BTE Publication Summary

Photochemical Pollution in Australian Airsheds

Occasional Paper

This report examines the factors which control the formation of photochemical smog in urban airsheds and reviews the present situation which exists in major Australian cities.





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BUREAU OF TRANSPORT ECONOMICS

PHOTOCHEMICAL POLLUTION IN AUSTRALIAN AIRSHEDS

DR. N.J. DALY

DEPARTMENT OF CHEMISTRY

AUSTRALIAN NATIONAL UNIVERSITY

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FOREWORD

Air pollution is a recognised problem in Australia's major urban areas. While increasing attention is being paid to controlling emissions from motor vehicles, there is a growing awareness of the need to measure and control photochemical smog precursors originating from all sources.

This report examines the effect of the type of control measure currently in force against a background of smog chemistry and the most recent research results. The report was prepared by Dr N.J. Daly of the Department of Chemistry, Australian National University, and was supervised by Mr L. Lawlor.

The BTE does not necessarily accept the findings of the Consultant's report, but considers that the information will be of value to many people concerned with air pollution control.

R.H. HEACOCK

Acting Assistant Director Transport Engineering Branch

Bureau of Transport Economics Canberra April, 1977

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SUMMARY

This report examines the factors which control the formation of photochemical smog in urban airsheds and reviews the present situation which exists in major Australian cities.

The onset of photochemical smog leads to substantial economic losses. These losses result from the damages to materials such as rubber based goods and certain synthetic textiles, and damages to a number of economically important crops such as leafy row vegetables and citrus plants. In addition, the economic costs of implementing strategies for controlling the intensity of the smogs are substantial.

Certain of the constituents formed in a photochemical smog pose a threat to the health of the public. Thus the standards set by such bodies as the Japanese Government, the US Federal Government, and the World Health Organisation (WHO) are designed to protect the health of the Public.

Photochemical smog is caused by the action of sunlight on mixtures of hydrocarbons and oxides of nitrogen. The main sources of these precursors are the emissions from the exhaust systems of motor vehicles. Accordingly policies aimed at controlling the occurrence of photochemical smogs seek to control the exhaust emissions from motor vehicles. At present in Australia the major controls are embodied in Australian Design Rule 27A.

The chemistry leading to the formation of photochemical smog is extremely complex and leads to the production of a number of toxic materials which are collectively termed oxidant. The major oxidant formed is ozone and the degree of advancement of the photochemical processes is measured by the concentration of ozone formed in the airshed. The complexity of the chemistry is such that the dependence of ozone formation on the concentration of each of the precursors,

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hydrocarbons and oxides of nitrogen, is extremely non-linear. The result of this non-linearity is that there are conditions for which a reduction of, say 50 percent, in the emissions of either hydrocarbons or oxides of nitrogen could have little effect on the quantity of ozone formed. Thus the introduction of effective control policies requires a detailed knowledge of the dependence of ozone formation upon the concentrations of the precursors, hydrocarbons and nitrogen oxides.

Laboratory simulations of photochemical smog formation are carried out in smog chambers in order to provide the necessary understanding of these ozone-precursor relationships. The results of these studies are reviewed in this work and their implications for Australian airsheds are discussed. The results appear to indicate that the beneficial aspects of ADR27A are likely to be minimal, and point up the strong need to develop smog chamber studies which examine ozoneprecursor relationships for conditions appropriate to Australian cities as an aid to policy decisions.

CHAPTER 1 - THE NATURAL HISTORY OF PHOTOCHEMICAL SMOG

Photochemical smog was first observed in Los Angeles in the mid-1940's and has since been a continuing problem. The phenomenon has now occurred in major cities throughout the United States and the rest of the Western world, and photochemical incidents of sufficient intensity to cause concern for public health have been experienced in Mexico City, major cities in Canada and Western Europe, the United Kingdom and Japan. In Australia, Sydney and Melbourne often experience photochemical smog.

The immediate effects observed during photochemical smog are eve and throat irritation⁽¹⁾ damage to vegetation^{(2),(3)} damage to materials such as rubber products $^{(3)}$ and reduced visibility. These effects have been established ^{(3),(4)} as due to pollutants which are formed in the airshed as a result of chemical reactions initiated in the airshed by the action of sunlight on the exhaust emissions from motor vehicles under special meteorological conditions.

The meteorological conditions required are those which provide a stable air mass to enable the reactions to proceed under conditions of sunshine. These conditions are found when there is a subsidence inversion accompanying a clear sky during the daylight period.

⁽¹⁾ Richardson, N.A. and Middleton, W.C. Evaluation of Filters for Removing Irritants from Polluted Air, University of California, Dept of Engineering, Los Angeles. Report No. 57-43, 1957. Advances in Environmental Science, Wiley Interscience, J. Wiley & Sons, New York, NY, 1971, Vol. 2 (2)

⁽³⁾ Air Quality Criteria for Photochemical Oxidants, U.S. National Air Poll. Control Administration, Publication No. AP-63, 1970

Haagen-Smit, A.J. Ind Eng. Chem., 1952, 44, 1342 (4)

PHOTOCHEMICAL OXIDANT

The constituents of photochemical smog which have the adverse effects are known collectively as oxidant or photochemical oxidant. This name is derived from the fact that they chemically oxidise solutions of potassium iodide to iodine⁽¹⁾, and this reaction formed the basis for their chemical analysis.

The oxidant which occurs in an airshed is mainly made up of $ozone, (0_3)$, nitrogen dioxide $(N0_2)$, peroxyacetyl nitrate (PAN) together with smaller quantities of aldehydes and alkenes. In practise the efficiency with which these various species react with potassium iodide varies from one oxidant to the next. Ozone is capable of oxidising potassium iodide at 100 percent efficiency whereas peroxyacetyl nitrate, and species such as nitrogen dioxide oxidise potassium iodide solution at about only 15 percent efficiency.

Apart from nitrogen dioxide, ozone is normally the major component present in a polluted airshed. Since the efficiency with which ozone oxidises potassium iodide solution is so much greater than that of other species it represents 90 percent or more of the total oxidising capacity of the sample of polluted air.

The traditional analytical method determines total oxidant without separating individuals. Specific methods now available measure ozone and nitrogen dioxide individually. Accordingly it is now practice to report individual oxidants. Since the concentration of ozone is essentially the same as

(1) Manahan, S.E. <u>Environmental Chemistry</u> Willard Grant Press, Boston, Massachusetts, 1975, pp.387 et seq.

that of the total oxidant, it is commonplace to use ozone concentration rather than that of oxidant.

ECONOMIC COSTS OF PHOTOCHEMICAL SMOG

Substantial economic losses result from occurrences of photochemical smog. Oxidant causes recognisable lesions in plants⁽¹⁾ and damage is caused to field crops, ornamental plants, and forest trees. Citrus fruits, leafy row vegetables and forest evergreens are particularly susceptible. For example in an experimental orange grove 56km east of Los Angeles citrus trees exposed to ambient air produce only half as much fruit as trees grown in the same air from which oxidants have been removed.⁽²⁾ The cost of plant damage in the State of California exceeded \$US100 million annually in 1970⁽²⁾

Occurrence of such oxidant damage need not be frequent in order to be significant. One episode is enough to damage an entire crop. For instance, on July 17 and 18, 1959,photochemical smog caused \$US5 million damage to tobacco crops in Connecticut⁽³⁾

A number of economically important products are sensitive to photochemical pollutants. Thus textile fabrics such as cotton, acetate, nylon and polyester suffer varying degrees of damage, while both natural and synthetic rubbers are highly sensitive to ozone⁽⁴⁾ Such materials damage has been reviewed by the U.S. Department of Health, Education and Welfare⁽⁵⁾

(1)	Advances in Environmental Science Wiley Interscience J. Wiley & Sons Inc. New York, NY, 1971, Vol.2
(2)	Larsen, R.I., J. Air Poll. Control Assoc. 1970, 20, 214
(3)	Heggistad, H.E. J. Air Poll. Control Assoc. 1966, 11, 691
(4)	Andrews, J.H. J. Rubber Chem. Technol, 1967, 40, 635
(5)	U.S. National Air Poll. Control Administration, op.cit.

The economic costs of oxidant episodes can be considered to be made up of a "damage" cost and an "avoidance" cost. These costs are most difficult to establish, but some national figures are available.

In the United States the national estimate of damage by photochemical oxidant has been reported⁽¹⁾ to range from \$0.5 to \$1.5 thousand million while the cost for implementing the program to control all air pollution has been evaluated at \$2.4 thousand million for 1972 and \$4 thousand million for 1973. Oxidant controls represent only a proportion of these total control costs.

In Japan the costs for implementing the 1972 abatement policies for oxidant was Yen 3.6 thousand million per year. Costs for the control devices themselves are not given.

HEALTH HAZARDS OF PHOTOCHEMICAL SMOG

In addition to causing property and plant damage oxidant is considered to have measurable adverse effects on public health. Thus both the Japanese Government and the U.S. Federal Government which have set legal standards governing ambient levels of oxidant have done so on the basis of health considerations.

In Japan evidence of acute disability to healthy persons became apparent during a photochemical episodes in Tokyo on July 18, 1970. Symptons observed were eye-irritation, respiratory troubles, and in many cases, numbress of the extremities. The episode occurred under conditions now recognised as a classical example of meteorological conditions favouring the creation of photochemical smog. The

⁽¹⁾ Guicherit R, Proceedings of the Symposium on Occurrence and Control of Photochemical Pollution, Clean Air Society of Australia and New Zealand, Sydney, 1976

incident led the Japanese authorities to undertake a program of epidemiological studies which led to the adoption of a standard for oxidants which states that a one-hour average concentration of oxidants exceeding 0.06ppm should not occur with a frequency greater than once per year.

The U.S. Federal Standard resulted from epidemiological studies which have been reviewed by the U.S. Department of Health Education and Welfare⁽¹⁾ The standard was chosen on the basis of studies which provided data on the relationship of oxidant levels to eye-irritation,⁽²⁾ impaired athletic performances⁽³⁾ ⁽⁴⁾ and the onset of asthmatic attacks⁽⁵⁾ The standard set as a legal requirement is that a one-hour average concentration of ozone of 0.08ppm is not to be exceeded more than once per year. This standard is considered necessary to protect the health of the community.

It is pertinent to note that the characteristic reduction in visibility associated with photochemical smog does not usually occur until oxidant concentrations are well in excess of those levels set as Public Health Standards. Since the term photochemical smog is generally applied to conditions for which visibility is reduced to a few kilometres it follows that standards set to safeguard Public Health are well exceeded during photochemical smogs.

- (1) U.S. National Air Poll. Control Administration, op.cit.
- (2) Richardson N.A. and Middleton, W.C., op.cit
- (3) Wayne, W.S., Wherle, P.F. and Carroll R.E. J. Amer. Med Assoc., 1967, 199, 901
- (4) Hasselblad, V., Lorimore, G. and Nelson, C.J. unpublished report quoted in <u>J.Air Poll. Control Assoc</u>. 1971, <u>21</u>, 544
- (5) Schoetlinn, C.E. and Landau, E. Air Pollution and Asthmatic Attacks in the Los Angeles Area, Public Health Reports, 1961, 76, 545

PRECURSORS TO PHOTOCHEMICAL SMOG

Photochemical oxidant has been shown to be formed in the airshed by the action of sunlight on mixtures of nitrogen oxides (NO_x) and non-methane hydrocarbons (HC). (1) (2) The overall process can be written as

 NO_x + SUNLIGHT + HC \longrightarrow OXIDANTS (incl O_3 , PAN) From this equation it can be seen that NO_x and hydrocarbons are the controllable precursors to oxidant formation. Thus the task for an oxidant abatement program is to limit the quantities of these precursors in the airshed to those values which do not form unacceptable levels of oxidant in the meteorological conditions prevailing in the particular airshed.

NEED FOR ABATEMENT STRATEGIES IN AUSTRALIA

The occurrences of photochemical smogs in Sydney and Melbourne have led to the initiation of abatement programs in Australia. In Sydney for example oxidant concentrations have been reported to exceed the WHO limits on 127 days in a year.⁽³⁾ The problem however, is more widespread.

Measurements carried out on an occasional basis rather than as part of a continuous air monitoring program have shown ozone concentrations for both Brisbane and Perth which exceed WHO and U.S. Federal Standards.⁽⁴⁾ In a study carried out for the Department of the Capital Territory

- (1) Haagen-Smit, A.J. op.cit.
- (2) Haagen-Smit, A.J. and Fox, M.M. J. Air Poll. Control Assoc., 1954, 4, 105
- (3) Canberra Times, November 25, 1976
- (4) Daly, N.J. and Steele, L.P. <u>Air Quality in Canberra</u>, Report to the Department of the Capital Territory, Canberra, 1976.

over an eight-month period in 1973-1974 a continuous air monitoring program showed that the relatively small city of Canberra experienced ozone concentrations which equalled the one-hour average set by WHO and the Japanese Government as Health Standards.⁽¹⁾ The forecast for the National Capital is that U.S. and WHO standards seem likely to be exceeded on a number of occasions by about 1980.

Some control of oxidant levels in cities is expected to result from legislation flowing from Australian Design Rule (ADR) No. 27A⁽²⁾ which came into effect on July 1, 1976 and which appears equivalent to the U.S. 1973 Light Duty Vehicle emission Standard. The regulation should lead to a reduction of about 15 percent in nitrogen oxides and about 50 percent in hydrocarbons. The expectation of improvement is based on the assumption that improvement results from any reduction in NO_X or hydrocarbons. However such is the complexity of the chemistry of oxidant formation that this apparently reasonable assumption is not always valid. The questions which need to be answered are:

- (i) to what extent, if any, is further NO_x control necessary,
- (ii) to what extent, if any, is further hydrocarbon control necessary.

Successful implementation of an oxidants abatement program requires accurate answers to these questions for Australian conditions.

- Daly, N.J. and Steele, L.P. <u>Air Quality in</u> <u>Canberra</u>, Report to the Department of the <u>Capital Territory</u>, Canberra, 1976.
- (2) Australian Design Rules for Motor Vehicle Safety, Commonwealth Department of Transport July, 1976.

PROPOSED SIMULATION STUDY AS A GUIDE TO POLICY FORMULATION.

An attractive goal in the implementation of an oxidants abatement program is the development of an "a priori" model which enables a computer simulation of the smog forming processes in any airshed. The application of such a model could enable Governments and planning authorities to evaluate the effects of alternative control strategies.

Thus the objectives of the study are to gain that knowledge of the photochemical and airshed processes necessary to enable the best possible decisions to be made in implementing oxidant control policies. The most complete description would be that provided by a computer model which quantifies the photochemical and airshed processes and accurately predicts oxidant concentrations. The tasks which such a model is required to carry out may be summarised as follows:

- (i) the model should be capable of "a priori" calculation of ambient concentrations of oxidant resulting from alternative control policies. For example it would be required to calculate the ozone concentration arising from, say, a proposal to reduce hydrocarbon emissions by 50 percent and NO_x emissions by 15 percent as in ADR27A, and to compare the result with those of an alternative proposal to reduce NO_x by 50 percent and leave hydrocarbons unchanged.
- (ii) standards for ozone and oxidant concentrations are set in terms of a one-hour average concentrations not to be exceeded more than once per year. For these standards the interest is not with maximum one-hour averages, but with the frequency with which these one-hour standards are exceeded. Accordingly the model should be able to calculate annual frequency distributions of one-hour averages.

- (iii) the model need not be concerned with great spatial resolution but does need considerable precision in predicting concentrations. This means that there may be no need to determine differences in concentration between one city block and the next, but that it must correctly calculate the oxidant concentration representative of say 2.5 sq.km of city. An uncertainty in concentration of 50 percent could represent failure. For example where an emergency level of 0.15 ppm oxidant is set for which certain industries must close, a model predicting 0.15 ppm where the true value would be an acceptable 0.10 ppm would have significant effects by the error.
- (iv) the model needs to describe Australian cities which presently have a problem and to describe growth centres which will develop a problem unless effective control strategies are introduced.
- (v) the model needs to be sufficiently simple to enable it to be used readily. The input data requirements should not be prohibitive.

In describing air quality in Canberra Daly and Steele⁽¹⁾ developed a simple planning model which calculated predicted annual frequency distributions for the Central business district and had minimal data requirements⁽²⁾.

- (1) Daly, N.J. and Steele, L.P. <u>Air Quality in Canberra</u> Report to the Department of the Capital Territory, Canberra, 1976.
- (2) Daly, N.J. and Steele, L.P. <u>A Predictive Model for</u> <u>Carbon Monoxide in Canberra</u>, Proceedings of the <u>Symposium on Air Pollution Diffusion Modelling</u>, Australian Environment Council, Canberra, 1976.

The complexity of the photochemical processes in the airshed is such that the adaptation of this model to the oxidants problem is inappropriate. The study did show⁽¹⁾ however, that the Canberra airshed has a number of advantages for the purposes of an oxidants study. These may be summarised as follows:

- Canberra has essentially no industrial sources of precursors to photochemical smog so that oxidants in the airshed are from motor vehicle emissions.
- (ii) the input of emissions is such that the airshed is poised at the point of exceeding WHO and U.S. Federal Standards for oxidants. Accordingly it represents the situation to which major cities should be reduced and at which growth centres should be halted.
- (iii) photochemical processes are established in the airshed.
- (iv) the dispersion of the precursors NO_x and hydrocarbons may be describable by the simple model⁽²⁾ used for carbon monoxide.

WORK PROGRAM FOR MODEL DEVELOPMENT

The computer model as described is a mathematical expression which calculates the concentrations of oxidant or ozone in airsheds as a function of a number of controlling parameters

- Daly, N.J. and Steele, L.P. <u>Air Quality in Canberra</u> Report to the Department of the Capital Territory, Canberra, 1976.
- (2) Daly, N.J. and Steele, L.P. <u>A Predictive Model for</u> <u>Carbon Monoxide in Canberra</u>, Proceedings of the <u>Symposium on Air Pollution Diffusion Modelling</u>, Australian Environment Council, Canberra, 1976.

such as concentrations of HC and NO_x , temperature, and wind speeds. The prime task is to determine which parameters are necessary to produce an expression which describes the test airshed. Accordingly the tasks necessary for the construction of the model are:

(i) measurement

- (ii) data processing and reduction
- (iii) modelling of measured values
- (iv) validation of predictive ability

The measurement task is the most demanding in that it needs to produce sufficient measurements to enable correct selection of controlling parameters and subsequent model development. Also since a year has a recognisable cycle of four different seasons it clearly represents the minimum period for a meaningful data base. Thus the measurement program must include a 12-month continuous air monitoring program. The measurements necessary fall into three classes:

- (i) meteorological measurements
- (ii) ambient air measurements
- (iii) emmissions inventory

The meteorological data required for the modelling carried out in the Canberra air quality study for the Department of the Capital Territory were provided by the courtesy of the Bureau of Meteorology. The original proposal for this study sought that this arrangement be extended. In theory the data requirements for a complete description of the airshed are enormous. In practice it seemed that a semi-empirical oxidants model might be constructed on the base of the following data:

- (i) diurnal values of wind velocities
- (ii) ambient temperature
- (iii) inversion heights

(iv) diurnal variations of humidity

Measurement of precursors and oxidants in the airshed requires the establishment of a continuous air monitoring program to obtain the ambient concentrations of the following pollutants:

- (i) ozone (0₃)
 (ii) nitric oxide (NO)
 (iii) nitrogen dioxide (NO₂)
- (iv) non-methane hydrocarbons (HC)
- (v) carbon monoxide (CO)

Carbon monoxide is included because of its recent implication in the formation of a species active in attacking hydrocarbons.⁽¹⁾

The instruments required to undertake the measurement programs for ozone and carbon monoxide were available from the study for the Department of the Capital Territory. The instruments necessary for the measurements of hydrocarbons and nitrogen oxides had to be purchased. Additionally a data-recording or data-logging system was required to process the vast body of information generated by such a measurement program. All indstruments used in the continuous air monitoring program required calibration against fundamental primary standards to ensure that the values measured in the airshed are absolute values. In general such calibration standards are not available within Australia and primary standards needed to be established using the facilities of ANU.

The guidelines for construction of an emissions inventory have been established by the United States EPA⁽²⁾ Within

Kerr, J.A., Calvert, J.G. and Demerjian, K.L., <u>Chem in</u> <u>Britain</u>, 1972, <u>8</u>, 252
 US EPA Office of Air Programs, <u>Compilation of Air</u> <u>Pollutant Emission Factors</u>, Research Triangle Park, <u>North Carolina</u>, 1973.

Canberra the task required is a traffic count along the road system. Such a count has been carried out by NCDC⁽¹⁾ for 1973 and it was hoped that this study could be readily updated. The relatively insignificant contribution from industrial sources is a simplification in constructing an inventory.

The establishment of the data bank from such a measurement program gives the potential to undertake the development and validation of an airshed model.

RESULTS EXPECTED AND IMPLICATIONS OF THE STUDY

The aims intended for the study were the production of a computer based airshed model which would describe the concentrations of oxidants produced in any particular airshed as a result of the emissions into that airshed. Such a model requires three submodels which are:

(i) an emissions submodel(ii) a meteorological submodel(iii) a chemical submodel

The function of the emissions model is the calculation of the quantities of NO_x and hydrocarbons which result from the emission sources. These quantities need to be processed by the meteorological model using the necessary meteorological operators to calculate ambient concentrations of NO_x and hydrocarbons. These precursor concentrations are input to the chemical model which calculates oxidant concentrations which are then processed by the meteorological model to calculate ambient concentrations of oxidant.

Daly, NJ, and Steele, LP, <u>Air Quality in Canberra</u>, Report to the Department of the Capital Territory, Canberra, 1976.

The question of the degree of emission control necessary to obtain acceptable air quality could be answered if the study aims were achieved to the necessary level of accuracy. The implications of the correct answer in terms of costs to both industry and consumers is well illustrated by the data of Figure 1.1 which shows the increase in costs to each US consumer as the degree of emissions control on each vehicle increases.⁽¹⁾

In addition, the value of research aimed at a more quantitative understanding of the relationship between ambient air quality and the control of emissions would be established as cost effective if it succeeded only in providing a basis for avoiding the implementation of unnecessary or even counterproductive controls.

An example of such a policy error is seen in the introduction and withdrawal less than 12 months later of the expensive (c. \$35 per car) retrofitted devices to control NO_x emissions from light duty motor vehicles in the South Coast Air Basin of Los Angeles county. The effects of this costly program on the ambient air quality ranged from no improvement in the oxidant concentrations to increased concentrations of oxidant. ⁽²⁾

Pierrard, J.N., <u>Innovation</u>, 1974, <u>5</u>, 6
 Pitts J.N., Lloyd, A.L., and Sprung, J.L. <u>Chem in</u> <u>Britain</u>, 1975, <u>11</u>, 247



FIGURE 1-1 THE COST TO THE US CONSUMER OF VARIOUS PERCENTAGE REDUCTIONS IN VEHICULAR EXHAUST EMISSION

CHAPTER 2 - ANALYSIS OF POLICY OPTIONS FOR AUSTRALIAN CITIES

In general terms existing Australian legislation dealing with air pollution has been largely derived from the United Kingdom legislation embodied in the Clean Air Act (1955) and the Alkali Act (1905). These acts cover emissions from stationary sources.

The U.K. Clean Air Act covers emissions of dark smoke, dust and grit from any building, chimney or plant, and requires that any plans for new plant be approved by the appropriate local authority.

The Alkali Act has been extended to cover emissions of so called noxious or offensive gases from a wide range of scheduled processes. Fundamental to this act and apparently to Australian legislation is the principle of "Best Practicable Means" which appears to mean that the most advanced technology should be applied to control emissions within the context of economics and local conditions.

This principle of "Best Practicable Means" appears to be implicit in the various legislations dealing with motor vehicle emissions. The 1976 application of ADR27A is the application of controls applied in 1973 in the United States. It does appear that the guidelines for the present oxidant abatement policies are being drawn from experience gained in the United States for conditions prevailing in the United States. There are three countries, the United States, Japan and the Netherlands conducting major roles in smog-research, and it is of value to review the positions adopted by each country.

THE UNITED STATES APPROACH

To the present the EPA have sought abatement of oxidant levels through control of hydrocarbons only. There are controls

on NO_X emissions but these are controls aimed at keeping ambient levels of nitrogen dioxide below the values at which adverse health effects were observed in epidemiological studies on NO₂, and are not required for ozone control.

This abatement strategy is based on relationships between ozone and hydrocarbons obtained from aerometric data collected mainly in Washington DC, Philadelphia, Denver and Los Angeles. Based on these data the EPA considers that the Federal Standard of 0.08ppm as a one-hour average for ozone can be met if the concentration of hydrocarbons is kept below 0.24ppm C as an average for the morning period 0600-0900 hrs. Because of the time taken for the photochemical processes to generate ozone it is considered that it is these 0600-0900 hr. hydrocarbon emissions which generate peak values of ozone later in the day.

More recently, the agency has given some renewed consideration to emissions of NO_X and has stated that control of nitrogen oxides may be necessary to meet the oxidant standards. The State of California considers NO_X control an essential part of the abatement strategies.

THE JAPANESE APPROACH

The Japanese air quality standard for oxidant is set at a one-hour average of 0.06ppm not to be exceeded more than once per year. In addition an air quality standard for NO_2 is set at 0.02ppm as a 24-hour average maximum in order to safeguard public health. It is considered that compliance with the standard for NO_2 should control NO_x levels to the extent that the oxidants standard would be achieved. Recently an expert committee has been established to examine the necessity for an air quality standard for hydrocarbons as part of the oxidant abatement program.

THE NETHERLANDS APPROACH

The view that seems to be adopted by the Netherlands is that control of oxidants is best achieved by controlling the ratio of ambient concentrations (HC/NO_x) to an optimum value (in excess of 10) which least favours ozone formations. Guicherit⁽¹⁾ has proposed a relationship (Figure 2.1) which shows ozone formation potential of precursors as a function of the ratio (HC/NO_y) .

This relationship shows a maximum in the ozone forming potential at (HC/NO_x) ratios around 3 to 4. Best controls of ozone are obtained by keeping the values of the ratio at higher values. Values in excess of 10 are nearing the optimum for ozone control.

Guicherit lists ${\rm HC/NO}_{\rm X}$ ratios for a number of cities as follows:

Los Angeles	ca 3		
Tokyo	7	-	10
Osaka	12	-	15
Netherlands	10	-	15
Sydney	ca 10)	
Canada (various)	10	_	20

The implication of the Sydney value is that NO_x control is more important that control of hydrocarbons. On this basis ADR27A which seeks to control HC to about 50 percent and NO_x to about 85 percent of former levels appears to decrease the (HC/NO_x) ratio to values below 10 which would, in the Netherlands view, make for a higher potential for ozone.

(1) Guicherit R. op.cit

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CONCLUSIONS FROM THESE APPROACHES

These apparent differences in national policies make it necessary to decide what action is appropriate for Australian conditions. Accordingly Australian studies are necessary.

An important deduction needs to be drawn from these three approaches. It does appear likely (and for the present will be assumed to be true) that successful implementation of either the United States Standard of 0.24ppm C as the average for the 0600-0900 hr period or the Japanese NO_x Standard of 0.02ppm as a 24 hr average would lead to the meeting of the National Standards. Given this, it is important to realise that each policy is a statement of what levels are necessary to meet the National Standard. They are not statements which describe the best means of getting to these standards.

By contrast the Netherlands strategy is not concerned with presently meeting the National Standards, but of lowering levels of oxidant which currently occur.

Australian cities at present experience levels of ozone which exceed Japanese or US Standards. The long term task is to achieve the concentrations of precursors which enable some standard to be achieved. The immediate task is however to seek the best methods of controls which result in progressive lowerings in present levels of ozone. This could well require a strategy based upon present levels of precursors in airsheds of Australian cities rather than dependence on US guidelines. It is the aim of this study to seek the guideline appropriate to Australian cities.

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CHAPTER 3 - FACTORS CONTROLLING PHOTOCHEMICAL POLLUTION

The chemical reactions which lead to the formation of photochemical oxidants in an airshed have been represented by the equation

This equation is an oversimplification and insofar as it leads to the conclusion that oxidants control is to be achieved by controlling to the limit the emissions of the primary pollutants NO_x and HC it can be an expensive and unproductive oversimplification.

The real issue which needs to be resolved in formulating policy is the determination of the extent of control of both NO_x and HC which is necessary to achieve the desired ambient air quality. This in turn requires that we gain an understanding of the relationship between oxidant levels in ambient air and the emissions of NO_x and HC.

The difficulties in gaining this understanding stem from the complexities of the chemical processes leading to photochemical pollution. These difficulties are exemplified by the fact that over 200 chemical reactions are involved in the photo-oxidation of just one hydrocarbon. ⁽¹⁾ Generally something like 50 different hydrocarbons can be found in an airshed. Over 60 have been identified in the Sydney basin. ⁽²⁾

⁽¹⁾ Demerjian K.L., Kerr J.A. and Calvert, J.G. <u>Advances</u> in Environ. Science & Technol. J. Wiley & Sons, N.Y. 1974.4, 1

⁽²⁾ Mulcahy MFR, Nelson PF, Smith MY, Murray KE and Whitfield FB, Smog Forming Hydrocarbons in Urban Air Proceedings of Symposium of Workshop Sessions Clean Air Society of New Zealand, Smog 76, Sydney 1976

The fundamental reactions in this complex set of processes have been widely studied and are reasonably understood.⁽¹⁾⁽²⁾⁽³⁾ The following description is aimed at summarising some major features with control implications. A more detailed description of the chemistry can be obtained from the literature.⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾

THE ROLE OF NITROGEN OXIDES

Since air is a mixture of nitrogen and oxygen the burning of any fuel in air is accompanied by the formation of some nitrogen oxides. The conditions of the internal combustion engine are such that it produces relatively large amounts of nitric oxide (NO). On release from the tail-pipe of the car a large proportion of this NO is converted to nitrogen dioxide (NO₂) by easy combination with the oxygen of the air.

$$NO + \frac{1}{2}O_2 \longrightarrow NO_2$$
 (1)

Nitrogen dioxide is able to absorb energy (hv) from sunlight and use this energy to break up into NO and oxygen atoms (O). This break-up is represented by equation (2)

....

$$NO_2 + hV \longrightarrow NO + O$$
 (2)

Demerjian K.L., Kerr J.A. and Calvert J.G. op.cit
 Leighton P.A. <u>The Photochemistry of Air Pollution</u>

- Academic Press Inc. New York, NY, 1961
 (3) Hecht T.A. Seinfeld J.N. and Dodge M.C. Environ
 Science and Technol 1974 8 327
- Science and Technol, 1974, 8, 327
 (4) Daly N.J. and Steele, L.P. The Chemistry of Photochemical Air Pollution, Proceedings of Symposium & Workshop Sessions, Clean Air Society of Australia and New Zealand, Smog 76, Sydney 1976.

The oxygen atoms formed in equation (2) are extremely reactive and combine with oxygen molecules in air to form ozone (0_2) . This formation of ozone is shown in equation (3).

 $0_2 + 0 \longrightarrow 0_3$ (3)

Apart from the natural methods of formation (3) represents the only source of ozone in an airshed.

Ozone is quite reactive and combines with NO to form NO_2 . This combination is represented by equation (4).

 $NO + O_3 \longrightarrow NO_2 + O_2$ (4)

Thus the role of reaction (4) is to remove some of the ozone formed in reaction (3).

The nett result of reactions (2), (3) and (4) is to form ozone in the airshed due to processes initiated by the photo-dissociation of NO_2 . The quantity of ozone formed is controlled by the amount of NO present since NO converts the ozone to oxygen via reaction (4). The accompanying conversion of NO to NO_2 starts the photo-initiated cycle once again.

Thus in the presence of sunlight the reactions of NO_2 set up a steady state system which forms ozone in the airshed. The concentration of the ozone is controlled by two factors:

(i) the intensity of the sunlight
(ii) the ratio of the concentrations (NO₂)/(NO)

The presence of hydrocarbons in the airshed leads to further chemical reactions which modify the steady state system, and the concentration of ozone present.

THE ROLE OF HYDROCARBONS

Hydrocarbons are emitted into an airshed from motor vehicles, a variety of industrial sources, and possibly some natural sources. The role of hydrocarbons in the smog forming processes is that they react with active species which are produced from the photolysis of NO_2 .

With the exception of methane all hydrocarbons found in the airshed have some reactivity. Although there is considerable variation in reactivity (see Chapter 3) from one hydrocarbon to another, the general features of the reactions of hydrocarbons are similar enough for the purposes of the following discussion.

The immediate active species from the photolytic steps are oxygen atoms and ozone. In addition a further species, hydroxyl (OH) is invariably formed when hydrocarbons and oxygen atoms are present, and is of major importance. The hydrocarbons combine with these species to form reactive products which react in such a way that they convert NOto NO₂. In addition, hydrocarbons undergo a sequence of reactions to form such toxic materials as PAN (peroxyacetyl nitrate) and methyl nitrate. A brief description of these major products is given by Manahan. (1)

Those reactions of hydrocarbons which convert NO to NO₂ have an important effect. They provide mechanisms which convert NO to NO₂ by means other than the reaction with ozone shown in equation (3). The existence of these alt ernatives lessens the control that NO exerts on ozone levels. Thus a major role of the hydrocarbon reactions is to intervene in such a way that ozone is enabled to accumulate.

(1) Manahan, S.E. op.cit

This accumulation of ozone brought about by the reactions of hydrocarbons indicates the degree of advancement of photochemical processes in the airshed. Beyond certain stated levels the ozone so formed is considered to be a health hazard. The time taken to achieve high levels of oxidant varies depending upon such factors as the reactivities of the hydrocarbons, the intensity of the sunlight, and the meteorological conditions controlling dispersion of the pollutants. Thus the US EPA considers (Chapter 2) that it is the hydrocarbons released in the morning period 0600 to 0900 which lead to ozone peaks later in the day.

SUMMARY OF THE CHEMISTRY

An extremely simplified summary of the chemistry of ozone formation in the airshed is given by the equations

NO2	+	hV	\longrightarrow	NO + (2	(2)	
0	+	0 ₂	>	0 ₃		(3)	
°3	+	ΝΟ	>	$0_2 + 1$	^{NO} 2	(4)	
HC	+	0)			_		
HC	+	$0^{)}_{3)}$	>	$NO \rightarrow \frac{1}{1}$	Produc	ts incl PAN	(5)
HC	+	OH)			2		

In the reaction sequence reaction (5) represents in excess of 200 individual reactions. Each reaction occurs at a particular rate which is determined by an individual parameter called the rate constant which is a characteristic of each molecule, the concentrations of the reacting species, and the temperature at which the reaction occurs.

The simultaneous occurrence of this very large number of reactions has the result that the dependence of oxidant formation upon concentrations of NO_x and hydrocarbons is complex and extremely non linear. That is, a halving of the concentration of either NO_x or hydrocarbons does not lead to a halving of the oxidant formed.

The processes which form oxidant take a time to develop Several hours of solar irradiation are necessary to form significant quantities of oxidant. In broad terms it is the hydrocarbons and NO_x which are emitted into the airshed in the morning period 0600 to 0900 hr. which lead to the oxidant maxima observed later in the day. The meteorological conditions which determine sunlight intensity, temperature, and dispersion influence the time taken for achieving the oxidant maxima as do the reactivities of the hydrocarbons involved in the reactions.

The major features of the abbreviated reaction scheme can be summarised as follows:

- (1) the production of the active species 0, 0_3 and 0H is brought about by the photo-dissociation of $N0_2$ and depends upon sunlight intensity.
- (ii) the concentration of ozone, and hence total oxidant is controlled in the airshed by NO via reaction (3).
- (iii) the reactions of hydrocarbons provide an alternative route which converts NO to NO₂. This firstly provides for the production of further chain carriers, 0, 0₃ and 0H, and secondly modifies the control reaction (3) exerts on ozone levels. The result is that ozone accumulates.
- (iv) the reactions of hydrocarbons lead to the formation of toxic species such as PAN.

It is the necessary goal for research to understand these processes sufficiently to determine the dependence of ozone formation on the concentrations of the precursors NO_x and hydrocarbons in order to enable the implementation of sound control policies.

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THE REACTIVITIES OF HYDROCARBONS

The reactivities of hydrocarbons in these photo-initiated oxidations in the airshed vary markedly from one chemical type to another as well as from one individual hydrocarbon to another. Thus in understanding the formation of photochemical oxidant it is desirable to have a scale of photochemical reactivity for hydrocarbons.

Smog chamber studies have provided the basis for the photochemical reactivity scale, and indices such as degree of eye irritation, rate of conversion of NO to NO2, rate of loss of hydrocarbon, and maximum ozone levels have been considered. The results depend upon the conditions chosen for the experiments and the criterion adopted for smogproduction. Altshuller and Bufalini⁽¹⁾ give an order of activity of hydrocarbon types on a scale ranked 0 - 3 in order of increasing ability to produce ozone under standard laboratory conditions. The scale is given in Table 3.1 The U.S. EPA have adopted a reactivity scale of 0 - 7 (Table 3.2) which is based on the rate of consumption of the hydrocarbon. In general the classifications in these Tables are consistent. Alkanes are regarded as having little reactivity whereas alkylbenzenes and alkenes are regarded as most reactive.

(1) Altshuller A.P. and Bufalini J.J., Environ. Science & Technol., 1971, 5, 39

TABLE 3.1 - RANKING OF HYDROCARBONS BY PRODUCTION OF OXIDANT UNDER STANDARD LABORATORY CONDITIONS

HYDROCARBON CLASS	EXAMPLE	RANK ^(a)
ACETYLENE		0
ALKANES (C ₁ -C ₅)	propane(C ₃ H ₈)	0
Alkanes (C ₆ -)	octane (C ₈ H ₁₈)	0-1
Ethylene		2
Monalkylbenzenes	toluene	2
Aldehydes	propionaldehyde	2-3
Alkenes (C ₃)	butene	3
poly-Alkylbenzenes	xylene	3

(a) On scale 0-3

SOURCE: Adapted from Altschuller A.P., et al, op.cit
TABLE 3.2 - SCALE OF HYDROCARBON REACTIVITY

HYDROCARBON CLASS	EXAMPLE	RANK ^(a)
Acetylene		0
Alkanes (C ₆ -)	octane	0-1
monoalkylbenzenes	toluene	3
ethylene		2
Alkenes (terminal) ^(b)	$C_2H_5CH = CH_2$	6
dialkenes	$CH_2 = CHCH = CH$	6
polyalkylbenzenes	-	6
internal alkenes ^(b)	$(CH_3)_2 C = C (CH_3)_2$	7

(a) On scale 0-7

(b) "terminal" and "internal" refer to the position of the double bond.

SOURCE: US EPA

Pitts⁽¹⁾ has pointed out that the reactivity of hydrocarbons continues to be of considerable interest because of plans for the revision of the reactivity scale. These plans are based on two major factors:

- (i) it has been realised that given relatively high HC/NO, ratios, and lengthy irradiation periods of up to 9-12 hours in summer, alkanes can generate as much ozone as alkenes or aromatics.
- (ii) such lengthy irradiation periods exist during stagnant air conditions characteristic of severe smog episodes, and during daily long range transport of pollutants across a given air basin.

The effect of increased irradiation time on the consumption of selected alkanes, alkenes and aromatics is shown by smog chamber studies carried out by Darnall, Winer and Pitts⁽²⁾ using irradiation periods of 10 to 12 hours. The results are shown in Figure 3.1. The mixture of hydrocarbons used in the experiments was a surrogate mixture representative of the mixture found in ambient air in Los Angeles.

The data in Figure 3.1 show that the alkene propene and the polyalkylbenzene, m-xylene, react rapidly. After the traditional 6-hour irradiation period both are essentially consumed and the ozone concentration is 0.25ppm. Beyond this 6-hour period the ozone concentrations continue to rise rapidly due

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Pitts J.N., Symposium on the Occurrence and Control of Photochemical Pollution, Smog 1976, Clean Air Society of Australia and New Zealand, Sydney, Feb 1976. (1)

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Darnall K.R., Winer A.M. and Pitts J.N., unpublished data reported in reference (1)



FIGURE 3-1 RATES OF DISAPPEARANCE OF CERTAIN HC IN THE LONG-TERM IRRADIATION OF A SURROGATE HC-NO_X MIXTURE IN THE SAPRC 6400-LITRE ALL-GLASS CHAMBER

to the significant contributions from the alkane (n-butane) and the alkylbenzene (toluene) and reaches a value of 0.50ppm after about 12 hours.

The reactivity scales based on short irradiation periods are heavily weighted in the direction of alkenes and polyalkylbenzenes. However the importance of alkanes and other apparently "unreactive" hydrocarbons is clearly demonstrated for long periods of irradiation.

Thus control of the hydrocarbons by replacing the more reactive hydrocarbons by those lower in the reactivity scale is of value during periods for which the irradiation period is shorter and of the order of 4-6 hours. On occasions where the irradiation period is longer, such as could be expected during a day of poor ventilation in summer (especially with daylight saving which places the 0600-0900 hr period earlier in the solar day), or during the operation of transport phenomena, the apparently "unreactive" hydrocarbons are important.

A further significant piece of evidence has emerged from laboratory studies on the reactivities of hydrocarbons. The monoterpene species a-pinene, b-pinene, and d-Limonene have been shown to have reactivities which range from about the same to about twice that of the alkene butene.⁽¹⁾ Additionally Grimsrud, Westberg and Rasmussen⁽²⁾ have shown that the terpenes terpinolene and a-phellandrene react so rapidly that their rate of reaction is controlled by the rate at which the reagents come together. Australian plants are rich in these terpenes and may contribute significantly to the hydrocarbon burden in parts of our cities.

(1)	Darnall K.R., et al, op.cit
(2)	Grimsrud E.P., Westberg H.A., and Rasmussen R.A.,
	Int. J. Chem. Kinetics, Symposium No. 1, 1975,
	183.

EFFECT OF SUNLIGHT INTENSITY

The primary effect of sunlight intensity is on the photodissociation processes. The concentrations of the chain carriers oxygen atoms, ozone, and hydroxyl (Chapter 3) are directly dependent upon the sunlight intensity. Thus the resultant effects on the formation of photochemical oxidant are that variation in the light intensity:

(i) alters the rate of conversion of NO to NO₂
(ii) alters the rate of consumption of hydrocarbons
(iii) affects the terminal ozone concentration.

These effects are illustrated in the simulation reported by Cuicherit⁽¹⁾ which shows (Figure 3.2) the diurnal variations in concentration of the major species for different seasons of the year for latitudes corresponding to that of the Netherlands. The data presented in the Figure shows that the ozone concentrations, rate of hydrocarbon consumption, and rate of NO₂ formation all increase as the sunlight intensity increases from (in the Northern hemisphere) mid January to mid-summer.

The photo-dissociation of NO₂ is brought about by absorption of sunlight with wavelengths varying from 290 to about 430 nanometres. Sunlight with wavelengths less than 290nm does not reach the earth's surface because it is absorbed by the ozone layer in the stratosphere. Sunlight with wavelengths longer than 430nm causes no photo-dissociation. The extent of the photo-dissociation depends directly on the intensity of the sunlight.

The intensity of sunlight which reaches the earth's surface varies with wavelength. Again, the intensity of sunlight

(1) Guicherit R, op.cit



SOURCE: Guicherit, R., op. cit



of each wavelength varies with latitude, time of year, time of day, and weather conditions. The absorption of sunlight by NO_2 also varies with the wavelength of the sunlight. Thus a quantitative evaluation of the effects of sunlight intensity must take account of these facts.

In this study the effects of the variation of intensity of sunlight upon the photo-dissociation of NO₂ have been modelled. The Solar Spectrum was divided into equal wavelength regions each spanning l0nm and the rate coefficients including the intensity factor have been calculated. The computer program which performs this calculation may easily be changed to perform the calculation for any time of the year and at any location in Australia.

Calculated values for rate coefficients for photo-dissociation of NO_2 are shown in Table 3.3. The rate coefficients in this Table are such that when their value is multiplied by the concentration of NO_2 (in suitable units) the resulting value is the quantity of NO_2 which photo-dissociates in appropriate concentration units per hour. Thus at 1200 hr. for an ambient concentration of NO_2 of 0.01ppm the sunlight intensity is such as to photo-dissociate 0.25ppm per hour of irradiation at that intensity. These values are calculated for a clear sunny day in Canberra for a zenith angle of 10° at noon which corresponds to a day near the summer solstice.

TABLE 3.3 - CALCULATION OF THE RATE COEFFICIENT FOR PHOTO DISSOCIATION OF NO2 FOR A CLEAR SUNNY DAY IN CANBERRA NEAR THE SUMMER SOLSTICE

TIME OF DAY	RATE COEFFICIENT
(Hours)	(Hours^{-1})
·····	· · · · · · · · · · · · · · · · · · ·
0600	4.3
0900	19.9
1200	25.1
1500	19.8
1800	4.2

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The relationship between solar zenith angle, latitude, and time of year can be used to show that from the equator to latitudes of at least 70° the light intensity is sufficient to induce photo-chemistry during some part of the year. For latitudes of 70° the intensity is sufficient to lead to photo-dissociation for about two months in the year. For latitudes of 50° the period during which photo-dissociation is possible is about 7 to 8 months. For latitude 30° the light intensity is sufficient to initiate photo-chemical processes for about 10 months of the year. These figures assume there is no screening effect of cloud cover.

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 those days for which cloud cover screens the effect, the time for which the sunlight intensity is sufficient to induce photochemical processes in the airshed is quite high.

CHAPTER 4 - THE ROLE OF METEOROLOGICAL PROCESSES

The meteorological conditions which favour the formation of ozone are those which provide sunny weather and poor dispersion of air pollutants and thus enable a sufficient period of solar irradiation of NO_x and hydrocarbons to allow the photo-initiated processes to become established.

Such 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. This subsidence inversion prevents vertical mixing creating the poor dispersion conditions.

OXIDANT FORMING CONDITIONS IN WESTERN EUROPE

The meteorological pattern leading to the formation of photo-chemical oxidants in Western Europe have corresponded to the synoptic conditions characterised by an anticyclone situated over central Europe and moving slowly westwards. Two such episodes have now been extensively documented.⁽¹⁾

The first episode well documented occurred over the period August 10 to 20, 1973. High ozone levels persisted for 11 days and extended over the whole area of Frankfurt in Western Germany, to Goteborg in Sweden and westwards across the Netherlands into the United Kingdom and Southern Ireland. Ozone values are given in Table 4.1. The synoptic conditions over this period were dominated by a large high pressure area which was quasi-stationary over the North Sea and

 OECD Workshop on Photochemical Air Pollution, Data from National Reports, Delft, Netherlands, 8-12 Sept 1975

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Scandinavia, and led to sunny skies, temperatures above normal, and low windspeeds over the whole region.

The second well documented episode occurred in August 1975 and lasted for 15 days, and corresponded to similar synoptic conditions. Ozone data from France and Austria were measured during this episode and are shown in Table 4.1.

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COUNTRY		l	DATES		· · · · · · · · · · · · · · · · · · ·	
	11.8.73 (OZ(14.8.73 DNE CONCENT	17.8.73 FRATIONS I	19.8.73 N PPM)	3.8.75	8.8.75
ENGLAND	0.09	0.13	0.14	0.12	0.11	0.15
FRANCE					0.20	0.13
GERMANY	0.13	0.08	0.17	0.12	0.09	0.09
ITALY					0.08	0.08
NETHERLANDS	0.12	0.13	0.19		0.10	0.12
SWEDEN		0.06	0.08		0.12	0.08
AUSTRIA						0.10

TABLE 4.1 - OZONE DATA FOR WESTERN EUROPE DURING SUSTAINED ANTICYCLONE CONDITIONS IN 1973 AND 1975

SOURCE: Guicherit R., op.cit

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In an earlier oxidants episode in 1971 ozone values were measured only in the Netherlands, the synoptic conditions of the slow moving anticyclone situated over eastern Europe were present.

OXIDANT FORMING CONDITIONS IN JAPAN

Episodes in which photochemical oxidant accumulates to unacceptable levels in Japanese cities are frequent occurrences during the rainy season and midsummer.

The episodes are associated with fronts in a high pressure system which persist for 3 to 4 days, setting up either a moving front or a subsidence temperature inversion with low wind speeds and poor dispersion conditions.

OXIDANT FORMING CONDITIONS IN AUSTRALIA

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 these systems is quite fast in comparison with systems in the Northern hemisphere, usually traversing the continent in 3 to 4 days.

At times a high pressure system develops in the Tasman sea and has the effect of blocking the movement of the anticyclone. Under these conditions the eastern capitals, Brisbane, Melbourne and Sydney, experience their worst air pollution episodes.

Miller and Holzworth⁽¹⁾ defined the Air Pollution Potential (APP) as an index to measure the ability of the airshed to

⁽¹⁾ Miller M.E. and Holzworth C.C., J.Air Poll. Control Assoc. 1967, <u>17</u>, 46

disperse pollutants. The higher the index the longer is the time required for dispersion and the worse the potential air pollution. All Australian capitals experience a high APP when under the influence of an anticyclone system. Shaw⁽¹⁾ has calculated the APP values for afternoon conditions in Australian capitals and compared them with those of selected overseas cities. Values are presented in Table 4.2 which shows Australia to be comparable with New York. Thus Shaw considers New York to be "an awful warning for Sydney and Brisbane if they allow either their size or source strengths or both to grow".

(1) Shaw, P.J., Clean Air, June 1969

TABLE	4.2	-	AFTERNOON	AIR	POLLUTION	POTENTIALS

CITY	CITY SIZE ^(a) (km)	Percentage of Afternoons for which AAP exceeds the tabulated value		
		10%	50%	90%
ADELAIDE	20	14	9	7
MELBOURNE	25	14	10	8
PERTH	25	15	11	8
BRISBANE	25	16	11.5	9
SYDNEY	30	17	12	10
NEW YORK	45	18	13	12
LOS ANGELES	60	35	18	14

(a) Along wind distance across city

SOURCE: Shaw P.J., Clean Air, June 1969

Under the influence of anticyclonic conditions Melbourne experiences calm sunny conditions for several days. Le Roy, Lau and Holden⁽¹⁾ reviewed the occurrence of photo-chemical smog in Melbourne and noted that photo-chemical smog became manifest as the major air pollution problem requiring attention in the industrially clean atmosphere of Melbourne. Major smog episodes have occurred in 1972, 1974 and 1975 and have persisted for up to 10 days continuously.⁽¹⁾ The photo-chemical smog tends to occur during late autumn and early winter during periods of calm meteorological conditions. It is however concluded⁽¹⁾ that at no matter what season during the year that smog occurs, it normally coincides with calm conditions.

Hawke and Iverach⁽²⁾ have made a study of days of high photo-chemical 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 values in Sydney.

TRANSPORT PHENOMENA IN CALIFORNIA

The transport of pollutants by wind has been extensively studied in a number of cities.

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

(2) Hawke JS, and Iverach D, Atmos. Envir. 1974, 8, 597

⁽¹⁾ Le Roy, PA, Lau WWP, and Holden GDS, <u>Proceedings of</u> the Symposium on the Occurrence and Control of Photochemical Smog, Clean Air Society of Australia & New Zealand, Sydney, 1976.

The results reported in Figure 4.1 give the oxidant levels for July 25, 1973 for Los Angeles and the cities of Pasadena, Pomona and Riverside which are downwind of Los Angeles. Appropriate distances are:

Los Angeles to Pasadena	14	km
Pasadena to Pomona	38	km
Pomona to Riverside	37	km

The delay in the arrival of the oxidant peak in the downwind cities is considered⁽¹⁾ support for the contention that significant amounts of the oxidants in the downwind sections of the 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.⁽¹⁾

A similar analysis of oxidant concentrations for West Los Angeles, Los Angeles, Azusa and Riverside has been carried out on the mean 1-hour average concentrations observed during October 1965.⁽²⁾ The station at West Los Angeles is about 16 km west, and that at Azusa about 32 km east of downtown Los Angeles. Riverside is about 48 km east of Azusa. The time of the peak in the oxidant concentrations follows the peak in West Los Angeles by 1 hr in Los Angeles, 2 hrs in Azusa, and 4 hrs in Riverside.

In each case study the oxidant concentrations at Riverside showed a double peak. The first peak around midday is attributed to pollutants generated at or near Riverside. The second around 1600 hrs is attributed to pollutants transported from the large, more densely populated Los Angeles metropolitan area. ⁽¹⁾

(1)	Pitts JN, Lloyd AC, and Sprung, JL, op.cit	
(2)	OECD Expert Group on Photo-chemical Oxidant	s and
	Precursors, Meeting of Rapporteurs, Sydney,	, April,
	1974	



DIURNAL VARIATIONS OF THE MAXIMUM HOURLY AVERAGE CONCENTRATION OF OXIDANT AT SEVERAL LOCATIONS ACROSS THE LOS ANGELES BASIN FOR 25 JULY 1973 Further information on the transport phenomenon is obtained by using the carbon monoxide concentrations present 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 suggested that the polluted airmass becomes diluted as it moved eastwards 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 oxidant continues to be formed during the transport process.

This view appears to be confirmed by the statement issued by the US National Academy of Sciences which reported ⁽¹⁾:

"Thus over a period of hours the mass of smogladen air from downtown Los Angeles experiences a growth in ozone concentration as it travels eastward so that a shift in the maximum ozone 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 NO, emissions."

TRANSPORT PHENOMENA IN AUSTRALIA

Hyde and Hawke⁽²⁾ have examined the meteorological factors which influence ozone levels in Sydney and have shown that irradiation during the transport of pollutants has some

 Report by the Coordinating Committee on Air Quality Studies, <u>Air Quality and Automobile Emission Control</u>, <u>The Relationship of Emissions to Air Quality</u>, National Academy of Sciences 1974, vol 3.
 Hyde R and Hawke GS, <u>Proceedings of the Symposium on</u> <u>Occurrence and Control of Photochemical Pollution</u>, <u>Clean Air Society of Australia and New Zealand</u>, Sydney 1976 importance. They concluded that the occurrence of ozone is related to the relative position of the monitor and the major precursor sources and to the mesoscale wind patterns in Sydney. Particularly high concentrations of ozone were in general associated with wind trajectories which pass through inland, city, or coastal source regions. High afternoon values generally result from a recirculation of pollutants carried eastward by the morning westerly drainage and then advected back inland with the seabreeze.

Wind trajectory analyses showed that the seabreeze will carry polluted air inland towards Liverpool and Campbelltown and to the southern half of the Hawkesbury Basin between Penrith and Camden. Hyde and Hawke suggest that subsequent monitoring may show that these areas experience prolonged periods of high concentration of ozone caused by local buildup of oxidants during the morning followed by oxidants advected inland by the seabreeze.

Similar analyses have not been carried out in other cities although similar situations could prevail.

The problem of drainage of pollutants in Melbourne in a southward direction followed by northwind advection under the influence of a bay breeze could be considered. Similarly the problem of transport into Perth of NO_x from power generation and hydrocarbons from the refining at Kwinana merits consideration.

SUMMARY OF METEOROLOGICAL CONDITIONS FAVOURING SMOG FORMATION .

The meteorological conditions which obtain during photochemical episodes in Tokyo, Los Angeles, Sydney and the Netherlands are compared in summary form in Table 4.3.

	токуо	LOS ANGELES	SYDNEY	HOLLAND
Periods of Highest Incidence	June-August (scattered April-Oct.)	August-Sept. (frequent May-Oct.)	October-April	SeptOct. (scattered incidence March-Oct.)
Distribution of Atmospheric Pressures	During and shortly after the rainy season (June-July) smog results in fronts in high pressure systems. During mid-summer (August) high pressure cells persist for 3- 4 days.	Incidence tends to occur when non-moving high pressure sys- tems dominate the eastern Pacific. Some flucuations occur in this general pattern.	High oxident levels occur when area is subject to stationary high pressure systems or is between two high pressure cells.	Anticyclonal (high pressure systems) conditions prevail over western Europe.
TempInversion	Mostly moving (front) type Sometimes settling, sub- sidence type.	Subsidence inversion.	Subsidence and frontal type.	Subsidence 200-2000m (sometimes absent)
Wind velocity (local)(m/sec)	Less than 4	Less than 3	Early morning less than 2	Less than 3
Humidity	60-80% (0900 hrs)falling afterwards	Approx.70%	50-80% (0900 hrs)	Less than 60%

TABLE 4.3 - SUMMARY OF METEOROLOGICAL CONDITIONS

Cont'd....

·	TOKYO	LOS ANGELES	SYDNEY	HOLLAND
Periods of Highest Incidence	June-Augustl (scattered April-Oct.)	August-Sept. (frequent May-Oct.)	October-April	Sept-Oct.(scattered incidence March-Oct.)
Visibility (Range in km)	Less than 2-3 km (Marunauchi)	0.8-1.6 km	3-24 km	Less than 2-15 km
Sunshine	At least 2-3 hours required before 1400 hrs	Always plenti- ful sunshine	At least 2-3 hours before 1400 hours (usually more)	Plentiful sunshine.
Temperature of adjacent Sea Water (°C)	(Tokyo Bay 24- 25	15-20	18-25	16-18
Conditions of Sea Wind	Area of high oxidant concen- tration corres- ponds to the movement of the sea-wind front for more than 40 km inland.	Same as for Tokyo except front extends up to 100 km inland	Generally same as for Tokyo except high concentration sometimes develop during calm and land-breeze condi- tions.	Sea wind plays no role in smoj ns episodes.
Wind Direction	Incidence occurs when wind moves inland from sea	West to East wind	E-NE to W-SW durin sea wind.NW to SE sometimes importan	ng Incidence occurs with wind from N, at E or S

TABLE 4.3 - SUMMARY OF METEOROLOGICAL CONDITIONS (CONT'D)

SOURCE: OECD Expert Group on Photo-Chemical Oxidants and Precursors, Meeting of Rapporteurs, Sydney, April 1974

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CHAPTER 5 - SIMULATION STUDIES

Simulation studies of the photochemical smog forming processes in an airshed may be carried out by constructing a computer model which describes the airshed or by undertaking laboratory simulations in smog chamber studies. The major features of these approaches are described below.

THE MODELLING APPROACH

The objectives, requirements, and advantages of an airshed model were described in Chapter 1. The development of such a model requires development of three major submodels to describe the meteorology of the airshed, the inventory of emissions to the airshed, and the chemistry of the processes in the airshed. The salient features of each of these submodels are described in the following sections.

THE METEOROLOGICAL SUBMODEL

The meteorological submodel needs to describe the ability of the airshed to disperse the emissions of hydrocarbons and NO_x and the oxidants formed in the airshed. The data required are such parameters as temperature, mixing height, wind speed and direction. These need to be combined with the temporal and spatial distribution of emissions from all sources to enable the concentrations of the precursors to be calculated. These concentrations then become input to the chemical model which has the task of calculating the resultant level of oxidant.

The meteorological submodel properly needs to provide a 3-dimensional flow pattern to describe the atmospheric transport and diffusion properties of the precursors and oxidants. However the theoretical difficulties and the enormous data requirements of this type of description are such that although 3-dimensional models have been attempted⁽¹⁾ they have yet to be developed to the stage of providing a description of sufficient accuracy to be useful.

The alternative approach is to develop a simpler, less detailed model using empirical constants. Such an approach is exemplified by the model of Enschroeder and Martinez⁽²⁾ which is based on the Lagrangian form of 3-dimensional flow, and neglects wind shear, vertical mean π otion, and horizontal dispersion. The assumptions implicit in these meteorological simplications are considered⁽³⁾ to be in keeping with the approximations implicit in the chemical submodel, although they appear to build an uncertainty into the concentrations of precursors which would make the resultant airshed model insufficiently accurate for policy purposes.

At present the achievements in the development of a meteorological model with the required accuracy to give reliable input into the chemical model are disappointing (4) and the future prospects do not look good.

THE EMISSIONS SUBMODEL

The emissions submodel has to provide a description of the concentrations of precursors at any time. Both hydrocarbons and $NO_{\rm X}$ are being continually added to an airshed from vehicular and industrial emissions, and these need to be summed.

(1)	Reynolds SD, Roth PM, and Seinfeld JH, Atmos Environ,
	1973 , <u>7</u> , 1033
(2)	Enschroeder AQ, and Martinez JR, Advan in Chem,
	1972, 113
(3)	Allen GH and Bilger RW, in reference (4)
(4)	Australian Environmental Council, Symposium on Air
	Pollution Diffusion Modelling, Canberra, 1976

Fluxes from automotive emissions are generally derived from traffic volume and speed data. The procedure is to divide the urban and suburban area into a suitable array of grid squares and assign an averaged speed and vehicle distance to each vehicle in the square. The emissions are calculated as a function of average speed which involves knowledge of the standard driving cycle. An example of the application of such a relationship is that used by Iverach⁽¹⁾ who gives concentrations of precursors as

HC =
$$\left[3.1 + 5.4 (\frac{s}{\sqrt{2}})^{-0.66}\right]$$
 g/km, and
NO₂ = 2.8 g/km

where S is the local average speed and V is the average speed over the US Federal driving cycle.

Emissions from stationery sources are included as a result of an inventory. Guidelines for carrying out such inventories have been laid down by the US Environmental Protection Agency.⁽²⁾ Such an inventory has been compiled for Sydney by Chambers⁽³⁾ Evaporative emissions from refineries needs to be included in the inventory. Thus Iverach⁽⁴⁾ sets the figure at 0.25 percent of refinery output.

THE CHEMICAL SUBMODEL

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

(1)	Iverach D, Mongon TR, Nielsen NJ, and Formby JR,
	J. Air Poll. Control Assoc, 1976, 26, 39
(2)	USEPA Office of Air Programs, op.cit
(3)	Chambers RJ, An Air Pollution Source Inventory for
	Sydney Airshed, M.Eng Sci. Thesis, University of
	Sydney, 1974
(4)	Iverach D, et al, op.cit

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

$$\frac{dC}{dt} = F - RC$$

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 $^{(1)}$ or determined by the methods of thermochemical kinetics. $^{(2)}$

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 (3)(4)

The photodissociation of NO₂ 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⁽⁵⁾ and have been incorporated in

(1)	Demerjian KL, et al, op.cit
(2)	Benson, SW, Thermochemical Kinetics, J. Wiley & Sons
	NY, 1968
(3)	Gear CW, Comm. Assoc. Comp. Mach., 1971, 4, 176
(4)	Gelinas RJ, J. Comp. Phys. 1972, 9, 222
(5)	Leighton PA, op.cit

the model developed in this study.

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 (2), (3), and (4).

In practical terms the vast number of chemical reactions becomes to 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⁽¹⁾ and the General Research Corporation model ⁽²⁾ 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⁽³⁾.

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.⁽⁴⁾ The description of airshed data still appears remote.

(1)	Hecht TA, Seinfeld JS, and Dodge MC, Environ Sci &
	Technology, 1974, 8, 327
(2)	Allen G, & Bilger RW, Proceedings of Symposium on Air
	Pollution Diffusion Modelling, Australian Envir. Council
	Canberra, 1976.
(3)	Pitts JN, Lloyd AC, and Sprung JL, Chem in Brit, 1975
	11 247

⁽⁴⁾ Kerr JA, Calvert JG, Demerjian KL, op.cit

THE AIRSHED MODEL

The major requirement of an airshed model is that it be sufficiently accurate to enable evaluation of alternative policies. The present stage of modelling necessitates the use of so many empiricisms that the models become too imprecise to be useful for this purpose. The major weaknesses inherent in the models are:

- (i) an accurate and comprehensive emissions inventory is generally not available. Those based on the guidelines set down by the (US) EPA⁽¹⁾ and adopted by Iverach use a US Standard driving cycle. Pitts⁽²⁾ has recently reported that the emissions of hydrocarbons into an airbasin may vary by a factor of 2 depending on the driving cycle.
- (ii) the severity of a photochemical smog has a dependence upon humidity, inversion height wind speed and direction. Since the smog takes a period of time to develop the variations of these data with time are needed. These data are either not generally available or available on a time instantaneous basis only. The data necessary to construct a sufficiently detailed meteorological model do not appear to be generally available.
- (iii) the basic kinetic reaction mechanism does not describe the periodic addition of primary pollutants. To gain understanding of these effects a series of smog chamber studies which examine the effects of repeated injections of precursors into the reacting system are required.

US EPA, <u>op.cit</u>
 Pitts JN, et al, <u>op.cit</u>

The nett result of these limitations is that while the chemical submodel has the capability of reasonably describing the results of the photo-oxidation of a single hydrocarbon in a smog chamber the multiplicity of hydrocarbons in the airshed introduces the need for simplifying the model. This, together with the lack of accuracy in the meteorological and emissions model makes the calculation of ambient concentrations of oxidant too inaccurate to be trustworthy as a quantitative guide to policy making. It does appear that chemical studies offer an understanding of the dependence of ozone on concentrations of NO_x and hydrocarbons which are necessary to sound policy formulation.

CHAPTER 6 - SMOG CHAMBER STUDIES

Smog chambers provide a laboratory simulation of the processes which take place in the airshed under solar irradiation, but are free of the complications of meteorological dispersion forces and intermittent emissions.

Fundamentally the apparatus consists of a large chamber with a volume of about 1500 litres in which surrogate mixtures representing the compositions of hydrocarbons and NO, found in the urban airshed can be admitted and subjected to ultraviolet irradiation which closely resembles the spectral distribution of solar irradiation.

The concentrations of hydrocarbons and NO, are monitored continuously throughout the irradiation period and a comprehensive picture of the functional dependence of oxidants on the initial concentrations of hydrocarbons and NO, can be established. Such experiments led initially to the development of the basic understanding of the formation of photochemical smog (1)(2)(3) and now offer useful guidelines for establishing policies.

The limitations of smog chamber studies are in the fact that while they provide an understanding of the chemistry of the processes occurring in the airshed, they do not provide a description of the meteorological dispersion processes. They do however lead to an understanding of the complex relationship between precursor concentrations and oxidant concentrations. Thus where existing concentrations of precursors in an airshed are known chamber studies may point the direction which emission control policies need to be aimed to achieve minimisation of oxidants levels in that airshed.

⁽¹⁾

Haagen Smit AJ, <u>op.cit</u> Haagen Smit AJ, et al, <u>op.cit</u> Kerr, JA, et al, <u>op.cit</u> (2)

⁽³⁾

RESULTS OF SMOG CHAMBER STUDIES

In the beginning the smog chamber studies of Haagen-Smit and his coworkers $^{(1)}(^{2)}$ showed that ozone was produced when diluted auto exhaust emissions or mixtures of NO_x and individual hydrocarbons such as alkenes, alkanes, alcohols, or carbonyls were irradiated with ultra violet light.

Since then a variety of experiments have reproduced these results under a range of conditions.⁽³⁾⁽⁴⁾⁽⁵⁾ Figure 6.1 shows a typical concentration versus time profile for major species in the photo-oxidation of a single hydrocarbon, in this case isobutene. In general such studies have provided the understanding of the chemical processes which take place in the airshed.

In terms of the implications for policy decisions three recent studies dealing with oxidant precursor relationships appear most important. One was carried out in the laboratories of the State wide Air Pollution Research Centre (SAPRC) of California and represents the opinions of that body; another originates from the Netherlands and represents at least an influential input into the OECD body concerned with photochemical air pollution; the third was reported at the International Conference on Photochemical Oxidant Pollution and its control held in Raleigh, NC, in September 1976 and appears likely to be that used by the US EPA in future. These studies are described in the following sections.

(1)	Haagen Smit AJ, op.cit
(2)	Haagen Smit AJ, et al, op.cit
(3)	Altshuller SZ, Kopcznski SL, Lonemann WA, Becker TL,
	and Slater R, Environ. Sci and Technol, 1967, 1, 899
(4)	Niki H, Daby EE, and Weinstock W, Advan in Chem
	1972 ser.113, 16
(5)	Pitts JN, and Finlayson BJ, Angew Chemie, 1975, <u>87</u>
	18



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

FIGURE 6-1 PRODUCTS AND THEIR VARIATION WITH TIME FOR THE IRRADIATION WITH ULTRAVIOLET LIGHT OF A MIXTURE OF ISOBUTENE AND NITRIC OXIDE

SAPRC SMOG CHAMBER STUDIES

The reactivity of hydrocarbon mixtures in an urban airshed depends upon the composition of that mixture. For this reason Pitts and his coworkers⁽¹⁾ have established a surrogate mixture of hydrocarbons which duplicates the balance of hydrocarbons found in the Los Angeles airbasin. The composition of this surrogate mixture is given in Table 1 of reference (1).

This surrogate mixture was irradiated for six-hour periods in a smog chamber; a range of various dilutions was chosen so that the effect of varying the initial concentrations of both the hydrocarbon mixture and NO_x could be determined. The experimental data are shown in Figure 6.2 which summarises the ozone levels reached after a 6-hour irradiation at various initial hydrocarbon and NO_y levels.

These results enable the evaluation of the effect on ozone levels of reducing the concentrations of either hydrocarbons or NO_x in the ambient air. From examination of the results Pitts argues that in all cases a policy which lowers the concentrations of hydrocarbons leads to a lowering of the ozone formed. By contrast, for many conditions, the lowering of NO_x actually leads to higher levels of ozone. For example if NO_x is held at 0.30 ppm, the progressive lowering of hydrocarbons concentration from 2.60 ppm C through 0.69 ppm C leads to progressive lowering of ozone levels. A similar lowering is effected at any other fixed NO_x value. On the other hand the reduction of NO_x levels does not always lead to lower ozone. Figure 6.2 shows that for a fixed concentration of 1.3 ppm C, lowering of NO_x from 0.25 to 0.10 ppm can actually increase ozone levels.

(1) Pitts JN, op.cit





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

These smog chamber results appear to confirm the importance of hydrocarbon controls and to support the US stand of effecting oxidant control through control of hydrocarbons. The conclusion is that the 1973 US Light Duty Vehicle Emission legislation is appropriate. Since ADR27A appears to be based on this 1973 legislation (Chapter 1) the implication is that ADR27A is appropriate to Australia.

A relationship showing the dependence of ozone concentrations on concentrations of both NO_x and hydrocarbons is contained in these SAPRC data. This relationship is shown by presenting the results in the Form shown in Figure 6.3. Figure 6.3 presents contour lines of approximately equal ozone concentrations as a function of both hydrocarbon and NO_x concentrations.

In Figure 6.3 each contour represents a narrow range of ozone concentrations (e.g. 0.35 to 0.40 ppm) which result from 6-hour of irradiation. Ozone values represented by each contour, or isopleth, are appended to each line. The lowest isopleth shows the ozone concentration which equals that set by the Japanese Government and the WHO as the standard.

DATA FROM SMOG RESEARCH IN THE NETHERLANDS

As a result of experiments and analysis of aerometric data gathered by TNO, Guicherit⁽¹⁾ has proposed a relationship which appears to lead to conclusions which differ from those of Pitts. Guicherit proposes that the ozone forming potential in an airshed is dependent upon the ratio HC/NO_x . The relationship between ozone potential and this ratio is curvilinear and has a maximum of ozone occurring at a value of HC/NO_x in the region of 3-4. The proposed relationship is shown in Figure 2.1.

Examination of this curve leads to the conclusion that lower ozone concentrations are obtained at higher values of the HC/NO_{v}

(1) Guicherit R, op.cit




ratio. Guicherit reports⁽¹⁾ that for Sydney HC/NO_x approximates 10. The implication of the model is that what is required in Australia is control of NO_x leading to higher values of the HC/NO_x ratio and a resultant lowering in the ozone forming potential in the airshed.

The further implication of importance is that the implementation of ADR27A which controls HC to about 50 percent and NO_x to about 85 percent of previous levels should result in a lowering of the HC/NO_x ratio and consequently increases the ozone forming potential in an airshed. On this basis ADR27A would prove to be a counter productive measure in this country.

THE DODGE-DIMITRIADES MODEL OF SMOG CHAMBER RESULTS

Dodge⁽²⁾ has recently developed a model aimed at extending the existing smog chamber data of Dimitriades⁽³⁾ to examine the precursor-oxidant relationships over a wider range. The features of the treatment are:

- photolytic rate constants are given value appropriate to the Los Angeles summer solstice (34^oN); these values are also appropriate for Sydney.
- (ii) the calculated isopleths assume that the precursors reach their assigned values at 0700 hrs and that no further emissions are added. A zero wind speed is assumed and a dilution rate of 3 percent per hour is allowed.

The model in effect calculates the results for smog chamber conditions with the addition that sunlight intensity is allowed

Guicherit R, <u>op.cit</u>
 Dodge MC, <u>Combined Use of Modeling Techniques and Smog</u> Chamber Data to Derive Ozone-Precursor Relationships Conference on the Control of Photo-chemical Oxidants Raleigh, North Carolina, Sept 1976.
 Dimitriades B, <u>Envir Sci & Technol</u>, 1972, <u>6</u>, 253 and references therein.

to vary over the irradiation period; the treatment is said to reproduce the smog chamber data of Dimitriades to within 15 percent.

The dependence of ozone concentrations on NO_x and hydrocarbons is shown by the isopleths given in Figure 6.4. The model has effectively extended smog chamber data to cover the regions of low hydrocarbons and NO_x concentrations for irradiation periods of 10 hours. Accordingly it extends the description to isopleths showing the dependence of ozone concentrations of 0.08 ppm - the US Federal Standard - on concentrations of both NO_x and hydrocarbons.

The model has not been validated for airshed data. Additionally, in view of the assumptions implicit in (ii) and the fact that the smog chamber data on which it is based were derived for auto exhaust emissions rather than the hydrocarbon balance in the airshed, the applicability to city airsheds is yet to be established.

COMPARATIVE ANALYSES OF THE STUDIES

Comparison of the results of each of these studies shows that they are essentially in agreement.

The most ready comparison of the data from the SAPRC smog chamber and those reported by Guicherit is obtained by plotting the SAPRC results in the form of potential ozone against the ratio HC/NO_v. Such a plot is presented in Figure 6.5.

Figure 6.5 shows that the smog chamber data from SAPRC forms a set of curves each of which has the same form as that presented by Guicherit. Each of these curves is constructed as follows:







FIGURE 6.5 VARIATION OF OZONE POTENTIAL WITH THE RATIO HC/NOX

- (i) an initial hydrocarbon concentration is selected.
- (ii) ozone values resulting from irradiation with various
 NO_x concentrations at this fixed hydrocarbon value are tabulated. The maximum ozone obtainable from that hydrocarbon concentration is also tabulated.
- (iii) each ozone value is expressed as a percentage of the maximum attainable at the chosen concentration of hydrocarbon.
- (iv) these ozone percentages are plotted against the appropriate values of the HC/NO_v ratio.

The results so obtained refer to potential ozone after a six hour irradiation period and corresponds closely with those of Guicherit. The SAPRC data show (Figure 6.5) that the maximum ozone forming potential for any chosen hydrocarbon concentration occurs in the range of HC/NO_x from about 4 to 12. The results also show that the position of the maximum alters with the initial concentration of hydrocarbon. The variations are summarised in the Table 6.1.

TABLE 6.1 -	VARIATION OF THE VALUE FOR THE RATIO HC/NO
	AT THE OZONE MAXIMUM WITH INITIAL HYDROCARBON
	CONCENTRATION

Initial Hydrocarbon Concentration	Value for HC/NO at Maximum ^(a) Ozone
0.46 ppm C	4 - 8
0.69 ppm C	6 - 10
1.30 ppm C	8 - 13
2.10 ppm C	9 - 14
2.60 ppm C	9 - 14

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

SOURCE: Pitts JN, op.cit

Guicherit fixed the maximum at 3-4 but did not give the range of hydrocarbons covered in the ambient air data from which the relationship was derived.

The important conclusion to be drawn from this relationship is as follows. For each particular concentration of hydrocarbon in ambient air there is a maximum ozone concentration which can be formed. If NO, concentrations are such that the HC/NO, ratio falls in the range at which this maximum occurs then this maximum will be realised. If the ratio falls outside the range in which the maximum falls, additional lowering in the ozone will result. Accordingly consideration should be given to the HC/NO_x ratio where possible. It follows that ADR27A would have been more effective if the NO, levels had been reduced to enable the ratio (HC/NO_v) to exceed 14. At present the HC/NO_x ratio for Sydney is reported (1) to be about 10. If this is the case the likely changes brought about by ADR27A will reduce this figure to about 6, which means that the most efficient use is not being made of the hydrocarbon controls contained in the legislation.

Comparison of the oxidant-precursor relationships emerging from the SAPRC smog chamber and the Dodge-Dimitriades smog chamber model is obtained by comparing Figures 6.3 and 6.4. The relationships are in general agreement and have the same form in the common region. The Dodge-Dimitriades model does however predict slightly higher values for ozone for given precursor concentrations. Thus to achieve an oxidant level of 0.10 ppm ozone by hydrocarbon control the Dodge-Dimitriade model requires the limiting of ambient levels to about 0.14 ppm C whereas Pitts data lead to a value around 0.24 ppm C. Correspondingly to achieve the same ozone level by NO_X control requires limiting NO_X to ambient concentrations of 0.01 ppm (Dodge-Dimitriades) compared with about 0.03 ppm according to the data of Pitts.

(1) Guicherit R, op.cit

The differences may be due to the longer (10 hours compared with 6 hours) period of irradiation in the Dodge-Dimitriades method. A further difference is found in the hydrocarbon mixture used in the experiments. Dimitriades irradiated diluted mixtures of exhaust gases from motor vehicles in his smog chamber studies. The SAPRC studies irradiated a mixture of hydrocarbons said to be representative of the airmass in Los Angeles. Whatever the origins of the differences, they clearly have significant implications for understanding the extent of controls needed to achieve any chosen air quality. The obvious need in Australia is for smog chamber data using hydrocarbon mixtures and irradiation periods appropriate to Australian cities.

PRECURSOR CONTROLS APPROPRIATE TO AUSTRALIAN CITIES

Each of the three studies described establish the extremely non-linear dependence of ozone concentrations on the concentrations of NO_X and hydrocarbons. In determining which direction Australian policies for control should take one firstly needs an accurate determination of present levels of both hydrocarbons and NO_X occurring in the airsheds of Australian cities.

At present Sydney and Melbourne are the only cities for which well documented data are published. Ambient levels of both NO_x and hydrocarbons appear similar in each city.

The extensive data published by the Victorian EPA report N0, N0₂ and ozone in terms of 1 hour and 24 hour average maxima. Similarly the SPCC of NSW reports these together with maximum averages of NO, NO₂ and hydrocarbons observed for the 0600 to 0900 hour period. In broad terms it is these 0600 to 0900 hour values which lead to ozone maxima later in the day so that it is these values which are needed for an initial approach to analysis. Unfortunately these 0600 - 0900 hour values cannot be extracted from the

published form of the Victorian values. Maximum values observed in Sydney for NO, NO₂ and hydrocarbon for this morning period are summarised in Table 6.2.

Period	Concentration ^(a) (ppm)				
	НС	NO	NO ₂	NOx	
1973	1.0	_	_	-	
Sept 1974	0.69	0.04	0.03	0.07	
Oct 1974	0.80	0.11	0.04	0.15	
Nov 1974	0.60	0.07	0.06	0.13	
Dec 1974	0.6	NA	NA	NA	
Jan-Mar 1975	0.59	NA	NA	_	
April-June 1975	NA	NA	NA	-	
July-Sept 1975	2.36	0.10	0.04	0.14	
April-June 1976	NA	0.08	0.01	0.09	
	-	0.19	0.02	0.21	

TABLE 6.2 - MAXIMUM 0600 - 0900 HR AVERAGES FOR HYDROCARBONS AND NO_x OBSERVED IN SYDNEY

(a) Concentrations converted to ppm assuming ideal gas behaviour.

SOURCES: Annual Reports, Sydney Pollution Control Commission 1973-1976

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Ambient air quality standards are written in terms of a frequency with which a given concentration of a pollutant is permitted. Thus the Japanese and US Federal standards for oxidant, and the WHO goal, refer to a stipulated one-hour average concentration of oxidant which is not to be exceeded more than once per year; that is, the level should not occur for more than one hour in each (365 x 24) hours, or about 0.01 percent of the time. Thus standards are concerned not so much with maximum reached, but rather with the frequency with which an acceptable level is exceeded. Accordingly pollutant concentrations are best treated in terms of an annual frequency distribution of concentrations. A more complete description of such frequency distributions is given by Daly and Steele. (1)

Thus the appreciation of the oxidant problem in an airshed requires a knowledge of the frequency with which one-hour average concentrations of ozone exceed the stated standard. Accordingly it follows that an oxidants problem needs to be concerned with the frequency with which simultaneously occurring concentrations of both hydrocarbons and NO, have the potential for forming ozone in quantities which exceed the standards. Accordingly an analysis of the existing situation in Australian cities requires an analysis of the frequency with which simultaneously occurring levels of NO_v and hydrocarbons have the potential for generating unacceptable levels of ozone. Were this analysis available it would be possible to apply a proposed policy reduction in either or both precursors and to determine the distribution resulting from this policy. Such an analysis would enable an evaluation of the impact of proposals in terms of the reduction of the frequency of potential occasions on which oxidant levels become unacceptable.

 Daly NJ and Steele LP, <u>Air Quality in Canberra</u>, Report submitted to the Dept of Capital Territory, Canberra, Jan 1975.

The data necessary for such an analysis are measured in both Sydney and Melbourne. They have not been published in a form which would permit such an analysis. The further limiting factor is that the smog chamber data presently available do not appear to be sufficiently precise to describe accurately the levels of NO_x and hydrocarbons which define the potential ozone formation for lower levels (such as 0.01 ppm ozone) for which standards apply.

Within these limits it is possible to generally locate the position of Australian cities and to point up general directions in which policies should move. It is not possible without these analyses to say what improvement in ambient air quality will result from a reduction in emissions of precursors.

Table 6.2 shows that Sydney experiences maximum hydrocarbon concentrations for the morning period 0600 - 0900 hours which generally fall in the range 0.6 to 1.0 ppm C. In 1975 a maximum of 2.4 ppm C was recorded. Similarly the Table 6.2 shows that the maximum values for NO_x generally fall in the range 0.07 to 0.15 ppm although a value as high as 0.21 ppm was recorded in June 1976.

The results of smog chamber experiments for concentrations in those regions are reported by Pitts⁽¹⁾ and are presented in a rearranged form in Figures 6.2 and 6.6. Figure 6.2 shows the ozone formed from various initial hydrocarbon concentrations plotted as a function of initial NO_x concentration. The irradiation period in the experiments was 6 hours and the hydrocarbon mixture was a surrogate said to be representative of the Los Angeles air.

(1) Pitts JN, op.cit



FIGURE 6.6 DEPENDENCE OF OZONE ON PRECURSOR CONCENTRATIONS AFTER 6 HOURS IRRADIATION

The data presented in Figure 6.2 show that where hydrocarbon concentrations are in the region of 2 ppm C or higher, and NO_x concentrations range up to 0.2 ppm, then a policy of reduction of NO_x emissions would lead to lower levels of ozone. On the other hand, where hydrocarbon concentrations range from about 0.5 to about 1.3 ppm C, a policy of reducing NO_x emissions has little beneficial effect on ozone levels until ambient NO_x concentrations reach about 0.08 ppm at the higher hydrocarbon concentration.

Figure 6.6 shows the ozone obtained with various initial NO, concentrations plotted as a function of initial hydrocarbon concentrations. Again the irradiation period was 6 hours and the hydrocarbon mixture was the surrogate representing Los Angeles air. The data show ozone dependences on hydrocarbon concentrations for initial NO, concentrations of 0.05, 0.10, 0.15 and 0.20 ppm. Where NO, concentrations are 0.05 ppm a policy of controlling hydrocarbon emissions has little effect on ozone until ambient levels are down to about 0.7 ppm C. Where NO_x levels are 0.10 ppm, control c^- hydrocarbons has little effect on ozone levels until hydrocarbon levels are down to about 0.9 ppm C: with initial NO, concentrations of 0.15 ppm, control of hydrocarbons begins to result in lower ozone levels when hydrocarbon levels are down to about 1.0 ppm C.

Taken together, the data of Figures 6.2 and 6.6 show that the major gains in terms of lower ozone levels should accrue when NO_x is controlled to ambient levels below about 0.05 ppm and hydrocarbons to levels below about 0.5 ppm C. The data of Dodge and Dimitriades (Figure 6.4) which is based on the irradiation of a hydrocarbon mixture taken from auto-exhausts and which

have been extended by calculations to an irradiation period of 10 hours suggest that hydrocarbons need to be controlled to better than 0.3 ppm C to achieve 0.10 ppm of ozone.

Analysis of the likely effects of ADR27A is difficult. The controls are expected to lower hydrocarbon emissions to about 50 percent of previous values and NO_x emissions to about 85 percent of previous values. These improvements assumed that the emissions from those Australian vehicles which preceded the design rules would be the same as those of their American counterparts before the appropriate US control in 1973. There is now some likelihood that Australian cars pre-ADR27A had lower emissions than previously thought, and although experments being undertaken to measure this are incomplete, there is the possibility that the percentage gain from the controls might be less than thought.

The effectiveness of the controls depends upon the ambient levels that obtain in the airshed. The data of Figures 6.2 and 6.6 show that the greatest improvement in ozone will result from NO_x control if hydrocarbons are in the range 1.5 to 3.0 ppm C or higher, and NO_x ranges up to 0.15 ppm. At higher NO_x both hydrocarbon and NO_x control is essential. For NO_x values above about 0.15 ppm decreasing NO_x could lead to increased ozone. Clearly a proper analysis requires construction of a frequency distribution of concentrations of hydrocarbon and NO_x levels as described earlier.

To establish the effects that control policies would have in Australia, it is necessary to have the dependence of oxidant on precursor concentrations established for conditions representative of Australia using surrogate mixtures which represent Australian airsheds.

SOURCES OF HYDROCARBONS AND NO

Hydrocarbons and NO, are emitted into an airshed from the exhausts of motor vehicles and from industrial sources. Notional figures are that roughly 60 percent of the levels found in city airsheds result from motor vehicle emissions. More precise figures need to be obtained by conducting an emissions inventory in each airshed of interest. The guidelines for such an inventory have been laid down by the US EPA⁽¹⁾ and have been applied in Sydney as part of the Sydney Area Transportation Study (SATS), which has been described by Mongon et al. (2) The breakdown of sources and contributions from each source have been described for Sydney in the Australian Report on oxidants and their precursors in the Atmosphere.⁽³⁾

The smog chamber data of Dodge and Dimitriades (4)(5) and Pitts (6) show that quite low ambient concentrations of NO_ and hydrocarbons can generate unacceptable levels of ozone. Thus it follows that implementation of a successful oxidant control policy requires correct identification of the sources of precursors and appropriate controls. For example, it seems to follow from the analysis of precursor levels in Australian cities (Chapter 6) that complete elimination of hydrocarbons and NO, from motor vehicle emissions might still leave ambient levels of hydrocarbon and NO, which are capable of forming ozone in concentrations which exceed standards.

(4) Dodge MC, op.cit

Pierrard JN, op. cit (1)

⁽²⁾

Iverach D, et al, op.cit Commonwealth Department Environment & Conservation (3) Oxidant and Their Precursors in the Atmosphere, National Summary Report, Canberra, February 1974.

⁽⁵⁾ Dimitriades B, op.cit

⁽⁶⁾ Pitts JN, op.cit

The reactivity of the hydrocarbons present in an airshed has considerable bearing on the smog forming potential of that airshed. The reactivities of hydrocarbons have been described in Chapter 3. Accordingly, it is possible to reduce the smog forming potential of an airshed if the use of the more reactive hydrocarbons in processes that are sources is replaced by use of a less reactive hydrocarbon for that process. Such an approach is seen in the United States, Rule 66, which bans the use of certain highly reactive hydrocarbons in favour of a less reactive species which will perform the same industrial function.

The contribution of natural sources to the hydrocarbon burden in cities is a possibility that merits consideration. Australian bush and trees are rich in natural oils and terpenes. The reactivity of terpenes has been examined by Pitts⁽¹⁾ and Grimsrud, et al⁽²⁾ who have shown them to be amongst the most reactive hydrocarbons. Additionally a monoterpene has been isolated in the Sydney airshed. Thus it is possible that natural bush has a role as a hydrocarbon source. The tree population of the Dandenongs near Melbourne and the Grose Valley near Sydney could contribute significantly if emissions from forests are significant. The hydrocarbon concentration in forests needs to be measured.

(1) Pitts JN, op. cit

(2) Grimsrud EP, et al, op.cit

CHAPTER 7 - CONCLUSIONS

The concentrations of oxidant formed in the airsheds of many Australian cities have reached levels which exceed the values set by the US Federal authorities, the Japanese Government and the WHO, as levels which represent the threshold necessary to safeguard public health.

The Japanese government and the WHO consider that this threshold is represented by a one-hour average concentration of ozone of 0.06 ppm, which should not be exceeded more than once per year. The US Federal government considers that a one-hour average concentration of 0.08 ppm of ozone should not be exceeded more than once per year in the interests of public health.

In both Sydney and Melbourne one-hour average concentrations of ozone ranging up to 0.35 to 0.40 ppm are now observed. Sydney records values which exceed the WHO limits on 127 occasions a year. In both Brisbane and Perth one-hour average values have been observed which exceed these various national and WHO standards; in the small inland city of Canberra a one-hour average concentration of ozone of 0.06 ppm has been observed over a eight month period and this level equals the limit set in both the Japanese standard and the WHO goal for a full one-year period.

The present Australian strategy for controlling these oxidant levels is one of controlling the quantities of NO_x and hydrocarbons emitted from the exhaust systems of motor vehicles. This strategy is based on the fact that oxidant in the airshed is formed by the reaction

and follows the lead of the United States. Thus the controls embodied in ADR27A limit the emissions of hydrocarbons, and to a smaller degree, of NO_{v} ; +hese controls are based directly

on the 1973 US Light Duty Vehicle Emissions regulation. Accordingly the strategy is derived directly from measurements carried out in the US for conditions prevailing in the US. Precursor concentrations in US cities, especially Los Angeles are generally higher than those found in Sydney and Melbourne.

The relationship between the quantity of ozone formed and the concentrations of NO_x and HC in the airshed have been discussed in Chapter 3 and are shown to be complex. The ozone concentrations depend upon such factors as:

- (i) concentrations of HC and NO
- (ii) time of irradiation, and
- (iii) the nature of the hydrocarbon mixture.

Smog chamber studies have shown that the dependence of ozone concentrations on the concentrations of HC and NO_x is extremely non-linear. Figure 6.3 shows the ozone isopleths as a function of NO_x and the concentrations which result from a 6-hour irradiation of a particular hydrocarbon mixture said to represent the ambient air in Los Angeles. The isopleths show that the effectiveness (in terms of minimising levels of ozone) of measures which:

- (i) reduce concentrations of HC, or
- (ii) reduce concentrations of NO_v, or
- (iii) reduce concentrations of both NO, and HC.

depends very much on what ambient concentrations of NO_X and HC are present. This dependence of the effectiveness of emission controls upon existing ambient concentrations can be shown by the following example:

EXAMPLE: Consider the effect of halving the hydrocarbon concentrations without changing the NO_x concentrations for two cases. Let the first case be one in

which initial hydrocarbon was 2.0 ppm C and NO_X was 0.12 ppm. According to the smog chamber data of Figure 6.3 about 0.35 ppm of ozone would be formed after 6 hours of irradiation. Halving the hydrocarbon to 1.0 ppm C would result in the lower ozone concentration of about 0.25 ppm.

Let the second case be the similar one in which the initial hydrocarbon concentration was 2.0 ppm and NO_x was 0.08 ppm. These conditions would lead to about 0.25 ppm of ozone after a 6-hour irradiation. Halving the hydrocarbon concentration to 1.0 ppm C would still result in the same ozone concentration of about 0.25 ppm.

Thus it can be seen that effective policy decisions on emission controls need to be made in terms of the knowledge of existing ambient levels of NO_x and hydrocarbons. Evaluation of the effects of proposed controls can then be made if appropriate smog chamber data are available. The factors that make smog chamber data appropriate to Australian conditions are:

- data are gathered from irradiations of hydrocarbon mixtures which are representative of those found in Australian airsheds; and
- the periods of irradiation cover the range of irradiation periods which would occur in Australian cities.

The evaluation of the effect of a policy which attempts to achieve a known reduction of emissions is difficult for Australian cities. The difficulty arises because the simultaneously occurring average values for the 0600 to 0900 hour concentrations of hydrocarbons and NO_x are not published. Instead the data are reduced and reported in the form of maximum averages recorded each month. Without these simultaneously occurring 0600 - 0900 hr averages for

NO, and hydrocarbons it is not possible to construct a frequency distribution of oxidant forming potential which is essential to policy evaluation.

At present, without the ability to describe the frequency distribution of the oxidant forming potential of the airshed it is not possible to distinguish between a policy which cuts down the maximum ozone recorded but leaves unchanged the number of occasions on which standards are exceeded, and one which cuts down the number of occasions on which the oxidant standard is exceeded.

One evaluation of ADR27A which can be made stems from the re-evaluation of the results reported by Guicherit⁽¹⁾ and Pitts⁽²⁾ and which is presented in Figure 6.5. The data in this figure show that the ozone forming potential of a mixture of hydrocarbons and NO, is at a maximum when the ratio HC/NO, falls in the range of about 3 to 12. The exact maximum varies slightly with the initial hydrocarbon concentration but is contained within the stated range.

At present the HC/NO_v ratio observed for Sydney is close to 10. The proposed changes likely to result from ADR27A would lower the vehicle contribution of this value to 6 which ensures that the maximum ozone forming potential of the hydrocarbons is more likely to be realised. To gain the utmost advantage, in terms of lower ozone concentrations, from any control which lowers hydrocarbons, it is necessary to stop those hydrocarbons from generating their full potential of ozone. To achieve this requires concomitant control of NO, to give values of the $\rm HC/NO_{v}$ ratio about 14 or higher. Thus ADR27A is not as efficient as it might be.

(2)

Guicherit R, <u>op.cit</u> Pitts JN, <u>op.cit</u> (1)

CHAPTER 8 - RECOMMENDATIONS

In implementing future policies for the control of photochemical oxidant in Australian cities it is essential to evaluate the impact of these controls to the fullest extent possible. To obtain guidelines for the most effective policies it is necessary to undertake the following major tasks:

- the evaluation of the frequency distribution of oxidant forming potential presently existing in Australian cities,
- the determination of the dependence of ozone concentrations on the concentrations of NO_x and hydrocarbons in major Australian cities,
- (iii) the identification of the makeup of the mixtures of hydrocarbons in Australian cities,
- (iv) the identification of the sources of NO and hydrocarbons in Australian cities.

The carrying out of tasks (ii) and (iii) should enable the construction of a graph, similar to that of Figure 6.4, which shows various ozone isopleths as a function of the hydrocarbon and NO_x concentrations. The achievement of task (i) should enable the location of each city studied on this graph, which should in turn point up the direction and extent of the controls needed to achieve stated goals. The achievement of task (iv) should point to possible ways of achieving these controls.

A brief description of the requirements for each of these tasks is given in the following sections.

EVALUATION OF THE FREQUENCY DISTRIBUTION OF OXIDANT FORMING POTENTIALS IN AUSTRALIA,

Standards for photochemical oxidant are written in terms of a one-hour average concentration of ozone or oxidant which is not to be exceeded more than once per year. As a result of this type of formulation the concern of policy decisions is directed not so much to the maximum ozone observed but rather towards the frequency with which the standard concentration is exceeded.

The amount of oxidant which may be formed in the airshed is determined interalia by the concentrations of hydrocarbons and NO_x in that airshed. Since in principle it is the concentrations of hydrocarbons and NO_x over the morning period 0600 to 0900 hours which determines the maximum ozone formed later in the day, it follows that it is the average concentration of NO_x and hydrocarbons over this period that determines the oxidant forming potential in the airshed.

The oxidant forming potential may thus be defined in terms of the concentrations averaged over the period 0600 to 0900 hours of both hydrocarbons and NO_x . This oxidant forming potential represents the potential ozone which may be generated if the meteorological conditions favour oxidant formation.

Appreciation of the effect resulting from an alteration in the emissions control policy requires the capability of comparing:

- the range and frequency distribution of ozone levels which could result from former concentrations of hydrocarbons and NO_v,
- (ii) the range and frequency distribution of ozone levels which could result from the altered concentrations of hydrocarbons and NO_v.

Where the dependence of ozone on the concentration of hydrocarbons and NO_x is established by the appropriate smog chamber data, then the range for the frequency distribution of potential ozone values from a proposed emissions policy can be computed if the percentage reductions in hydrocarbons and NO_x are known, and the existing averages for the 0600 to 0900 hour period are known for simultaneously occurring hydrocarbon and NO_x concentrations.

The task required is the collection of the average values for the 0600 to 0900 hr period for both hydrocarbon and NO_x concentrations for each day. Each set of hydrocarbon and NO_x data has an ozone forming potential which can be evaluated from smog chamber data. Thus the potential ozone which could be formed from each set of NO_x and hydrocarbon data can be computed, and a frequency distribution of the potential ozone concentrations can be calculated.

Where a known reduction is planned for one, or both precursors the reduction can be passed on to the ambient concentrations as appropriate and a new set of distribution of potential ozone concentrations can be calculated for comparison purposes.

The prime task is the construction of the frequency distribution of potential ozone presently encountered in Australian cities. The data necessary for such an analysis is presently measured in both Sydney and Melbourne, although they are not reported in a suitable form. The gathering of the necessary data appears to be a considerable job of data retrieval, but the overall usefulness of the result appears to make the job worthwhile.

OZONE-PRECURSOR RELATIONSHIPS FOR AUSTRALIA

The two major smog chamber studies discussed in Chapter 6 provide very similar relationships for the dependence of ozone on hydrocarbon and NO_x concentrations. The differences

however, are significant in terms of implementing emissions control policies. The SAPRC smog chamber data leads to the conclusion that major gains in oxidant control to levels of 0.10 ppm ozone will accrue at hydrocarbon concentrations of 0.5 ppm C. The Dodge-Dimitriades data suggests that this hydrocarbon level needs to be 0.3 ppm C.

Factors which lead to this type of discrepancy between wellconducted smog chamber studies are:

- (i) the nature of the hydrocarbon mixture,
- (ii) the length of the irradiation period.

Accordingly it is apparent that the vitally important dependence of ozone concentrations on hydrocarbon and NO_X concentrations be established in smog-chamber experiments designed to represent Australian airshed conditions.

The construction of an Australian smog chamber would enable the study of such important variables as:

- (i) the length of the irradiation period
- the effect of "subsequent irradiations" as would occur during stagnation periods in Melbourne when the same airmass may be irradiated over several days,
- (iii) the effect of repeated injections of hydrocarbons and NO as happens during the course of irradiation in a city air mass.

Such irradiations would need to be carried out on a hydrocarbon mixture which truly represents that occurring in the airshed of interest, and needs to cover the range of concentrations of hydrocarbon and NO, which occurs in that airshed.

The development of such an ozone-precursor relationship for Australian conditions is necessary to provide the basis for informed control policies.

IDENTIFICATION OF THE HYDROCARBON MIXTURES

The reactivities of hydrocarbons were discussed in Chapter 3 and it was established that all hydrocarbons except methane undergo photo-oxidation to produce ozone. There is however a scale of reactivity and certain hydrocarbons such as alkenes and terpenes react very much faster than others such as alkanes. Thus it follows that the actual composition of the hydrocarbon mix in a city airshed affects the composite reactivity of that airshed. Accordingly, when planning control policies for a city the knowledge of the ozone-precursor dependence needs to be established for the hydrocarbon mixture found in the city. Thus it is necessary to identify the makeup of the mixture in the city.

It has been noted in Chapter 3, that something like 50-60 different hydrocarbons occur in an urban airshed. Thus the analytical task of determining the composition of the urban hydrocarbon mixture is enormous. Presently this work is being undertaken for the Sydney airshed by Mulcahy and his coworkers ⁽¹⁾ at CSIRO. Successful completion of this task is a necessary prerequisite to smog-chamber studies.

SOURCE INVENTORY FOR PRECURSORS

Implementation of effective control measures requires an accurate evaluation of the contributions to hydrocarbon and NO_X levels from all sources. It would, for example, be mistaken policy to control emissions from motor vehicles by means of a moderately expensive converter to lead to a HC/NO_X ratio of 14 if power generation in the airshed emitted NO_x in amounts sufficient to adjust the ratio to 10.

(1) Mulcahy MFR, et al, <u>op.cit</u>

The present methods for conducting source inventories have been described in Chapter 3. Clearly one method of modifying the oxidants problem in an airshed is to cut down where possible, the reactivities of the hydrocarbons in the airshed. An example of this might be the replacement of some of the more reactive dry-cleaning solvents with solvents equally effective for drycleaning purposes but less reactive photochemically.

An issue of potential importance arises from the high reactivity of terpenes. Terpenes are present in Australian trees in large quantities and it is possible that these could contribute to the hydrocarbon burden in a city. An evaluation of the contribution of natural bush to the hydrocarbon levels in cities needs to be carried out.

The results of such a program could lead to an ability to determine what quantities, if any, of hydrocarbons are advected from the natural background into the city airshed. The outcome of the study could have significant implications for policies of controlling hydrocarbons, and optimising the HC/NO, ratio.

ANNEX A

DIFFICULTIES ENCOUNTERED IN CARRYING OUT THE CONTRACT BRIEF

Contract No. C9788 was offered to the University by telex on March 26, 1975, and a Research Officer was appointed to undertake the agreed study. The appointment was dated from March 4, 1975.

The construction of the model envisaged in the study plan required a data base provided by a minimum period of 12 months measurement of ambient air quality and selected meteorological parameters. The minimum period is necessary to embrace the full cycle of the seasons. It was initially agreed that necessary meteorological data would be obtained from the Bureau of Meteorology through the Department of Transport which would form a continuation of an arrangement made previously by the Department of the Capital Territory.

In practise the meteorological data required fell outside the chartered area of responsibility of the Bureau of Meteorology. Previous data⁽¹⁾ on wind speed measurements using a Woelfle anemometer were collected as part of a Special Program of Study and are not routinely measured. The Bureau very courteously allowed us to use the Woelfle anemometer at the Belconnen site, and wind speeds were measured for the period September 1975 to December 1975. The program had to be discontinued when it became impossible to obtain the usage of a special purpose vehicle needed to service an instrument atop a 10-metre pole.

The major instruments required to complete the program of measuring ambient air quality were:

⁽¹⁾ Daly NJ, and Steele LP, <u>A Predictive Model for Carbon</u> <u>Monoxide in Canberra</u>, Proceedings of the Symposium on an Air Pollution Diffusion Modelling, Australian Environment Council, Canberra, 1976.

- (i) a nitrogen oxides analyser,
- (ii) a hydrocarbon analyser.

These instruments were described as available in Australia from American suppliers on a delivery time quoted as varying from 1 to 4 weeks following the placement of the order.

In the event a number of difficulties arose. The ANU administration experienced undefined difficulties in finalising the contract and did not release funds to enable purchase of equipment until the week ending June 26, 1975. Thus the order for the nitrogen oxides analyser was placed on June 30, 1975 by telephone using order No. G76133, this was confirmed in writing on July 29, 1975. Delivery of the instrument was partly effected on August 5, 1975, although vital circuit boards were not delivered until October 15, 1975.

The hydrocarbon analyser presented a more complex problem. The present technology is based on the use of the flame ionisation detector (FID) and uses an apparatus employing two FID systems. One of these FID units is used to determine all hydrocarbons in the airshed including methane; the other FID unit is used to determine the simultaneously sampled air parcel from which all hydrocarbons except methane have been removed. The reactive hydrocarbons are determined by taking the difference between the two measurements. Methane, which is unreactive to the photochemical processes in the airshed, comprises up to about 60 percent of the hydrocarbon burden in the airshed. Accordingly, the method based on difference is subject to some error. Calculations from specified instrument performance figures lead to an estimate of about 25 percent for the uncertainty of values measured in the Canberra airshed, and this is unacceptable for the purposes. Further the instruments do not distinguish between non methane hydrocarbons. Accordingly it was considered desirable to develop an instrumental method of analysing

hydrocarbons which would have improved accuracy over the existing method, and would distinguish between the reactive alkenes and other hydrocarbons.

A suitable analytical scheme seemed possible using the principle of chemiluminescence. The method in principle operates as follows:

At present ozone is analysed on the basis of a chemiluminescent reaction; that is ozone reacts with ethylene to produce a chemiluminescent reaction. The quantity of light is proportional to both the quantity of ozone, and the quantity of ethylene. Thus where the quantity of ethylene is held c constant, the light emitted depends only upon the quantity of ozone. By suitable calibration procedures the quantity of ozone can be determined from measurements of the intensity of light emitted. The relevance of these ozone measurements Ethylene is a specific example of the class of is this. hydrocarbons known as alkenes. Accordingly it is possible in principle to construct an ethylene analyser by building an ozone generator which supplies a fixed constant stream of ozone which reacts with ethylene to give light. Measurement of the light under these conditions leads to determination of the concentration of ethylene.

A supplementation grant was given to enable development of this concept. Studies carried out showed that the method could be used for determining ethylene and other alkenes found in urban airsheds. Accordingly an ambient Air Quality Analyser was purchased from Monitor Labs Inc. to provide the basis for the accurate flow control and calibration needed to establish the hydrocarbon analysis. The instrument was ordered on November 17, 1975, and delivery was effected on May 5, 1976. The 12-month tenured position of the Research Officer was terminated by the University on March 3, 1976.

During the tenure of the Research Officer no ambient concentrations of hydrocarbons could be measured. Four months data for NO_x levels were possible. In the absence of the provision of meteorological data a limited wind-speed program of measurement was undertaken. However no effective data bank was provided for the modelling project.

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