PHOTOCHEMICAL SMOG IN GREATER CAPE TOWN

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Thesis submitted in fulfillment of the requirements towards the Degree of Master of Science in the Department of Environmental and Geographical Science

UNIVERSITY OF CAPE TOWN

1988

This is to declare that this dissertation has not been previously submitted for a degree at any University

ABSTRACT

Photochemical smog is the name given to a complex sequence of chemical reactions that occurs in the presence of sunlight. These reactions comprise a mix of organic and inorganic compounds, including a number of toxic secondary pollutants such as ozone (O_3) and peroxyacetyl nitrate. These substances are commonly referred to as oxidants and are the result of numerous reactions of primary pollutants or precursors (including nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHC)) emitted from vehicle exhausts and to some extent industry. O_3 is the major constituent of the photochemical oxidants, and its concentration is often used to determine the severity of photochemical smog.

Limited research on photochemical smog in Cape Town has been undertaken, and this study has concentrated on providing a more detailed understanding of photochemical precursor and oxidant levels in the urban atmosphere of Greater Cape Town. This was approached by the investigation and assessment of the spatial and temporal behaviour of photochemical pollutants, making use of automatic monitor data collected from 1984 to 1986, and supplemented by data collected during a spatial survey in April and May of 1987.

Precursor levels were found to be strongly influenced by the seasonal cycle of the weather and were highest in winter when stable atmospheric conditions prevailed, particularly during morning rush hours. O_3 behaviour was complex and lacked any definite relationship to season or to selected meteorological variables, although the limited data indicated high levels during the early spring months. Peak levels were generally experienced on fair weather days during the early afternoon hours at the time of maximum ultraviolet radiation. O_3 levels did not exceed the USEPA 1-hour standard of 0.12ppm during 1985 and 1986. The spatial distribution of precursor and oxidant concentrations showed the NO_x levels to be spatially dependent, following the major arterial roads. NMHC levels were spatially less well defined than NO_x, and O_3 levels were spatially relatively uniform, exhibiting depletion due to scavenging by nitric oxide (NO) in areas close to main traffic routes. High NO_x levels were experienced predominantly in the city centre, while the suburbs tended to experience the higher O_3 levels. Cape Town was not considered to have a photochemical smog problem of the same magnitude as Los Angeles or Sydney, due to a number of factors which contributed to the complex situation (such as high NO levels, relatively low NMHC levels and strong winds in summer). However in the Northern Suburbs, the absence of high NO levels together with additional NMHC emissions from nearby industry led to the recognition of this area as one of potential photochemical smog formation.

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ACKNOWLEDGEMENTS

There are many people without whose help this thesis would not have been possible. I am indebted to my supervisors, Dr. Cecil Keen and Prof. R.K. (Dick) Dutkiewicz for their support, guidance, wisdom and advice from the inception of the thesis. I am also appreciative of their help during the research and in the writing up.

I would like to thank Roy Nates for his encouragement and assistance, and Mike Silberbauer for the many hours spent on the mainframe sorting out the monitor data and plotting numerous graphs.

The field research was accomplished with the help and cooperation of City Council and Regional Services Council members from the Health Departments, Town Planning Branch and the Traffic Department to all of whom I am indebted.

A special thank you to Derrick Oxley, Danie, Dries, Ed, Rob and Hans of the City Council Air Pollution Section for their help and assistance. I must also extend my gratitude to Lionel Tucker of State Health for the provision of the one and only NMHC analyser for my survey. Likewise I must also thank the Scientific Services Branch of the City Council for the provision of data, and especially Grant Ravenscroft for his time, support and advice in the early stages of the research and during the field work.

Also to Hugh Ballard, for his cheerful assistance - best of luck for the smog chamber in the next phase of the project.

The funding from the CSIR FRD as a Masters Research Bursary during the first year and as an official project during the

second year is gratefully acknowledged.

Finally, I would like to thank Andrew, my fiancé, for his unfailing support, encouragement, patience and optimism from start to finish.

Lee Loewenheim

CHAPTER 1

THESIS INTRODUCTION

INTRODUCTION

Deteriorating air quality is a serious problem in many cities where emissions of air pollutants into the atmosphere frequently exceed the capacity of the environment to disperse them. The London smogs of the 1950's were examples of severe pollution episodes which were essentially formed from a mixture of smoke and fog (and hence the name 'smog'). These episodes occurred under conditions of poor dispersion, particularly in places where large amounts of coal burning increased the sulphur oxide content of the air. A new type of oxidising air pollution was noticed in the Los Angeles Basin in the 1940's, where effects such as eye and throat irritations, and damage to vegetation and materials were experienced. This type of air pollution became known as photochemical smog. In the 1950's, similar complaints and damage were reported in the San Francisco Bay area and in New York. The problem of photochemical air pollution has grown rapidly in recent decades, and has affected many major metropolitan cities around the world. Urban air quality and the role of motor vehicle and industrial emissions have become increasingly important concerns, and have prompted research aimed at improving the general understanding of photochemical pollution and the physical processes involved in its formation.

Photochemical smog is the designation given to a particular mixture of pollutants that form in the atmosphere as a result of chemical transformations that occur in the presence of sunlight. It comprises a complex mix of organic and inorganic compounds, consisting of a number of toxic secondary pollutants including ozone (O_3) and peroxyacetyl nitrate (PAN). These substances are commonly referred to as oxidants and are the result of numerous chemical reactions of certain primary pollutants or precursors, including nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHC), in the presence of ultraviolet radiation. O_3 is the major constituent of the photochemical oxidants, and its

concentration is often used to determine and measure the severity of the photochemical smog, even though more toxic substances are often present in smaller concentrations.

HISTORICAL OVERVIEW

During the 1940's, an awareness of the deterioration of air quality in Southern California became apparent. In the Los Angeles Basin, hot sunny days with temperature inversions gave rise to typically hazy conditions, obscuring the mountains that provide a barrier to air pollutant dispersion. Of greater concern was the damage to vegetable crops which displayed unfamiliar 'bronzing' after such episodes. Rubber companies were also aware of the cracking of tyres at an accelerated rate in the Los Angeles area. Attempts to explain these effects led to the first research projects on photochemical smog.

Middleton *et al* (1950) recognised that air pollution was the cause of the observed damage to vegetation. The 'traditional' air pollutants, such as sulphur dioxide, were not found to be the cause, but a new kind of pollution with 'oxidising' power was found to be responsible. Numerous experiments in the late 1940's involving plant fumigation with various chemical vapours failed to produce the anticipated damage symptoms. Haagen-Smit (1952) hypothesised that smog symptoms were due to partially oxidised hydrocarbons from petroleum products containing olefins, such as gasoline. His experiment involved the fumigation of a test plant with the O_3 products of gasoline exhaust gases, which produced the classic 'bronzing' effect of photochemical smog. Continued work led to the confirmation that the combination of NO_X and sunlight with NMHC led to the formation of O_3 and produced the characteristic plant damage (Haagen-Smit, 1952; Haagen-Smit *et al*, 1952; Haagen-Smit *et al*, 1953; Haagen-Smit and Fox, 1955). Vehicle emissions were therefore recognised as being major air

contaminants and as the predominant sources of the precursors of photochemical smog. A later discovery found that Haagen-Smit's assertion, that photolysis of hydrocarbons with nitrogen dioxide (NO_2) produces O_3, remained accurate. However, his statement that O_3-olefin reactions cause the oxidant plant damage did not prove so, as shortly afterwards PAN was isolated as the smog toxicant that produced the observed plant damage (Stephens, 1961).

In the late 1950's, tobacco growers north of Lake Erie experienced significant crop yield losses due to 'weather fleck' on sunny days with high temperatures and dew points, and poor visibility. Further investigation confirmed that high O_3 concentration correlated directly with the observed 'weather fleck' (MacDowell *et al*, 1964; Mukammal, 1965).

In 1961, Leighton presented the chemical and mechanistic aspects of photochemical smog in the atmosphere and laboratory (Leighton, 1961). This definitive monograph, which still provides a basis for the present understanding of photochemical smog, was followed by California State Legislation to mandate statewide control. Studies were initiated to further define the physical processes involved in photochemical smog formation, the social and economic implications, and to formulate strategies applicable to the control of photochemical pollution.

During the 1960's, O_3 began to draw serious attention as a pollutant in urban areas with the risks of both health and plant damage. Los Angeles became the focus of photochemical air pollution studies with its abundant sunlight, nocturnal inversions, persistent anticyclonic stagnant air masses and not least, high motor vehicle numbers. Limited measurements in other urban areas demonstrated by the late 1960's that photochemical pollution, although most severe in Los Angeles, was to be found in many other urban locations. By 1970, the United States Environmental Protection Agency (USEPA) promulgated National Ambient Air Quality Standards

for oxidants and published procedures for determining the necessary precursor reductions to control the high oxidant levels (US Federal Register, 1971).

In the early 1970's, the growing recognition of the adverse effects of photochemical air pollution initiated the deployment of precursor and oxidant monitoring systems in Western Europe, Japan, Australia and Canada, together with the expansion of the monitoring network in the United States. The function of these networks was initially to gauge the pollutant levels in order to establish standards, and thereafter to monitor for episodes and the appropriate control strategies. Studies thus tended to be geographically localised and empirically based. Certain cities with concentrated petrochemical industries and high traffic densities were highlighted as potential areas for the production of photochemical smog (OECD, 1975). Evaluation of the various methods for the control of photochemical smog was made, involving control of either NMHC emissions, NO_x emissions, or a combination of both methods, depending on the degree of O_3 reduction required (Bilger, 1978). The first control strategies were introduced into the United States, to reduce emissions of petroleum vapour from oil refineries and limit both NO_x and NMHC emissions from vehicles (Tiao *et al*, 1975).

In the Netherlands, high O_3 concentrations of up to 0.25ppm were recorded in the data from 1969 to 1975 and inference to the NO_x method of control was made (Guicherit and Van Dop, 1977). Greater London began monitoring O_3 in 1972, and elevated levels of up to 0.20ppm were observed during an episode in 1976 (Ball and Bernard, 1978). The variations in the incidents of high O_3 concentrations in Western Europe were ascribed to differing meteorological conditions rather than changing precursor emission patterns, although the latter was forecast to be a matter of concern for future decades (Guicherit and Van Dop, 1977; Ball and Bernard, 1978).

In Japan during 1971, the city of Osaka experienced classic atmospheric conditions for the formation of photochemical smog. Some 15 high school children were hospitalised after acute systematic symptoms of eye and throat irritations, paraesthesia and muscle spasms were diagnosed (WHO, 1978). This incident aroused much public concern throughout Japan, causing the formulation of air pollution warnings and the initiation of a large statistical survey on the effects of photochemical pollution on the urban population (OECD, 1975). Stringent standards were also introduced as part of the abatement policy (Bilger, 1978).

Sullivan (1962) recognised the potential for photochemical smog development in the Sydney Basin, an area similar in latitude, topography and sunshine to Los Angeles. Photochemical smog was perceived to be a serious problem in 1971, when the first significant oxidant values were recorded (Mitchell, 1983). A wide-ranging research project entitled The Sydney Oxidant Study was initiated in 1974 by the State Pollution Control Commission. Its objectives were to determine the extent, severity and control options for photochemical smog in Sydney (Post, 1983). Details of precursor emissions, oxidant formation, related meteorology and model applications were covered in this extensive study.

The occurrence of photochemical smog episodes and the relationship of such incidents to meteorology has, until recently, tended to dominate the literature (Hawke and Iverach, 1974; Guicherit and Van Dop, 1977; Ball and Bernard, 1978; Evans *et al*, 1981; Hawke *et al*, 1983). The potential hazards of photochemical pollution have stimulated smog chamber experiments, and the concurrent development of empirical, kinetic and computerised models (Dodge, 1977; Derwent and Hov, 1980; Johnson, 1983; Smith and Johnson, 1984). Such models have aided in the prediction of oxidant concentrations, source areas of precursor emissions, and the

formulation of optimum control strategies for the maintenance of pollutant levels within acceptable limits.

CHEMISTRY OF PHOTOCHEMICAL SMOG

Photochemical air pollution is the generic term given to a particular mixture of reactants and products that exists when NMHC and NO_x occur together in the presence of sunlight. The complex reactions that occur in the formation of photochemical smog are numerous (see Appendix 1.1), and although many studies on the complex chemical reactions for the formation of oxidants have been carried out (Leighton, 1961; Demarjian *et al*, 1974; Graedel *et al*, 1976), complete understanding of the sequence of reactions and the ultimate controlling precursors is still not completely understood (Innes, 1981; Johnson, 1983; Kelly *et al*, 1984). The simplified reactions are, however, well known. The three most important inorganic reactions are illustrated in Figure 1.

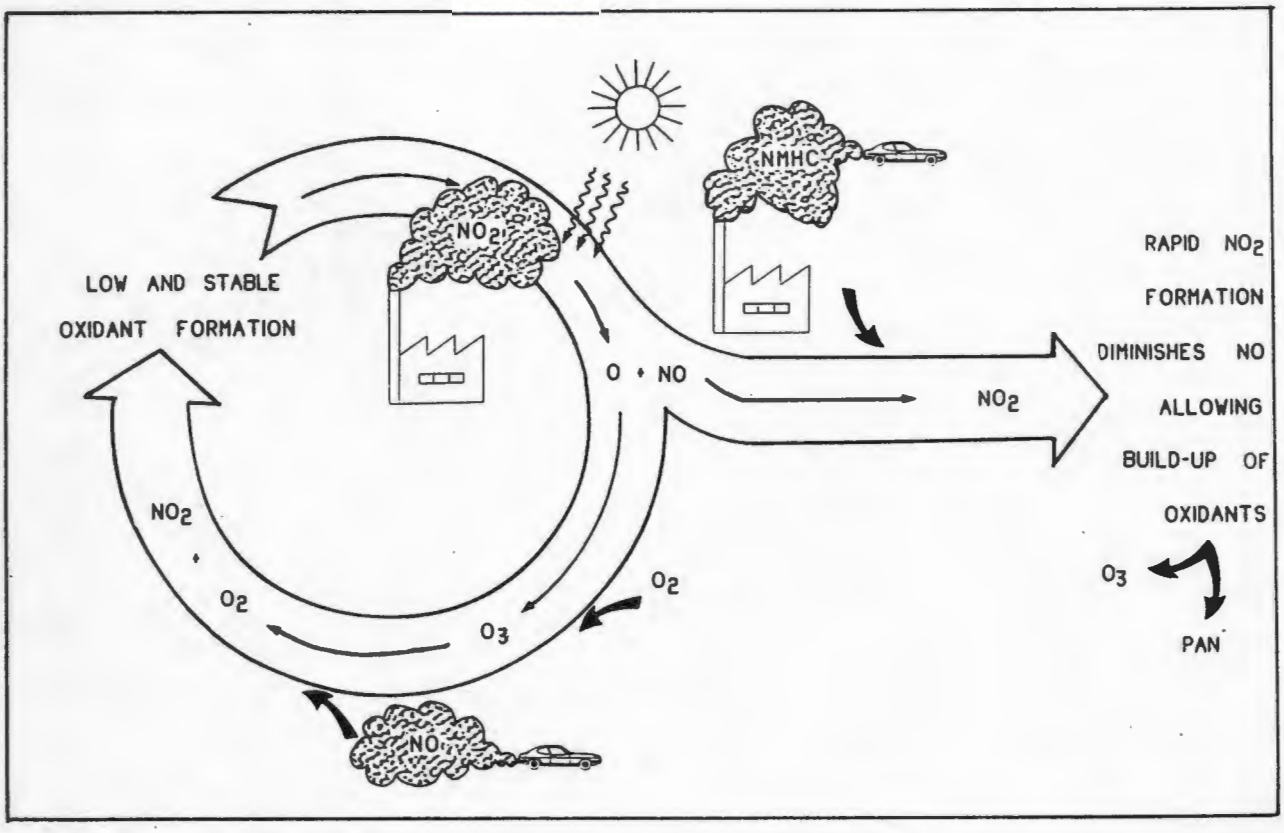

Figure 1: A schematic of the basic reactions involved in the formation of photochemical smog.

After irradiation, nitric oxide (NO), a primary pollutant emitted from vehicle exhausts, is readily oxidised to NO_2. NO_2, which is also a primary pollutant emitted mainly from industrial sources, undergoes photodissociation which produces atomic oxygen (O) and NO. The combination of O with O_2 results in the formation of O_3, the chief constituent of photochemical smog. The combination of NO and O_3 giving NO_2 and O_2 restarts the cycle. The NO_2 concentration reaches a maximum when its rate of formation from NO is just balanced by depletion reactions to form NO and organic nitrates. The formation of O_3 continues until a dynamic equilibrium is reached, where a low but stable O_3 concentration is maintained. However, in the presence of active NMHC, this equilibrium is disturbed, and high O_3 concentrations are rapidly formed. NMHC oxidise and promote the formation of NO_2 from NO, thus reducing the NO which would normally reduce the O_3. This causes the build-up of O_3, PAN,

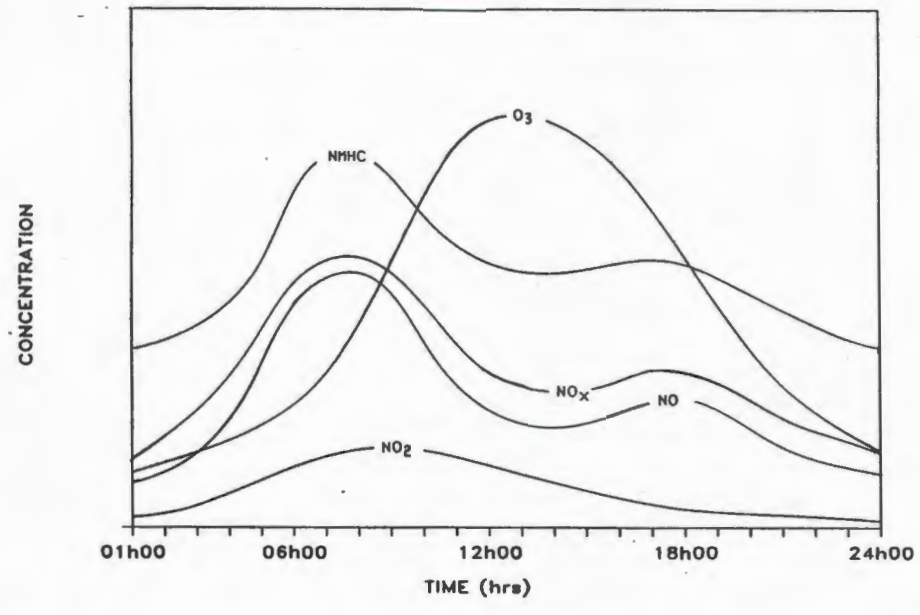

Figure 2: A schematic of the average diurnal variation of photochemical pollutants.

aldehydes. and organic nitrates. Termination of this reaction occurs when high NO_2 concentrations are reached, which inhibit the overall reaction.

Meteorological conditions are known to influence the formation of photochemical smog. Low wind speeds and subsidence inversions allow increases in the NO_X and NMHC concentrations, while intense sunlight (strong ultraviolet radiation) and high temperatures favour the formation of photochemical oxidants. Other variables such as vehicular and industrial emissions are also known to affect the general levels of the precursors and oxidants, and result in an average daily pattern depicted in Figure 2. During the early morning, increased levels of NMHC and NO_X are evident due to peak traffic and by mid-morning, maximum NO_2 levels are reached. From midday to mid-afternoon, maximum solar radiation occurs with a simultaneous maximum in the O_3 concentration.

BACKGROUND INFORMATION

Oxides of Nitrogen

NO_X are emitted naturally during lightning discharges and by decomposition of nitrates in terrestrial and aquatic systems (Aneja *et al*, 1984). Although concentrations of man-made NO_X are far smaller than natural forms, the high concentrations produced on a localised scale by combustion processes, industrial boilers, refineries, explosive manufacture and nitric acid production often cause man-made levels to be far greater than background levels. The primary anthropogenic sources of NO_X are motor vehicle exhaust gases.

The World Health Organisation (WHO) has suggested that NO_2 levels of between 0.1ppm and 0.17ppm for one hour be exceeded only once per month (WHO, 1977). Concentrations of about 400ppm of NO_2 for a short time could result in fatal

pulmonary oedema, whilst levels of 25ppm to 75ppm could cause pneumonia. Japan recommends a maximum level of 0.04ppm for one hour, whilst California recommends a level of 0.25ppm (OECD, 1975).

Hydrocarbons

Hydrocarbons are emitted naturally by various forms of vegetation, but their contribution is relatively insignificant in urban areas. Hydrocarbons generally tend not to be problems in air pollution, but they are essential in the formation of photochemical smog. One of the largest anthropogenic sources of hydrocarbons occurs in emissions of incomplete combustion products by internal combustion engines, and by the evaporation of fuels and solvents. Not all hydrocarbons participate equally in photochemical reactions. Methane is considered to be unreactive, and hence the hydrocarbons involved in the problem of photochemical smog are referred to as NMHC. A simplified classification of the hydrocarbons results in three groups (neglecting any overlap between groups) in increasing order of reactivity: paraffins, which react very slowly; aromatic hydrocarbons; and olefins which react most quickly, and are thus most important in photochemical reactions. Differences in the relative reactivities of the NMHC have led to reactivity classifications (Altschuller *et al*, 1971; Pitts *et al*, 1977), which have enabled the development of selective control strategies for the various hydrocarbons based on reactivity.

The USEPA guideline for NMHC maxima is 0.24ppm for the time period from 06h00 to 09h00, whereas a level of 0.20ppm is recommended in Japan (OECD, 1975).

Ozone

O_3, a powerful oxidising agent, occurs naturally in the stratosphere and is formed by the photolysis of O_2 by

sunlight with a wavelength of less than 430nm. O_3 is produced photochemically within the troposphere and also transported dynamically from the stratosphere into the troposphere by vertical turbulent mass exchange. Fabian and Pruchniewicz (1977), support the latter concept as being the predominant process, found the most active area of stratospheric O_3 transport to be between latitudes 30°N to 60°N, with springtime injections being the largest. Levy *et al* (1985) found that in general, stratospheric sources of O_3 were at a maximum in late winter and early spring, and that the production of summertime O_3 was due to photochemical processes associated with NO_X emissions and NMHC from fossil fuels. Logan and Kirchoff (1986) found high O_3 levels in spring in the Southern Hemisphere to be equal to the levels experienced in the summer, when photochemical sources of O_3 are most prevalent. It was further noted that the behaviour of O_3 in the troposphere was more complex in nature than previously thought and that photochemical processes could be of greater importance to maximum O_3 concentrations in certain locations. Natural hydrocarbons from trees and vegetation can give rise to photochemical reactions during daylight hours which can produce O_3 (Rasmussen, 1972). Other natural sources are associated with the passage of cold fronts (Ripperton *et al*, 1971) and atmospheric phenomena (U.S. Dept.of Health, Education and Welfare, 1970).

O_3 is a photochemical product and not a direct emission. It is known to accelerate the deterioration process of natural and synthetic rubbers at concentrations of 0.01 to 0.02ppm Damage to plants and trees, including petunias, morning glory, hibiscus, poplar and tobacco as well as loss of crop yield, are also recognisable at these levels (OECD, 1979; WHO, 1978). O_3 is known to interfere with the normal functions of the lung in healthy adults at levels above 0.25ppm. Increased susceptibility to infectious pulmonary disease, systematic biochemical changes, eye, nose and throat irritation, nausea and cellular alterations have been noted as primary effects of O_3 (WHO, 1978).

In the United States, the primary (health) and secondary (welfare) national ambient air quality standards are set at a one hour (1-h) average level of 0.12ppm, not to be exceeded on more than one day per year (US Federal Register, 1979). The Australians use the same goal for 1-h average O_3 (NSW, 1984) whereas the Japanese and the World Health Organisation long term goal is 0.06ppm (Tokyo, 1985).

PHOTOCHEMICAL SMOG IN CAPE TOWN

In South Africa, very few studies on photochemical smog have been conducted. Various studies on pollutant levels in South Africa have been carried out (Kemeny and Halliday, 1974; Kemeny, 1977) although the emphasis was placed on smoke and sulphur dioxide. Studies by Louw *et al* (1977) have detailed vehicle pollution in the Pretoria area, and Stevens (1987) studied photochemical smog in the Greater Johannesburg Region. During 1974, measurements of pollutant levels were carried out in Cape Town and Prof. Lovelock of Reading University suggested the potential for photochemical smog. This marked the start of measurements of photochemical precursor and oxidant concentrations in the Greater Cape Town area.

Air Pollution Survey of Greater Cape Town

An air pollution survey was commissioned by the City Council of Cape Town at the end of 1975 in order to assess the levels of selected pollutants in Cape Town. The decision to investigate photochemical pollutants was prompted by the earlier measurements taken in 1974 (which suggested that Cape Town had the potential for photochemical smog). Monitoring of pollutant concentrations during the survey, including the precursors of photochemical smog (namely NO_x, O_3 and total hydrocarbons), was undertaken using a mobile laboratory equipped with the relevant instrumentation.

Results obtained from the two week survey in February 1977 and July 1978, covering both summer and wintertime conditions showed:

(a) O_3 levels to be extremely high in Oranjezicht (a suburb near the city centre), the highest 1-h level being 0.2ppm (250% of the USEPA Standard);
(b) the maximum 1-h average oxidant level to be 0.52ppm (518% of the California Standard);
(c) the maximum 1-h average of NO_x levels to be 0.16ppm (300% of the USEPA Standards);
(d) total hydrocarbons to be above acceptable limits, approximately 1.3ppm for the 3-h average (500% of the limits in the United States).

(The standards referred to above can be found in Appendix 1.2)

Based on the results of the Air Pollution Survey of Greater Cape Town, where high levels of precursors and oxidants were measured, it was suggested that an in-depth study of photochemical smog in Cape Town be undertaken in the near future (Dutkiewicz *et al*, 1980).

Consultant's viewpoint: Dr. M.Y. Smith

A brief visit by Dr. M.Y. Smith from the Commonwealth Scientific and Industrial Research Organisation in Sydney, Australia was made in 1984 to survey aspects of urban air pollution with particular reference to Cape Town. From the initial data collected, which was sparse compared to that in Sydney, it was suggested that Cape Town had a photochemical smog problem. In comparing precursor and oxidant levels between Cape Town and Sydney, the levels of NO_x were generally found to be considerably higher. The O_3 readings measured by Dutkiewicz (1979) at Oranjezicht were found to be high compared to Sydney, but those taken at the City Hall were significantly lower. Edgemead data for 1984 revealed

three occasions when O_3 values exceeded the USEPA 1-h standard of 0.12ppm, thus indicating the likely presence of photochemical smog, although difficulties had been experienced with the calibration of the O_3 monitor at that time. Mention was made of the lack of precursor and oxidant data and in particular, the absence of summertime data.

The recommendations for research and investigation can be summarised as follows:

(a) to fully assess Cape Town's photochemical air pollution situation by further data collection;
(b) to interpret the meteorology of Cape Town together with the levels of precursors and oxidants;
(c) to upgrade the existing monitoring system by obtaining additional instrumentation such as a NMHC analyser, a separate calibration apparatus for all the monitors and a PAN chromatograph;
(d) to build a smog chamber to allow for the characterisation of local hydrocarbon sources;
(e) to apply a predictive model particular to the Cape Town situation.

APPROACH AND AIMS OF THE STUDY

Past studies have indicated the presence of photochemical smog in Cape Town (Dutkiewicz *et al*, 1980; Smith, 1984), but no detailed research has been conducted to ascertain the nature and extent of this problem. This study was therefore aimed at providing a more detailed understanding of photochemical precursor and oxidant concentrations in the urban atmosphere of Greater Cape Town. This was approached by the investigation and assessment of the spatial and temporal behaviour of photochemical pollutants, and viewed as a concern of Cape Town's atmospheric environment requiring identification and assessment, rather than one of complex air chemistry analysis.

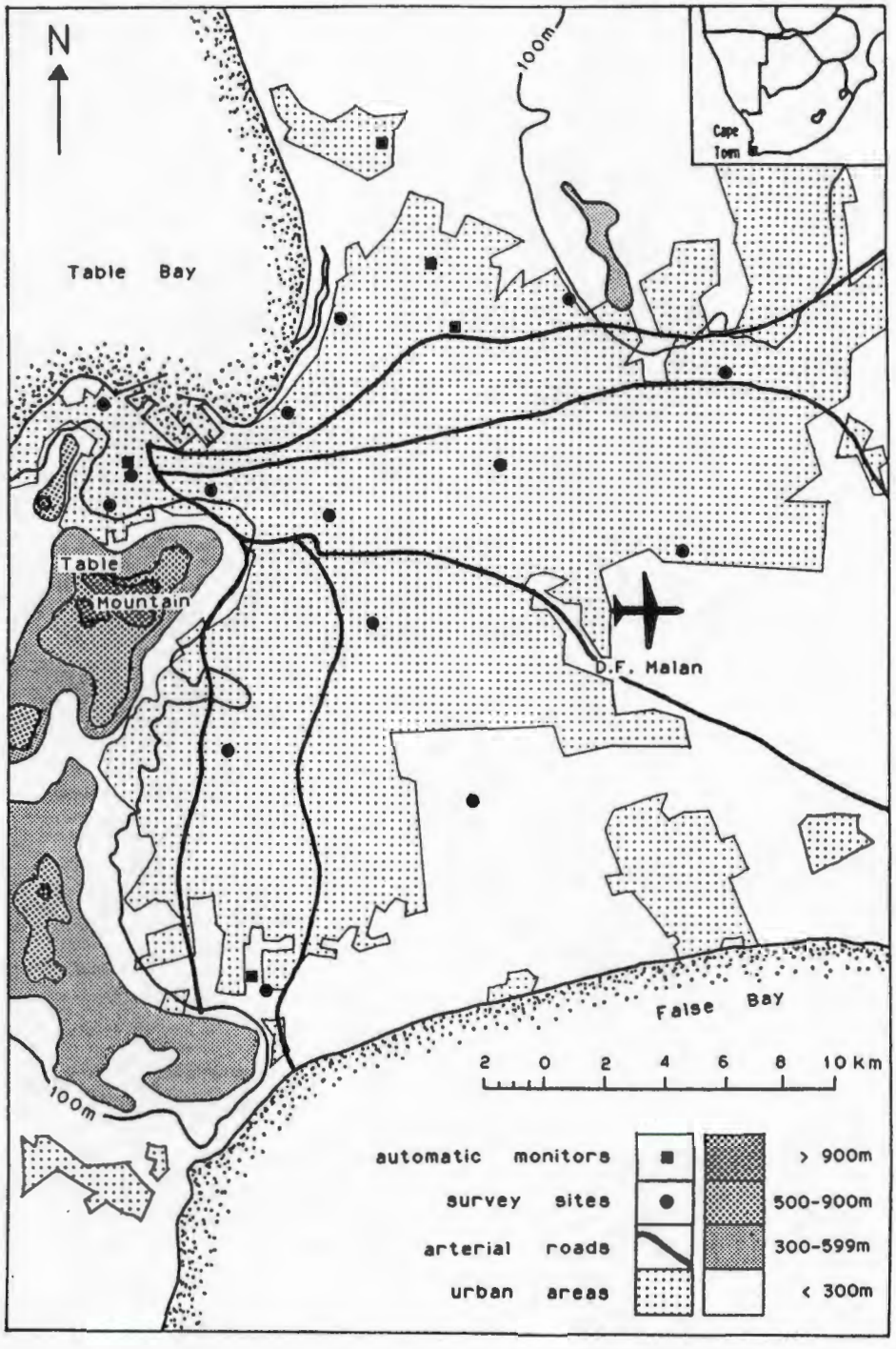

Figure 3: Location map of the study area showing the urban area, surrounding topography, arterial roads and the automatic monitor and survey sites.

The collection of continuous data of precursors and oxidants by the Cape Town City Council and the Regional Services Council since 1984 provided an adequate initial data set for such a study. The monitor data was limited to very few sampling sites and thus had to be supplemented by a comprehensive field program which was undertaken in April and May of 1987. A large number of sampling sites were chosen for this field program, which made use of bag samples and a single automatic monitoring system. The locations of automatic monitors and sampling sites in relation to the surrounding topography, urban areas and chief arterial roads are illustrated in Figure 3. The trends in the data and its relationship to meteorology were initially analysed. This was followed by a consideration of the spatial distribution of the precursor and oxidant concentrations and their variation over time. This was followed by a closer interpretation of the combined data sets to make an assessment of photochemical smog in Greater Cape Town.

The approach adopted for the presentation of this thesis is one whereby the body of the text consists of three chapters in the form of scientific papers in journal format. Three different aspects of photochemical smog in Greater Cape Town have been approached and thus each is reported in a separate chapter (paper), where the data relevant to each chapter are given in the appropriate appendix (ie. Ch.2's data can be found in Appendix 2). Titles of each chapter and short descriptions outlining the aspects covered in each are provided below:

Chapter 2

TREND ANALYSIS OF PHOTOCHEMICAL PRECURSOR AND OXIDANT CONCENTRATIONS AND METEOROLOGICAL INFLUENCES IN GREATER CAPE TOWN

This chapter analyses the seasonal, diurnal and hourly trends and variations of precursor and oxidant concentrations in the Greater Cape Town area. Peak O_3 events

are also examined, together with the relationship of pollutants to selected meteorological parameters.

Chapter 3

A SPATIAL SURVEY OF PHOTOCHEMICAL PRECURSOR AND OXIDANT CONCENTRATIONS IN GREATER CAPE TOWN.

This chapter is an investigation of the spatial distribution of precursor and oxidant concentrations and their variation over time. A field survey comprising a program of bag sampling from fifteen sites was performed in order to detail the spatial variations of photochemical pollutants in and around the city.

Chapter 4

AN ASSESSMENT OF PHOTOCHEMICAL SMOG IN GREATER CAPE TOWN.

This chapter examines the factors controlling precursor and oxidant levels, and the chemical relationships evident in the empirical data. Pollutant levels are compared to selected standards and to levels experienced in other cities, in order to gauge the relative severity of photochemical smog in Greater Cape Town.

These chapters are followed by a thesis conclusion and a complete reference list incorporating all references used in the thesis.

CHAPTER 2

TREND ANALYSIS OF PHOTOCHEMICAL PRECURSOR AND OXIDANT CONCENTRATIONS AND METEOROLOGICAL INFLUENCES IN GREATER CAPE TOWN

Concentrations of nitrogen oxides, non-methane hydrocarbons and ozone (O_3) were monitored in Greater Cape Town from 1984 to 1986, and have been analysed in terms of trends in the data and influences of meteorology. It was found that variations in the precursor concentrations were directly influenced by the seasonal cycle of the weather, whereas O_3 behaviour was complex and lacked a simple seasonal trend. Daily fluctuations in precursor levels were largely determined by the weather, with a clear weekday/weekend difference resulting from the change in emissions. O_3 showed no strong relationships to selected meteorological parameters, although marginally higher O_3 levels were found with warmer temperatures, and with southerly winds at the northerly located sites. O_3 displayed no differences between weekdays and weekends. The hourly patterns of precursors were directly dependent on traffic flow and density while O_3 levels tended to increase with greater ultraviolet radiation. O_3 levels did not exceed the 1-h USEPA standard of 0.12ppm but equalled or exceeded the WHO 1-h goal of 0.06ppm on 26 occasions. High O_3 levels were generally found on fair weather days with the South Atlantic Anticyclone to the west of Cape Town, or with a Coastal Low over the Peninsula.

INTRODUCTION

Photochemical smog is the name given to a complex sequence of chemical reactions that occurs in the presence of sunlight. These reactions involve the formation of secondary pollutants, known as photochemical oxidants, which are produced from a number of primary pollutants or precursors that are commonly associated with vehicular and industrial emissions. The reactions between the precursors and oxidants that constitute photochemical smog possess extremely complicated mechanisms, in which prevailing meteorology, pollutant emissions, and chemical reactions all play important roles.

The complexities of the chemical reactions are not yet well understood (Innes, 1981; Johnson, 1983; Kelly *et al*, 1984), but the basic reactions are well known and are illustrated in Figure 1. In the atmosphere nitric oxide (NO), which is a product of a range of combustion processes, is oxidised to

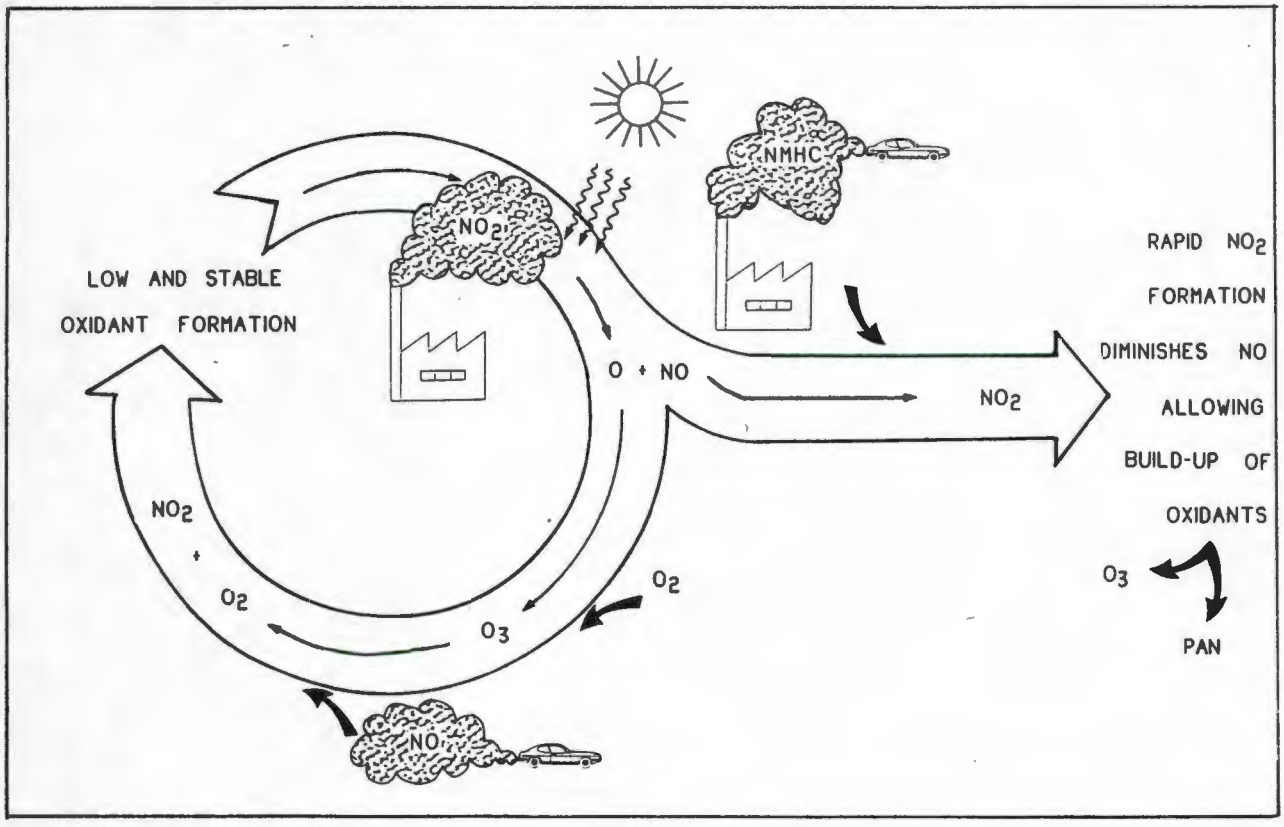

Figure 1: A schematic of the basic reactions involved in the formation of photochemical smog.

nitrogen dioxide (NO_2). This oxidation process is greatly accelerated by the presence of non-methane hydrocarbons (NMHC), which are emitted from sources such as vehicles, and petrochemical and solvent based industries. NO_2 is reduced to NO and atomic oxygen (O) by photodissociation. This is followed by a reaction between O and molecular oxygen (O_2) to produce ozone (O_3), the chief constituent of photochemical smog. O_3 concentrations can become depleted by significantly large quantities of NO, thereby resulting in the formation of O_2 and NO_2. Other more complex reactions involving NMHC, O_3 and NO_2 yield products such as peroxyacetyl nitrate (PAN), organic peroxides and aldehydes. O_3 is quantitatively the most important reaction product and its concentration is often used as an index of the severity of the above processes in the atmosphere.

Photochemical smog was first identified by Haagen-Smit (1952) in Los Angeles where much of the initial analysis of photochemical smog was conducted. A definitive monograph by Leighton (1961) presented the mechanisms and chemical aspects of photochemical smog in the atmosphere and laboratory, and today still provides a basis to the understanding of photochemical smog.

The growing recognition of the adverse effects of photochemical air pollution led to the establishment of monitoring systems in many cities around the world, initially to gauge pollutant levels in order to establish standards, and thereafter to monitor for the occurrence of episodes. Hence, geographically localised and empirically based studies have tended to dominate the literature. Such studies include those performed in the United States (Edinger, 1973; Bruntz *et al*, 1974; Tiao *et al*, 1975; Elkus and Wilson, 1977; Trijonis *et al*, 1978; Vukovich, 1986), Europe (Guicherit and Van Dop, 1977; Ball and Bernard, 1978) and Australia (Sullivan, 1962; Hawke and Iverach, 1974; Post, 1981; Post and Carruthers, 1983). In an effort to improve the existing knowledge on photochemical smog,

comprehensive surveys such as the Sydney Oxidant Study were undertaken (Carras and Johnson, 1983). The concurrent development of smog chamber analyses (Kamens *et al*, 1982; Smith and Johnson, 1983; Evans *et al*, 1986) and modelling (Dodge, 1977; Derwent and Hov, 1980; Johnson, 1983) have aided in the formulation of optimum control strategies for the maintenance of pollutant levels within acceptable limits.

In Cape Town, photochemical smog was investigated as part of an Air Pollution Survey of Greater Cape Town (Dutkiewicz and Fuggle, 1977; Dutkiewicz, 1979; Dutkiewicz *et al*, 1980). The study concluded that Cape Town experiences photochemical smog for a limited number of hours during the year. Consequently, monitors were installed at a few selected sites around the city. More recently an investigation by Smith (1984) based on the initial data available, indicated the likelihood of photochemical smog formation in Cape Town. It was recommended that further studies be conducted with more detailed data collection.

Since 1984 routine monitoring has further expanded the data set, both in time and in the range of pollutants sampled. It has been suggested that the value of data resulting from routine monitoring appears to be only to find out how often a standard is exceeded, after which the data are archived (Stevens and Rimmer, 1984). The need thus exists to use the data constructively to broaden the basis of knowledge on photochemical smog. Trend analysis is one such method that constitutes a fundamental part of the feedback approach towards the understanding and control of air pollution (Trijonis *et al*, 1978; Ball and Bernard, 1978).

This study presents the trends of selected precursor and oxidant concentrations in Cape Town, as revealed by analysis of long-term trends through to small-scale hourly fluctuations. Relationships between pollutant levels and influencing factors, in particular meteorology, are

highlighted, with emphasis given to days with high O_3 concentrations.

DATA BASE AND INSTRUMENTATION

Although NO_X levels have been monitored since 1975 at the City Hall as part of general pollutant measurements, specific monitoring of photochemical smog constituents only began in 1984, when an automatic air pollution monitoring system was installed at the City Hall (sometimes referred to as the central business district, or CBD). Monitors initially recorded O_3, NO, NO_2 and NO_X data, after which additional monitors recording NMHC and ultraviolet radiation became operational in 1986. A mobile monitoring system recording NO, NO_2, NO_X and O_3 data was located in Edgemead in 1984 and was moved to Bothasig in 1986. A third system recording NO, NO_2, NO_X, NMHC and O_3 data was installed at Lakeside in 1985 and was relocated to Table View in 1986. In this study all the above sites, except the City Hall, are generally referred to as the suburbs. The relative location of the abovementioned sites and the times during which corrected data were available are illustrated in Figure 2. During the four months in 1984 that O_3 was recorded in Edgemead, surprisingly high O_3 levels were continuously measured. These O_3 readings were however excluded from this study, upon consideration of the calibration problems that were encountered at that time.

NO, NO_2 and NO_X were monitored by chemiluminescence principles using Monitor Labs Model 8840 and Model 14D/E instruments. O_3 was monitored by ultraviolet absorption detectors, using Monitor Labs Model 8810 and Dasibi instruments. NMHC were monitored by an HNU Model PI201 analyser, operating on the principle of photoionisation. Stevens (1987) found close agreement between NMHC readings taken by the non-standard HNU analyser and the US Environmental Protection Agency (USEPA) approved Byron

analyser. Actinic flux was monitored using an ultraviolet radiometer. Raw data were collected via a Monitor Labs Model 8350 datalogger, which provided hourly averages of each pollutant. Hourly data were recorded on magnetic tape and were regularly downloaded onto a microcomputer (Fortune 16:32). Calibration procedures can be found in Appendix 2.1.

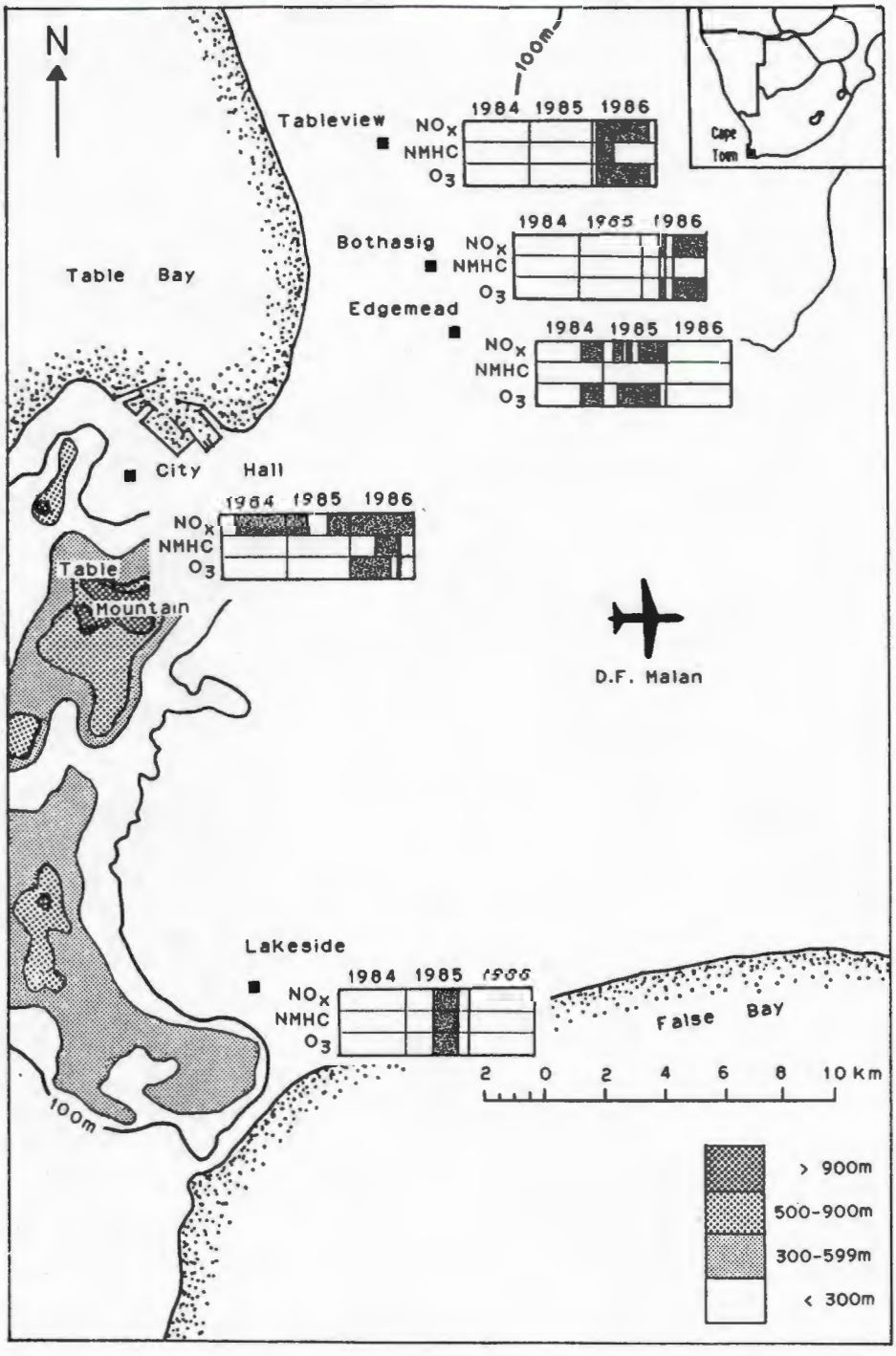

Figure 2: Location of automatic sampling sites, the pollutants sampled and the duration of data collection.

Meteorological data were obtained from the weather station at D.F. Malan airport (Figure 2) which included measurements of temperature, wind speed, wind direction, and inversion heights and strengths. Reference was also made to Fuggle (1978) and Keen (1979) for further knowledge on the surface wind field and meteorological aspects of air pollution transport in Greater Cape Town.

RESULTS AND DISCUSSION

Long-term trends and variations

Figure 3a, b and c illustrate the average monthly precursor and oxidant levels measured from 1984 to 1986. NO_x levels at the City Hall date back to 1975, and have remained remarkably similar over the last ten years, with monthly means ranging between 0.05ppm and 0.20ppm. No significant trends in the NO_x data at the City Hall were apparent, although a marginal decrease from 1984 to 1986 was evident. NMHC data were largely incomplete, but values appeared to be centred around 0.15ppm. The more continuous O_3 data varied according to location, with the majority of monthly means below 0.025ppm. Given that the parameters controlling precursor and oxidant concentrations such as vehicle numbers, industry and meteorology have not undergone any major changes in recent years, and are not expected to do so in the near future, it is anticipated that the present levels and trends will only undergo minimal changes over the next few years.

The month to month variations for the majority of data showed a definite seasonal influence. These fluctuations in concentration were predominantly a function of the changing meteorological regimes found during the year in Cape Town, with the individual pollutants each displaying different degrees of response to the varying conditions.

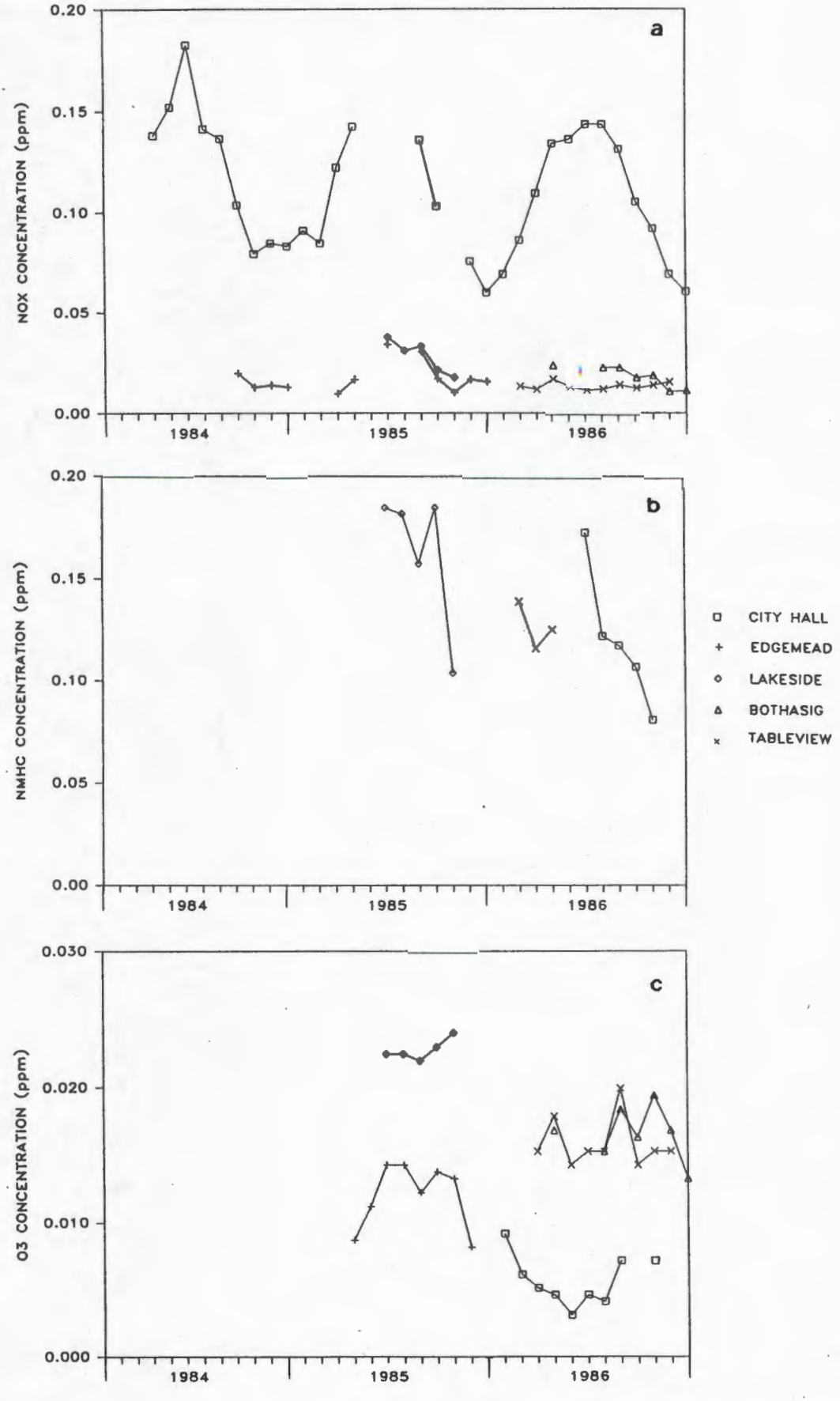

Figure 3: Average monthly variations of (a) NO_X, (b) NMHC, and (c) O_3 concentrations at all sites from 1984 to 1986.

NO_X

The NO_X levels were closely correlated to the seasonal cycle of the weather. This is clearly illustrated in the comparison of monthly NO_X levels to monthly wind speeds in Figure 4. Summer months (October to March) are typified by higher wind speeds and a well mixed atmosphere, and hence possess a reduced pollution potential (Keen, 1979). This influence was reflected in the lower concentrations

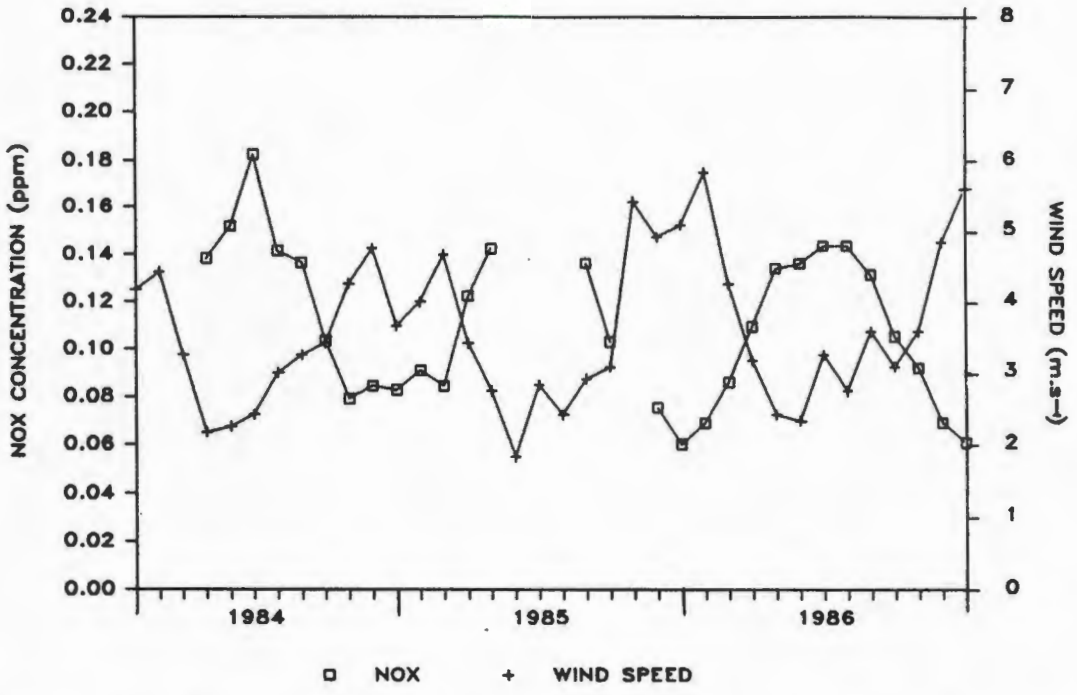

Figure 4: Monthly NO_X levels at the City Hall and monthly wind speeds.

measured, with monthly averages of about 0.013ppm in the suburban areas, and a range of levels from 0.053ppm to 0.093ppm in the CBD. NO_X minima generally occurred between October and December when wind speed was at a maximum, and increased gradually until late summer. Winter months (April to September) in Cape Town are characterised by lower wind speeds and the frequent occurrence of surface inversions (Tyson *et al*, 1976). These conditions of increased air pollution potential during winter resulted in elevated NO_X levels of about 0.027ppm in the suburban areas, and a range from 0.133ppm to 0.160ppm in the CBD.

The frequency distributions of NO_X for typical summer and winter months at the City Hall and Lakeside are given in Figure 5. The proportion of high values in winter in the CBD was characterised by a more even distribution of NO_X up to 0.15ppm compared to summer, when the decreased frequency of high NO_X values were reflected in the correspondingly increased frequency of lower values. The NO_X concentrations in Lakeside (with reduced vehicle emissions) were skewed towards lower NO_X values but showed similar seasonal tendencies to the CBD.

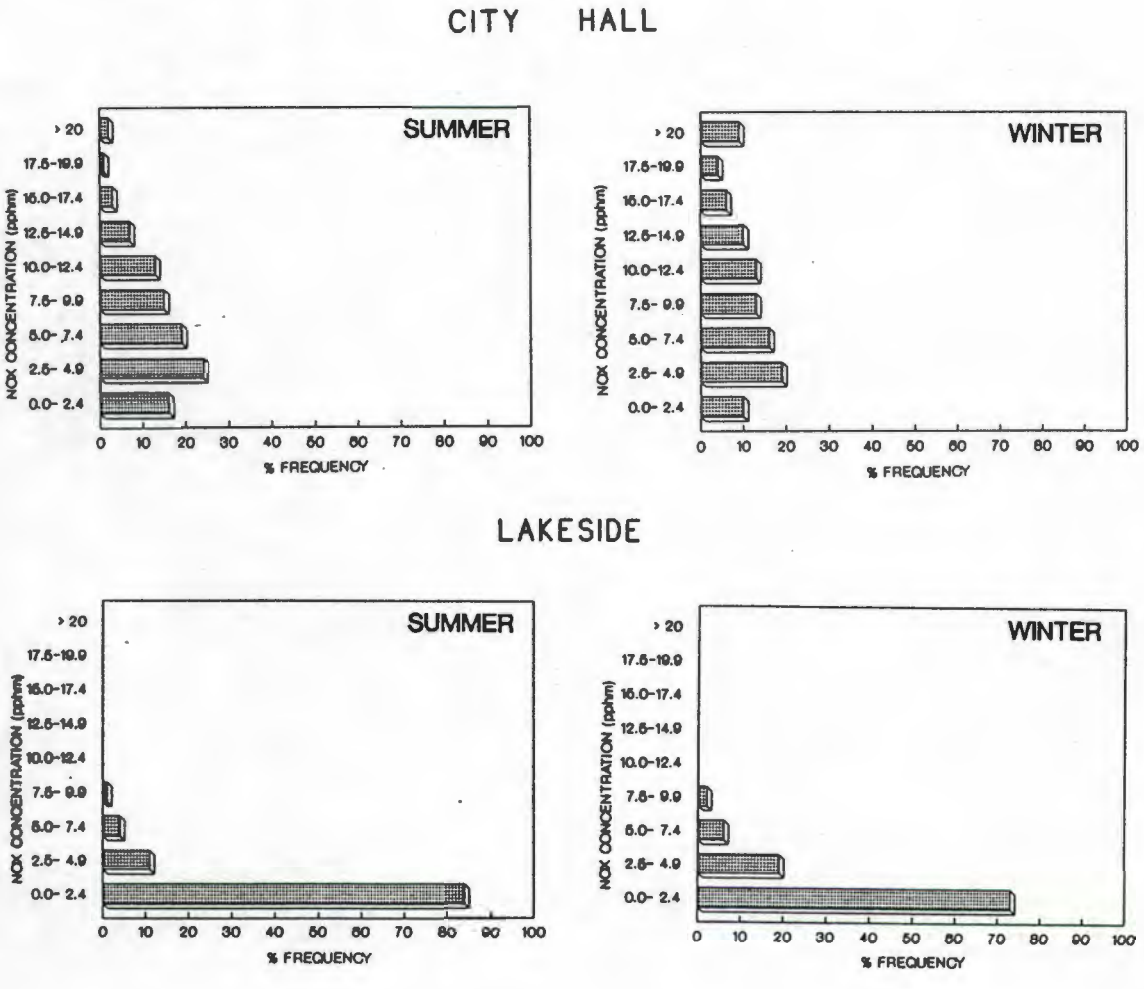

Figure 5: Percentage frequency distributions of NO_X at the City Hall (February and July) and Lakeside (October and June) for typical summer and winter months respectively.

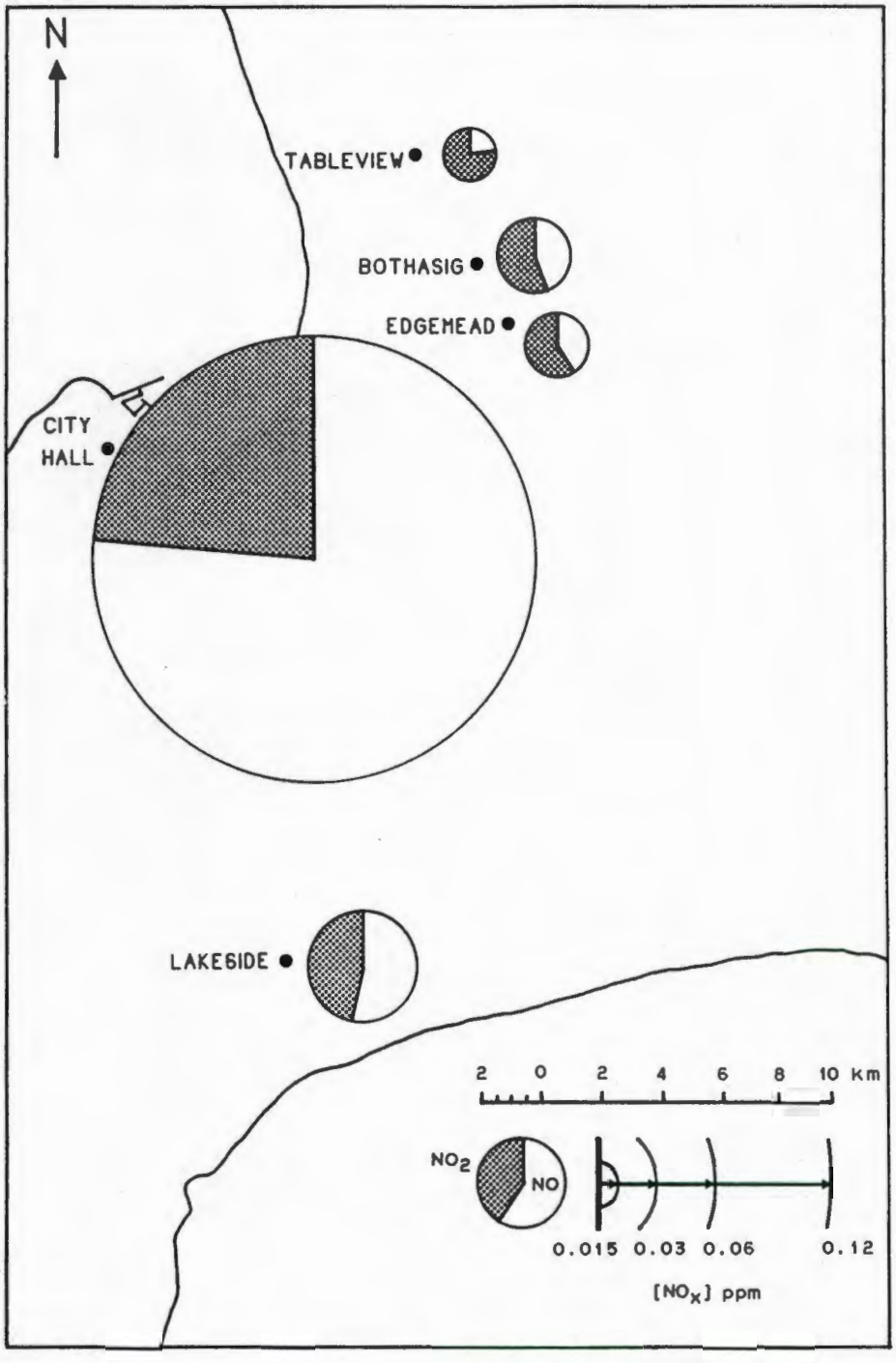

Figure 6: Proportions of NO and NO_2 to the NO_x concentration at all sites.

The high proportion of NO in the CBD atmosphere, compared to the suburbs, was a direct consequence of the different emission patterns associated with the respective areas. The proportions of NO and NO_2 to the NO_x concentration for the CBD and suburbs are depicted in Figure 6. Greater traffic densities in the CBD maintained a high NO ratio compared to the suburbs, where the NO supply was lower and the relative proportion of NO_2 was greater. The likelihood of O_3 depletion in the CBD was therefore enhanced relative to the suburban areas.

NMHC

Although the NMHC data were very limited, a general decrease in levels from winter to summer was evident. The behaviour

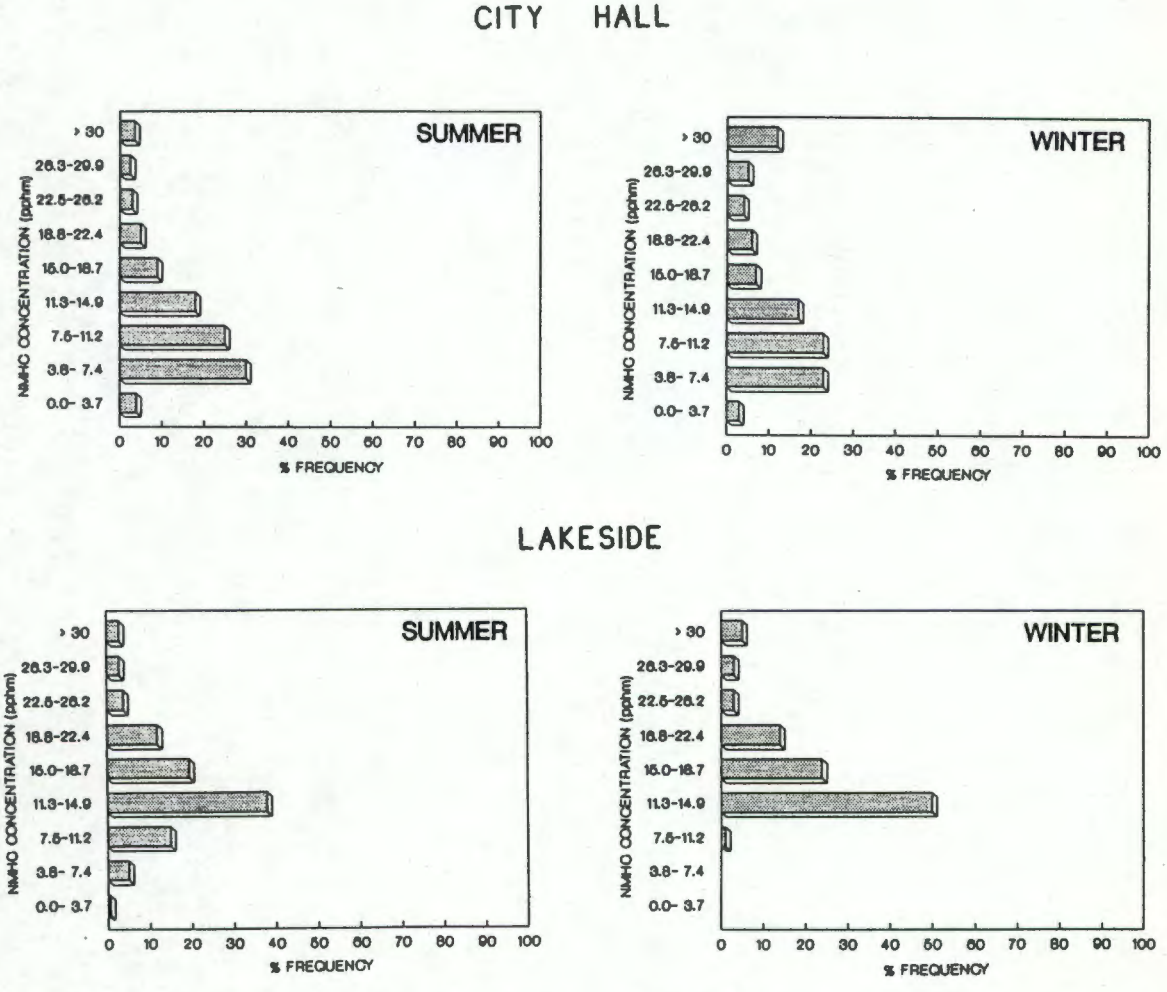

Figure 7: Percentage frequency distributions of NMHC at the City Hall (October and June) and Lakeside (October and July) for typical summer and winter months respectively.

of NMHC approximated that of NO_x, both being primary pollutants emitted by similar sources and subject to the same meteorological influences. NMHC levels were generally greater in winter and lower in summer, even though increased evaporative emissions in summer might be expected to occur at higher temperatures. Unlike NO_x, NMHC levels appeared to be of the same order of magnitude at all sites (average monthly concentrations fluctuated between 0.075ppm and 0.190ppm), contrary to the more localised variations found in Sydney, Australia by Post (1981). The frequency distributions of NMHC for typical winter and summer months at the City Hall and Lakeside are shown in Figure 7. NMHC values remained within a relatively narrow range at the suburban site due to consistent emission patterns, while the CBD was characterised by a much broader spread of data augmented by the diurnal vehicle patterns. The higher values in winter can be seen at City Hall in the less skewed distributions for this period, and the corresponding shift from the lower ranges to the mid ranges at Lakeside.

O_3

The monthly trends in the O_3 data were more complex in nature than those of the primary pollutants. This was attributed to the conflict between the meteorology of Cape Town and the formation mechanisms of photochemical smog. The increased dilution potential offered by the higher wind speeds in summer occurs at the same time as the strongest ultraviolet radiation which promotes the formation of photochemical smog.

The available O_3 data (see Figure 3) revealed a peak during August and September. This period of maximum O_3 formation corresponds to a recorded increase in the background levels at Cape Point (approximately 50km south of Cape Town) during late winter and early spring (Brunke and Allen, 1985), and also to the well documented Southern Hemisphere tropospheric O_3 peak (Fabian and Pruchniewicz, 1977; Logan and Kirchhoff,

1986). The somewhat lower O_3 levels experienced in early summer (October, November and December) were possibly a result of the higher wind speeds experienced at this time of year. Increased temperatures and the somewhat decreased wind speeds present during late summer (January and February) may have led to slightly higher O_3 levels, but verification of the above statements would require a more complete summer data set.

Figure 8 illustrates the higher O_3 values experienced in summer at both the City Hall and Tableview sites. In the CBD, a downward shift in concentration occurred from summer to winter, while a similar but more damped pattern was found at Tableview. Reduced O_3 levels occurred in late autumn and

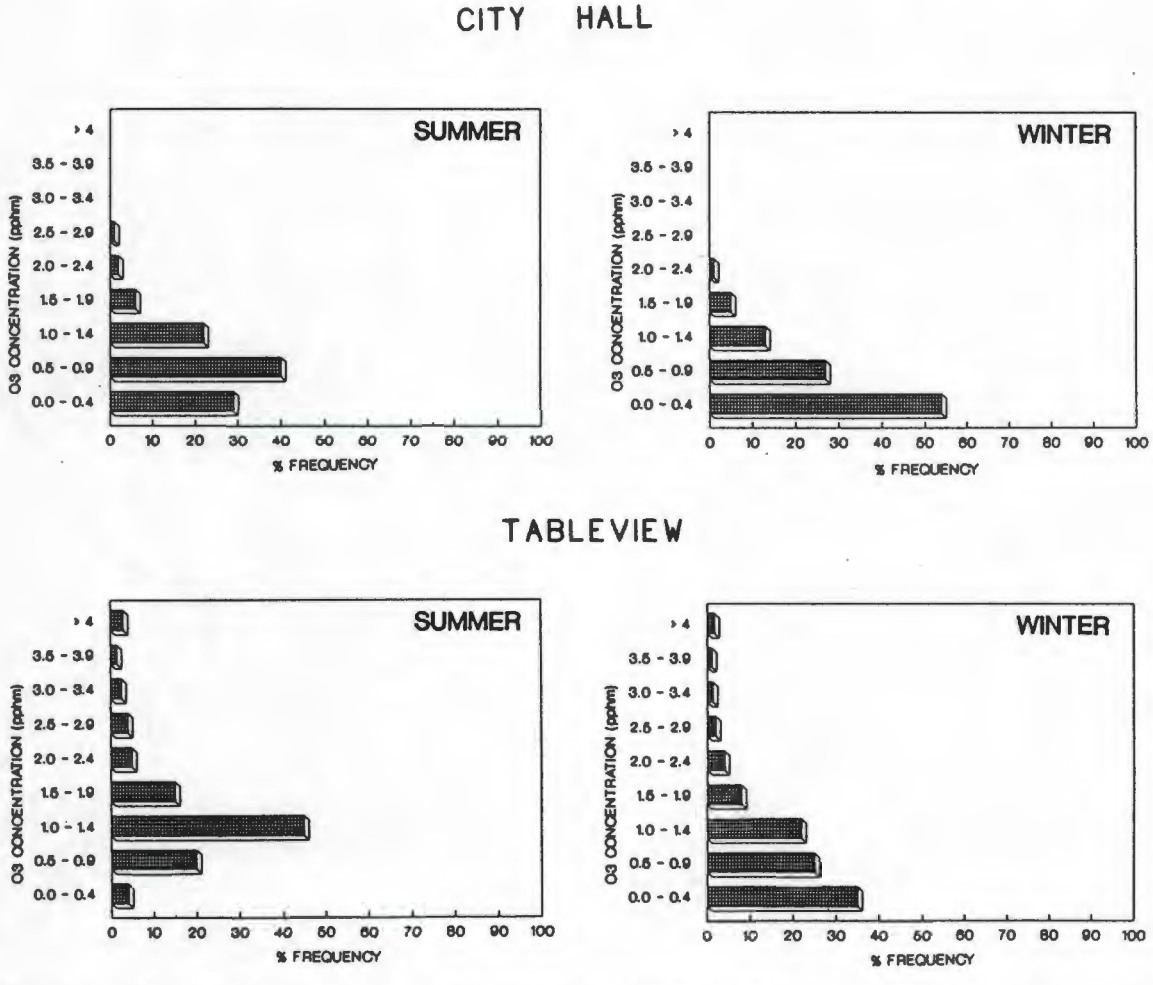

Figure 8: Percentage frequency distributions of O_3 at the City Hall (February and July) and Tableview (March and July) for typical summer and winter months respectively.

winter, together with diminished sunlight intensity. More importantly, the predominance of low wind speeds (see Figure 4) and surface inversions possibly resulted in the trapping of primary pollutants and the scavenging of O_3 by high NO levels. This effect was most pronounced in the CBD, being the main source area of NO. In the city the NO/NO_2 ratio increased from approximately 2 to greater than 4 from summer to winter, whereas in Tableview this ratio remained around 0.5 throughout the year. Thus the greater proportion of NO had the effect of exaggerating the natural depression of O_3 values in the CBD in winter, compared to Tableview. The relationships between O_3 and the various meteorological variables are however extremely complex, and defy any easy explanation of observed patterns (see below).

Daily variations

The pronounced daily fluctuations present in the measured pollutant concentrations were largely determined by variations in the weather. The behaviour of primary pollutants closely followed conditions for air pollution potential, and was strongly related to factors such as wind speed and inversions. The behaviour of a secondary pollutant such as O_3 is not as simple, and its relationship to meteorological parameters is considered highly complex in nature (Ball and Bernard, 1978; Mitchell *et al*, 1983; Post and Carruthers, 1983). A more detailed analysis of the O_3 to weather relationship was thus undertaken, using a relatively complete data set obtained in 1986.

O_3 AND METEOROLOGICAL PARAMETERS

O_3 levels were recorded across a full range of maximum temperatures from 10^0C to 35^0C (see Figures 9a, b and c). A wide range of scatter was present, showing no relationship between the O_3 concentrations and temperature maxima. Figure 10 (a, b and c) depicts a similar but somewhat more positive relationship between O_3 maxima and the 11h00 ultraviolet

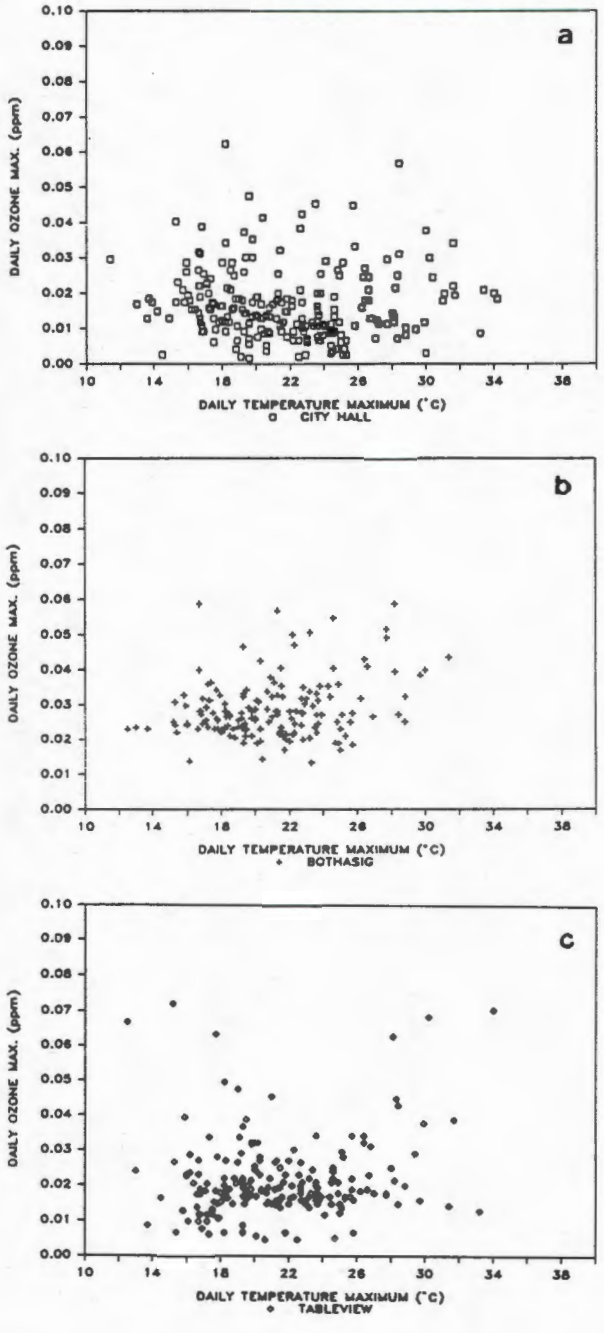

Figure 9: Daily O_3 maximum as a function of the daily temperature maximum at (a) City Hall, (b) Bothasig, and (c) Tableview during 1986.

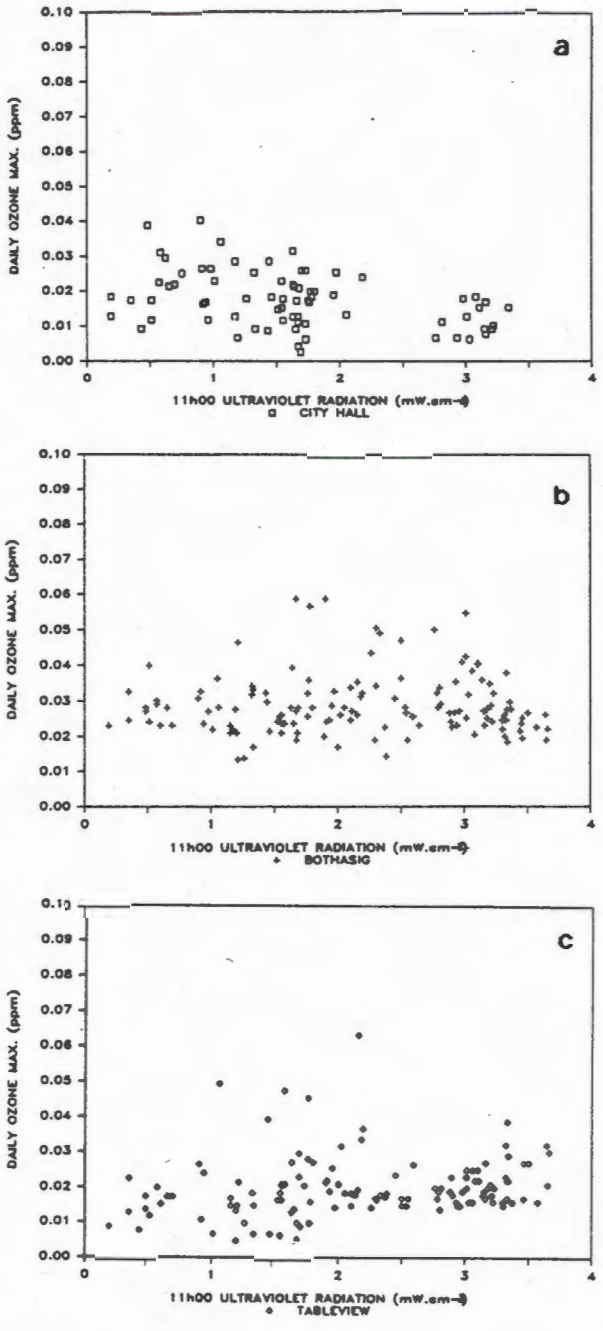

Figure 10: Daily O_3 maximum as a function of the 11h00 ultraviolet radiation at (a) City Hall, (b) Bothasig, and (c) Tableview during 1986.

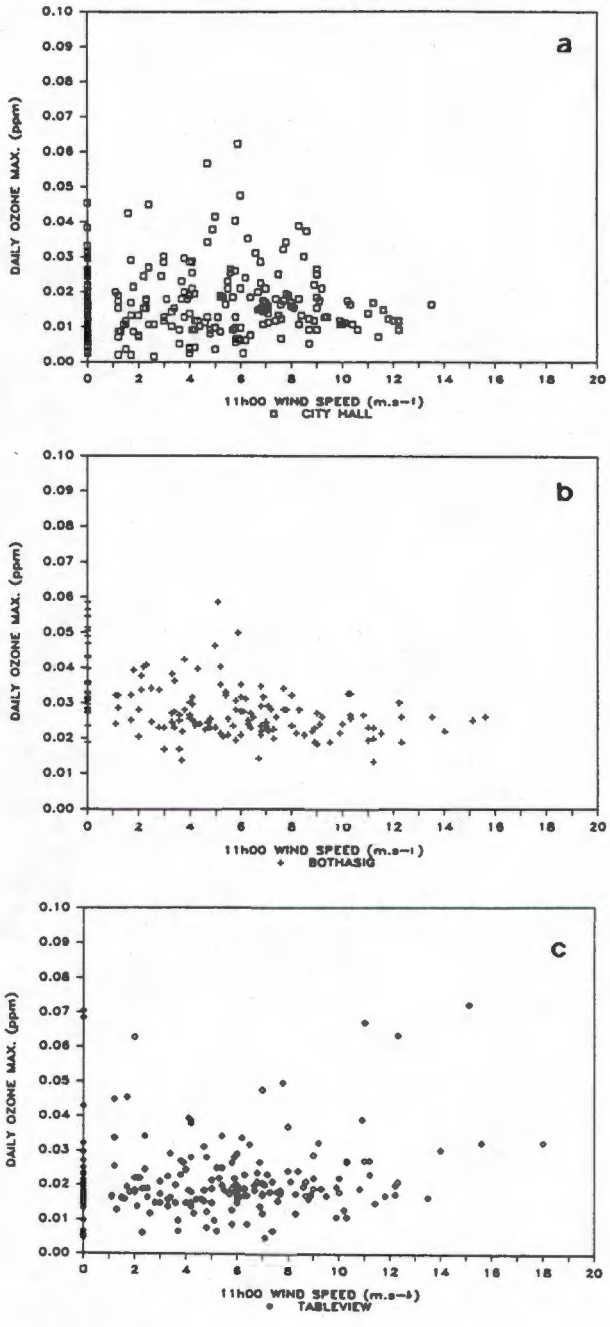

Figure 11: Daily O_3 maximum as a function of the 11h00 wind speed at (a) City Hall, (b) Bothasig, and (c) Tableview during 1986.

radiation measurements. As seen in Figures 11a, b and c, wind speed appeared to have a negligible effect on the O_3 levels, with a wide range of high and low O_3 values at all wind speeds. Wind direction appeared to have a more direct relationship to the O_3 concentrations. Illustrated in Figure 12 are the O_3 concentration roses for three sites during 1986. Higher concentrations were independently experienced at all sites with a southerly O_3 vector (E to WSW inclusive). This was partially attributable to the more northerly location of the sampling sites in the city and the influence of the transport of local urban emissions towards them. In the Bothasig and Tableview area, average O_3 maxima were about 0.024ppm. Under northerly wind conditions this

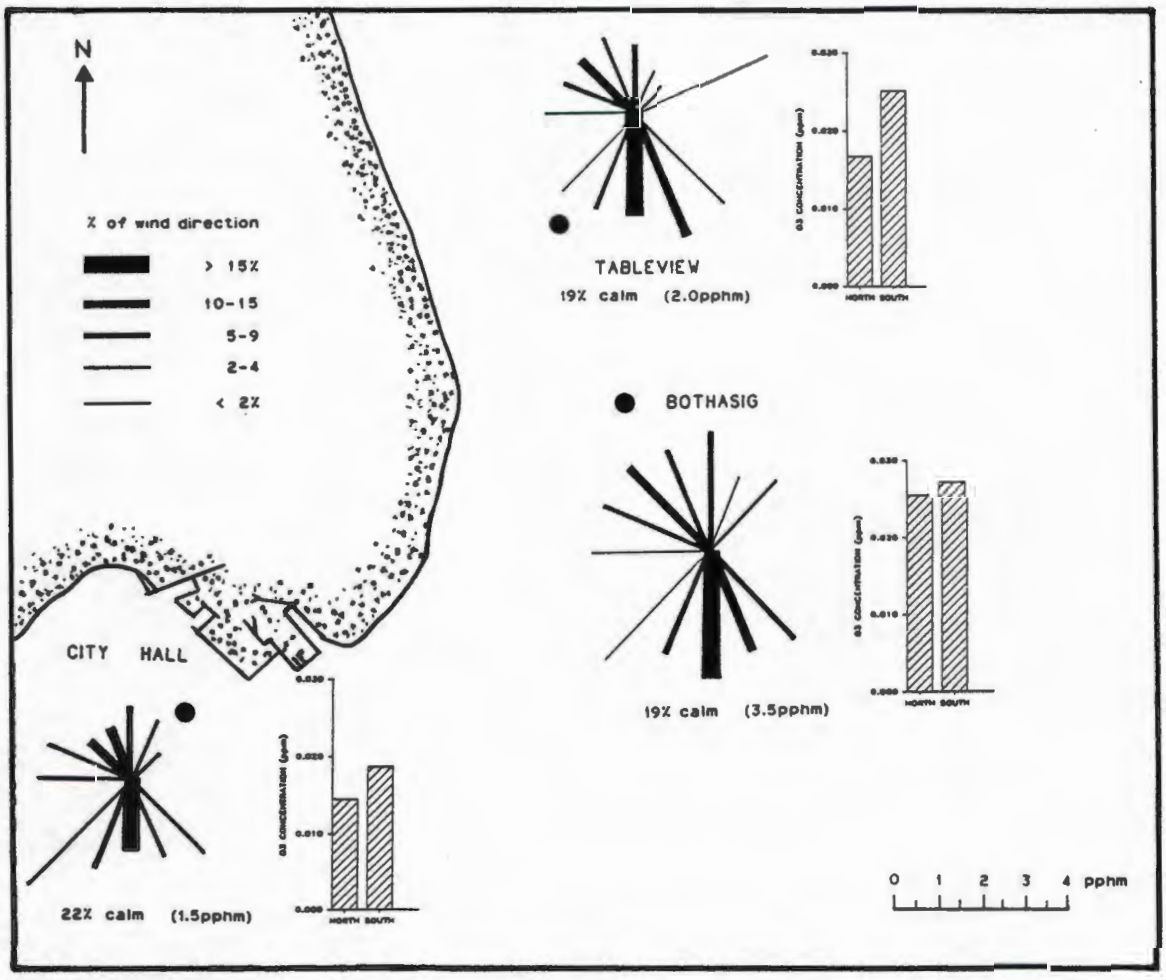

Figure 12: Concentration roses of O_3 maxima and vector averages of the 11h00 wind direction at three sites during 1986.

level was generally maintained at Bothasig (a few kilometres within the urban area), while at Tableview (located on the boundary of the urban area) the absence of precursor sources to the north possibly led to the drop in O_3 levels to about 0.016ppm.

WEEKDAY VERSUS WEEKEND VARIATIONS

It has been found by researchers that during any given year, day to day variations in emissions of precursors and oxidants are small, except for weekday and weekend differences (De Mandel *et al*, 1979). Illustrated in Figures 13a, b and c are examples of the average hourly NO_X, NMHC and O_3 concentrations for the weekdays and weekends during 1986 at the City Hall site. The large reduction in vehicle numbers during the weekends caused NO_X and NMHC levels to show the expected decrease at all sites. Over the weekends, the higher values occurred on Saturdays at all sites due to greater commercial activity in the morning, with more pronounced variations in the CBD. The minimal traffic flow on Sundays resulted in the lowest weekly precursor concentrations with the least variation in levels. The weekly pattern of O_3 as depicted in Figure 13 showed no significant differences between weekdays and weekends. The above patterns of precursors did not appear to influence the O_3 levels to any degree, a conclusion that appears to be typical for many locations. Such situations were found, for example, in New Jersey and New York (Cleveland *et al*, 1974), in Los Angeles for locations close to the sea (Elkus and Wilson, 1977), in Tel-Aviv (Ganor *et al*, 1978) and in Zagreb (Von Tomislav *et al*, 1979).

Hourly variations

POLLUTANT LEVELS AND BEHAVIOUR

Figures 14a, b and c illustrate the mean hourly fluctuations of NO_X, NMHC and O_3 for 1986 for the CBD and suburban sites.

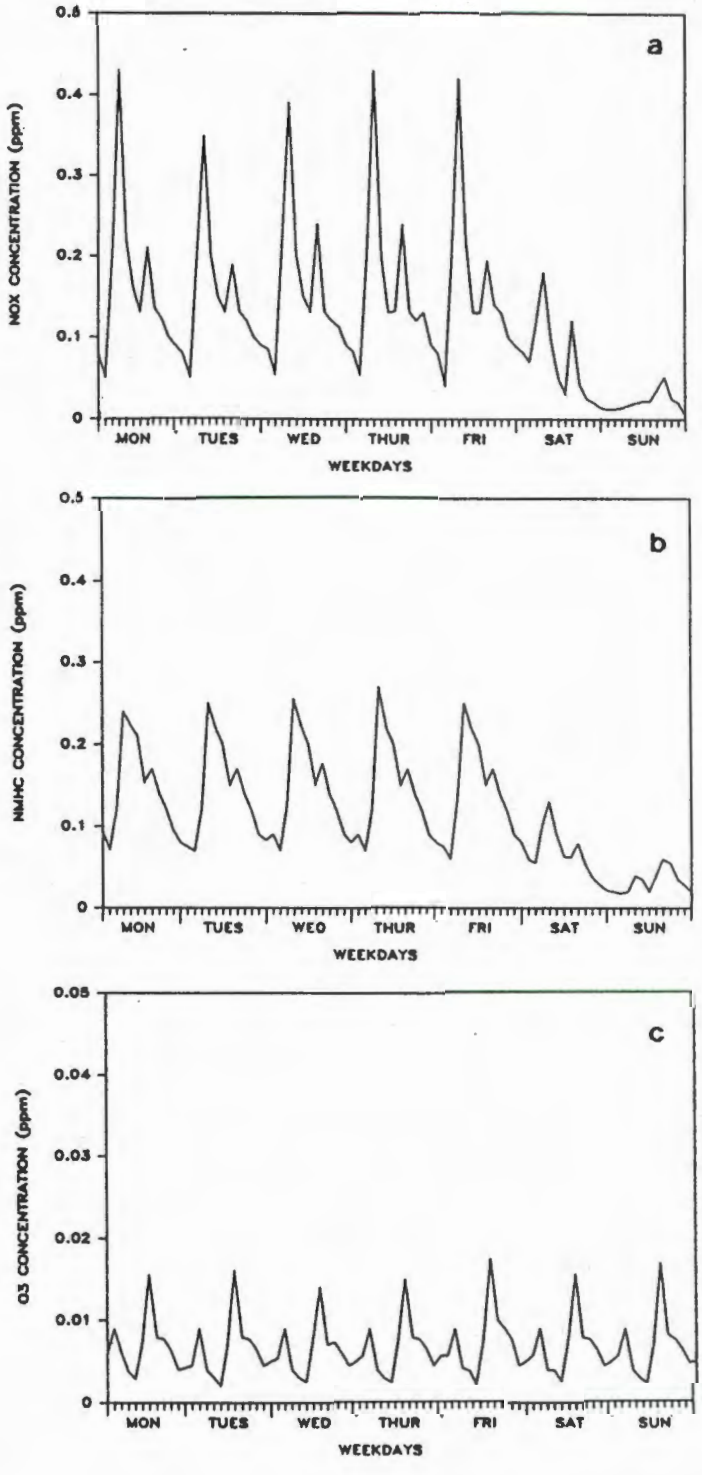

Figure 13: Mean hourly levels of (a) NO_X, (b) NMHC, and (c) O_3 averaged for weekdays and weekends during 1986 at the City Hall.

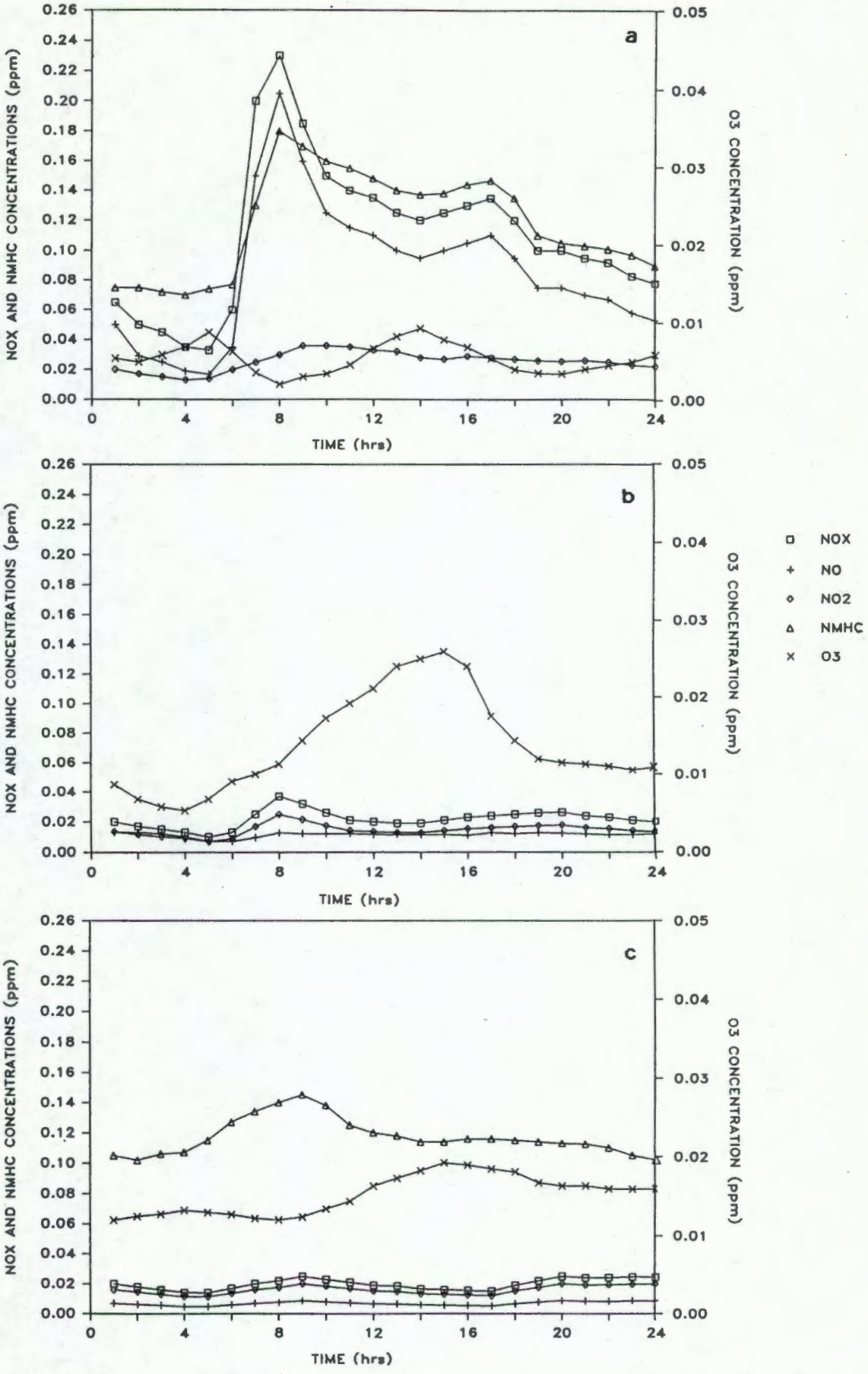

Figure 14: Mean hourly fluctuations of NO_X, NO, NO_2, NMHC and O_3 at (a) City Hall, (b) Bothasig, and (c) Tableview during 1986.

The NO_X levels in the CBD behaved as expected, and showed two distinct daily maxima corresponding to peak rush hour traffic at 08h00 and 17h00. The 17h00 peak was diminished to about half the morning peak owing to increased dispersion by higher wind speeds during the afternoon hours (see Figure 15). Daily variations were far greater in the CBD with higher vehicle numbers and road densities, whilst suburban areas showed much less variation being further away from the influence of concentrated traffic. The morning peak was evident in the suburbs and a slight increase in NO_X levels occurred during the evening hours around 20h00. The

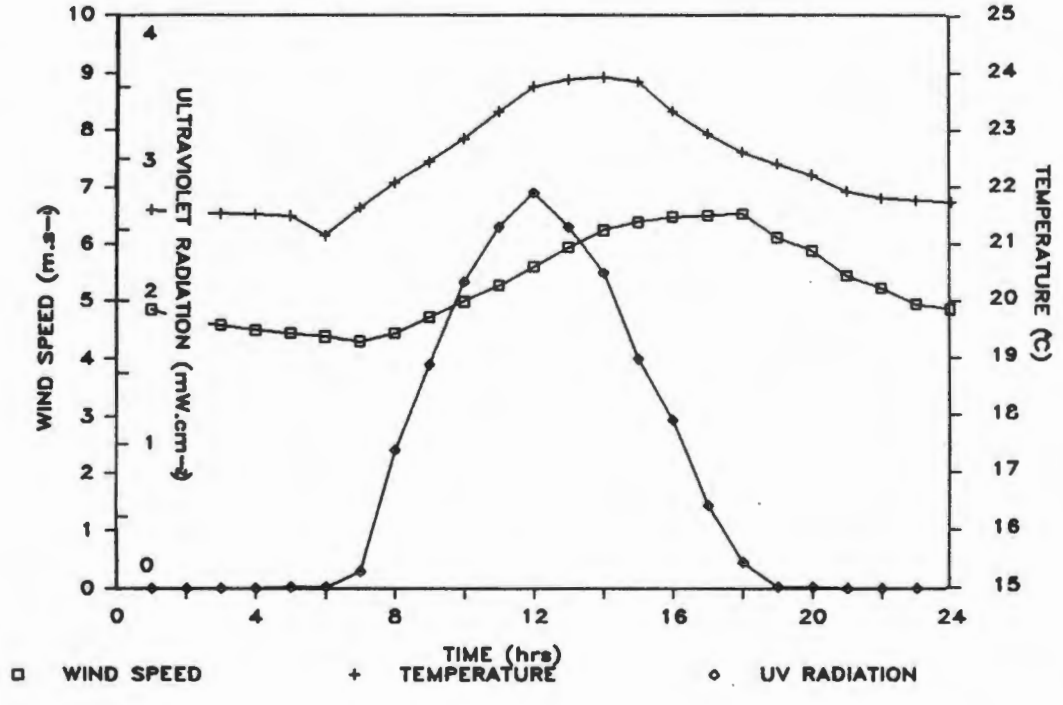

Figure 15: Diurnal variations of wind speed, ultraviolet radiation and temperature for 1986.

absence of a definite afternoon peak in the suburbs is explained by increased wind speeds and a more evenly spread traffic peak, while possible explanations for the evening peak include continued traffic in the early evening and emissions from a nearby industrial plant, with increased levels due to greater atmospheric stability. The hourly NO_x levels recorded in the CBD were particularly high compared to the suburbs, with an average hourly mean during 1986 of 0.10ppm and 0.02ppm respectively. The CBD also experienced 16 cases when the hourly NO_x concentrations exceeded 1ppm, and a maximum in recent years of 1.62ppm (recorded in June 1984). The 06h00-09h00 hourly average for 1986 was about 0.18ppm in the CBD and 0.015ppm in Tableview, with CBD values considerably higher than those found in other studies, such as Stevens (1987), where the Johannesburg City Hall recorded a mean hour-averaged value of 0.08ppm for the period 06h00-09h00 during 1984/85.

NO levels in the CBD reflected the NO_x pattern, exhibiting both morning and afternoon peaks. In the suburbs, the relatively low NO concentrations exhibited a minor peak during morning rush hour and remained fairly consistent throughout the day, although NO levels at the suburban sites near to main roads (such as Bothasig) corresponded more closely to the NO_x patterns. NO_2 levels in the CBD showed the expected increase from the morning rush hour peak, and decreased slightly to a minimum in the early morning hours. The suburbs however displayed NO_2 behaviour that shadowed that of NO_x, with a morning peak around 08h00 dropping off during the day and increasing in the evening hours.

Trends in NMHC levels in the CBD were similar to the trend of NO_x with both morning and afternoon peaks, although there was less variation during the day. Again the suburbs did not exhibit an afternoon peak. The average hourly mean NMHC concentration in the CBD was 0.11ppm for 1986, and exceeded 0.4ppm on 49 occasions, with a maximum of 0.85ppm in the CBD in August 1986. The 06h00-09h00 hourly average for NMHC was

about 0.158ppm in the CBD and 0.137ppm in Tableview. These values were somewhat lower than other cities such as Sydney (Mitchell *et al*, 1983) and Johannesburg, where the latter had recorded a mean hour-averaged value of 0.36ppm for the period 06h00-09h00 at the City Hall during 1984/85 (Stevens, 1987).

O_3 levels generally showed a characteristic minimum in the early morning, corresponding to peak NO concentrations. During the day, O_3 levels increased with ultraviolet radiation and temperature (see Figure 15), reaching a maximum after peak insolation around 14h00 and decreasing during the late afternoon and evening. The average hourly mean O_3 concentration in the CBD was 0.005ppm, and 0.016ppm in the suburbs. The generally depressed O_3 levels in the CBD were largely due to scavenging by the very high NO levels in the city air. A peak was sometimes present in the early morning hours, and was most pronounced in the CBD. This phenomenon has been related to the trapping of O_3 in the descending inversion during the night, causing an elevation in levels near the ground (Steinberger and Ganor, 1980), and also to the lack of high NO levels in the CBD at this time, which promote O_3 formation.

Figure 16 illustrates the average hourly O_3 concentrations for City Hall and Bothasig during 1986, grouped according to season. The summer months exhibited a broader peak with higher values extending into the early evening, whilst the winter months displayed a narrower peak just after midday due to reduced amounts of ultraviolet radiation. The O_3 trace at the CBD site was irregular, with sharp peaks corresponding to the periods of lowest NO during the daylight hours. The suburban site displayed a more regular pattern, increasing gradually around midday and decreasing gently after the peak insolation hours. An extension of increased O_3 levels further on into the early evening hours resulted, which was possibly associated with the persistence of NO_x levels at this time.

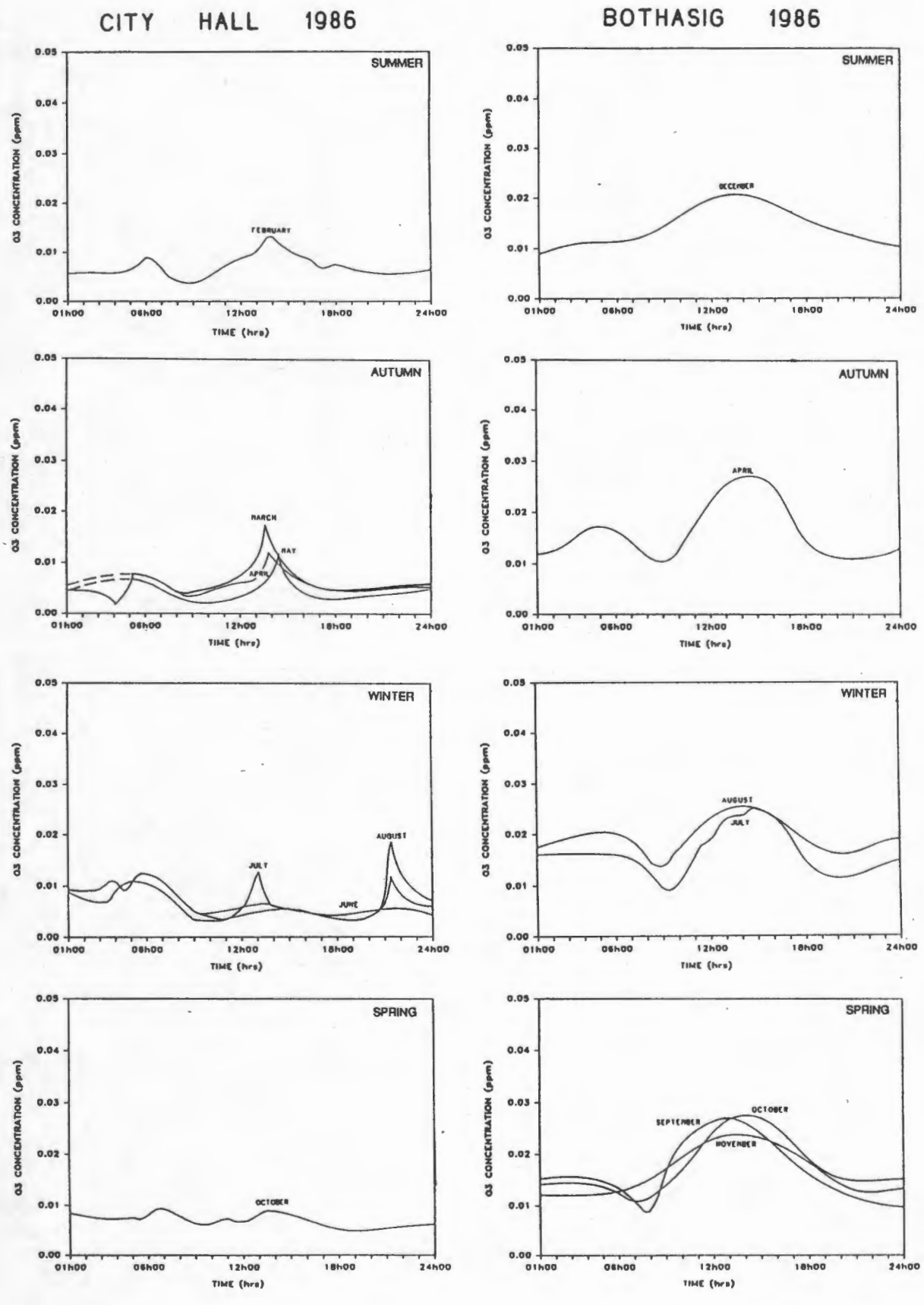

Figure 16: Average hourly O_3 concentrations grouped according to season at City Hall and Bothasig during 1986.

PEAK O_3 EVENTS

The maximum hourly O_3 data recorded in Cape Town during 1985 and 1986 at the respective sites were examined for high O_3 levels (O_3 events). Values were relatively low compared to most O_3 studies, for example Ball and Bernard (1978), De Mandel *et al* (1979), Hawke *et al* (1983), Mitchell *et al* (1983) and Stevens (1987), and did not exceed the 1-h USEPA standard of 0.12ppm at any time during this period. It was thus decided to define an O_3 event as values equalling or exceeding the World Health Organisation (WHO) 1-h goal of 0.06ppm.

From the maximum hourly O_3 averages for 1986 illustrated in Figures 17a, b and c, the highest values occurred in the period from June to October (late winter and early spring). Very few readings were taken in the hotter summer months, and the patterns for this time are thus tentative and require the confirmation of an increased data set. Taking all data into account, the highest maximum hourly value recorded was 0.071ppm recorded in August 1986 at Tableview. A total of 14 days (26 hours) were found to have concentrations equalling or exceeding the 1-h WHO goal, with 43% of these days and 65% of the hours falling in the month of August. As mentioned previously, this period coincides with the natural increase in background levels associated with the Southern Hemisphere tropospheric O_3 maximum. The simultaneous occurrence of O_3 events at more than one site did not take place, indicating possible localised influences such as the amount of NO scavenging. The high degree of variability in the precursor concentrations was sufficient to result in localised O_3 behaviour, with little correlation evident in the O_3 levels between any of the sites. During O_3 events, the NO/NO_2 ratio usually showed a corresponding decrease, with the ratio at Tableview showing the greatest decrease from approximately 0.33 to 0.20.

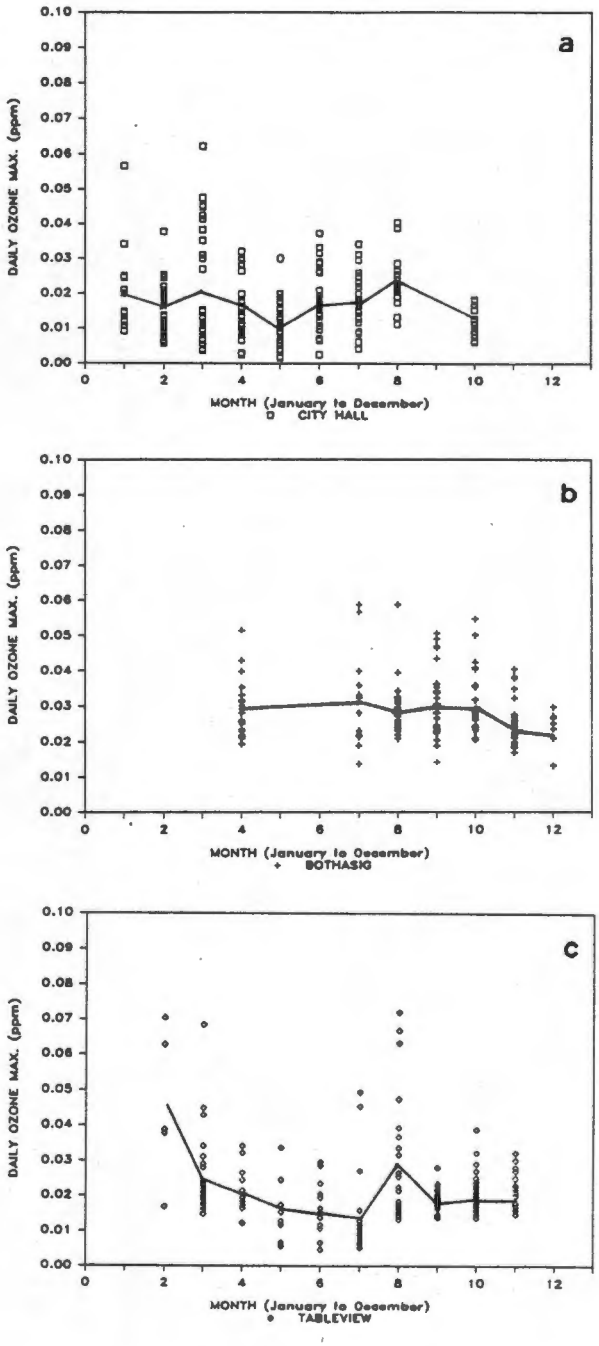

Figure 17: Maximum hourly O_3 concentrations grouped according to month at (a) City Hall, (b) Bothasig, and (c) Tableview during 1986.

On examination of the highest O_3 levels and the associated meteorological conditions, it was found, as for the O_3 levels generally, that no definitive relationships existed (see Figures 9,10,11 and 12). This is contrary to the many papers that have found significant relationships between local meteorological conditions and high O_3 levels (Guichert and Van Dop, 1977; Von Tomislav *et al*, 1979; Hawke *et al*, 1983). O_3 events were experienced on days with both low and high temperatures, with only a slight bias emerging towards warmer temperatures (greater than 25^0C), and increased ultraviolet radiation, especially under conditions of fair weather. The O_3 events on cooler and more overcast days remained largely unexplained. Surface inversions at 01h00 were present on half the days when O_3 levels were high, but by midday (13h00) on the majority of days surface inversions had dissipated. Although no direct relationship existed between O_3 levels and inversions during daylight hours, increased NO concentrations under inversion conditions most likely caused indirect secondary influences by increasing the amount of NO scavenging. A wide range of wind speeds was present on high O_3 days at most sites. Bothasig was the exception, where high levels were experienced generally under very low wind speed conditions (less than $1ms^{-1}$). In contrast, high levels were experienced at Tableview either under low (less than $3ms^{-1}$) or high wind speeds (greater than $10ms^{-1}$). Wind direction proved to be the more determinate variable, with southerly winds prevailing at northerly located sites on high O_3 days. Thus the transport of higher NO_x and NMHC downwind of local urban source areas to these monitoring sites was reflected. During 1985 at Lakeside in the south, observation of the one high O_3 level experienced under a moderate strength ($5ms^{-1}$) northerly wind could perhaps indicate the downwind influence of local urban sources.

The synoptic weather conditions present on days with high O_3 concentrations fell into two broad categories. The major group comprised 64% of the cases, and was characterised by

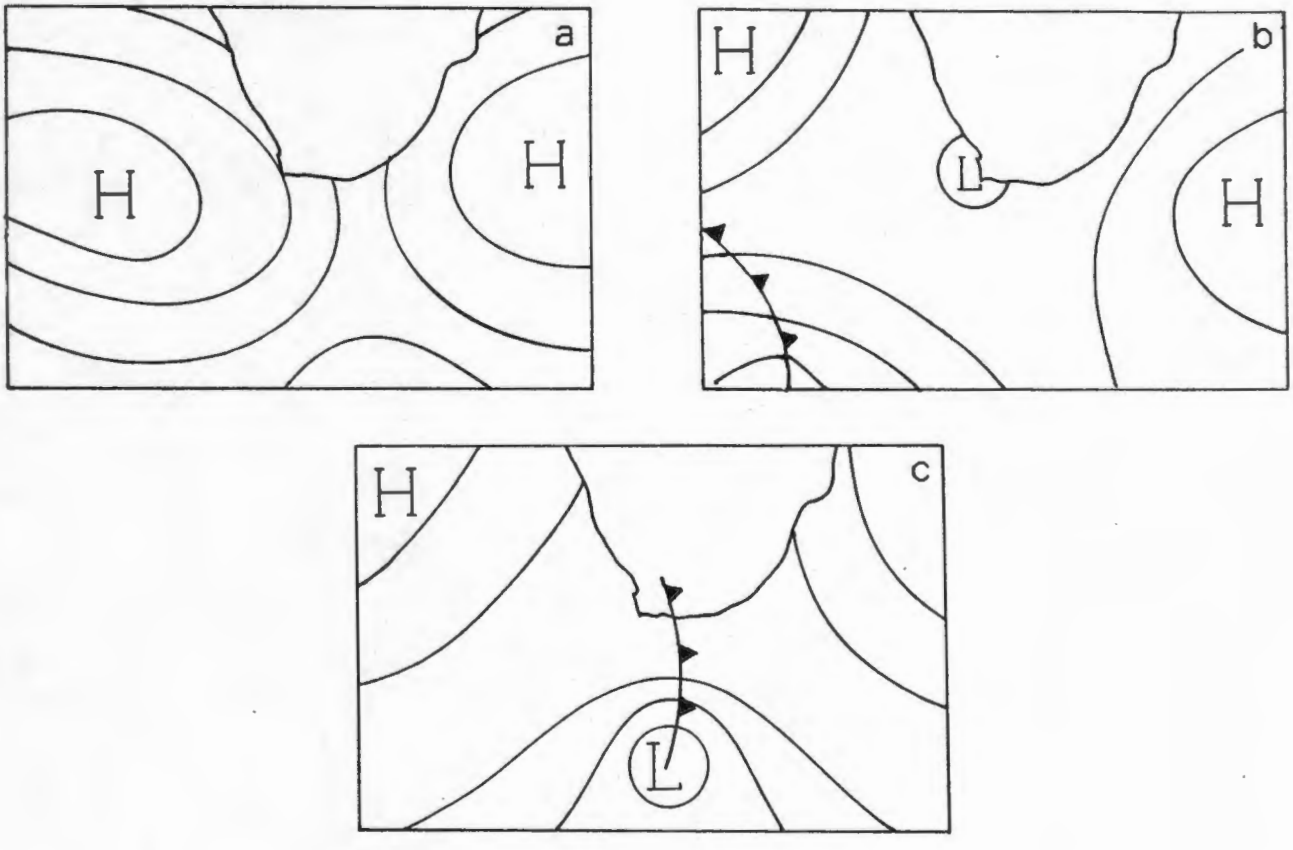

Figure 18: Typical synoptic weather conditions found on high O_3 days with (a) the South Atlantic Anticyclone to the west of Cape Town, (b) a Coastal Low over the Peninsula, and (c) post-frontal conditions.

fair and sunny weather with warmer temperatures. These conditions were the result of two synoptic situations illustrated in Figure 18a and 18b: firstly, the location of the South Atlantic Anticyclone to the west of Cape Town which caused southerly winds and warm temperatures (6 out of 9 cases); and secondly, the presence of a Coastal Low over the Peninsula which was associated with hot and generally calm conditions at the surface (3 out of 9 cases). Fair weather conditions and warmer temperatures have been associated with O_3 episodes in numerous studies, including Hawke and Iverach (1974), Guichert and Van Dop (1977), Ball and Bernard (1978), Hawke *et al* (1983) and Heidorn and Yap (1986). The remaining 36% of days on which O_3 events occurred all possessed cloudy and cool weather resulting mostly from post-frontal conditions (see Figure 17c). No ready explanation for these events could be found either in other meteorological parameters or in precursor concentrations. This further emphasised the complexity of O_3 formation and the necessity to steer away from clear cut explanations of oxidant behaviour.

SUMMARY AND CONCLUSIONS

This paper has sought to analyse the trends in precursor and oxidant concentrations over a spectrum of time scales in Greater Cape Town using monitor data from 1984 to 1986. O_3, being the more important constituent of photochemical smog, was investigated in more detail, in particular on days with high O_3 levels. Consideration was given to any possible relationships between O_3 levels and selected meteorological parameters, as well as the synoptic conditions prevailing on high O_3 days. This study has shown that:

1) Precursor and oxidant concentrations considered in this study have not undergone significant changes over the last few years, and are not anticipated to do so in the near future;

2) Month to month variations in precursor concentrations were strongly influenced by the seasonal cycle of the weather. Increased levels of NO_x and NMHC coincided with periods of high air pollution potential, namely in the winter months when lower wind speeds and frequent inversion conditions occurred. Conversely, the higher wind speeds and lack of strong surface inversions in summer resulted in lower precursor levels. NO_x levels in the CBD were significantly higher than in the suburbs (approximately sevenfold) and contained the largest proportion of NO, while NMHC levels were similar at both the CBD and suburban sites;

3) Monthly O_3 behaviour was highly complex and lacked a simple seasonal trend, although O_3 levels showed a small peak in late winter and early spring, corresponding to the Southern Hemisphere tropospheric O_3 maximum. However, increased summer data are needed to confirm this behaviour. The decreasing NO/NO_2 ratio in the CBD from winter to summer could have positively influenced the formation of O_3 and aided in the observed seasonal pattern, while in the suburbs the relatively constant ratio possibly led to the absence of such a pattern;

4) The day to day fluctuations in the precursor levels were largely determined by variations in the weather. O_3 levels were not closely related to meteorological factors. Slight increases in the O_3 levels were found under warmer temperatures and higher ultraviolet radiation. O_3 levels showed a negligible relationship to wind speed. At the northerly located sites, higher O_3 levels were generally experienced under southerly winds, and diminished levels under northerly winds. In particular, Tableview showed the more marked effect of a northerly wind, where the potential for O_3 formation was diminished due to the implicit reduction of precursor levels;

5) The most consistent day to day variation in the precursor concentrations was evident in the decrease of levels from the weekdays to the weekend. O_3 however showed no significant weekday to weekend differences;

6) Hourly patterns of precursors showed maxima during rush hour traffic and minima during the early morning hours. The suburbs tended to show a more muted pattern with the absence of an afternoon peak and small increases in the evening (possibly enhanced by the contribution of emissions in these areas);

7) O_3 levels characteristically increased during the day with increased insolation, peaking around 14h00 and decreasing slowly at night. The CBD patterns were more irregular than the suburbs, showing a narrow afternoon maximum, thus indicating the influence of the high NO concentrations;

8) O_3 concentrations did not exceed the 1-h USEPA standard of 0.12ppm during 1985 and 1986. The WHO 1-h goal of 0.06ppm was equalled or exceeded on 26 occasions with a maximum of 0.071ppm, with the majority of days occurring in August. The simultaneous occurrence of O_3 events at more than one site did not take place and was thought to be influenced by localised NO scavenging;

9) The majority of high O_3 levels occurred on fair weather days with the South Atlantic Anticyclone to the west of Cape Town, or with a Coastal Low over the Peninsula.

This paper has outlined the trends and patterns evident in the long and short-term data and their relationship to meteorology. The nature of precursor levels was relatively simple compared to the more complex patterns revealed in the analysis of O_3. It is recommended that further data be collected (particularly during the summer months), which

would enable a more in-depth analysis of photochemical smog in Greater Cape Town.

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CHAPTER 3

A SPATIAL SURVEY OF PHOTOCHEMICAL PRECURSORS AND OXIDANTS IN GREATER CAPE TOWN

Analysis of the spatial distribution of selected precursors and oxidants in Greater Cape Town was performed in April and May of 1987 using bag samples, a mobile O_3 monitor and a single automatic monitoring system. Weekday and Saturday mornings were found to experience high levels of nitrogen oxides (NO_X) and non-methane hydrocarbons (NMHC) compared to levels during the afternoons. High precursor levels in the morning were concentrated in the commercial areas of the Northern and Southern Suburbs and in the city centre. These levels were the result of a stable atmosphere and a high traffic density. High wind speeds and greater diffusion occurred during the day, with increased levels from vehicle emissions in the late afternoon. NO_X levels exhibited a great spatial variation and were dependent on the location of traffic routes and the combination of meteorology and the sheltering influence of topography. The distribution of NMHC levels was less localised than NO_X, although generally higher levels were experienced near midday in the industrial areas of the Northern Suburbs. Levels of ozone (O_3) were low, and remained spatially uniform over the study area. Lower levels of O_3 were experienced in areas of concentrated NO_X, while higher levels were experienced towards the edge of the city, away from the influence of vehicle emissions. Saturday afternoon and Sunday exhibited the least spatial variation for all pollutants, with relatively even levels over the whole city.

INTRODUCTION

The spatial distribution of precursors and oxidants is an essential consideration in the assessment of photochemical smog. Effective monitoring and control require a comprehensive knowledge of precursor and oxidant patterns, in particular, the location and extent of potential problem areas. Photochemical smog likelihood at any one site is a function of the complex chemical relationships between its constituents. Spatial patterns of photochemical smog are also affected by local influences of vehicle and industrial emissions, meteorology and topography. The complexity of the above factors require a detailed spatial study as part of a complete evaluation of photochemical smog.

In some cities with well-known photochemical smog problems, such as Los Angeles and Sydney, comprehensive networks of permanent monitoring sites have been established, facilitating spatial analyses (Trijonis *et al*, 1978; Mitchell *et al*, 1983). Cities where photochemical smog is less apparent are often not as well equipped. In the absence of an extensive monitoring network, it is necessary to conduct periodic surveys in order to gauge the spatial distribution of photochemical pollutants. Spatial surveys are commonly achieved using a mobile laboratory, airborne sampling, regular relocation of monitors, or a program of bag sampling. In Cape Town, there are three monitoring systems, two of which are periodically relocated to various sites of anticipated concern. Considering the limited spatial extent of the data, it was decided to use extensive bag sampling to provide a comprehensive spatial analysis of photochemical precursors and oxidants in Greater Cape Town.

Photochemical smog was first investigated in Cape Town in the late 1970's as part of the Air Pollution Survey of Greater Cape Town (Dutkiewicz and Fuggle, 1977; Dutkiewicz, 1979; Dutkiewicz *et al*, 1980). This study included, amongst others, the measurement of photochemical precursors and

oxidants in areas within and surrounding the city. Although no direct spatial interpretation was given, areas of possible concern were highlighted. Results indicated the evidence of photochemical smog for a limited number of hours during the year. As a result of the above survey, a small number of monitors were installed in the Cape Town area in 1984. More recently, Smith (1984) indicated that Cape Town experiences photochemical air pollution, based on the findings by Dutkiewicz *et al* (1980) and a rather sparse data set collected at two sites in Cape Town during 1984. It was recommended that a complete assessment of Cape Town's photochemical air pollution be carried out by further data collection and analysis.

It is the aim of this paper to examine the spatial and temporal distribution of selected photochemical smog precursor and oxidant concentrations in Greater Cape Town. Consideration is given to emissions, prevailing meteorology and local topography. It is intended to identify the spatial distribution patterns of precursors and oxidants and highlight areas of low and high photochemical smog potential.

EXPERIMENTAL METHOD

Surveys involving the use of bag samples have been employed in a number of air pollution studies. Bag samples were used for example by Post and Bilger (1978), Nelson (1981) and Evans *et al* (1982). In South Africa, bag sampling was used by Louw *et al* (1977), Louw and Richards (1977) and Louw *et al*, (1979).

The sampling process used for this survey involved the collection of bag samples filled with ambient air at various preselected sites around the city. These samples were then analysed at an automatic monitoring system. The pollutants to be sampled were the chief precursors and oxidant, namely

nitrogen oxides (NO_x), non-methane hydrocarbons (NMHC) and ozone (O_3). The experimental method was found to be satisfactory for both the NO_x and NMHC, but not for O_3. Preliminary tests showed O_3 levels to decrease with time, pointing to an absorption mechanism, and thus bag sampling was restricted to NO_x and NMHC, and a mobile O_3 monitor was used to measure O_3 concentrations. The automatic instruments used were:

1. Monitor Labs 8840 for the analysis of NO_x. This is a gas phase chemiluminescence detection device which performs continuous analysis of NO, NO_2 and total NO_x.
2. HNU analyser Model PI 201 for the analysis of NMHC. This instrument operates on the principle of photoionisation.

3. Thermo Electron UV absorption detector for the measurement of O_3 concentrations.

Calibration of the NO_x monitor was carried out using gas dilution, a nitrogen dioxide permeation tube and O_3/NO gas phase titration. Calibration of the NMHC analyser was carried out using iso-butene, and results were expressed as methane. The O_3 analysers were calibrated by an external O_3 generator and cross-calibrated with another O_3 monitor with an internal calibrator. Calibration of the pollutant analysers was carried out each week during the survey.

Bag tests

The samples were collected in 'Tedlar' bags (DuPont Corp.) which are chemically inert and do not absorb or contaminate air samples normally encountered in air monitoring. Tests were carried out in order to gauge possible variations of an air sample by using these bags. Polyvinyl flouride has been found to release organic compounds in smog chamber experiments, but the levels have not been quantified (Von Ham, 1978). For this experiment, the testing of 'Tedlar' bags was carried out by filling them with ambient air and

analysing them. An increase of about three to five percent from the initial levels of the NO_x and NMHC was observed.

In order to test sample decay, bags were filled with ambient air and well mixed. A portion of the air sample was analysed immediately and thereafter at regular intervals for three hours. Marginal decreases of about three to five percent were experienced within this period, after which the errors became more pronounced. It was thus decided that a cut-off time of two and a half hours be applied to this experiment, thus ensuring only negligible variations of less than five percent in pollutant concentrations.

It was assumed that the above two sources of variation were minimal (with variations of below five percent) and were considered negligible for this experiment.

Sampling procedure

A bag volume of ten litres was found to be sufficient to obtain stabilised readings of NO_x and NMHC during analysis (considering the differing flow rates and response times of the monitors). A sampling time of approximately ten minutes was chosen as the minimum required to obtain a representative sample at each site. This factor, together with the time constraints of sample decay allowed an optimum of fifteen sites around the city to be surveyed at regular times during the day (see Figure 1). Sites were located away from the direct influence of major traffic routes and heavy industries.

Sampling took place between 06h00 and 18h00, thus including both the morning and afternoon traffic peaks. Precursors were sampled about five times per day at each site and O_3 only three times, owing to the greater distances to be covered by the O_3 monitor.

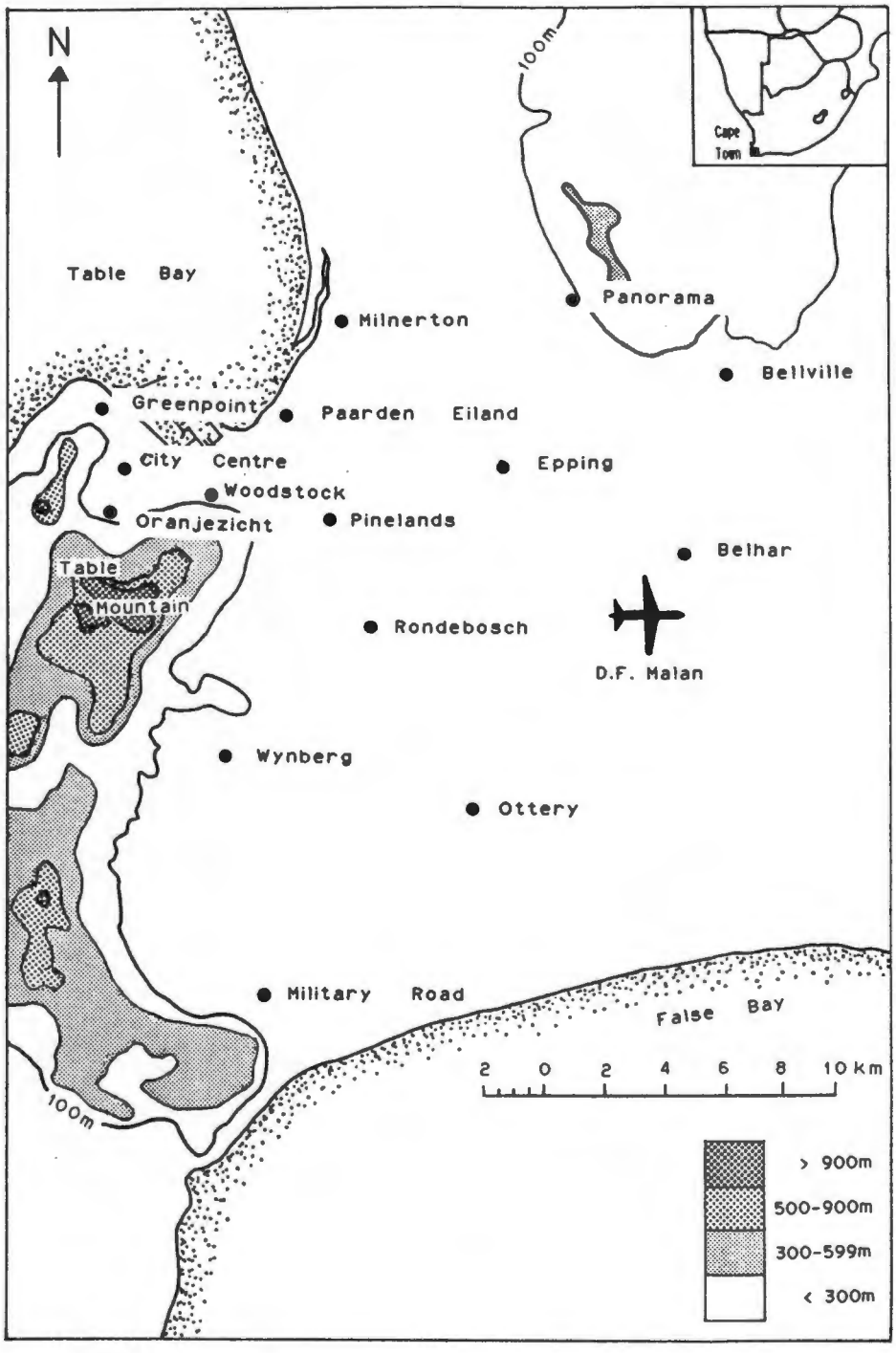

Figure 1: Location of the survey sampling sites in Greater Cape Town.

On arrival at each site, a sampling bag was placed in an airtight container and filled by displacement of air from the container itself, by means of a vacuum pump. This caused the bag to expand with ambient air, taken from a sampling height of three metres in order to avoid direct exhaust emissions. Inert materials such as 'Teflon' tubing, and stainless steel pipes and fittings were used throughout. The filled bag was then placed in a light-proof container to eliminate any further photochemical reactions. The bag samples were taken to the automatic monitoring system for analysis, after which the bags were flushed twice with high purity nitrogen. The data were collated, ordered chronologically and plotted, after which contour maps for each pollutant were constructed for various times during the day using simple linear interpolation.

The data were collected on 14 days during the study period from 21 April to 10 May 1987. This time period was selected due to the high frequency of calm conditions which are more favourable for the definition of spatial patterns of air pollutants. A range of weather conditions typical of that experienced in Cape Town throughout the year provided a representative range of spatial patterns of air pollutants. Figure 2 is an inventory of data collected on the sampling days, including relevant meteorological conditions and equipment efficiency for the survey period.

BACKGROUND

Examination of the characteristic factors influencing precursor and oxidant concentrations in Greater Cape Town was carried out prior to the analysis of the survey data.

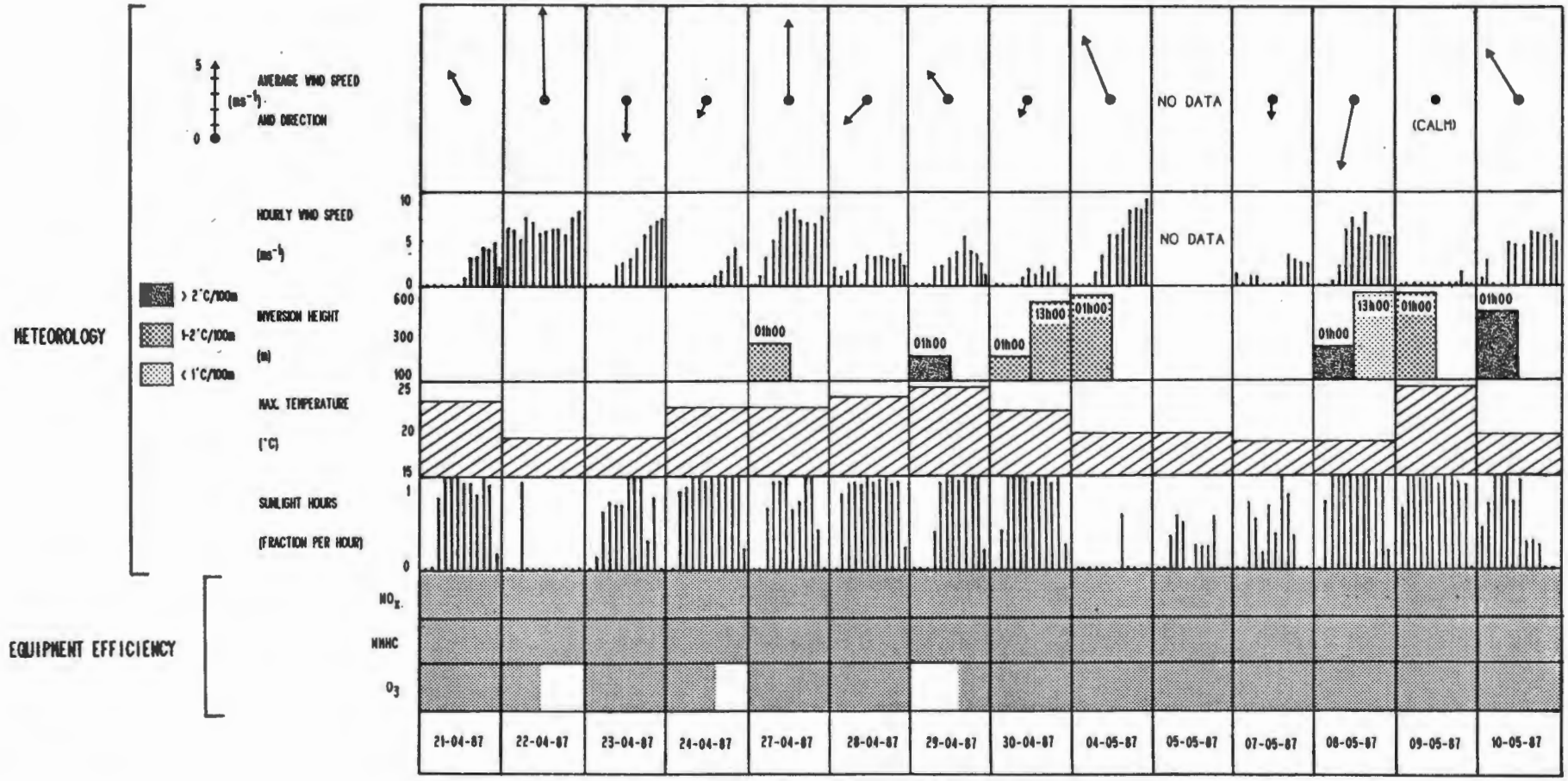

Figure 2: Data inventory of the sampling days of the survey, from 06h00 to 18h00.

Factors influencing pollutant levels

EMISSIONS

Spatial patterns of photochemical pollutants are primarily influenced by the nature and distribution of motor vehicle and industrial emissions. Motor vehicle exhaust emissions contribute substantially to the levels of photochemical precursors (Stewart *et al*, 1983; Nelson and Quigley, 1984). Weekday traffic flow patterns in Cape Town exhibited the usual daily trends, with peak rush hour traffic at approximately 08h00 and 17h00, while weekend patterns showed a substantial decrease in vehicle numbers, especially after 12h30 on Saturdays (Eadie *et al*, 1987; Thompson, 1985). Figure 3 illustrates the arterial roads in Greater Cape Town (referred to in the text by the abbreviated names) and the average daily traffic volume in both directions for weekdays. The area immediately to the east of the Central Business District (CBD) contains the greatest traffic flows with the roads extending further eastward into the industrial areas being heavily used by trucks and buses. Commercial areas (see Figure 3) with consistently higher traffic concentrations are likely nodes for photochemical precursors.

Emissions of photochemical precursors by industry are of some importance when considering the spatial distribution of NO_x and NMHC. Stationary sources of NO_x emissions are associated with industrial combustion, refineries and nitric acid production (Eiser *et al*, 1983). Principle stationary sources of NMHC emissions have been identified as oil refineries, petrochemical plants, industrial process emissions and evaporation associated with the storage of petroleum products (Nelson *et al*, 1983). In Cape Town, Dutkiewicz (1979) found Paarden Eiland (petrochemical storage) and Milnerton (oil tank farm) to be possible source areas of NMHC. Illustrated in Figure 3 are the major

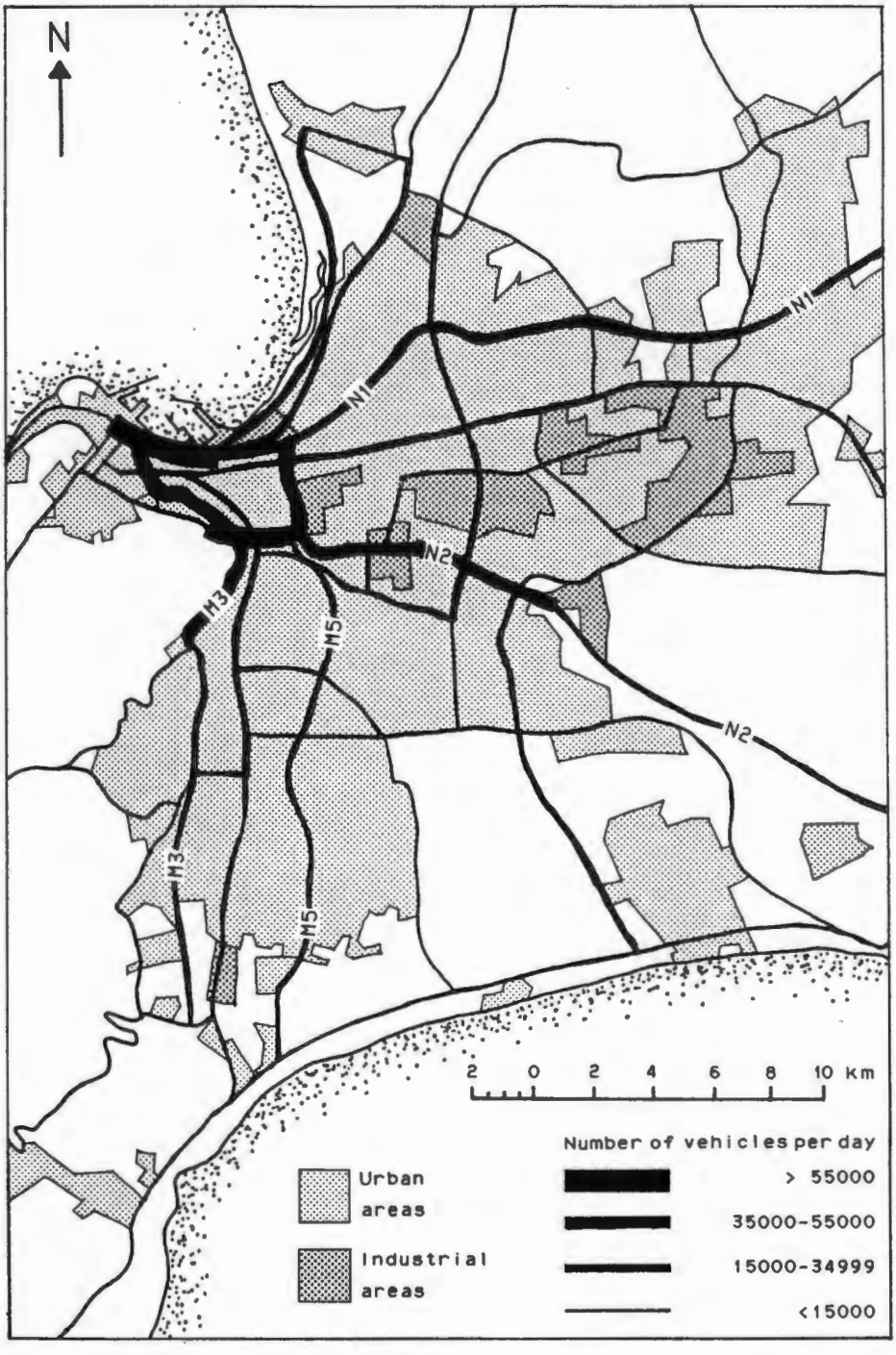

Figure 3: Location of urban and industrial areas, with the major arterial roads and their average weekday traffic volume.

industrial areas in Cape Town, which are likely to enhance the levels of NO_x and NMHC in the study area.

METEOROLOGY AND TOPOGRAPHY

Meteorology is well known to be the most dominant influencing factor affecting the daily variations in the distribution of photochemical smog (Sullivan, 1962; Hawke and Iverach, 1974; Hawke *et al*, 1983). In Cape Town, the interaction of the meteorology with the unique complex topography (see Figure 1) further affects the spatial distribution of pollutants. Fuggle (1978), Keen (1979), Dutkiewicz *et al* (1980) and Keen (1984) examined the meteorology of Greater Cape Town with emphasis given to areas possessing high pollution potential. It was found that the protected city amphitheatre had the highest air pollution potential, followed by areas bordering the mountain, while well ventilated areas such as the outlying suburbs away from the mountain had the least potential.

The weather in Cape Town is typified by three synoptic conditions (see Figure 4): (a) in summer, the well-developed South Atlantic Anticyclone occurs, with associated warm temperatures, fair weather, clear skies and a frequent strong south east wind; (b) the regular passage of frontal systems occurs predominantly in winter, with associated north west winds, cool temperatures, rain and overcast skies, and (c) calmer periods which occur most frequently in late summer and autumn and are characterised by the persistence of weak pressure gradients. It is under the latter conditions that the highest air pollution potential exists.

The effects of a weak pressure gradient are most severely experienced in the early morning with the occurrence of surface inversions and low wind speeds. These factors, together with the local topography, serve to intensify the resulting spatial differences in pollutant concentrations.

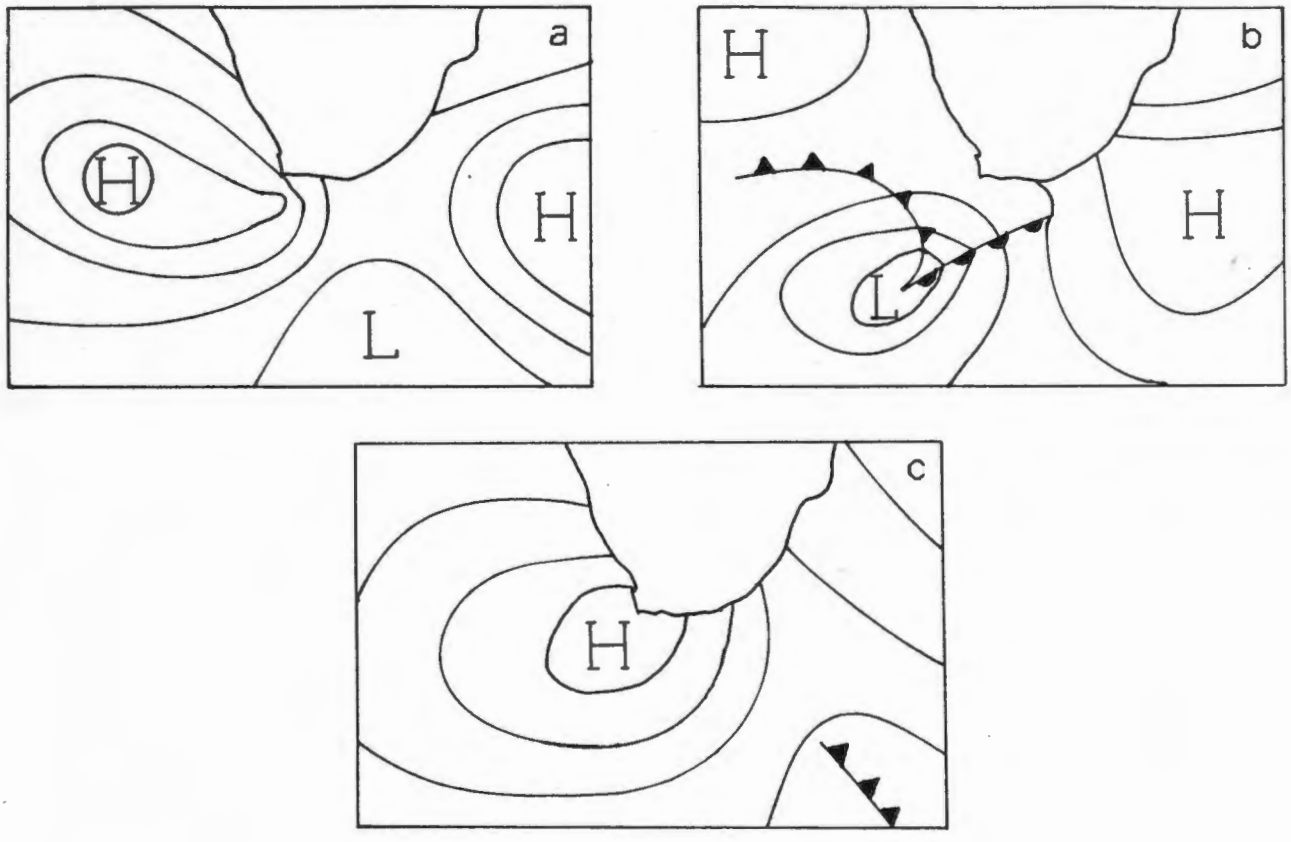

Figure 4: Typical synoptic patterns of weather influencing air pollution in Greater Cape Town: (a) strong SE winds and fair weather; (b) NW winds and overcast conditions; and (c) calm conditions conducive to limited pollution dispersion.

Changes in wind speed and direction and the resulting atmospheric transport serve to diffuse the localised levels during the day.

RESULTS AND DISCUSSION

Weekday patterns

NO_x

Figure 5 illustrates the NO_x distribution for 23-04-87 at selected times during the day. During peak traffic at 08h00, the NO_x levels displayed the highest spatial contrast compared to any other time of the day. Nodes of high values were recorded within the CBD extending eastwards to Epping and Belhar, and the Southern Suburbs. In particular, the Wynberg site, sheltered from the influence of the southerly wind, exhibited exceptionally high values. The area between the N2 and M5 (see Figure 3), possessing good ventilation potential, experienced lower NO_x levels.

At 10h00, the influence of the slightly increased wind speed led to greater pollutant dispersion, with the Wynberg, City Centre and sites surrounding the N1 experiencing the high values. The southerly wind displaced the concentrated NO_x levels northwards, causing an extension of the area of influence from the City Centre northeast towards Milnerton.

From midday (12h00) to the afternoon (14h00), further dilution of NO_x concentrations occurred, particularly at coastal sites where increased ventilation was present. The City Centre and Paarden Eiland sites continued to maintain the higher values in the study area, whilst Oranjezicht and the sites away from major arterial routes maintained the lower readings.

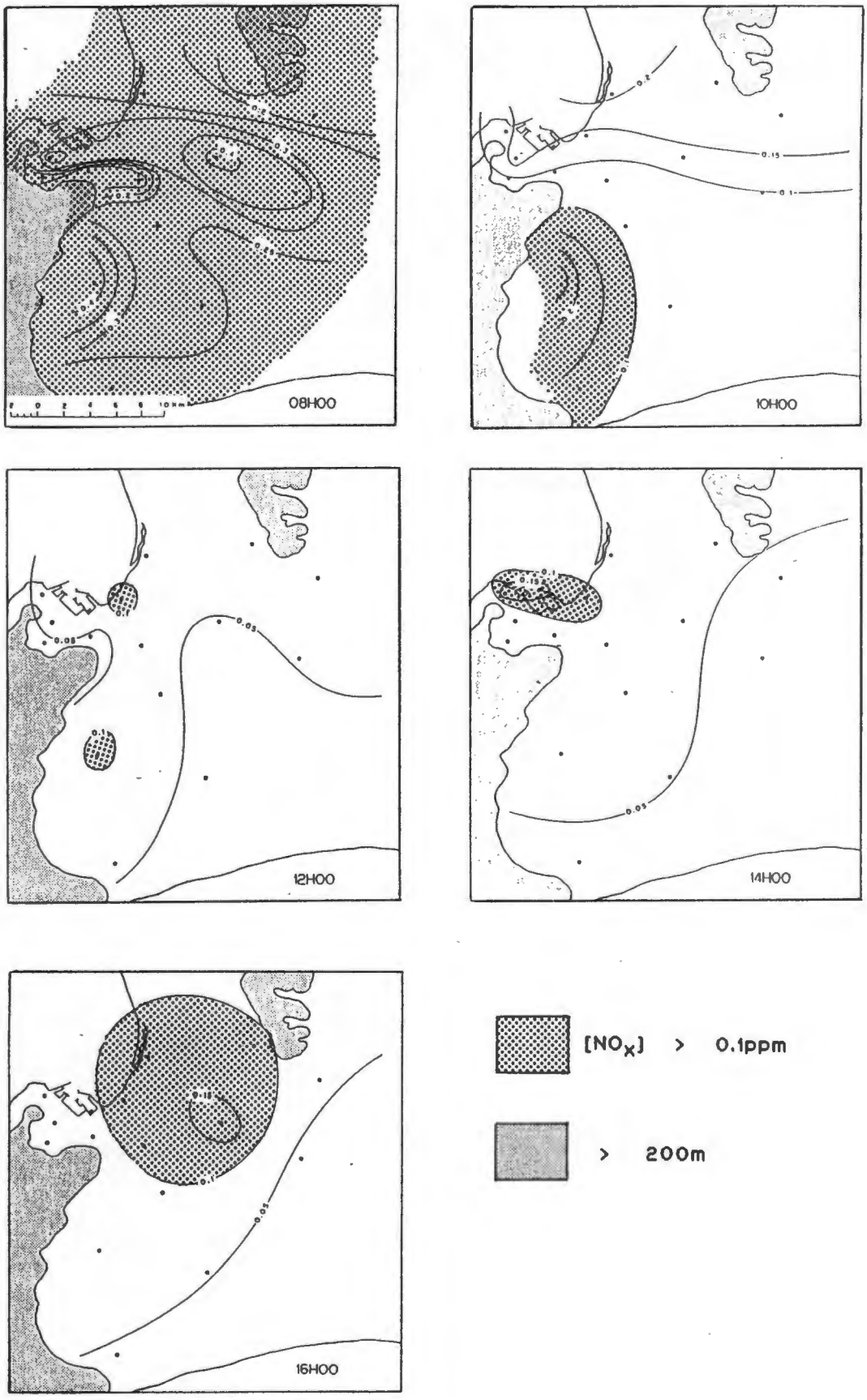

Figure 5: A sequence of NO_x distributions at selected times on 23-04-87.

During the later afternoon (16h00), the departure of vehicles from the CBD caused levels of NO_x to increase in the surrounding area, particularly in the regions of high vehicle numbers, decreasing outwards towards the southern and eastern edges of the city.

NO_x levels exhibited strong localised patterns during the survey, with the anticipated high NO_x values during peak rush hours and during the day being experienced within the CBD and immediate surrounding area. The Wynberg site, however, experienced surprisingly high NO_x values. Although no SE winds capable of diffusing pollutants in this area were experienced during the survey, the trapping of NO_x in the sheltered area of the mountain, with inversion conditions and gentle southerly through to northerly winds, resulted in the high levels being observed in the morning. Bellville also experienced high NO_x levels on some days in the morning rush hour, owing to the combination of morning inversions, topography and commercial activity. Areas near main traffic throughflows experienced higher NO_x levels (particularly during rush hour), while lower NO_x levels were found away from major traffic routes, particularly in the area between the N1 and M5.

These patterns are somewhat different to those documented by Dutkiewicz (1979), where areas of high NO_x were located in the City Centre and the immediate surrounding area. However, the study area for photochemical pollutants covered in Dutkiewicz (1979) was somewhat smaller than that of the present study. The influence of industry was not apparent in the NO_x distribution. Higher wind speeds resulted in greater dispersion of pollutants and a more even spatial distribution, whilst lower wind speeds and inversions persisting throughout the day, caused increased levels of NO_x with greater spatial differentiation.

NMHC

Illustrated in Figure 6 are the NMHC patterns for the 30-04-87 at selected times during the day. During the morning rush hour peak at 08h00, the levels of NMHC were most concentrated in the City Centre and Bellville sites. The area north of the N2 experienced generally higher concentrations decreasing southwards, with Wynberg exhibiting the lowest value. The presence of a surface inversion resulted in greater spatial contrast in the NMHC levels, although this contrast was not as marked nor as localised as that of the NO_x.

At 10h00, the NMHC concentrations levelled out, with the City Centre, Epping and Belhar experiencing the higher levels, and marginal increases in the Southern Suburbs and area immediately surrounding the CBD.

During midday and the early afternoon, a marginal increase in the NMHC levels was evident in the Northern Suburbs, particularly north of the N2, with higher levels extending from the CBD eastwards to include the Panorama site. The levels decreased gradually further southwards.

At 16h00, the NMHC levels began increasing with greater traffic flow, with the City Centre and areas surrounding the N1 in the Northern Suburbs experiencing the higher values, and lower values towards the south (between the N2 and M5).

NMHC levels were more spatially uniform in distribution than the NO_x levels, in contrast to the findings of Post (1981), although significant spatial variation was displayed on certain days around midday. Higher NMHC levels were experienced within the City Centre extending eastwards to include the Northern Suburbs (especially north of the N1), and areas near the main arterial roads, in particular, the N2 and M3. Bellville also experienced higher NMHC values when inversion conditions prevailed. Evident from the data

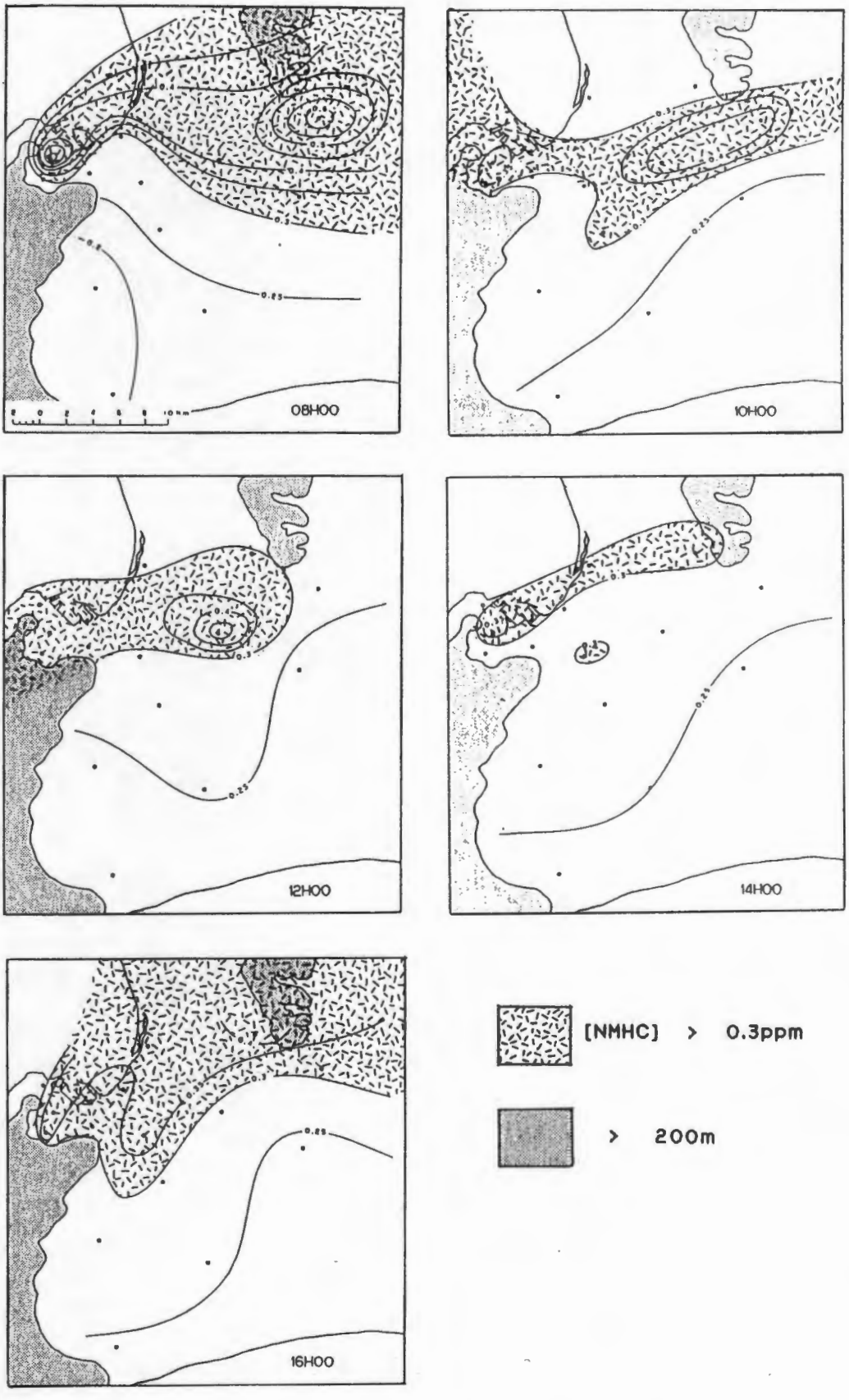

Figure 6: A sequence of NMHC distributions at selected times on 30-04-87.

were the abnormally high NMHC values experienced in the Northern Suburbs at midday. The industrial areas of Epping, Maitland, Paarden Eiland and Milnerton repeatedly experienced higher NMHC levels. This was coincident with the findings of Dutkiewicz (1979). These localised peaks were likely to be associated with emissions from industrial areas, the petrochemical plant and increased evaporation from the oil tank farm.

Lower levels of NMHC were predominantly experienced in the area between the N2 and M3, including Military Road, Ottery and Pinelands sites. Greenpoint, Oranjezicht and Woodstock sites also experienced lower levels, all the above sites being located away from industrial areas and concentrated traffic flows. This was in agreement with Dutkiewicz (1979), although the present survey, by covering a far greater area, highlights the Northern Suburbs as the area of highest NMHC levels. Under northerly winds, elevated levels were experienced at the Wynberg site and lower levels in the area immediately to the east of the CBD, while southerly winds covered the area extending from the Southern Suburbs northwards to the CBD in the early morning, leaving only a narrow band of concentrated NMHC from the City Centre to Milnerton in the late morning. High levels of NMHC were evident on low wind speed days and under inversion conditions, where prolonged sheltering in the lee of the mountain occurred, whilst lower levels were evident on higher wind speed days.

O_3

Figure 7 illustrates the spatial distribution of O_3 for 8-05-87 at selected times during the day. The levels of O_3 were all low and fairly homogeneous throughout the study area. Greater ultraviolet radiation caused an increase in O_3 values, particularly in areas of low precursor concentration. Areas of depleted O_3 were experienced around the CBD, with higher levels away from main traffic routes,

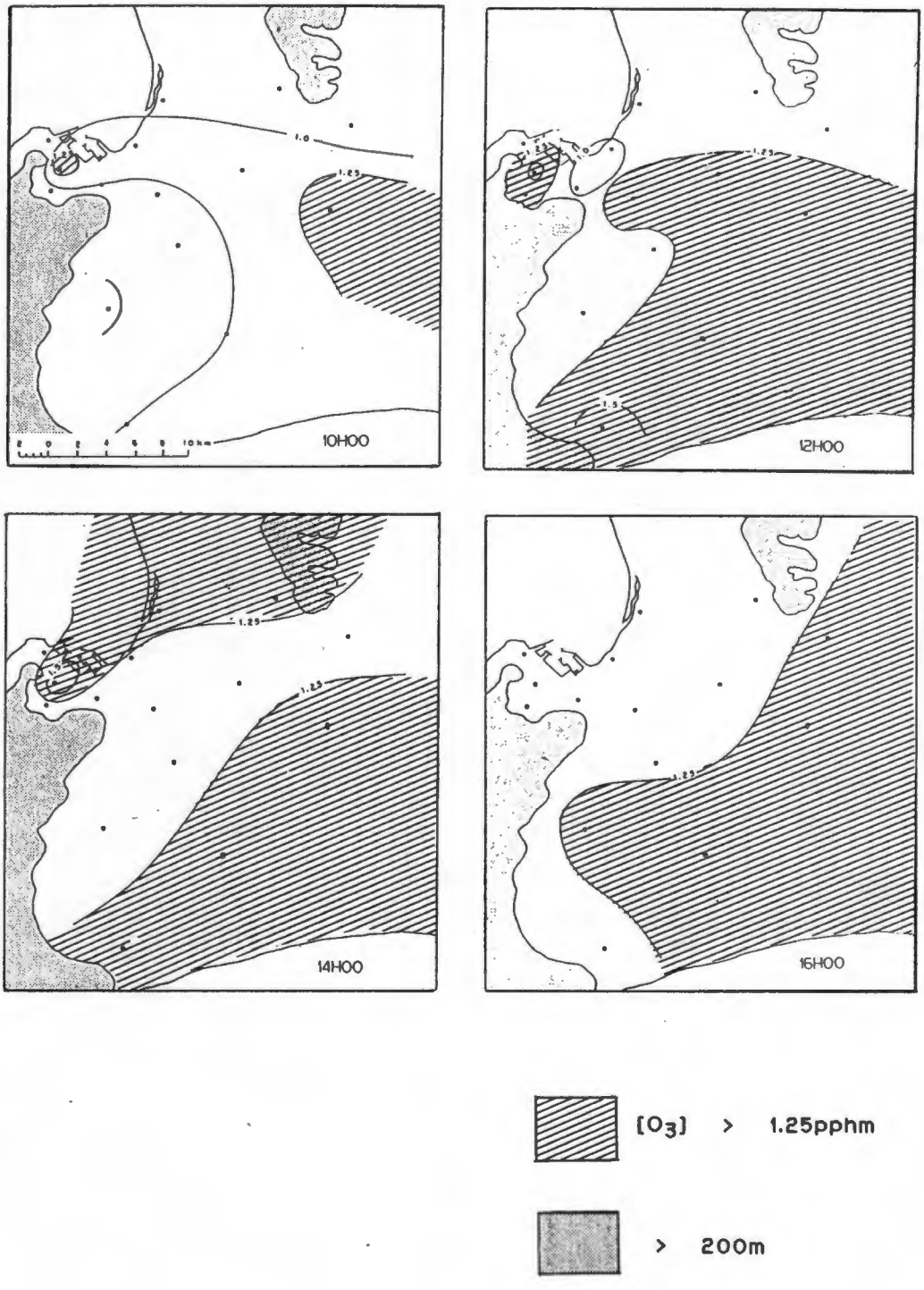

Figure 7: A sequence of O_3 distributions at selected times on 08-05-87.

between the N1 and the M5. The City Centre itself and the Oranjezicht site exhibited marginally higher readings at midday. O_3 levels decreased in the late afternoon, with diminished ultraviolet radiation and increased precursor levels.

Higher O_3 readings were evident on sunny days, with lower values recorded under cloudy and overcast conditions. On calmer days, localised high NO_x concentrations prevented the build-up of O_3 on a local scale, resulting in greater spatial variation in the O_3 levels. Higher wind speeds led to increased mixing and dispersion of the precursors, decreasing the spatial variation in O_3 levels. O_3 exhibited greater spatial uniformity than the primary pollutants, although it was sensitive to very localised variations in destruction rates in the vicinity of NO_x sources. Stevens (1987) also found O_3 levels to be similar at different sites in Johannesburg, especially under well-mixed conditions.

The O_3 readings recorded during the survey were particularly low and very little variation was evident over the study area. This was attributed to the relatively stable conditions that occurred during the survey which promoted the formation of high NO_x concentrations, particularly NO. It is anticipated that the O_3 levels on such days would increase near the borders of the metropolitan region where the NO_x concentrations are diminished and the NO_2/NO ratio is greater (Loewenheim, 1988).

Weekend patterns

SATURDAY

Saturdays are characterised by a change in emission patterns, with high traffic volume in the morning, biased towards the commercial areas and less to the industrial areas. Figure 8 illustrates NO_x patterns at selected times during Saturday 9-05-87. NO_x levels showed far less spatial

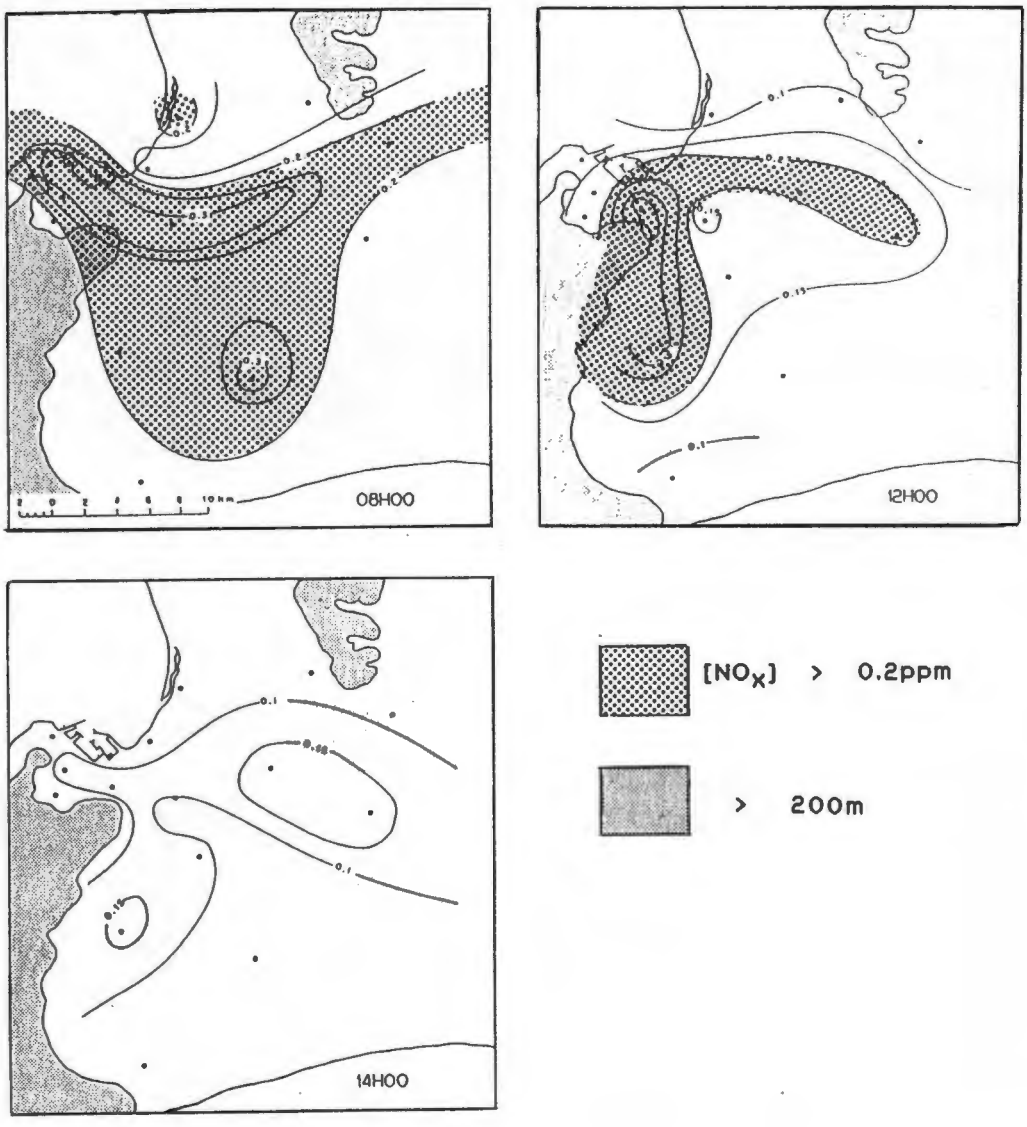

Figure 8: NO_x distributions for selected times on 09-05-87.

contrast than on weekdays, with the concentrated areas located from the CBD around the mountain to the Southern Suburbs with an extension out to the Northern Suburbs. This area encompassed the commercial areas and regions of high traffic volume within the city, with readings in the CBD being somewhat lower than the decentralised commercial areas. At midday, the departure of vehicles from the City Centre and commercial areas is indicated by the noticeable drop in NO_x levels between 12h00 and 14h00. NO_x levels decreased further in the late afternoon.

Figure 9 shows the NMHC patterns at 16h00 on 9-05-87. NMHC levels were remarkably constant throughout the study area for the entire day, with marginally lower values experienced in the area between the N2 and the M5, away from the influence of industrial and vehicle emissions.

Figure 10 shows the O_3 pattern at 12h00 on 9-05-87. O_3 levels were slightly lower in commercial areas where the NO_x levels were greatest. Thus the eastern part of the study area experienced the higher O_3 levels, which extended progressively westward after midday, when decreased NO_x levels were experienced.

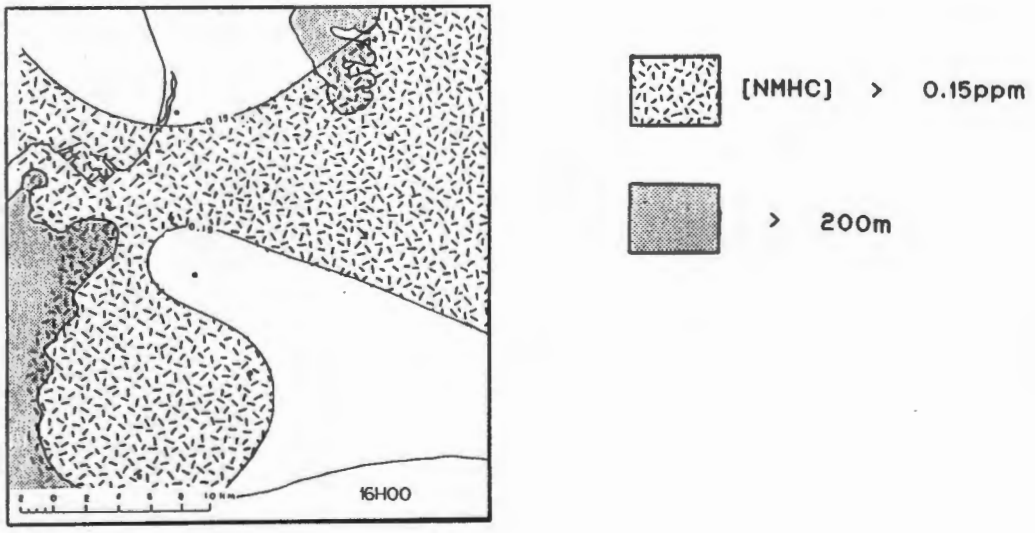

Figure 9: NMHC distribution at 16h00 on 09-05-87.

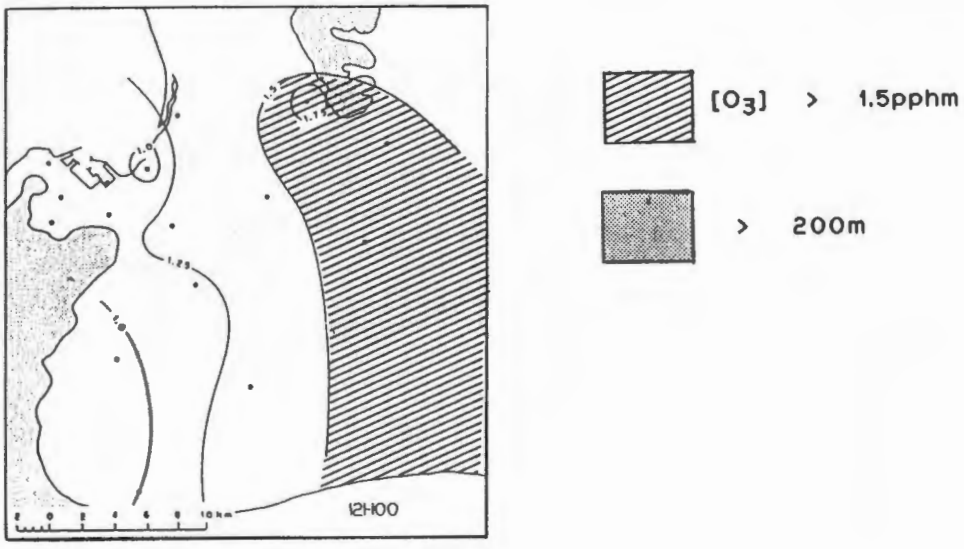

Figure 10:O_3 distribution at 12h00 on 09-05-87.

SUNDAY

Precursor concentrations were generally low over most of the city, with some increases occurring in areas near the major traffic routes. Sunday exhibited the least spatial variation of NMHC, O_3 and NO_X, with similar distributions to Saturday afternoon. Precursor values remained relatively constant during the day due to low traffic flow, although a localised NO_X increase was experienced at the Wynberg site in the morning. Higher precursor levels were experienced uniformly over the city in the late afternoon, when vehicle numbers showed a small increase. Thus, as expected, Sunday with the lowest emissions displayed the least spatial variation, with levels remaining consistent over the study area.

SUMMARY AND CONCLUSIONS

This paper has considered the spatial distribution of precursors and oxidants in Greater Cape Town. Measurements achieved using bag samples and an O_3 monitor were used to analyse the spatial structure of NO_X, NMHC and O_3 over time. This study has shown that:

1) Bag sampling together with an automatic monitoring system can be successfully used for spatial measurements of precursors. However, volatile substances such as O_3 require *in situ* measurements with mobile monitoring equipment;

2) NO_X distributions exhibited a high spatial dependency. NO_X readings were strongly influenced by vehicle emissions, following the most well-used arterial roads with expected nodes of concentration in the CBD and adjacent area to the east. The areas away from commercial, industrial and heavily travelled routes experienced the lower NO_X levels. NO_X patterns were most intense during morning rush hour, diffusing to a more regular distribution during the day with localised increases in regions of afternoon peak rush hour traffic. A combination of atmospheric stability and the sheltering influence of topography resulted in the high NO_X readings experienced at the Wynberg site;

3) NMHC patterns were less exaggerated than NO_X, with the more concentrated levels experienced in the CBD in the morning. During midday and the early afternoon, there was a build-up of NMHC in the Northern Suburbs, where evaporative and industrial process emissions are located;

4) O_3 levels exhibited a low spatial dependency being relatively uniform over the study area. Contrasts were more evident on calmer days when localised NO_X build-up depleted O_3 levels. This occurred in the areas of high traffic

density and in areas protected by the topography, leaving higher O_3 levels in areas of low NO_X;

5) Photochemical smog patterns on Saturday morning were similar to weekday mornings, although less sharp contrasts were evident. The patterns of NO_X showed concentration nodes in commercial areas while NMHC levels remained relatively uniform;

6) Precursor patterns on Saturday afternoon through to Sunday evening displayed weaker spatial contrasts, with more evenly spread levels over the study area. This resulted in a net decrease in precursors and an increase in O_3 levels in the areas commonly associated with high NO_X.

In conclusion, classic photochemical smog problems over the city area are unlikely, due to exceptionally widespread high NO_X concentrations. NO_X pollution in itself is an existing problem under calm conditions. The areas with higher photochemical smog potential are predicted to be in the region of the Northern Suburbs, especially where the combination of high NMHC and lower NO_X could lead to high O_3 levels. It should be kept in mind that the problems and conclusions outlined above apply largely to relatively calm periods in Cape Town. Given the high frequency of north west and south east winds with good diffusion potential, these calm conditions rarely persist for more than a few days. Photochemical smog episodes are thus likely to be spatially limited and of relatively short duration in the Greater Cape Town area.

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CHAPTER 4

AN ASSESSMENT OF PHOTOCHEMICAL SMOG IN GREATER CAPE TOWN

Photochemical precursor and oxidant concentrations in Greater Cape Town were examined with respect to controlling factors, chemical relationships, and peak levels. These were compared to standards and measurements in other cities. The database for this study comprised continuous monitor measurements and data collected for a spatial survey. It was found that precursor levels were more influenced by wind speed than by traffic emissions, while ozone (O_3) concentrations displayed a negative relationship to vehicle emissions and a positive relationship to temperature. The low nitric oxide (NO) levels in the early morning in the city resulted in elevated O_3 levels at this time, while NO scavenging was responsible for low O_3 values during the remainder of the day. An $NO:NO_2$ ratio of approximately 2:1 was found in the city, and roughly 1:1 at the suburban site. Maximum O_3 formation at the suburban site occurred for non-methane hydrocarbon (NMHC) values between 0.09ppm and 0.14ppm where the $NMHC:NO_x$ ratio was about ten times that at the city site. The EKMA/Dodge Model proved adequate for O_3 prediction in the city data but overpredicted O_3 for the suburban data. The potential for peak O_3 levels was highest just after midday at both sites, as well as during the early morning hours in the city. The areas potentially most exposed to high O_3 levels were those away from high NO concentrations, in particular the Northern Suburbs.

INTRODUCTION

Located on the South Western coast of Southern Africa at a latitude of 34^{0} S, Cape Town is a city with a population of approximately two million. It is both an industrial and commercial centre, with an urban area that extends outwards in a semicircle from the city centre for about 20 km, bounded to the west and south by the Atlantic Ocean (see Figure 1). The central business district (CBD) is contained in the northern part of the Peninsula in the amphitheatre of Table Mountain, and the suburban areas extend outwards from the mountain, spread across the region between the coastlines. Cape Town is situated at almost the same latitude as Los Angeles and Sydney, two cities which are well known for their photochemically induced air pollution problems (Sullivan, 1962; Hawke and Iverach, 1974). Photochemical smog occurs largely as a result of vehicle emissions and is known to contain chemicals that cause damage to vegetation, health and materials (Haagen-Smit *et al*, 1952). Despite vehicle numbers in Cape Town not being as great as those in Los Angeles or Sydney, concern has been raised with regard to the possible photochemical smog pollution in the city.

Photochemical smog is the result of a complex sequence of chemical reactions, initiated by the action of sunlight on nitrogen oxides (NO_x), and promoted by reactive non-methane hydrocarbons (NMHC), both referred to more generally as precursors. The precise mechanisms involved in the chemical reactions that produce photochemical pollution are complex and are still not well understood (Innes, 1981; Johnson, 1983; Kelly *et al*, 1984). The simplified reactions are however well known and can be followed in Figure 2. Emissions of nitric oxide (NO), a primary pollutant chiefly emitted from motor vehicle exhausts, are converted to nitrogen dioxide (NO_2) by oxidation. NO_2, also a primary pollutant emitted mainly from industrial sources, absorbs ultraviolet radiation and undergoes photodissociation which

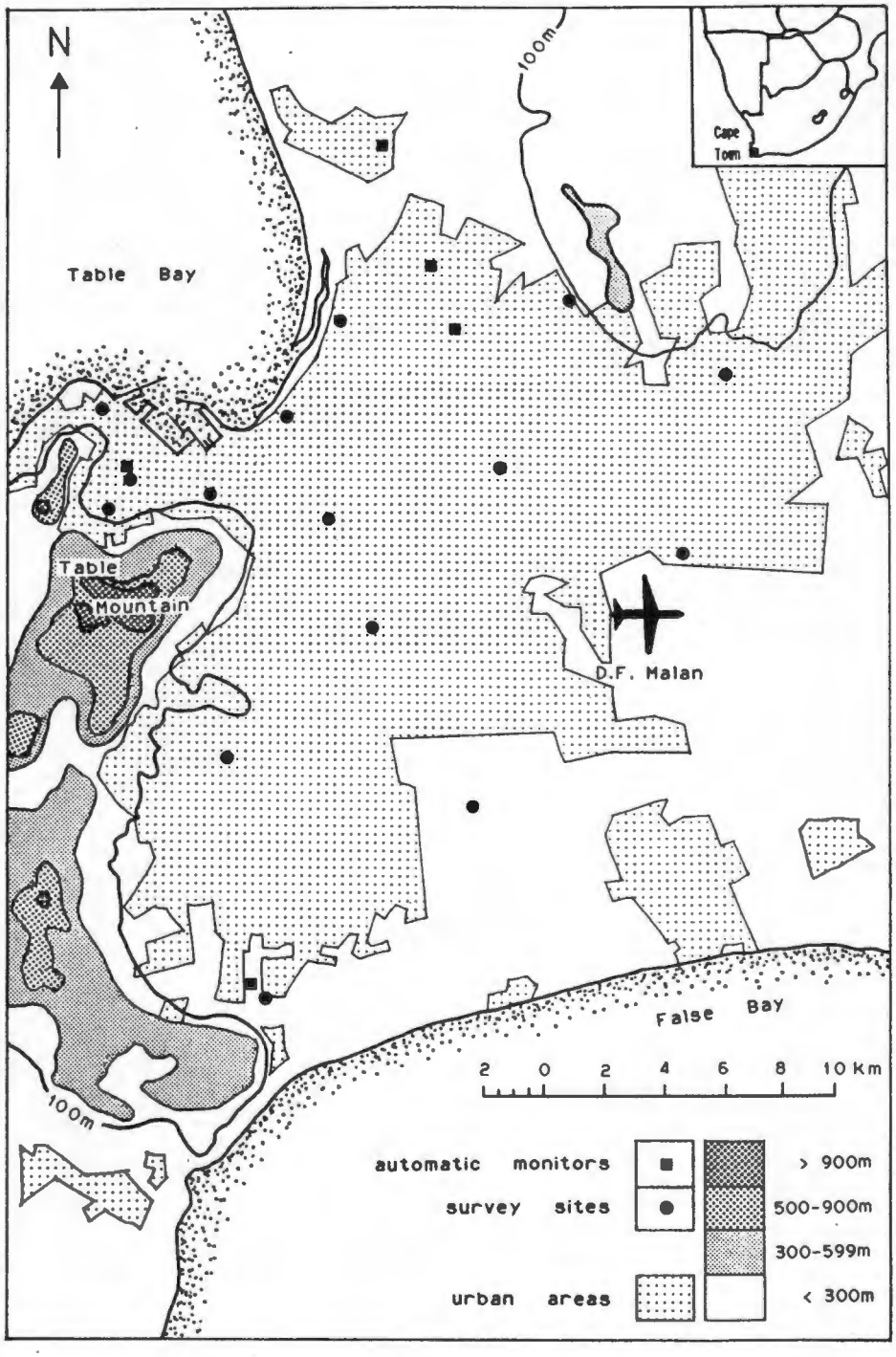

Figure 1: Location map of the study area showing the urban area and surrounding topography with the automatic monitoring and survey sites.

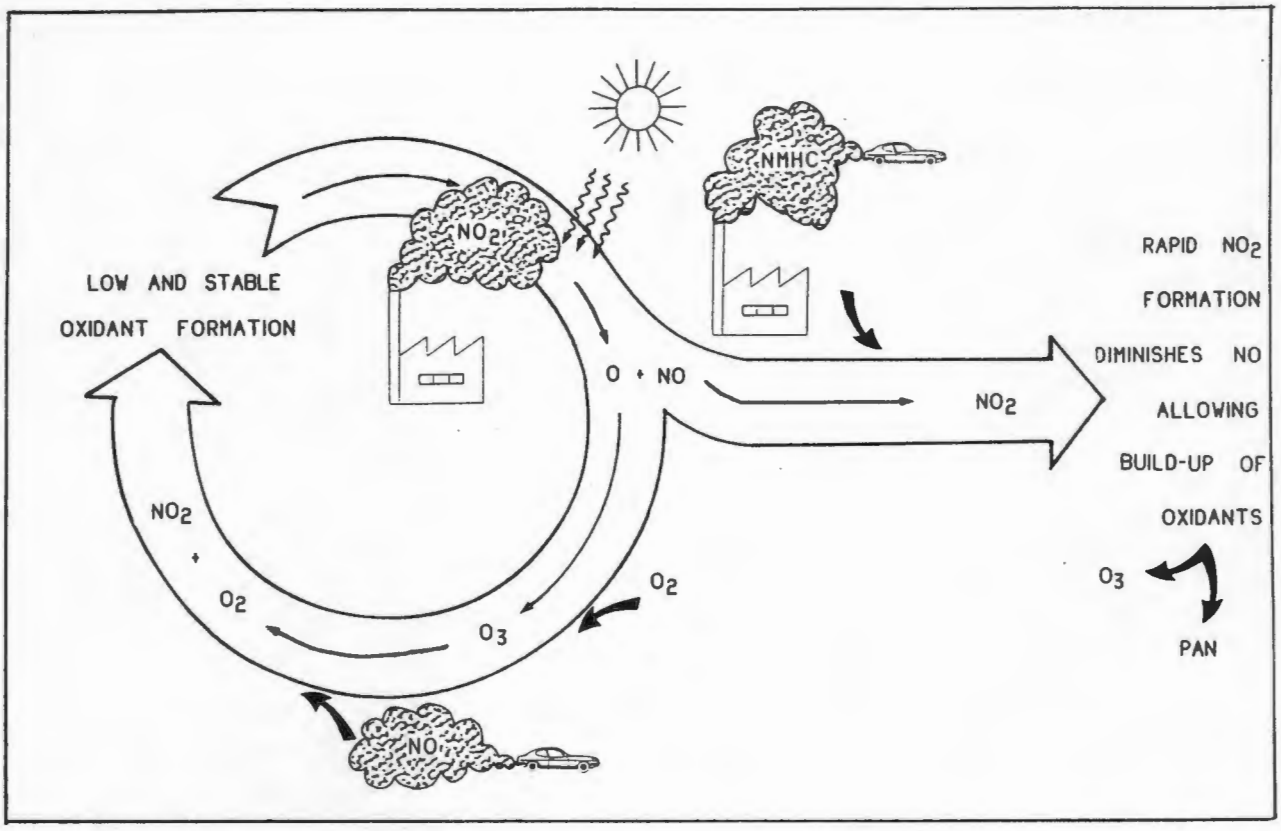

Figure 2: A schematic of the basic reactions involved in the formation of photochemical smog.

produces atomic oxygen (O) and NO. The combination of O with molecular oxygen (O_2) results in the formation of ozone (O_3), the chief constituent of photochemical smog. The combination of NO and O_3 giving NO_2 and O_2 restarts the cycle. A stabilised concentration of O_3 is thus rapidly reached. However, NMHC tend to modify the steady-state reaction by converting NO to NO_2 without consuming O_3. The NO concentration then becomes low enough to cause a rapid and marked increase in the O_3 concentration. Although other reaction products such as organic peroxides and peroxyacetyl nitrate (PAN) are produced, O_3 quantitatively forms the major contribution to the oxidant level, and its concentration is often used as a measure of the severity of photochemical smog.

The analysis of photochemical smog present in many metropolitan cities has been well documented, and has covered topics such as the occurrence of photochemical pollution incidents and high oxidant levels (Hawke and Iverach, 1974; Ball and Bernard, 1978; Trijonis *et al*, 1978; Post, 1979; Evans *et al*, 1981; Mitchell *et al*, 1983; Stevens, 1987). Details of the relationship of such incidents to meteorology and to weekday/weekend differences have also been covered in the literature (Elkus and Wilson, 1977; Guicherit and Van Dop, 1977; Ganor *et al*, 1978; De Mandel *et al*, 1979; Hawke *et al*, 1983) . Studies of the more complicated concepts evident in the chemistry have been performed (Leighton, 1961), and more recently the development of empirical and chemical kinetic models making use of smog chamber experiments have been documented (Dodge, 1977; Johnson, 1983; Smith and Johnson, 1984).

In Cape Town, initial studies into photochemical smog began with The Air Pollution Survey of Greater Cape Town (Dutkiewicz and Fuggle, 1977; Dutkiewicz, 1979; Dutkiewicz *et al*, 1980). This survey concluded from the measured levels of O_3 that Cape Town experienced photochemical smog for a limited number of hours during the year. Reports from this study prompted the installation of automatic monitoring systems at a few selected sites around the city for further data collection. A more recent investigation by Smith (1984) suggested that from the initial data available, Cape Town does indeed experience photochemical smog, and recommended that further research be done to fully assess Cape Town's photochemical pollution.

In order to make a comprehensive assessment of the photochemical smog situation in Cape Town, it was found necessary to consider both the temporal and spatial aspects of the precursors and oxidants. The basic analysis of monitor data from 1984 to 1986 was dealt with in Loewenheim (1988a) and covered the temporal behaviour of precursor and oxidant levels and the associated meteorological influences.

The spatial patterns of photochemical smog was emphasised in Loewenheim (1988b) and was based on a survey conducted during 1987. Figure 1 shows the locations of the various automatic monitors as well as the sites covered by the spatial survey. In order to complete the analysis of photochemical smog, identification of the physical relationships evident in the data and the implications of the spatial and temporal behaviour of photochemical smog was needed.

It is the aim of this paper to supplement the existing knowledge on photochemical smog in Greater Cape Town by examining the factors influencing and controlling the levels of selected precursors and oxidants, and the chemical interactions and relationships evident from the empirical data. Considering both the temporal and spatial data, areas of concern with regard to specific pollutant levels and their respective areas of influence are investigated and synthesised. Comparisons of levels and the frequency of episodes in Cape Town to other cities worldwide are made, in order to place Cape Town in perspective in terms of its present and possible future status with regard to photochemical smog.

BACKGROUND

The current photochemical smog situation in Cape Town was assessed by consideration of the following points:

a) controlling factors promoting its formation, persistence and dispersion;
b) chemical relationships between the specific pollutants;
c) temporal and spatial behaviour of the pollutants.

It was decided to make use of data from two sources. Firstly, monitor data collected during the period 1984 to 1986, and secondly, data collected during a spatial survey

during April and May 1987. The methods of measurement and instruments used for both data sets are described in Loewenheim (1988a) and Loewenheim (1988b) respectively.

Controlling factors

The investigation into the controlling factors affecting the precursor and oxidant levels was carried out in order to identify those applicable to Cape Town. NO_x, NMHC and O_3 concentrations at all of the fifteen survey sites in and around Cape Town were utilised. Seven weekdays were selected so as to cover a full range of meteorological conditions with the same patterns of vehicle emissions (see Appendix 4.1). Meteorological data, namely hourly averaged 10m wind speeds and temperatures, were recorded at D.F. Malan airport (see Figure 1). Traffic counts around Cape Town (obtained from the City Engineer's Department) were used to calculate vehicle numbers as an average of weekday vehicle counts taken at random times at locations as close to each sampling site as possible. This provided a direct measure of traffic flow with which to compare the precursor and oxidant levels. For comparative purposes, pollutant concentrations and controlling factors were then normalised as a proportion of their maxima. Moving averages (of 61 points) were also calculated to identify patterns. The results are naturally subject to the constraints of the database limited by the survey period and the prevailing conditions.

Chemical relationships

To illustrate the interrelationships between the precursor and oxidant levels, and the relative behaviour of the pollutants over time and at different locations, monitor data were used to distinguish between examples of a city and suburban site. Two months of data collected under similar meteorological conditions were used, namely October 1986 for the City Hall and March 1986 for Tableview, where virtually

complete data sets of hourly averaged data were available. The city site was located in the CBD, and the suburban site was located in a residential area towards the edge of the urban boundary, which at times came under the influence of a nearby industrial area.

It was decided to make use of the Empirical Kinetic Modelling Approach (EKMA) (originally proposed by the USEPA) to further examine the relationships between NO_X, NMHC and O_3. The EKMA method (Dodge, 1977; USEPA, 1977) is based on smog chamber analyses and is used for the estimation of maximum potential O_3 concentrations using the 06h00 to 09h00 NMHC and NO_X data. The standard isopleth diagram used in EKMA was tested for its applicability using monitor data, for all days when the relevant readings were available from City Hall and Tableview, which comprised a total of 105 days during 1986. This allowed comparison of O_3 levels estimated by EKMA with the observed O_3 maxima. Since very low O_3 levels were experienced in Cape Town during this time (always less than 0.08ppm), extrapolation of the O_3 curves was required to include the 0.05ppm curve.

Levels and episodes

Knowledge of the occurrence and duration of high concentrations of photochemical smog precursors and oxidants, the characteristic conditions surrounding them and the areas susceptible to high levels is required for the determination of the potential environmental and physical impacts of high levels. For this study, the calculation of the means and standard deviations of the precursor and oxidant levels was performed for a sample month at City Hall and Tableview, following which a comparison of the hourly variability and the monthly range and standard deviations was made. Thereafter, a general overview of photochemical pollutant levels in Cape Town was made, including reference to selected standards and the levels in other cities.

RESULTS AND DISCUSSION

Controlling factors

Illustrated in Figure 3 are the mean levels of the respective pollutants and selected influencing factors, each normalised as a function of their maxima for the weekdays chosen. Figure 3a shows the NO_x concentrations, traffic counts and wind speed over time. The behaviour of NO_x in the early morning followed the general traffic curve until approximately 09h30, when the wind speed had increased to about half of its daily maximum. A further increase in wind speed led to the stabilising of the NO_x level around a value of about 40%, while traffic remained constant at roughly 65% of its maximum. Peak traffic at the 17h00 rush hour coupled with the wind speed maximum in the afternoon prevented a significant increase in the NO_x level and resulted in the somewhat damped NO_x increase of about 10%. The influence of low wind speed was evident in the high NO_x concentrations during the morning rush hour, while higher wind speeds during the afternoon rush hour diluted traffic emissions and resulted in correspondingly lower levels.

Figure 3b shows the normalised curves of NMHC levels, wind speed and temperature. NMHC concentrations increased gently to a peak at rush hour during the morning, and tended to remain relatively constant throughout the day at about 80% of the maximum. The increased wind speed and temperature in the early afternoon resulted in a marginal increase in the NMHC level, which decreased slowly during the later afternoon. During the afternoon, NMHC levels were slightly influenced by the diluting effect of the wind speed, and higher temperatures could have caused increased evaporative emissions of NMHC, especially in industrial areas. However, in general the NMHC levels did not show strong relationships to any of the factors, with peak rush hour traffic having little influence on the NMHC concentrations.

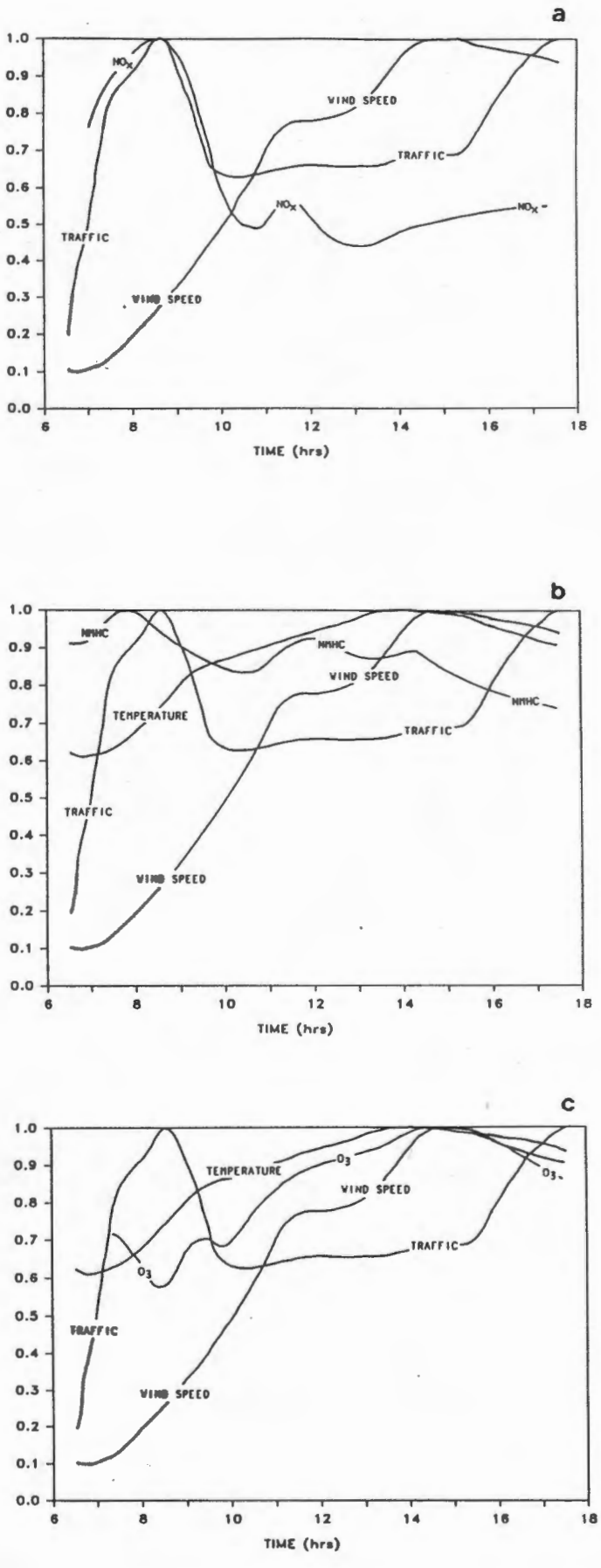

Figure 3: Average normalised levels of (a) NO_X, (b) NMHC, and (c) O_3 and selected influencing factors over time for seven weekdays during the survey.

Illustrated in Figure 3c are the normalised curves of O_3, temperature, wind speed and traffic counts over time. The O_3 concentration decreased to a minimum of about 50% at peak rush hour traffic before increasing steadily, together with rising temperature, to a maximum around 14h00. The temperature peak occurred approximately half an hour before the peak O_3 concentration. The O_3 level began to decrease to about 80% of its maximum with the onset of evening rush hour traffic and the concurrent drop in temperature. Unlike the NO_x and NMHC levels, O_3 showed little direct dependency on wind speed, but showed a definite positive relationship to temperature, and an inverse relationship to traffic flow.

Chemical relationships

DIURNAL VARIATION

For a more comprehensive description of the diurnal variation of the photochemical pollutants over time, a more consistent and complete database was used, comprising hourly averages from continuous monitors for a month at a city and at a suburban site. Figures 4a to 4e correspond to each of the pollutants discussed below.

NO_x, NO and NO_2

At the city site, the NO_x, NO and NO_2 levels reached their minimum at 04h00 before rising to their maxima at about 07h30 with peak rush hour traffic (see Figures 4a to 4c). However the NO_2 maximum was delayed by roughly an hour. During the day, the NO_x and NO levels dropped to approximately half the morning peak and remained relatively constant, unlike the NO_2 level which exhibited a far broader peak, only dropping to its afternoon low at 13h00 with increased wind speed and mixing, before peaking again at 17h00 together with NO_x and NO. The suburban site experienced levels approximately a tenth of the city site, with damped responses to rush hour traffic. The NO_2 level

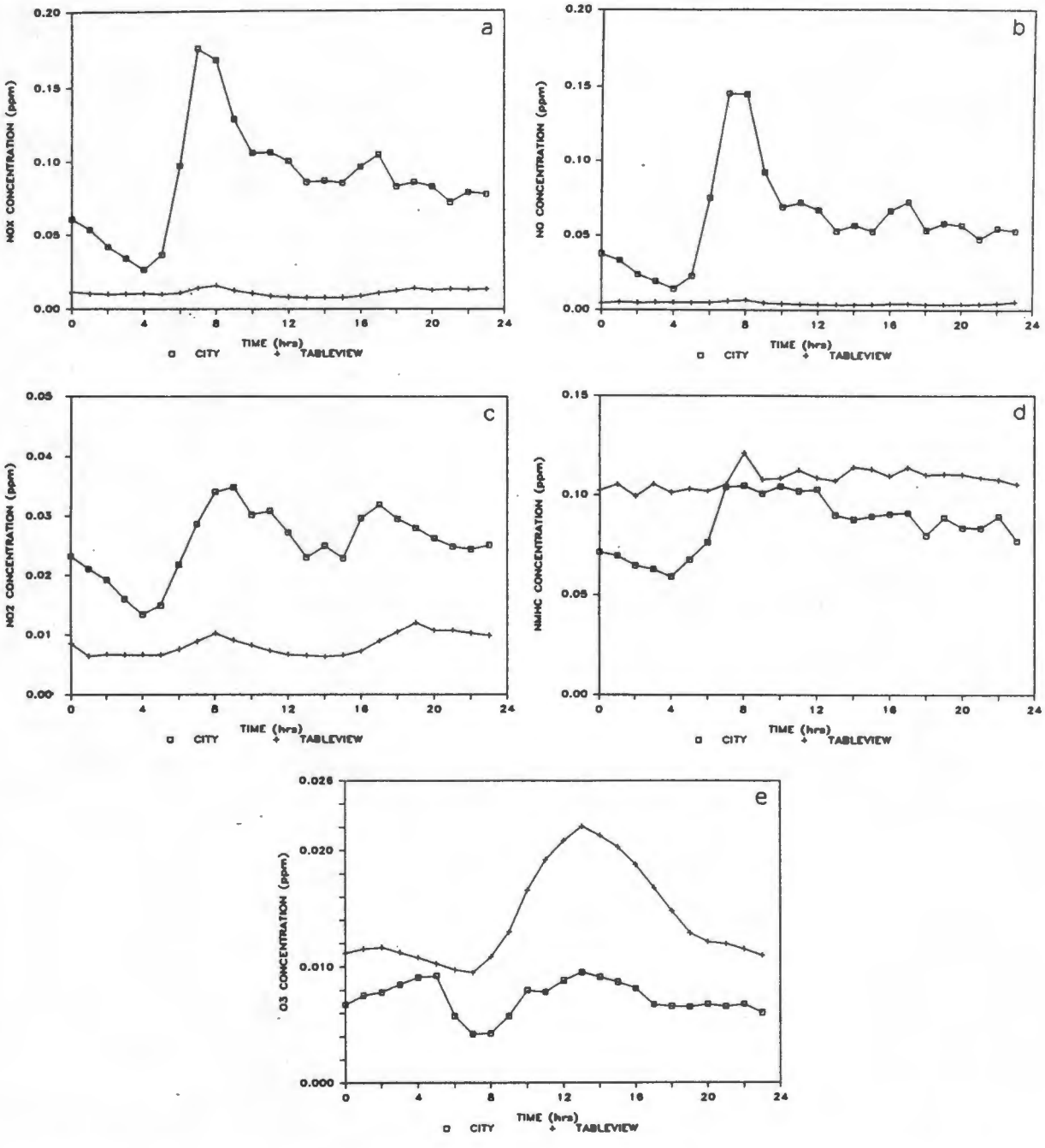

Figure 4: Mean hourly levels of NO_X, NO, NO_2, NMHC and O_3 at (a) a city (City Hall) and (b) a suburban site (Tableview).

constituted a larger proportion of the NO_X at the suburban site, although both sites displayed similar trends. The evening rush hour peak at the suburban site occurred two hours after the traffic peak and showed only a slight decrease until 01h00, before dropping to a minimum at 04h00.

The relatively higher levels experienced after 18h00 showed the possible influence of background industrial emissions in the area when wind speed dropped to its minimum. The levels at the city site showed the large influence of vehicular emissions, experiencing lower levels in the absence of traffic during the early morning hours and with particularly high levels during the morning rush hour.

NMHC

The NMHC levels at the suburban site were generally higher than in the city and remained constant throughout the day showing only a minor peak during the morning rush hour (see Figure 4d). In the city the NMHC levels exhibited far greater variation during the day. Levels reached a minimum at 04h00 and rose to a maximum at 07h00. This level was maintained until 12h00 before dropping steadily to about half its maximum for the rest of the day. As with the NO_x, the NMHC concentrations at the city and suburban site showed the respective influences of traffic and industry.

O_3

The O_3 curve at the suburban site displayed the typical convex shape with a minimum at rush hour around 07h00 and a maximum just after peak insolation at about 13h00 (see Figure 4e). The pattern at the city site exhibited a more complicated behaviour with a peak in the early morning at roughly 05h00 equal in magnitude to its afternoon maximum. Although decreased wind speeds and increased stability occurred during the early morning hours, a possible cause for this peak may be found in the NO concentrations. At the city site the NO levels were extremely low in the early morning, largely due to the lack of vehicular emissions, thus diminishing the scavenging by NO and promoting the O_3 formation. At the suburban site however, emissions from a nearby industrial area possibly maintained precursor levels (including NO) at relatively elevated concentrations, thus depressing the O_3 levels.

CHEMICAL INTERRELATIONSHIPS

NO to NO_2

Illustrated in Figures 5a and b are scatterplots of NO vs NO_2 at the city and suburban sites. At the city site, the curve begins with a gradient of approximately 1, but at NO values above 0.05ppm, the curve flattens to a slope of about 0.5, with increased scatter. At the suburban site the NO vs NO_2 relationship was not nearly as well defined as the city site as it covered a distinctly limited range of NO and NO_2 levels, although the basic pattern at both sites was similar. The NO and NO_2 levels at the suburban site were

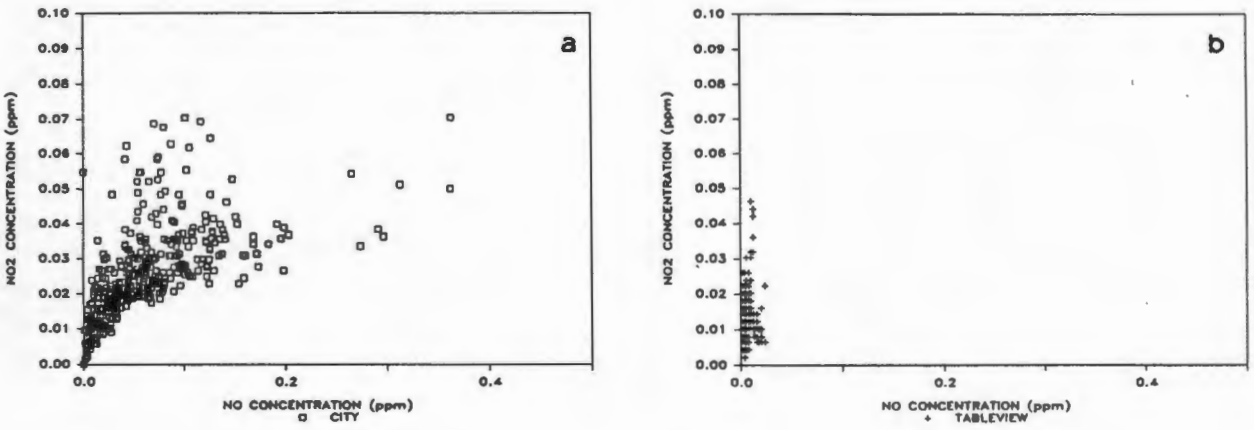

Figure 5: NO versus NO_2 at (a) a city (City Hall) and (b) a suburban site (Tableview).

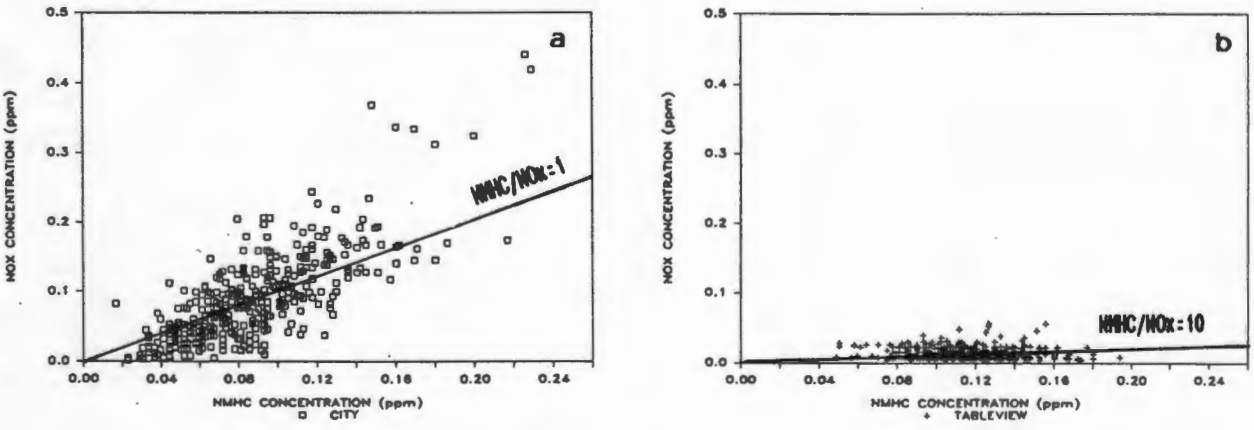

Figure 6: NMHC versus NO_x at (a) a city (City Hall) and (b) a suburban site (Tableview).

clustered closer to the vertical axis where the $NO:NO_2$ ratio was 1:1 while at the city site, the NO values were for the most part generally greater than the NO_2 levels, again showing the influence of high vehicle traffic.

NMHC to NO_X

Figures 6a and b show the NMHC to NO_X relationship. It is apparent from this scatter diagram that the city site has a $NMHC:NO_X$ ratio of almost 1:1 whilst at the suburban site, the data are clustered around the diagonal corresponding to a ratio of 10:1. The relative proportion of NMHC at the suburban site was thus far greater than in the city, which further emphasised the largely vehicular influence in the city and the likely industrial influence at the suburban site. The NMHC levels at both sites spanned a similar range while the NO_X values were significantly lower at the suburban site.

NO_X, NO and NO_2 to O_3

The definite inverse relationship of NO_X to O_3 is illustrated in Figure 7a and b. The shape of the hyperbolic curve was as expected and showed a sharp decrease in O_3 with increased NO_X. Likewise the NO to O_3 scatterplot (Figures 7c and d) behaved in a similar fashion to the NO_X versus O_3 curve and displayed a slightly more compact pattern closer to the axes. The higher O_3 at the suburban site was attributed to the low NO_X and NO concentrations at this site (all below 0.1ppm), and conversely the low O_3 at the city site was related to the very high NO_X and NO levels (extending as far as 0.4ppm). From these graphs it was deduced that an NO level less than 0.02ppm for these data would result in the O_3 level being greater than the World Health Organisation (WHO) goal of 0.06ppm. The basic inverse relationship between NO_X and O_3 highlighted the NO_X concentration as being a strong and influential factor in affecting O_3 formation. Figures 7e and f show the NO_2 versus

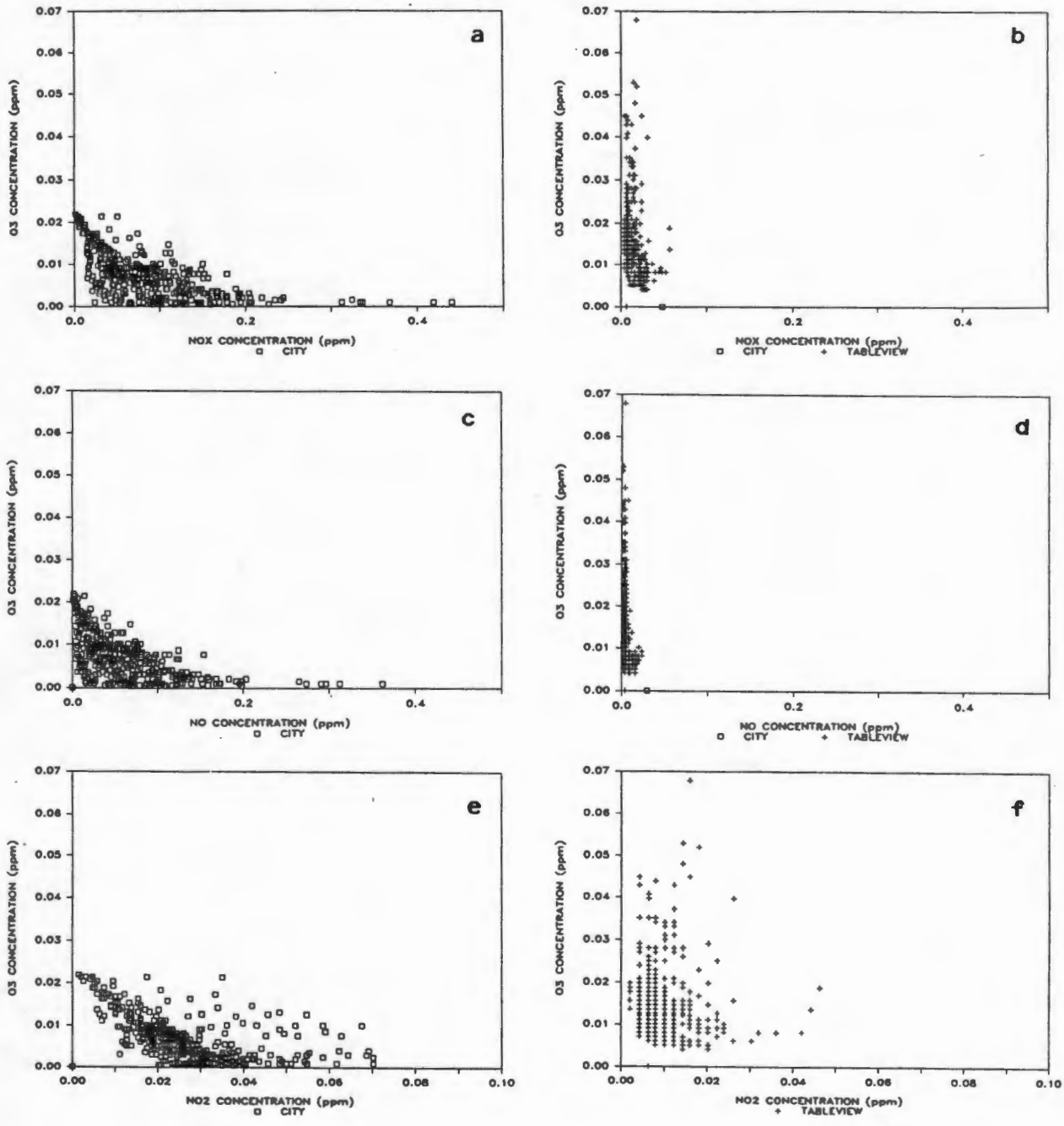

Figure 7: NO_X, NO and NO_2 versus O_3 at a city site (City Hall-(a), (c) and (e) and suburban site (Tableview-(b), (d) and (e).

the O_3 concentration. The increased scatter evident in this plot was far greater than the previous two plots although the basic pattern of decreased O_3 with increased NO_2 was evident. At the city site, there was a more defined relationship with less scatter and diminished O_3 concentrations, whereas at the suburban site the scatter was more pronounced, with higher O_3 levels experienced when the NO_2 concentration was below 0.02ppm.

NMHC to O_3

Figures 8a and b show the NMHC to O_3 scatterplot. The relationship between NMHC and O_3 at the city site was strongly influenced by the NO_X to NMHC ratio of approximately 1. With high NMHC and thus high NO_X, the O_3 level was suppressed. At the suburban site there appeared to be a period of increased O_3 formation, for NMHC values between 0.09ppm and 0.14ppm in the given data range. This

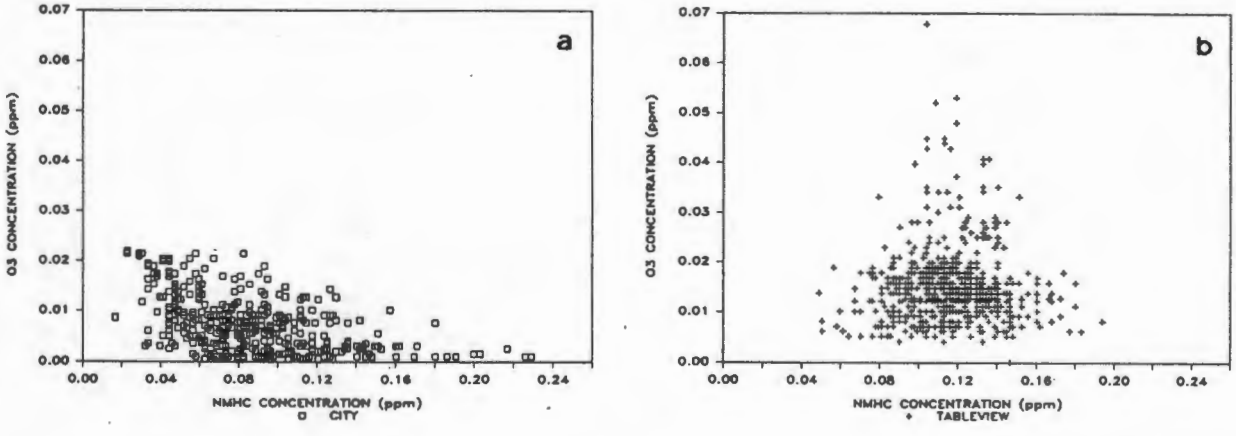

Figure 8: NMHC versus O_3 at (a) a city (City Hall) and (b) a suburban site (Tableview).

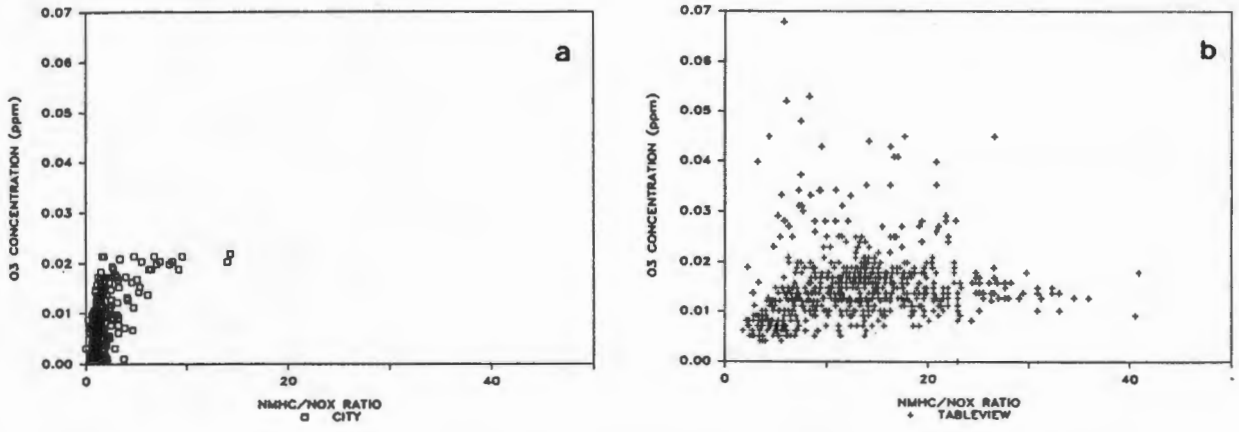

Figure 9: $NMHC/NO_X$ versus O_3 at (a) a city (City Hall) and (b) a suburban site (Tableview).

was the expected pattern where the NMHC levels contributed to the formation of O_3, within the constraints of the relationship between NMHC and NO_X. The inhibitive effect of the NO_X can be seen at the city site and is illustrated by the suppression of the curve, whereas the more normal distribution evident at the suburban site showed both an inhibition by NO_X and a promotion by NMHC when the NO_X was low.

$NMHC/NO_X$ to O_3

Illustrated in Figures 9a and b are the $NMHC/NO_X$ versus O_3 relationship at the city and suburban sites. At the city site the $NMHC:NO_X$ ratio was very low with the majority of data falling between 0.5 and 2, with the NO_X values at unusually high levels relative to other cities and compared to the NMHC concentrations. At the suburban site a similar range was present for the higher $NMHC/NO_X$ values, although most values were greater than 2 and reached a maximum of 40. The resulting $NMHC/NO_X$ versus O_3 graph for both sites thus

gave an exponential curve starting near zero where the NMHC/NO_x ratio was less than 1 and which grew rapidly up until about 10, whereafter a more constant relationship with increased scatter was found. From other authors (Post, 1979; Martinez and Ludwig, 1979), the optimum ratio of NMHC to NO_x for maximum O_3 formation lies between 10 and 20. This ratio was rarely reached in the city, but was more frequent at the suburban site, which experienced the higher O_3 concentrations.

The EKMA/Dodge Model

In order to test the EKMA/Dodge Model for applicability to Cape Town, it was necessary to extrapolate the 0.05ppm O_3 isopleth to allow for the relatively low O_3 levels experienced in Cape Town. Figures 10a and b show the O_3 isopleth diagram for the city and suburban site data respectively. The position of the EKMA isopleths and the observed maximum O_3 concentrations (for the relevant NMHC and NO_x concentrations) are also annotated. The data compared reasonably well to the EKMA isopleths at the city site, with almost all O_3 values below 0.05ppm placed below the relevant isopleth. The correlation between the suburban site data and the EKMA isopleths was not as good, and the observed O_3 values were generally underpredicted by about 50%. The shape of the curves for the observed data did however tend to follow the isopleth curves for both sites.

Following the relationships in the EKMA Model, possible reductions in NO_x concentrations with an increase in the NMHC level might result in a substantial increase in the O_3 concentration in the city. Using the EKMA isopleth diagram and typical NMHC and NO_x values for the city, by halving the NO_x level and doubling the NMHC concentration, which would be more representative of the situation in other metropolitan cities, approximately a sixfold increase in the O_3 level could be expected. Such precursor variations at the suburban site could possibly cause a slight increase in the

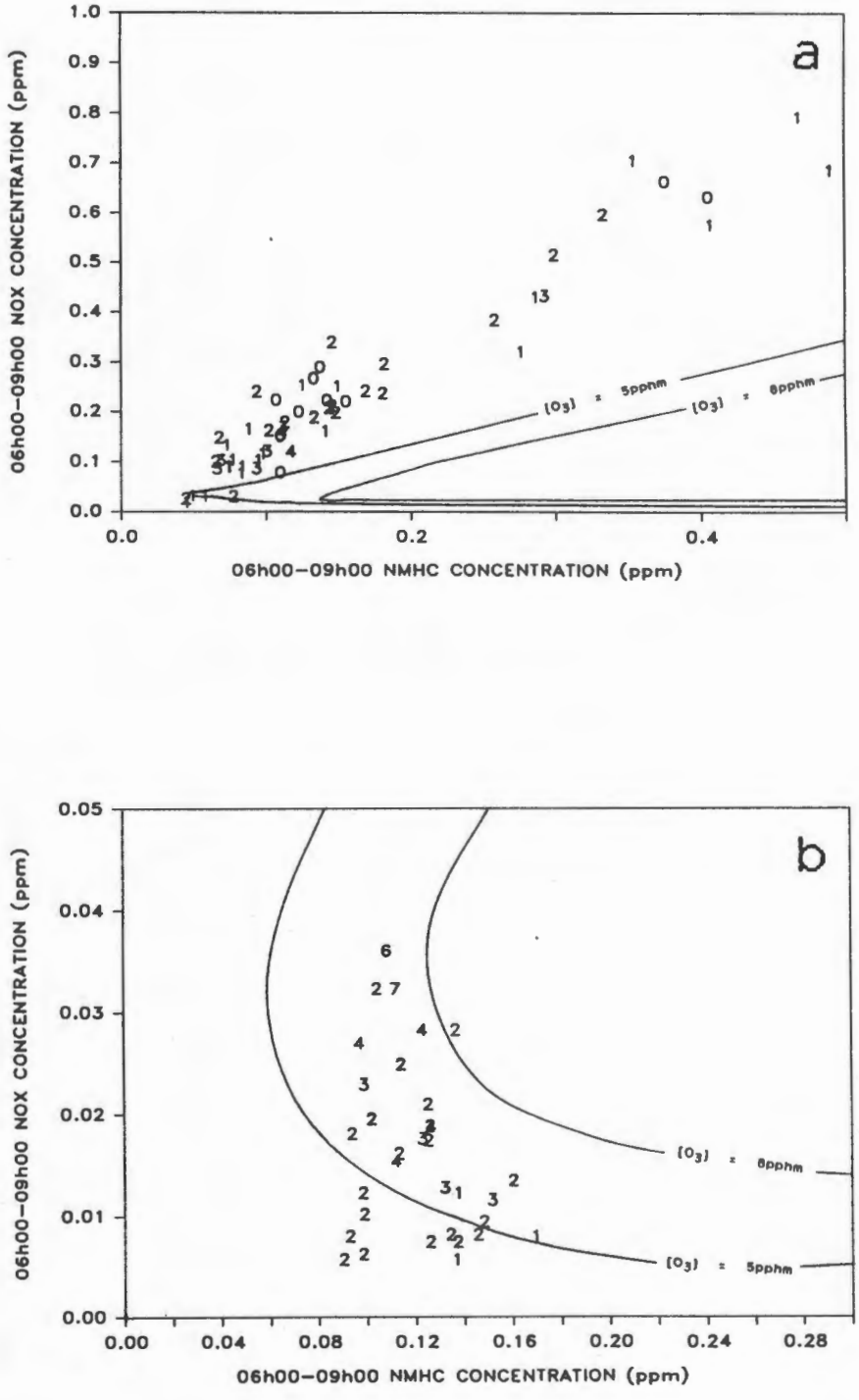

Figure 10: The EKMA/Dodge isopleths and the observed O_3 values at (a) a city (City Hall) and (b) a suburban site (Tableview). Note the considerably different NO_x values at the two sites which affect the form of the isopleths.

O_3 levels (to perhaps double the present values), but not nearly as marked as the possible change within the city where the USEPA standard might then be exceeded.

Levels and episodes

It is important to consider the likelihood of episodes both spatially and temporally, together with knowledge of the characteristic conditions for smog formation, the pollutant levels and their likely duration. Loewenheim (1988a) dealt with trends in the data and covered the general cycles of high and low precursor and oxidant levels at the selected sampling sites.

In order to locate the most likely times for episode potential (or exaggerated peaks) in the precursor and oxidant concentrations on a diurnal basis, the standard deviations for a month of complete data at each of the sites for NO_x, NO, NO_2, NMHC and O_3 were consulted.

STANDARD DEVIATIONS

NO_x, NO and NO_2

Standard deviations indicate the amount of variability contained within a sample. With regard to pollutant levels, the greatest values of standard deviations when added to the mean may thus indicate the locations and times when peak levels are most likely to be experienced. Standard deviations thus provide an index from which the potential for episodes may be gauged. Figures 11a, b and c show the standard deviations of the NO_x, NO and NO_2 concentrations respectively. The city site showed relatively little variation in the NO_x and the NO levels during the early morning hours, while the greatest variation occurred during the morning rush hour, followed by relatively low variation during the day. At the suburban site the position was somewhat reversed, with the least variation occurring during

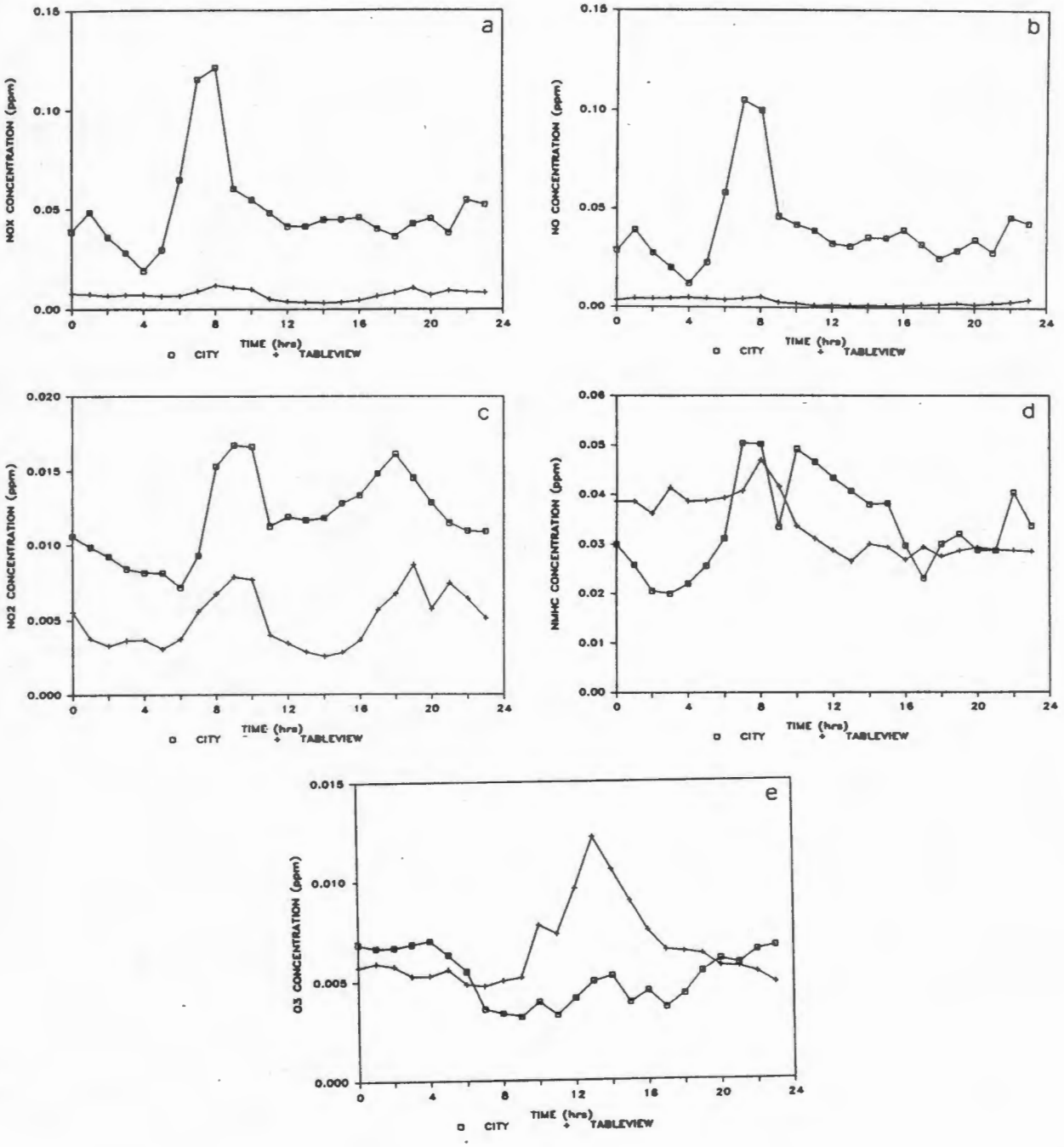

Figure 11: Standard deviations of NO_x, NO, NO_2, NMHC and O_3 (a to e) at a city (City Hall) and suburban site (Tableview).

the afternoon and most variation during the night-time and early morning through until the 07h30 rush hour. A possible explanation for this behaviour was the likely presence of emissions from a nearby petrochemical plant with the simultaneous drop in wind speed. The NO_2 levels varied considerably at both sites (although on different scales), mostly just after the rush hour peaks. The period likely to experience high NO_x levels was thus during morning rush hour, when low wind speeds occurred and traffic was at a maximum. Significant inhibition of O_3 formation was thus most likely, especially in the city for the major portion of the morning.

NMHC

The NMHC levels at the city site showed higher standard deviations than the suburban site, as shown in Figure 11d. The NMHC levels at the city site followed the traffic pattern and showed the greatest variation during morning rush hour through until noon, after which the standard deviations decreased gradually into the evening. The suburban site showed only minor variations during the day with a peak at about 08h00 and 19h00. The standard deviations were remarkably consistent during the day, again showing the possible effect of industrial emissions. It was anticipated that in the city, the higher NMHC levels promoting O_3 formation would occur concurrently with high NO_x levels would be inhibiting them, thus producing relatively lower O_3 levels. For the suburban site, the constant NMHC levels with low standard deviations indicated increased episode potential for O_3, particularly during the afternoon when the NO_x levels were low.

O_3

Illustrated in Figure 11e are the O_3 levels for the two sites. The suburban site showed the greatest standard deviation at the time of maximum O_3 concentration, just

after midday. Exaggerated peaks or possible episodes were therefore most likely to occur at this time. At the city site the opposite was true where the greatest standard deviations occurred outside of daylight hours, between 20h00 and 06h00. At midday the O_3 level was relatively high but the standard deviation was lower resulting in similar episode potential in the early morning as just after midday.

MONTHLY VARIATIONS

Figure 12 shows the maxima, minima, means and standard deviations for a selected month of complete data at each site. The city site, with a greater and more variable traffic flow, showed far higher NO_x and NO values with a large range and standard deviation. The suburban site with limited vehicular influence and perhaps more constant industrial effects showed NO_x and NO means of almost 10% and 7% of the city values respectively, and with a limited range and standard deviation. The NO_2 means and standard deviations at the suburban site compared to the city site were more similar than the NO_x and NO relationships above, and were about a third of the city values. The NMHC behaved somewhat differently to the NO_x with very similar values experienced at both sites. Values at the suburban site showed a slightly higher mean value than the city, although the city experienced the larger maximum, and could perhaps be explained by the respective contributions of industry and vehicles. The O_3 values again showed definite discrepancies, with the suburban site experiencing values approximately double those in the city and a range almost three times greater, although the standard deviation in both cases was relatively similar.

SPATIAL AND TEMPORAL SENSITIVITY OF PEAK PHOTOCHEMICAL POLLUTANTS

In assessing the current air quality situation, information regarding the spatial distribution of precursor and oxidant levels and particularly the possibility of high levels or

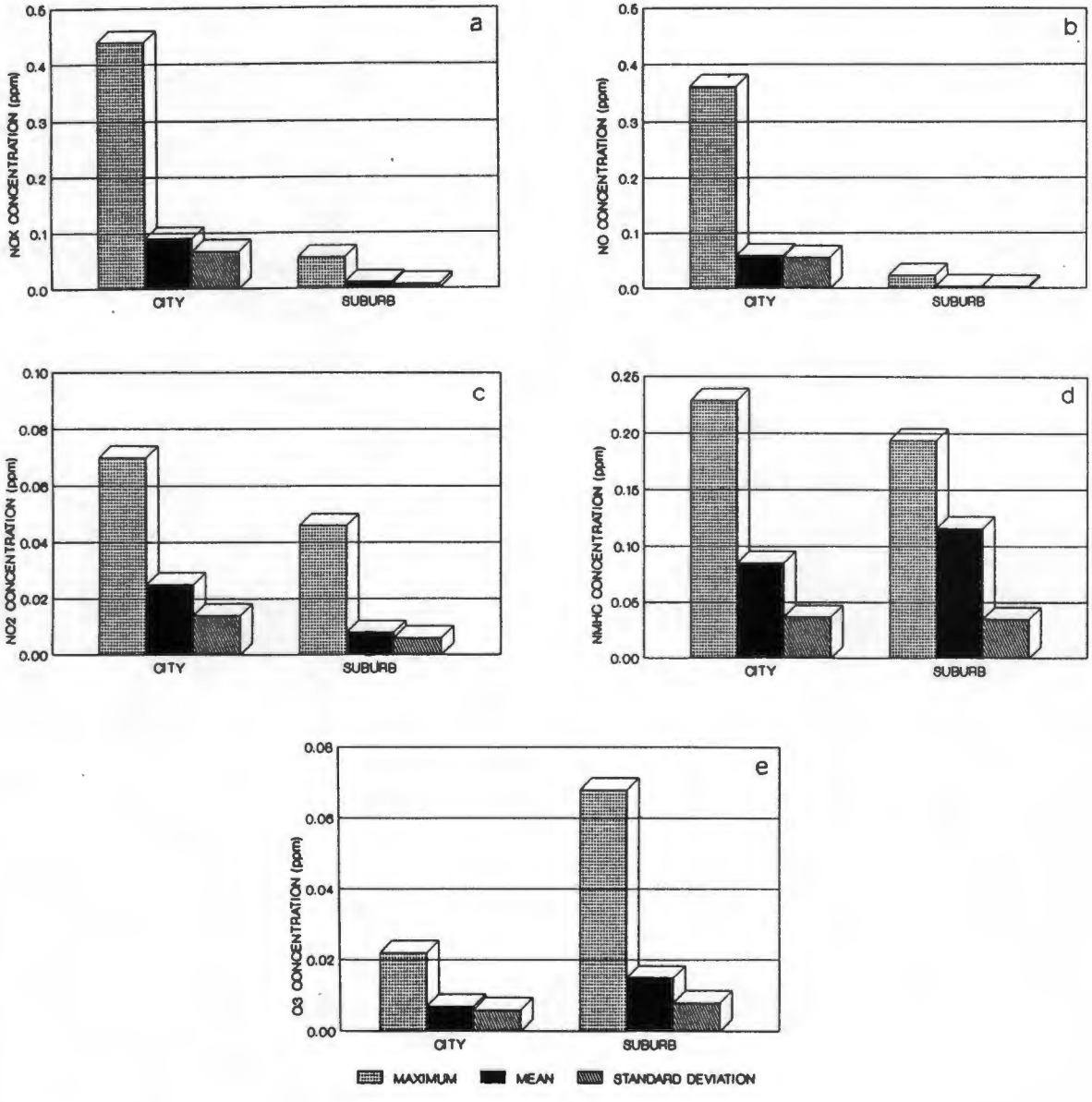

Figure 12: Monthly maxima, means and standard deviations of NO_x, NO, NO_2, NMHC and O_3 (a to e) at a city (City Hall) and suburban site (Tableview).

episodes is required. Figures 13a, b and c provide a composite view of high NO_x, NMHC and O_3 levels and the time of occurrence in Greater Cape Town, based on Loewenheim (1988a) and Loewenheim (1988b). These areas correspond fairly closely to those assigned a high air pollution potential in Keen (1979). High NO_x concentrations were experienced during the calmer winter months and were most concentrated during the morning rush hour, particularly in the Southern Suburbs and the city centre. Although there was only a small quantity of NMHC data, it was deduced, from the location of industry and the consistently high levels experienced in this area, that the Northern Suburbs were likely to experience the higher NMHC levels particularly during morning rush hour and especially during the winter period. Given the database of this study it was estimated that for O_3 pollution, the areas most likely to be affected were the the Northern Suburbs where NO_x levels were lowered and the NMHC were raised, as well as the areas between the main arterial roads (see Figure 13). Loewenheim (1988a) found from the limited data (1985 and 1986) the time of peak O_3 concentrations to be early spring and late summer, and not the expected summer months, as the latter were associated with the highest wind speeds during the year. At the diurnal scale, O_3 maxima tended to occur around 14h00, a little after the maxima of ultraviolet radiation and temperature.

METEOROLOGICAL INFLUENCES

Summer meteorological conditions prevailing over the Western Cape area are significantly different to those experienced over both Los Angeles and Sydney during their summer seasons. Los Angeles and Sydney both experience much warmer temperatures, frequent and strong nocturnal inversions and protracted periods of calm wind conditions. However Cape Town is generally well ventilated during the summer months when strong, pulsating southerly winds prevail (Keen, 1983). It was thus concluded that, although maximum ultraviolet

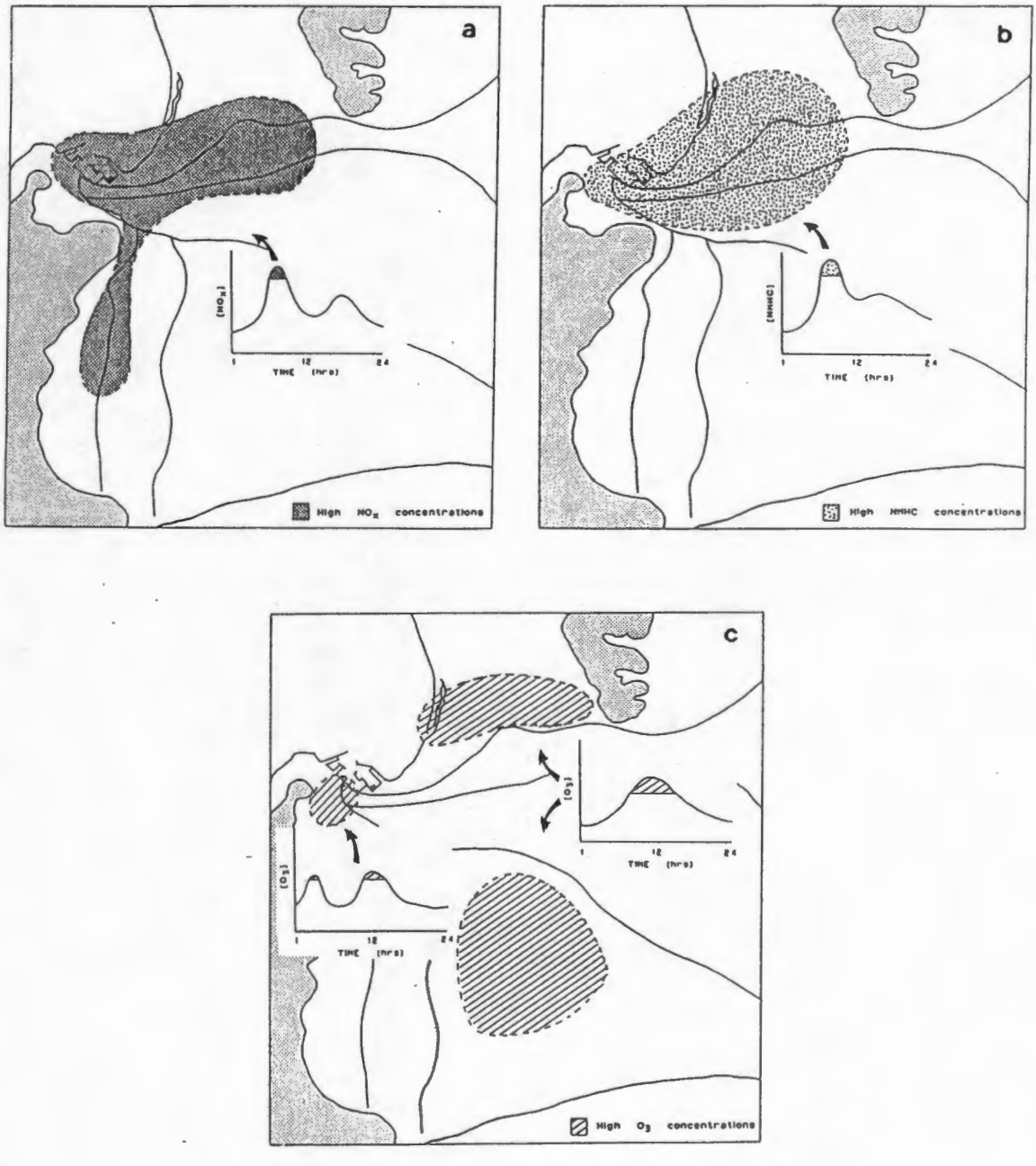

Figure 13: A summary diagram showing (a) NO_X, (b) NMHC, and (c) O_3 levels and the times and areas of high concentration in Greater Cape Town.

radiation and temperatures are experienced during the summer in Cape Town, greater dispersion of photochemical precursors would result in infrequent occurrences of photochemical smog episodes. However on calmer days (with reduced pollutant dispersion) it was anticipated that the likelihood of a photochemical episode would be increased. Extremely calm conditions and the presence of strong inversions would however not necessarily be most favourable for increased O_3 formation, as high pollutant levels (particularly NO) would result in increased O_3 depletion (see Loewenheim, 1988a).

POLLUTION STANDARDS

The NO_x levels were particularly high on occasion at the city centre, with the 06h00 to 09h00 levels averaging at about 0.18ppm for 1986. The USEPA yearly NO_x standard of 0.05ppm and the Japanese NO_x standard of 0.02ppm were not exceeded. The NMHC levels at the same time tended to average around 0.16ppm in the city, with very few cases showing 06h00 to 09h00 values greater than the USEPA guideline of 0.24ppm. Past data show only a small frequency of high O_3 concentrations. During 1985 and 1986, there were no O_3 concentrations equal to or above the 1-hour average USEPA standard and the Australian goal of 0.12ppm. Only 14 days were found to exceed the WHO goal of 0.06ppm, with an hourly maximum of 0.071ppm.

COMPARATIVE STATUS

A comparison between data collected in Cape Town and that collected elsewhere in the world showed some significant differences. The maximum daily average NO_x concentration in Cape Town's city centre during the months from October 1985 to April 1986 was 0.18ppm. This value is almost double that experienced in the city centre of Sydney, Australia at Lidcombe (Mitchell *et al*, 1983) during the same months in 1980/1981. Winter levels of NMHC in Cape Town were generally greater than in the summer. The former averaged around

0.20ppm, hence inferring that the NMHC values in summer would be less than this value. The city centre in Sydney showed a daily maximum average for the summer months of 0.27ppm at Rozelle and 0.20ppm at Lidcombe (*ibid.*). Thus the NMHC levels measured in Cape Town are lower than those in Sydney. In Johannesburg, South Africa the mean NO_X hourly averaged value for the city centre was 0.08ppm for the period 06h00 to 09h00 during 1984/1985 and the corresponding NMHC value was 0.36ppm. In Cape Town's city centre the equivalent NO_X and NMHC levels for 1985/1986 were 0.11ppm and approximately 0.08ppm respectively. NMHC levels in Cape Town are thus generally lower than the norm in other cities with recognised photochemical smog problems. The difference in the precursor levels in Cape Town compared to other cities was thus not surprising, showing the resultant dissimilarity in the O_3 levels. As seen above, there were no exceedances of the USEPA standard during the monitoring period of 1985 and 1986. Cape Town can therefore be described as a city which is not consistently experiencing the occurrence of photochemical smog. It therefore cannot be compared to cities like London (Ball and Bernard, 1978), Melbourne (Evans *et al*, 1981), Tel-Aviv (Ganor *et al*, 1978), Sydney (Mitchell *et al*, 1983) or Los Angeles (Trijonis *et al*, 1978).

ASSESSMENT

A broad assessment of the current and possible future of Cape Town with regard to photochemical smog was made, on consideration of Loewenheim (1988a) and Loewenheim (1988b) and the findings in this study. In the city centre a unique position existed whereby the NMHC were generally much lower than other metropolitan cities that experience photochemical smog, whilst the NO_X concentrations were significantly higher. The suburbs however did not have such high NO_X levels but experienced very similar NMHC concentrations to the city centre. The Northern Suburbs with the likely addition of NMHC from the petrochemical plant and petrol

storage tanks in the vicinity, and with lower NO concentrations which inhibit O_3 formation, possess at present a greater chance of exposure to photochemical pollution than the city centre.

By the turn of the century, expansion of the Northern Suburbs is likely to include many new residential areas. Furthermore, it is anticipated that both vehicle numbers and industrial emissions would also increase over this area. Thus, with the concomitant increases in NO_x and NMHC levels, the Northern Suburbs could possibly be a potential problem area with regard to photochemical smog formation. The proposed changeover to an ethanol blend of fuel may also have a significant influence on pollution patterns and photochemical smog occurrence in the area. Vehicle emissions would contain increased aldehydes that would raise the reactivity of the NMHC content of the air and hence the oxidant levels.

SUMMARY AND CONCLUSIONS

This paper has aimed to supplement the current state of knowledge pertaining to photochemical smog precursor and oxidant concentrations particularly as it applies to the Greater Cape Town area. A database comprising both a continuous monitoring network as well as a spatial sampling analysis was employed. An examination of the controlling factors, chemical relationships, and peak levels was undertaken, followed by an assessment of photochemical smog levels in Cape Town in comparison to other standards and cities. For the limited database under consideration, this study has shown that:

1) The diluting effect of wind speed showed the greatest influence on the precursor levels, particularly in the afternoon when wind speed was at its maximum. The influence of traffic emissions was most prominent during the morning

rush hour when wind speed was at a minimum. Although wind speed had little influence on the O_3 levels, traffic emissions displayed a negative relationship to the O_3 levels, while temperature showed a positive relationship;

2) The variation of the precursor and oxidant levels followed the recognised diurnal patterns. The city site experienced far greater NO_x levels than the suburban site, but similar NMHC levels. In the early morning (05h00) at the city site, the influence of extremely low NO levels diminished the amount of O_3 scavenging, and resulted in inflated O_3 levels almost equal to the midday peak. At the suburban site the possible influence of industry was evident in the precursor concentrations, which tended to be maintained at constant levels throughout the day and night;

3) The $NO:NO_2$ proportion in the city was high, with a ratio of about 2:1, while at the suburban site the NO_2 values were generally equal in value to the NO levels. The $NMHC:NO_x$ ratio was approximately 1 at the city site and 10 at the suburban site. This difference was largely due to the disparity in the NO_x levels and not the NMHC concentrations, which were similar for both sites;

4) A strong inverse relationship of the NO_x and NO concentrations to O_3 was found. High O_3 levels were found only below an NO value of 0.02ppm. Owing to the almost direct relationship of NMHC to NO_x at the city site, the NMHC level showed little effect in aiding the photochemical reaction. At the suburban site, however, an area of increased O_3 formation for NMHC values between 0.09ppm and 0.14ppm was evident;

5) The $NMHC/NO_x$ to O_3 relationship at the city site was restricted to the lower values by the presence of very high NO_x levels. At the suburban site the $NMHC/NO_x$ ratio was higher and resulted in increased O_3 levels;

6) The EKMA/Dodge isopleths for Los Angeles compared reasonably to the data from the city site, and tended to overpredict the O_3 concentrations at the suburban site by about 50%. It was estimated that possible future reductions in NO_x and increases in the NMHC levels would result in a substantial increase in the O_3 levels in the city. Should control mechanisms be required at any stage, the limited data suggest that the NMHC reduction method might presently be most appropriate;

7) Precursor concentrations at the city site had the greatest means and standard deviations (and hence likelihood of highest levels) during the morning rush hour, with minimal variation in the early morning hours. NMHC levels showed a broader peak than NO_x, which extended to about midday. The episode potential for NMHC levels at the suburban site was not easily detected owing to the relatively consistent levels during the day, with only minor increases during the rush hours. NO_x and NO variability was elevated during the early morning hours, showing the possible influence of industry;

8) The standard deviations of O_3 at the suburban site displayed a maximum just after midday. At the city site, however, the greatest episode potential occurred outside of daylight hours in the early morning, during the period of reduced NO scavenging. Peak values were thus likely to occur both during the early morning hours and during the afternoon. Precursor and oxidant variations over a period of a month showed relationships similar to the above at each site;

9) The areas most likely to experience high O_3 levels were the Northern Suburbs and the areas towards the edge of the city, where O_3 inhibition was limited by the lack of high NO_x levels. The early spring was anticipated to produce increased O_3 episodes and not the windier summer months;

10) In terms of USEPA standards and measurements in other cities, it was deduced that at present, Greater Cape Town does not have a serious photochemical smog problem of the same scale as, for example, Los Angeles or Sydney.

Three main factors have been found to contribute to the complexity of the photochemical smog situation in Greater Cape Town: the presence of high NO levels causing scavenging of O_3; low NMHC levels slowing the process of O_3 formation; and high wind speeds in the summer months. An increase in vehicle numbers and industrial expansion will result in changes in the levels of photochemical smog in Greater Cape Town, and this should be considered together with any future plans regarding fuel changes and new residential and commercial developments, particularly in the Northern Suburbs. Continued research and monitoring of precursor and oxidant levels is recommended with emphasis on PAN, especially in the potentially sensitive areas likely to undergo further industrial, commercial and residential expansion.

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CHAPTER 5

THESIS SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

This thesis has considered the temporal and spatial aspects of photochemical smog in Greater Cape Town. Automatic monitor data collected during the period 1984 to 1986 was used for the analysis of trends and patterns evident in the precursor and oxidant levels, and their relationship to meteorology. Data obtained by a survey during April and May 1987 supplemented the existing database, allowing an examination of the spatial distribution of precursor and oxidant levels and their variation over time. Selected data were used for the investigation of factors influencing pollutant levels and chemical relationships evident in the data. Comparison of precursor and oxidant concentrations in Greater Cape Town to air quality standards, and levels experienced in other cities was also made. The results of the above three general aspects of this study have been written up as individual chapters (papers), which together form the body of this thesis. The overall conclusions reached by this study can be summarised as follows:

1) Precursor levels were directly influenced by the seasonal cycle of the weather, showing higher levels during the calmer winter months. A definite 'weekend effect' was evident in the precursor levels, which decreased simultaneously with reduced vehicle emissions. On a diurnal basis, NO_x and NMHC levels were inversely related to wind speed and directly dependent on traffic flow, showing the highest levels and episode potential during the calmer morning rush hours;

2) O_3 behaviour was complex and lacked a simple and defined seasonal trend. O_3 levels showed no 'weekend effect'. A strong inverse relationship of O_3 to the NO levels (and thus to traffic) was evident, showing O_3 concentrations to be highly sensitivity to NO scavenging. O_3 levels peaked just after midday, and showed a positive relationship to increased ultraviolet radiation. The greatest potential for

O_3 episodes occurred at this time, although at the city site, high O_3 levels and episode potential were also experienced in the early morning hours when NO levels were significantly reduced;

3) Increased precursor levels were generally experienced under very stable atmospheric conditions, while high O_3 levels were experienced on fair weather days with the South Atlantic Anticyclone to the west of Cape Town or with a Coastal Low over the Peninsula. Peak O_3 levels did not occur during the windier summer months, but occurred in early spring, thus coinciding with the Southern Hemisphere tropospheric O_3 maximum;

4) Spatially, the higher precursor concentrations were experienced in the city centre and in the commercial and industrial areas of the Northern and Southern Suburbs, especially during the morning rush hour when wind speeds were low. NO_x levels exhibited a high spatial dependency, with increased levels following the pattern of the major arterial roads. A combination of atmospheric stability and topographic influence resulted in the high NO_x levels at the Wynberg site. The NMHC patterns were less defined, although higher levels were experienced in the city centre during morning rush hour and during the early afternoon in the Northern Suburbs, possibly as a result of evaporative and industrial process emissions. O_3 levels were spatially relatively uniform, although localised O_3 depletion occurred close to main traffic routes (where high NO_x levels were experienced);

5) NO_x levels in the city centre and in the suburbs were significantly different, while the NMHC levels were similar. NO_x levels were high in the city centre (about 0.18ppm from 06h00 to 09h00), whilst NMHC levels were relatively low in the city and suburbs (roughly 0.16ppm from 06h00 to 09h00);

6) During 1985 and 1986, O_3 levels did not exceed the USEPA 1-h standard of 0.12ppm, but equalled or exceeded the WHO goal of 0.06ppm on 26 occasions, more frequently at the suburban sites;

7) A high $NO:NO_2$ ratio was present in the city centre compared to the suburbs, indicating extensive NO scavenging in the city. The $NMHC:NO_x$ ratio at the city site was a tenth of the ratio at the suburban site, the latter revealing optimum O_3 formation at a ratio of 5:1 to 10:1;

8) The EKMA/Dodge model proved adequate for O_3 prediction at the city site, but overpredicted at the suburban site. It was thus estimated that significantly increased O_3 concentrations might occur with an increase in the NMHC levels.

At present, the occurrence of severe photochemical pollution is infrequent, although a limited number of cases with relatively high O_3 concentrations are possible in certain areas and under certain conditions. By way of a summary diagram, Figure 1 illustrates the areas and times of precursor and oxidant pollution potential. The main reasons for the current status of photochemical smog in Cape Town can be summarised as follows:

1. the general absence of high oxidant levels;
2. the comparatively small numbers of emission sources;
3. the low $NMHC:NO_x$ ratio which slows oxidant formation;
4. the diluting effect of strong winds during the late spring and hot summer months;
5. the calm conditions during autumn and winter which produce high NO_x levels that inhibit O_3 formation.

It may therefore be concluded from the limited data available that levels of photochemical smog in Greater Cape Town are not high enough to constitute a significant air pollution problem.

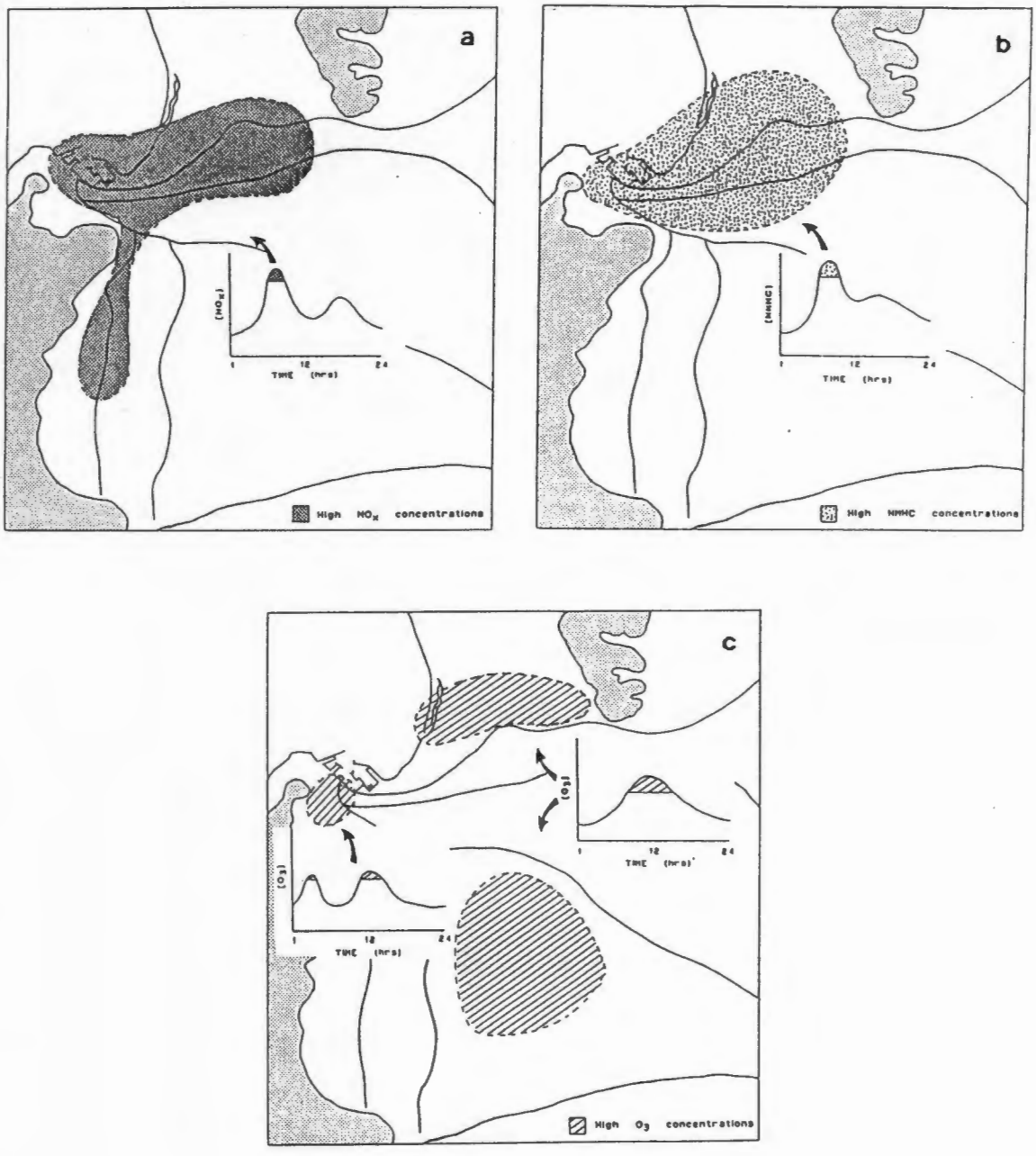

Figure 1: A summary diagram showing (a) NO_X, (b) NMHC, and (c) O_3 levels and the times and areas of high concentration in Greater Cape Town.

Perhaps a more immediate point of concern are the relatively high NO_X levels that are frequently experienced in the city centre. A proposed fuel changeover to an ethanol blend could increase the reactivity of the NMHC levels and thus increase the potential for high oxidant formation. It is suggested that smog chamber experiments be conducted in order to characterise local hydrocarbon sources and estimate the effect of precursor variations. It is further recommended that PAN concentrations be measured to verify the oxidant levels recorded. An application of an empirical model would also aid in the prediction of future oxidant concentrations. An increased data set (especially summertime data) comprising concurrent measurements of NO_X, NMHC and O_3 at appropriately located sites is recommended, in order to clarify and further examine the conclusions of this study.

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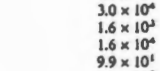
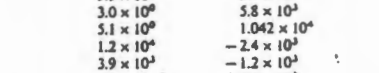
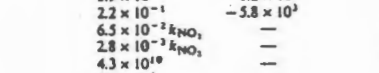
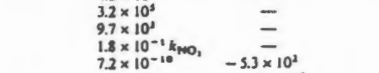
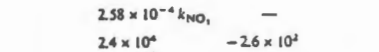
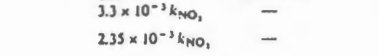
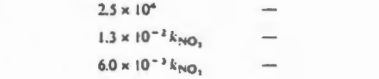
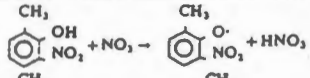
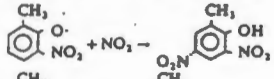
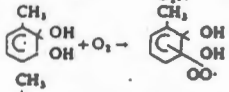
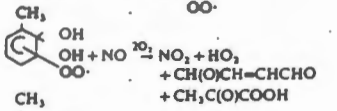
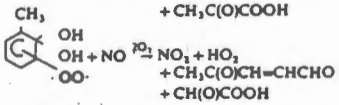
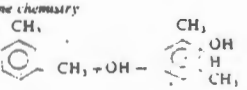
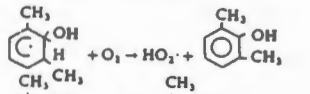
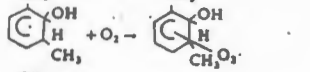
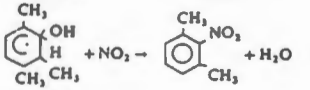
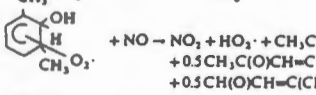
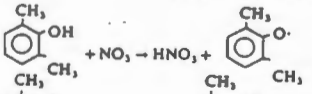
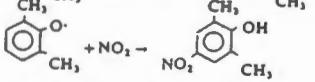
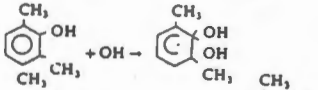
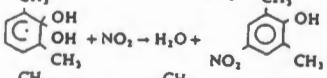
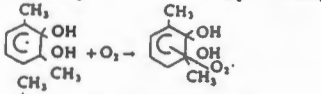
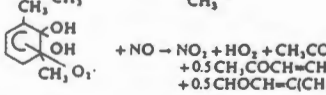
APPENDIX 1

1.1: Chemical reaction mechanisms for photochemical smog

Reaction†	Rate constant‡	Activation energy (K)	Note
Inorganic reactions			
(1) $NO_2 + h\nu \rightarrow NO + O(^3P)$	*	—	
(2) $O(^3P) + O_2 \rightarrow O_3$	2.6×10^4	-5.1×10^2	
(3) $O_3 + NO \rightarrow NO_2 + O_2$	2.7×10^1	1.5×10^2	
(4) $O(^3P) + NO_2 \rightarrow NO + O_2$	1.4×10^4	—	
(5) $O_3 + NO_2 \rightarrow NO_3 + O_2$	4.7×10^{-2}	2.45×10^3	
(6) $NO_3 + NO \rightarrow 2NO_2$	3.0×10^4	—	
(7) $HO_2 + NO_2 \rightarrow HO_2NO_2$	1.6×10^3	—	
(8) $NO_2 + OH \rightarrow HNO_3$	1.6×10^4	—	
(9) $O_3 + OH \rightarrow HO_2 + O_2$	9.9×10^1	9.7×10^2	
(10) $O_3 + HO_2 \rightarrow OH + 2O_2$	3.0×10^0	5.8×10^3	
(11) $HO_2NO_2 \rightarrow HO_2 + NO_2$	5.1×10^0	1.042×10^4	
(12) $HO_2 + NO \rightarrow NO_2 + OH$	1.2×10^4	-2.4×10^2	
(13) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.9×10^3	-1.2×10^3	
(14) $HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + H_2O$	2.2×10^{-1}	-5.8×10^3	
(15) $O_3 + h\nu \rightarrow O(^3P) + O_2$	$6.5 \times 10^{-2} k_{NO_2}$	—	1
(16) $O_3 + h\nu \rightarrow O(^1D) + O_2$	$2.8 \times 10^{-3} k_{NO_2}$	—	1
(17) $O(^1D) \rightarrow O(^3P)$	4.3×10^{10}	—	
(18) $O(^1D) + H_2O \rightarrow 2OH$	3.2×10^4	—	
(19) $NO + OH \rightarrow HONO$	9.7×10^3	—	
(20) $HONO + h\nu \rightarrow NO + OH$	$1.8 \times 10^{-1} k_{NO_2}$	—	1
(21) $NO + NO + O_2 \rightarrow 2NO_2$	7.2×10^{-10}	-5.3×10^2	
(22) $NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$	5.9×10^{-1}	1.23×10^3	
(23) $NO_3 + NO_2 \rightarrow N_2O_5$	1.6×10^3	—	
(24) $N_2O_5 \rightarrow NO_2 + NO_3$	3.1×10^0	1.108×10^4	
(25) $N_2O_5 + H_2O \rightarrow 2HNO_3$	0.0	—	
(26) $H_2O_2 + OH \rightarrow HO_2 + H_2O$	2.5×10^3	—	
(27) $H_2O_2 + h\nu \rightarrow 2OH$	$8.4 \times 10^{-4} k_{NO_2}$	—	
(28) $CO + OH \xrightarrow{O_2} HO_2 + CO_2$	4.0×10^2	—	
(29) $NO_2 + h\nu \rightarrow 0.3NO + 0.7NO_2 + 0.7O(^3P)$	$1.55 \times 10^1 k_{NO_2}$	—	
Aldehyde reactions and PAN formation			
(30) $CH_3CHO + h\nu \xrightarrow{2O_2} CH_3O_2\cdot + HO_2 + CO$	$2.58 \times 10^{-4} k_{NO_2}$	—	1
(31) $CH_3CHO + OH \xrightarrow{O_2} CH_3C(O)O_2\cdot + H_2O$	2.4×10^4	-2.6×10^2	
(32) $CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot$	1.1×10^4	—	
(33) $CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$	2.1×10^0	1.35×10^3	
(34) $CH_3O\cdot + NO_2 \rightarrow CH_3ONO_2$	2.2×10^4	—	
(35) $CH_3O_2\cdot + HO_2 \rightarrow CH_3OOH + O_2$	9.2×10^3	-1.3×10^3	
(36) $CH_3C(O)O_2\cdot + NO \xrightarrow{2O_2} NO_2 + CH_3O_2\cdot + CO_2$	1.1×10^4	—	
(37) $CH_3C(O)O_2\cdot + NO_2 \rightarrow PAN$	6.9×10^3	—	
(38) $CH_3C(O)O_2\cdot + HO_2 \rightarrow CH_3C(O)O_2H + O_2$	4.4×10^3	—	
(39) $PAN \rightarrow CH_3C(O)O_2\cdot + NO_2$	2.2×10^{-2}	1.354×10^4	
(40) $HCHO + h\nu \rightarrow H_2 + CO$	$3.3 \times 10^{-3} k_{NO_2}$	—	1
(41) $HCHO + h\nu \xrightarrow{2O_2} 2HO_2 + CO$	$2.35 \times 10^{-3} k_{NO_2}$	—	1
(42) $HCHO + OH \xrightarrow{O_2} HO_2 + CO + H_2O$	1.6×10^4	—	
α-Dicarbonyl chemistry			
(43) $CH_3C(O)CHO + OH \xrightarrow{O_2} CH_3C(O)O_2\cdot + CO + H_2O$	2.5×10^4	—	
(44) $CH_3C(O)CHO + h\nu \xrightarrow{2O_2} CH_3C(O)O_2\cdot + HO_2 + CO$	$1.3 \times 10^{-2} k_{NO_2}$	—	
(45) $CH_3C(O)CHO + h\nu \xrightarrow{2O_2} CH_3O_2\cdot + HO_2 + 2CO$	$6.0 \times 10^{-3} k_{NO_2}$	—	
(46) $(CHO)_2 + OH \xrightarrow{O_2} HO_2 + 2CO + H_2O$	1.7×10^4	—	
(47) $(CHO)_2 + h\nu \rightarrow 0.13HCHO + 0.87H_2 + 1.87CO$	$8.0 \times 10^{-3} k_{NO_2}$	—	
Toluene abstraction pathway			
(48) $C_6H_5\text{-}CH_3 + OH \xrightarrow{O_2} C_6H_5\text{-}CH_2O_2\cdot + H_2O$	7.5×10^2	—	
(49) $C_6H_5\text{-}CH_2O_2\cdot + NO \rightarrow NO_2 + C_6H_5\text{-}CH_2O\cdot$	9.0×10^3	—	
(50) $C_6H_5\text{-}CH_2O_2\cdot + NO \rightarrow C_6H_5\text{-}CH_2ONO_2$	1.0×10^3	—	
(51) $C_6H_5\text{-}CH_2O\cdot + O_2 \rightarrow C_6H_5\text{-}CHO + HO_2$	1.0×10^1	6.9×10^2	
(52) $C_6H_5\text{-}CH_2O\cdot + NO_2 \rightarrow C_6H_5\text{-}CH_2ONO_2$	1.9×10^4	—	

Reaction†	Rate constant‡	Activation energy (K)	Note
(53) $C_6H_5\text{-}CHO + h\nu \rightarrow$ stable products	1.6×10^{-3}	—	
(54) $C_6H_5\text{-}CHO + OH \xrightarrow{O_2} C_6H_5\text{-}C(O)O_2\cdot + H_2O$	1.9×10^4	—	
(55) $C_6H_5\text{-}C(O)O_2\cdot + NO \xrightarrow{O_2} NO_2 + C_6H_5\text{-}O_2\cdot + CO_2$	1.0×10^4	—	
(56) $C_6H_5\text{-}C(O)O_2\cdot + NO_2 \rightarrow C_6H_5\text{-}C(O)O_2NO_2$	6.9×10^3	—	
(57) $C_6H_5\text{-}C(O)O_2NO_2 \rightarrow C_6H_5\text{-}C(O)O_2\cdot + NO_2$	9.6×10^{-3}	1.304×10^4	
(58) $C_6H_5\text{-}O_2\cdot + NO \rightarrow NO_2 + C_6H_5\text{-}O\cdot$	9.0×10^3	—	
(59) $C_6H_5\text{-}O_2\cdot + NO_2 \rightarrow NO_3 + C_6H_5\text{-}O\cdot$	1.0×10^4	—	
(60) 	2.2×10^4	—	
(61) 	3.0×10^{-3}	—	
(62) 	2.2×10^4	—	
(63) 	7.4×10^3	—	
Toluene addition pathway			
(64) 	8.7×10^3	—	
(65) 	1.0×10^4	6.9×10^2	
(66) 	4.4×10^4	—	
(67) 	4.9×10^1	—	
(68) 	1.0×10^4	—	
(69) 	0.0	—	
(70)	4.9×10^3	9.0×10^2	
(71) 	1.5×10^4	—	
(72) 	2.2×10^4	—	
(73) 	5.6×10^4	—	
(74) 	4.4×10^4	—	

	Reaction†	Rate constant‡	Activation energy (K)	Note
(75)		1.5×10^{-4}	—	
(76)		2.2×10^{-4}	—	
(77)		4.9×10^{-1}	—	
(78)		1.0×10^{-4}	—	
(79)		0.0	—	
(80)	$CH(O)COOH + OH \xrightarrow{O_2} HO_2 + H_2O + CO + CO_2$	2.2×10^{-4}	—	
(81)	$CH_3C(O)COOH + h\nu \rightarrow CH_3CHO + CO_2$	$1.4 \times 10^{-3} k_{NO_2}$	—	
	Conjugated γ-dicarbonyl chemistry			
(82)	$HC(O)CH{=}CHCHO + OH \xrightarrow{O_2} HC(O)CH{=}CHC(O)O_2\cdot + H_2O$	4.4×10^{-4}	—	
(83)	$HC(O)CH{=}CHC(O)O_2\cdot + NO \xrightarrow{O_2} NO_2 + CO_2 + HC(O)CH{=}CHO_2\cdot$	1.0×10^{-4}	—	
(84)	$HC(O)CH{=}CHO_2\cdot + NO \xrightarrow{O_2} NO_2 + HC(O)CH(O_2\cdot)CHO$	1.0×10^{-4}	—	
(85)	$HC(O)CH(O_2\cdot)CHO + NO \rightarrow HC(O)CH(ONO_2)CHO$	4.0×10^{-2}	—	
(86)	$HC(O)CH{=}CHC(O)O_2\cdot + NO_2 \rightarrow HC(O)CH{=}CHCO_3NO_2$	6.9×10^{-3}	—	
(87)	$HC(O)CH{=}CHCO_3NO_2 \rightarrow HC(O)CH{=}CHC(O)O_2\cdot + NO_2$	2.2×10^{-4}	—	
(88)	$HC(O)CH(O_2\cdot)CHO + NO \xrightarrow{O_2} (CHO)_2 + HO_2 + NO_2 + CO$	1.0×10^{-4}	—	
(89)	$HC(O)CH{=}CHO_2\cdot + NO \rightarrow HC(O)CH{=}CHONO_2$	4.0×10^{-2}	—	
(90)	$HC(O)CH{=}CHO_2\cdot + NO_2 \xrightarrow{O_2} HC(O)CH(O_2\cdot)CHO + NO_2$	1.0×10^{-4}	—	
(91)	$CH_3C(O)CH{=}CHCHO + OH \xrightarrow{O_2} H_2O + CH_3C(O)CH{=}CHC(O)O_2\cdot$	2.2×10^{-4}	—	
(92)	$CH_3C(O)CH{=}CHCHO + OH \xrightarrow{O_2} CH_3C(O)CH(OH)C(O_2\cdot)HCHO$	7.4×10^{-3}	—	
(93)	$CH_3C(O)CH(OH)C(O_2\cdot)HCHO + NO \xrightarrow{O_2} NO_2 + HO_2 + CH_3C(O)CHO + (CHO)_2$	1.0×10^{-4}	—	
(94)	$CH_3C(O)CH{=}CHC(O)O_2\cdot + NO \xrightarrow{O_2} NO_2 + CO_2 + CH_3C(O)CH{=}CHO_2\cdot$	1.0×10^{-4}	—	
(95)	$CH_3C(O)CH{=}CHO_2\cdot + NO \xrightarrow{O_2} NO_2 + CH_3C(O)CH(O_2\cdot)CHO$	1.0×10^{-4}	—	
(96)	$CH_3C(O)CH(O_2\cdot)CHO + NO \rightarrow CH_3C(O)CH(ONO_2)CHO$	8.0×10^{-4}	—	
(97)	$CH_3C(O)CH{=}CHC(O)O_2\cdot + NO \rightarrow CH_3C(O)CH{=}CHCO_3NO_2$	6.9×10^{-3}	—	
(98)	$CH_3C(O)CH{=}CHCO_3NO_2 \rightarrow CH_3C(O)CH{=}CHC(O)O_2\cdot + NO_2$	2.2×10^{-4}	—	
(99)	$CH_3C(O)CH(O_2\cdot)CHO + NO \xrightarrow{O_2} NO_2 + CH_3C(O)O_2\cdot + (CHO)_2$	5.0×10^{-3}	—	
(100)	$CH_3C(O)CH(O_2\cdot)CHO + NO \xrightarrow{O_2} NO_2 + HO_2 + CH_3C(O)CHO + CO$	5.0×10^{-3}	—	
(101)	$CH_3C(O)CH{=}CHO_2\cdot + NO \rightarrow CH_3C(O)CH{=}CHONO_2$	8.0×10^{-4}	—	
(102)	$CH_3C(O)CH{=}CHO_2\cdot + NO_2 \xrightarrow{O_2} NO_3 + CH_3C(O)CH(O_2\cdot)CHO$	1.0×10^{-4}	—	
	m-Xylene chemistry			
(103)		3.4×10^{-4}	—	

	Reaction†	Rate constant‡	Activation energy (K)	Note
(104)		1.0×10^{-2}	6.9×10^{2}	
(105)		4.7×10^{-1}	—	
(106)		4.4×10^{-4}	—	
(107)		1.0×10^{-4}	—	3
(108)		2.2×10^{-4}	—	
(109)		2.2×10^{-4}	—	
(110)		1.1×10^{-3}	—	
(111)		4.4×10^{-4}	—	
(112)		4.7×10^{-1}	—	
(113)		1.0×10^{-4}	—	3
(114)	$CHOCH{=}C(CH_3)CHO + OH \xrightarrow{O_2} HCOC(OH)HC(CH_3)CHO$ (with $O_2\cdot$)	7.4×10^{-3}	—	
(115)	$HCOC(OH)HC(CH_3)CHO + NO \xrightarrow{O_2} 0.88\,NO_2 + 0.88\,(CHO)_2 + 0.88\,HO_2\cdot$	1.0×10^{-4}	—	
(116)	$CHOCHO{=}C(CH_3)CHO + OH \xrightarrow{O_2} HCOCH{=}C(CH_3)CO_3\cdot + H_2O$	4.4×10^{-4}		
(117)	$HCOCH{=}C(CH_3)CO_3\cdot + NO \xrightarrow{O_2} NO_2 + HCOCH{=}C(CH_3)CO_2\cdot + CO_2$	1.0×10^{-4}		
(118)	$HCOCH{=}C(CH_3)CO_3\cdot + NO_2 \rightarrow HCOCH{=}C(CH_3)CO_2NO_2$	6.9×10^{-3}	—	
(119)	$HCOCH{=}C(CH_3)CO_2NO_2 \rightarrow NO_2 + HCOCH{=}C(CH_3)CO_3\cdot$	2.2×10^{-4}	1.354×10^{4}	
(120)	$HCOCH{=}C(CH_3)CO_2\cdot + NO \xrightarrow{O_2} NO_2 + CH_3(O)CH(O_2\cdot)CHO$	1.0×10^{-4}	—	

Reaction†	Rate constant‡	Activation energy (K)	Note
(121) $HCOCH{=}C(CH_3)CO_3\cdot + NO \rightarrow HCOCH{=}C(CH_3)CO_3NO_2$	8.0×10^3	—	
(122) $HCOCH{=}C(CH_3)CO_3\cdot + NO_2 \rightarrow NO_3 + CH_3C(O_3\cdot)(CHO)_2$	1×10^4	—	
(123) $CH_3C(O_3\cdot)(CHO)_2 + NO \rightarrow CH_3C(ONO_2)(CHO)_2$	8.0×10^2	—	
(124) $CH_3C(O_3\cdot)(CHO)_2 + NO \xrightarrow{O_2}$ 0.75 $HO_2\cdot$ + 0.75 CO + 0.75 CH_3COCHO + 0.25 $(CHO)_2$ + 0.25 $CH_3C(O)O_2\cdot$ + NO_2	1×10^4	—	
Ethene chemistry			
(125) $CH_2{=}CH_2 + OH \xrightarrow{O_2} HOCH_2CH_2O_2\cdot$	1.2×10^4	-3.82×10^2	
(126) $HOCH_2CH_2O_2\cdot + NO \rightarrow NO_2 + HOCH_2CH_2O\cdot$	1×10^4		
(127) $HOCH_2CH_2O\cdot \rightarrow HCHO + \cdot CH_2OH$	5.6×10^5		
(128) $HOCH_2CH_2O\cdot + O_2 \rightarrow HOCH_2CHO + HO_2\cdot$	1.0×10^1	6.9×10^2	5
(129) $\cdot CH_2OH + O_2 \rightarrow HCHO + HO_2\cdot$	3×10^3		
(130) $CH_2{=}CH_2 + O_3 \xrightarrow{O_2}$ HCHO + 0.4 CH_2OO + 0.18 CO_2 + 0.42 CO + 0.12 H_2 + 0.42 H_2O + 0.12 $HO_2\cdot$	2.5×10^{-3}	2.56×10^3	
Propene chemistry			
(131) $CH_3CHCH_2 + OH \xrightarrow{O_2}$ 0.65 $CH_3CH(O_2\cdot)CH_2OH$ + 0.35 $CH_3CH(OH)CH_2O_2\cdot$	3.7×10^4	-5.37×10^2	
(132) $CH_3CH(O_2\cdot)CH_2OH + NO \rightarrow NO_2 + CH_3CH(O\cdot)CH_2OH$	1×10^4		
(133) $CH_3CH(O\cdot)CH_2OH \rightarrow CH_3CHO + \cdot CH_2OH$	1×10^5	—	
(134) $CH_3CH(OH)CH_2O\cdot \rightarrow HCHO + CH_3CHOH$	1×10^2	—	
(135) $CH_3CH(O_2\cdot)CH_2OH + NO \rightarrow CH_3CH(ONO_2)CH_2OH$	1×10^4	—	
(136) $CH_3CH(OH)CH_2O_2\cdot + NO \rightarrow NO_2 + CH_3CH(OH)CH_2O\cdot$	400	—	
(137) $CH_3CH(OH)CH_2O_2\cdot + NO \rightarrow CH_3CH(OH)CH_2ONO_2$	3×10^3	—	
(138) $CH_3CHOH + O_2 \rightarrow HO_2\cdot + CH_3CHO$	1.6×10^{-2}	1.897×10^3	
(139) $CH_3CHCH_2 + O_3 \rightarrow$ 0.5 CH_3CHO + 0.2 CH_3COO + 0.06 CH_4 + 0.27 CO_2 + 0.33 CO + 0.20 $HO_2\cdot$ + 0.1 OH + 0.22 $CH_3O_2\cdot$ + 0.03 $CH_3O\cdot$ + 0.2 CH_2OO + 0.06 H_2 + 0.21 H_2O			
trans-2-butene chemistry			
(140) $CH_3CH{=}CHCH_3 + OH \xrightarrow{O_2} CH_3CH(OH)CH(OO\cdot)CH_3$	1.0×10^3	-5.42×10^2	
(141) $CH_3CH(OH)CH(OO\cdot)CH_3 + NO \rightarrow NO_2 + CH_3CH(OH)CH(O\cdot)CH_3$	1.0×10^3	—	
(142) $CH_3CH(OH)CH(OO\cdot)CH_3 + NO \rightarrow CH_3CH(OH)CH(ONO_2)CH_3$	8.0×10^2	—	
(143) $CH_3CH(OH)CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CHOH$	1.0×10^4	—	
(144) $CH_3CH{=}CHCH_3 + O_3 \rightarrow CH_3CHO$ + 0.4 CH_3COO + 0.12 CH_4 + 0.36 CO_2 + 0.24 CO + 0.29 $HO_2\cdot$ + 0.19 OH + 0.05 $CH_3O\cdot$ + 0.43 $CH_3O_2\cdot$	2.7×10^{-4}	1.051×10^3	

Reaction†	Rate constant‡	Activation energy (K)	Note
(145) $CH_2OO + NO \rightarrow NO_2 + HCHO$	1.0×10^4	—	
(146) $CH_2OO + NO_2 \rightarrow NO_3 + HCHO$	1.0×10^3	—	
(147) $CH_2OO + H_2O \rightarrow HCOOH + H_2O$	6.0×10^{-3}	—	
(148) $CH_3CHOO + NO \rightarrow NO_2 + CH_3CHO$	1.0×10^4	—	
(149) $CH_3CHOO + NO_2 \rightarrow NO_3 + CH_3CHO$	1.0×10^3	—	
(150) $CH_3CHOO + H_2O \rightarrow CH_3COOH + H_2O$	6.0×10^{-3}	—	
Propane chemistry			
(151) $CH_3CH_2CH_3 + OH \rightarrow H_2O +$ 0.85 $CH_3CH(OO\cdot)CH_3$ + 0.15 $CH_3CH_2CH_2O_2\cdot$	2.3×10^3	6.8×10^2	
(152) $CH_3CH(OO\cdot)CH_3 + NO \rightarrow NO_2 + CH_3CH(O\cdot)CH_3$	1.1×10^4	—	
(153) $CH_3CH_2CH_2O_2\cdot + NO \rightarrow NO_2 + CH_2CH_2CHO\cdot$	1.1×10^4	—	
(154) $CH_3CH(O\cdot)CH_3 + O_2 \rightarrow HO_2\cdot + CH_3C(O)CH_3$	4.4×10^1	—	
(155) $CH_3CH_2CH_2O\cdot + O_2 \rightarrow HO_2\cdot + CH_3CH_2CHO$	1.0×10^2	6.9×10^2	
n-Butane chemistry			
(156) $CH_3CH_2CH_2CH_3 + O(^3P) \xrightarrow{O_2}$ OH + 0.88 $CH_3CH_2CH(OO\cdot)CH_3$ + 0.12 $CH_3CH_2CH_2CH_2O_2\cdot$	3.3×10^1	2.099×10^3	
(157) $CH_3CH_2CH_2CH_3 + OH \rightarrow H_2O +$ 0.86 $CH_3CH_2CH(OO\cdot)CH_3$ + 0.14 $CH_3CH_2CH_2CH_2O_2\cdot$	3.8×10^2	5.59×10^2	
(158) $CH_3CH_2CH_2CH_2O_2\cdot + NO \rightarrow CH_3CH_2CH_2CH_2O\cdot + NO_2$	1.0×10^4	—	
(159) $CH_3CH_2CH_2CH_2O_2\cdot + NO \rightarrow CH_3CH_2CH_2CH_2ONO_2$	8.0×10^2	—	
(160) $CH_3CH_2CH_2CH_2O\cdot + O_2 \rightarrow HO_2\cdot + CH_3CH_2CH_2CHO$	1.0×10^1	6.90×10^2	
(161) $CH_3CH_2CH_2CH_2O\cdot \xrightarrow{O_2} \cdot OOCH_2CH_2CH_2CH_2OH$	7.2×10^6	4.20×10^3	
(162) $\cdot OOCH_2CH_2CH_2CH_2OH + NO \rightarrow NO_2 + \cdot OCH_2CH_2CH_2CH_2OH$	1.0×10^4	—	
(163) $\cdot OOCH_2CH_2CH_2CH_2OH + NO \rightarrow O_2NOCH_2CH_2CH_2CH_2OH$	8.0×10^2	—	
(164) $\cdot OCH_2CH_2CH_2CH_2OH \rightarrow HOCH_2CH_2CH_2CHOH$	3.6×10^7	—	6
(165) $HOCH_2CH_2CH_2CHOH + O_2 \rightarrow HO_2\cdot + OHCH_2CH_2CH_2CHO$	1.0×10^1	6.90×10^2	
(166) $CH_3CH_2CH(OO\cdot)CH_3 + NO \rightarrow NO_2 + CH_3CH_2CH(O\cdot)CH_3$	1.0×10^4	—	
(167) $CH_3CH_2CH(ONO_2)CH_3 + NO \rightarrow CH_3CH_2CHCH_3$	8.0×10^2	—	
(168) $CH_3CH_2CH(O\cdot)CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_3 + HO_2\cdot$	4.4×10^1	—	
(169) $CH_3CH_2CHCH_3 \xrightarrow{O_2} C_2H_5O_2\cdot + CH_3CHO$	4.0×10^6	7.0×10^3	
(170) $C_2H_5O_2\cdot + NO \rightarrow C_2H_5O\cdot + NO_2$	$1.1^* \times 10^6$	—	
(171) $C_2H_5O\cdot + NO_2 \rightarrow C_2H_5ONO_2$	2.2×10^4	—	
(172) $C_2H_5O\cdot + NO \rightarrow C_2H_5ONO$	4.4×10^4	—	
(173) $C_2H_5O\cdot + O_2 \rightarrow CH_3CHO + HO_2\cdot$	1.0×10^1	6.90×10^2	
2,3-dimethyl butane chemistry			
(174) $(CH_3)_2CHCH(CH_3)_2 + O(^3P) \rightarrow (CH_3)_2CHC(O_2\cdot)(CH_3)_2 + OH$	3.1×10^2	1.25×10^3	
(175) $(CH_3)_2CHCH(CH_3)_2 + OH \rightarrow$ 0.14 $(CH_3)_2CHC(CH_3)CH_2O_2\cdot$ + 0.86 $(CH_3)_2CHC(O_2\cdot)(CH_3)_2$	9.3×10^3	—	
(176) $(CH_3)_2CHC(CH_3)CH_2O_2\cdot + NO \rightarrow$ 0.9 NO_2 + 0.9 $(CH_3)_2CHC(CH_3)CH_2O\cdot$ + 0.1 $(CH_3)_2CHC(CH_3)CH_2ONO_2$	1.0×10^4	—	

Reaction†	Rate constant‡	Activation energy (K)	Note
(177) $(CH_3)_2CHCH(CH_3)CH_2O\cdot + O_2 \rightarrow HO_2\cdot + (CH_3)_2CHCH(CH_3)CHO$	1.0×10^1	6.90×10^2	
(178) $(CH_3)_2CHCH(CH_3)CH_2O\cdot \xrightarrow{O_2} \cdot OOCH_2CHCH(CH_3)CH_2OH$	1.4×10^7	4.20×10^3	
(179) $\cdot OOCH_2CHCH(CH_3)CH_2OH + NO \rightarrow 0.9\,NO_2 + 0.9\cdot OCH_2CHCH(CH_3)CH_2OH + 0.1\,O_2NOCH_2CHCH(CH_3)CH_2OH$	1.0×10^4		
(180) $\cdot OCH_2CHCH(CH_3)CH_2OH \xrightarrow{O_2} 0.8\,HOCH_2CHCH(CH_3)CHOH + 0.2\,HOCH_2CHCH(CH_3)CH_2OH$	1.4×10^7	4.20×10^3	
(181) $HOCH_2CHCH(CH_3)CHOH + O_2 \rightarrow HO_2\cdot + HOCH_2CHCH(CH_3)CHO$	1.0×10^1	6.90×10^2	
(182) $HOCH_2CHCH(CH_3)CH_2OH + NO \rightarrow 0.9\,NO_2 + 0.9\,HOCH_2CHCH(CH_3)CH_2OH + 0.1\,HOCH_2CHCH(CH_3)CH_2OH$	1.0×10^4	—	
(183) $HOCH_2CHCH(CH_3)CH_2OH \xrightarrow{O_2} 0.8\,HOCH_2CHCH(CH_3)CH_2OH + 0.2\,HOCH_2CHCH(CH_3)CH_2OH$	1.4×10^7	4.20×10^3	
(184) $HOCH_2CHCH(CH_3)CH_2OH + O_2 \rightarrow HO_2\cdot + OHCCHCH(CH_3)CH_2OH$	1.0×10^1	6.90×10^2	
(185) $HOCH_2CHCH(CH_3)CH_2OH + NO \xrightarrow{O_2} 0.9\,NO_2 + 0.9\,HO_2\cdot + 0.9\,(HOCH_2)_2CHCHCHO + 0.1\,HOCH_2CHCH(CH_3)CH_2OH$	1.0×10^4	—	
(186) $(CH_3)_2CHC(O_2\cdot)(CH_3)_2 + NO \rightarrow 0.9\,NO_2 + 0.9\,(CH_3)_2CHC(O\cdot)(CH_3)_2 + 0.1\,(CH_3)_2CHC(ONO_2)(CH_3)_2$	1.0×10^4	—	
(187) $(CH_3)_2CHC(O\cdot)(CH_3)_2 \xrightarrow{O_2} CH_3C(O)CH_3 + CH_3CH(O_2\cdot)CH_3$	3.0×10^7	6.44×10^3	
(188) $CH_3CH(O_2\cdot)CH_3 + NO \rightarrow CH_3CH(ONO_2)CH_3$	4.0×10^2	—	
(189) $CH_3CH(O_2\cdot)CH_3 + NO \rightarrow NO_2 + CH_3CH(O\cdot)CH_3$	1.0×10^4	—	
(190) $CH_3CH(O\cdot)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2\cdot$	4.4×10^1	—	
Propionaldehyde chemistry			
(191) $C_2H_5CHO + OH \xrightarrow{O_2} H_2O + C_2H_5CO_3\cdot$	2.8×10^4	-2.5×10^2	
(192) $C_2H_5CHO + NO_3 \xrightarrow{O_2} HNO_3 + C_2H_5CO_3\cdot$	2.2×10^9	—	7
(193) $C_2H_5CHO + h\nu \xrightarrow{O_2} C_2H_5O_2\cdot + HO_2\cdot + CO$	$8.4 \times 10^{-4}\,k_{NO_2}$	—	8
(194) $C_2H_5CO_3\cdot + NO_2 \rightarrow C_2H_5CO_3NO_2$	6.9×10^3	—	
(195) $C_2H_5CO_3\cdot + NO \xrightarrow{O_2} C_2H_5O_2\cdot + NO_2 + CO$	1.1×10^4	—	
(196) $C_2H_5CO_3NO_2 \rightarrow C_2H_5CO_3\cdot + NO_2$	2.2×10^{-2}	1.354×10^4	

Reaction†	Rate constant‡	Activation energy (K)	Note
Butyraldehyde chemistry			
(197) $C_3H_7CHO + OH \xrightarrow{O_2} H_2O + C_3H_7CO_3\cdot$	3.7×10^4	—	
(198) $C_3H_7CHO + NO_3 \xrightarrow{O_2} HNO_3 + C_3H_7CO_3\cdot$	2.2×10^9	—	7
(199) $C_3H_7CHO + h\nu \xrightarrow{O_2} C_3H_7O_3\cdot + HO_2\cdot + CO$	$8.4 \times 10^{-4}\,k_{NO_2}$	—	8
(200) $C_3H_7CO_3\cdot + NO_2 \rightarrow C_3H_7CO_3NO_2$	6.9×10^3	—	
(201) $C_3H_7CO_3\cdot + NO \xrightarrow{O_2} NO_2 + CO_2 + C_3H_7O_2\cdot$	1.1×10^4	—	
(202) $C_3H_7CO_3NO_2 \rightarrow C_3H_7CO_3\cdot + NO_2$	2.2×10^{-2}	1.354×10^4	
(203) $C_3H_7O_2\cdot + NO \rightarrow NO_2 + C_3H_7O\cdot$	1.1×10^4	—	
(204) $C_3H_7O\cdot + NO \rightarrow C_3H_7ONO$	4.4×10^4	—	
(205) $C_3H_7O\cdot + NO_2 \rightarrow C_3H_7ONO_2$	2.2×10^4	—	
(206) $C_3H_7O\cdot + O_2 \rightarrow HO_2\cdot + C_2H_5CHO$	1.0×10^1	6.90×10^2	
Acetone chemistry			
(207) $CH_3C(O)CH_3 + OH \xrightarrow{O_2} H_2O + CH_3C(O)CH_2O_2\cdot$	4.1×10^2	1.23×10^2	
(208) $CH_3C(O)CH_3 + h\nu \xrightarrow{O_2} CH_3CO_3\cdot + CH_3O_2\cdot$	$1.7 \times 10^{-4}\,k_{NO_2}$	—	9
(209) $CH_3C(O)CH_2O_2\cdot + NO \rightarrow CH_3C(O)CH_2O\cdot + NO_2$	1.0×10^4	—	
(210) $CH_3C(O)CH_2O_2\cdot + NO \rightarrow CH_3C(O)CH_2ONO_2$	4.0×10^3	—	
(211) $CH_3C(O)CH_2O\cdot + O_2 \rightarrow HO_2\cdot + CH_3C(O)CHO$	1.0×10^1	6.9×10^2	
MEK chemistry			
(212) $C_2H_5C(O)CH_3 + OH \xrightarrow{O_2} H_2O + CH_3CHC(O)CH_3$ (OO)	8.1×10^2	—	
(213) $C_2H_5C(O)CH_3 + h\nu \xrightarrow{O_2} CH_3CO_3\cdot + C_2H_5O_2\cdot$	$1.7 \times 10^{-3}\,k_{NO_2}$	—	
(214) $C_2H_5C(O)CH_3 + OH \rightarrow H_2O + C_2H_5C(O)CH_2\cdot$	4.9×10^2	—	10
(215) $CH_3CHC(O)CH_3$ (OO·) $+ NO \rightarrow NO_2 + CH_3CHC(O)CH_3$ (O·)	1.0×10^4	—	
(216) $CH_3CHC(O)CH_3$ (OO·) $+ NO \rightarrow CH_3CHC(O)CH_3$ (ONO_2)	8.0×10^2	—	
(217) $CH_3CHC(O)CH_3$ (O·) $\xrightarrow{O_2} CH_3CHO + CH_3CO_3\cdot$	7.8×10^6	6.44×10^3	

* The k_1 profile used in these simulations is (in 60-min intervals): 0.30, 0.39, 0.44, 0.46, 0.47, 0.46, 0.41.
† Only one isomer is shown, even when many are possible.
‡ 298 K, ppm min^{-1} units.

Notes:

1. These photolysis rates represent averages over zenith angles ranging from 30 to 60 degrees.
2. Abstraction pathway neglected.
3. 50/50 split of the two γ-dicarbonyls is assumed.
4. 12 per cent nitrate formation assumed.
5. Reactions of glycolaldehyde are ignored.
6. Hydroxy substituted aldehydes are assumed to react the same as un-substituted aldehydes.
7. Rate constants based on estimates by Atkinson and Lloyd (1984).
8. Photolysis rate assumed to be the same as acetaldehyde.
9. Photolysis rate from Atkinson *et al.* (1982).
10. Reactions of the $C_2H_5C(O)CH_2\cdot$ species are neglected.

Source: Leone and Seinfield (1985)

1.2: Standards used in the Air Pollution Survey of Greater Cape Town

Pollutant	Organisation	Level	Averaging time
O_3	USEPA Primary	0.08ppm	1 hour
Oxidant	California	0.10ppm	1 hour
NO_x	USEPA Primary	0.05ppm	1 year
NO_x	United States*	0.36ppm	1 hour
Total hydrocarbons	United States guideline	0.24ppm	06h00-09h00

* This value was obtained from the relationship between various standards, and based on a 1 hour averaging time (Dutkiewicz, 1979).

APPENDIX 2

2.1: Monitor calibration and editing

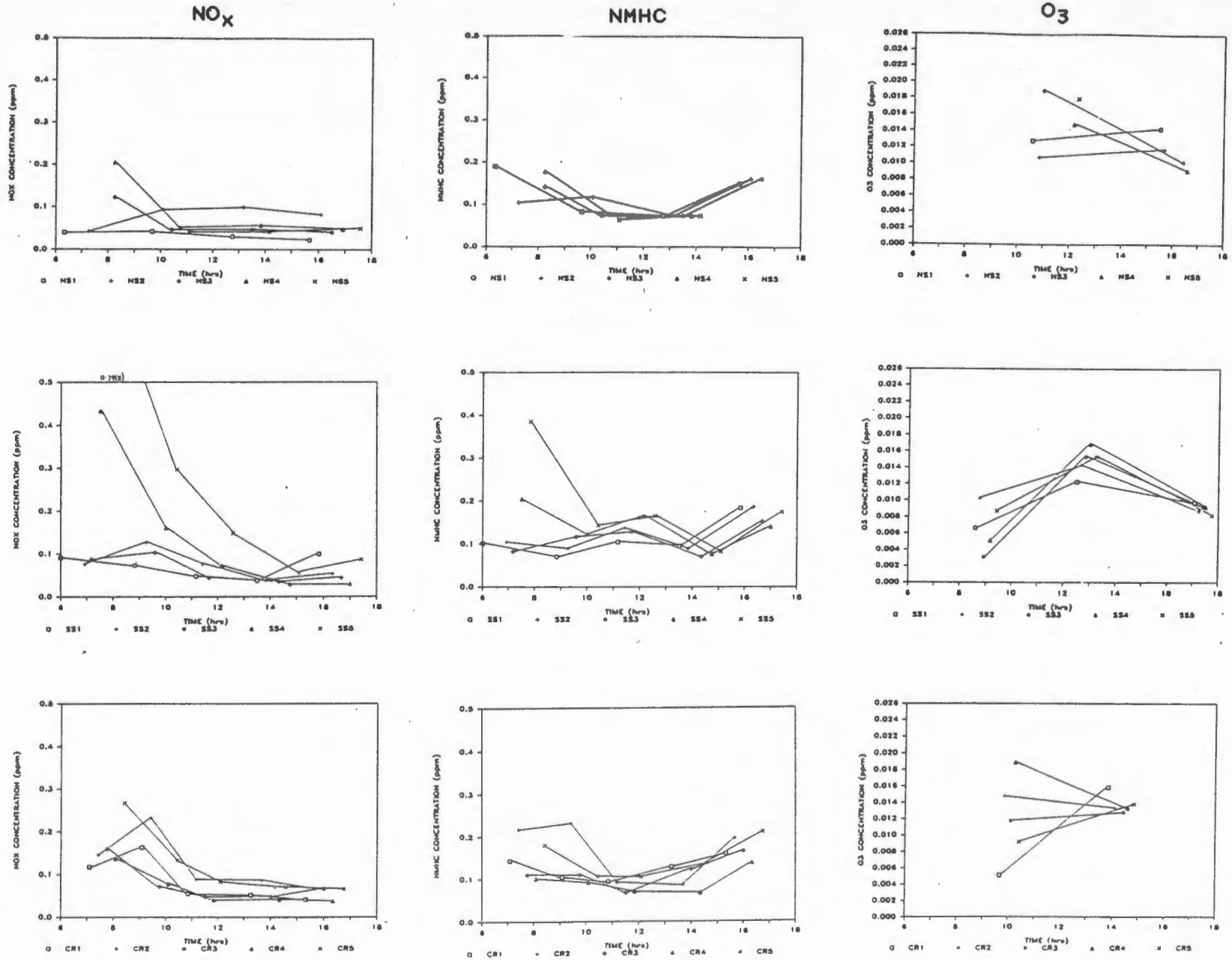
Weekly calibration of the NO and NO_2 monitors was performed using gas dilution (NO), a NO_2 permeation tube and O_3/NO gas phase titration. The O_3 analysers were calibrated to an external O_3 generator and cross-calibrated with another O_3 monitor with an internal calibrator. The NMHC analyser was calibrated using iso-butene, and results were expressed as methane.

Routine correction and editing of the data affected by calibration and instrument malfunctions took place. The preparation of annual reports covering compliance with standards, monitor operation and general comments are published annually by the Scientific Services Branch of the Cape Town City Council.

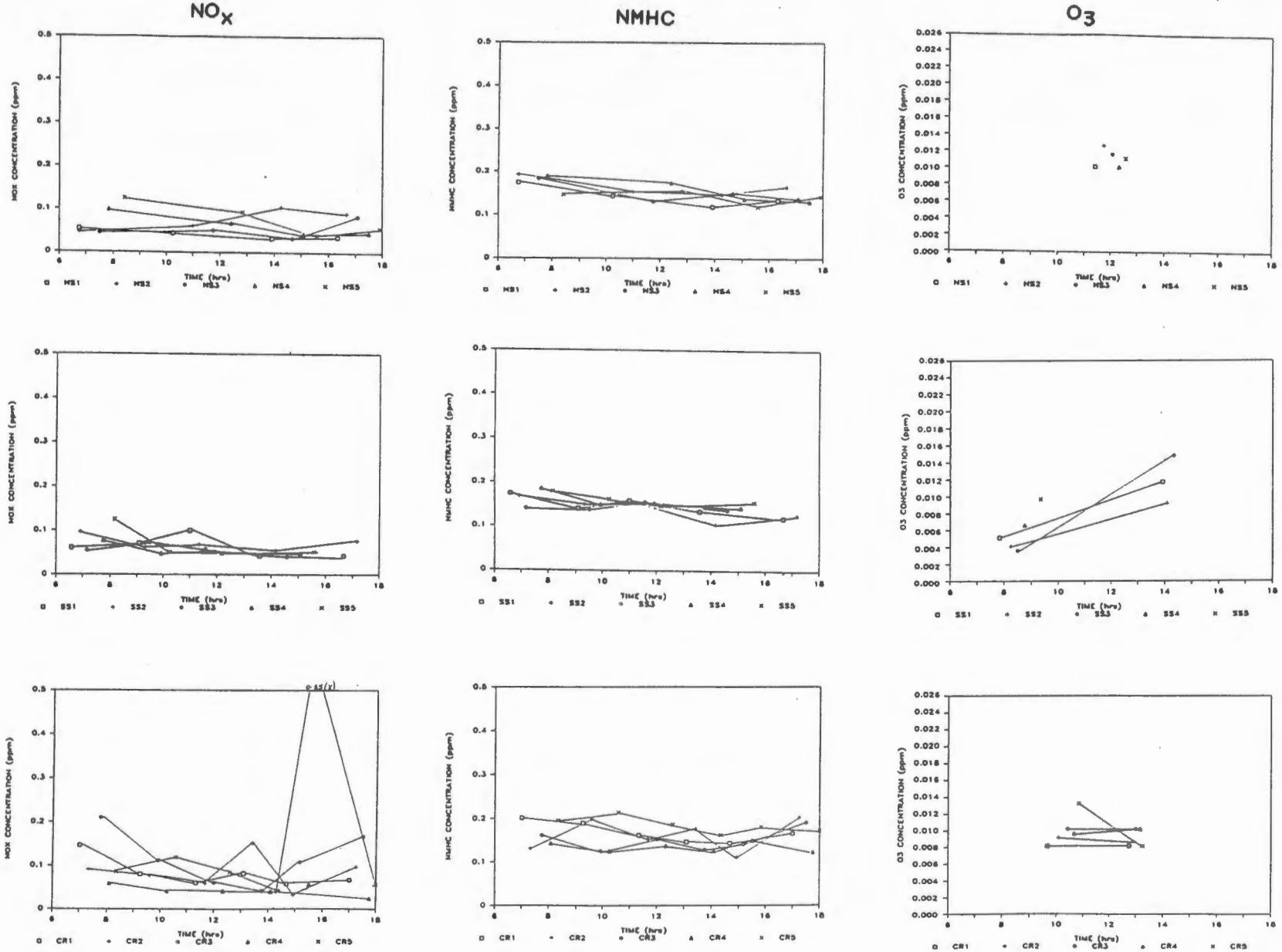
APPENDIX 3

3.1: Data collected during the survey from 21-04-87 to 10-05-87 are illustrated in graphical format on the following pages. Each graph shows either NO_x, NMHC or O_3 levels (for that day) for five sites grouped accordingly:

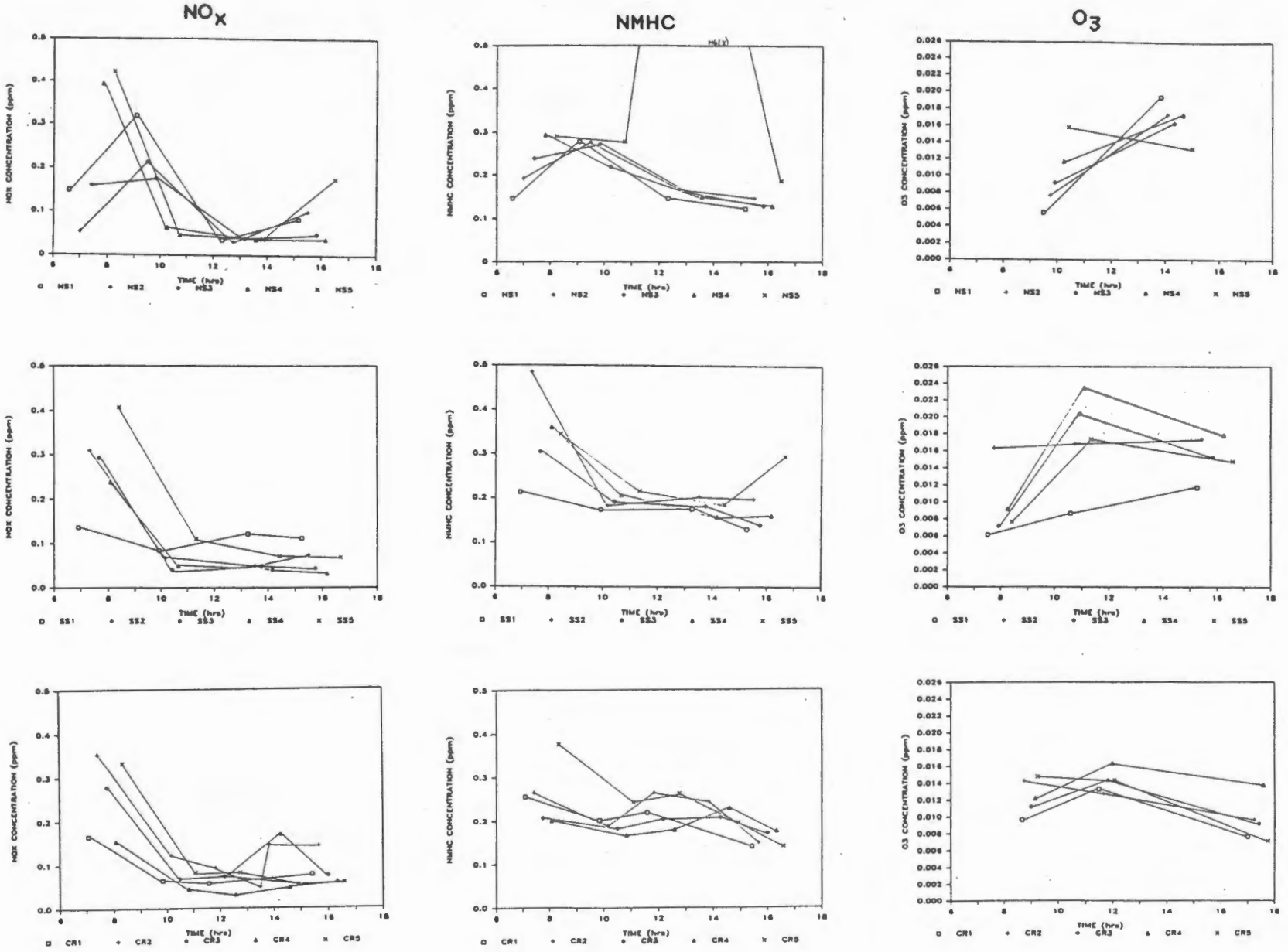
NS1	Milnerton
NS2	Panorama
NS3	Bellville
NS4	Belhar
NS5	Epping
SS1	Pinelands
SS2	Rondebosch
SS3	Ottery
SS4	Military Road
SS5	Wynberg
CR1	Woodstock
CR2	Paarden Eiland
CR3	Greenpoint
CR4	Oranjezicht
CR5	City Centre


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

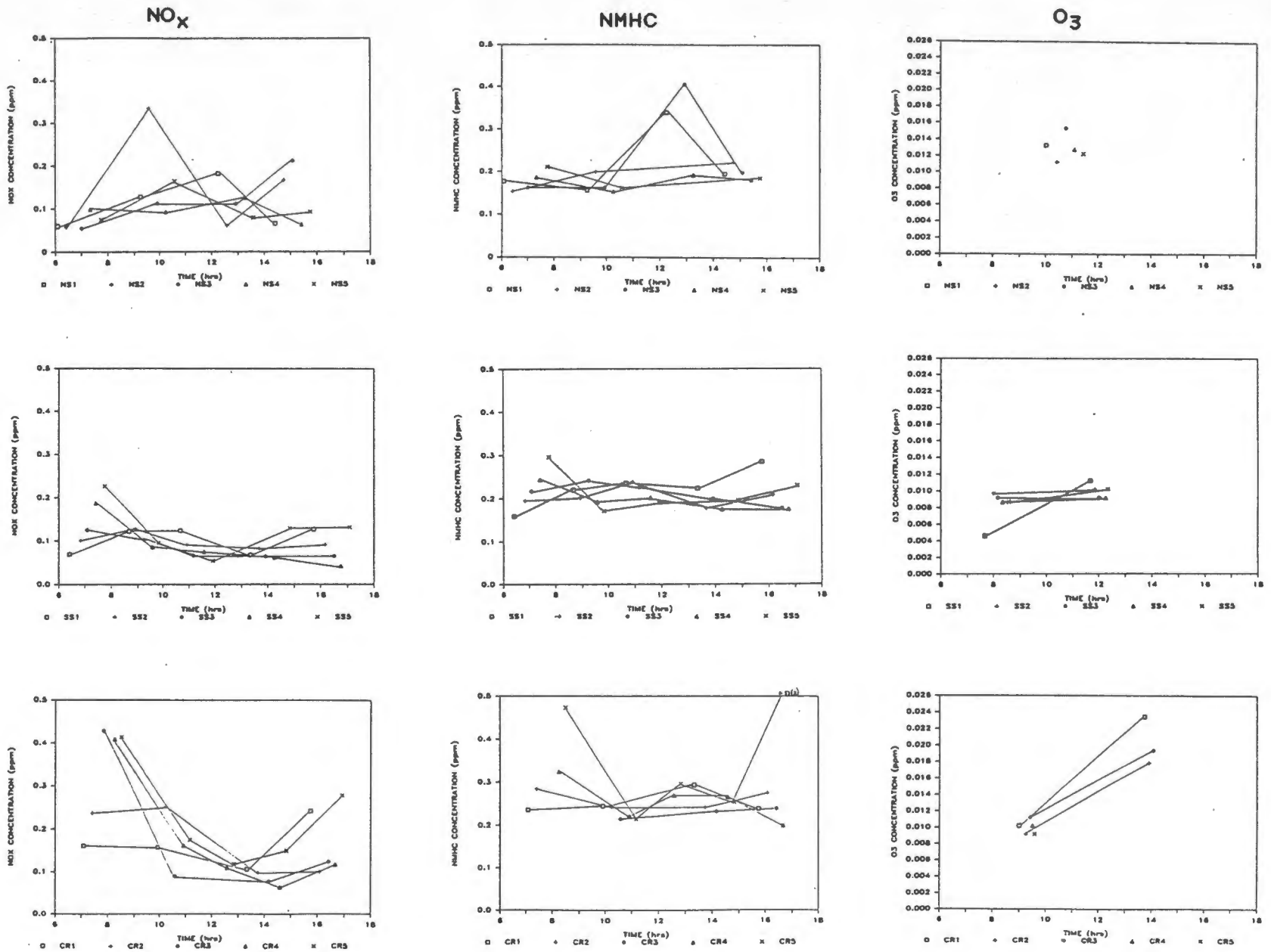
21-04-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

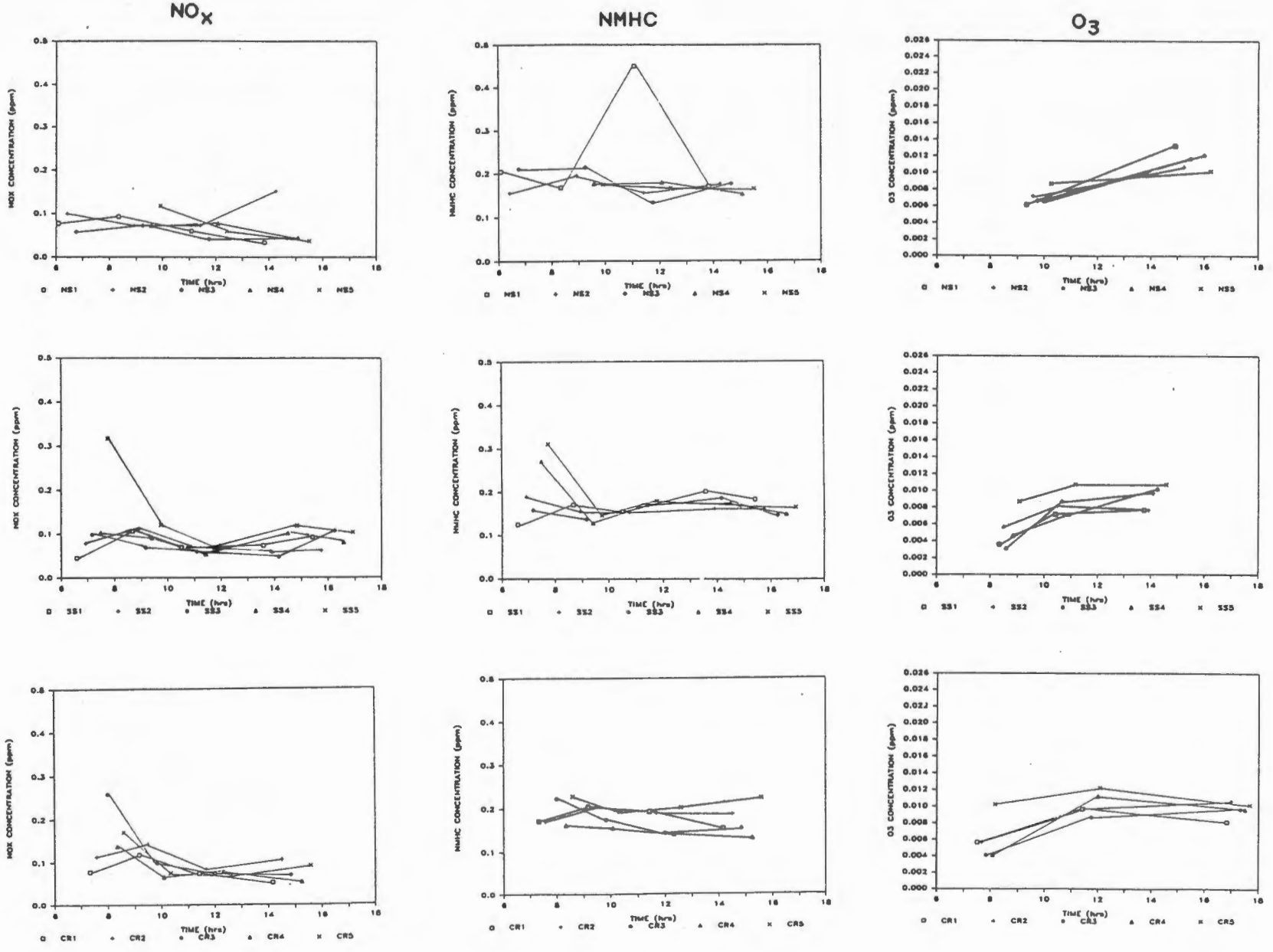
22-04-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

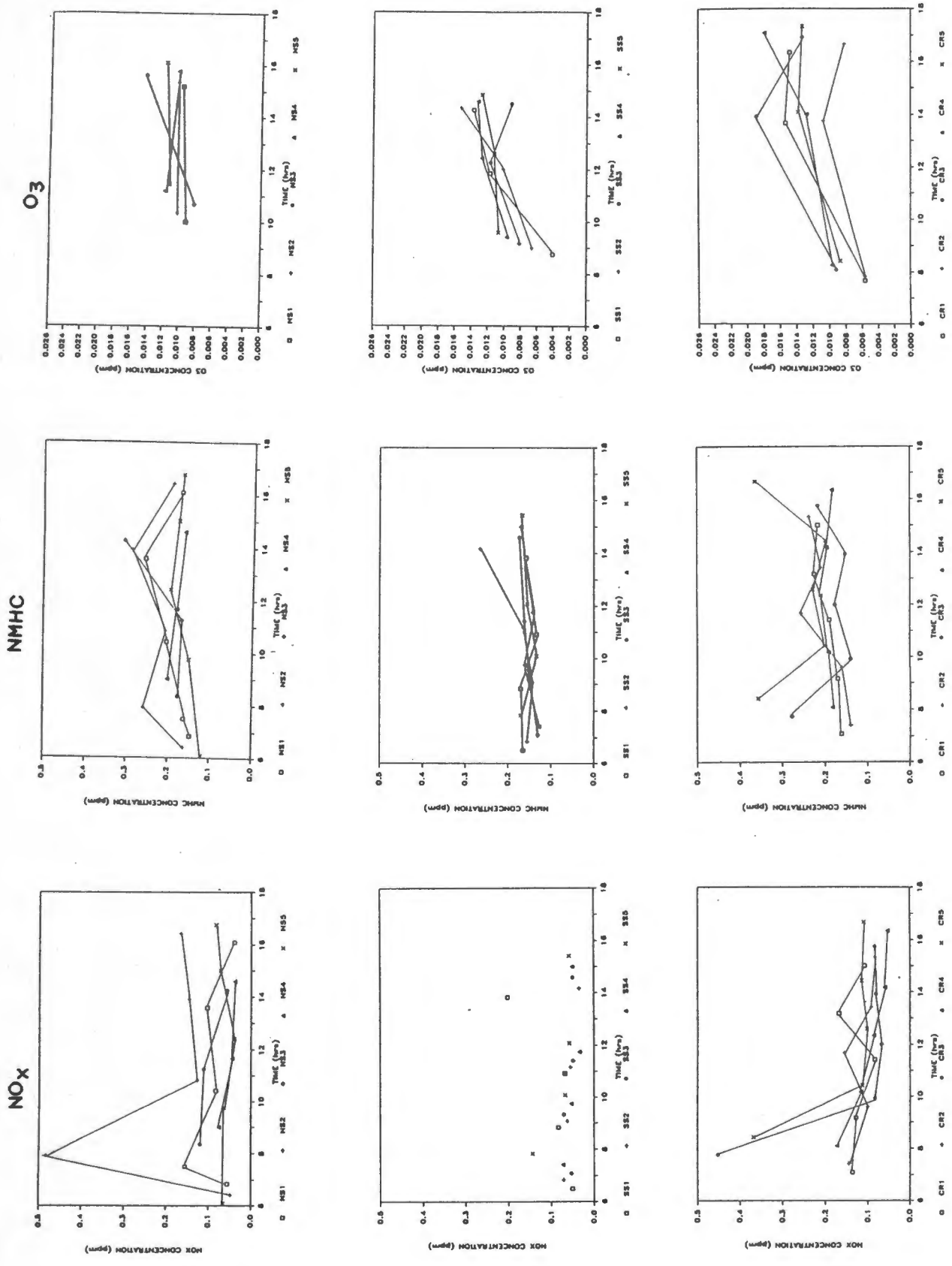
23-04-87

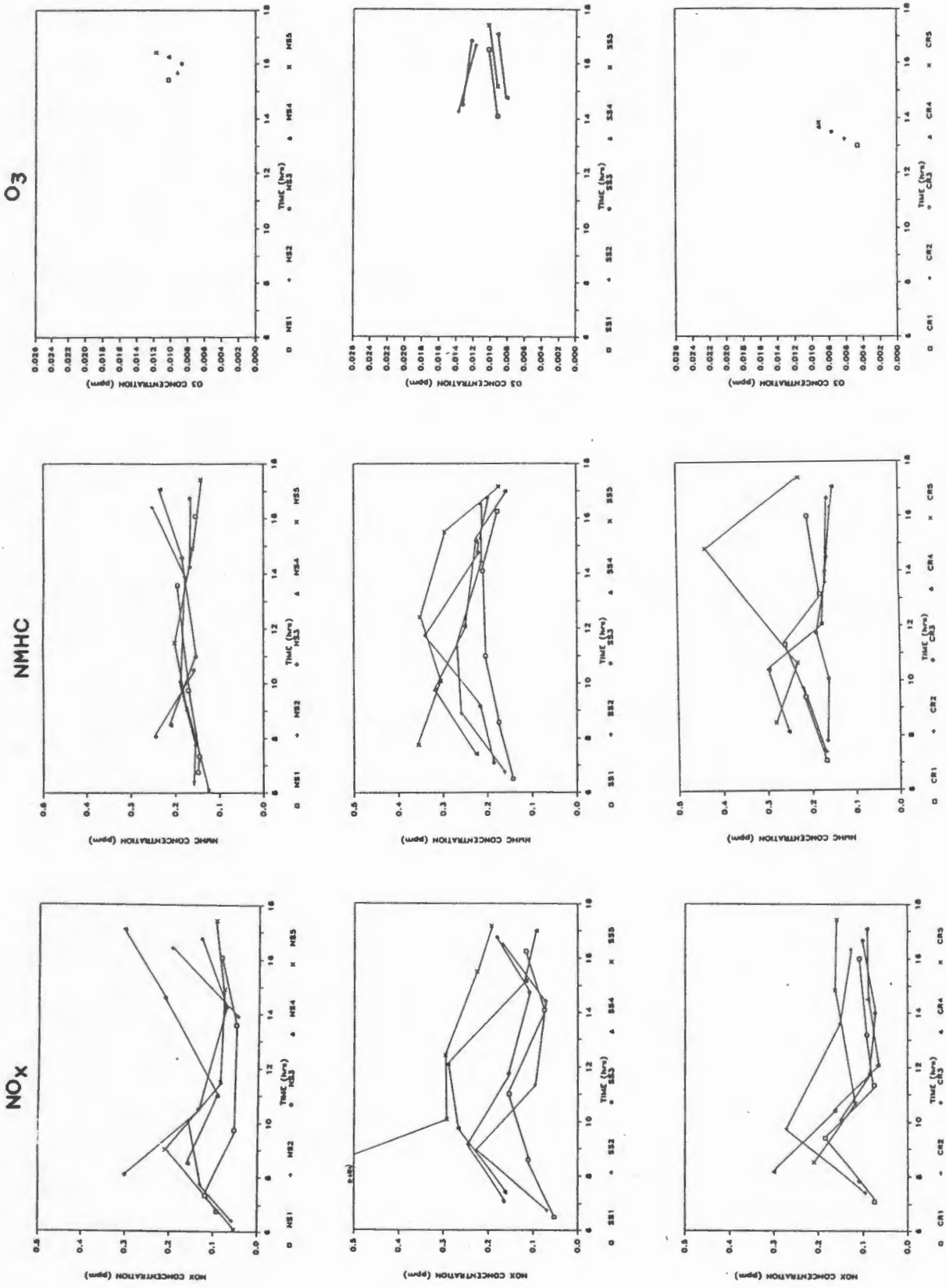

NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

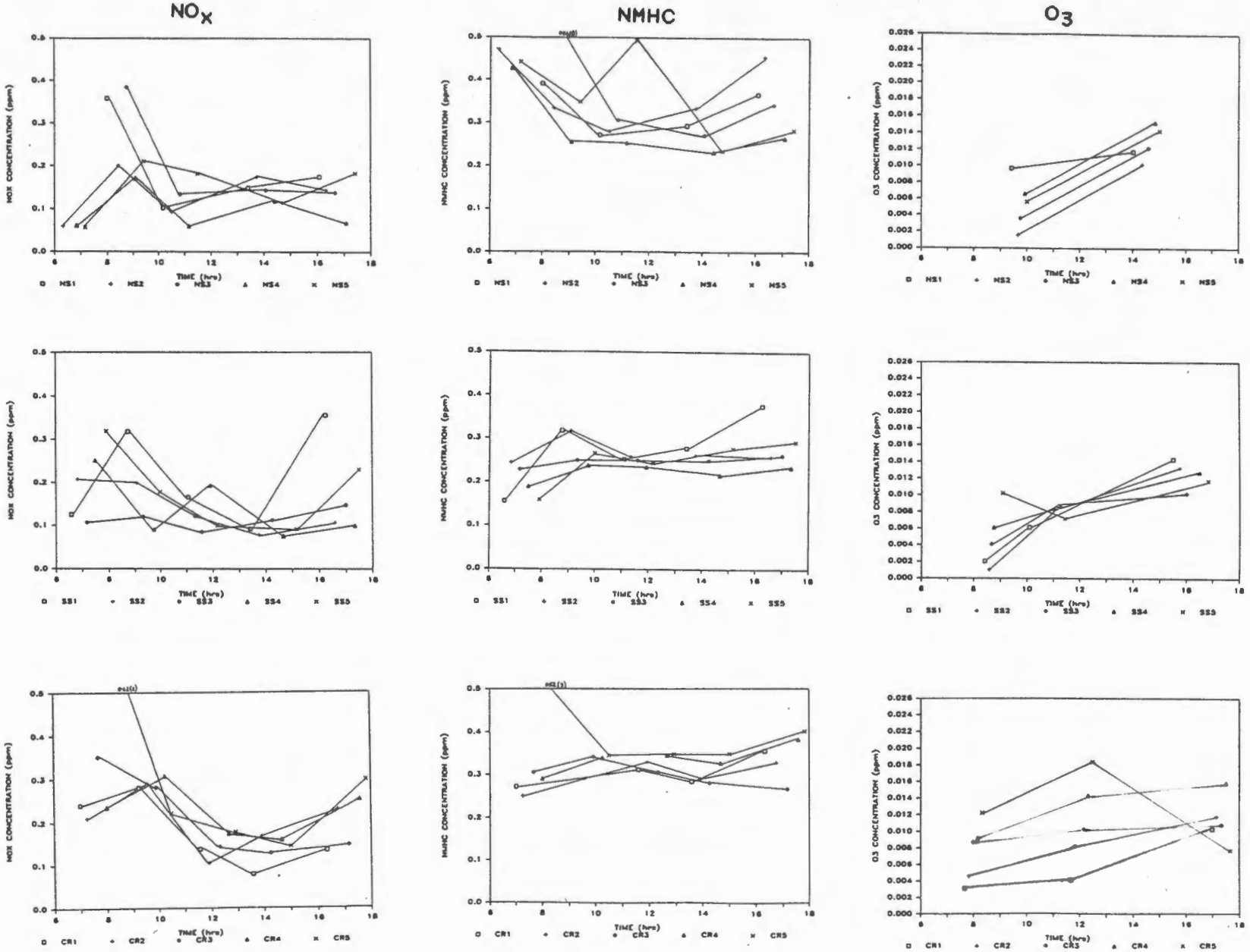
24-04-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

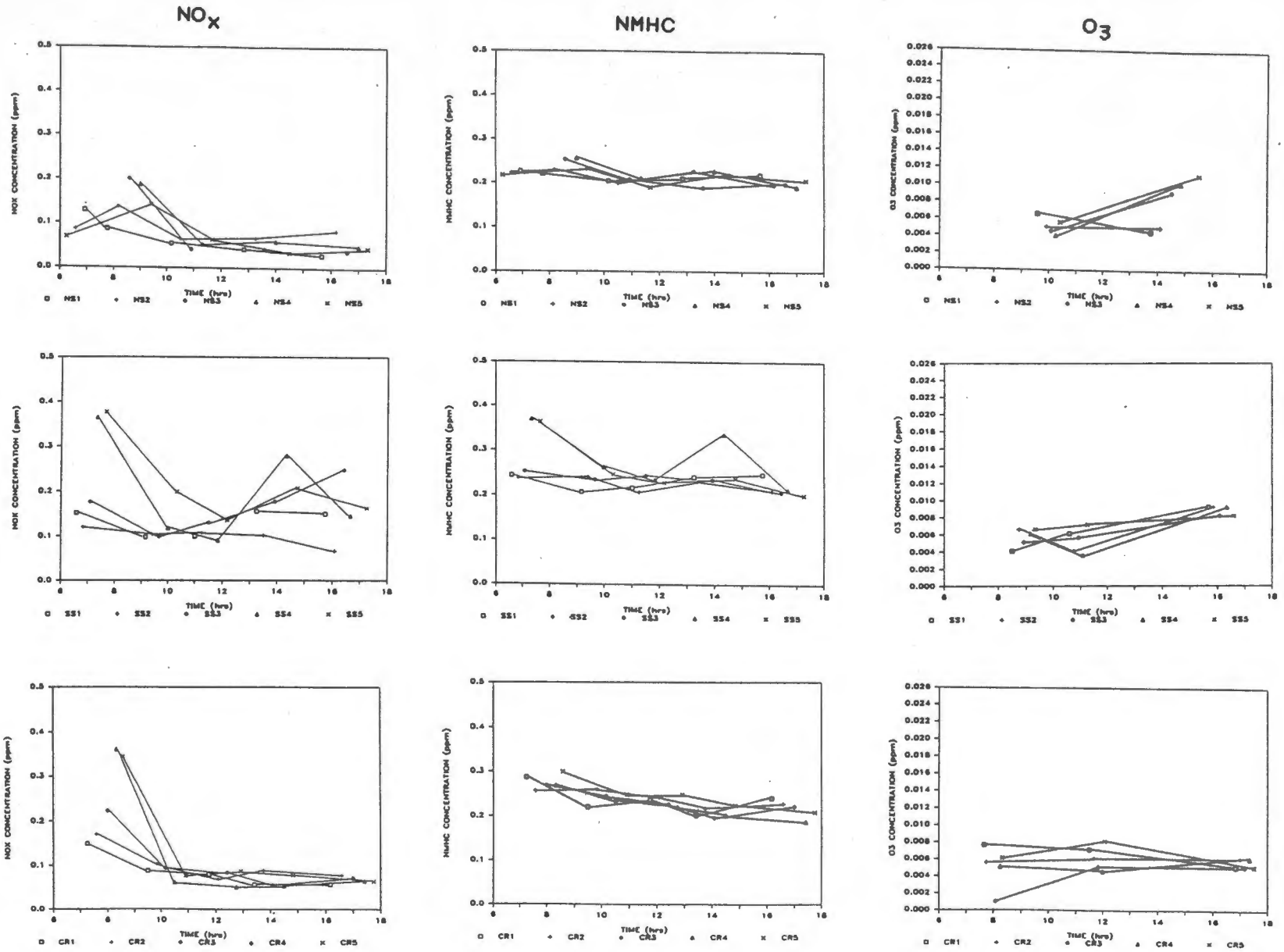
27-04-87


O3
NMHC
NOx
28-04-87

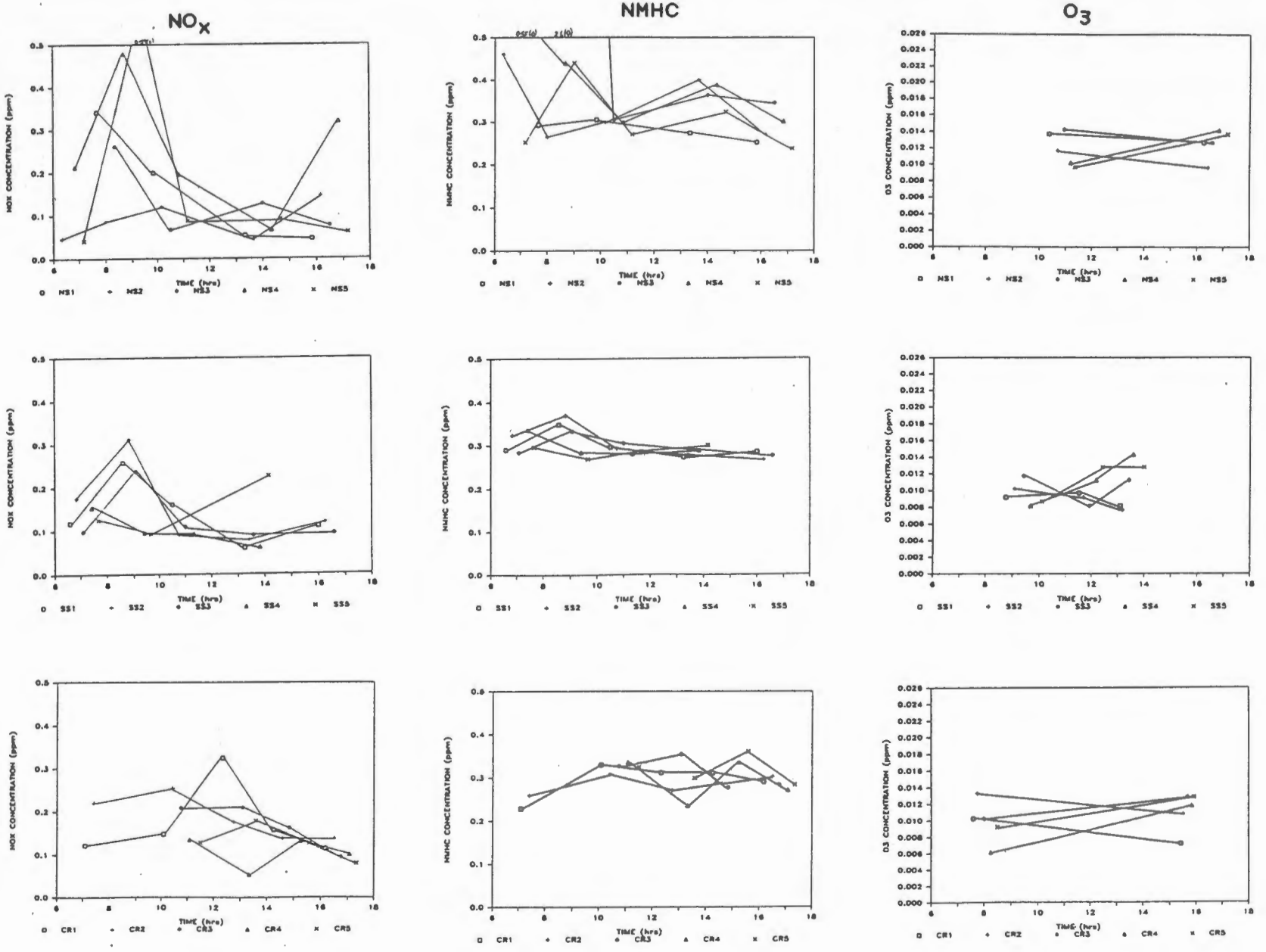

O3
NMHC
NOx
29-04-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

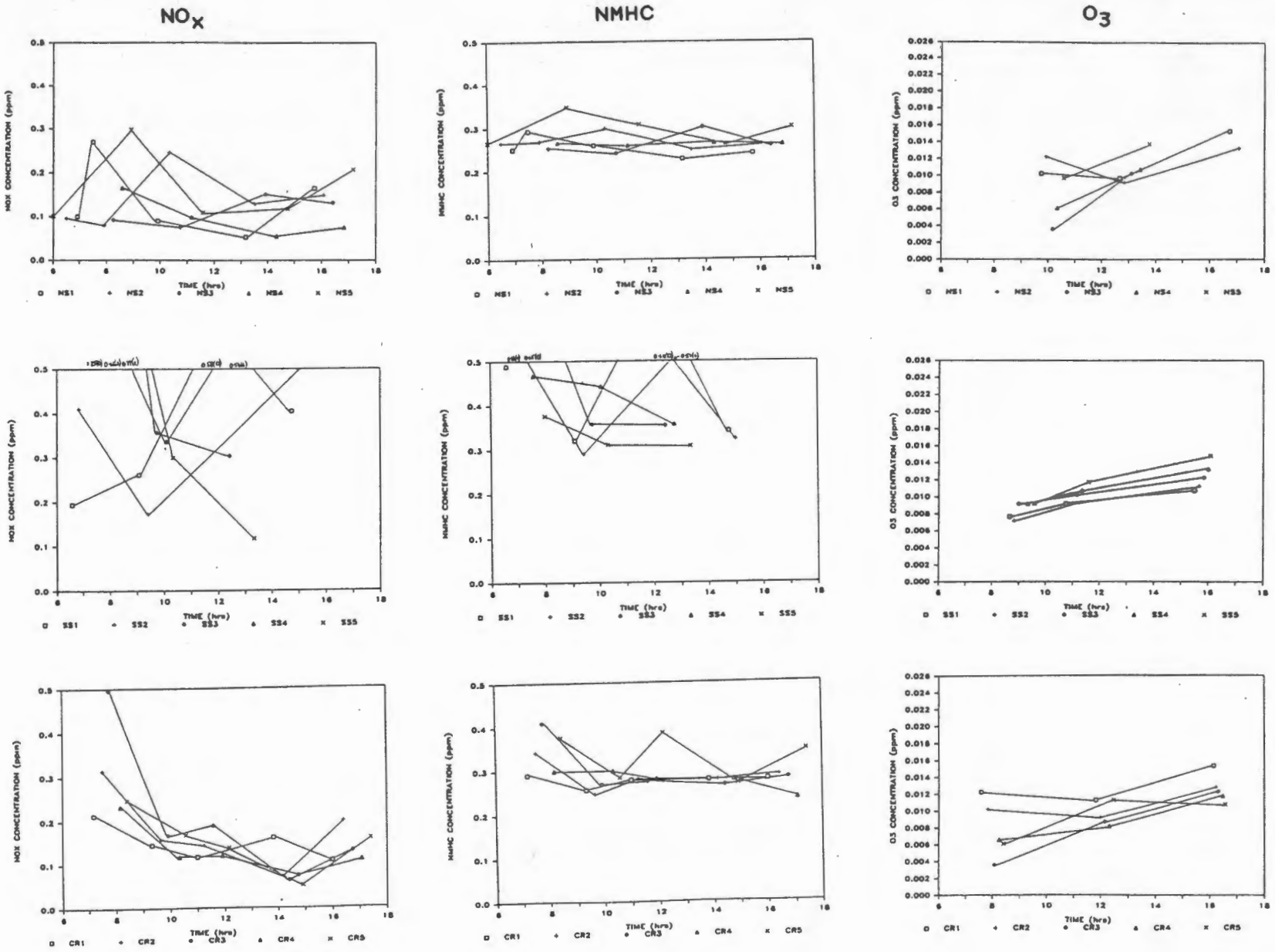
30-04-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

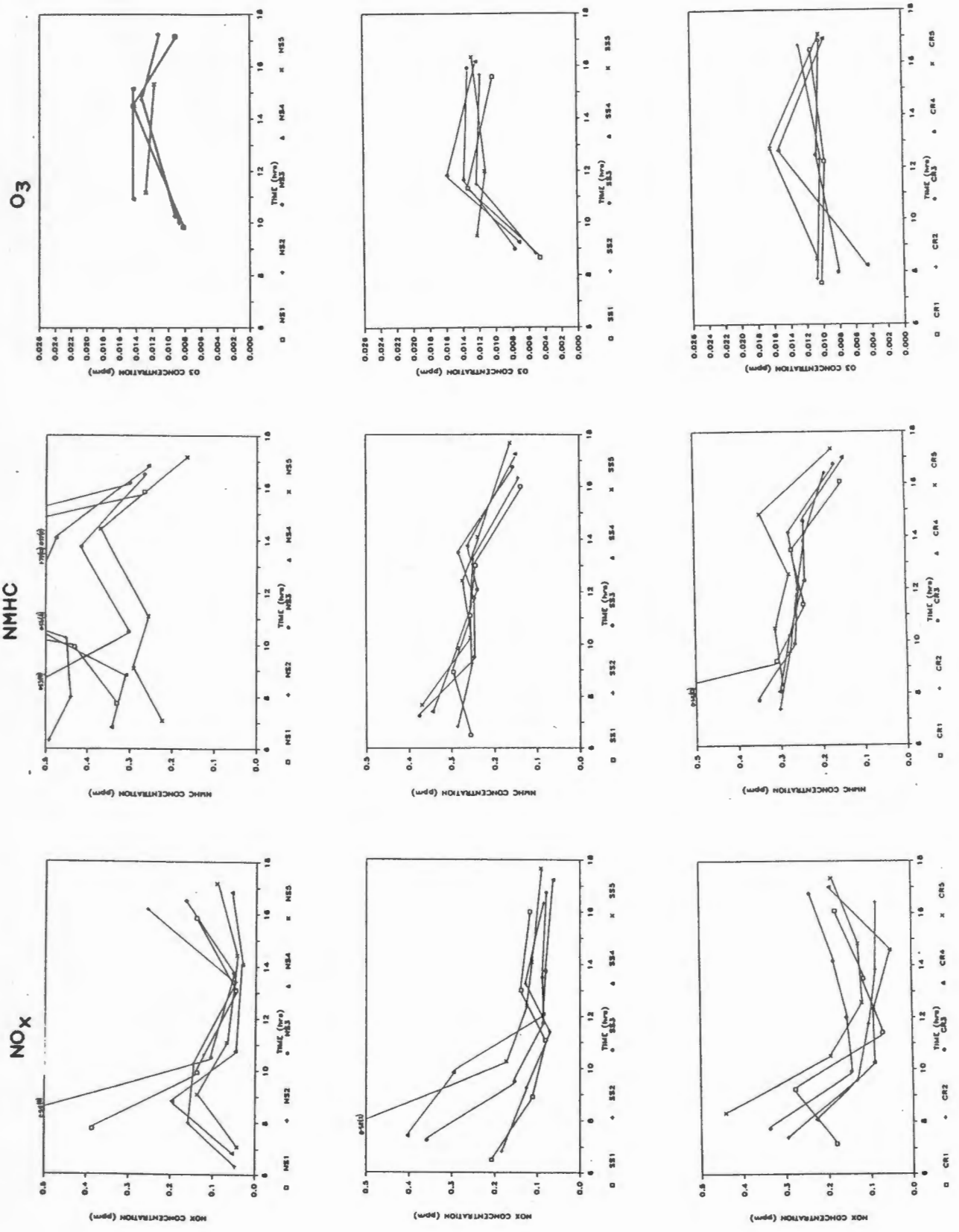
04-05-87

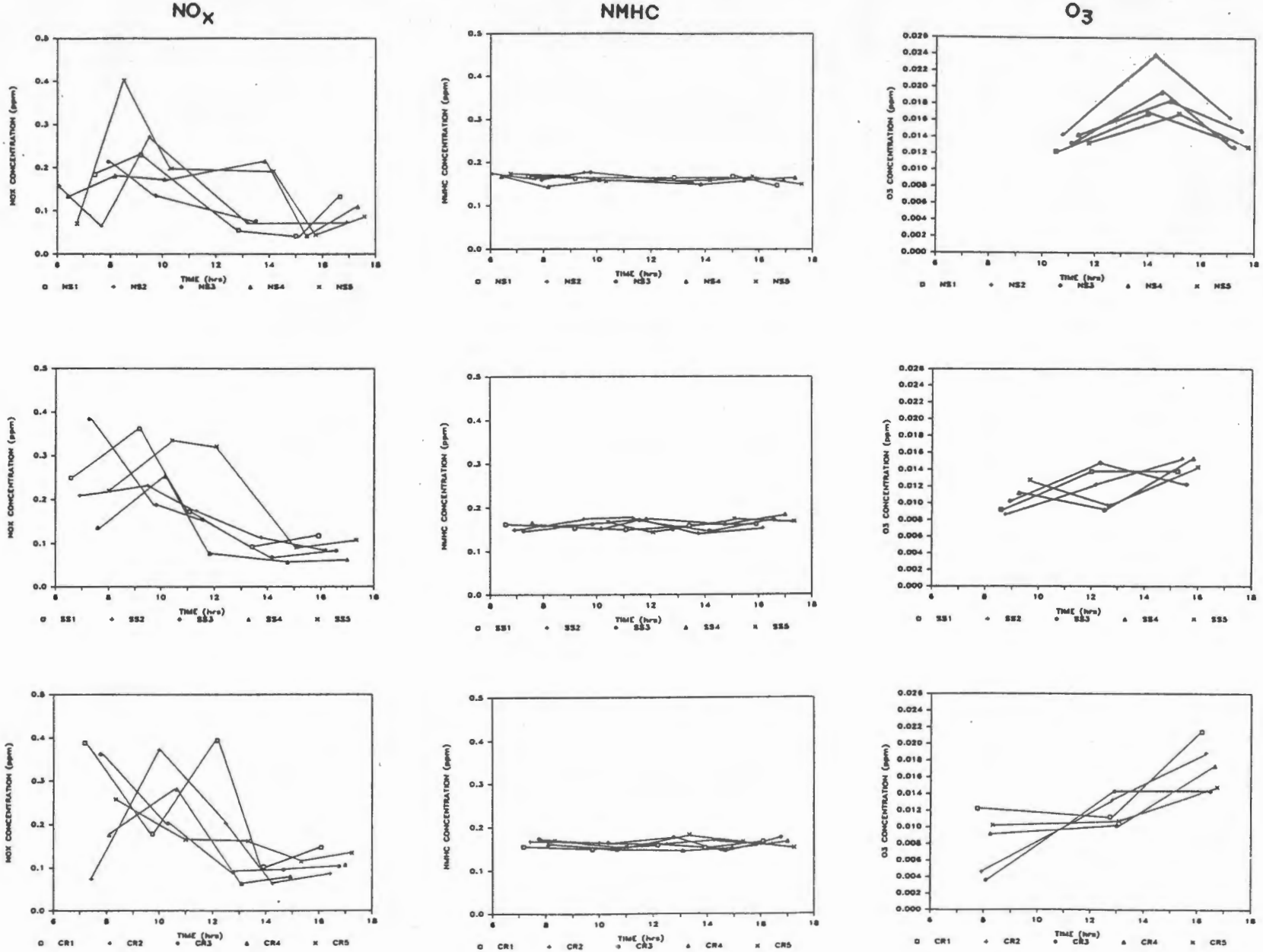

NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

05-05-87

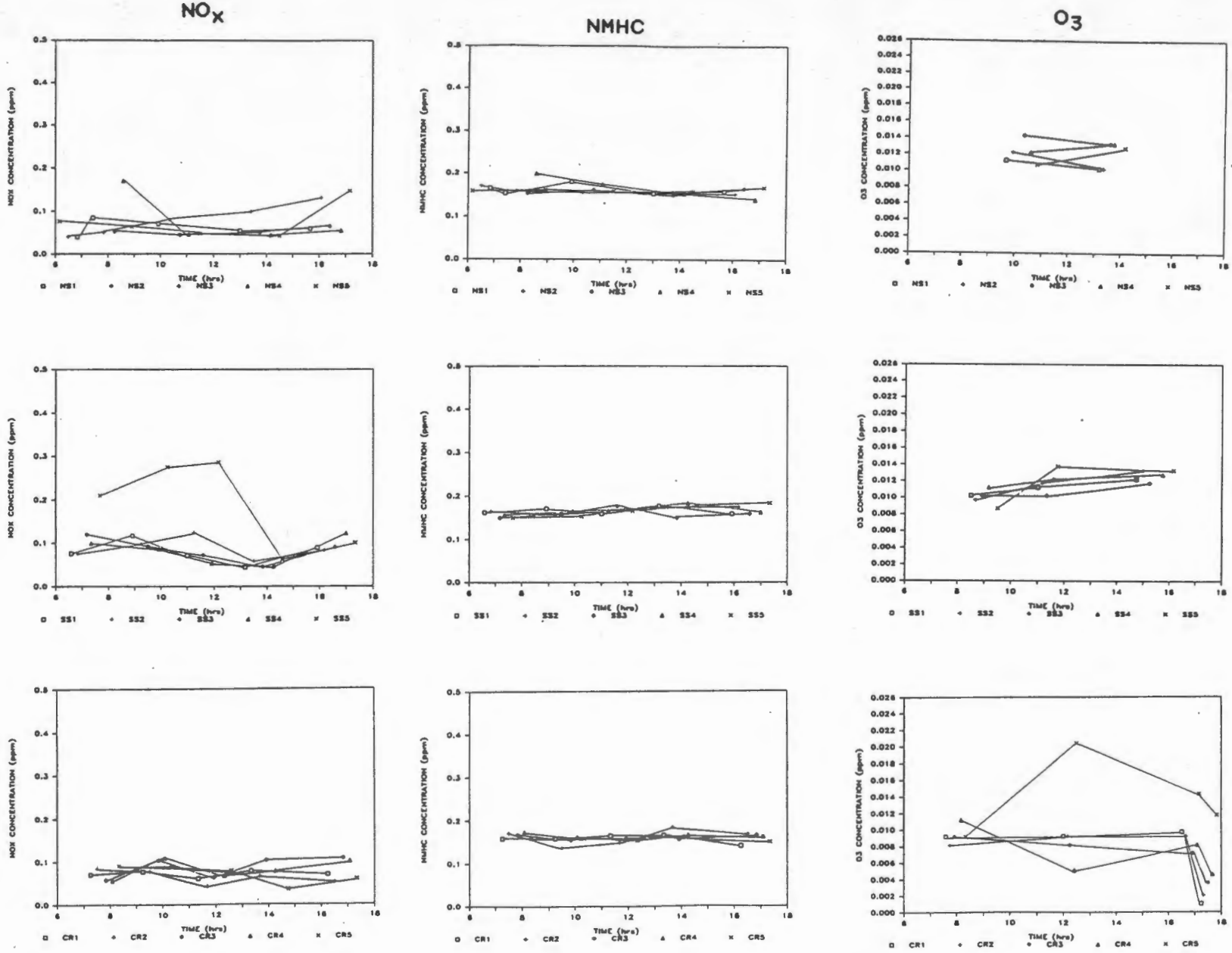

NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

07-05-87


O3
NMHC
NOx
08-05-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

09-05-87


NOx
NMHC
O3
NOX CONCENTRATION (ppm)
NMHC CONCENTRATION (ppm)
O3 CONCENTRATION (ppm)
TIME (hrs)
NS1 NS2 NS3 NS4 NS5
SS1 SS2 SS3 SS4 SS5
CR1 CR2 CR3 CR4 CR5

10-05-87

APPENDIX 4

4.1: Survey days selected for normalising

23-04-87
27-04-87
28-04-87
30-04-87
04-05-87
07-05-87
08-05-87