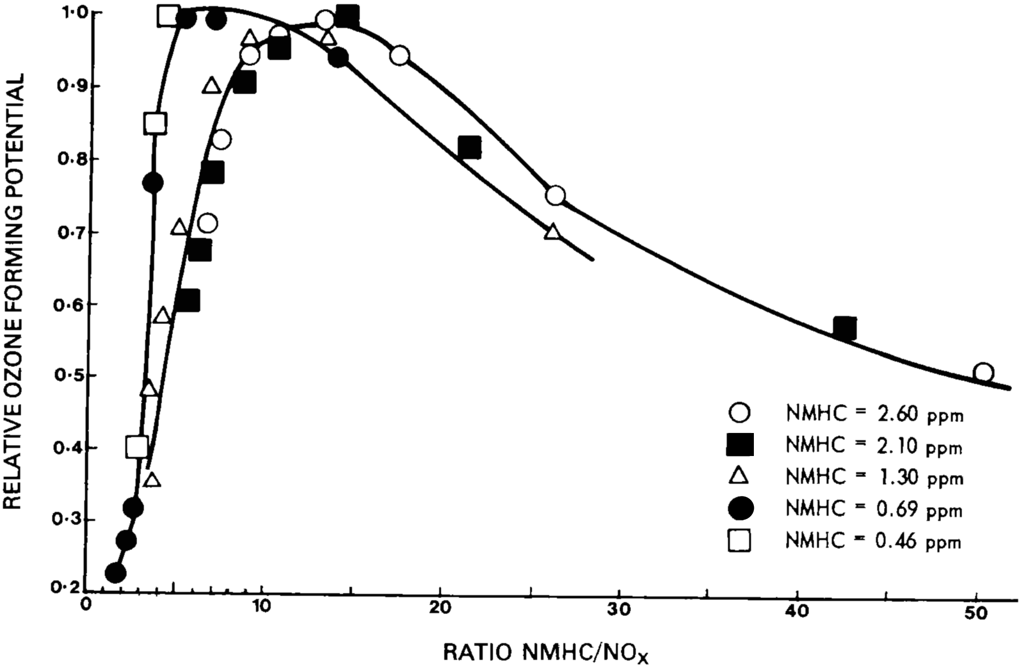


FIGURE 2.5
VARIATION OF OZONE POTENTIAL WITH THE RATIO
NMHC/NOx

SOURCE : Daly N.J., (1977)

4 to 14. The position of the maximum varies slightly with the initial concentration of hydrocarbon. These variations are summarised in Table 2.2.

TABLE 2.2 - VARIATION OF THE VALUE FOR THE RATIO NMHC/NOx AT THE OZONE MAXIMUM WITH INITIAL HYDROCARBON CONCENTRATION

Initial Hydrocarbon Concentration (ppm C)	Value for NMHC/NOx at Maximum Ozone[(a)]
0.46	4 - 8
0.69	6 - 10
1.30	8 - 13
2.10	9 - 14
2.60	9 - 14

(a) Maximum taken for region for which the ozone formed exceeds 95 per cent of potential ozone.

Source : Daly 1977.

The position of the maximum from the Netherlands airshed data falls in the range of NMHC/NOx from 3 to 4 and applies (Guicherit 1976) to ambient concentrations of hydrocarbons from 0.2 to 1.0 parts per million carbon. The smog chamber data show that the position of the maximum appears to vary with hydrocarbon concentration (Table 2.2). For hydrocarbon concentrations in the range 0.2 to 1.0 parts per million carbon the maxima occur in the range NMHC/NOx from about 4 to 12. This agreement between smog chamber and airshed values is considered excellent in view of the differences in reaction conditions such as the nature of the hydrocarbon mixture, the period of irradiation and the ambient temperature. The positioning of the maximum merits further study.

These results show that the ozone concentrations achieved in one-day irradiations depend on:

- the concentration of hydrocarbons; and
- the ratio of airshed values of NMHC/NOx

These results lead to the conclusion that the criteria for oxidant controls are to :

- lower ambient concentrations of hydrocarbons; and
- optimise the ratio of NMHC/NOx in the airshed.

OXIDANT-PRECURSOR RELATIONSHIPS FOR EXTENDED IRRADIATIONS

Ozone-precursor relationships for extended irradiations are not generally as well-established as those for one day irradiations. It is however established that during extended irradiations both hydrocarbons of low reactivity and the low concentrations of hydrocarbons and nitrogen oxides which result from atmospheric dilution during the period of irradiation can lead to the formation of significant quantities of ozone. Thus high concentrations of ozone may be formed during a period of transport and affect remote rural areas (Rasmussen et al 1974) (Guicherit 1976) (Pitts 1976).

Of more immediate importance in Australia are those conditions of transport which make for recirculation of air-masses within the urban airshed thus leading to the possibility of second and subsequent-day irradiation. Such conditions may occur in Melbourne, where lengthy periods of stagnation have occurred, and in Sydney when storage aloft of polluted air-masses and subsequent recirculation have been noted. These meteorological effects are discussed in Chapter 3.

Ripperton et al (1976) have studied oxidant-precursor relationships under conditions encountered during transport and multi-day irradiations. Their results are shown in Figure 2.6 which summarises data from a 3 day irradiation. The reaction conditions were such that the reacting mixture was diluted by 95 per cent during the first 24 hours. The results show that,

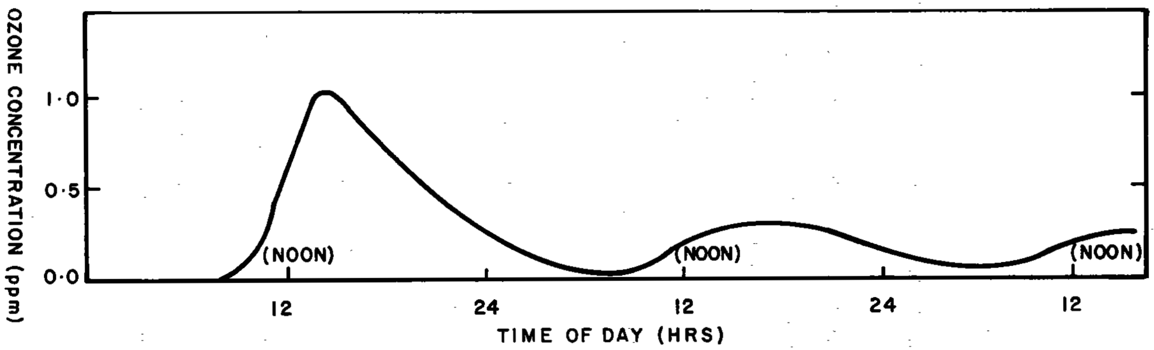


FIGURE 2.6
OZONE CONCENTRATIONS FORMED DURING MULTI–DAY IRRADIATION AND DILUTION IN SMOG CHAMBERS

SOURCE : Ripperton L.A., Eaton W.C., and Sickles J.E.

despite this dilution, the multi-day irradiation produced high concentrations of ozone on the second and third days. Thus the low concentrations of hydrocarbons and nitrogen oxides resulting from the atmospheric dilution remained capable of generating significant ozone concentrations during the second and third days of irradiation.

Jefferies et al (1975) studied the effects of reducing the concentrations of hydrocarbons in a 2-day irradiation using natural sunlight. The results are summarised in Figure 2.7. Figure 2.7 clearly shows that hydrocarbon controls are effective in reducing ozone formed from fresh emissions on the first day of irradiation. The results additionally show that the effectiveness of hydrocarbon controls is not carried over to the second day of irradiation since on the second day, with the fixed initial NOx concentration of 0.36 parts per million, initial hydrocarbon concentrations of 2.90 and 1.30 parts per million gave 0.41 and 0.38 parts per million ozone respectively. That is, for this experiment, a 55 per cent reduction of hydrocarbons at fixed NOx concentration gave only a small (7.3 per cent) reduction in the ozone maximum reached on the second day.

Sickles, Ripperton and Eaton (1977) have studied oxidant-precursor relationships in transport simulation in smog chambers. In a series of experiments they carried out 3-day chamber runs in which the chemical pollutant systems were irradiated with natural sunlight for multi-day periods, and subjected to periods of dilution with clean air to simulate atmospheric dilution during transport.

The ozone maxima recorded on the second and third days of the irradiation were shown to depend upon the ratio of the concentrations of non-methane hydrocarbons to nitrogen oxides measured on the second day. This relationship is shown in Figure 2.8.

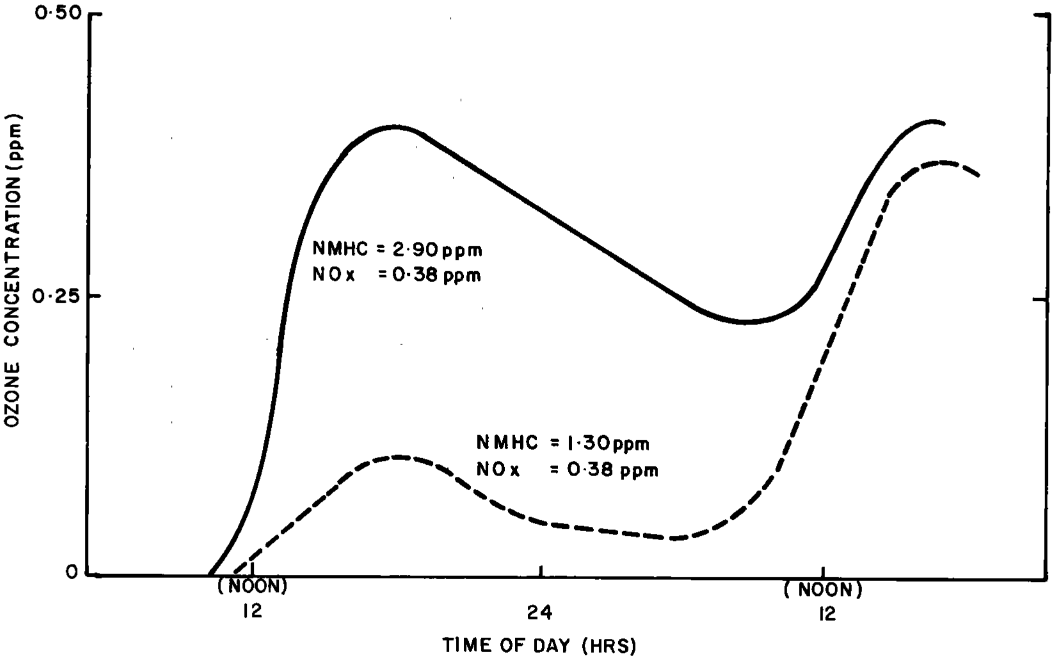


FIGURE 2.7
OZONE FORMED DURING TWO-DAY IRRADIATIONS
IN SMOG-CHAMBERS

SOURCE : Jeffries H.E., Fox D.L., and Kamens R.M.

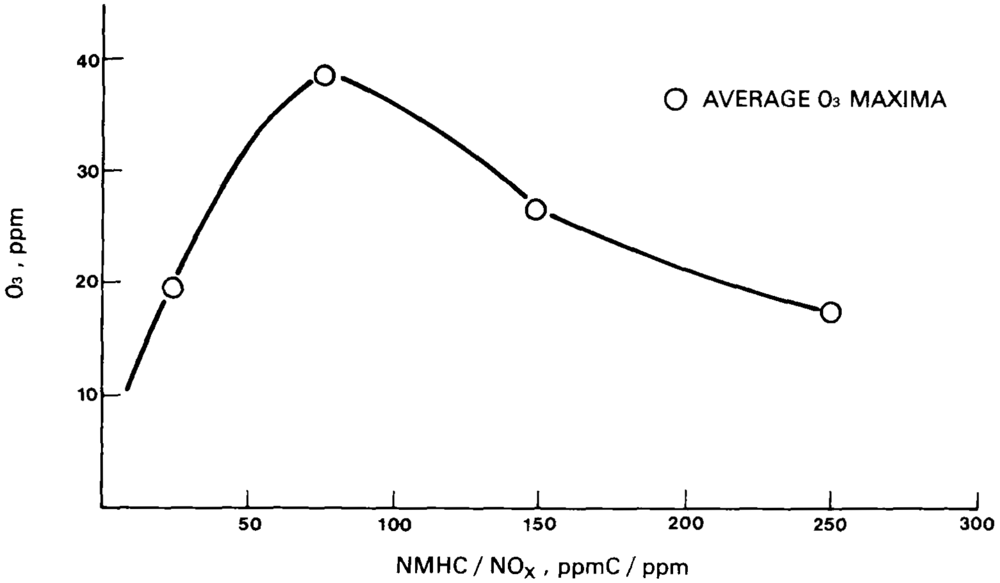


FIGURE 2.8
VARIATION OF THE NMHC/NOx RATIO MEASURED AT SUNRISE ON THE SECOND DAY OF IRRADIATION WITH MAXIMUM OZONE ACHIEVED ON THE SECOND DAY

SOURCE : Sickles et al.,

The values of the ratio plotted in Figure 2.8 are values which were obtained for concentrations on the second and third days after commencing dilution processes on the first day and after the consumption of the reagents by the smog forming processes. These high values of the ratio stem from initial values which ranged between about 5 and 18.

For example, initial values of the ratio of 5.5, 7.3 and 10.8 led to values of 96, 120, and 275 on the second day. From the air management point of view it would be appropriate to plot the ozone maxima against the values of the ratio in the urban airshed on the first day. The necessary data to do this are not reported in the paper (Sickles et al 1977) but it seems that first day values of the ratio are roughly one-twentieth to one-thirtieth those for the second day. To a rough approximation the maxima in ozone which span the ratio from about 50 to 120 for second-day values would normalise to a range of about 2.5 to 6 for first day values. This range closely approximates the range within which the maximum ozone potential occurs during one-day irradiations (Guicherit 1976) (Daly 1977).

Sickles et al also showed the operation of the so-called dilution effect on ozone formation (Sickles et al 1977) in which a dilution of the concentrations of reagents without alteration of the initial ratio NMHC/NOx does not produce a corresponding proportional reduction in ozone. Examples of this phenomenon are shown in Figure 2.9 in which dilutions of the reacting mixtures of zero, 77 and 95 per cent do not lead to corresponding proportional reductions in second-day ozone maxima.

These results show firstly that reducing the absolute concentrations at fixed NMHC/NOx ratio does not exert a major controlling influence on the concentrations of ozone reached during multi-day irradiations, and secondly, that control of the ratio to optimum values can exert a valuable control on ozone concentrations on second and later days.

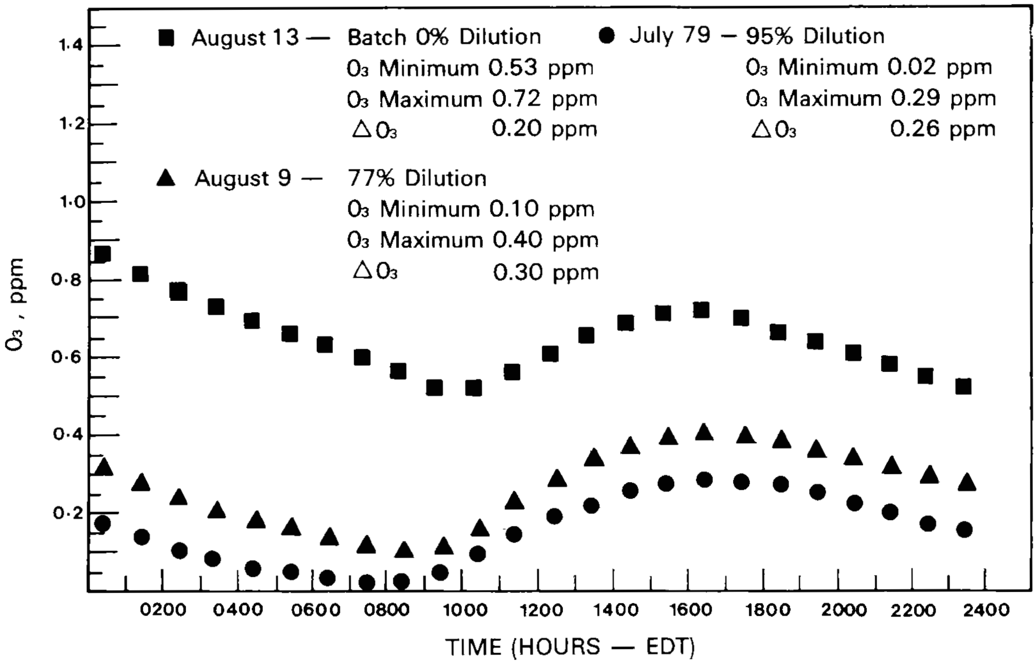


FIGURE 2.9
OZONE PROFILES OVER THE SECOND DAY IRRADIATIONS
FOR SAME INITIAL CONDITIONS AND DIFFERENT DILUTIONS

SOURCE : Sickles et al.,

Guicherit (1976) has pointed out that control of hydrocarbon concentrations alone merely delays the production of ozone rather than affecting the final concentration. Although absolute percursor concentrations have an effect on the maximum ozone concentration, these ozone maxima are to a great extent governed by the ratio NMHC/NOx.

These studies lead to the conclusions that for extended irradiations the control of hydrocarbon concentrations alone does not have the effectiveness that it achieves in one-day irradiations, and that ozone is best controlled by optimising airshed values of the ratio NMHC/NOx. The evidence reviewed here indicates that the ozone forming potential during extended irradiations peaks around similar values of the ratio to those for one-day irradiations. Study of these influences is clearly warranted. Thus the principles

- control of hydrocarbon concentrations, and
- optimisation of the ratio NMHC/NOx

enunciated for the control of the effects of irradiations for one-day episodes also encompass the strategy necessary for the control of ozone produced during extended irradiation periods.

THE WEEKEND EFFECT

Statistical analysis of air quality data in both the United States and the Netherlands show the occurrence of similar or slightly higher ozone concentrations on summer weekends compared with weekdays despite significantly different traffic patterns and thus different concentrations of hydrocarbons and nitrogen oxides (Lebron 1975) (Blokziyl and Guicherit 1978). The weekend effect has been reviewed by Blokziyl and Guicherit (1978) who point out that the ratios of NMHC/NOx for both parts of the week are more or less identical, despite the differences in the relative concentrations of emissions. These observations correspond with the smog chamber results of Sickles et al (1977) who showed that dilution of the concentrations of reagents without alteration of the initial ratio of NMHC/NOx does not produce an equivalent reduction in the ozone maximum.

The effect has also been studied by Graedel et al (1977) who used calculations based on the photochemistry of the system to show that, despite differences in the concentrations of precursors, the formation and destruction rates for ozone for both parts of the week are about equal, so that no differences in ozone levels would be detected. There is a tight balance between ozone production from photodissociation of nitrogen dioxide and ozone scavenging due to nitric oxide.

Blokziyl and Guicherit (1978) point out that the higher levels of NOx on weekdays have other consequences such as the high concentrations of organic and inorganic nitrates on weekdays compared with weekends.

PHOTOCHEMICAL MODELS

In recent times there has been considerable progress in the development of photochemical models which seek to describe the dependence of oxidant concentrations upon those of the precursors, non-methane hydrocarbons and nitrogen oxides, for various sets of airshed conditions. The models seek to provide a simulation of the key chemical reactions, the variation of sunlight intensity, and the operation of meteorological dispersion forces in the airshed. The purpose of the simulations is to provide oxidant-precursor relationships which permit the evaluation of the effects of alternative strategies for reducing emissions.

The major variables which influence the oxidant dependence upon precursor concentrations are:

- the nature of the hydrocarbon mixture;
- the ratio of nitric oxide to nitrogen dioxide in the mixture of nitrogen oxides;
- the intensity of solar irradiation used;
- the values assigned to the individual rate constants used in the reduced chemical mechanism for smog formation;
- the rate of atmospheric dilution; and
- the reaction time for which the mixture undergoes irradiation.

Accordingly, the results obtained for an analysis based on any particular photochemical model are valid only within the limits with which the chosen model describes the airshed of interest.

Examples of models which have been used to explore aspects of the oxidant-precursor relationships are the model developed in the Netherlands at the TNO Research Institute for Environmental Hygiene (Nieboer et al 1978) (Nieboer and Duyzer 1978) and that developed at the US Environmental Protection Agency, North Carolina (Dodge 1977a). Summaries of the elementary chemical reactions used in describing the smog forming sequence are given in Appendix A for these two models.

The model developed by Dodge has provided a criterion for evaluating control needs in Australia. The model extends data from smog chamber studies to provide sets of ozone isopleths as a function of hydrocarbon and nitrogen oxides concentrations. These isopleths are shown in Figure 2.10. Key conditions used to generate these ozone isopleths include:

- a mixture of hydrocarbons which is made up of 25 per cent propene and 75 per cent butane. Initial nitrogen dioxide levels are taken as 25 per cent of initial nitrogen oxides;

- diurnal variations of one-hour average values of the photolytic rate constants which correspond to the summer solstice at 34°N;

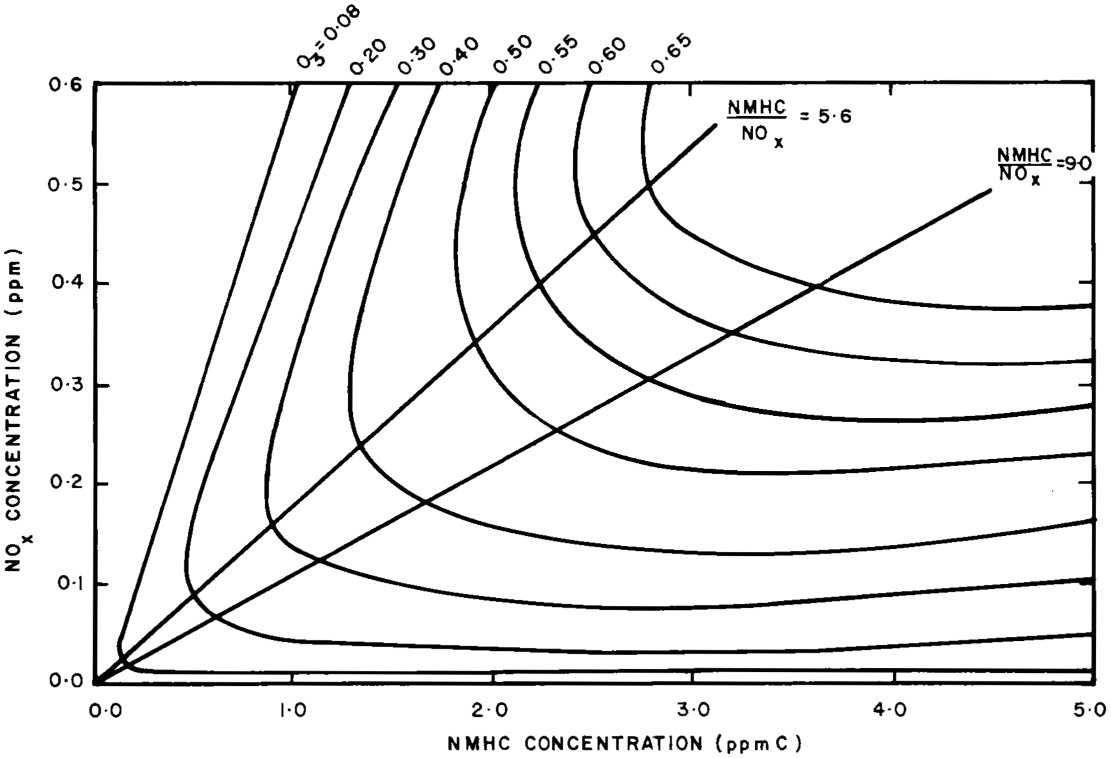


FIGURE 2.10
OZONE–PRECURSOR RELATIONSHIPS CALCULATED FROM
THE DODGE MODEL

SOURCE : Dodge M.C., (1977)

- simulations which apply to the 9-hour period from 0800 to 1700 hours;
- simulations which commence with a fresh charge of nitrogen oxides to which no further emissions are added; and
- an atmospheric dilution rate of 3 per cent per hour.

Sensitivity tests show that the absolute dependence of the ozone isopleths upon non-methane hydrocarbons and nitrogen oxides concentrations varies as each of these conditions is varied. However, the ozone isopleths hold their relative positions on the hydrocarbons and nitrogen oxide scales as the conditions are varied, and the model is considered of use in developing oxidant strategies for various airsheds (Dodge 1977b). Bilger (1977) has followed this approach and has presented the ozone isopleths as a function of the logarithm of the hydrocarbon and nitrogen oxides concentrations to stress the applicability of the model to the calculation of the effects of fractional reductions in emissions of hydrocarbons and nitrogen oxides.

The conditions of the Dodge model are such that it describes the maximum one-hour average concentration of ozone formed during one-day irradiations of fresh emissions. The ozone concentrations predicted are computed from initial concentrations of hydrocarbons and NOx which represent the average of the 0600-0900 hours concentrations in the airshed. Thus the conclusions reached from the application of the model do not apply to :

- the effects of multi-day irradiations and irradiations of aged mixtures which occur where air-packets move across and recirculate within an airbasin;
- the effects of continuous addition of hydrocarbons and nitrogen oxides; and

- the question of whether ozone is always an adequate surrogate for oxidants such as PAN, nitrates and aerosols, or whether combinations of pairs of oxidants need to be considered in evaluating the impact on health.

Thus these issues need to be considered as additional items when evaluating the results obtained from a model such as the Dodge model.

Recent evaluations of the parameters of certain elementary reactions such as those involving aldehydes (Nieboer and Duyzer 1978) and reactions of nitric oxide such as

$$RO_2 + NO \longrightarrow RO + NO_2$$
$$HO_2 + NO \longrightarrow HO + NO_2$$
$$RCO_3 + NO + O_2 \longrightarrow RO_2 + NO_2 + CO_2$$

have shown that the rate constants may have values up to 10 times those previously accepted (Smith 1979). Use of such new values in the Dodge model may have the effect of almost doubling the values of the ozone isopleths. It is also not clear whether the isopleths would continue to hold their relative positions as before. Thus the applicability of the model to the development of policy for a chosen airshed must be considered limited until the parameters for the reaction mechanism are established.

SUMMARY OF CHEMICAL FACTORS

The concentration of ozone formed in the airshed depend upon the major chemical variables:

- the concentrations of hydrocarbons and nitrogen oxides;
- the ratio of NMHC/NOx;
- the duration of the period of the irradiation;
- the rate of dilution of the reacting mixture; and
- the composition of the hydrocarbon mixture.

The relative importance of these factors depends upon the duration of the irradiation. For example where the irradiation periods are short, only the most reactive hydrocarbons generate ozone. Where irradiation periods are extended, essentially all non-methane hydrocarbons can generate ozone.

Because of the interplay of factors the dependence of ozone upon precursors needs to be described by sets of ozone-precursor relationships derived for the following types of conditions:

- partial or one-day irradiations of fresh emissions;
- partial or one-day irradiations of 'aged' mixtures;
- partial or one-day irradiations of mixtures of fresh and 'aged' mixtures; and
- multi-day irradiations.

Evidence to date suggests two guidelines for the control of photochemical oxidants:

- limit hydrocarbon concentrations in ambient air; and
- control the ambient air ratios NMHC/NOx to optimise the distribution of airshed values.

Clearly this involves control of both hydrocarbons and NOx.

For situations in which extended periods of irradiation occur the control of hydrocarbons appears to be much less effective than for one-day irradiations and control of the ratio NMHC/NOx appears to become the more crucial factor. Thus in the Netherlands where extended irradiations seem to occur frequently, control of the ratio NMHC/NOx is seen as the only policy likely to permit compliance with oxidant goals (Guicherit et al 1976).

In the Australian situation the distribution of the periods of irradiation are not well established for cities with present or pending photochemical problems, although it appears that extended irradiation periods may occur with significant frequencies. This matter is discussed further in Chapter 3.

CHAPTER 3 - METEOROLOGICAL FACTORS IN OXIDANT FORMATION

INTRODUCTION

The meteorological factors which have a major role in determining the extent to which the photochemical reactions proceed in an airshed are those which control the following:

- the length of the irradiation periods;
- the solar intensity during the irradiation;
- the temperature of the reacting system; and
- the concentrations of the reacting species.

The length of time during which the photochemical reactions occur and the concentrations of the reacting species are broadly controlled by the atmospheric dispersion forces which operate in the air-basin. The intensity of the solar irradiation, and to an extent the ambient temperature at which reactions take place, are determined by the zenith angle of the sun and the extent of cloud cover.

OXIDANT FORMING CONDITIONS

The meteorological conditions which favour the formation of photochemical oxidants are those which provide bright sunshine during periods of poor dispersion of air pollutants and thus allow a sufficient time for solar irradiation of the mixtures of hydrocarbons and nitrogen oxides so that the photochemically initiated sequence of reactions can become established.

In general terms these conditions are provided by anticyclones which are characterised by sunny weather, gentle winds, and inhibited vertical motions, leading to poor dispersion conditions. Mass divergences around the anticyclones result in subsidence of the atmosphere which results in the air above being heated adiabatically by compression, thus forming a subsidence inversion in the higher air strata.

The Australian climate is controlled by a regular progression of high pressure systems which move across the continent from West to East. The centres of these highs are normally around latitude 40°S in summer and 30°S in winter. The rate of progress of the system is quite fast, and they usually traverse the continent in 3 to 4 days.

At times high pressure systems develop in the Tasman Sea and have the effect of blocking the movement of the anticyclones. Under these conditions the eastern capitals Brisbane, Melbourne, and Sydney experience their worst pollution episodes.

Hawke and Iverach (1974) studied days of high photochemical pollution in Sydney and concluded that a high pressure region situated in the mid-Tasman Sea was the synoptic system that favoured the production of high ozone concentrations in Sydney. Le Roy, Lau and Holden (1976) reported that major photochemical episodes occurred in Melbourne in 1972, 1974, and 1975 and persisted for up to 10 days continuously. They observed that photochemical oxidants tend to form during late autumn and early winter during periods of calm meteorological conditions. It was however concluded that for whatever the season of the year that oxidants were formed in Melbourne, the formation normally coincided with calm conditions (Le Roy et al 1976).

These results make it clear that lengthy periods of irradiation are an important feature of oxidant episodes in both Sydney and Melbourne. In the case of Melbourne the problems of multi-day irradiations seem well developed.

EFFECT OF SUNLIGHT INTENSITY

The primary effect of sunlight is on the photo-dissociation processes which control the concentrations of the free radicals which carry the reaction sequence (Leighton 1961). The resultant effect on the formation of photochemical oxidants is that an increase in the intensity of incident sunlight leads to increases in (Guicherit 1976) (Daly 1977):

- the rate of conversion of NO to NO_2;
- the rate of consumption of hydrocarbons; and
- the terminal ozone concentration.

The intensity of sunlight depends upon the solar zenith angle, the latitude, and the time of year. The relationship between these factors can be used to show that from the equator to latitudes of at least 70° the light intensity is sufficient to induce photochemistry during some part of the year (Nieboer et al 1976) (Daly 1977). For latitudes around 50° the period during which photodissociation in airsheds is possible is about 7 to 8 months of the year. For latitudes around 30° the light intensities are sufficient to initiate photochemical processes for at least 10 months of the year. These figures assume that cloud cover is absent.

Australian capital cities have latitudes which fall in the range of about 26°S (Brisbane) to about 38°S (Melbourne) with the exception of Hobart which is about 43°S. Clearly, with the exception of days for which cloud cover screens the effect, the period for which sunlight intensity is sufficient to initiate photochemical smog forming processes is quite long.

The rates of chemical reactions tend to increase exponentially with increasing temperature. During conditions of poor dispersion the ambient temperature tends to follow the sunlight intensity, which also favours the establishment of the photochemical reaction sequence.

TRANSPORT OF OXIDANTS

The transport of photochemical pollutants by air-mass movements has been well documented (OECD 1974) (US National Academy of Sciences 1974). The phenomenon occurs when an air-mass moves as a coherent entity, taking with it the burden of pollutants, under the influence of prevailing winds.

The effect of transport is to create an oxidants problem at a location removed from the original source of the hydrocarbons and nitrogen oxides, and to increase the length of time during which the chemical reactions occur. The transported air-mass may undergo dilution by normal atmospheric processes as it moves from the source to the receptor area, but the increased reaction time may produce significant quantities of ozone and other oxidants at the receptor area. These observations are well illustrated by the data from the Los Angeles region.

In Los Angeles, most wind trajectories enter the basin from the west, and in spring and fall surface winds from ocean to land are the predominant ones. These give a general eastward transport of pollutants which is illustrated by the diurnal variations of oxidant concentrations across the basin.

Measurements of oxidants made on 25 July 1973 for Los Angeles and the cities of Pasadena, Pomona, Riverside, and Palm Springs, which are downwind of Los Angeles, show the effects of the transport phenomenon. The results are reported in Figure 3.1. Approximate distances between the cities are:

Los Angeles	to	Pasadena	:	14 km
Pasadena	to	Pomona	:	38 km
Pomona	to	Riverside	:	37 km
Riverside	to	Palm Springs	:	120 km

The times at which the oxidant peaks occur in the downwind cities show that significant amounts of the oxidants in the downwind air basin are formed from pollutants emitted earlier in the day in areas to the west and south-west such as Los Angeles and Orange county. Oxidant concentrations at Riverside show a double peak. The first occurs around midday and is attributed to pollutants formed from hydrocarbons and nitrogen oxides emitted at or near Riverside. The second occurs around 1600 hours and is attributed to transport from the large, more densely populated Los Angeles metropolitan area (Pitts et al 1975). The double

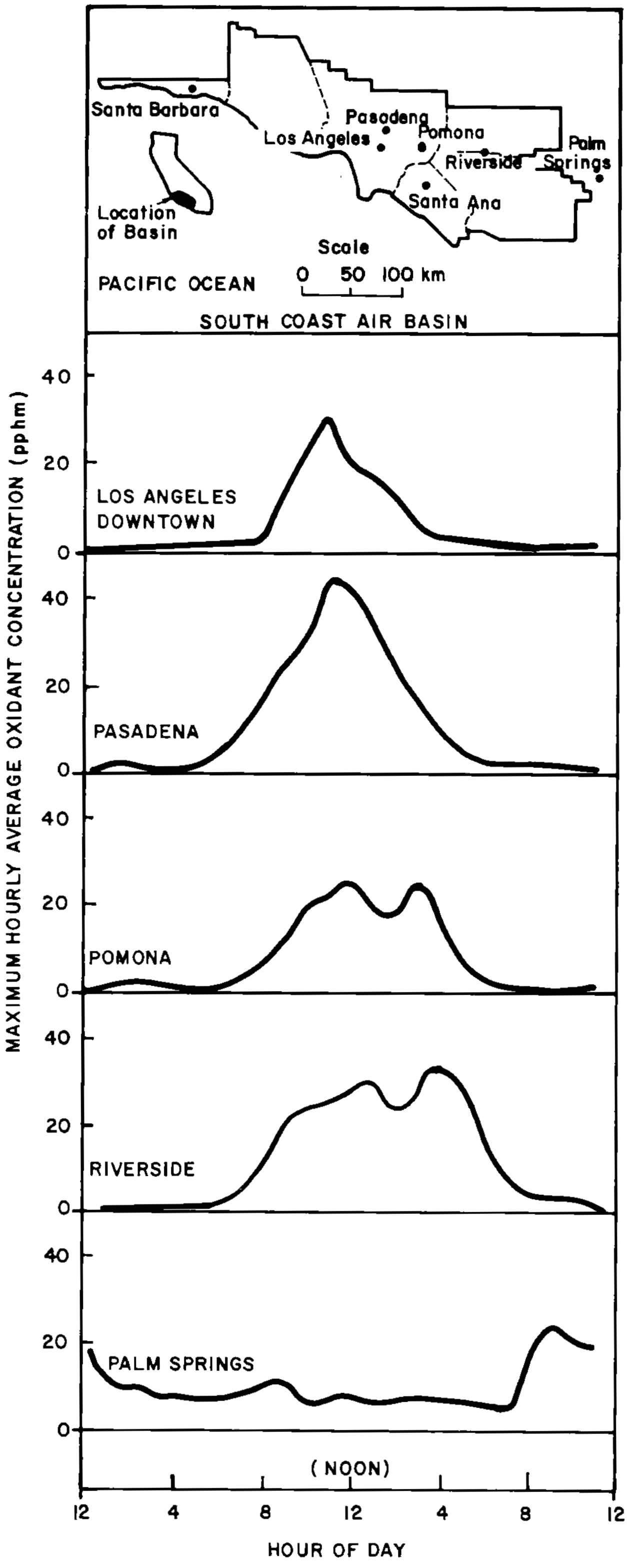


FIGURE 3.1
DIURNAL VARIATION OF OZONE CONCENTRATIONS AT SEVERAL LOCATIONS IN THE SOUTH COAST AIR BASIN

SOURCE : Pitts J.N., Lloyd A.C., and Sprung J.L.

peak in the oxidant concentrations observed at Pomona shows the corresponding balance between locally generated and transported oxidants.

The data for the city of Palm Springs show that the peak of oxidant concentrations occurs around 2200 hours indicating that transport is the main source of the oxidants problem.

Further information of the transport phenomena is obtained by using the concentrations of carbon monoxide in the air mass as a tracer. The afternoon peak concentration of carbon monoxide observed at Riverside was much smaller than that observed in Los Angeles. This suggests that the air mass becomes diluted as it moves eastward to Riverside. The afternoon peak concentration of oxidant at Riverside was about the same as that in Los Angeles and this appears to show that oxidants continue to be formed during the transport process.

This view appears to be confirmed by the US National Academy of Sciences (1974) which reported:

> 'Thus over a period of hours the mass of smog laden air from downtown Los Angeles experiences a growth in ozone concentration as it travels eastward so that a shift in the maximum concentrations eastward should be expected, and has been confirmed by measurements. The shift in ozone concentrations to the east also has been enhanced by the growth in urbanisation in that region which causes increases in local hydrocarbon and NOx emissions.'

TRANSPORT EFFECTS IN THE SYDNEY BASIN

The roles of both long and medium range transport of oxidants and their precursors in contributing to photochemical smog forming processes have received little study in the airsheds of Australian cities with the notable exception of the excellent work on the Sydney airshed by Hyde and his co-workers.

In a preliminary analysis of the influence of meteorology on ozone levels in the Sydney Basin, Hyde and Hawke examined air-mass trajectories across the basin and concluded that transport of pollutants within the sea-breeze appeared likely. The west and south-west sectors of the basin appeared to be receptor areas for air passing over Lidcombe and Marrickville, and were likely to experience prolonged high concentrations of ozone (Hyde and Hawke 1976) (Hyde and Hawke 1977).

Hyde, Hawke, and Heggie (1978a) studied the transport and recirculation of ozone within the inland regions of the Sydney basin and examined the effects on the concentrations of ozone observed at Campbelltown. Three main mechanisms were considered important in determining the movement of air-masses within the inland areas:

- transport of oxidants and precursors from the city and the coastal source regions into the south-west of the region by the afternoon sea-breeze;
- transport from the inland source area by north-easterly gradient winds; and
- recirculation of oxidants and precursors into the Sydney basin by nocturnal flows.

In an examination of the effects of transport and recirculation of oxidants and precursors in the coastal region of the Sydney Basin, Hyde et al (1978b) studied ozone concentrations and surface air-mass trajectories at Coogee, and concluded that two mechanisms were important. These were:

- horizontal transport and recirculation of air advected offshore by westerly drainage flow, and then back inland within the sea-breeze; and

- vertical recirculation of air within a shallow, slow moving sea-breeze.

These investigations of both inland and coastal regions of the Sydney basin show that the polluted air-masses may be transported over long distances, and recirculated within the basin from one day to the next. These long range transport and recirculation phenomena are considered to have several implications for the control of oxidant pollution within the Sydney region (Hyde et al 1978a).

The implication of the long-range transport of the air-masses is that extensive inland areas downwind of the precursor source areas may experience high oxidant concentrations during afternoon and evening. The implication of the recirculation of oxidants and their precursors from one day to the next is that the time available for chemical reactions within the air-mass is increased. In addition the recirculation introduces the problems associated with the irradiation of aged smogs (Pitts et al 1977) which include rapid increases in oxidant concentrations and reactions of the 'less reactive' hydrocarbons.

TRANSPORT EFFECTS IN OTHER STATE CAPITALS

In general the role of long-range transport and recirculation of air-masses has not been as extensively studied in other Australian cities as it has in Sydney. Superficially at least there are indications that such effects may be important in a number of air basins.

In Melbourne it is possible that polluted air-masses could be advected to the south and south-east by nocturnal and early morning drainage, and later returned northward and recirculated under the influence of a shallow, slow-moving bay breeze, a gradient wind, or a sea breeze (Daly 1977). Such a pattern of recirculation of oxidants and precursors could make for long reaction times and multi-day irradiations. In Perth the possibility exists of transport into the Perth air basin of NOx from power generation and hydrocarbons from refining operations at Kwinana. Again such long-range transport could make for lengthy reaction times. In Brisbane the problems of the poorly drained Brisbane Valley (Report from the Senate Select Committee 1969) justify consideration of the possibility of a weak drainage to the sea followed by recirculation on a sea breeze.

The identification of such effects in airsheds would have important implications for oxidant control programs. To the extent that they operate, they tend to:

- increase the time-period over which chemical reactions may occur;
- lead to the result that all non-methane hydrocarbons need to be treated as reactive; and
- introduce the problem of irradiation of aged smogs.

Thus the development of suitable oxidant controls requires an appreciation of the proportion of oxidant episodes which have short irradiation periods, the proportion for which long-range transport effects operate, and the proportion for which recirculation effects are important for each airshed of concern.

CHAPTER 4 - SETTING GOALS FOR OXIDANTS

THE CHALLENGE TO EXISTING STANDARDS

The standards at present set for a number of countries which are summarised in Table 1.5 show that the one-hour average concentrations of ozone or oxidants considered acceptable range from 0.06 parts per million to 0.12 parts per million. The differences between these standards apparently reflect different value judgments over the safety margins appropriate for oxidant control programs.

The recently updated Federal Standard of the United States of 0.12 parts per million is based on epidemiological evidence and was deemed necessary to protect asthmatics and other 'at-risk' sections of the community (US Federal Register 1979). The original Japanese Standard of 0.06 parts per million appeared to include a greater margin of safety and was based on epidemiological assessment and the belief that natural levels of ozone do not exceed 0.06 parts per million as a one-hour average.

The values set by these standards have been challenged as unrealistic on the grounds that they underestimate the background of natural ozone (Stasiuk and Coffey 1974) and the threshold necessary to protect public health.

PROBLEMS OF RURAL OZONE

The previous US standard of a one-hour average concentration of ozone of 0.08 parts per million was questioned because ozone values measured in rural areas of North America were found to exceed this value. Stasiuk and Coffey described the standard as one which 'has no meaning in terms of abatement action without better defining man's relative contributions to the violations that have been recorded'. This judgement was based on a study of urban and rural ozone in New York State over a 17 day period in August 1973 which showed that ozone concentrations frequently exceed the air quality standard at widely separated monitoring points situated over the entire State of New York (Stasiuk and Coffey 1974).

Stasiuk and Coffey found that the daily rural ozone concentrations correlated well with daily maximum urban concentrations averaged over one hour, and suggested the possibility of a common natural source for ozone. They suggested that all ozone concentrations represented predominantly naturally occurring ozone. Urban ozone concentrations were held to approach rural concentrations only when the removal of the nocturnal inversion layer permitted mixing with ozone-rich background air and when urban nitric oxide was oxidised to nitrogen dioxide. They believed that some additional ozone may be photochemically generated so that urban values at times rise above rural values.

Ripperton also found concentrations of ozone above expected levels at sites far removed from urban centres and discussed the results in terms of movement of a pollution system away from an urban area. As the system undergoes transport the hydrocarbons and nitrogen oxides were believed to undergo reaction to form ozone, and were thus depleted by reaction as well as dilution (Ripperton 1974). In a system containing unreactive alkanes and low nitrogen oxides, ozone accumulates at a greater generation-to-destruction rate than in a classically described system with higher concentrations of precursors (Ripperton 1974) (Ripperton et al 1977).

Subsequent studies have established that long range transport of oxidants and their precursors lead to the observation of rural levels of ozone in excess of 0.08 parts per million. The violations of the US Federal standard in south-eastern New England have been attributed to transport effects (Dobbin et al 1977), and the high ozone values measured 250 km east of New York city have been attributed to that city's emissions (Siple et al 1977). Emissions from the New York City metropolitan region have been transported by prevailing winds on a 300km northeastern trajectory through Connecticut as far as Northeastern Massachussets (Cleveland et al 1977). The plume of emissions from St Louis has been shown to lead to violations of the oxidants standard 160 km or more downwind (White et al 1977).

The possibility of the occurrence of high concentrations of ozone at ground level due to downward transport of ozone from the lower stratosphere has been examined (Mohnen et al 1977) (Reiter 1977) (Hathorn and Walker 1977). The operation of such stratospheric intrusions are believed to contribute in part to the high values observed (Hathorn and Walker, 1977). An assessment of the sources of ozone in the lower troposphere has been made by Chatfield and Rasmussen (1977).

RURAL OZONE IN AUSTRALIA

Little is known of the pattern of rural ozone levels in Australia. What evidence there is appears to pose problems for standards set at 0.06 or 0.08 parts per million ozone.

Daly and Steele studied ozone concentrations in Perisher Valley, NSW, and Canberra, ACT, and found that the maximum one-hour average concentration recorded during the 2 month study at Perisher was 0.08 parts per million, and the maximum one-hour average concentration during the 8-month study in Canberra was 0.06 parts per million. Comparison of the frequency distributions of the one-hour average concentrations shows that ozone levels in Perisher Valley were generally higher than in Canberra (Figure 4.1). The pattern was further established by the average diurnal variations of ozone for these locations (Figure 4.2). Concentrations of ozone in Canberra were about half those for Perisher Valley.

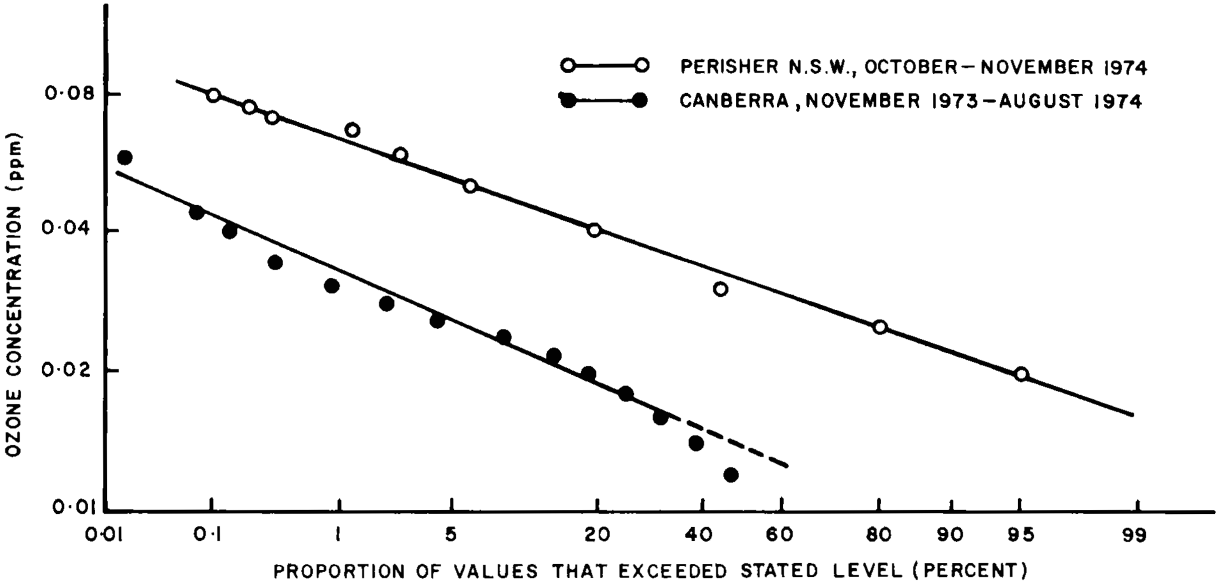


FIGURE 4.1
FREQUENCY DISTRIBUTION OF HOUR–AVERAGE OZONE CONCENTRATIONS IN CANBERRA AND PERISHER VALLEY

SOURCE : Daly N.J., and Steele L.P. (1975)

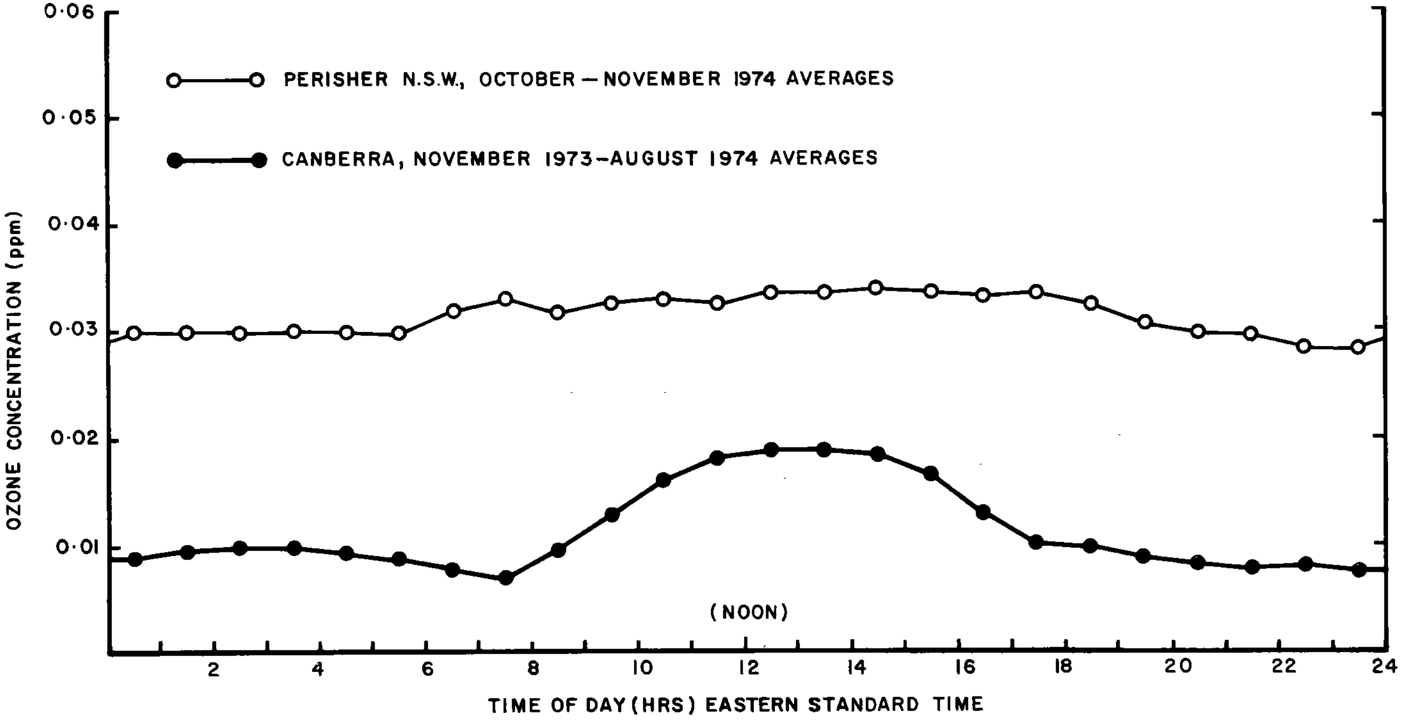


FIGURE 4.2
DIURNAL VARIATIONS OF OZONE CONCENTRATIONS IN
CANBERRA AND PERISHER VALLEY

SOURCE : Daly N.J., and Steele L.P. (1975)

The lower ozone concentrations in urban air were considered to be due to control by nitric oxide emissions. The hypothesis was tested by simulating the addition of nitric oxide to a stable air-mass containing natural levels of ozone (Daly and Steele 1975). The calculation assumed that no other reagents were present, that there was perfect mixing, and that there was no physical addition or removal of reagents (other than addition of nitric oxide) during the simulation. The program for the simulation (Daly and Steele 1975) described the steady addition of nitric oxide to the system from sunrise on. The initial concentration of ozone was set at 0.03 parts per million which is an average value for the rural airmass, and nitrogen oxides were set initially at zero. Nitric oxide was added at a constant rate of 0.001 parts per million per hour. The solar zenith angle reached 10^{o} at noon in the simulation. This simulation is regarded as describing the effect of the impact of motor vehicle emissions in a rural airshed assuming that hydrocarbon reactions have not become important. The results are summarised in Figure 4.3 and show that ozone values decreased monotonically throughout the addition.

The simulation led Daly and Steele to propose three broad classes of behaviour under different wind regimes. With strong winds the residence time of pollutants is insufficient to allow any significant extent of reaction, and the ozone recorded in urban air is essentially that of rural air. Diurnal variations of ozone concentrations tend to the pattern recorded for rural areas in New York State such as Whiteface and Utsayantha (Figure 4.4) and Perisher Valley (Figure 4.2). With moderate winds, the residence time of pollutants becomes such that the rapid sequence of nitric oxide, nitrogen dioxide, and ozone reactions become established, and the nitric oxide emissions from the city result in ozone concentrations lower than rural values. This was proposed as the likely norm for cities (Daly and Steele 1975). Under conditions of poor dispersion the hydrocarbon reaction sequence becomes established and leads to the diurnal variation of the type seen for New York City (Figure 4.4).

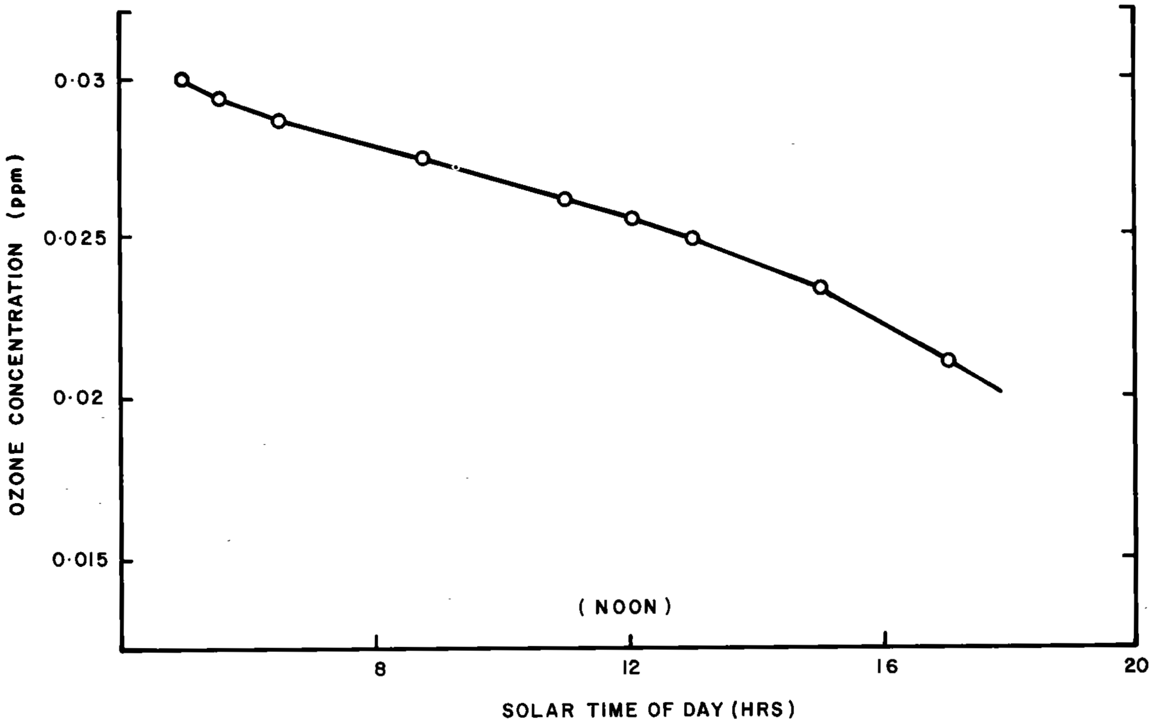


FIGURE 4.3
SIMULATED EFFECT OF ADDITION OF NITRIC OXIDE
TO A RURAL AIRSHED

SOURCE : Daly N.J., and Steele L.P. (1975)

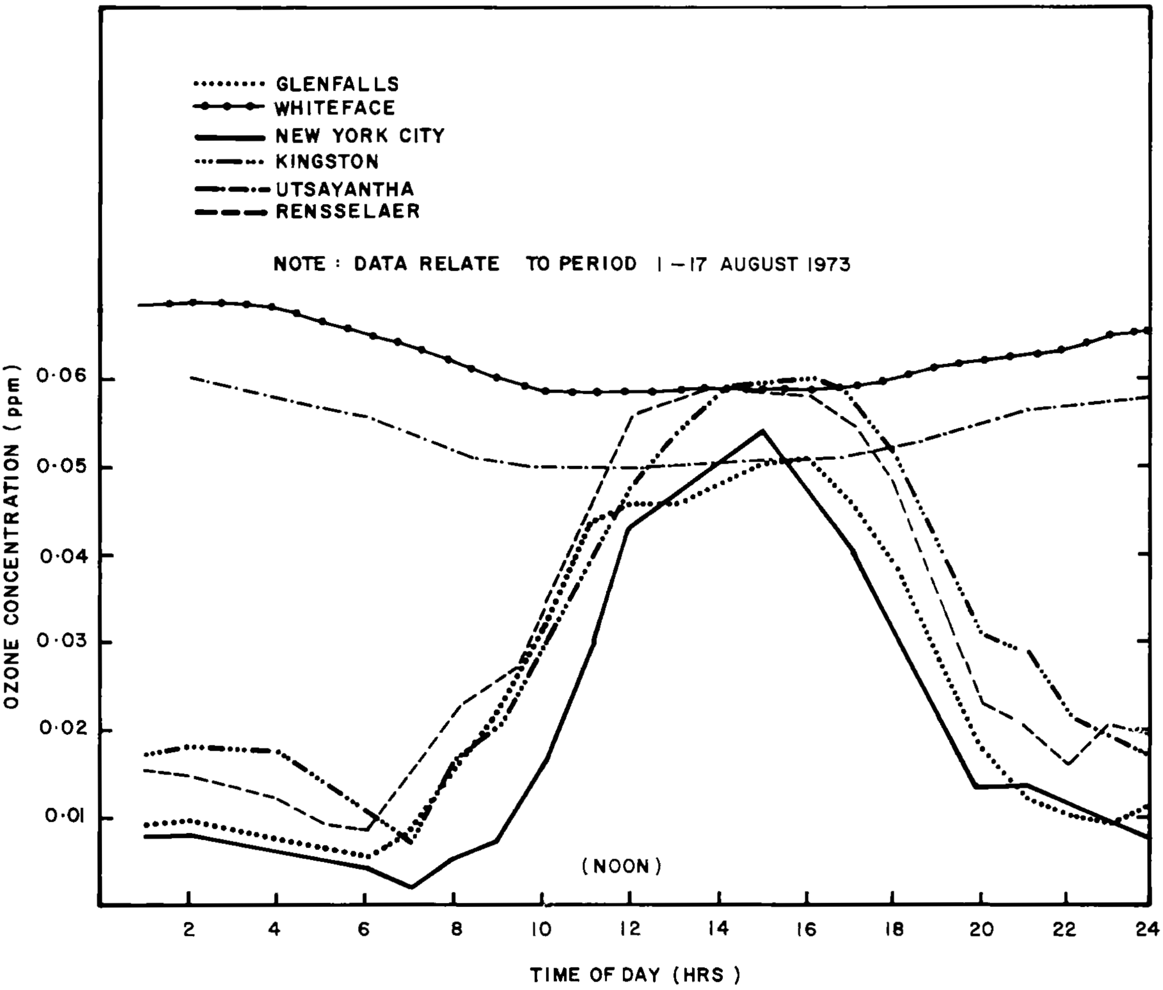


FIGURE 4.4
AVERAGE HOURLY OZONE VALUES IN SELECTED U.S. CITIES

SOURCE : Stasiuk M.N., and Coffey P.E.

The variations of ozone concentrations in Canberra illustrate these broad classes. Figure 4.5 shows the diurnal variation on a Sunday on which the average wind speed was 8.2 metres/second. Comparison with the Perisher Valley data of Figure 4.2 shows these values are essentially rural levels. Figure 4.5 also shows the patterns observed for three weekdays of the study for which the daily average wind speed exceeded 7.0 metres/second. For the bulk of the day, ozone values are essentially rural values except during traffic peaks when the emissions bring about a reduction in ozone due to the controlling effect of nitric oxide. On most occasions in the city, the emissions lead to ozone levels lower than rural as shown by the data of Figure 4.2.

On a weekday morning in Canberra for which the average wind speed over the period 0800 to 1200 hr was less than 2.5 metres/second, the ozone concentration rose smoothly from 0.01 parts per million at 0800 to 0.06 parts per million at 1200 hr and declined to about 0.02 parts per million at sunset. The pattern resembled that of New York City (Figure 4.4).

An important result which should be borne in mind when assessing the oxidants standard is that the standard was arrived at by correlating health effects with levels of ozone in cities. This correlation stands although we may tend to the error of regarding ozone as total oxidants because of the ability to monitor ozone conveniently. Although oxidants are mainly ozone, they do include many species such as peroxyacetyl nitrate and higher analogues which have toxic properties. There is also the possibility that some species synergise the toxicity of others. Clearly there is scope for a considerable body of investigative work.

An example of the ozone standard perhaps masking the effect of other materials is seen by comparing the suggestion by Larsen (1970) that an oxidants standard which specifies an 8 hour average of ozone not exceeding 0.03 parts per million is

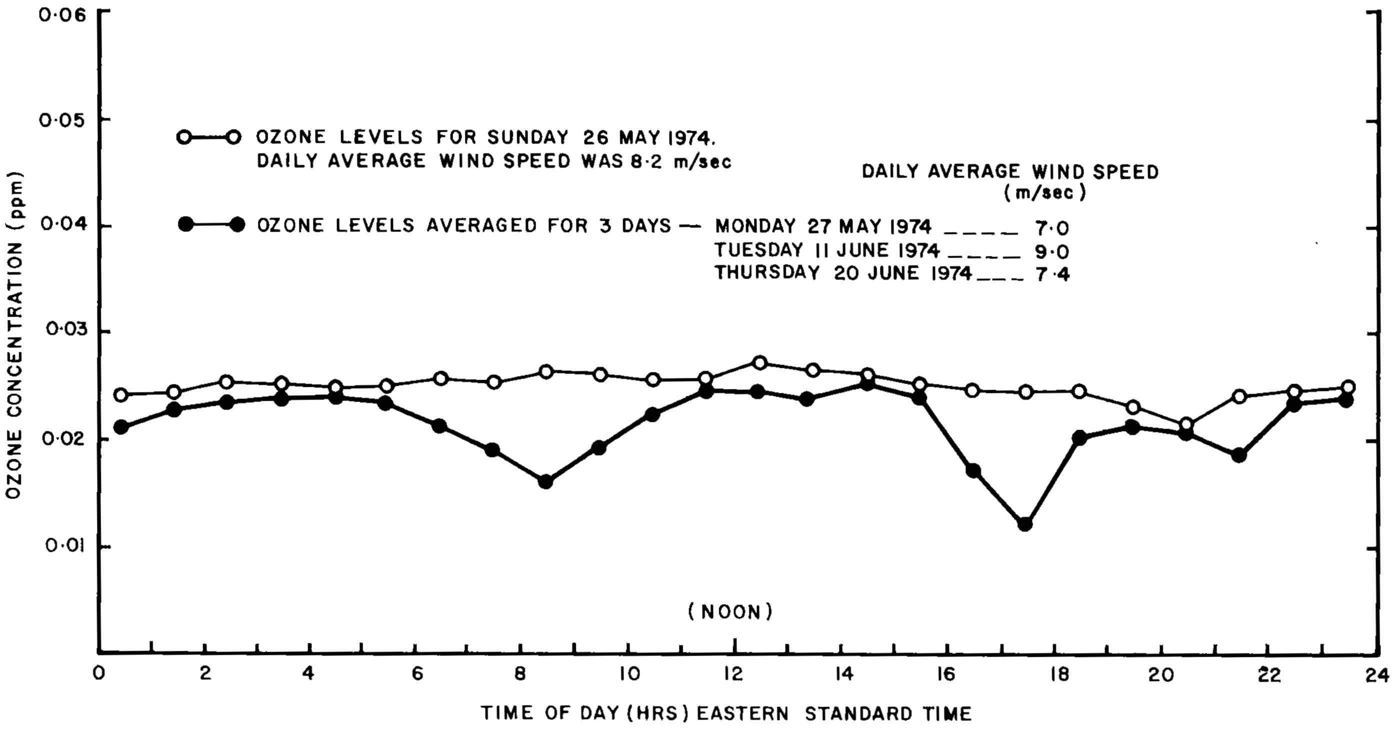


FIGURE 4.5
DIURNAL VARIATIONS OF OZONE CONCENTRATIONS ON SELECTED DAYS IN CANBERRA

SOURCE: Daly N.J., and Steele L.P. (1975)

necessary to preserve leaf crops with the speculation by Pitts and Finlayson (1975) that a hydroperoxide is the phyto-toxicant. Natural ozone exceeding the proposed concentration may be quite innocuous. Urban based generation of ozone exceeding the proposed standard could be harmful because of the other oxidants present.

The extent to which these Perisher Valley results represent natural background and the extent to which they are perturbed by interaction with a polluted plume from, say, the Sydney-Wollongong region is not known. Certainly evidence from the United States shows that city plumes have been known to move 300 km given suitable conditions (Cleveland 1977). Until these issues are resolved there is a strong case for caution in applying ozone standards in Australia.

HEALTH EFFECTS OF OXIDANTS

Photochemical oxidants such as ozone, nitrogen oxides, and peroxyacetyl nitrates exert their toxic effect by entering the body through inhalation. In addition some cause eye irritation. The toxicological effects of the major pollutant groups ozone, oxidants, and peroxyacetyl nitrates have been reviewed by the US Department of Health, Education and Welfare (US National Air Pollution Control Administration 1970) and are discussed below.

Physiological Effects of Ozone

The effects of prolonged exposure of humans to ozone were summarised as follows:

- no apparent effects were observed at concentrations up to 0.20 parts per million;
- the threshold level at which nasal and throat irritation will result appears to be about 0.30 parts per million; and

- concentrations of 0.50 parts per million have caused a 20 per cent decrease of forced expiratory volume observed after eight weeks of intermittent exposure. This change returned to normal during a post-exposure period of six weeks.

Experimental appraisal of short-term exposure to ozone gave the following results (US National Air Pollution Control Administration 1970):

- up to 0.10 parts per million for 1 hour is apparently without significant effect;
- concentrations of 0.10 to 0.40 parts per million for one hour have not been shown to produce effects, but there is a lack of information for this concentration range;
- exposure to concentrations of 0.50 to 1.00 parts per million for periods of 1 to 2 hours produces changes in pulmonary function; and
- some people are unable to tolerate concentrations of 1.00 to 3.00 parts per million over a period of about 2 hours. Extreme fatigue and lack of co-ordination are experienced.

Oxidants and Eye-Irritation

The effects of oxidants on humans has not been as widely studied as the effects of ozone. Thus, apart from the production of eye-irritation, no studies on the effects of photochemical oxidant mixtures had been carried out until 1970 (US National Air Pollution Control Administration 1970).

In the study of eye-irritation in humans, Richardson and Middleton (1975) established a statistically significant correlation between eye-irritation and the concentration of oxidant in Los Angeles. The results are summarised in Figure 4.6 and were taken as showing that the threshold of eye-

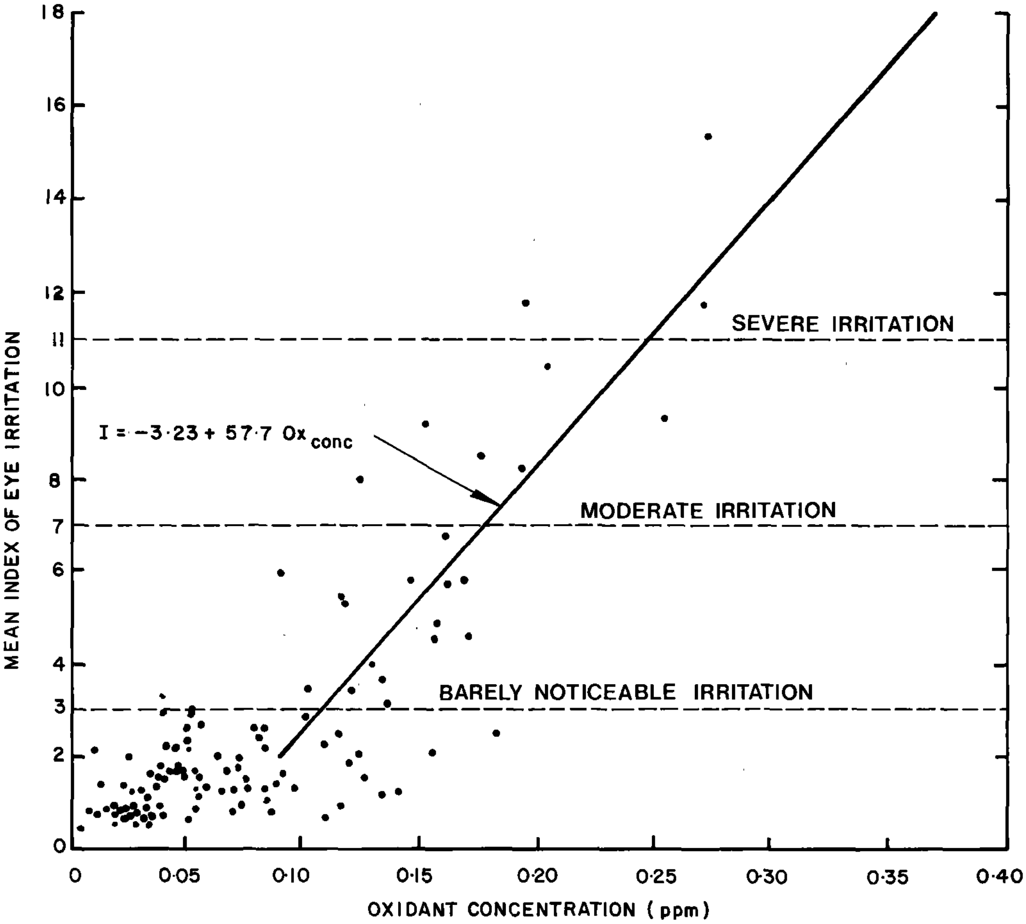


FIGURE 4.6
CORRELATION OF EYE IRRITATION WITH OXIDANT CONCENTRATIONS

SOURCE : US NATIONAL AIR POLLUTION CONTROL ADMINISTRATION., irritation occurs at an oxidant concentration of about 0.10 parts per million. It should be noted that ozone, the principal component of photochemical oxidant, is not an eye-irritant. The major photochemical oxidants identified as eye-irritants are acrolein, peroxyacetyl nitrate, and peroxybenzoyl nitrate. Peroxybenzoyl nitrate has an eye-irritation potency 200 times that of formaldehyde (US National Air Pollution Control Administration 1970).

Physiological Effects of Oxidants

The physiological effects of photochemical pollution are due to a mixture of oxidants. The complexity of the mixture makes the task of identifying the causes of the effects a difficult one. Mizoguchi and his co-workers have used simple and multiple correlation analysis and multi-variate analysis to investigate the relationship between photochemical oxidants and physiological symptoms in humans (Mizoguchi et al 1977).

Mizoguchi and co-workers studied the daily incidences of acute subjective symptoms in 515 students of a junior high school in Tokyo for a 61 day period. In the study, incidences of symptoms connected with predispositions such as allergy, asthma, and orthostatic disregularity were examined for different oxidant levels. Eye irritation, throat irritation, shortness of breath, and headache correlated significantly with ozone. Throat irritation, cough, and phlegm correlated significantly with sulphur dioxide. Studies on multiple correlations between different pairs of environmental factors showed that associations were found between oxidant paired with a number of other pollutants and a range of health symptoms. See Table 1.6.

Mizoguchi and his co-workers noted that on days on which oxidant levels exceeded 0.15 parts per million there was a significant increase in the incidence of cough in the asthma group, and significant increases in the incidence of headache and lethargy in the orthostatic disregulation group.

The health effects of short-term exposure to mixtures of ozone and nitrogen dioxide have been studied by Ehrlich et al (1977). The study used concentrations of nitrogen dioxide which ranged from 1.5 to 5.0 parts per million, and of ozone which ranged from 0.05 to 5.0 parts per million.

The study showed that the effects of a single exposure of test mice to the mixture was additive, whereby the excess mortality rates were equivalent to those induced by the inhalation of each individual pollutant. Excess mortalities observed after 20 daily 3-hour exposures were taken as suggesting a synergistic effect of the pollutant mixtures that made them more effective in reducing resistance to respiratory infection. The results were considered to show the need for the establishment of primary air quality standards for short term exposures to nitrogen dioxide.

The problems presented by nitrogen oxides have also been considered by Pitts who discussed factors which make their control important (Pitts 1977). These are:

- although NOx emissions decrease ozone levels in the immediate area, they seem to raise ozone levels in areas downwind;
- control of NOx reduces ambient levels of toxic nitrogen dioxide;
- reduction of NOx emissions will lower ambient levels of secondary nitrate aerosols;
- NOx is changed into many compounds such as PAN, organic nitrates, and nitric acid for which no air quality standards exist.

Such evidence suggests that the sum of ozone and nitrogen oxides concentrations may need to be considered as well as the ozone concentration when developing oxidant control strategies.

HEALTH DAMAGE FUNCTIONS

Among the categories of receptors of damage affected by air pollution is the health of people living in an airshed. It is important to review the evidence which associates effects on human health with varying levels of air pollution.

Composite Damage Function

Bradley et al used the dose-response curves discussed earlier in the chapter to develop a composite damage function (Bradley et al 1977). They weighted each subgroup by an estimate of the relative size of the population of the group in California, and weighted each of the three levels of health impairment by a factor based upon estimated medical treatment costs and productivity loss for that level. The weightings used were: discomfort 1, disability 6.6, and incapacity 54.5.

The 42 functions were combined to give a composite per capita damage function. As with the dose-response curves on which they were based, best, low, and high estimates were reported for the function.

The combination of these estimates of the per capita damage function with population data and the oxidant concentrations recorded in the airshed gave best, low and high estimates of the population weighted damage function for an airshed.

Bradley et al consider that the important characteristics of the damage functions are:

- zero or minimal damage occur at low oxidant concentrations which correspond to low or negligible risk to people experiencing oxidant levels at or below the air quality standard;

- health damage increases as oxidant levels increase; and

TABLE 4.1 - PER CAPITA OXIDANT HEALTH DAMAGE AND SELECTED OXIDANT INDICATOR VALUES FOR UPLAND AND SAN JOSE (USA) IN 1974

Location	Annual per capita health damage ($ US-1974)	1974 maximum 1-hour average oxidant conc. (ppm)	Annual average oxidant conc. (ppm)	Annual average of daily maximum 1-hour average conc. (ppm)	Annual hours above 0.08 ppm conc. (No.)
San Jose	0.68	0.22	0.020	0.052	162
Upland	60.43	0.44	0.050	0.144	1 360
San Jose as % of Upland	1.1%	50.0%	40.0%	36.1%	11.9%

Source: Bradley et al 1977.

- the rate of change of health damage increases as oxidant levels increase.

Bradley et al (1977) compared the health damage between San Jose and Upland, in the South Coast Air Basin of Los Angeles, with the effect indicated by commonly used oxidant air quality parameters. The results are shown in Table 4.1. The comparison of the relative effects observed shows that the air quality parameters fail to reflect the large difference that exists in health effects between the two locations.

A major finding which emerges from the study is that the greatest amount of damage occurs at the highest oxidant levels. Thus at Azusa, one of the more heavily impacted areas of the South Coast Air Basin, between 61 and 79 per cent of health damage resulted from the 23 per cent of the observations for which ozone levels exceeded 0.20 parts per million. The proportion of per capita damage at various oxidant levels was tabulated by Bradley et al and is reproduced in Table 4.2.

TABLE 4.2 - PROPORTION OF PER CAPITA OXIDANT HEALTH DAMAGE AT OR ABOVE SELECTED OXIDANT LEVELS AT AZUSA (USA) IN 1974

Oxidant level	Hours at or above level	Proportion of damage at or above level (%)		
(ppm)	No.	Low	Best	High
0.10	987	99	99	96
0.15	505	94	93	84
0.20	223	79	78	61
0.25	71	51	49	32
0.30	14	22	20	11
0.35	3	8	7	3

Source: Bradley et al 1977.

Further analysis of the data in Table 4.2 shows that the proportion of per capita health damage is normally distributed about the mean oxidant levels. Thus plots of the cumulative frequency of the proportion of per capita damage are a linear function of the one-hour average concentrations of oxidant. Figure 4.7 shows distributions for each of the estimates: low, best and high.

Delphi Survey Approach

Leung, Goldstein and Dalkey (1975, examined the dose-response relationships for health effects due to oxidants, and conducted a delphi survey of 14 medical professionals familiar with air pollution health effects. Each professional was asked to estimate the oxidant level at which 0, 10, 50 and 90 per cent of 14 population subgroups would experience each of the effects, discomfort, disability and incapacity. The population subgroups considered were:

- old age;
- children;
- influenza;
- asthma;
- chronic respiratory disease;
- severe chronic lung disease;
- heart condition (mild);
- heart condition (severe);
- hay fever;
- upper respiratory infection;
- acute viral bronchitis;
- acute bacterial pneumonia; and
- mild chronic obstructive lung disease.

The impairments due to oxidants were described by the equation:

$$\ln \frac{F}{(1-F)} = A + B \ln(Ox)$$

where F is the fraction of the population affected, (Ox) is the concentration of oxidant at which the effect was noted, and A and B are parameters giving the intercept and slope for each function.

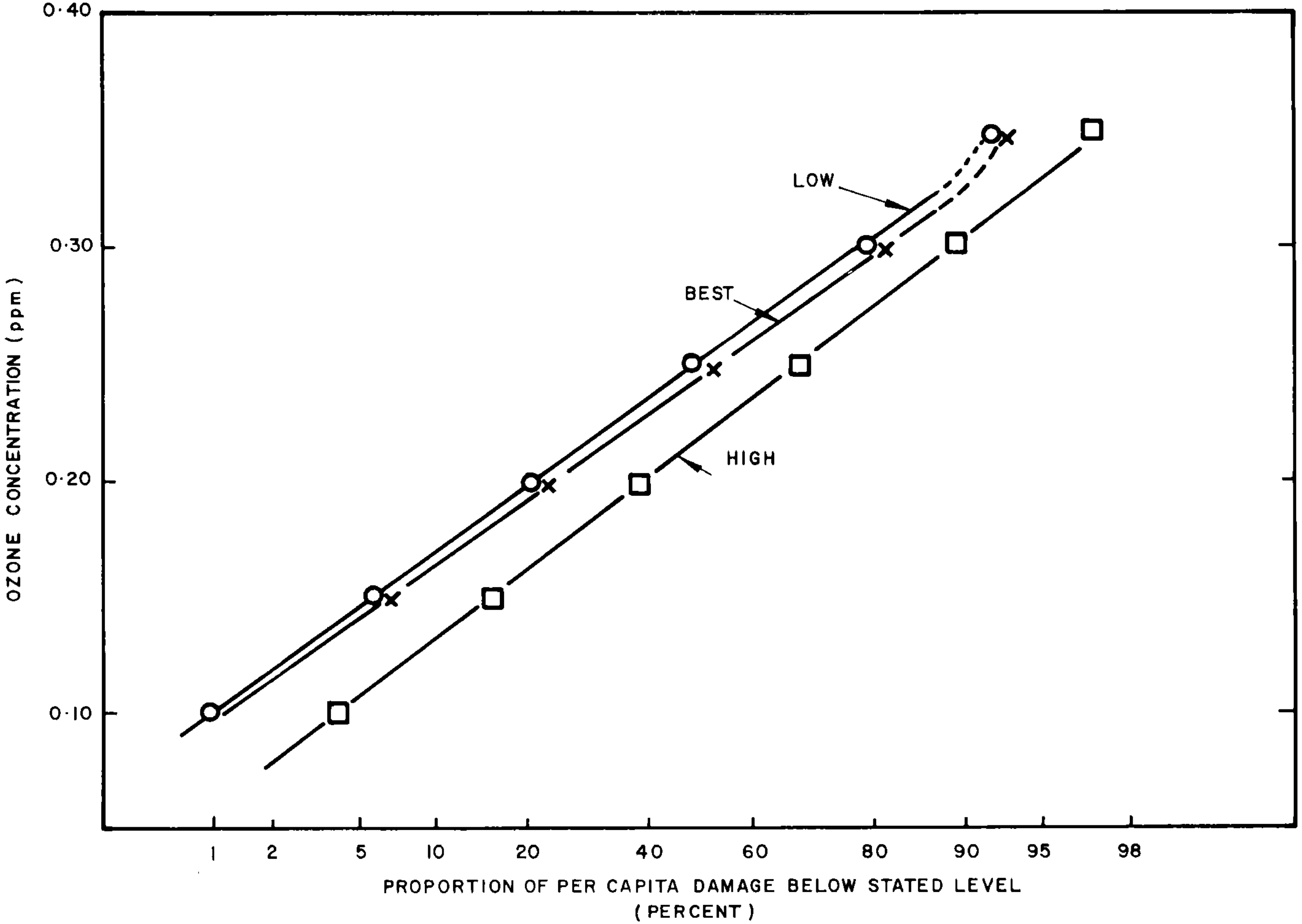


FIGURE 4.7
DISTRIBUTION OF HEALTH DAMAGE AS A FUNCTION OF OZONE CONCENTRATIONS

The study gave dose-response functions for each of the three symptoms, discomfort, disability, and incapacity, for each of the 14 subgroups. The 42 dose-response functions gave the fraction of the population of each subgroup affected by the hourly oxidant concentrations. Three estimates, best, low, and high were given for each dose-response function. Best represented the median; low and high estimates differed from the median by two standard deviations.

The data presented in Figure 4.7 clearly show that the greatest gains in reducing the probability of health damage come from controlling the high concentrations of oxidant. On the basis of using the best estimate of the Californian based data of Bradley et al (1977), Figure 4.7 shows that about 22 per cent of the health damage occurs below a one-hour ozone concentration of 0.20 parts per million while about 7 per cent occurs below 0.15 parts per million, which was suggested as an interim standard in the previous section of this Chapter. Extrapolation of the data in Figure 4.7 shows that about 99.8 per cent of health damage occurs above the World Health Organisation oxidant goal of 0.06 parts per million.

The combination of the cumulative distribution of per capita health damage with population statistics and the frequency distribution of potential ozone provides a good guideline for evaluating the comparative effectiveness of alternative controls.

AN OXIDANT GOAL FOR AUSTRALIA

Air quality standards are classically set on the basis of public health considerations. The objective has been to select a concentration which relates to a threshold which if crossed poses a threat to the health of the public, and provides an adequate safety margin for the effective operation of an air quality program (see Table 1.5).

The adoption of this form of standard or guideline for oxidants control requires the exercise of value judgments on the frequency of episodes in excess of the threshold concentration which should be tolerated, and the proportion of the public which should be protected. Many of the problems in choosing a standard arise because of the difficulties in determining the threshold concentrations. Photochemical smog is a complex mixture with a composition which varies with factors such as the nature of the hydrocarbon mixture, the ratio of hydrocarbons to nitrogen oxides, the length of the insolation period, and the number of irradiations. At present it is not known to what extent the effects of the pollutants are independent, additive, or involve synergism.

It seems evident that in the immediate future, despite its limitations, the concentration of ozone will remain the most practical way of measuring the intensity of a photochemical episode. Accordingly the ozone concentration used as a guideline needs to truly indicate the activity of the total mixture of oxidants. In this respect the long term goal of the World Health Organisation is not satisfactory since it would classify as a health threat the occurrence in a wilderness area of a one-hour average concentration of ozone exceeding this goal. However, the physiological evidence is that pure ozone does not affect humans for one-hour exposures of concentrations up to 0.20 parts per million (US National Air Pollution Control Administration 1970).

At present there is insufficient medical evidence on the physiological effects of smog mixtures in Australia to use as a base for an oxidant goal. There are, however, sufficient data to justify an interim goal to operate as a guideline for a period sufficient to enable the conduct of the necessary research to establish the appropriate oxidant goal.

The existing evidence suggests that a concentration of 0.15 parts per million of ozone as a one-hour average is a reasonable interim goal for oxidant control. The advantages are:

- the concentration never seems to be exceeded in rural airsheds;
- a one-hour average of 0.15 parts per million is a good surrogate for total oxidants; and
- the concentration appears to be a health threshold for a large percentage of "at risk" community groups.

The suggested goal is a practical one for a period of say 5 years. The selected ozone concentration is a realistic compromise between the present high urban ozone levels and the (low) WHO goal since the maximum ozone concentrations currently recorded in Sydney and Melbourne are often about twice this value, and the immediate task is one of getting down to more acceptable levels. If later studies show that more stringent goals are necessary, the achievement of the 0.15 parts per million mark during the 5 year period would represent a substantial advance in oxidant control.

The suggested goal of 0.15 parts per million represents a reasonable estimate of the health threshold for a substantial proportion of the population. Mizoguchi et al (1977) studied the relationship of subjective symptoms to oxidant concentrations and showed that there was a significant increase in the symptoms of groups with predispositions on days on which oxidant concentrations exceeded 0.15 parts per million. Until an assessment is made of the Australian photochemical mixture it seems prudent to accept that the Japanese evidence applies locally.

CHAPTER 5 - EVALUATION OF STRATEGIES FOR OXIDANT CONTROL

AVAILABLE CONTROL OPTIONS

The options available for the control of the incidence and intensity of photochemical smog-forming episodes involve reductions in the ambient concentrations of the precursors. The various options are:

- control of emissions of non-methane hydrocarbons;
- control of emissions of nitrogen oxides; and
- control of emissions of both nitrogen oxides and non-methane hydrocarbons.

Which of these options is the most efficient in terms of reducing ozone depends upon the whole range of oxidant forming conditions experienced in the airsheds of interest. The overall analysis of efficiency needs to include an assessment of the costs and benefits of the various methods considered.

The oxidant forming conditions which occur in an airshed are determined by the meteorology of the airshed. Where a particular airshed, with its characteristic regime of sunlight and temperature is considered, the prime factor which determines the concentrations of oxidants formed from any set of non-methane hydrocarbons and nitrogen oxide concentrations is the length of the reaction time.

The reaction time is determined by the meteorological forces which control rates of dispersion and transport, and recirculation effects. The meteorological conditions in a given airshed may lead to a variety of reaction times which range from several hours to several days. Each different class of reaction times may lead to a different dependence of oxidant upon precursor concentrations from the other classes.

The meteorological conditions observed in Sydney (Hyde et al 1978a) (Hyde et al 1978b) appear to provide a range of reaction times, and the corresponding pattern seems likely for other State Capitals. The relevant meteorological conditions for Australia have been briefly reviewed in Chapter 3.

The assessment of costs requires a detailed economic analysis which evaluates additional costs incurred over and above those already associated with existing control programs. Estimation of benefits is a complex issue which properly involves social judgments.

DISTRIBUTION OF REACTION TIMES

The range of meteorological conditions which occur in an airshed can be classified broadly into those which lead to the following reaction conditions:

- partial-day or one-day irradiations of fresh emissions;
- partial-day or one-day irradiations of aged mixtures;
- partial-day or one-day irradiations of mixtures of fresh emissions and aged mixtures; and
- multi-day irradiations.

Each of these classes of reaction conditions has its own characteristic set of oxidant-precursor relationships.

The chemical factors which lead to the different relationships between the quantity of oxidant and the concentrations of non-methane hydrocarbons and nitrogen oxides have been discussed in Chapter 2. The general result accepted is that irradiation of aged smog mixtures rapidly produces high ozone concentrations because the species of reactive hydrocarbon which undergo reaction to consume ozone have themselves been consumed in the early stages of the reactions. The more aged the smog mixture, and the lower the proportion of reactive hydrocarbons in the hydrocarbon mixture, the greater is the ability of the system to conserve the ozone it generates.

The range of meteorological conditions which can occur means that proposed oxidant controls need to be evaluated against the oxidant-precursor relationships for the various reaction conditions which are normal to the airshed. This evaluation requires a knowledge of the various oxidant-precursor relationships and the proportion of the oxidant forming episodes which fall into each of the four categories.

The study of the meteorological conditions which permit the classification of reaction conditions has been undertaken for the Sydney-Liverpool air basins by Hyde et al (1978a) (1978b). Such detailed studies are not available for other airsheds.

FREQUENCY DISTRIBUTIONS OF POTENTIAL OZONE

Oxidant goals such as those of the World Health Organisation, the United States Government and the Japanese Government fix a one-hour average concentration of oxidant which is not to be exceeded more than once per year (which is a frequency of approximately 0.01 per cent of the year). An implication of such a goal is that the concern is not only with maximum values, but also with how often the goal is exceeded.

Accordingly one approach to the development of the optimum control strategy is to determine which set of fractional reductions in emissions minimises the frequency with which the desired oxidant goal is exceeded. A useful method for evaluating the likely effects of alternative options for emissions controls combines the use of photochemical models with real airshed data to calculate the oxidant forming potential of the resulting alternative distributions of hydrocarbons and nitrogen oxides in the airshed (Daly 1977) (Daly (1978a) (Daly (1979).

An airshed has a potential for forming oxidants because of the various concentrations of nitrogen oxides and hydrocarbons which occur. This potential is realised only when the necessary conditions of atmospheric stability and clear skies occur simultaneously. If the necessary meteorological conditions which promote oxidant formation are treated as occurring at random intervals, the task of controlling oxidant becomes one of controlling the ambient concentrations of hydrocarbons and nitrogen oxides so as to minimise the frequency with which oxidant has the potential for exceeding the stated goal of concentration. The oxidant potential of an airshed can be estimated with the aid of a suitable photochemical model and is valid within the limits for which the model is valid. Most present day models such as that of Dodge lead to the oxidant potential of the airshed being expressed as an ozone potential for one-day irradiations of fresh emissions only.

Photochemical models follow the 'Appendix J' method (US Federal Register 1971) and assume that the average of the 0600 to 0900 hr concentrations of hydrocarbons and nitrogen oxides gives the ozone peak observed - albeit at a different location - later in the day. Thus for a chosen year the 365 sets of the averaged 0600 to 0900 hr concentrations of hydrocarbons and nitrogen oxides represent the annual ozone potential of the element of the airshed represented by the monitoring station. The maximum one-hour average concentration of ozone which can potentially be formed from each set of hydrocarbon and nitrogen oxides data is calculated from the photochemical model, and the annual frequency distribution of these ozone concentrations is prepared. Such a distribution is taken as defining the ozone potential of the existing ambient concentrations of hydrocarbons and nitrogen oxides in the airshed for oxidant episodes due to one-day irradiations of fresh emissions under the conditions set by the model.

If it is accepted that fractional reductions in emissions of hydrocarbons and nitrogen oxides lead to corresponding fractional reductions in ambient levels of these precursors, it is possible to make a planned reduction in the concentrations of each of the hydrocarbons and nitrogen oxide sets and to recalculate the resultant distribution of potential ozone. Such a procedure gives a method for evaluating the likely impact of alternative control strategies. It must be stressed that such an evaluation applies only within the limits implicit within the assumptions of the model used. Where the Dodge model is used, the results apply only to the control of the maximum one-hour average concentrations of ozone formed in one-day irradiations of fresh emissions.

The choice of a year as the basic time interval for evaluating the frequency distribution is arbitrary although it has the advantage of corresponding to the period chosen in the various oxidant goals and standards set by authorities such as the World Health Organisation and the US Federal Government. It may, as has been suggested elsewhere (Daly 1978), be more appropriate to examine the oxidant potential of an airshed over the period for which oxidants are, or are likely to be, a problem in the airshed. Thus, for example, it may be necessary to evaluate the impact of precursor concentrations during summer and early autumn in one airshed, and in late spring and summer in another (Daly 1979).

INTERPRETING SYDNEY'S OXIDANT-PRECURSOR RELATIONSHIPS

It would be useful to examine the airshed data measured in Australian airsheds and to assess the likely impact of alternative control strategies on the ozone potentials. In carrying out such an assessment it should be noted that existing photochemical models confine the results to the class of episodes which arise from one-day irradiations of fresh emissions so that the impact of extended irradiations and the problems of irradiation of 'aged' mixtures would need to be evaluated separately.

In general, however, the data in the form of the 0600 to 0900 hr average concentrations of hydrocarbons and nitrogen oxides which are necessary for the Appendix J based approach have not been published. Nonetheless an approach to the assessment has been made using airshed data measured during the Sydney Oxidant Study.

Post (1979a) and Post and Bilger (1978) have analysed 836 sets of half-hour averaged concentrations of hydrocarbons and NOx measured between 0600 and 1000 hr in the Sydney Oxidant Study. The results of their calculations of potential ozone are presented in Figure 5.1. Of the 836 sets of precursor data observed, 226 were obtained at one or other of the sample sites visited on field days during the Sydney Oxidant Study. The remainder were obtained from the base sample site at Sydney University.

In Figure 5.1 the numbers shown in individual elements refer to the number of half-hour average observations within the concentration ranges given by the bottom and left-hand axes. Broken lines show the assumed ozone-precursor relationships. Dotted lines show these relationships replotted according to the top and right hand axes which have been adjusted to simulate a shift in the precursor distribution resulting from a 60 per cent and 20 per cent reduction in emissions of NMHC and NOx respectively.

This analysis assumes that the basic conditions of the Dodge model apply within the airshed, that airshed conditions are bounded by the model, and that the 836 sets typify the ozone forming precursors in the airshed.

The Dodge model as originally formulated converts a concentration of fresh emissions of hydrocarbons and NOx into a maximum one-hour average concentration of ozone on the basis of a nine-hour irradiation. The calculations of Post depart from the conditions of the model in several important respects:

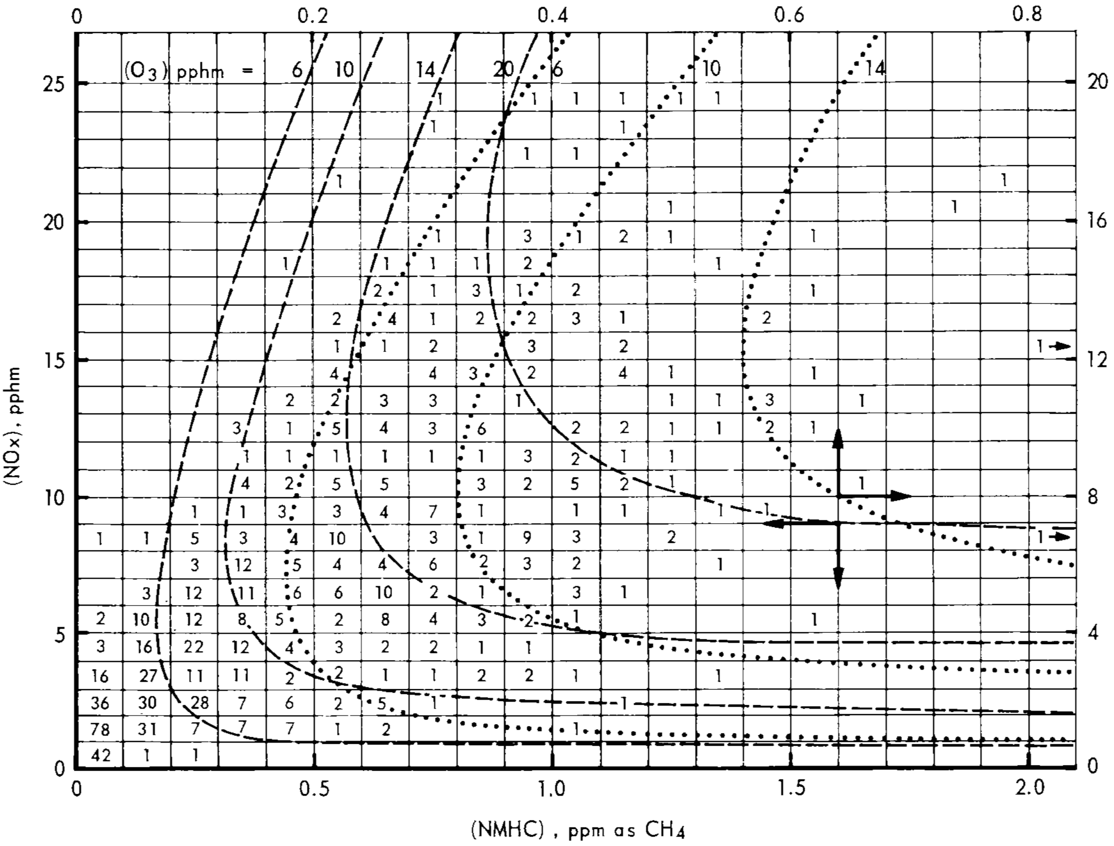


FIGURE 5.1
JOINT DISTRIBUTION OF NMHC AND NOx
OBSERVATIONS FOR SYDNEY FOR SUMMERS OF 1975–76 AND
1976–77

SOURCE: Post K., (1979a)

- precursor concentrations are averaged over half-hour intervals in the expectation that each half-hour air packet would randomly move to a different part of the airshed, and contribute to the ozone values within the airshed;

- data are treated as 8 half-hour averages between 0600 and 1000 hours. Thus in principle these generate 8 maximum one-hour average concentrations for the day. The daily one-hour maximum in the real airshed and implied by Dodge is normally associated with the average concentrations of precursors over the 0600 to 0900 hour period;

- the Dodge model does not apply to multi-day irradiations or to continuous emissions of hydrocarbons and NOx. The empirical correction factor aggregates such episodes along with single day irradiations despite the mechanistic differences in ozone production. Such an aggregation factor could have an extremely non-linear dependence on reaction conditions and time; and

- no temporal or spatial correlations between precursors and ozone maxima are established. Thus it is not clear that the precursor set and the ozone maximum with which it correlates occur on the same day, or that the air packet containing these sets actually moves to a position in the air basin where ozone is observed.

The oxidant potentials of these sets of data are discussed in the following section in terms of the potential ozone (Daly 1977) (Daly 1978) which could result from a range of control options.

OZONE PRECURSOR MODELS FOR SYDNEY

Two models have been put forward to describe ozone-precursor relationships in the Sydney airshed. These are a modified version of the Dodge model (Post and Bilger 1978) and an empirical relationship proposed (Post 1979a) to correlate observed ozone concentrations with precursor concentrations. These are briefly described below.

The Modified Dodge Model

The Dodge model has been described earlier and is based on an assumed kinetic reaction mechanism (Appendix A) with assigned rate constants and a defined time of reaction. For fixed reaction conditions the model is considered useful in determining the relative dependencies of ozone formed in one-day irradiations upon the concentrations of fresh emissions of hydrocarbon and NOx. The model is not considered to apply to the absolute calculation of ozone concentrations (Dodge 1977b). No standard deviations for curve-fitting relationships are given, but errors in the reproduceability of smog chamber data are typically 15 to 20 per cent (Dodge 1977b) (Dodge 1977a).

Post and Bilger (1978) have proposed that the ozone concentrations formed in the Sydney airshed are well described by the Dodge model providing that the ozone concentrations calculated by the model are multiplied by the empirical factor 0.67. This conclusion extends the model to the calculation of absolute concentrations of ozone and is based on the evidence offered by 16 sets of concentrations of ozone, hydrocarbon, and NOx measured during the Sydney Oxidant Study. These 16 sets are shown together with the ozone isopleths they are said to validate in Figure 5.2.

The hydrocarbon and NOx concentrations in Figure 5.2 are plotted on a logarithmic scale. The numbers appended to the points list the observed averaged ozone concentrations. Figure 5.2 shows that the apparent fit of the airshed data to the adjusted Dodge isopleths is poor. This is confirmed by considering the magnitudes of the adjustments in either hydrocarbons or NOx concentrations necessary to make the observed averaged ozone concentrations fit the adjusted isopleths of the model. Typical

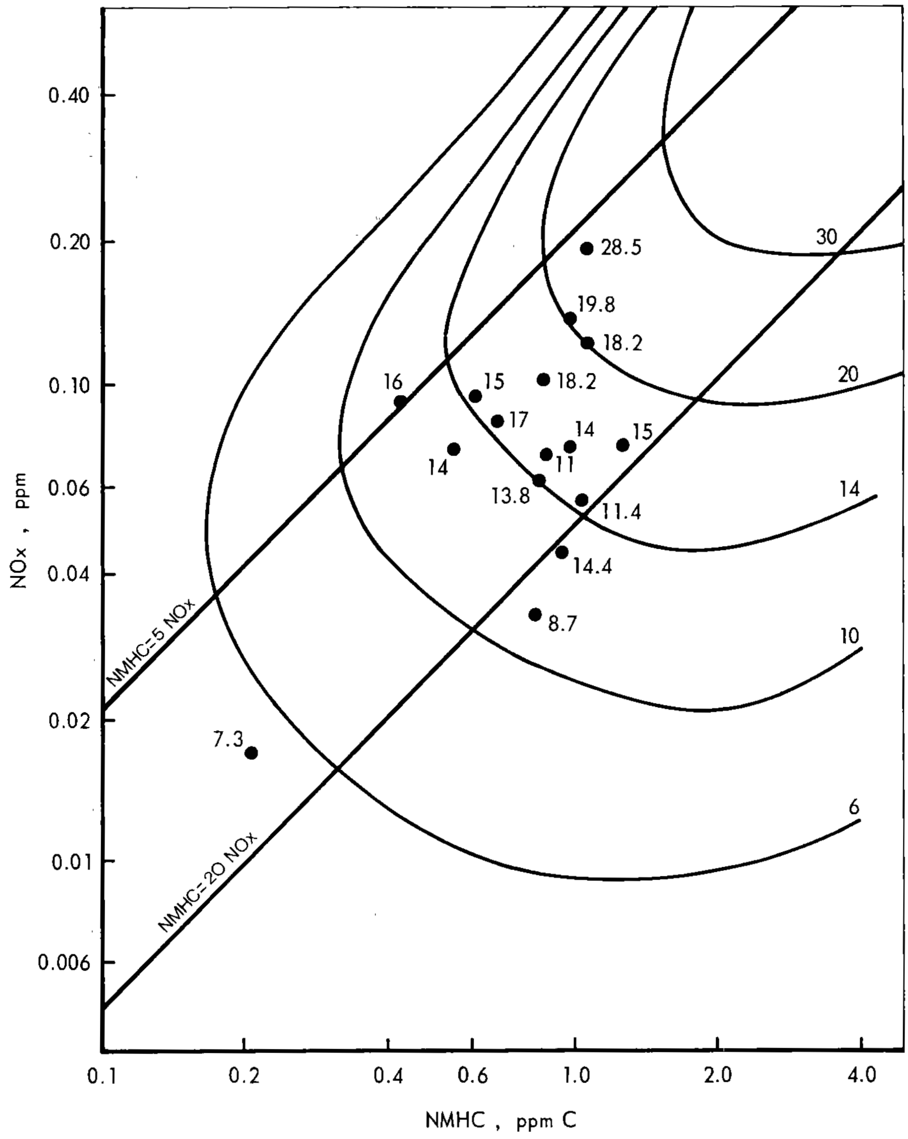


FIGURE 5.2
COMPARISON OF AIRSHED VALUES
WITH ISOPLETHS FROM MODIFIED DODGE MODEL

SOURCE· Post K., and Bilger R.W.,

adjustments required in either hydrocarbons or NOx involve both increases and decreases of about 50 per cent in the airshed concentration. Some adjustments to accommodate the higher ozone concentrations are greater than this level.

The airshed data offered as validation of the modified Dodge model are such that, even were the fit satisfactory, the correlation could conceal important mechanistic differences between the airshed and the model. The model, for example, correlates initial concentrations of hydrocarbons and NOx with the maximum one-hour average concentration of ozone formed in a nine-hour irradiation. This is not the case for the airshed correlation. Thus, for example, the airshed concentrations NMHC = 0.93 ppmC and NOx = 0.044 ppm are correlated with the ozone concentration O_3 = 0.144 ppm in Figure 5.2 (Post et al 1976a). These data appear to stem from the average of the 3 minute averages NMHC = 1.05 and 0.81 ppmC and NOx = 0.045 and 0.043 ppm observed at 0930 and 0940 hr at Leichhardt Park on 12 December, 1975, which are correlated with the average of five three-minute averages of ozone concentrations obeserved at Canterbury Racecourse on the same day, viz., 0.117 ppm (at 1020 hr), 0.150 ppm (1030 hr), 0.133 ppm (1040 hr), 0.163 ppm (1050 hr) and 0.157 ppm (1100 hr). Hydrocarbon and NOx concentrations observed earlier in the airshed are considered to make no contribution to the ozone averaged between 1020 and 1100 hr. This correlation allows only 40 to 60 minutes between the selected initial hydrocarbon and NOx concentrations and the designated oxidant peak. This seems an insufficient reaction time to permit maximum ozone formation by the Dodge mechanism when about 30 per cent of the NOx sampled at the times mentioned above was in the form of nitric oxide.

All of the airshed data sets used to validate the Dodge model for Sydney are biased towards short irradiation times between the chosen initial concentrations and the onset of the oxidants peak. This is shown in Table 5.1.

TABLE 5.1 - DISTRIBUTION OF IRRADIATION TIMES FOR OZONE PRECURSORS

Irradiation Time (hr)	Proportion of Ozone Precursor Pairs (cum. per cent)
≤ 1	13
≤ 2	39
≤ 3	78
≤ 4	87
> 4	100

Source: Post and Bilger 1977.

The ozone isopleths of the Dodge model are explicitly derived for one day irradiations of freshly emitted hydrocarbons and nitrogen oxides, and apply within stated limits for defined mechanisms of ozone formation. The airshed observations for Sydney suggest not only that ozone levels are not satisfactorily described by the modified model, but that there are conditions for oxidant formation in Sydney which differ from those of the model. For example, oxidant levels in Campbelltown may involve a contribution from extended irradiation periods due to the operation of certain meteorological factors. The relative importance of this contribution is likely to increase from its present level of significance as the population of receptors in Campbelltown grows, and as emissions into the Sydney airshed grow. Again the observation (Post et al 1976b) of ozone peaks of 0.140 and 0.145 ppm at Concord as early as 0910 and 0920 hr on 12 December, 1975 suggests the importance of photochemical processes other than the one-day irradiations described by the Dodge model.

These considerations lead to the conclusion that the applicability of the Dodge model to the problem of calculating ozone concentrations in the Sydney basin has not been established between the limits of NMHC/NOx ratios of 5 to 20 for which airshed values are reported.

No verification of the steeply reverse-angled isopleths outside these limits has been reported. Extrapolation of airshed values, especially those for which the NMHC/NOx ratios are below 5, is based on the assumption that the Dodge model holds, and that the mechanism of and all the conditions for oxidant formation in the Sydney airshed conform to those of the model. Thus the applicability of the models in this region where the isopleths change more rapidly as a function of NMHC and NOx is also not justified.

The likely reason for the general lack of applicability of the models is that the airshed processes are more complex than those used in the Dodge model.

The Empirical Model

Post (1979a) has extended the method of correlating frequency distributions, used by Daly and Steele (1975) (1976) to describe inert pollutants, to the analysis of ozone concentrations in the Sydney airshed, and has shown that, between the limits of NMHC/NOx from 5 to 20, the observed ozone concentrations are described by the empirical relationship:

$$(O_3) = 0.39 \left[(NOx) \quad (NMHC) \right]^{0.36}$$

The relationship correlates the 836 sets of half-hour average concentrations of hydrocarbons and NOx obtained in the Sydney Oxidant Study and analysed by Post and Bilger.

The application of such a model to the prediction of future trends requires that major variables which influence the formation of oxidants maintain the present relativity of their contributions. Thus the present meteorological dispersion forces and geographical distributions of precursor sources and receptors would be required to satisfactorily typify the airbasin in the future.

Post (1979a) showed that with certain adjustments of frequencies the modified Dodge model correlates the same 836 sets of half-hour average concentrations of hydrocarbons and NOx with ozone maxima accumulated across the basin as well as does the empirical relationship. This observation also applies between the limits of NMHC/NOx from 5 to 20. Again no spatial or temporal correlations between precursors and ozone are established, and the empirical model must be regarded as an empirical correlation of observed data within the stated limits.

ASSESSMENT OF JOINT AND SINGLE EMISSION CONTROLS

The results obtained from the analysis of distributions of potential ozone based on airshed data for Sydney depend upon the airshed model used to evaluate the potential ozone. Post has assumed that the modified Dodge model describes oxidant formation in the Sydney basin (Post 1979a) and has applied the technique (Daly 1977) (Daly 1978) of evaluating potential ozone for several emission reduction strategies to the 836 sets of half-hour ozone precursor averages.

The results of the analysis led Post to conclude firstly (Post 1979a), that hydrocarbon control is the most effective strategy for containing oxidant in the Sydney airshed, and secondly (Post 1979b) that

> 'it is unproductive, and in fact counterproductive, to pursue a policy of constraining NOx emissions to present levels whilst reducing NMHC emissions.'

Joint Emission Controls

Calculations have been made of the potential violations of ozone concentrations of 0.12, 0.14, 0.15 and 0.20 parts per million for a range of combinations of joint control, based on the 836 sets of precursor concentrations (Daly 1979). They have been presented as a function of percentage reductions in both hydrocarbons and nitrogen oxide concentrations. The computations for example, show that a 33 per cent equal reduction of both hydrocarbons and nitrogen oxides levels has the same relative effect as a 54 per cent reduction of hydrocarbons only in reducing potential violations of both the 0.10 and 0.14 parts per million level of ozone and becomes more effective in reducing potential violations of the 0.20 parts per million level (Daly 1979).

The computations also reproduce the ozone distribution reported for Sydney by Ferrari et al (1979). Equal joint controls are not necessarily the optimal strategy for joint emission reduction. Even if they were optimal in theory, it could be difficult in practice to achieve equal reduction across the range of sources in an airshed.

Examples of joint emission reduction strategies not involving equal joint control are shown in Table 5.2. This Table shows the alternative strategies that could be applied to eliminate all ozone levels exceeding 0.20 parts per million in Sydney, based on the 836 sets of data obtained during the Sydney Oxidant Study.

The computations discussed above do not support the conclusion by Post (1979a) (1979b) that Sydney ozone concentrations are not favoured by reductions in nitrogen oxide concentrations.

These computed results are relative rather than absolute, but show that, within the limits of the empirical model, less stringent controls of both hydrocarbons and nitrogen oxides are as effective as more stringent controls of hydrocarbons alone.

TABLE 5.2 - ALTERNATIVE JOINT EMISSION REDUCTION STRATEGIES TO ELIMINATE OZONE LEVELS ABOVE 0.20 PPM IN SYDNEY

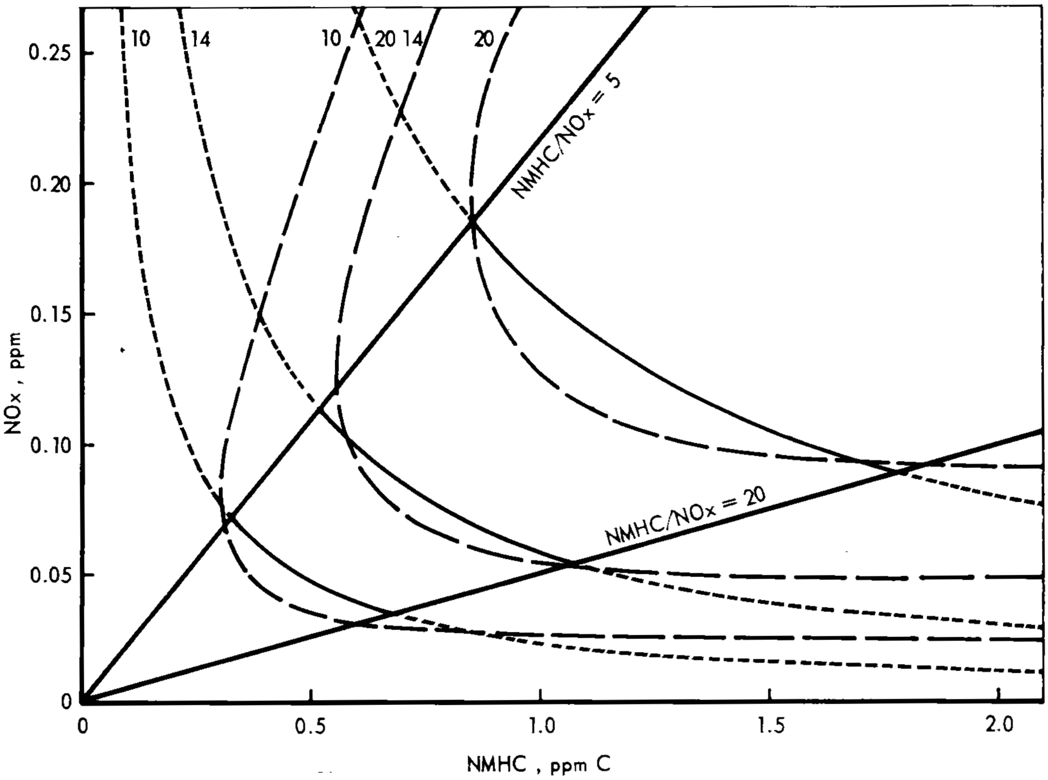
Reduction of HC (%)	Reduction of NOx (%)
63	0
54	20
47	30
40	39
0	63

Source: Daly 1979.

Figure 5.3 illustrates the isopleths for ozone concentrations of 0.10, 0.14 and 0.20 parts per million upon the concentrations of hydrocarbons and nitrogen oxides derived from both the empirical and the modified Dodge models. Within the area bounded by the lines showing the loci of NMHC/NOx = 5 and NMHC/NOx = 20, both models are essentially in agreement because the corresponding isopleths for each model are in close proximity. Thus both models imply that the reduction of the frequency of occurrence of ozone episodes is equally sensitive to reductions in hydrocarbons and in nitrogen oxides. Joint control of these emissions is likely to confer further benefits in ozone control during extended irradiations, and in limiting accumulations of nitrogen dioxide and perhaps nitrate aerosols.

Hydrocarbon only Controls

Implementation of combined controls on both hydrocarbon and NOx concentrations should not significantly alter the distribution of NMHC/NOx ratios, and so the distribution should remain in the region of NMHC/NOx of 5 to 20 for which validation has been attempted. However, when the impact of large scale controls on



NOTE: Ozone isopleths for empirical model ________
Ozone isopleths for modified Dodge model — — — —

FIGURE 5.3
COMPARISON OF ISOPLETHS FOR MODIFIED DODGE AND EMPIRICAL AIRSHED MODELS

hydrocarbons only is assessed, the effect of such reduction is to move significant numbers of the sets of precursor concentrations into the region below the NMHC/NOx ratio of 5. No airshed correlations of hydrocarbon, NOx, and ozone exist for this region. Neither the Dodge model nor the empirical model have been validated for this region. Since results are subject to the limits of the models used, evauation of the effect of hydrocarbon only controls must be regarded as speculative.

Comparison of the isopleths in Figure 5.3 shows that the isopleths based on the Dodge model give an advantage to hydrocarbon controls in comparison with those conferred by the empirical model. Thus predictions for the effects of hydrocarbons only controls appear to be more optimistic when based on the Dodge model than they are when based on the empirically observed correlation of observed airshed data when both are extrapolated into the region where precursor sets have NMHC/NOx ratios less than about 3.

This apparent advantage originates because the chemical component of the Dodge model shows that the addition of nitric oxide depresses ozone concentrations. This type of suppression behaviour is seen at low values of the NMHC/NOx ratio for short-term irradiations in smog chambers although the exact positioning of the ozone isopleths depends upon experimental conditions.

These effects have been discussed earlier in this work and elsewhere (Daly 1977). Thus were the formation of oxidant in Sydney to approximate to the conditions of a well-mixed smog chamber in which each episode is a short-term irradiation of fresh emissions, and were ozone formation to be the only criterion rather than total oxidant or the sum of selected constituents of oxidant, and were ozone able to be described in the low ratio area by Dodge, the NOx depression of ozone could be an advantage provided it did not lead to increased ozone downwind. However, in reality, evidence is accumulating that oxidants other than ozone also need to be considered, and that irradiations of aged mixtures and transport and recirculation effects do occur in the basin and are likely to become more important as the population in the basin grows.

It could seem that the results from the modified Dodge model should be used in the case of examining the effect of hydrocarbon only controls since the original model is based on a chemical reaction scheme and a number of smog chamber experiments and thus has physical meaning. Such usage does not take into account the knowledge that:

- the original Dodge model is not validated for the airshed, for which conditions may differ markedly from model conditions, especially in the region of interest;
- there is the uncertainty described earlier over values assigned to certain of the rate constants in the model;
- the model refers specifically to 9-hour irradiations;
- no account is taken of the effects of accumulation of NO_2; and
- the results accrue from methods which depart from the physical conditions of the model.

In addition to these factors, Dodge (1977a) has stressed with respect to the Dodge model isopleths of Figure 2.10 (and therefore also Figure 5.3) that:

> 'the extreme upper left and lower right portions which correspond to very low and very high HC-to-NOx ratios, should be viewed with caution.'

The five points mentioned above become important since the regions mentioned by Dodge are those where single control strategies gain their advantage over joint controls.

Meteorological studies described earlier show that multi-day irradiations presently contribute to oxidant formation in Sydney and are likely to become more important as the region grows. The effects of extended irradiations have been described earlier, and lead to a set of ozone precursor relationships quite different from those of Dodge. A likely effect would be to make ozone formation less sensitive to hydrocarbons and more sensitive to NOx which would contribute to moving an averaged position of the ozone isopleths from the Dodge location towards that of the empirical model in the regions of low NMHC/NOx ratios where the models appear to differ. Study of this region is clearly warranted.

THE DIVIDING LINE CONCEPT

Dodge has proposed the 'dividing line' concept as an aid to deciding the comparative effects of alternative emission control strategies (Dodge 1977b).

Originally the line was positioned to locate the 'apex' points of the ozone isopleths on the Dodge model and was described by the equation NMHC = 5.6 NOx (Dodge 1977b). The line is shown in Figure 2.10 and was believed to divide the diagram into two regions for control purposes (Dodge 1977a).

The first of these regions is described as predominantly hydrocarbon-rich and is characterised by values of the ratio NMHC/NOx exceeding 5.6. In this region reduction of nitrogen oxides was seen to offer the most effective means of ozone control. The second region is described as predominantly NOx-rich and is characterised by values of the ratio NMHC/NOx less than 5.6. In this region control of hydrocarbons was seen to offer the most effective means of ozone control.

Bilger (1977) has accepted the 'dividing line' concept and proposed that the criterion for selecting the dividing line be that the line describe the points for which fractional reductions in hydrocarbons yield the same reductions in ozone concentrations as the corresponding fractional reduction in nitrogen oxides. Using this more satisfactory criterion, the dividing line has the equation NMHC = 9.0 NOx. On this basis it was concluded that, where hydrocarbon and nitrogen oxides controls are equally costly, the oxidant control strategies required are: control of hydrocarbon emissions for an airshed characterised by a ratio below 9.0, and control of nitrogen oxides emissions for an airshed characterised by a ratio in excess of 9.0.

The use of the dividing line concept in an airshed involves three important assumptions which need to be examined. These are:

- the oxidant problem involves one-day irradiations of fresh emissions only;
- the Dodge model describes the ozone-precursor relationships for the one-day irradiations; and
- the optimum control strategy is taken as <u>either</u> control of hydrocarbons <u>or</u> control of NOx emissions. Simultaneous controls on both species are not examined.

In addition, problems arise in applying the dividing line concept when deciding what value of the ratio NMHC/NOx characterises the airshed. Thus the State Pollution Control Commission reported that the average ratio for the Sydney basin based on predicted mass emissions of NMHC and NOx is 9.3, whereas that obtained for the geographical areas of highest oxidant potential is 7.8 (State Pollution Control Commission of NSW 1977). These values of the ratio fall on different sides of the value of 9.0 used as the basis for the dividing line concept.

The difficulty of applying the dividing line concept is shown by examining sets of airshed data. Figure 5.3 shows the cumulative frequency distribution (Daly 1978) of NMHC/NOx based upon 836 sets of hydrocarbon and nitrogen oxides concentrations measured (Post and Bilger 1978) during the Sydney Oxidant Study for the years 1975-76 and 1976-77 by the Sydney University team. While the ratio is seen to have fallen from one year to the next, the distribution of airshed values straddles the dividing line value NMHC/NOx = 9.0. Thus in 1975-76 the ratio was less than 9.0 for about 62 per cent of the values, and for 1976-77 was less than 9.0 for 84 per cent of the values.

Such a straddling of the dividing line shows the difficulties inherent in regarding the policy options as either control of hydrocarbons or control of nitrogen oxides. This evidence, when compounded with the assumptions implicit in the dividing line concept, the chemical evidence (Chapter 2) suggesting the necessity for hydrocarbon controls and for optimising the ratio NHMC/NOx to high values, and the effectiveness of combined controls in evaluations based on Sydney airshed data, justifies full examination of the effectiveness of combinations of controls in reducing oxidants.

It is instructive to determine the cause of the decline in the overall NMHC/NOx ratio. The data of Post (1979) show that during the years of observation the distribution of maximum hydrocarbon concentrations remained unaltered and the distribution of maximum NOx concentrations showed an increase in the population of higher levels. From the 1975-76 year to the 1976-77 year the growth in median (50th percentile level) NOx concentrations were:

. over all sites,	28%
. at Sydney University site,	25%
. sites other than Sydney University	35%

The causes of this rapid increase need to be examined given that nitrogen dioxide is a toxic substance and there is the possibility that the effects of nitrogen dioxide and ozone are cumulative (Mizoguchi et al 1977) (Ehrlich et al 1977). Such an increase, if established, would have control implications, since it would show that emissions of hydrocarbons and NOx are not strongly coupled. It is also possible that the strategy of hydrocarbon only control if implemented would be less effective in reducing oxidant levels across the basin if NOx emissions are on this rising trend. In general terms the dividing line approach to the formulation of policy is made difficult because of the range of airshed concentratins of hydrocarbons and NOx which commonly occur in an airshed. This leads to a wide range of values in the distribution of the ratio NMHC/NOx. Thus the average value of this range does not necessarily reflect a sensible characterisation of the airshed. Additionally, the dividing line approach is an either-or approach and does not consider all the possible options.

The alternative approach of applying the two criteria of reducing hydrocarbons and also reducing NOx to optimise the airshed distribution of the ratios of NMHC to NOx across the airshed appears to contain guidelines which incorporate safeguards against known and potential effects of oxidant formation over the range of airshed conditions observed.

CONTROL MEASURES ADOPTED

Some control of oxidant levels is expected to result from the implementation of Australian Design Rule (ADR) 27A which came into effect on 1 July 1976, and which seeks to reduce emissions of non-methane hydrocarbon and nitrogen oxides from light duty motor vehicles (Australian Design Rules for Motor Vehicle Safety, 1976). Exactly what the reductions will be is uncertain, but likely figures are that average emissions of non-methane hydrocarbons could fall by about 25 to 50 per cent and nitrogen oxides could fall by up to 15 per cent (Daly 1977). There seems to be no agreement on the rate at which the vehicle emissions will deteriorate from the standards set by ADR 27A as the engines of vehicles built to these standards increase in age.

Emissions from stationary sources are either controlled or are in the process of being controlled to conform with standards recommended by the National Health and Medical Research Council (Proceedings of the Workshop on the Air Pollution 1977), although the rates of emissions of hydrocarbons and nitrogen oxides do not specifically relate to the objectives of an oxidants control program.

There is general acceptance that further controls on emissions will be necessary to meet the desired oxidant goals, although there are differences between authorities as to what these controls should be. There is still debate over whether oxidant control is best achieved by control of emissions of hydrocarbons, or control of emissions of both hydrocarbons and nitrogen oxides (State Pollution Control Commission of NSW 1977) (Daly 1977).

Impact of Australian Design Rule 27A

The major initiative in the program to control the concentrations of photochemical oxidants in Australian airsheds has been the implementation of the controls on motor vehicle emissions contained in ADR 27A. At present there is an interest in evaluating the impact of these controls.

In principle, the impact of the Rule can be calculated from the application of photochemical models. It is assumed that:

- one-day irradiations occur;
- ADR 27A leads to a 50 per cent reduction in hydrocarbon emissions and a 20 per cent reduction in NOx emissions, using ADR 27 as a basis for comparison;
- all vehicles meet the standards 9 years into the program; and
- the motor vehicle fleet increases in size at a rate of 3 per cent per annum over the period.

It is possible to apply the Dodge model to present airshed concentrations of precursors to estimate the potential ozone distribution in the ninth year of the program. If it is assumed that the present sets of hydrocarbon and nitrogen oxides concentrations averaged over the 0600 to 0900 hr period are due entirely to motor vehicles, the hydrocarbon concentrations in year 9 would be reduced to 67 per cent of present values, and nitrogen oxides would remain unchanged. The potential ozone distribution resulting from these assumptions is compared with the existing distribution in Figure 5.4. Such a change in emissions would give an airshed a potential for exceeding 0.20 parts per million of ozone, the level above which 78 per cent of health damage is said to occur (Figure 4.7), with a probability of 2.5 per cent compared with the present probability of about 15 per cent. In practice this analysis holds only to the extent to which the assumptions hold, which appears to be limited to an unknown proportion of all oxidant forming episodes.

In Sydney, air basin episodes such as that of 22 December 1976 involved a tail-pipe contribution to emissions of from 8 to 20 per cent (Hawke et al 1978). Additionally, oxidant episodes in the Parramatta valley are likely to involve recirculation of precursors to permit second-day irradiation (Hyde et al 1978a), while in Melbourne episodes have occurred in which multi-day irradiations operate (Le Roy et al 1976). The data required to permit some quantification of the ozone-effectiveness of the controls require a classification of oxidant episodes into groups by proportion of industrial and motor vehicle emissions and by length of irradiation times.

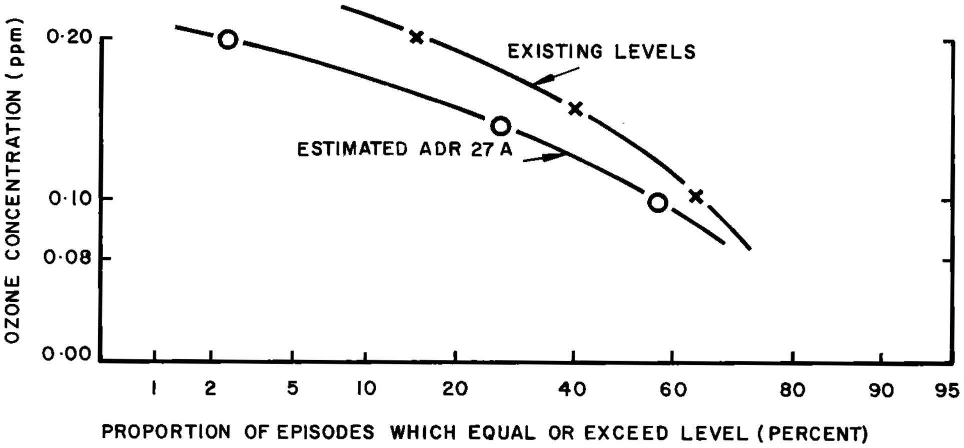


FIGURE 5.4
ESTIMATED EFFECTS OF ADR 27A CONTROLS ON
OXIDANT EPISODES ARISING FROM MOTOR VEHICLE EMISSIONS ONLY

CHAPTER 6 - CONCLUSIONS

The controllable factors which determine the intensity of an oxidant-forming episode are the ambient concentrations of hydrocarbons and nitrogen oxides. The amount of control necessary depends upon particular airshed conditions.

The extent to which the precursors form oxidants, as measured by ozone concentrations, depends upon the length of the period of solar irradiation. In broad terms this irradiation-time is determined by the meteorology of the air basin and needs to be determined for each airshed of concern.

The chemical factors described in Chapter 2 lead to the conclusion that the irradiation of 'aged' smog mixtures produces a different set of ozone-precursor relationships from those due to the irradiation of fresh mixtures. Thus the evaluation of the impact of the range of ambient concentrations of hydrocarbons and nitrogen oxides in an airshed requires a knowledge of the range of meteorological conditions in the airshed.

The range of meteorological conditions should be classified for airsheds of concern into categories which permit the assessment of the relative proportions of each of the following reaction conditions:

- partial-day or one-day irradiations of fresh emissions;
- partial-day or one-day irradiations of 'aged' mixtures;
- partial-day or one-day irradiations of mixtures of fresh emissions and 'aged' mixtures; and
- multi-day irradiations.

This compilation would also permit an evaluation of the effectiveness of selected controls on hydrocarbons such as those of the Californian Rule 66 (Chapter 2).

To complement these meteorological classifications, a set of ozone-precursor relationships needs to be developed for each of the meteorological categories which are found to be important in the airshed of concern. Such a data-base is a necessary adjunct to the evaluation of the emissions controls required to meet some selected oxidants goal. It follows that the necessary ozone-precursor relationships should be developed for the airsheds of concern.

The development of emissions controls requires the identification of the sources of oxidant-forming precursors. The trajectory analyses observed in Sydney (Chapter 4) show that some oxidant forming episodes may arise substantially from industrial emissions, while, one presumes, others are substantially due to motor vehicle emissions. Three broad classes of oxidant episodes may need to be recognised:

- episodes in which the precursors arise substantially from industrial emissions;
- episodes in which the precursors arise substantially from motor vehicle emissions; and
- episodes in which both industrial and motor vehicle emissions contribute to precursor concentrations.

Consideration of the chemical and meteorological factors involved in ozone formation lead to the conclusion that effective oxidant control requires limits to be placed on emissions of both hydrocarbons and nitrogen oxides (Chapters 3 and 4).

The required extent of control on the gross emissions of hydrocarbons and nitrogen oxides depends upon the oxidant goal which the community judges to be the best compromise between the adverse effects of air pollution and the advantages from minimal controls. The classical approach is to set an oxidant goal which represents a threshold which if crossed constitutes a threat to public health. There are indications that the physiological effects of the additivity of oxidants need to be considered in addition to the yardstick provided by the ozone concentration alone. At present the physiological evidence is not conclusive and further studies are required.

Until such studies provide the evidence necessary for choosing an oxidant goal, it seems prudent to set an interim goal which, while not too stringent, would represent a notable success for an oxidant abatement program.

An interim objective of a one-hour average maximum concentration of ozone of 0.15 parts per million may be regarded as a desirable goal. Such a temporary goal is sensible at the present time, since it marks the concentration at which health damage may become significant, and is greatly exceeded in Sydney and Melbourne, where the maximum ozone concentrations observed are about twice this value.

A recent approach to the problems of oxidant goals is the examination of health damage functions as described in Chapter 4. Progress made in this area to date suggests that the classical 'threshold-level' approach to the setting of oxidant goals does not lead to a correlation between the severity of episodes at alternative receptor areas and the magnitude of the health damage which occurs at the locations.

The analysis of health damage functions offers the advantage of describing the relative intensities of oxidant episodes in terms of per capita health damage. The Californian study reviewed in Chapter 4 clearly shows that the greatest gains in reducing the possibilities of health damage come from controlling the highest concentrations of oxidant.

Combining health damage functions with analyses of distributions of potential ozone permits the estimation of the total benefits and costs of control alternatives as far as health effects are concerned. It appears to be highly desirable that health damage functions appropriate to Australian conditions be developed.

In principle, the methodology for the development of materials-damage functions should parallel that of health damage. Such functions are necessary to permit assessment of the total benefits and costs of emission controls, and should be developed where possible.

The choice between alternative strategies for oxidant control requires information on the relative costings of alternative measures. At present the information on costs for the high degrees of control often discussed is extremely sketchy, and estimates can differ sufficiently to lead to different strategies being proposed. A definitive statement on the cost structures of emission controls across the major mobile and industrial sources is lacking at present.

Chapter 5 contains a discussion of two models which have been put forward to describe ozone-precursor relationships in the Sydney airshed. They are a modified version of a model by Dodge and a simplification of the modified Dodge model.

Both models are claimed to be validated by observed airshed values for which the ratios of concentrations of non-methane hydrocarbons and nitrogen oxides (NMHC/NOx) are between 5 and 20. It is shown that the relationship proposed between these compounds and ozone has not been established between these NMHC/NOx limits. Thus ozone levels observed in Sydney are not satisfactorily explained by these models. The likely reason for this is that the mechanisms associated with the formation of ozone in the airshed are more complex than those assumed in the modelling process.

It is also shown that the extrapolation of the models to evaluate ozone formation outside the NMHC/NOx range of 5 to 20 is not justified on present evidence. Consequently neither model can be used to predict the outcome of emission control strategies involving large proportional reductions in non-methane hydrocarbons only, since these strategies would have the effect of reducing the NMHC/NOx ratios of ozone precursor concentrations below the value of 5 which represents the lower limit of combined observations of non-methane hydrocarbons, nitrogen oxides and ozone concentrations in Sydney.

The analysis presented in Chapter 5 shows that in terms of present information Sydney's ozone concentrations appear to be equally dependent on changes in nitrogen oxide concentrations as on changes in non-methane hydrocarbon concentrations. Computations are discussed which support this contention.

Given the limitations of available models in defining the relationship between ozone precursors and ozone levels in Sydney, analysis of the models indicates that strategies based on the combined control of hydrocarbons and nitrogen oxide emissions can be as effective in reducing oxidant levels as strategies involving reduction of hydrocarbons only, and would require less stringent control standards to achieve this result. Such an approach does not require major extrapolation of the existing models beyond the regime for which they have been claimed to be validated or apply in order to predict the resultant reductions in ozone formation. These less stringent controls, since they incorporate controls on nitrogen oxides, are likely to confer additional benefits not available when hydrocarbons only are controlled.

APPENDIX A - SUMMARY OF ELEMENTARY REACTIONS USED IN PHOTOCHEMICAL MODELS

When a large set of chemical reactions goes to make up a chemical mechanism this can be translated into a set of complex, non-linear, first-order differential equations.

The differential equation for each chemical reaction shows the variation with respect to time of the concentration of any species C, and has the general form

$$\frac{dC}{dt} = (F - R)C$$

F is the summation of all rates forming C and R is the summation of all rates removing C. Appropriate values for F and R for each species need to be measured (Demerjian et al 1974) or determined by the methods of thermochemical kinetics (Benson 1968).

For the reactions which occur in the airshed the range of values for R and F differ by several orders of magnitude and accordingly the times associated with meaningful changes in the concentrations of species also differ by several orders of magnitude. The computational difficulties introduced by these differences are satisfactorily handled by use of the 'STIFF' routine (Gear 1971) (Gelinas 1972).

The photodissociation of NO_2 is the step which initiates the reaction sequence and is brought about by sunlight with wavelengths from 290-430 mm as described in Chapter 3. Calculation of the intensity of solar irradiation at the earth's surface needs to include the ability to vary latitude, time of year, time of day and wavelength across the spectral region of interest. The guidelines for such a model have been set down by Leighton (1961).

The set of differential equations which make up the chemical model can be solved by the methods of numerical integration.

This has been successfully carried out on reactions (1), (2) and (3).

$$NO_2 + h\nu \longrightarrow NO + O \qquad (1)$$
$$O + O_2 \longrightarrow O_3 \qquad (2)$$
$$O_3 + NO \longrightarrow O_2 + NO_2 \qquad (3)$$

In practical terms the vast number of chemical reactions becomes too unwieldy to process. Accordingly there is a need to reduce this number and to replace individual values of F, R and C by lumped parameters thereby making the model 'semi-empirical'. Thus Hecht et al have described the photochemistry by 50 reactions (Hecht et al 1974) and the General Research Corporation model (Allen and Bilger 1976) reduces the number to 16. Such empiricisms lead to great simplifications, but the representation of the reactivities of whole classes of hydrocarbons by a 'lumped parameter' is considered to make the model lose specificity and possibly integrity (Pitts et al 1975).

Because of the loss of specificity the integrity of the reduced model can be guaranteed only for the range of conditions for which it can be validated by airshed data. The validation amounts to a calibration in which the 'lumped parameters' are adjusted empirically to provide the best fit of measured data.

At present computer models based on a moderately detailed reaction mechanism have the capability of describing the processes occurring during laboratory simulations in smog chambers (Kerr et al 1972). The description of airshed data still appears remote, although the use of models and real airshed data to calculate frequency distributions of potential ozone offers a useful technique for comparing the relative effects of alternative strategies (Daly 1979).

The reaction mechanism and the rate constraints for the elementary reactions are given for the TNO models (Tables A.1 and A.2) and the Dodge model (Table A.3).

TABLE A.1 - REACTION SCHEME 1 - TNO MODEL 1

no.	k(25°C)(a)	Reaction(b)		
1	4.0 E-01	$NO_2 + \underline{h\nu}$	$\rightarrow$	$NO + O$
2	2.1 E+01	$O + O_2 + (M)$	$\rightarrow$	$O_3 + (M)$
3	2.5 E+01	$O_3 + NO$	$\rightarrow$	$NO_2 + O_2$
4	5.0 E-02	$O_3 + NO_2$	$\rightarrow$	$NO_3 + O_2$
5	1.3 E+04	$NO_3 + NO$	$\rightarrow$	$2\ NO_2$
6	5.6 E+03	$NO_3 + NO_2$	$\rightarrow$	N_2O_5
7	2.4 E+01	N_2O_5	$\rightarrow$	$NO_3 + NO_2$
8	5.0 E-06	$N_2O_5 + H_2O$	$\rightarrow$	$2\ HNO_3$
9	5.0 E-07	$NO + NO_2 + H_2O$	$\rightarrow$	$2\ HNO_2$
10	1.4 E-03	$2\ HNO_2$	$\rightarrow$	$NO + NO_2 + H_2O$
11	1.3 E-01	$HNO_2 + \underline{h\nu}$	$\rightarrow$	$OH + NO$
12	1.0 E-03	$O_3 + \underline{h\nu}$	$\rightarrow$	$O_2 + O^1D$
13	5.0 E-03	$O_3 + \underline{h\nu}$	$\rightarrow$	$O_2 + O$
14	8.7 E+10	$O(^1D) + (M)$	$\rightarrow$	$O + (M)$
15	1.0 E+05	$O(^1D) + O_3$	$\rightarrow$	$2\ O_2$
16	5.0 E+05	$O(^1D) + H_2O$	$\rightarrow$	$2\ OH$
17	1.8 E+03	$HO_2 + NO$	$\rightarrow$	$OH + NO_2$
18	8.8 E+03	$OH + NO_2 + (M)$	$\rightarrow$	$HNO_3 + (M)$
19	8.8 E+03	$OH + NO + (M)$	$\rightarrow$	$HNO_2 + (M)$
20	2.0 E+01	$HO_2 + NO_2$	$\rightarrow$	$HNO_2 + O_2$
21	4.0 E+03	$HO_2 + HO_2$	$\rightarrow$	$H_2O_2 + O_2$
22	2.0 E-04	$H_2O_2 + \underline{h\nu}$	$\rightarrow$	$2\ OH$
23	1.2 E+00	$HO_2 + O_3$	$\rightarrow$	$OH + 2\ O_2$
24	8.7 E+01	$OH + O_3$	$\rightarrow$	$HO_2 + O_2$
25	2.1 E+02	$OH + CO$	$\rightarrow$	$HO_2 + CO_2$
26	3.8 E+04	$O1 + OH + (O_2)$	$\rightarrow$	$ROHO_2$
27	1.8 E+03	$ROHO_2 + NO$	$\rightarrow$	$ROHO + NO_2$
28	3.0 E+05	$ROHO + (O_2)$	$\rightarrow$	$RCHO + CH_2O + HO_2$
29	3.8 E+03	$Pa + OH + (O_2)$	$\rightarrow$	$RO_2 + H_2O$
30	1.8 E+03	$RO_2 + NO$	$\rightarrow$	$RO + NO_2$
31	1.0 E+00	$RO + O_2$	$\rightarrow$	$\gamma RCHO + (1-\gamma)CH_2O + HO_2$
32	1.9 E-02	$O1 + O_3 + (O_2)$	$\rightarrow$	$OH + 0.98\ RCHO + 0.02\ CH_2O + 0.98\ HCO_3 + 0.02\ RCO_3$
33	3.0 E-03	$CH_2O + \underline{h\nu}$	$\rightarrow$	$CO + H_2$
34	3.0 E-04	$CH_2O + (O_2) + \underline{h\nu}$	$\rightarrow$	$HCO_3 + HO_2$
35	2.0 E-04	$RCHO + (O_2) + \underline{h\nu}$	$\rightarrow$	$HCO_3 + RO_2$
36	1.0 E+04	$CH_2O \bullet OH + (O_2)$	$\rightarrow$	$HCO_3 + H_2O$
37	1.0 E+04	$RCHO + OH + (O_2)$	$\rightarrow$	$RCO_3 + H_2O$
38	1.5 E+03	$RCO_3 + NO_2$	$\rightarrow$	PAN
39	2.4 E-02	PAN	$\rightarrow$	$RCO_3 + NO$
40	4.9 E+03	$RCO_3 + NO + (O_2)$	$\rightarrow$	$RO_2 + CO_2 + NO_2$
41	4.9 E+03	$HCO_3 + NO$	$\rightarrow$	$HO_2 + CO_2 + NO_2$
42	4.0 E+03	$HO_2 + RO_2$	$\rightarrow$	products
43	1.0 E+04	$HO_2 + HCO_3$	$\rightarrow$	products
44	1.0 E+04	$HO_2 + RCO_3$	$\rightarrow$	products
45	1.0 E+04	$HO_2 + ROHO_2$	$\rightarrow$	products
46	5.0 E-05	(W)	$\rightarrow$	NO_2
47	1.0 E-03	$(W) + O_3$	$\rightarrow$	products
48	5.0 E-04	(W) + PAN	$\rightarrow$	products
49	1.0 E+00	$(W) + HO_2$	$\rightarrow$	products
50	1.0 E+00	$(W) + RO_2$	$\rightarrow$	products
51	1.0 E+00	$(W) + ROHO_2$	$\rightarrow$	products
52	1.0 E+00	$(W) + HCO_3$	$\rightarrow$	products
53	1.0 E+00	$(W) + RCO_3$	$\rightarrow$	products

(a) Rate constant in units of $ppm^{-1}\ min^{-1}$ unless otherwise indicated.
(b) *Compounds within brackets do not determine kinetics*

Note: 4.0 E-01 = 4.0×10^{-1}
W = wall, 01 = olefin, PAN = peroxyacetyl nitrate, Pa = parafin aliphatic hydrocarbon,
M = inert third body molecule (N_2 or O_2).

TABLE A.2 - REACTION SCHEME 2 - TNO MODEL 2

no.	k(25 °C)$^{(a)}$	Reaction$^{(b)}$		
1	5.0×10^{-1}	NO_2 + $\underline{h\nu}$	⟶	$NO + O$
2	$3.8 \times e^{510/T}$	$O + O_2 + (M)$	⟶	$O_3 + (M)$
3	$1.4 \times 10^3 e^{-1200/T}$	$O_3 + NO$	⟶	$NO_2 + O_2$
4	1.3×10^4	$O + NO_2$	⟶	$NO + O_2$
5	5.0×10^{-2}	$O_3 + NO_2$	⟶	$NO_3 + O_2$
6	1.3×10^4	$NO_3 + NO$	⟶	$2\ NO_2$
7	$1.8 \times 10^2 e^{1030/T}$	$NO_3 + NO_2$	⟶	N_2O_5
8	$3.4 \times 10^{16} e^{-10600/T}$	$N_2O_5 + (M)$	⟶	$NO_3 + NO_2 + (M)$
9	5.0×10^{-6}	$N_2O_5 + H_2O$	⟶	$2\ HNO_3$
10	2.0×10^{-7}	$NO + NO_2 + H_2O$	⟶	$2\ HNO_2$
11	1.4×10^{-3}	$2\ HNO_2$	⟶	$NO + NO_2 + H_2O$
12	1.6×10^{-1}	HNO_2 + $\underline{h\nu}$	⟶	$OH + NO$
13	$2.2 \times 10^2 e^{1110/T}$	$NO_2 + OH + (M)$	⟶	$HNO_3 + (M)$
14	$2.2 \times 10^2 e^{1110/T}$	$NO + OH + (M)$	⟶	$HNO_2 + (M)$
15	2.1×10^2	$CO + OH + (O_2)$	⟶	$CO_2 + HO_2$
16	2.0×10^1	$HO_2 + NO_2$	⟶	HO_2NO_2
17	$8.0 \times 10\ e^{-1250/T}$	$HO_2 + O_3$	⟶	$OH + 2\ O_2$
18	1.8×10^3	$HO_2 + NO$	⟶	$OH + NO_2$
19	$2.5 \times 10^4 e^{-540/T}$	$2\ HO_2$	⟶	$H_2O_2 + O_2$
20	2.0×10^{-3}	H_2O_2 + $\underline{h\nu}$	⟶	$2\ OH$
21	3.8×10^4	$Ol + OH + (O_2)$	⟶	$ROHO_2$
22	$1.1 \times 10\ e^{-1900/T}$	$Ol + O_3 + (O_2)$	⟶	$OH + 0.98\ RCHO + 0.02\ CH_2O$ $+ 0.98\ HCO_3 + 0.02\ RCO_3$
23	3.5×10^3	$Ol + O + (O_2)$	⟶	$0.5\ RCO_3 + 0.5\ HCO_3$
24	8.0×10^3	$Ar + OH + (O_2)$	⟶	$ROHO_2$
25	3.8×10^3	$Pa + OH + (O_2)$	⟶	$RO_2 + HO_2$
26	1.8×10^3	$ROHO_2 + NO + (O_2)$	⟶	$NO_2 + RCHO + CH_2O + HO_2$
27	1.8×10^3	$RO_2 + NO$	⟶	$RO + NO_2$
28	1.0	$RO + (O_2)$	⟶	$0.5\ RCHO + 0.5\ CH_2O + HO_2$

TABLE A.2 (CONT'D) - REACTION SCHEME 2 - TNO MODEL 2

no.	k(25°C)[(a)]	Reaction[(b)]		
29	8.0×10^{-4}	$CH_2O + \underline{h\nu} + (O_2)$	⟶	$HCO_3 + HO_2$
30	7.0×10^{-3}	$CH_2O + \underline{h\nu}$	⟶	CO + (M)
31	1.0×10^{-3}	$RCHO + \underline{h\nu} + (O_2)$	⟶	$RO_2 + HCO_3$
32	1.0×10^{4}	$CH_2O + OH + (O_2)$	⟶	$HCO_3 + H_2O$
33	1.0×10^{4}	$RCHO + OH + (O_2)$	⟶	$RCO_3 + H_2O$
34	4.9×10^{3}	$HCO_3 + NO + (O_2)$	⟶	$HO_2 + NO_2 + CO_2$
35	4.9×10^{3}	$RCO_3 + NO + (O_2)$	⟶	$RO_2 + NO_2 + CO_2$
36	1.5×10^{3}	$RCO_3 + NO_2$	⟶	PAN
37	$1.5 \times 10^{17} e^{-12900/T}$	PAN	⟶	$RCO_3 + NO_2$
38	1.0×10^{4}	$HCO_3 + HO_2$	⟶	M
39	1.0×10^{4}	$RCO_3 + HO_2$	⟶	M
40	4.0×10^{3}	$RO_2 + HO_2$	⟶	M
41	4.0×10^{3}	$ROHO_2 + HO_2$	⟶	M
42	4.0×10^{3}	$2\ ROHO_2$	⟶	M
43	1	HO_2 + aerosol	⟶	M
44	1	$ROHO_2$ + aerosol	⟶	M
45	1	HCO_3 + aerosol	⟶	M
46	1	RCO_3 + aerosol	⟶	M
47	1×10^{-3}	O_3 + aerosol	⟶	M
48	1×10^{-3}	PAN + aerosol	⟶	M
49	1×10^{-3}	NO_2 + aerosol	⟶	M
50	1×10^{-3}	H_2O_2 + aerosol	⟶	M
51	1×10^{-3}	CH_2O + aerosol	⟶	M
52	1×10^{-3}	RCHO + aerosol	⟶	M
53	1×10^{-4}	O_3 + ground	⟶	M
54	5×10^{-5}	PAN + ground	⟶	M
55	1×10^{-4}	NO_2 + ground	⟶	M
56	1×10^{-4}	H_2O_2 + ground	⟶	M

TABLE A.2 (CONT'D) - REACTION SCHEME 2 - TNO MODEL 2

no.	k(25°C) [(a)]	Reaction [(b)]		
57	1×10^{-4}	CH_2O + ground	→	M
58	1×10^{-4}	RCHO + ground	→	M
59	$6.2 \times 10^{17} e^{-11700/T}$	HO_2NO_2	→	$HO_2 + NO_2$

(a) Rate constant in units of $ppm^{(1-q)}$ min^{-1} where q is reaction order.
(b) Compounds within brackets do not determine kinetics.

Note: Ar = aromatic hydrocarbon, Pa = parafin aliphatic hydrocarbon, PAN = peroxyacetyl nitrate, 01 = olefin, M = inert third body molecule (N_2 or O_2).

Source: Nieber H., van den Eikhoff J. and Whittebrood L.J.J., 1978.

TABLE A.3 - REACTION MECHANISM USED TO GENERATE O_3 ISOPLETHS

No.	Reaction		Rate Constant[(a)]
1	$NO_2 + h\nu$	$\rightarrow NO + O(^3P)$	k_{vary}
2	$O(^3P) + O_2 + (M)$	$\rightarrow O_3 + M$	2.0×10^{-5} $ppm^{-2}min^{-1}$
3	$O_3 + NO$	$\rightarrow NO_2 + O_2$	2.5×10^{1}
4	$NO_2 + O_3$	$\rightarrow NO_3 + O_2$	4.5×10^{-2}
5	$NO_2 + O\ (^3P)$	$\rightarrow NO + O_2$	1.3×10^{4}
6	$NO_3 + NO$	$\rightarrow 2\ NO_2$	1.3×10^{4}
7	$NO_2 + NO_3$	$\rightarrow N_2O_5$	5.6×10^{3}
8	N_2O_5	$\rightarrow NO_2 + NO_3$	22.0 min^{-1}
9	$N_2O_5 + H_2O$	$\rightarrow 2\ HNO_3$	2.5×10^{-6}
10	$NO + NO_2 + H_2O$	$\rightarrow 2\ HONO$	1.0×10^{-9} $ppm^{-2}min^{-1}$
11	$2\ HONO$	$\rightarrow NO + NO_2 + H_2O$	1.0×10^{-3}
12	$HONO + h\nu$	$\rightarrow OH + NO$	k_{vary}
13	$OH + NO_2 + (M)$	$\rightarrow HNO_3\ (M)$	8.0×10^{3}
14	$OH + NO + (M)$	$\rightarrow HONO\ (M)$	3.0×10^{3}
15	$HO_2 + NO$	$\rightarrow NO_2 + OH$	1.2×10^{3}
16	$HO_2 + HO_2$	$\rightarrow HOOH + O_2$	8.4×10^{3}
17	$HOOH + h\nu$	$\rightarrow 2\ OH$	k_{vary}
18	$O_3 + h\nu$	$\rightarrow O(^1D)$	k_{vary}
19	$O_3 + h\nu$	$\rightarrow O(^3P)$	k_{vary}
20	$O(^1D) + M$	$\rightarrow O(^3P) + M$	8.7×10^{4}
21	$O(^1D) + H_2O$	$\rightarrow 2\ OH$	5.1×10^{5}
22	$OH + O_3$	$\rightarrow HO_2 + O_2$	8.4×10^{1}
23	$O_3 + HO_2$	$\rightarrow OH + 2\ O_2$	2.4
24	PROP + OH	$\rightarrow$ ADD	2.5×10^{4}
25	ADD + NO	$\rightarrow X + NO_2$	1.0×10^{3}

TABLE A.3 (CONT'D) - REACTION MECHANISM USED TO GENERATE O_3 ISOPLETHS

No.	Reaction	Rate Constant$^{(a)}$
26	ADD + ADD → 2 X	1.2×10^{4}
27	ADD + MeO_2 → X + MeO	1.0×10^{3}
28	ADD + C_2O_2 → X + C_2O	1.0×10^{3}
29	ADD + C_3O_2 → X + C_3O	1.0×10^{3}
30	ADD + C_4O_2 → X + C_4O	1.0×10^{3}
31	ADD + ScO_2 → X + ScO	1.0×10^{3}
32	X → HCHO + ALD2 + HO_2	1.0×10^{5} min^{-1}
33	PROP + O_3 → OH + HO_2 + ALD2	8.0×10^{-3}
34	PROP + O_3 → OH + C_2O_3 + HCHO	8.0×10^{-3}
35	BUT + OH → ScO_2	1.8×10^{-3}
36	BUT + OH → C_4O_2	1.8×10^{3}
37	NO + C_4O_2 → NO_2 + C_4O	1.8×10^{3}
38	NO + ScO_2 → NO_2 + ScO	1.8×10^{3}
39	NO + C_3O_2 → NO_2 + C_3O	1.8×10^{3}
40	NO + C_2O_2 → NO_2 + C_2O	1.8×10^{3}
41	NO + MeO_2 → NO_2 + MeO	1.8×10^{3}
42	C_4O → HCHO + C_3O_2	7.5×10^{4} min^{-1}
43	ScO → ALD2 + C_2O_2	1.0×10^{5} min^{-1}
44	C_3O → HCHO + C_2O_2	8.0×10^{3} min^{-1}
45	C_2O → HCHO + MeO_2	4.0×10^{3} min^{-1}
46	C_4O + O_2 → ALD4 + HO_2	7.0×10^{-1}
47	ScO + O_2 → MEK + HO_2	1.4
48	C_3O + O_2 → ALD3 + HO_2	5×10^{-1}
49	C_2O + O_2 → ALD2 + HO_2	4×10^{-1}

TABLE A.3 (CONT'D) - REACTION MECHANISM USED TO GENERATE O_3 ISOPLETHS

No.	Reaction			Rate Constant[(a)]
50	MeO + O_2	→	HCHO + HO_2	4×10^{-1}
51	HCHO + $h\nu$	→	stable products	k_{vary}
52	HCHO + $h\nu$	→	2 HO_2	k_{vary}
53	HCHO + OH	→	HO_2	1.5×10^4
54	ALD2 + $h\nu$	→	stable products	k_{vary}
55	ALD2 + $h\nu$	→	MeO_2 + HO_2	k_{vary}
56	ALD2 + OH	→	C_2O_3	1.5×10^4
57	ALD3 + $h\nu$	→	stable products	6.0×10^{-5} min^{-1}
58	ALD3 + $h\nu$	→	C_2O_2 + HO_2	2.5×10^{-3} min^{-1}
59	ALD3 + OH	→	C_3O_3	4.5×10^4
60	ALD4 + $h\nu$	→	stable products	6.0×10^{-5} min^{-1}
61	ALD4 + $h\nu$	→	C_3O_2 + HO_2	1.9×10^{-3} min^{-1}
62	ALD4 + OH	→	C_4O_3	4.5×10^4
63	C_4O_3 + NO	→	C_3O_2 + NO_2	8.0×10^2
64	C_3O_3 + NO	→	C_2O_3 + NO_2	8.0×10^2
65	C_2O_3 + NO	→	MeO_2 + NO_2	8.0×10^2
66	C_4O_3 + NO_2	→	PAN	1.0×10^2
67	C_3O_3 + NO_2	→	PAN	1.0×10^2
68	C_2O_3 + NO_2	→	PAN	1.0×10^2
69	C_4O_2 + HO_2	→	stable products	4.0×10^3
70	C_3O_2 + HO_2	→	stable products	4.0×10^3
71	ScO_2 + HO_2	→	stable products	4.0×10^3
72	C_2O_2 + HO_2	→	stable products	4.0×10^3
73	MeO_2 + HO_2	→	stable products	4.0×10^3

TABLE A.3 (CONT'D) - REACTION MECHANISM USED TO GENERATE O_3 ISOPLETHS

No.	Reaction	Rate Constant[(a)]
74	$C_4O_3 + HO_2 \longrightarrow$ stable products	4.0×10^3
75	$C_3O_3 + HO_2 \longrightarrow$ stable products	4.0×10^3
76	$C_2O_3 + HO_2 \longrightarrow$ stable products	4.0×10^3

Note: M = inert third body molecule (N_2 or O_2).

(a) Units of $ppm^{-1}min^{-1}$ unless otherwise indicated.

Symbol	Definition
k_{vary}	Diurnal 1-hour average photolytic rate constant
PROP	C_3H_6
BUT	$n\text{-}C_4H_{10}$
ADD	$CH_3CH(OH)CH_2OO$
X	$CH_3CH(OH)CH_2O$
MeO_2	CH_3O_2
C_2O_2	$CH_3CH_2O_2$
C_3O_2	$CH_3CH_2CH_2O_2$
C_4O_2	$CH_3CH_2CH_2CH_2O_2$
ScO_2	$CH_3CH(O_2)CH_2CH_3$
ALD2	CH_3CHO
ALD3	CH_3CH_2CHO
ALD4	$CH_3CH_2CH_2CHO$
C_2O_3	CH_3CO_3
C_3O_3	$CH_3CH_2CO_3$
C_4O_3	$CH_3CH_2CH_2CO_3$

Source: Dodge 1977a.

APPENDIX B - EMISSION CONTROL COST MODELS

GENERAL COMMENTS

A major consideration in the selection of the appropriate emission controls for oxidant abatement is the cost of the proposed program. In principle it is possible to make reasonable estimates of the effectiveness of proposed controls in reducing oxidants by the use of photochemical models. It then becomes desirable to have the means of evaluating the relative costs of implementing the various control alternatives. In practice, the estimation of costs of controls across the range of emitters in an airshed appears to be difficult.

It does appear, however, that there is a general agreement on the way in which relative costs of reductions of emissions vary with the degree of emission control. Thus the US National Academy of Sciences use a cost model which shows that costs increase with an exponential or power series dependence upon the degree of fractional reduction in emissions (Pierrard 1974). In a study of the economics and technology of the control of hydrocarbon emissions from stationary sources Bowey showed a similar dependence of cost upon the proportion of total reduction in emissions (Bowey 1977).

These cost models have implications for the costing of the control measures for oxidant control. At present there is controversy over whether controls should be exerted through limiting hydrocarbon emissions only, or through less stringent reductions on both hydrocarbons and nitrogen oxides. Where the rate of increase of costs of controls increases sharply with the percentage reduction in emissions it is clear that for any percentage reduction in emissions of one precursor there is a corresponding smaller percentage reduction in emissions of both precursors to be had for the same cost.

In addition, it follows that the higher the percentage reduction of one precursor sought, the more competitive becomes the option of joint controls. Thus for airsheds where a high degree of control of one precursor is sought - e.g. reductions of hydrocarbons between 75 and 86 per cent have been proposed for Sydney (Bilger 1978) - smaller joint reductions of both precursors merit attention on cost grounds.

The results of the estimation of the relative costs of alternative reduction programs depend upon the cost model used. At present cost models appear to be insufficiently developed to enable any but the most crude comparisons of the costs of projected controls.

COST MODELS FOR SYDNEY

Recently, from consideration of the Dodge model for ozone production, and the assumption that the relative cost of controlling nitrogen oxides emissions are twice those of controlling emissions of hydrocarbons, Bilger has claimed that control of hydrocarbons is the optimum control strategy for photochemical oxidant (Bilger 1978).

The following assumptions are inherent in the proposal:

- the oxidants problem is one of ozone formed during one-day irradiations of fresh emissions;
- NOx controls are twice as costly as those of hydrocarbons;
- the choice of controls is intended to limit either hydrocarbons or NOx emissions; and
- a cost model which is unspecified.

The proposal does not consider the possibility of less stringent joint controls, nor takes into account the increasing rate at which costs increase with the degree of reduction in emissions. No estimation of benefits is included.

Because of the importance of the conclusion of Bilger, it is pertinent to examine the result for its sensitivity to a second cost model. Such a sensitivity test is given by considering an example. The following assumptions are made in the second cost model:

- following Bilger, costs of nitrogen oxides controls are taken as twice those of hydrocarbon controls for the same degree of fractional reduction; and

- costs of control are taken as increasing with a first-order dependence upon the fractional reduction in emissions for both hydrocarbon and nitrogen oxides controls. This rate of cost increase with extent of control rises less sharply than the near-exponential rate used by Pierrard.

On the basis of these assumptions, it follows that a reduction of about 50 per cent in emissions of hydrocarbons has the same cost as a reduction of 33 per cent in both hydrocarbons and nitrogen oxides emissions.

Analysis of airshed data shows that each of these reduction programs would be equally as effective in controlling ozone formed in one-day irradiations as calculated by the modified Dodge model (Daly 1979).

Daly and Fuller (1979) have examined the relative effectiveness of equal joint controls versus hydrocarbon only controls in reducing violations of various ozone concentrations based on Sydney airshed data reported (Post 1979a) for the oxidant seasons 1975-76 and 1976-77. These comparisons were based on the empirical airshed model (Chapter 5). The results show that both joint reductions and reductions of hydrocarbons only can lead to the same distribution of ozone formed in the airshed. These results clearly show that the choice of the optimum control strategy is most sensitive to the cost model chosen, where it becomes necessary to evaluate costs of more stringent hydrocarbon controls only versus that of less stringent joint controls.

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