

MODELLING ATMOSPHERIC CHEMICAL TRANSFORMATIONS UNDER SOUTH AFRICAN CONDITIONS

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Hierdie verhandeling word opgedra aan my ouers.

"Environmentalism has been a great force for good.....if the world is to work in the 21st century it will be because nature, humanity, and technology work together" – Walter Truett Anderson, "A new shade of green", TIME, March 23, 1998.

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South Africa is in the process of adapting to new social and economical structures. The government has made it clear that the creation of work and economic growth is of the utmost importance. This policy will put South Africa's limited resources under enormous pressure and will have an adverse impact on the environment. In order to facilitate sound decision making, all aspects of the environmental impacts must be investigated, e.g. the necessary knowledge on atmospheric chemical transformations of air pollutants has to be obtained. This study is aimed at extending the existing knowledge of air pollutants at selected sites and developing a mathematical model that can be used to predict the future impact of air pollutants under southern African conditions.

Against this background, it should be noted that volatile organic compounds (VOC's) and their photochemical products are a potential threat to sustainable development due to their role in the formation of tropospheric oxidants. A VOC sampling survey was conducted in this study in order to determine the concentration profiles of selected VOC's in the vicinity of a petrochemical plant. A commercially available passive sampler was used in the study. Benzene, toluene, xylene, acrylonitrile, butanol, propanol, acetone, hexane and pentane, were identified as problem species at the petrochemical plant, and these species were measured in terms of different seasonal variations. The summer survey was successful in obtaining ambient concentrations for the selected VOC's, but during the winter survey none of the selected VOC's were detected in measurable amounts on the samplers. Follow-up surveys must be initiated in order to validate these results, and to explore or develop other sampling techniques for the sampling of ambient VOC's under these conditions.

In order to test our understanding of atmospheric processes, it is essential to construct models to help interpret their chemistry. A photochemical box model was designed to study the irradiation of a mixture of NO_x and non-methane hydrocarbon (NMHC) gases by solar ultraviolet radiation, which leads to the formation of photochemical smog. This photochemical box model was used to

model the chemical transformations in biomass and petrochemical diffusive plumes in southern African conditions.

Results from the modelled biomass plume show that biomass burning emissions lead to high ozone concentrations, and that this O₃ formation in the plume is NO_x limiting.

The results from the modelled petrochemical diffusive plumes showed that the aromatic compounds in the plume are very stable, even in bright sunlight. It also follows from the results that the ozone production in the plumes is NO_x limiting.

A great deal of research had been undertaken in South Africa on the horizontal and vertical transport of aerosols and trace gases over southern Africa. This research addresses the need to understand the extent of trace gas transport and deposition over South Africa, its neighbours and other African countries in order to assess the extent of transboundary pollution transport. It is therefore important to understand the relationship between the emission of pollutants from major industrial sources and their distribution over the globe.

A trajectory transformation model was developed to explore the transport of trace gases and deposition over the subcontinent from the Mpumalanga highveld region, the centre of power generation and chemical industries of South Africa. Five distinctive trajectory patterns were identified and obtained from the Climatological Research Group at the University of the Witwatersrand. The model represents a box-shaped parcel of air, which traverses with a specific trajectory over an emissions grid of southern Africa. The chemistry within this box, and the concentrations of all the species were modelled throughout this navigation process along the trajectory.

The values simulated by the trajectory transformation model are slightly higher than those measured along a trajectory. It follows from validation results that realistic SO₂ residence times and chemical conversion can be obtained from the model. The total sulphur deposition values obtained from the model were also of realistic magnitude.

This study succeeded to quantify the transport and deposition of trace gases in such a way that a better description of the transfer of pollutants over international borders was obtained.

This study has highlighted the need for the operation of an increase in the number of long term atmospheric monitoring stations which should be spaced in strategic locations throughout the southern African region.

Suid Afrika is tans besig om 'n nuwe maatskaplike en ekonomiese bestel aan te neem. Die regering het dit duidelik laat blyk dat die klem op werkskepping en ekonomiese groei geplaas gaan word. Hierdie klemverskuiwing bring mee dat daar toenemende druk op die land se beperkte natuurlike hulpbronne sal wees, wat 'n negatiewe impak op die omgewing tot gevolg het. Ten einde sinvolle besluitneming moontlik te maak, moet alle omgewingsimpakte ondersoek en kennis aangaande chemiese transformasies van besoedelstowwe verkry word. Hierdie studie is daarop gemik om kennis aangaande atmosferiese besoedelstowwe uit te brei en 'n rekenaarmodel te ontwikkel, wat toekomstige impakte van besoedelstowwe onder verskillende Suid Afrikaanse toestande, kan voorspel.

Teen bogenoemde agtergrond, bestaan die wete dat vlugtige organiese verbindings (VOV's) (of sogenaamde "VOC's") en hulle fotochemiese produkte moontlik 'n bedreiging vir volhoubare ontwikkeling in hou. Dit kan toegeskryf word aan die rol, wat VOV's in die vorming van troposferiese oksideermiddels speel. 'n Proefsteekopname is in hierdie ondersoek uitgevoer om die konsentrasieprofile van geselekteerde VOV's in die nabyheid van 'n petrochemiese aanleg te bepaal. 'n Kommersieel beskikbare diffusie-monsternemer is in hierdie ondersoek vir dié doel gebruik. Benzeen, tolueen, xileen, akrilonitriël, butanol, propanol, asetoon, heksaan en pentaan is geïdentifiseer as probleemverbindings in die petrochemiese aanleg. Die voorkoms van hierdie verbindings is onder verskillende seisoene ondersoek. Tydens die someropname is daarin geslaag om troposferiese konsentrasies van die geselekteerde VOV's te bepaal, terwyl die winteropname geen van die geselekteerde VOV's in kwantifiseerbare hoeveelhede opgelewer het nie. Verdere studies word aanbeveel met die oog op die verifieëring van hierdie resultate, asook op die verkenning en ontwikkeling van verdere monsternemingstegnieke, wat verband hou met die bepaling van troposferiese VOV's, onder hierdie bepaalde toestande.

Met die oog op uitbreiding van kennis oor atmosferiese prosesse, is dit noodsaaklik om rekenaarmodelle te ontwikkel waarmee die chemiese prosesse, wat hierdie verbindings ondergaan, verklaar kan word. 'n Fotochemiese blokmodel (of sogenaamde "box model") is vir die doeleindes van hierdie ondersoek ontwerp. Die model is geprogrammeer om die effek wat ultravioletbestraling op 'n mengsel van stikstofoksiedspesies (NO_x) en nie-metaankoolwaterstofgasse (of sogenaamde "NMHC"-gasse) het, te voorspel. Hierdie proses het die vorming van fotochemiese rookmis tot gevolg. Die fotochemiese blokmodel is gebruik om die chemiese veranderinge, wat in biomassa- en petrochemiese diffusepluime onder suider-Afrikaanse toestande voorkom, te modelleer.

Die resultate, wat vanuit die biomassaverbranding verkry is, het getoon dat vrystellings aanleiding tot hoë osoonkonsentrasies gee en dat die proses van osoon produsering in die pluim beperkend ten opsigte van NO_x -konsentrasies optree.

Die gemodelleerde diffusepluim resultate het getoon dat die aromatiese verbindings baie stabiel, selfs onder helder sonlig omstandighede, is. In hierdie geval het die resultate weereens getoon dat osoonproduksie in die pluim beperkend ten opsigte van NO_x -konsentrasie is.

Heelwat navorsing is in Suid-Afrika onderneem om die horisontale- en vertikale vervoer van aerosols en spoorgasse ("trace gases") oor suidelike Afrika te bepaal. Dit is om politieke en volhoubare ontwikkelings redes belangrik om die verhouding tussen die industriële vrystelling van besoedelingstowwe vanuit hoofbronne en die verspreiding van hierdie stowwe in suidelike Afrika aan die ander kant, beter te verstaan.

'n Chemiese transformasiemodel is aan 'n transportmodel gekoppel om die vervoer van transformasie van spoorgasse en die daaropvolgende neerslag in die sub-kontinent beter te kwantifiseer. Vir die doel, is die oorsprong van hierdie gasse die sentrum van kragopwekkings- en chemiese industriële in die Mpumalanga-Hoëveld beskou. Vyf onderskeibare transportweë is geïdentifiseer en die empiriese data van die transportweg is vanaf die Klimatologie Navorsingsgroep ("Climatological Research Group") by die Universiteit van die

Witwatersrand verkry. Die chemiese reaksies in die blok, tesame met die konsentrasies van die teenwoordige chemiese verbindings, is deurgaans gemodelleer volgens die gegewe transportweg, soos geïdentifiseer deur die Klimatologie groep.

Die waardes verkry vanuit die chemiese transformasie model, was oor die algemeen effens hoër as dié ooreenstemmende gemete waardes. Hierdie gevalideerde resultate bevestig dat realistiese SO₂ konsentrasies en chemiese omskakelingstempo's vanuit die teoretiese model verkry word. Die totale swawelneerslag, soos deur die model voorspel, is ook van 'n realistiese omvang.

In hierdie studie is dus daarin geslaag om die mate van chemiese element vervoer en neerslag te kwantifiseer. Hierdeur is dit nou moontlik om die transport van industriële emissies oor lands grense beter te kwantifiseer.

Hierdie ondersoek ondersteun die behoefte aan die daarstelling van 'n groter hoeveelheid langtermyn atmosferiese moniteringstasies, wat op strategiese punte binne suidelike Afrika geplaas behoort te word, ten einde volhoubare ontwikkelingsbehoefte en risiko's te kan bepaal.

CHAPTER 1

MOTIVATION AND GOALS

In this Chapter...

The project is motivated by looking at the pollution sources and pollution capabilities of volatile organic (Par. 1.1.2) and sulphur (Par. 1.1.3) compounds in the South African atmosphere, problems related to it and the atmospheric relevance of the project. Par. 1.1.3 gives a short overview of the trajectory transport of trace gases over southern Africa, the problems associated with the deposition of trace gases and the motivation to model this phenomenon. This short chapter is concluded by Par 1.2, which sets the scope of the project.

1.1 PROJECT MOTIVATION

1.1.1 Introduction

Atmospheric constituents follow a series of steps or processes from the time of their introduction into the atmosphere until their eventual removal from it. This atmospheric pathway is but one portion of the overall biogeochemical cycle that links the origins and fates of all environmental chemical species. The main processes that comprise the atmospheric pathway are emissions, transformation, transport and deposition (Figure 1.1). Section 1.1.2 of this dissertation will deal with the emission and transformation sections of the atmospheric pathway while the section on trajectory transport (Par 1.1.3) will deal with the transport and deposition section of the atmospheric pathway. Understanding the atmospheric pathways of important species and quantifying the flux of material along these pathways are fundamental to the study of atmospheric chemistry.

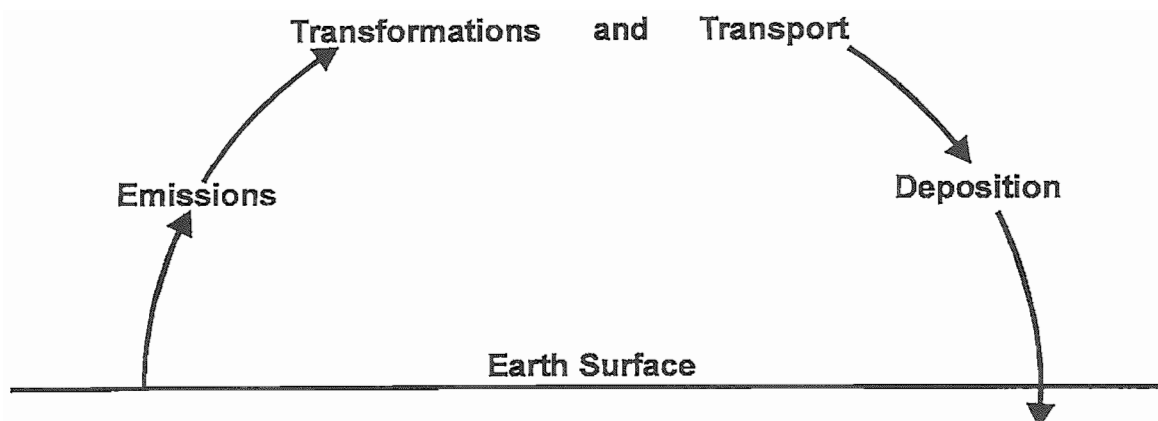


Figure 1.1 – Schematic presentation of the atmospheric cycle and its component processes.

1.1.2 Volatile organic compounds

Exposure to air pollutants including hydrocarbon species (commonly referred to as volatile organic compounds or VOC's) is believed to result in significant risks to human health. The VOC's in the air originate from both anthropogenic and biogenic sources. Major anthropogenic sources include fossil fuel combustion, chemical industries, oil refineries, biomass burning, landfill sites and motor vehicles. The biogenically emitted volatile organic compounds are released into the atmosphere by plants, animals and micro-organisms and contribute significantly to VOC's present in the atmosphere. In sub-Sahara Africa, up to one quarter (1/4) of available biomass is combusted in veld and forest fires each year (van Wilgen *et al.*, 1997).

Biogenic VOC's have recently received renewed attention for their role in ozone and haze formation (Bloemen *et al.*, 1993). Isoprene is one of the most abundant and most reactive biogenic VOC's. Chronic exposures to many of these compounds have been linked to carcinogenic, mutagenic, teratogenic and neurological health problems (Keith and Walker, 1995). Many of the compounds can be related to acute health effects such as irritation and skin reactions (Keith and Walker, 1995). Some of the VOC's are associated with photochemical smog, which in turn decreases visibility and produce adverse reactions in humans as well as vegetation and wildlife population. Smog exposure can

damage lung tissue, cause serious respiratory illness in humans and also harm farm crops (Keith and Walker, 1995).

The rate of VOC emissions and degradation mechanisms are still poorly understood. A need therefore exists to identify and quantify the VOC's in the atmosphere and to establish an inventory of the sources which contribute to their existence.

Research in atmospheric chemistry has also clearly established the important role of VOC's in tropospheric processes. The emissions of VOC's lead to complex chemical and physical transformations in the atmosphere contributing directly or indirectly to diverse effects such as acid deposition and global climate modification.

Both anthropogenic and biogenic VOC's considerably enhance the rate of oxidation of NO to NO₂ and hence the production of tropospheric ozone (see Figure 2.2). The oxidised VOC's formed in radical chain processes contribute to aerosol haze and can pose further environmental hazards. The extent of photochemical air pollution depends on the nature of the VOC's. It is therefore important to identify species and the amount of VOC's present in the atmosphere.

Because of the reactivity of VOC's and their significance in atmospheric chemistry, detailed information is required to understand the major sources of their existence, their composition, concentration and transport. Only with this information on VOC's can the identification, quantification and modelling of the impact of VOC emissions be achieved.

1.1.3 Trajectory atmospheric transport

The transport section of the complete atmospheric pathway (Figure 1.1) consists of those processes that mix atmospheric species in the troposphere, and occasionally even the stratosphere. The transport section therefore carries material from where it is introduced into the atmosphere to where it is eventually deposited on the earth's surface. The initial mixing of emitted pollutants, vertical-exchange processes, clouds, and advection are important aspects of this part of the atmospheric cycle. The importance of these various physical processes that

influence transport depends on the spatial scale of the transport process.

The influence of a chemical species emitted into the atmosphere on the receiving environment depends on both the atmospheric residence time of the species and the prevailing meteorological conditions. Chemical species may reside in the atmosphere for times ranging from a second to as long as several centuries. In the context of acid deposition, the important contributors, that is, gaseous sulphur dioxide, nitric oxide, and ammonia, tend to have relatively short residence times in the order of days, and thus meteorology is crucial in their distribution over tens to thousands of kilometres. Oxidation products, such as particulate sulphate and nitrate or sulphuric acid and nitric acid, have longer residence times of a few days. The range of influence of a species with a short residence time depends on wind speed and atmospheric stability near the source. A species with a longer residence time can be distributed over hundreds and thousands of kilometres by large-scale meteorology. Meteorological factors are less important for a longer-lived species that has been distributed throughout the hemispheric or global atmosphere.

Atmospheric chemical and trajectory analysis results from the Ben MacDhui High Altitude Trace Gas and Transport Experiment (BHATTEX) (Piketh *et. al.*, 1998) which showed that industrial sulphur peaks could be traced back to transports from the Mpumalanga highveld.

Trajectory analysis over South Africa over the past seven years has indicated that air parcels are transported most frequently over the Indian and Atlantic oceans. There is evidence, however, to suggest that material generated on the Mpumalanga highveld could be transported over neighbouring and other countries in southern Africa (Piketh *et. al.*, 1998). This transboundary transport of pollutants from the industrialised Highveld has not yet been quantified.

1.2 SCOPE OF THE PROJECT

The first aim of the proposed study is to model chemical transformations of selected VOC's in ambient air and to determine their role in the formation of ozone and other secondary pollutants in a biomass burning plume and an industrial petrochemical environment.

The second aim of the study is to establish the extent to which air pollutants are transported over the borders of other countries in southern Africa, and to predict deposition values for the major trajectory transport routes.

To achieve these goals, the study aims to:

- I. Explore passive sampling techniques for quantifying VOC concentrations in an industrial environment.
- II. Determine the concentrations of selected VOC's in the ambient air in the vicinity of petrochemical industries using passive sampling techniques.
- III. Model chemical transformations of selected VOC's under local conditions.
- IV. Model the deposition of sulphur compounds from the Mpumalanga highveld on typical trajectory routes for southern Africa.

The study hopes to answer the following questions:

- I. Can passive sampling methods for the sampling of selected VOC's be introduced into a modern air quality-monitoring network?
- II. Can a suitable photochemical air pollution transformation model be developed applicable to southern African conditions?
- III. What portion of the total sulphur deposition, along identified transboundary transport pathways of air pollutants, originates from emissions over the Mpumalanga highveld of southern Africa?

These questions will be addressed in Chapters 3, 4 and 5 respectively.

CHAPTER 2

LITERATURE SURVEY

In this Chapter...

An overview of the relevant literature is given. An introduction to air pollution in the industrialised world (Par 2.1) is provided. Par 2.2 gives a short overview on the environmental aspects and implications of volatile organic compounds in the atmosphere. Par 2.3 focuses on various sampling and analytical methods of volatile organic compounds in the ambient atmosphere. Par 2.4 gives an overview of the deposition of pollutants in the atmosphere. Par 2.5 focuses on the mathematical modelling of atmospheric processes. Par 2.6 concludes the chapter by summarising what will be done in the following chapters in view of the completed literature survey.

2.1 INTRODUCTION

The dramatic increase in public awareness and concern about the state of the environment which has occurred in recent decades, has been accompanied and partly prompted by an ever-growing body of evidence on the extent to which pollution has caused severe environmental degradation. The introduction of harmful substances into the environment has revealed many adverse effects on human health, agricultural productivity and natural ecosystems.

A widely used definition of pollution is “the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment” (Alloway *et al*, 1997). Some experts make a distinction between contamination and pollution. Contamination is used for situations where a substance is present in the environment, but not causing any obvious harm, while pollution is reserved for cases where harmful effects are apparent (Alloway *et al*, 1997).

Pollutants consist of two types: *primary pollutants* which exert harmful effects in the form in which they enter the environment, and *secondary pollutants*, which are formed as a result of chemical processes by often less harmful precursors within the environment.

In all cases of pollution there is a particular source of pollutants, in addition to the pollutants themselves, as well as the transport medium (air, water or direct dumping onto land), the target (or receptor) which includes ecosystems, individual organisms (e.g. humans), and structures. Pollution can be classified in several ways according to the source (e.g. agricultural pollution), the media affected (e.g. air pollution or water pollution) or by the nature of the pollutant (e.g. heavy metal pollution) (Alloway *et al*, 1997).

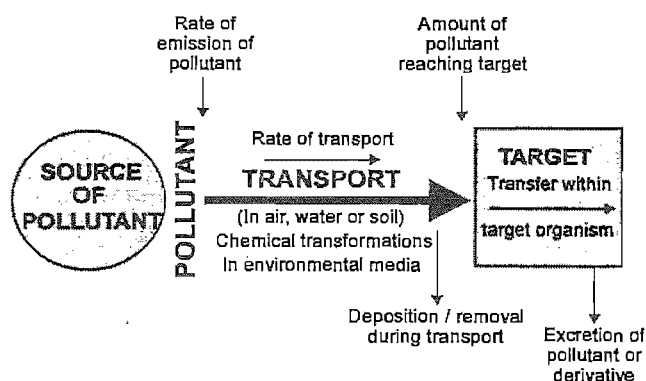


Figure 2.1 – A simplified model of environmental pollution (Alloway *et al*, 1997).

2.2 ENVIRONMENTAL ASPECTS AND IMPLICATIONS OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

2.2.1 Atmospheric relevance of VOC chemistry

A potential threat to sustainable development in southern Africa is the detrimental effects caused by species emitted during the burning of fossil fuels. This is further enhanced by the atmospheric oxidation of these species. Air pollutants are mostly emitted as reduced or partly oxidised molecules. The removal of these pollutants from the atmosphere usually requires a chemical transformation, that is, the oxidation thereof, in the atmosphere. The oxidation of a pollutant molecule can be a complex process. Depending on the chemical and physical conditions, it may take place *via* different reaction pathways.

VOC's in ambient air are primarily of interest because they participate in photochemical reactions which lead to the formation of photochemical smog and ozone in the ambient atmosphere.

The U.S. Environmental Protection Agency (EPA) has designated ozone as a criterion pollutant. Ambient air quality standards for O₃ have been set to protect against adverse health and welfare effects.

The only known way by which ozone is produced in the troposphere is photolysis reactions of nitrogen dioxide (NO₂) (Wayne, 1985).

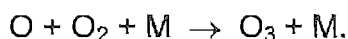
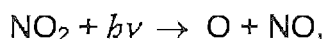


Figure 2.2 shows the NO_x catalyzed oxidation of organic compounds in the troposphere.

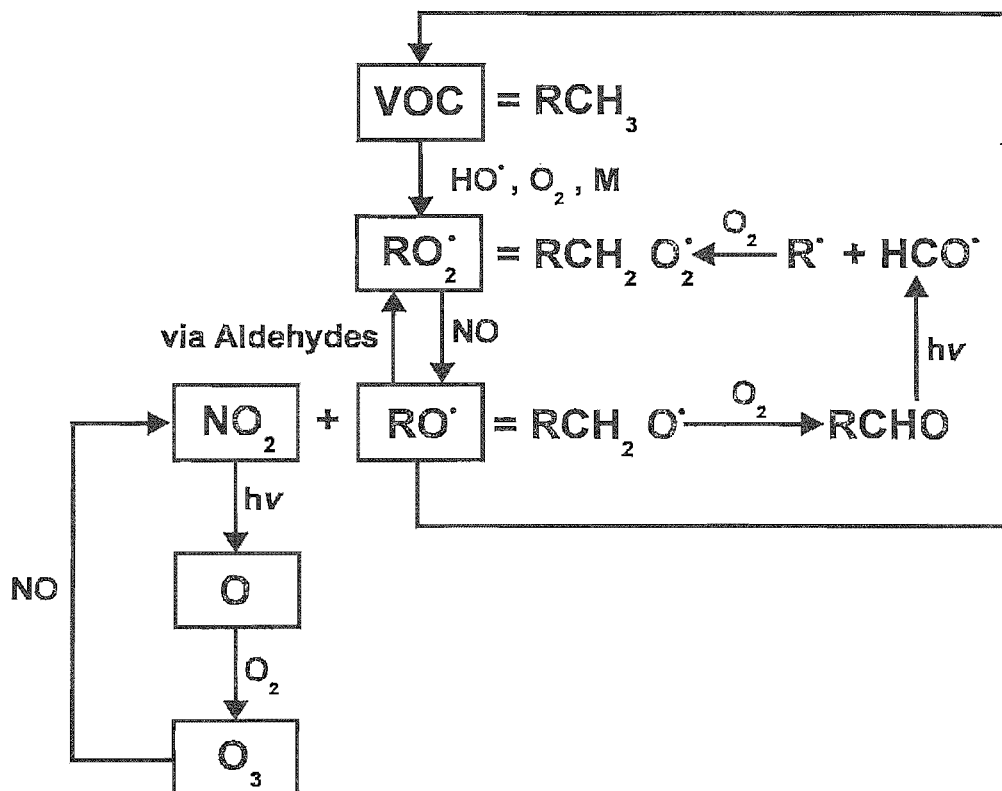


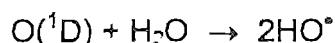
Figure 2.2 – Schematic diagram of the oxidation of organic compounds in the troposphere. Organic compounds are the fuel for NO_x catalyzed ozone production (Colbeck *et al.*, 1994).

Thus both urban air pollutants arising from combustion processes and the products of biomass burning play an important role in the formation of tropospheric ozone concentrations.

Photolysis reactions of ozone (O_3) are considered to be the "trigger" of all atmospheric oxidation reactions (Seinfeld, 1998).



The singlet oxygen atoms, $O(^1D)$, that are produced react with water to generate two hydroxyl radicals.



The hydroxyl radicals ($HO^\bullet$), unlike many other molecular fragments and radicals formed from carbon containing molecules, are unreactive towards nitrogen and oxygen molecules and survive collisions with these molecules to react with atmospheric trace species such as hydrocarbons (RCH_3), carbon monoxide (CO) and aldehydes ($RCHO$). Due to the relatively high concentration levels of CO and methane (CH_4) in the atmosphere, it is estimated that about 70% of the hydroxyl radicals react with CO to produce carbon dioxide (CO_2) and hydrogen radicals ($H^\bullet$). The rest react with CH_4 to produce water and methyl radicals ($CH_3^\bullet$), assuming an unpolluted atmosphere. The hydrogen and methyl radicals then react with oxygen to produce hydroperoxyl ($HO_2^\bullet$) and methylperoxyl ($CH_3O_2^\bullet$) radicals. The atmospheric oxidation rates of organic, nitrogen and sulphur species are, to a large extent, determined by the concentration of these oxygen based radicals (Wayne, 1985; Seinfeld, 1998).

Furthermore, tropospheric ozone is linked to the production of atmospheric hydrogen peroxide. The reaction of atmospheric ozone with isoprene and terpenes emitted by vegetation results in the formation of a wide variety of radicals with subsequent reactions contributing to the formation of hydroperoxides (Seinfeld, 1998). In an unpolluted atmosphere, hydrogen peroxide is mainly formed by reactions between two $HO_2^\bullet$ radicals. The formation of $HO_2^\bullet$ radicals is, however, also linked to photolysis reactions of ozone.

To control the formation of ambient ozone, EPA has emphasised the control of VOC emissions from both mobile and stationary sources.

The petrochemical industries and related activities are generally assumed to be the major sources of VOC's in ambient air. Significant sources that have contributed to the degradation of urban air quality include waste lagoons, activated sludge treatment plants, chemical waste sites, and automobiles. Ubiquitous background sources of VOC's are animal and plant matter, forest and grass fires and seepage of crude oil. The diversity of sources causes a complex chemical mixture of volatile organic compounds in the ambient air. VOC's have been found in remote regions of the North Pacific marine atmosphere implying a global distribution and transport for some refractory compounds (Casserly *et al*, 1985).

A large number of VOC's have been regularly found in urban centres through out the world: 20 mutagenic VOC's in seven U.S. cities; 25 VOC's at three urban sites in New Jersey; 22 halogenated hydrocarbons in Louisiana; and 48 VOC's regularly found in Sydney, Australia, with an estimated contribution of 90% of the non-methane hydrocarbons measured (Casserly *et al*, 1985).

Through photo-oxidation, VOC's react to produce hydrogen peroxide, reactive carbonyl compounds, organic acids and organic oxidants. There are many oxidation reactions that give rise to the formation of organic acids in the atmosphere, such as formic and acetic acid. Formaldehyde (CH_2O) is formed by the interaction of $\text{HO}^\bullet$ radicals and CH_4 or by ozonolysis of alkenes. The CH_2O may then be oxidised by hydroperoxyl radicals ($\text{HO}_2^\bullet$). The reaction proceeds *via* an electrophilic attack of ozone on the carbon atoms sharing the double bond of the alkene. This results in the formation of a five member ring with two carbon and three oxygen atoms. The mixture of aldehydes and acids are formed when the strained five member ring breaks (Seinfeld, 1998).

Figure 2.3 shows the oxidation of VOC's in the formation of photochemical smog and acid deposition.

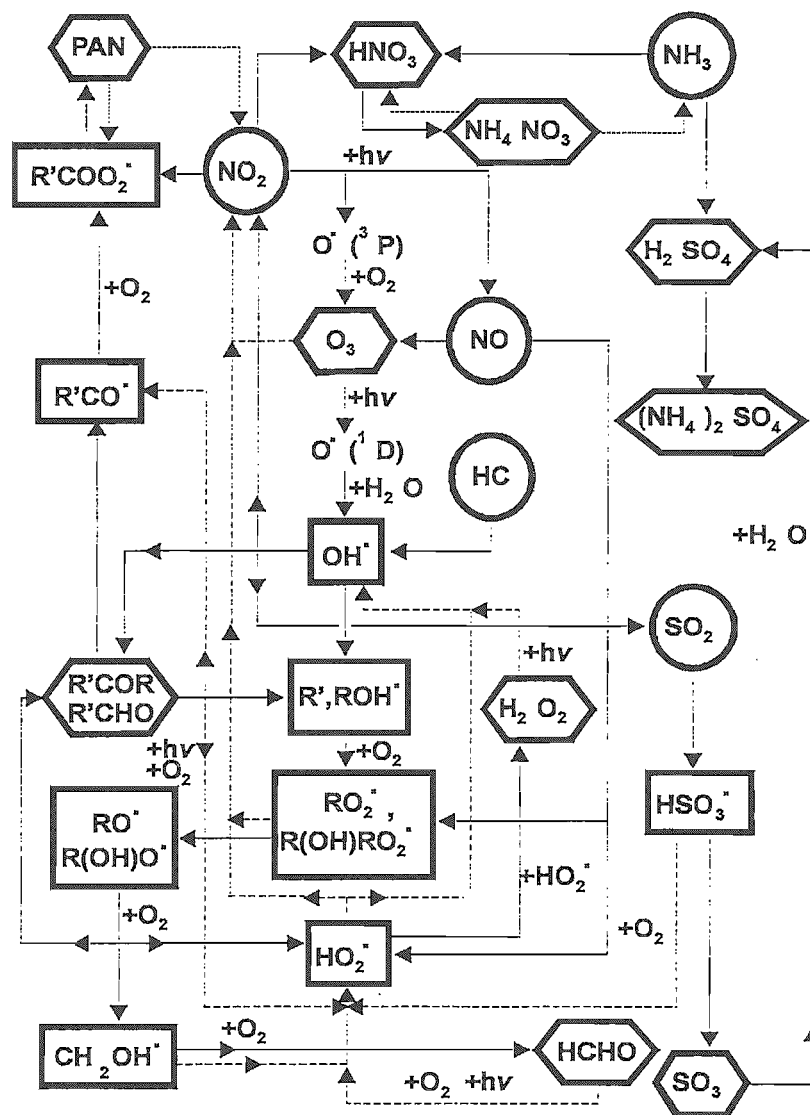


Figure 2.3 – Schematic diagram of the main daytime reactions contributing to photochemical smog formation and dry acid deposition (Bloemen *et al.*, 1993).

2.2.2 Carcinogenicity and toxicity of VOC's

In recent years there has been an increasing interest in the human health effects associated with exposure to hazardous air pollutants (HAP's). To assess the extent of the human health impact due to exposure to HAP's, it is necessary to have available accurate determinations of their atmospheric concentrations under a variety of ambient conditions. Many of the HAP's designated by the EPA as candidates for possible regulatory action are present in the environment at ppb level concentrations (Shepson *et al.*, 1987).

VOC's form part of the HAP's. To find rational mitigation methods, we need to

fully characterise VOC concentrations in as many situations as possible. The spatial and temporal variations of VOC's, and the factors that influence their concentrations, must be determined. These three elements can be investigated only if there is a valid method to measure VOC concentrations. Concern about the occurrence of these compounds in the environment is well justified, since not only have many been proven to have carcinogenic and/or mutagenic properties but these species are also known to be ubiquitous in ambient air to which the general public is exposed. It is generally believed that long term chronic exposure to environmental carcinogens is of greater significance than short-term acute exposure. It is accepted that there will always be some risk, however small, to a population exposed to carcinogenic compounds on a continuous basis. Assessment of the risk from VOC's in air depends on a detailed knowledge of their concentration, particle size distribution and phase distribution.

A further aspect of the risk assessment is the capability of identification and quantification of airborne VOC's present in indoor and outdoor environments. In general the existing sampling, analytical, and bio-assay capabilities have been inadequate to provide sufficient and reliable data for this purpose. Considerable improvements in the analytical methodologies within the last decade, have however enhanced the ability to provide a better measure of exposure levels to the complex mixture of VOC's in ambient air (Larsen,1996).

Polycyclic aromatic hydrocarbon compounds (PAH's) are formed during incomplete combustion or pyrolysis of organic material and in connection with the worldwide use of oil, gas, coal and wood in energy production. Additional contributions to ambient air levels in micro environments arise from tobacco smoking, while the use of unvented heating sources can increase PAH concentrations related to indoor air. Because of such widespread sources, PAH's are present almost everywhere. PAH's are complex mixtures of hundreds of chemicals, including derivatives of PAH's, such as nitro-PAH's and oxygenated products, and also heterocyclic PAH's. The biological properties of the majority of these compounds are as yet unknown. Benzo[a]pyrene (3,4-Benzpyrene) (BaP) is the PAH most widely studied and the abundance of information on toxicity and occurrence of PAH's is related to this compound.

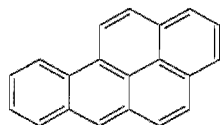


Figure 2.4 - Benzo[a]pyrene (BaP)

Data from animal studies indicate that prolonged exposure to VOC's and several PAH's may induce a number of adverse effects, such as immunotoxicity, genotoxicity, carcinogenicity, reproductive toxicity (affecting both male and female offspring), and possibly also influence development of atherosclerosis (Larsen,1996).

2.2.3 Sampling methods of VOC's

The determination of VOC's in ambient conditions is a difficult task, as concentrations of these compounds are generally low and many of them are unstable and volatile. As a result, a large air sample is required in order to collect sufficient VOC's in order to enhance the accuracy of the measurement. Conversely, short duration sampling is recommended to minimize evaporative losses and to avoid the formation of chemical artifacts during sampling (Baek *et al*, 1990).

It is important to note that volatilization and reaction losses of VOC's collected on filters either by filtration or impactation would inevitably take place during sampling and hence the results may not be expected to yield an accurate distribution of VOC's between the gaseous and particulate phases. Most of the literature is ambiguous concerning the significance of these factors on measuring VOC's, even though any degree of loss during the collection procedure further reduces the accuracy of the data. This issue is particularly important because it may not affect all compounds in an equal manner.

Improvements in sampling methods to capture VOC's present in the vapour phase or to minimize the losses during sampling have relied on the use of various vapour traps such as impregnated filters, solid adsorbents, cryogenic traps and gas bubblers. Glass fibre filters impregnated with glycerotricaprylate captured larger amounts of volatile PAH than untreated filters, but the impregnated filters also lost volatile PAH when sampling was extended to

several weeks (Baek *et al.*, 1990). A variety of solid adsorbents are used to trap vapour phase PAH, including Bondpak C18 on Porasil, XAD, Chromosorb and Tenax. Recently owing to the low pressure drop and ease of handling, polyurethane foam (PUF) plugs have been increasingly used for the collection of organic compounds, and have also been reported to be an effective means of trapping volatile PAH, particularly with high-volume samplers. Cryogenic traps and impingers have not been commonly used for ambient PAH sampling, but these techniques have often been applied for source sampling (Baek *et al.*, 1990).

2.2.3.1 Active sampling of VOC's

In general one of two approaches is used to sample volatile organics in ambient air: whole air collection into specially treated canisters or bags, or selective collection by solid adsorbents.

Tedlar (polyvinyl fluoride) bags and metal canisters are used for VOC sampling. A grabbed or integrated air sample is pumped into the bag or canister and brought back to the laboratory where the hydrocarbons in the sample, including VOC's, are determined with gas chromatography after cryogenic sample preconcentration. VOC's have also been monitored successfully using an on-site gas chromatograph equipped with a photoionization detector (Fung *et al.*, 1985).

A common method of active sampling for VOC's is by adsorption on charcoal in adsorbent tubes. Air is drawn through the tube at a known flow rate using a pump. This technique must not be mistaken for passive sampling, because a pump is used to draw the ambient air through the adsorbent tubes and there is no "natural" diffusion of the ambient air into the tubes. At the completion of sampling, the VOC's adsorbed by the charcoal or adsorbent resin are eluted with a solvent or released by thermal methods and determined by gas chromatography (Fung *et al.*, 1985).

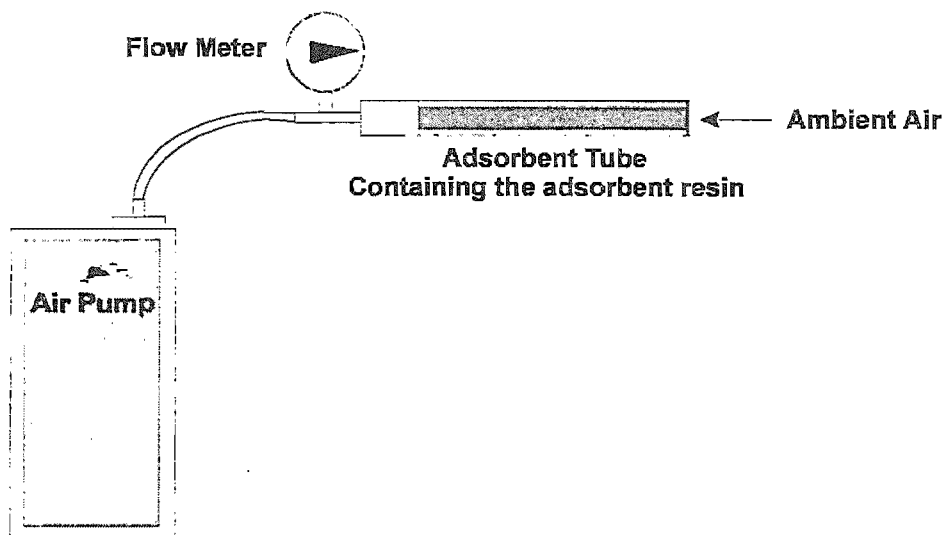


Figure 2.5 – Active VOC Sampling

By far the most widely employed adsorbent resin for volatile organic compounds is Tenax[®] (a porous polymer based on 2,6-diphenyl-p-phenylene oxide) (Hanson *et al*, 1981). Tenax has the advantage of good thermal stability which allows for efficient desorption of higher boiling compounds (e.g., C-12 hydrocarbons) during analysis. A primary limitation of Tenax is the low retention volume of highly volatile compounds (e.g., vinyl chloride, 1,2-dichloroethane, etc.). In order to extend the applicability of solid adsorbent collection to more volatile compounds, a combination of various adsorbents could be used in place of, or in combination with Tenax. The two most promising materials for this purpose are a polyimide material formed from pyromellitic anhydride and 4,4'-diaminodiphenylsulfone, and carbon molecular sieves (CMS) sold under the tradenames Sphero carb[®], Carbosieve[®], or Carbosphere[®] (Holdren *et al*, 1985).

2.2.3.2 Passive sampling of VOC's

While active sampling techniques will yield reliable VOC data, their application to large-scale field monitoring may be costly. A sampling pump and sorbent tube are typically required, which can be a costly venture. Maintenance and flow calibrations all make such programmes even more expensive. Availability of power, instrument noise, and equipment security are major problems in some monitoring situations (Fung *et al*, 1985).

A passive sampler is a cost effective alternative to active sampling for VOC's in

ambient and indoor environments. This commercially available device is inexpensive, lightweight for easy placement and handling, and requires no associated sampling equipment. Passive samplers have been used routinely as personnel monitors in industrial hygiene applications in place of the adsorbent tube/pump (active sampling) method. Due to the potentially high variability of VOC concentrations, investigations of the chronic health effects of VOC's may also require a sampler with a longer exposure duration than the typical <12 hours used for active VOC sampling (Cohen *et al*, 1990).

The passive sampling technique is based on the property of molecular diffusion of gases, hence the term "diffusive sampling". The gas molecules diffuse into the sampler, where they are quantitatively collected on an impregnated filter or an adsorbent material, giving a concentration value integrated over time. No electricity, pump or other equipment is needed at the sampling point.

Inorganic gases are adsorbed by chemical reaction on a filter, impregnated with a solution specific to each pollutant measured. The reaction product, which is washed out with water prior to analysis, is specific to the particular gas in question. Organic gases do not react sufficiently fast with other chemicals and are instead trapped on an adsorbent material. Organic gases are thermally desorbed or dissolved in organic solvents from the adsorbent during analysis (Ferm *et al*, 1991).

The diffusive sampling technique is reliable. Figure 2.6 above shows the correlation between a diffusive and an active sampler for Benzene, Toluene, Ethylbenzene and Xylene collectively known as BTEX (IVL, 1998).

There are two approaches used in passive VOC sampling in the ambient air: diffusive sampling onto an adsorbent resin in a tube, or diffusion onto a charcoal sorbent pad or strip.

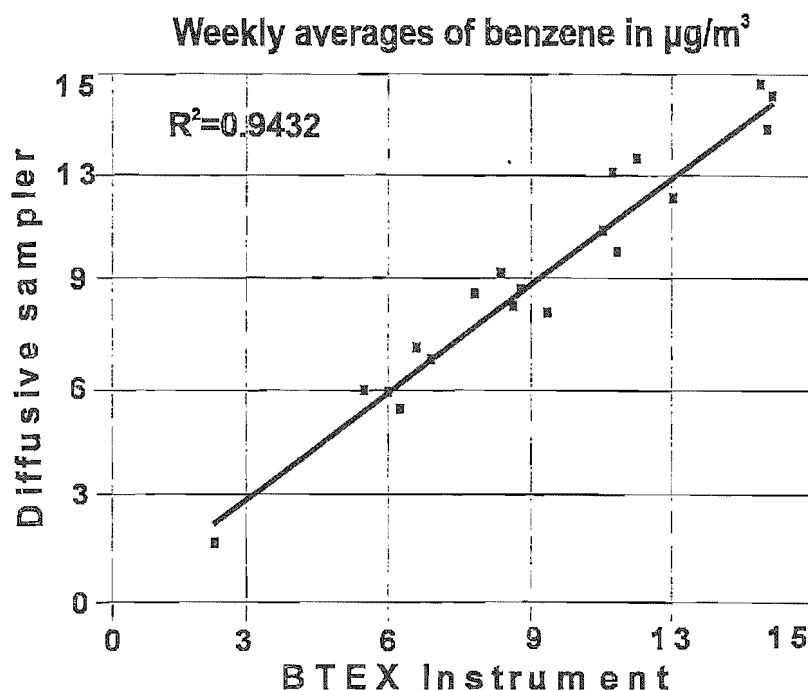


Figure 2.6 – Comparison between weekly averages of benzene obtained using diffusive samplers (Tenax) and weekly averages calculated from a parallel BTEX (active sampling) instrument.

The major disadvantage associated with the use of a passive monitor to sample volatile organics in ambient air is the relatively long sampling period required to collect sufficient material for analysis. Most uptake rates for this sampler lie between 15 and 35 cm^3/min . Studies that employ active sampling to collect VOC's typically use flow rates in the range of 100 to 150 cm^3/min . Thus, it may take five times as long to collect the same amount of a given compound with passive sampling as in the case with active sampling. For this reason active sampling is better suited to monitoring short term fluctuations in concentrations of organic species. Passive sampling is less accurate than active sampling, because of the following disadvantages: 1) For certain polar species, especially amines and nitro compounds, the carbon sorbent pads are not reliable sampling media. 2) The passive sampler is not an appropriate collector for unsaturated compounds such as hexene which can undergo reactions on the surface of the charcoal sorbent. 3) Finally, poor analyses are frequently obtained for low boiling compounds. Best results are obtained for compounds with boiling points between 100°C and 300°C (Ferm *et al*, 1991).

In addition to equipment considerations, passive sampling has several analytical advantages over active sampling as a collection approach. 1) With active sampling, a fraction of the more volatile compounds are commonly lost during the sampling period. This is due to vacuum desorption of the trapped analytes. With passive sampling, vacuum desorption is not a concern. 2) Tenax is frequently used as a sorbent for active sampling. Unfortunately, data obtained using Tenax is plagued by severe artifact problems in the case of benzaldehyde, acetophenone, and benzonitrile; there are also possible artifact or retention problems with benzene, toluene, and styrene. These artifact problems are not present with a passive sampler that utilizes a carbon sorbent. 3) Finally, with active sampling airborne particles must be filtered out of the sampling stream; subsequent 'blowoff' of organics from particles collected in the upstream filter can result in non-representative sampling of ambient vapours. With the passive sampler the diffusion screen prevents diffusion of particles to the sorbent surface, and, because there is no pumping, blowoff does not occur (Cohen *et al*, 1990).

Only charcoal pad adsorbent samplers were investigated in this study. A more detailed description of passive sampling of VOC's will follow in Chapter 3.

2.3 ATMOSPHERIC DEPOSITION

In recent years, "acid rain" has received great attention as a global environmental problem, because of the effect of acidic deposition within various ecosystems. Extensive studies were undertaken in order to understand how acid forming precursor gases (SO_2 and NO_x) would be deposited in the environment (Obasi, 1996).

There are two pathways according to which chemical species are removed from the atmosphere: wet deposition and dry deposition. Wet deposition is the removal by precipitation scavenging and, to a lesser extent, impaction of fog or cloud droplets on vegetation. Dry deposition includes the direct adsorption or deposition of gases on the surface of particles, and the settling and impaction of particles. On a global scale, precipitation scavenging and dry deposition are by far the most efficient methods. Fog and droplet deposition can be locally important, especially in cloudy, high elevation regions in South Africa (WMO,

1996).

2.3.1 Wet deposition

Precipitation scavenging is an effective mechanism for removing soluble trace gases and small particles from the troposphere. The gases and particles are incorporated into cloud droplets and precipitation in several ways. Those trace particles in the atmosphere that act as ice-forming nuclei or condensation nuclei can be incorporated into hydrometeors during the nucleation process itself. This is the process that generates cloud droplets from which raindrops form. In many parts of the world, sulphate particles are the most commonly found condensation nuclei in the atmosphere. The cloud droplets that are generated continue to scavenge gases and particles in cloud as they grow in size. As they grow, the droplets fall faster until they leave the cloud base and are deposited as rain, carrying all of the scavenged pollutants with them. It is not only particulate sulphate that is scavenged in this way, gaseous sulphur dioxide can also be dissolved in cloud droplets, whereupon it can be oxidized to sulphate by means of aqueous-phase chemical reactions (Summers, 1992).

Hydrometeors falling from a cloud can scavenge other pollutants with which they come in contact. This sub-cloud scavenging is often relatively inefficient in comparison to in-cloud processes, especially in the case of convective cells. In these cloud "processes" a steady stream of air passes through, scavenging pollutants from the stream in a continuing dynamic process. In short, convective precipitation cells are among the most efficient mechanisms for cleaning the atmosphere (Summers, 1992).

Clearly, the actual wet-deposition flux of chemical species to the surface depends on many factors. The most important ones are precipitation from (rain, snow, etc.) and precipitation rate, both of which are strongly related to cloud type, as well as ambient air concentrations within and below a cloud. These complex physicochemical processes can be integrated into several parameters such as scavenging ratio, scavenging efficiency, and scavenging rate. These quantities have varying degrees of applicability, depending on the kind of precipitation system that is considered, but all of them can be formulated from observations giving the "bulk" characteristics of precipitating weather systems.

For example the mass scavenging ratio (S_R) is defined as the concentration of the dissolved chemical species per unit mass of cloud water or rain (C_r) divided by the total concentration of the same species (or its precursor) per unit mass of ambient air, including the mass water in the air (C_a):

$$S_R = C_r / C_a \quad (2.1)$$

The typical liquid water content of precipitating clouds is 1 g of water per 1 m³ of air at STP (but it ranges from 0.1 to 5.0). Since 1 m³ of air weighs approximately 1 kg (STP), if all the trace species in 1 m³ of air were dissolved in the cloud water (i.e., 100% scavenging efficiency), the species concentration in the rain would be magnified by a factor of 1000 and the scavenging ratio would be 1000. In practice, the efficiency of removal of either pollutants or of water itself is not 100%, and hence the scavenging ratio can vary greatly. At a few locations in North America (Barrie, 1988) and Europe where concentrations of sulphur and nitrogen species have been simultaneously measured in the air and precipitation, values of S_R varied from 100 to a few thousand (Barrie, 1988).

The wet-deposition rate (D_W) is given by the precipitation rate (R) times the species concentration in the rain (C_r):

$$D_W = C_r R = S_R R C_a \quad (2.2)$$

The ratio $S_R R$ is thus analogous to the dry-deposition velocity in the formulation of the dry-deposition flux. However, for wet deposition, C_a refers to the air concentrations at various atmospheric elevations where the species are being incorporated into cloud- and rainwater, whereas for dry deposition, C_a refers to the air concentration immediately above the surface (Barrie, 1988).

The wet deposition in a given precipitation event is calculated as the product of the total precipitation (P) times the measured concentration (C_r) of the species within the precipitation. In many regions the day-to-day variation in wet-chemical deposition is controlled more by the precipitation amount than by trace-chemical concentrations (Barrie, 1988).

One overwhelming characteristic of wet deposition is how much the total wet deposition of one chemical species can vary from one event to another.

Precipitation itself is a highly intermittent phenomenon occurring about 5% of the time in the midlatitude cyclonic belt, with amounts varying for a given trace with several centimeters from one event to the next; the concentration of a chemical species can vary by an order of magnitude. The largest difference between events occurs on the periphery of industrial regions where emission rates are high. There, depending on air-mass trajectories, the air can be clean or heavily polluted. Within regions with high emissions and in remote areas, the concentrations vary less. Thus, in southeast Canada and southern Scandinavia, wet-deposition episodicity is the highest, with less than 10% of the wet days accounting for 50% or more of the annual wet deposition of sulphate being typical. In extreme cases a single precipitation event can contribute up to 30% of the annual chemical deposition (Summers, 1992).

2.3.2 Dry deposition

Dry deposition must always be considered in any calculation of total deposition of an acidifying compound, whether it is related to a specified receptor or to a large area. The dry-deposition process involves close interaction between the atmosphere and the surface in which the characteristics of individual underlying surfaces often determine the mass-transfer rates. Depending on the characteristics of the surface, the ability to "capture" pollutants from the air may vary by more than an order of magnitude, causing highly varied dry-deposition rates even over small areas. Forests, especially coniferous forests, normally receive relatively high dry deposition of acidifying compounds, whereas lake surfaces receive much lower ones. Deposition extremes are often observed at forest edges or in forests on mountain slopes.

In any circumstance dry-deposition rates are proportional to the concentrations of air immediately above (or surrounding) the receptor under consideration. The "constant" of proportionality is referred to as a deposition velocity (V_d) which depends on factors mainly associated with turbulence and related to characteristics of the air near the surface, as well as the composition of the surface itself. Depending on the chemical in question, different factors assume important roles in determining the magnitude of V_d . In the case of sulphur dioxide, for example, the surface moisture and the photosynthetic activity of

vegetation are important factors. The dominant terrestrial surface sink of sulphur dioxide is via open stomata into plant mesophyll tissue. Actively respiring vegetation presents a good sink for SO_2 , whereas the same vegetation suffering under water stress does not (Sheih *et al.*, 1979).

In practice, using a standardized deposition velocity in numerical models is an engineering approximation that is particularly attractive in relation to large-scale simulations because it combines the effects of many complex processes into a single term (Wesely and Hicks, 1977).

In conclusion, we note that the use of a deposition velocity approach in large-scale numerical models is a simplification of complicated processes that results in substantial computational convenience. This is in contrast to the complexity with which chemical reactions are addressed in advanced Eulerian models. If deposition processes were described with the detail permitted by current understanding, much greater surface detail would be required and computation time would be increased considerably (WMO, 1996).

2.3.3 Effects of acidic deposition

Acid deposition and accompanying effects were first noticed as a large-scale environmental problem at the end of the 1960's. During the 25 years since it was originally observed, acidification effects have occurred in many ways and in various ecosystems. Early observations of acidification effects in lakes and streams were followed by later observations of groundwater acidification and, later still, soil acidification. Acid deposition had a considerable negative impact on materials (WMO, 1996).

Acidification effects are primarily associated with the atmospheric deposition of sulphur and nitrogen compounds. Deposition may occur in the form of strong acids (sulphuric acid, nitric acid, and infrequently hydrochloric acid) or compounds, which, after deposition, may be converted to strong acids (e.g., sulphur dioxide and nitrogen dioxide). In this context ammonia is also a potentially strong acid. In soils it may be converted to nitric acid and thus cause acidification. In tropical areas organic-acid deposition may contribute as much as 50% of the deposition of acids in precipitation. It is, however, assumed that

these acids are absorbed or oxidized in soil and will not contribute to soil acidification (McDowell, 1988).

Acid deposition has been of interest not only for its role in acidification but also for effects associated with the deposition of nitrogen as a nutrient. Also, direct effects from sulphur dioxide and nitrogen oxides have sometimes been considered as acidification effects. It is, however, important to note that in many areas of the world, concentrations of sulphur and nitrogen oxides exceed ambient air quality standards, and considerable emission reductions are necessary to protect human health. Sulphur and nitrogen compounds may also affect physical and chemical properties of the atmosphere (Isaksen and Hov, 1987; Langner *et al.*, 1992).

2.3.3.1 Pathways of sulphur deposition

The primary emissions of sulphur are in the form of SO₂, with a small proportion already oxidized to sulphate. SO₂ is quite readily dry deposited, but is relatively insoluble in cloud water, since dissolved SO₂ comes to an equilibrium which depends on the cloud water acidity. However, conversion of the gas to soluble sulphate aerosol, and chemical reactions within cloud droplets, results in wet deposition being an equally important process related to sulphur emissions.

Anthropogenic sulphur is mostly deposited from the atmosphere as S(IV) (sulphur dioxide) and S(VI) (sulphates or sulphuric acid). Sulphur dioxide is deposited through dry deposition processes, mainly by means of direct uptake by plants through their stomata. After uptake, sulphur dioxide is, to a large extent, oxidized to sulphuric acid, which may be transferred to the surface of the leaves and then washed off by precipitation. Particulate sulphur is deposited to the ground by different mechanisms (e.g., turbulent diffusion and sedimentation). Rough surfaces, such as forests, receive relatively more dry deposition than open flat areas such as agricultural land. Much of the sulphur deposited on vegetation is washed off through the process of precipitation (Hultberg and Grennfelt, 1991).

Dry deposition varies considerably depending on the receptor type. Some receptors that are at risk from acidification effects may themselves increase dry

deposition. This is the case in coniferous forests, which may increase their relative sensitivity to damage because of their high filtering efficiency. Dry deposition on such receptors may be more than twice of the wet deposition, although dry deposition to adjacent open land may only comprise a small fraction of the wet deposition. Deposition to forests may be enhanced at forest edges or in the case of forests growing on slopes or ridges in mountain areas (Ivens, 1990; Fowler *et al.*, 1993).

In tropical or other well-weathered soils, significant sulphur deposited from the atmosphere is retained in the soil. Retention of sulphate is accompanied by retention of an equal amount of hydrogen ions. Sulphate retention may then be regarded as retention of sulphuric acid (Eriksson, 1988).

2.4 MATHEMATICAL MODELLING

It is becoming common in the environmental sciences to describe complex systems of interacting physical, chemical, and biological processes through the design of numerical "models." These models consist of sets of mathematical equations that attempt to describe processes observed in nature, allowing scientists to create replicas of natural systems with a computer so that the causes and effects of system behaviour may be better understood. Although we can study individual interactions within a system by using laboratory simulations or, under favourable conditions, by directly observing nature, the complexity of Earth system processes makes the use of these mathematical models necessary, in order to comprehend the behaviour of the system as a whole (Graedel *et al.*, 1997).

Once scientists are sufficiently convinced of a model's validity, they begin to use the model to predict future conditions arising from changes in important variables within the system such as natural processes, solar activity, volcanic eruptions, anthropogenic factors, and emissions of industrially produced trace gases. Models can also be used to study the past, which in turn provides additional opportunities for testing the models or for learning more about past processes, such as continental drift, etc. It is the ability of models to explore situations remote from current conditions and unavailable in reality - as well as their ability to allow numerical experiments aimed at the question, "what would happen if...?"

- that makes them potentially valuable.

Numerical atmospheric models differ greatly in complexity, especially in their degree of spatial and temporal resolution. Ideally, a model should be able to generate predictions specific to large and small geographical areas and for long and short time intervals. In practice, though, the information required to perform the calculation may not be available, or the capabilities of computers may be insufficient. All computer modelling efforts at best represent trade-offs: scientists must choose spatial and temporal resolution at the expense of physical, chemical, and meteorological detail, or vice versa. For example, smog chemistry may be calculated in great detail, but only for a single city, or climate could be calculated for a century, but only for continents instead of individual regions. Each choice has its uses and limitations; no single model can serve all needs (Graedel *et al*, 1997).

It is recognised that chemistry affects climate and environmental change in many ways. Yet programmes which incorporate chemistry into atmospheric models are not as advanced or well-defined as models for coupled atmospheric and oceanic dynamics are. There are several reasons for this drag in progress. First, the climate modelling community and air pollution researchers have each had their own separate development, measurement and validation programmes over the years. Similarly, the atmospheric chemistry community has worked independently. Secondly, solving the atmospheric chemistry problem in three dimensions is more daunting than solving dynamics and radiation problems in similar dimensionality, because of the large number of species involved and the extreme difference in the time scale for chemical reactions and atmospheric models, ranging from the micro scale in the former to days in the latter. This is called numerical "stiffness" in the equations that govern their behaviour.

2.4.1 Modelling needs

"Traditional" air pollution problems are local scale ones, that is, those occurring in the surroundings of isolated sources. More recently, environmental policy has to a large extent been confronted with global scale problems (global warming, ozone depletion). Other important policy issues related to the atmospheric environment are acidification, eutrophication, photo-oxidant formation, urban air

pollution and the problem of air toxics (Table 2.1).

Acidification is related to the emissions of sulphur dioxide, nitrogen oxides and ammonia. Nutrifaction refers to nutrients added to the environment. A combination of maps of critical loads of acidity and deposition matrices from air pollution models show that excess of the critical loads is found in large areas of Europe (Downing *et al.*, 1993). Originating from emissions of nitrogen oxides and ammonia, eutrophication of the ecosystem through excess nitrogen deposition is a problem of growing concern (Skeffington and Wilson, 1988). Finally, the emissions of nitrogen oxides and VOC's create high levels of near surface ozone and other toxic photochemical compounds. Critical levels of ozone are frequently exceeded during the summer season in many parts of Europe according to the WHO. Also, the European ozone concentration levels are above the critical level for plants during the growing season in the largest part of Europe (Anttila, 1993).

Co-ordinated, longterm international actions are needed for solving regional scale air pollution problems. On the other hand, air quality at local scale, typically in urban agglomerations, may be improved with a proper abatement strategy of local character, e.g. interventions tailored to the specific situation in the area of interest. Being indispensable for optimising such abatement strategies, air pollution models may substantially support local environmental policy making (Batterman *et al.*, 1997).

At present there are clear needs to develop new protocols for the reduction of acidifying compounds created by emissions of NO_x and NH_3 and low level ozone originating from emissions of NO_x and VOC's. Regional scale models will have to play an important role in the development of these protocols. Souncereceptor relationships, "blame matrices" quantifying the contribution from one country in relation to the air pollution of another country, total loads to the ecosystem, and emission scenario analysis will be important tools needed and extrapolated from the models. The inclusion of both the acidification problem and the surface ozone problem into these protocols will inevitably put greater demands on the capabilities of the models.

Table 2.1 - Policy issues related to the atmospheric environment and corresponding scale(s) of dispersion phenomena.

Policy issue	Scale of dispersion phenomenon			
	Global	Regional-To-Continental	Local-to-Regional	Local
Climate change	X			
Ozone depletion	X	X		
Tropospheric ozone		X		
Tropospheric change		X		
Acidification		X		
Nutrification		X		
Summer smog		X	X	
Winter smog		X	X	
Air toxics		X	X	X
Urban air quality			X	
Industrial pollutants			X	X
Nuclear emergencies		X	X	X
Chemical emergencies		X	X	X

Detailed and time consuming models are needed to build proper control strategies based on analysis of the interactions between different air pollutants. Such simulations need to be performed either for longer time periods or, in an attempt to reduce the computational effort, for individual representative scenarios (Moussiopoulos *et al.*, 1996).

2.4.2 Instruments for air quality assessment studies

During air pollution assessment, information on all the relevant aspects of the cause-effect chain has to be collected. The physical/chemical description of ambient air has to be presented in such a way that it can be compared with

effective threshold values, and the relation between this effect quantity and the atmospheric emissions from sources (e.g. source categories, countries, regions, economical sectors) should be quantified. Only when all three elements, (threshold or critical values, ambient parameters and emissions) are available, can an optimal abatement strategy be developed. Three types of instruments are used in assessment studies: emission inventories, atmospheric dispersion and transport models, as well as air quality measuring programmes (Moussiopoulos *et al.*, 1996).

Air quality monitoring may be defined as the systematic collection of information from measurements or other means in order to determine the levels and the time evolution of quantities relevant to air quality. Such quantities include air concentrations, fluxes of air pollutants to land or water surface, and the exposure of human beings, materials, and ecosystems to air pollution.

Although measurements form an important aspect of monitoring, measurements alone are rarely sufficient to determine the impact of air pollution on the environment. Models are often needed to establish larger scale average exposure and deposition fields, which cannot easily be derived from measurements. The reason is simply that observations are made at a few locations only and may therefore not be very representative of larger areas. Substantial uncertainty can be introduced if measured data are extrapolated or interpolated into larger domains. Models are therefore used to generate best estimates in situations where measurements are lacking or cannot be made. Models are also necessary if the relative impact of various sources (source categories, emissions from different regions or countries) or emission scenarios have to be investigated. A consistent mass budget of emission, transport and deposition can only be obtained by means of employing models.

2.4.3 Application areas of air quality models

A wide range of different models have been published in scientific papers, and even a larger number of unpublished models and special model versions exist. Models can be distinguished on many grounds: e.g. the underlying physical concepts, the temporal and spatial scale, and the type of component involved. Contemporary air pollution models deal with "conventional" primary pollutants

(mainly SO₂, CO, NO_x and VOC's). At present the need is recognised for extending the models to include heavy metals and persistent organic pollutants (POPs). Modelling of visibility, particulate concentrations (particulate matter with a size distribution smaller than 10 µm - PM 10) and aquatic phase chemistry are among the most important current model developmental trends (Moussiopoulos *et al.*, 1996).

Four groups of application areas are defined for air pollution models: *regulatory purposes, policy support, public information and scientific research.*

2.4.4 Model validation and evaluation

Analysing the potential for the practical use of mathematical models for air quality assessments implies investigating the following aspects:

- Which kind of statements can be made by the aid of models (qualitative approach).
- The accuracy of these statements (quantitative approach).

It appears that the former approach is easier, because it only requires knowledge of the characteristics and the application range of a model. In addition to this, quantification of the accuracy of the model results presupposes insights into the following:

- Input data accuracy and how the latter affects the accuracy of model results.
- Uncertainties in model assumptions and parameterisations.
- Methodologies for judging to which extent model results represent reality.

As a consequence of the above, model validation (typically with the aid of available analytical solutions) should be considered as an indispensable part of the model development process, whereas a model which has been validated already, should be subject to a more thorough evaluation procedure in order to ensure that potential users can assess the degree of reliability and accuracy inherent in the given model. High quality field data which is needed for evaluation purposes is, however, very rare (Moussiopoulos *et al.*, 1996).

2.4.5 Overview of different approaches to air quality modelling

Air quality modelling involves the investigation of individual processes in laboratory experiments as well as field observations. The use of numerical models enables the description of complex, interacting, often non-linear processes encountered in atmospheric chemical processes.

2.4.5.1 Definitions

Air pollution dispersion phenomena are decisively influenced by atmospheric processes, which are commonly classified with regard to their spatial scale. The latter is in turn related to the characteristic time of the individual process. Orlanski (1975) recommends distinguishing the following scales:

- **Macroscale** (characteristic lengths exceeding 1,000 km); at this scale, the atmospheric flow is mainly associated with synoptic phenomena, that is, the geographical distribution of pressure systems. Such phenomena are mainly due to large-scale inhomogeneties of the surface energy balance. Global dispersion phenomena (as well as the majority of regional-to-continental scale) are related to macroscale atmospheric processes, for which the hydrostatic approximation can be considered as valid.
- **Mesoscale** (characteristic lengths between 1 and 1000 km); the flow configuration in the mesoscale is dependent both on hydrodynamic effects (e.g. flow channelling, roughness effects) and inhomogeneties of the energy balance (mainly due to the spatial variation of area characteristics (e.g. land use, vegetation, water)), but also as a consequence of terrain orientation and slope. From the air pollution point of view, thermal effects are the most interesting, as they are of particular importance at times of weak synoptic forcing, that is, bad ventilation conditions. As a minimum requirement mesoscale meteorological models should be capable of simulating local circulation systems, for instance sea and land breezes. Mesoscale atmospheric processes affect primarily local-to-regional scale dispersion phenomena, of which urban studies are the most important examples. The description of such phenomena requires, even for practical applications, the utilisation of fairly complex modelling tools.
- **Microscale** (characteristic lengths below 1 km); in general, air flow is

exceedingly complex at this scale, as it depends strongly on detailed surface characteristics (that is, form of buildings, their orientation with regard to the wind direction, etc.). Although thermal effects may contribute to the generation of these flows, they are mainly determined by hydrodynamic effects (e.g. flow channeling, roughness effects) which have to be described well in an appropriate simulation model. In view of the complex nature of such effects, local scale dispersion phenomena (which are to a large extent associated with microscale atmospheric processes) are mainly described with robust "simple" models in the case of practical applications, such as street canyon models, etc.

2.4.5.2 Air pollution model types

Models describing the dispersion and transport of air pollutants in the atmosphere can be distinguished on many grounds, for example:

- The spatial scale (global, regional-to-continental, local-to-regional, local).
- The temporal scale (episodic models, (statistical) long-term models).
- The treatment of transport equations (Eulerian, Lagrangian models).
- The treatment of various processes (chemistry, wet and dry deposition).
- The complexity of the approach.

Following Zannetti (1993), the following model categories can be distinguished:

- Plume-rise models. In most cases, pollutants injected into ambient air are at a higher temperature than the surrounding air. Most industrial pollutants, moreover, are emitted from smoke stacks or chimneys and therefore possess an initial vertical momentum. Both factors (thermal buoyancy and vertical momentum) contribute to increasing the effective stack height. Plume-rise models calculate the vertical displacement and general behaviour of the plume in this initial dispersion phase. Both semi-empirical and advanced plume-rise formulations are available.
- Gaussian models. The Gaussian plume model is the most common air pollution model. It is based on the assumption that the plume concentration at each downwind distance has independent Gaussian distributions both in the horizontal and in the vertical axis. Almost all the models recommended by the

EPA are Gaussian. Gaussian models have been modified to incorporate special dispersion cases. A simplified version of the Gaussian model, the Gaussian climatological model, can be used to calculate long-term averages (e.g. annual values).

- **Semi-empirical models.** This category consists of several types of models which were developed mainly for practical applications. In spite of considerable conceptual differences within the category, all these models are characterised by drastic simplifications and a high degree of empirical parameterisations. Among the members of this model category are box models and various kinds of parametric models.
- **Eulerian models.** The transport of inert air pollutants may be conveniently simulated by the aid of these models which numerically solve the atmospheric diffusion equation, that is, the equation for conservation of mass of the pollutant (Eulerian approach). Such models are usually embedded in prognostic meteorological models. Advanced Eulerian models include refined sub-models for the description of turbulence (e.g. second-order closure models and large-eddy simulation models).
- **Lagrangian models.** As an alternative to Eulerian models, the Lagrangian approach consists in describing fluid elements that follow the instantaneous flow of air. They include all models in which plumes are broken up into elements such as segments, puffs, or particles. Lagrangian models use a certain number of fictitious particles to simulate the dynamics of a selected physical parameter. Particle motion can be produced by both deterministic velocities and semi-random pseudo-velocities generated using Monte Carlo techniques. Hence, transport caused by both the average wind and the turbulent terms due to wind fluctuations is taken into account.
- **Chemical modules.** Several air pollution models include modules for the calculation of chemical transformation. The complexity of these modules ranges from those including a simple, first-order reaction (e.g., transformation of sulphur dioxide into sulphates) to those describing complex photochemical reactions. Several reaction schemes have been proposed for simulating the dynamics of interacting chemical species. These schemes have been implemented into both Lagrangian and Eulerian photochemical models. In Eulerian photochemical

models, a three-dimensional grid is superimposed to cover the entire computational domain, and all chemical reactions are simulated in each cell at each time step. In the Lagrangian photochemical models a single cell (or a column of cells or a wall of cells) is advected according to the main wind in a way that allows the injection of the emissions encountered along the cell trajectory.

- **Receptor models.** In contrast to dispersion models (which compute the contribution of a source to a receptor as the product of the emission rate multiplied by a dispersion coefficient), receptor models start with observed concentrations within a receptor and seek to apportion the observed concentrations at a sampling point among several source types. This is done based on the known chemical composition of source and receptor materials. Receptor models are based on mass-balance equations and are intrinsically statistical in the sense that they do not include a deterministic relationship between emissions and concentrations. However, mixed dispersion-receptor modeling methodologies have been developed recently and are very promising.

- **Stochastic models.** Stochastic models are based on statistical or semi-empirical techniques to analyse trends, periodicities, interrelationships of air quality, atmospheric measurements and to forecast the evolution of pollution episodes. Several techniques are used to achieve this goal, e.g., frequency distribution analysis, time series analysis, Box-Jenkins and other models, spectral analysis, etc. Stochastic models are intrinsically limited because they do not establish cause-effect relationships. However, stochastic models are very useful in situations such as real-time short-term forecasting, where the information available from measured trends in concentration is generally more relevant (for immediate forecasting purposes) than that obtained from deterministic analyses.

Table 2.2 gives a summary of each scale of dispersion phenomenon.

Table 2.2 – Summary of each scale of dispersion phenomenon: 1. Regulatory purposes; 2. Policy support; 3. Public information and 4. Scientific research.

Scale of atmospheric process	Microscale	Mesoscale	Macroscale	
Scale of dispersion phenomenon	Local	Local-to-regional	Regional-to-continental	Global
Model type				
Plume-rise	1,2,4			
Gaussian	1,2,4	1,2		
Semi-empirical	1,2,3,4	1,2,4		
Eulerian	1,2,4	2,3,4	2,4	2,4
Lagrangian	4	4	2,4	
Chemical	1,2,4	2,3,4	2,4	2,4
Receptor		2,4		
Stochastic		2,4		

2.4.6 Introduction to box models

The simplest model for atmospheric applications is the box model, envisioned as a box into which some chemical species are added, from which some chemical species are taken away, and within which chemical changes occur. The focus of this study will be on box models and these will therefore be discussed in more detail.

Chemical species enter the box in two ways: they are emitted from sources within the box, or they enter by entrainment (the addition of air and its chemicals into the box from the surroundings as a consequence of atmospheric motions). Conversely, detrainment (the loss of air and its chemicals into the surroundings), advection and surface deposition represents a loss of chemical species. Often a box model of atmospheric chemistry is "placed" at ground level at a specified location so that the chemical effects of emissions from the geographical region

into the air immediately above it can be studied (Graedel *et al*, 1997).

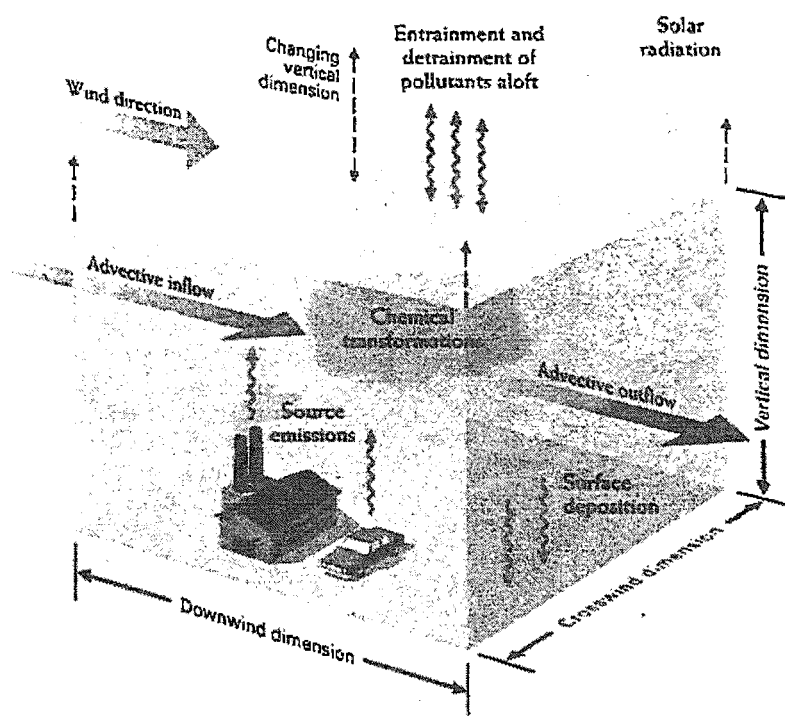


Figure 2.7 – Schematic diagram showing the features of a box model of atmospheric chemistry (Graedel *et al*, 1997).

The dimensions and placement of the box are normally dictated by the particular problem of interest. If one wishes to study the influence of urban emissions on the chemical composition of the air leaving an urban area, for instance, then the box may be designed to cover the entire urban area, and emissions may be assumed to be mixed thoroughly throughout the box. Chemical species from outside the box are "blown" into the box. The chemical composition of the air within the box is then determined by the model. Chemical reactions must, of course, be taken into account. Key assumptions are the following: the pollutants are completely uniformly mixed within the box and that uniform atmospheric properties prevail throughout the box. Because a few of the chemical reactions within the box are driven by solar radiation, appropriate wavelength-dependent solar fluxes must be incorporated into the calculations. The ensuing reactions could be considered as sources of new chemical species as well as sinks for existing molecules and atoms. Not only gasphase reactions but also chemical reactions on the surfaces of aerosol particles, in cloud or fog droplets, or in

raindrops are often considered in the box model. Many investigators are at least as interested in the products of chemical reactions as in the primary emissions themselves. These products include the generation of ozone from hydrocarbons and oxides of nitrogen and the formation of sulphate particles from sulphur dioxide.

In many calculations in traditional scientific fields, the relevant equations are set up, the required input data supplied, and if everything is formulated properly, the result will be generated by the computer. An Earth system calculation, however, is generally more complicated because of the investigator's interest in the system's progress over time. In other words, most models of atmospheric chemistry are time dependent. Thus, the results of the first calculation must be related to a new calculation, along with appropriate new information on emissions, radiation, and so forth, in order to compute a result for a later stage in the system's development. The interval between the times represented by the sequential calculations is known as the "time step". It can be large if all the factors are changing slowly, but must be quite small if factors (such as emissions from rush-hour traffic) are rapidly changing. A complete model result, therefore, may encompass hundreds or thousands of calculations as scientists attempt to mimic the changing world from the beginning to the end of the time span at hand (Graedel *et al*, 1997).

An example of a time-dependent box model might be one designed to compute urban air quality for a 24-hour day. Any variations over that period of time in any of the influential factors would need to be accurately supplied to the model; these variables would certainly include hourly variations in traffic and other pollution sources, diurnal wind-speed patterns, variations in the height of the well mixed layer in the lowest kilometer or so of the troposphere, and the variation of solar radiation.

To construct a box model, the builder first defines the dimensions of the box and an appropriate approach to time variations. Next, pertinent variables-source fluxes, surface depositions, advection and entrainment rates, and so forth, are represented by mathematical formulas, and initial and boundary flux conditions are specified. The suitable description of each of these factors has been and

continues to be a topic of inquiry, which entails that representing them mathematically is a complicated exercise requiring many decisions, some well constrained, some not. The appropriate chemical reactions in the box must then be decided on. This is a potentially difficult task because the Earth systems are chemically so complex that often not all reactions of interest are identified. Furthermore, sometimes the rate constants or absorption coefficients for a known reaction have not been determined in the laboratory, in which case estimates must be used instead. There is always the risk that some key processes have not even been discovered yet or those chemical reactions that were rather unimportant or were unknown to investigators (in the past), have become important because of human-induced changes in atmospheric conditions.

The box model is sometimes called a "zero-dimensional" model because of its inability to calculate variations in any spatial dimension, horizontal or vertical. Rather, the set of results it computes, at each time step, is an estimate of the average meteorological conditions and chemical composition within the box at a given point in time. As a consequence, box models are generally best used for a first assessment of a particular problem. It is not intended to be definitive but to provide a quick and rough idea of the most important processes, without the tedious and exacting requirements for determining the details of horizontal wind speeds, vertical mixing times, emissions fluxes in different locations, etc.

The simplest improvement over the zero-dimensional box model is to compute changes in the concentrations of chemical species as a function of a single spatial dimension. This approach allows the model to capture, for example, the variation of ozone with height. The earliest models of this type were constructed for studying the chemistry of the middle atmosphere (the stratosphere and mesosphere), and therefore altitude was chosen as the variable dimension in the past. In more recent years the troposphere has also been simulated with one-dimensional models, again with altitude as the variable dimension.

2.4.6.1 Equations and chemistry for box models

Chemical kinetics must obey the law of mass action. The notation used to describe chemical reactions is widely understood. The simplest reaction to

occur is an irreversible one in which one species (*A*) is converted to another species (*B*) with a known rate coefficient. The chemical notation for this is as follows:



where $[A]$ and $[B]$ represent the concentrations of species A and B respectively, and k_f is the known rate coefficient of the reaction. Mathematically, this would be formulated as follows:

$$\frac{d[A]}{dt} = -r_f \quad (2.4)$$

$$\frac{d[B]}{dt} = r_f \quad (2.5)$$

where $r_f = k_f[A]$ is the rate of conversion of A to B.

When considering the unimolecular gas phase decomposition of the species N_2O_5 as an example, the chemical reaction of which would be as follows:



where k_f is the chemical rate constant for the decomposition process. The rate of N_2O_5 depletion and the corresponding forming rate of NO_2 and NO_3 is given by the following differential equation:

$$-\frac{d[N_2O_5]}{dt} = k_f[N_2O_5] \quad (2.7)$$

$$= \frac{d[NO_2]}{dt} \quad (2.8)$$

$$= \frac{d[NO_3]}{dt} \quad (2.9)$$

where the notation $[N_2O_5]$ means the concentration of the species. Reversible reactions in the model are treated as a series of irreversible reactions (Facsimile Users Guide, 1998).

All the chemical species in the box has been defined as variables in the model.

Each chemical reaction related to a specific species in the box is specified as a differential equation. The chemical mechanism for a specific problem therefore results in a series of differential equations. The complexity of a chemical mechanism requires the simultaneous solution of hundreds of coupled differential equations in real time.

The rate of chemical change of a chemical species i within the box can be described as follows:

$$\frac{dc_i}{dt} = P_i - L_i c_i - \frac{V_i c_i}{h} - k_h c_i \quad (2.10)$$

where c_i is the concentration of the species in the box, P_i is the production term, $L_i c_i$ describes the loss due to homogeneous chemical and photolysis reactions, V_i is the deposition velocity of the species i over height h , and k_h is the rate of loss of the species by heterogeneous processes (Jenkin *et al.*, 1997).

The integration of all the differential equations over time delivers the numerical solution for each chemical species. This integration of the chemical equations can often act as a limiting part of the process. Depending on the particular integration programme which is used, the numerical solution for each species is given as a concentration value at a specific time. The total integration time constitutes the distance the box has travelled.

2.4.7 Model evaluation

The way to evaluate air pollution models seems to be straightforward: model predictions are compared against appropriate measurements and identified deviations are statistically analysed to allow for quantification of model uncertainties. In spite of the simplicity of this method, there are considerable difficulties both in defining the evaluation procedure and in interpreting its results – these are listed below:

- Different evaluation procedures should be applied to the various model categories. In other words, the experimental data set needed to evaluate the models in addition to the evaluation of software, which should be tailored for the specific application.

- Deviations between model results and observations may be caused by a variety of such as the following reasons: shortcomings in model assumptions and parameterisations, errors and inaccuracies in input data (particularly emission data and meteorological data), uncertainties related to the stochastic nature of atmospheric processes, uncertainties in observations, uncertainties in the representativeness of both observed and modelled data, etc.

2.5 CONCLUSIONS

This literature survey will be tested and clarified as the analyses unfold in the subsequent chapters of this dissertation. VOC's and their oxidation products remain a persistent threat to sustainable development in southern Africa. These compounds have to be fully characterised and sampled under southern African conditions. Chapter 3 will deal with VOC sampling under southern African conditions.

Chapter 4 gives a perspective on the modelling of photochemical transformations, with a biomass burning plume suite and an industrial waste disposal site as examples of a photochemical plume.

In conclusion, the key issue of the transboundary transport of air pollutants, and the modelling of the deposition of trace gases will be discussed in Chapter 5.

CHAPTER 3

VOLATILE ORGANIC COMPOUND SAMPLING

In this Chapter...

The objectives of the study are briefly stated (Par 3.1). Par 3.2 gives a detailed description of the passive sampler that was used, while Par 3.3 focuses on the sampling and analysis of the passive sampler. Par 3.4 focuses on the summer field survey, while Par 3.5 gives an overview of the winter field survey. Par 3.6 concludes the chapter by summarizing and pointing out the possible limitations of the sampling method.

3.1 OBJECTIVES

The main objective of this VOC sampling survey is to determine the concentration profiles of selected VOC's in the vicinity of a petrochemical plant. The selected VOC's identified as problem species from the petrochemical plant, are benzene, toluene, xylene, acrylonitrile, butanol, propanol, acetone, hexane and pentane. The Occupational Exposure Levels (OEL) for South Africa (SA) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) standards are the most cited airborne standards in the world. These standards for the selected VOC's are given in Table 3.1.

To achieve this goal, the sampling survey carried out here were aimed at achieving the following:

- 3.1.1 Determining the selected VOC concentration profiles as a function of time. 12-Hour passive sampling at sampling sites during different cycles of day and night conditions were conducted.
- 3.1.2 Determining the VOC concentration gradients as a function of distance from the petrochemical plant. 12-Hour passive sampling at different sampling sites distributed over a distance of 0 to 20 km from the petrochemical plant (see Figure 3.2 and 3.6) were conducted.

Table 3.1 - Airborne VOC standards (ppb).

VOC	OEL (SA)	TLV (ACGIH)
Benzene	5	0.5
Toluene	50	50
Xylène	100	100
Acrylonitrile	2	2
Butanol	200	200
Propanol	200	200
Acetone	750	500
Hexane	20	50
Pentane	600	600

3.2 CHARCOAL SORBENT PAD PASSIVE SAMPLERS

Charcoal sorbent pad passive samplers were used in this study. The sampling procedure depended on diffusion processes for eventual contact between vapours in the atmosphere and an adsorbing charcoal pad (passive sampling). Due to the low concentrations of contaminants in ambient conditions, a very long sampling interval was required.

The passive sampler consisted of a diffusion screen (white film), a spacer, and a charcoal sorbent pad assembled in a disk shaped plastic holder. (This sampler is commercially available from 3M; see Figure 3.1.)

3.3 SAMPLING AND ANALYTICAL METHODS

The manufacturer seals each organic vapor monitor in an aluminium can. Sampling begins by opening the lid of the can removing the monitor from the can and recording the time. During the sampling period, the monitor should be placed in a location with adequate air movement (at least $1.0 \text{ m} \cdot \text{min}^{-1}$). Stagnant air at the face of the sampler will result in nonrepresentative sampling. All the samplers that were used in this study were connected to physical structures (fences, trees, etc.) which were approximately two meters above the ground. At the end of the sampling period, the white film on the face of the monitor was

removed and replaced with an impermeable cap and the time was recorded again. Badges are typically analyzed soon after the conclusion of sampling, and this procedure was adhered to in this study.

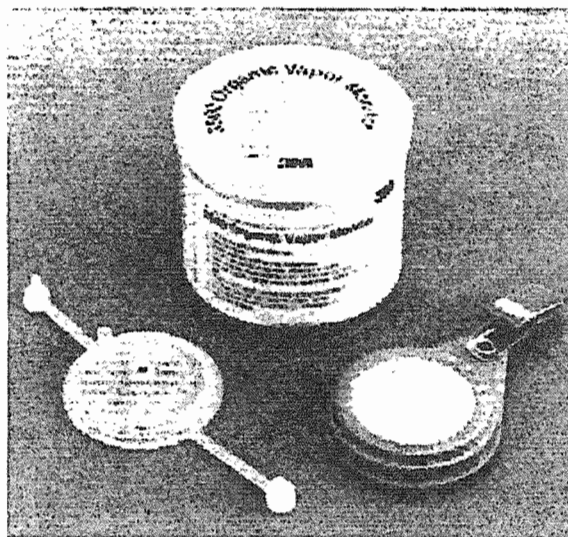


Figure 3.1 – Charcoal Sorbent Pad Sampler (3M, 1993)

During the sampling, the diffusion screen (white film) creates a concentration gradient from its surface to the carbon sorbent pad. At the surface of the screen the concentration of a substance is its ambient concentration (C_a) (assuming adequate air movement); at the sorbent pad the concentration (C_f) is effectively zero. The behaviour of the substance along the diffusion path (l), and the gap determined by the spacer, is described by Fick's First Law of Diffusion (flux is proportional to the concentration gradient), as follows:

$$\text{flux} = -D \left(\frac{dc}{dl} \right) \quad (3.1)$$

where "flux" is the amount of substance migrating through a unit area in a unit time, D is the diffusion coefficient, and $\left(\frac{dc}{dl} \right)$ is the concentration gradient. For the conditions and sampler employed in this study, Fick's law can be restated as follows:

$$\frac{m}{tA} = D \frac{(C_a - C_f)}{l} \quad (3.2)$$

where m = mass of substance that diffuses in μg

t = sampling interval in s

A = cross sectional area through which diffusion occurs = 7.07 cm^2 for the OVM #3500 (3M Sampler)

D = diffusion coefficient in $\text{cm}^2.\text{s}^{-1}$

C_a = ambient concentration of substance in $\mu\text{g}.\text{cm}^{-3}$

C_f = concentration of substance just above sorbent pad (= 0).

l = path over which diffusion occurs = 1.0 cm for the OVM #3500.

Equation 2 can be rearranged as follows:

$$\frac{m}{tC_a} = D \left(\frac{A}{l} \right) \quad (3.3)$$

The quantity $u = \frac{m}{tC_a}$ is commonly referred to as the "uptake rate" or "sampling rate" for diffusive samplers. For a given substance and type of sampler, the uptake rate is a constant as long as the amount of material collected remains significantly less than the capacity of the sorbent used in the device. Once an uptake rate for a particular substance and sampler has been determined, it can be used to calculate the ambient concentration (C_a) of that substance:

$$C_a = \frac{m}{(t)(u)(r)} \quad (3.4)$$

where m = mass of substance adsorbed by the sampler

t = sampling interval

u = uptake rate, as defined above

r = recovery coefficient, a factor used to adjust for incomplete extraction of a substance from the sorbent pad.

The uptake rate, when expressed in units of volume per unit time, provides a useful comparison to sampling rates employed with pumped samplers.

Prior to the analysis each badge was spiked with an internal standard, typically 1 μl of a 1.0 $\text{mg}\cdot\text{ml}^{-1}$ cyclo-octane/carbon disulfide solution. The badge is extracted with 1.5 ml of carbon disulfide. Carbon disulfide is among the more efficient solvents for extracting organic species that are adsorbed on carbon. The charcoal pad is kept in contact with the solvent for at least 45 minutes, with occasional mild agitation. The extract is then decanted into a 2 ml conical vial (the cone begins at 0.5 ml, 48 mm from base of cone to lip of vial, 8 mm I.D.). Aliquots of 1-3 μl are injected into the GC/MS.

Organic compounds contained in the extract are separated and identified using standard gas chromatograph/mass spectrometer (GC/MS) procedures. It is important that samplers used as field blanks, laboratory blanks, and for actual sampling originate from the same batch number, since the background compounds present on an unexposed sampler vary from batch to batch.

Given the small amounts being collected with the passive sampler in this application, it is extremely important that the background amounts associated with the samplers are well characterized. Unexposed badges are analysed with each set of samples. As mentioned above, unexposed monitors and actual sampling monitors should come from the same manufacturing lot. Both laboratory blanks (unexposed monitors that remained in the laboratory during sampling) and field blanks (unexposed monitors sent into the field along with sample monitors) have been analysed. The resulting analyses for badges from the same lot are indistinguishable, illustrating the effective vapour barrier presented by the can in which they were sealed. Occasionally multiple blanks had to be analysed in conjunction with a particular set of samples yielding comparable analyses. Blank corrections are normally necessary in the analysis.

3.4 SECUNDA SUMMER FIELD SURVEY

3.4.1 Scope and logistics of project

Two 12-hour day cycles and one 12-hour night cycle were measured during the sampling period of 26 to 27 February 1999 at SASOL Secunda. February was selected on the bases that it exhibits typical southern African summer month conditions. The average exposure time of all the samplers was 11 hours.

Twelve sampling sites were selected based on existing meteorological information obtained from the SASOL environmental office. Financial restraints limited the total sampling sites to twelve. The selected twelve sites were distributed into three different sets in the following manner:

- I. Four sites situated at the borders around the plant.
- II. Six sites situated down wind over a maximum distance of 15 km from the plant.
- III. Two sites situated upwind to the plant.

Each site was equipped with 4 sets of passive samples for the purpose of measuring VOC's. The sites were numbered A to L. Figure 3.2 provides a layout of the summer survey sampling sites on a regional map, while Table 3.2 provides a layout of the co-ordinates for the twelve sampling sites.

Table 3.2 – Co-ordinates of the twelve sampling sites.

Site	South	East	Altitude / ft
A	26°32'43.6"	29°06'49.4"	5193
B	26°32'23.4"	29°07'40.7"	5084
C	26°33'41.1"	29°08'41.6"	5013
D	26°32'21.5"	29°08'53.0"	4969
E	26°32'42.9"	29°10'57.1"	5410
F	26°33'56.3"	29°10'46.5"	5194
G	26°35'48.7"	29°10'34.1"	5219
H	26°34'44.6"	29°11'43.6"	5505
I	26°32'46.6"	29°12'57.7"	5149
J	26°32'21.4"	29°14'33.1"	5410
K	26°35'18.1"	29°13'37.7"	5553
L	26°32'40.7"	29°17'03.1"	5410

All co-ordinates were taken with a GARMIN Communication & Navigation 95 XL Global Positioning System (GPS).

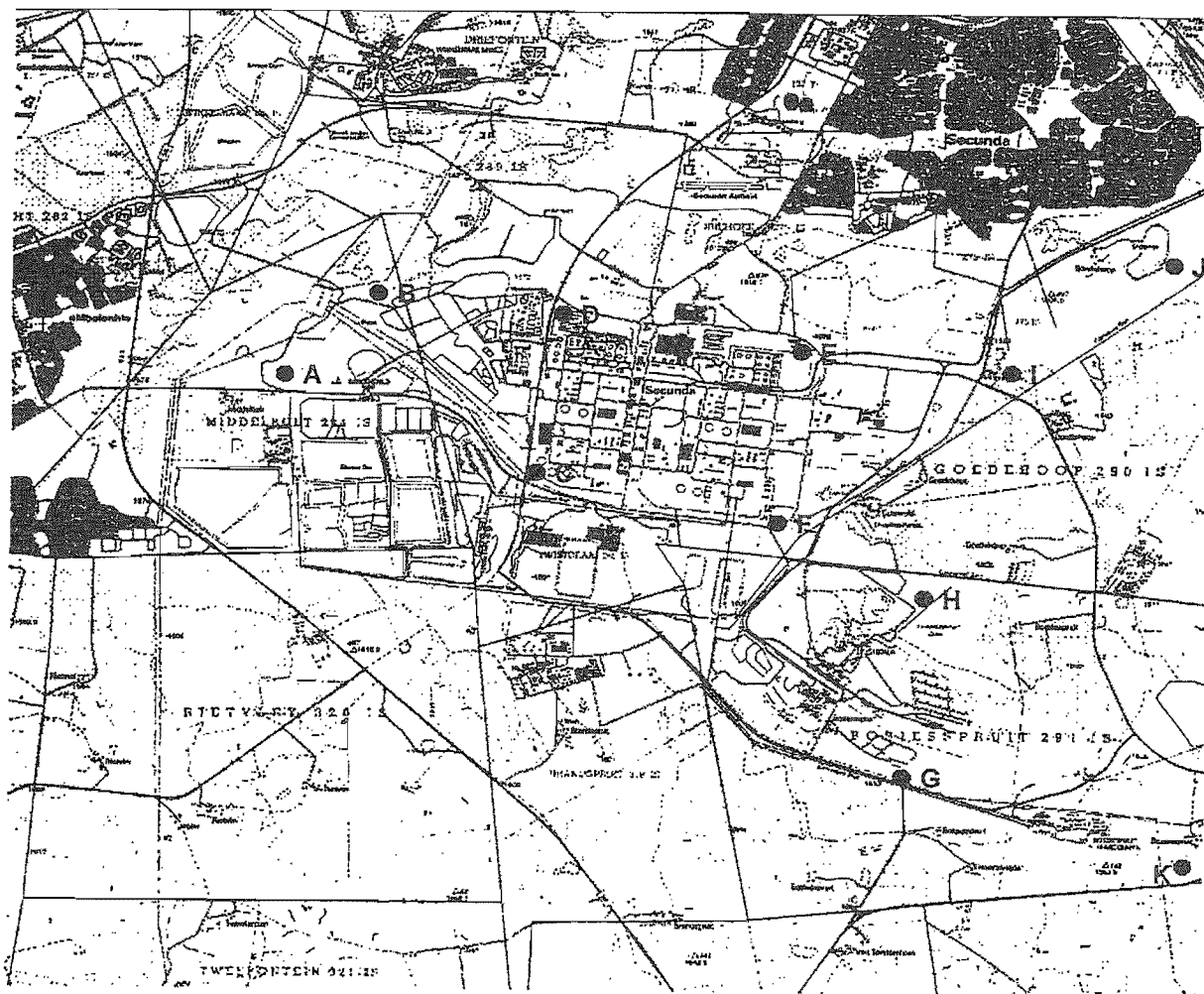


Figure 3.2 – Layout of the sampling sites for the summer survey.

Table 3.3 - Different VOC's measured at the twelve sampling sites.

VOC's measured		
Benzene	Toluene	Xylene
Acrylonitrile	Butanol	Propanol
Acetone	Hexane	Pentane

3.4.2 Meteorological data

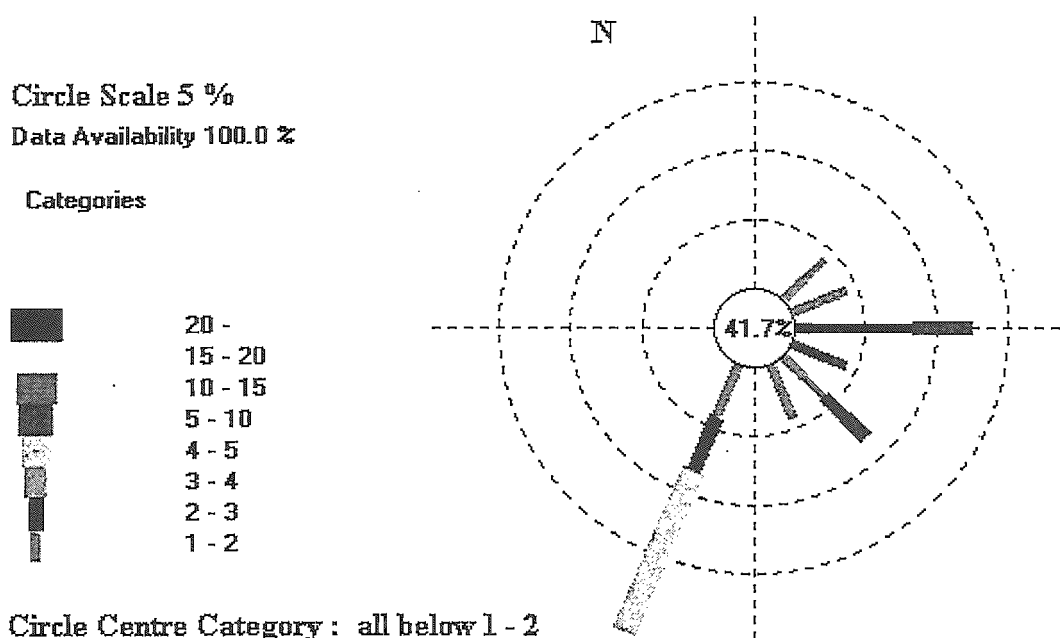


Figure 3.3 – The prevailing wind direction at Secunda on 26 February 1999.

Figure 3.3 and 3.4 shows the prevailing wind direction for the specified time period. On 26 February the prevailing wind was predominantly from a south southwesterly direction. The wind speed during the day varied from windless to a maximum of 8.7 m.s^{-1} . The mean wind speed for 26 February was 3.27 m.s^{-1} .

The prevailing wind direction on 27 February was from a southeasterly direction as is graphically depicted by Figure 3.4. The wind speed varied from a minimum of 0.05 m.s^{-1} to a maximum of 5.41 m.s^{-1} . The mean wind speed was 3.21 m.s^{-1} .

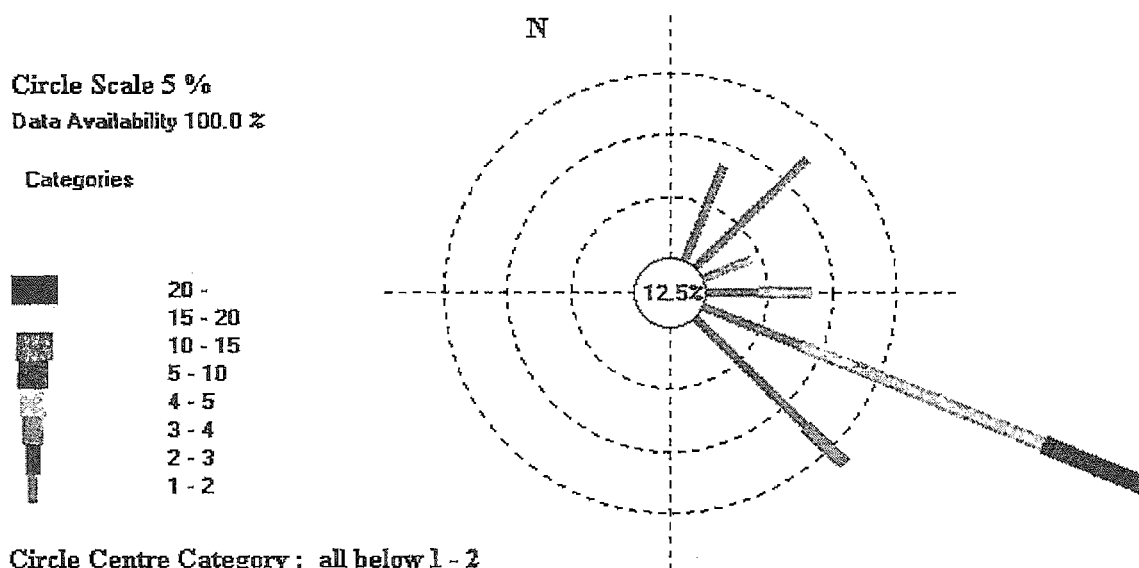


Figure 3.4 - The prevailing wind direction at Secunda on 27 February 1999.

The temperature profiles during the two sampling days stayed almost identical, with the exception that the temperature dropped (on 27 February) to a lower value at 19:00. The temperature profiles are graphically represented in Figure 3.5. The highest temperature values were measured at 14:00 with a maximum of 28°C.

No wet precipitation (rain or fog) occurred during the sampling period.

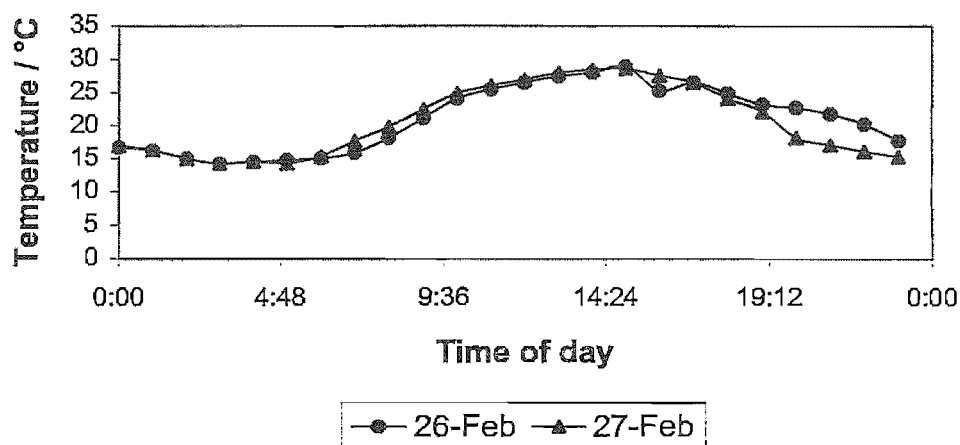


Figure 3.5 - Temperature profiles at Secunda on the 26 and 27 February 1999.

3.4.3 Results

No detectable concentrations of ambient VOC's were measured at sampling sites A, E and F. This could be the result of the prevailing wind direction which occurred from a south-easterly direction and thus no plume movement occurred over these sampling sites. The remaining sampling sites showed detectable amounts of ambient VOC's.

Table 3.4 summarises all the VOC species detected at the sampling sites during the two sampling days. All the VOC species were detected at very low ambient concentrations and only acrylonitrile showed ambient values higher than the recommended OEL (SA) and TLV (ACGIH) standards. At Site J acrylonitrile levels of 89.42 ppb were detected, and the prescribed standards only allows 2 ppb for ambient air.

3.4.4 Problems identified

Very low ambient concentrations of VOC's were measured during the day and night cycles of the sampling survey. These low ambient concentrations could be the result of numerous factors. The first possible cause for the low concentrations is the wind direction during the sampling time. The prevailing wind direction of the region was totally opposite (180°) (a south-easterly wind) to the expected average direction (north-westerly wind), as shown in Figure 3.3 and 3.4. The samples were placed in a south-easterly direction to accommodate a typical north-westerly wind, which would have enabled a concentration gradient from the petrochemical plant to be obtained.

The second problem was the distance of the samples from the plant. The typical height of release from the stack would have been 300 meters, thus samples allocated close to the plant would only pick up emissions from ground sources such as valves and dams. A previous study showed that sites 10-20 km from such tall stacks show maximum values (G. Held personal communication).

Table 3.4 - VOC species detected at the sampling sites.

Site	VOC / ppb								
	Benzene	Toluene	Xylene	Acrylonitrile	Butanol	Propanol	Acetone	Hexane	Pentane
A	<0.005	<0.5	<1.0	<0.02	<2.0	<2.0	<5.0	<5.0	<5.0
B	0.04	<0.5	<1.0	<0.02	<2.0	<2.0	<5.0	<5.0	<5.0
C	0.06	<0.5	<1.0	<0.02	<2.0	<2.0	<5.0	<5.0	<5.0
D	0.03	<0.5	<1.0	77.76	<2.0	3.39	<5.0	<5.0	<5.0
E	<0.005	<0.5	<1.0	<0.02	<2.0	<2.0	<5.0	<5.0	<5.0
F	<0.005	<0.5	<1.0	<0.02	<2.0	<2.0	<5.0	<5.0	<5.0
G	<0.005	<0.5	<1.0	65.99	<2.0	<2.0	<5.0	<5.0	<5.0
H	0.035	<0.5	<1.0	51.4	<2.0	15.94	<5.0	<5.0	<5.0
I	<0.005	<0.5	<1.0	73.03	<2.0	<2.0	<5.0	<5.0	<5.0
J	<0.005	<0.5	<1.0	89.42	<2.0	8.4	<5.0	<5.0	<5.0
K	0.07	<0.5	<1.0	63.85	<2.0	<2.0	<5.0	<5.0	<5.0
L	0.07	<0.5	<1.0	75.7	<2.0	<2.0	<5.0	<5.0	<5.0

3.5 SECUNDA WINTER SURVEY

3.5.1 Scope and logistics of project

Two 12-hour day cycles and one 12-hour night cycle were chosen during the sampling period of 16 to 18 August 1999 at SASOL Secunda. The average exposure time of all the samplers was 11 hours in accordance with the summer survey.

Twenty-two sampling sites were selected on existing meteorological information and average wind directions obtained from the environmental office at SASOL Secunda (Figure 3.6). Financial constraints again determined the amount of sampling sites, but each of the twenty-two sites was equipped with 2 sets of passive samplers for measuring VOC's, and not 4 sets of passive samplers as in the summer survey. Therefore twenty two sampling sites were selected and were distributed in four different sets in the following manner:

- I. Four sites situated at the borders around the plant.
- II. Eleven sites situated on a radius of approximately 2 km from the factory boundary.
- III. Six sites situated approximately 6 km from the plant.
- IV. One site approximately 10 km from the plant.

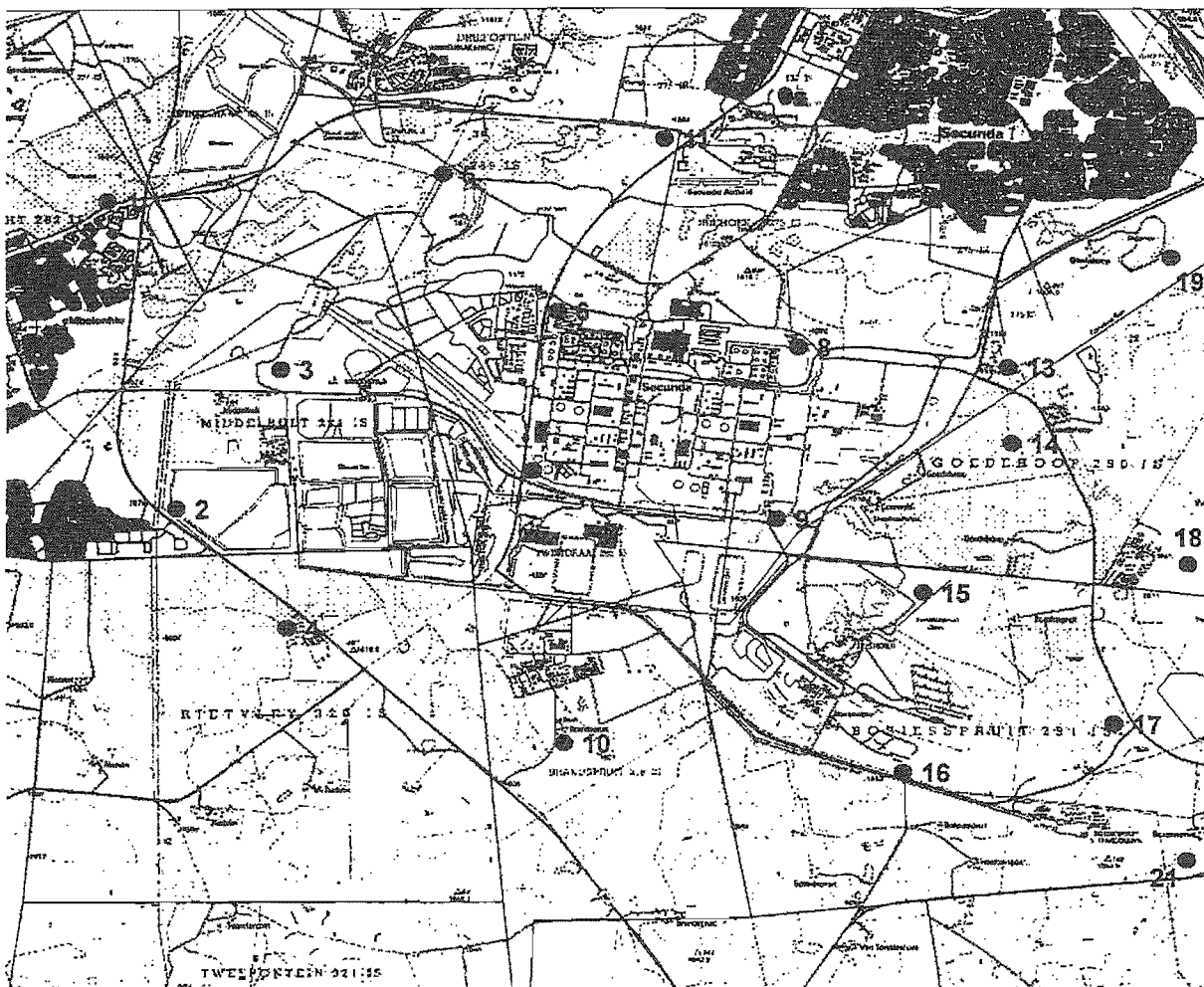


Figure 3.6 – Layout of the sampling sites for the winter survey.

Table 3.5 - Coordinates of the twenty-two sampling sites.

Site	South	East	Altitude / ft
1	26°31'42.1"	29°05'49.2"	5530
2	26°34'16.6"	29°06'53.7"	5231
3	26°32'43.9"	29°06'50.2"	5289
4A	26°33'46.7"	29°07'22.8"	5360
4B	26°34'02.7"	29°07'29.2"	5224
5	26°31'23.7"	29°08'13.4"	5480
6	26°32'23.9"	29°08'53.7"	5155
7	26°33'39.6"	29°08'40.6"	4941
8	26°32'43.4"	29°09'34.9"	5071
9	26°33'56.6"	29°10'48.1"	5481
10	26°35'26.8"	29°08'36.7"	5390
11	26°31'05.0"	29°09'53.8"	5033
12	NA	NA	NA
13	26°32'42.2"	29°12'15.0"	5244
14	26°32'47.4"	29°12'55.5"	5479
15	26°34'44.1"	29°11'44.2"	5544
16	26°35'56.8"	29°10'52.7"	5283
17	26°35'49.1"	29°13'30.6"	5538
18	26°35'18.3"	29°13'37.0"	5401
19	26°32'23.1"	29°14'33.2"	5279
20	NA	NA	NA
21	26°32'40.3"	29°17'02.8"	5406

All coordinates were taken with a GARMIN Communication & Navigation 95 XL Global Positioning System (GPS).

Table 3.6 - Different VOC's measured at the twenty-two sampling sites. Three VOC's were measured per passive sampler.

VOC's measured	
Benzene	Toluene
Acrylonitrile	Xylene
Acetone	Propanol

3.5.2. Meteorological data

The wind directions during the three sampling days are graphically represented in Figures 3.7 to 3.10. The prevailing wind direction during the sampling period was predominantly from an east to north-easterly (30° to 110° from North) direction.

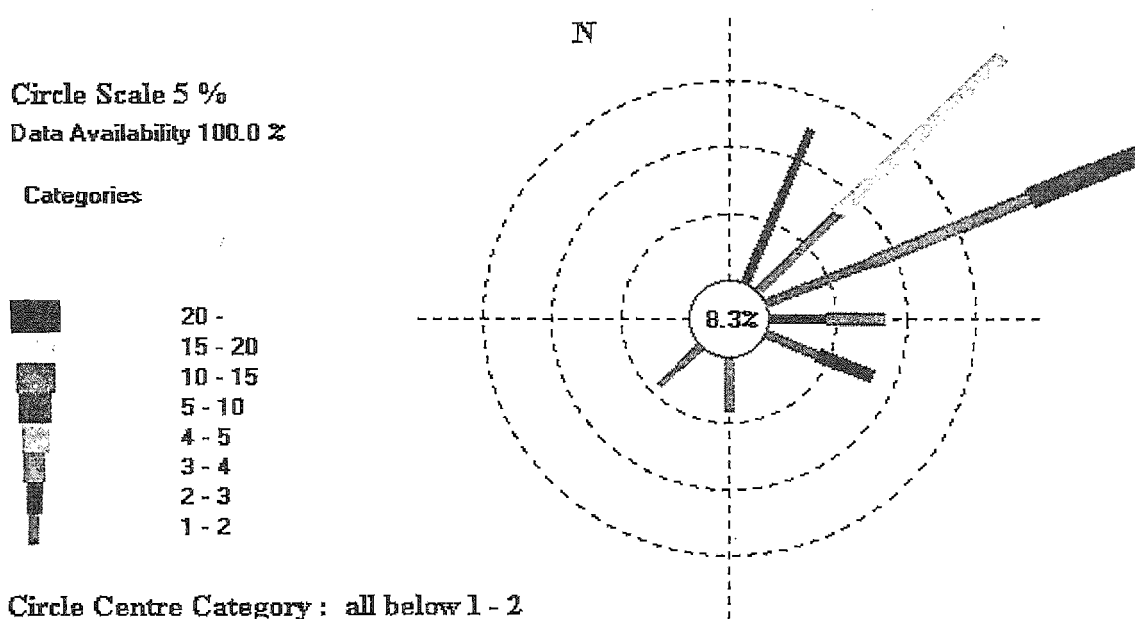
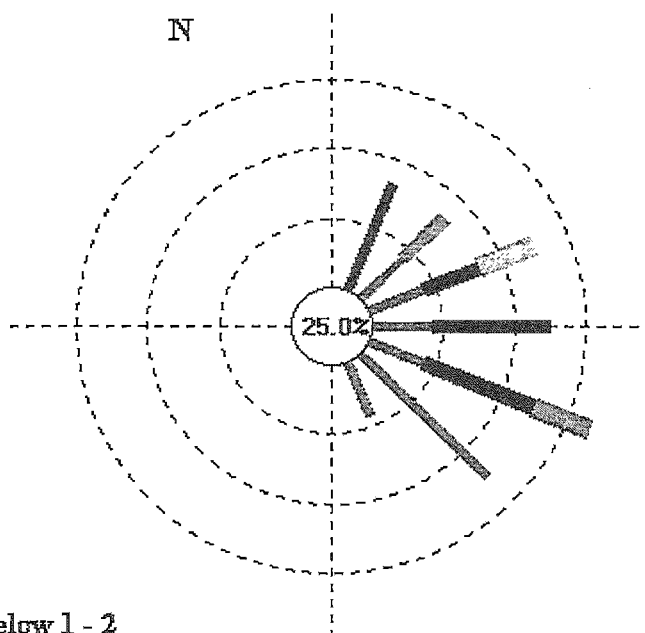
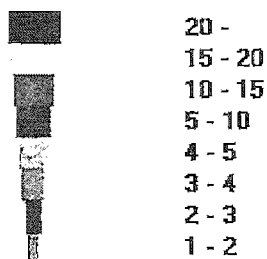


Figure 3.7 - The prevailing wind direction at Secunda on 16 August 1999.

Circle Scale 5 %
Data Availability 100.0 %

Categories

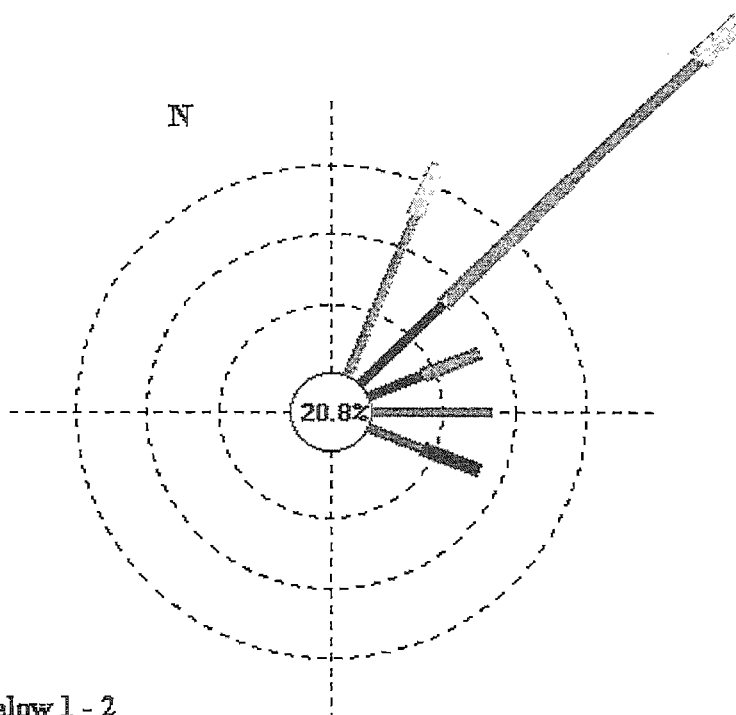
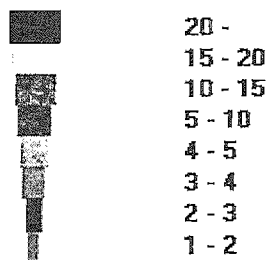


Circle Centre Category : all below 1 - 2

Figure 3.8 - The prevailing wind direction at Secunda on 17 August 1999.

Circle Scale 5 %
Data Availability 100.0 %

Categories



Circle Centre Category : all below 1 - 2

Figure 3.9 - The prevailing wind direction at Secunda on 18 August 1999.

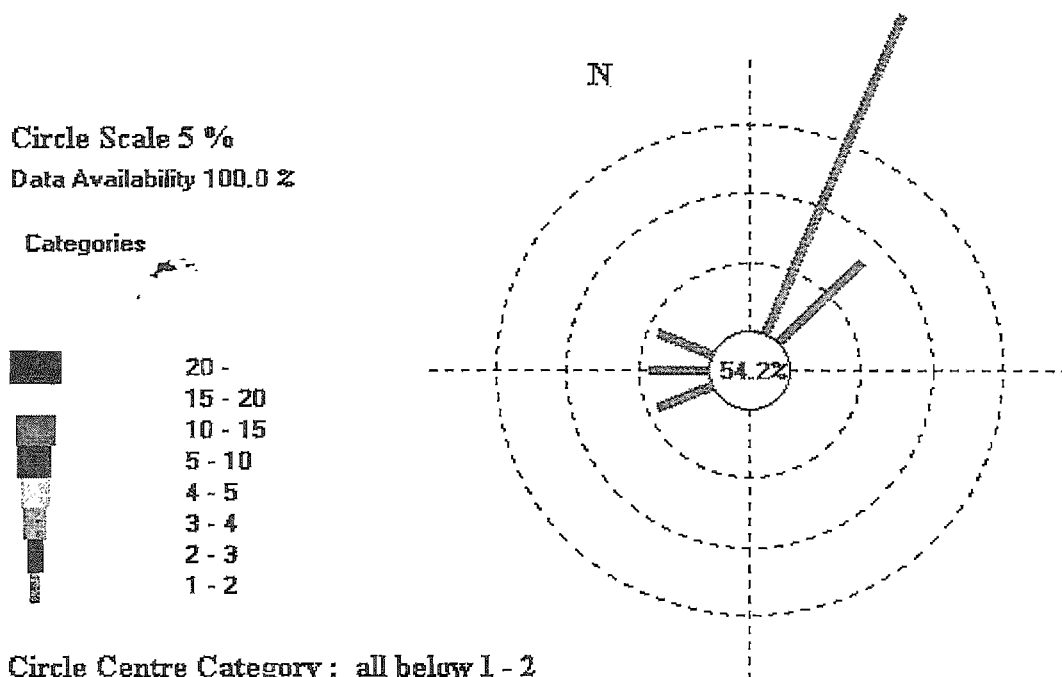


Figure 3.10 - The prevailing wind direction at Secunda on 19 August 1999.

The wind speed during the specified sampling time of 17 to 19 August varied from a minimum of 0.08 m.s^{-1} to a maximum of 5.15 m.s^{-1} . The mean wind speed for the four sampling days was 1.92 m.s^{-1} .

The temperature profiles during the three sampling days stayed the same. The highest temperature value was measured at 14:00 with a maximum of 22°C . The lowest minimum value of 1°C was measured at 06:00 in the morning. The temperature profiles are graphically presented in Figure 3.11. No wet precipitation (rain or fog) occurred during the sampling period.

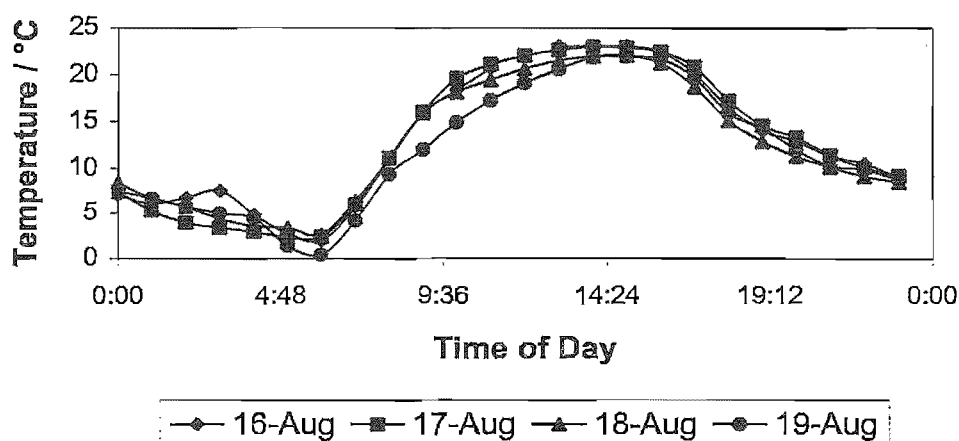


Figure 3.11 - Temperature profiles at Secunda on the 16 to 19 August 1999.

3.5.3 Results

The twenty-two sampling sites showed no detectable ambient concentrations of VOC's. These results are summarized in Table 3.7.

Table 3.7 - VOC species detected at the sampling sites.

Site	VOC / ppb					
	Benzene	Toluene	Acrylonitrile	Xylene	Acetone	Propanol
1	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
2	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
3	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
4	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
5	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
6	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
7	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
8	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
9	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
10	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
11	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
12	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
13	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
14	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
15	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
16	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
17	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
18	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
19	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
20	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0
21	<0.005	<0.5	<0.02	<1.0	<5.0	<2.0

3.6 CONCLUSIONS

The summer survey was successful in obtaining VOC concentrations for selected VOC's. However, a concentration gradient for the summer conditions could not be obtained due to the unexpected change in meteorological conditions. Due to this a follow-up survey could be beneficial in which certain parameters, such as a denser sampler network, could be changed. The first suggested change includes a denser distribution of the samples around the plant to accommodate a change in wind direction. This, however would be a costly venture. A second suggestion would be to place some of the samples further away (± 20 km) from the plant, to obtain a better estimate of VOC concentrations from high stack emissions.

During the winter survey none of the selected VOC's was detected in measurable amounts on the samplers. The twenty-two sampling sites also showed no concentration levels of VOC's higher than the specified health standards.

These low ambient concentrations of VOC's during the winter survey could be the result of a number of factors. The first possible cause for the low concentrations is that the sampling method and selected passive samplers were not capable of measuring the low ambient VOC concentrations. Due to the low concentrations of contaminants in the ambient air, a very long sampling interval was required. Shields *et al.* (1987) extended the sampling interval times on 3M samplers from the eight hour intended application to intervals as long as twelve weeks, with typical periods between two and four weeks. Even with these extended sampling intervals, the amount of material collected by the charcoal pad was three to four orders of magnitude less than the amounts which would have been collected by active sampling.

Chung *et al.* (1999), reports that the 3M passive sampler is compound specific and is highly dependent on ambient air factors such as concentration, temperature and humidity. Recovery rates in a controlled exposure chamber showed negative biases when compared to calculated chamber concentrations, with exposure times of up to 24 hours.

Better sampling techniques and extended sampling intervals should thus be exploited or developed for follow-up surveys.

The low temperature in winter may also result in less evaporation of VOC's and lower ground level sources of VOC's.

Another possibility can be that the measured ambient VOC concentrations were correct, and that the results showed the typical VOC concentrations to be lower than the detection limit of the passive samplers. This would be a positive result to the petrochemical industry.

Another shortcoming is that both sets of experiments are not really suited or designed to address influences on ambient air quality due to high stack emissions.

Follow-up surveys must be initiated in order to validate these results, and to exploit or develop other sampling techniques for the sampling of ambient VOC concentrations under these conditions.

CHAPTER 4

PHOTOCHEMICAL MODEL

In this Chapter...

Firstly an introduction to the photochemical model (Par 4.1) is provided. Par 4.2 points out the various stages in the model development, whilst Par 4.3 focuses on the modelling results from the photochemical model. Par 4.4 focuses on the evaluation and validation of the photochemical model. Par 4.5 concludes the chapter by summarizing and pointing out the limitations of the photochemical model.

4.1 INTRODUCTION

VOC's and their photochemical products are a potential threat to sustainable development due their role in the formation of tropospheric oxidants, as mentioned in Chapter 2. In order to test our understanding of atmospheric processes, it is essential to construct models to help interpret the chemistry. The hydroxyl radical ($\text{HO}^\bullet$) is the primary tropospheric oxidant and is largely responsible for oxidizing many anthropogenic pollutants, as well as a significant number of biogenic species. The $\text{HO}^\bullet$ radical is formed in the troposphere primarily through the photolysis of ozone (O_3) at wavelengths below 330 nm, followed by the reaction of the excited state oxygen atom with water vapour:



Ozone (O_3) is a secondary pollutant formed in the atmosphere from photochemical reactions involving sunlight, volatile organic compounds (VOC's) and nitrogen oxides (NO_x). Ozone concentrations reach their maximum in the afternoon after several hours of UV radiation, atmospheric transport, dispersion and chemical reactions. During this time, industrial emissions can be transported long distances. Thus, ozone pollution can be regarded as a long range effect. At short range NO_x emissions have been shown to decrease

ambient ozone concentrations since nitrogen monoxide (NO) emissions react rapidly with ambient ozone (O₃), thereby depleting it. This suggests different mechanisms of accounting for tropospheric ozone concentrations in short and long range transport models. Changes in ozone concentrations (decreases in the short term and increases in the long term) can be modelled as a function of changes in the NO:NO₂ ratio.

4.2 PHOTOCHEMICAL MODEL DEVELOPMENT

4.2.1 Background

The irradiation of a mixture of NO_x (NO+NO₂) and non-methane hydrocarbon (NMHC) gases by solar ultraviolet radiation leads to photochemical smog formation in which ozone is the major secondary pollutant. The formation of is catalysed by NO_x. The overall photochemical reaction scheme can be expressed as follows:



NMHC are important for ozone formation, but CO and NO₂ have to be present in the plume in order to initiate the oxidation reaction. The CO and NO₂ from biomass burning and/or industrial emissions are thus as important, or even more important than VOC's for the formation O₃.

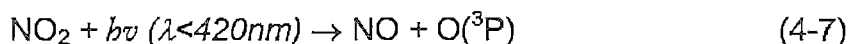
The details of the above-mentioned ozone (O₃) formation process is a complex photochemical chain reaction involving reactive VOC's, NO_x and ultraviolet radiation (from sunlight). Reactive hydrocarbons (RH) react with hydroxyl radicals to form organic radicals (R^{*}):



These organic radicals then react with oxygen to form peroxy radicals, which in turn react with nitrogen monoxide to form nitrogen dioxide:



Nitrogen dioxide absorbs ultraviolet radiation and is photodissociated (broken apart) to form nitrogen monoxide again and ground state oxygen atoms, which then react with oxygen to form ozone:



It has been shown that photochemical ozone production is controlled by both ambient NMHC as well as NO_x levels, unless either of these species is depleted and becomes rate limiting. Figure 4.1 shows this limiting effect, through a series of isopleths of constant O_3 concentration.

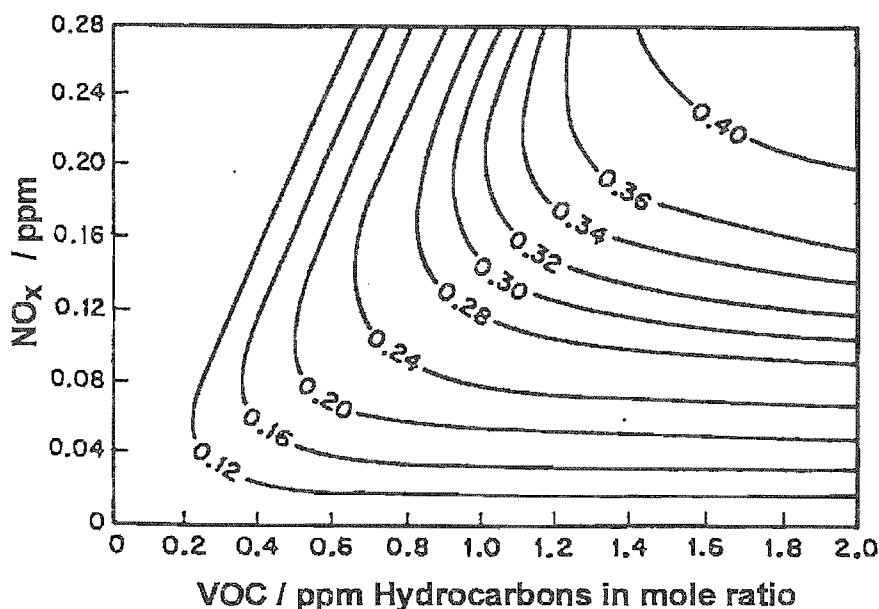


Figure 4.1 – Peak ozone concentrations as a function on initial NO_x and VOC concentrations from the US EPA standard EKMA model (Colbeck *et al.*, 1994).

The oxidation of hydrocarbons is coupled closely to the NO_x – O_3 photostationary state: oxidation of VOC compounds by $\text{HO}^\bullet$ produces $\text{RO}_2^\bullet$ radicals (where R is some organic substituent) which convert NO to NO_2 without destroying O_3 . The concentration of O_3 will therefore increase, providing more $\text{HO}^\bullet$ via reactions (4.1) and (4.2), and so increasing the rate at which VOC is oxidised. It is this feedback that gives photochemical smog chemistry its characteristic non-linearity (Figure 4.1). For maximum ozone production, a balance of NO_x and VOC

concentrations is required. At low NO_x concentrations, insufficient HO[•] is produced to oxidise the VOC; too little VOC and RO₂ concentrations do not alter the position of the photostationary state significantly. Hence the top-left of Figure 4.1 ozone formation is hydrocarbon-limited, and towards the bottom-right ozone formation is NO_x-limited.

The sustained ozone production in aged biomass fire plumes is due to the recycling of NO_x from PAN and possibly other organic nitrates produced in the fresh plumes. Formation of these organic nitrates is facilitated by the low NO_x:NMHC emission ratio and is a major factor responsible for the short NO_x lifetime in the plumes (Jacob *et al.* 1992; Wofsy *et al.* 1992).

Ozone also absorbs solar radiation (near-ultraviolet) and dissociates, creating an excited oxygen atom which in turn leads to the formation of two hydroxyl radicals (4-1 and 4-2).

The hydroxyl radicals thus produced are available again for Reaction (4-4) in order to sustain this photochemical chain reaction which eventually produces ozone.

However, significant buildup of ozone is prevented until nitrogen monoxide is converted to nitrogen dioxide, because nitrogen monoxide reacts quickly with ozone, thereby depleting it:



This reaction (4-9) actually reduces the ambient ozone concentrations in plumes close to the source (<50 km).

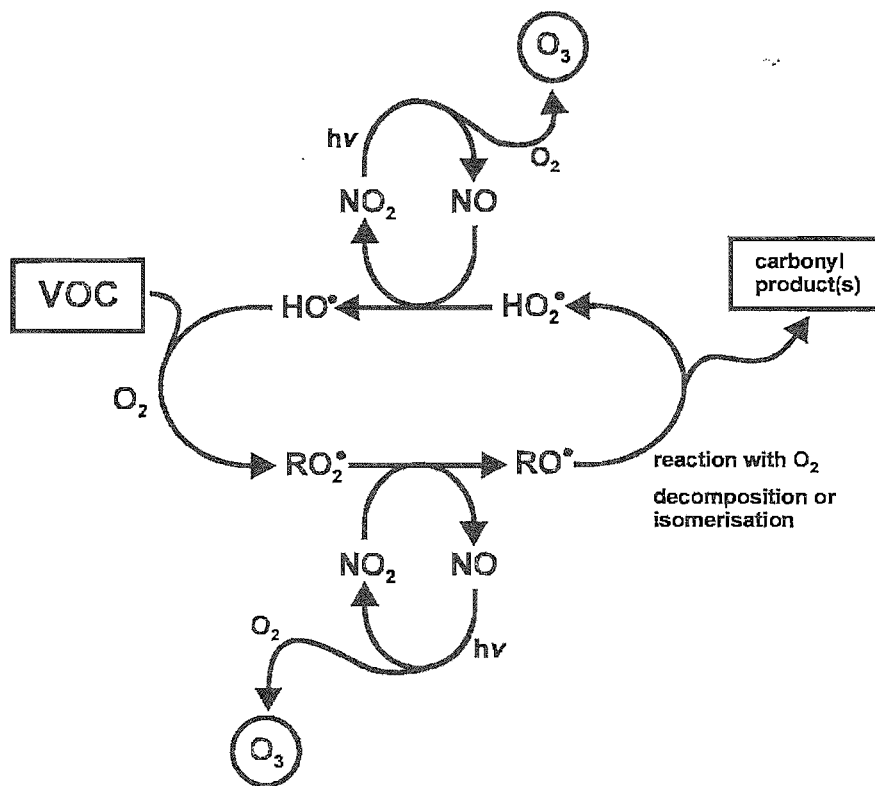


Figure 4.3 – Schematic representation of the free radical catalysed oxidation of a VOC into its first generation carbonyl product(s) in the presence of NO_x, and the associated generation of ozone (O₃) (Jenkin *et al.*, 1999).

The ozone buildup in plumes generally occurs in the afternoon after significant VOC's and NO_x have been emitted into the atmosphere, solar radiation is still intense, and nitrogen monoxide has been consumed. After the sun sets, the chain reaction stops, and ozone concentrations drop due to reaction (4-9) and due to deposition (surface reactions).

Figure 4.3 shows a schematic representation of the free radical catalysed oxidation of a VOC to form O₃ as the product, while Figure 4.4 shows the complete photochemical oxidant cycle in the atmosphere.

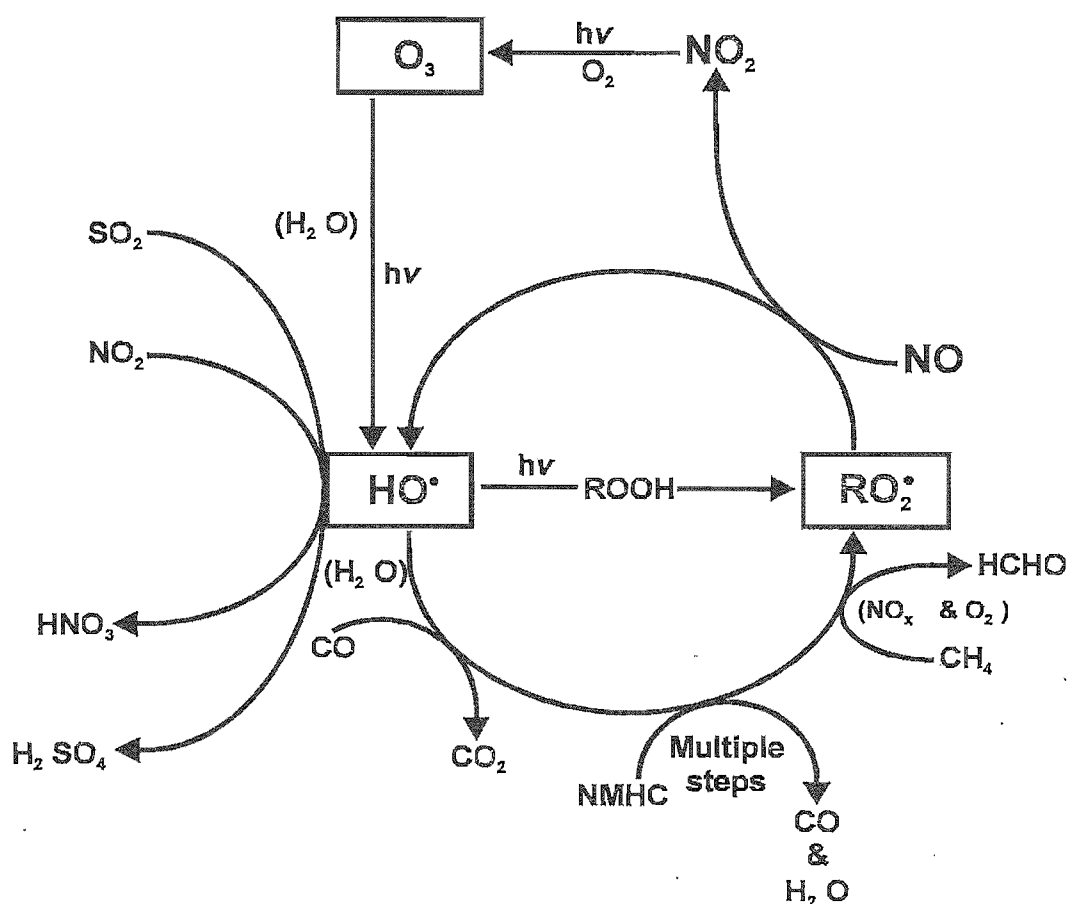


Figure 4.4 – The photochemical oxidant cycle in the atmosphere (Crutzen *et al.*, 1993). R represents H, CH₃ or higher alkyl radicals.

4.2.2 Model description

Owing to their short lifetimes, HO[•] and HO₂[•] reacts quickly to changes in local ambient conditions (solar flux, concentration of NO_x, and non methane hydrocarbons), but are unaffected by transport. It is therefore sufficient to use a zero-dimensional box model with no spatial resolution in order to describe these fast chemical processes. The vertical extent of the box is determined by the altitude of the mixing height (boundary layer), which varies throughout the day.

At dawn the boundary layer is relatively shallow (300 meters), but as the earth's surface is warmed by solar irradiation, convective currents are produced which cause an increase in the depth of the layer. This increase continues until early afternoon (maximum height of the boundary layer is 1300 meters), when the mixing height levels off and remains stable until the early evening, after which

the boundary layer collapses to its early morning height. This is due to the decrease in solar irradiation and hence a reduction in the convective heating. A simplified, step-like representation of this behaviour has been adopted in the model. The absence of high turbulence, which would destroy the boundary layer, is assumed consistent. It is also assumed that the relief over which the box moves is relatively flat, to avoid any disturbance to the box's shape or path.

The changes in the boundary layer height will cause changes in the concentrations of chemical species present in this layer in two ways. Firstly the concentrations of the species emitted into the boundary layer will be inversely proportional to the boundary layer height. That is, as the boundary layer expands those species emitted into the layer will have to occupy a larger volume and so they will be less concentrated. Secondly, as the boundary layer expands, air from above with a different chemical composition, will be mixed in. The material above the boundary layer can be considered as a second layer. The upper layer is that which is between the boundary layer and the maximum height to which the boundary layer expands. This implies that there is no upper layer whilst the boundary layer is at its maximum depth. When the boundary layer collapses in the evening there is no change in the concentration of the chemical species. The concentrations in the upper layer are held constant at these levels.

The chemical mechanisms and rate coefficients for the photochemical box model (PBM) have been taken from the master chemical mechanism (MCM) by Jenkin *et al.*, (1997). The MCM is believed to be the most comprehensive chemical mechanism available, treating the degradation of 123 volatile organic compounds (VOC's) that are emitted into the atmosphere (Jenkin *et al.*, 1997). The VOC's in the MCM provide 97% mass coverage of the UK emissions of uniquely identifiable chemical species (Jenkin *et al.*, 1997). The remaining 3% result from minor emissions of about a further 100 compounds (Carslaw *et al.*, 1999). The MCM has been constructed by consideration of the chemical kinetics data concerning rate coefficients, absorption cross sections, and reaction products, including several recent evaluations and reviews (Jenkin *et al.*, 1997). The MCM is an explicit mechanism and, as such, does not suffer from the limitations of a lumped scheme or one containing surrogate species to represent the chemistry of many species.

The MCM includes the oxidation of the 123 VOC's by HO^{*}, NO₃, and O₃, as well as the chemistry of the subsequent oxidation products. These oxidation steps continue until CO₂ and H₂O are yielded as final products of the oxidation. Therefore it is possible to have many reactions in some hydrocarbon schemes: the isoprene scheme alone contains over 300 reactions (Jenkin *et al.*, 1997).

The inorganic section of the PBM has been updated from the Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III, from IUPAC's Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry.

In addition to chemical reactions, physical processes such as dry deposition and heterogeneous loss must be considered. The rate of chemical change of a chemical species *i* within the box is described in Chapter 2 of this study, see Equation 2.10.

The model contains a large number of distinct, often generic photochemical reactions involving inorganic species, aldehydes, ketones and organic hydroperoxides. The photolysis coefficients for these reactions have been calculated after the method described by Jenkin *et al.*, (1997), and take the following form:

$$J = I \times \cos Z^m \times \exp(-n \times \sec Z)$$

where *I*, *m* and *n* are coefficients that have been determined for each photolysis reaction by fitting the *J*-values calculated (using the two stream scattering model of Hough (1988)) to the functional form given above.

Reaction 4.7 as an example:



$$J = 1.165 \times 10^{-2} \times (\cos Z^{0.244}) \times \exp(-0.267 \times \sec Z)$$

$$\frac{d\text{NO}}{dt} = J \times \text{NO}_2$$

These coefficients have been calculated by considering a combination of the

solar actinic flux, the quantum yield and the absorption cross-section between 200 and 700 nm. The zenith angle (Z) is calculated at each time-step during the model run, from knowledge of the latitude, longitude and time of year. In this way, the photolysis coefficients can be calculated for any location, time of year and time of day. These values have been calculated assuming clear skies. Therefore, to properly represent the conditions in the atmosphere, the effect of clouds must be taken into account. This has been achieved by considering the difference between the model predicted maximum of $J(\text{O}^1\text{D})$ with that observed in the atmosphere. The attenuation in the atmosphere gives an indication of the cloudiness, and this factor can be applied to the photolysis parameters that are not determined experimentally in the model.

The dry deposition terms have been taken from Derwent (1996). It is assumed that the deposition rate for PAN analogs in the PBM (Photochemical Box Model) can be calculated with the same parameters as in the case of PAN. In order to account for the increased deposition that occurs at nighttime in a much smaller boundary layer, the boundary layer height is varied in the model, at different times of the day.

The rate coefficient of heterogeneous loss on the surface of aerosols (e.g. SO_2 dissolution in fog droplets) is described by the following equation:

$$k = \frac{1}{4} c A g$$

where g is the experimentally determined accommodation coefficient, A is the surface area of aerosol (cm^2), and c is the mean speed (ms^{-1}) of the air molecules (Ravishankara, 1997). c is defined by the expression $\left(\frac{8kT}{\pi M}\right)^{1/2}$, where $k = 1.381 \times 10^{-23} \text{ JK}^{-1}$ (Boltzmann's constant), T is the temperature in Kelvin and M is the molar mass in kg. The aerosol surface area in this expression has been measured. In this model, heterogeneous loss of the following species are included: $\text{N}_2\text{O}_5^{2-}$, NO_3^- , $\text{HO}_2^\bullet$, $\text{CH}_3\text{O}_2^\bullet$, $\text{HO}^\bullet$, $\text{CH}_3\text{SO}_3\text{H}$ and HNO_2 . Once the species are lost on the aerosol surface, they are considered to take no further part in the chemistry. This is realistic for a model containing only gas phase chemistry and no heterogeneous phase chemistry.

4.2.3 Computer implementation

The model is written in a 'language' called FACSIMILE (Flow And Chemistry SIMulator). FACSIMILE is a series of FORTRAN subroutines, which are designed to solve stiff differential equations using a variable order Gear's method. This Gear's method integrates the differential equations numerically using stiffly stable techniques. At the beginning of each time-step, the solution is estimated using a polynomial fit, and this is improved upon by using a Newton-type iteration 'predictor-corrector' method.

Because of the large program size, the source code for the model (±350 pages) is not attached as an appendix.

The Facsimile computer language is available from AEA Technology, A32 Winfrith, Dorchester, Dorset DT2 8DH, United Kingdom.

4.3 MODELLING RESULTS

4.3.1 Biomass burning

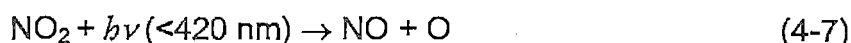
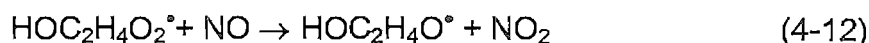
Biomass burning is an important source of VOC's. Biomass burning refers to the burning of the world's forests, grasslands and agricultural lands following either the harvest for land clearing and/or land conversion, or by natural occurrences. Estimates of the amount of biomass burned each year around the globe suggest that savanna fires are the single largest source of pyrogenic emissions (van Wilgen *et al.*, 1997). Africa contains about two thirds of the world's savanna regions, and the fires in the African savannas alone account for about 30% of the biomass burned in the tropics worldwide. The biomass burned annually in African savannas has been estimated at 2000 Tg dm.yr⁻¹ (1 Tg = 10¹²g = 1 million tonnes; dm = dry matter), and the area exposed to fire in African savannas covers 440 million hectares (van Wilgen *et al.*, 1997).

The pyrolytic decomposition of plant matter is the first step in the combustion of vegetation. It releases a wide array of reduced and partially oxidized organic compounds, with methane being the most abundant species. The largest fraction of the non-methane hydrocarbons (NMHC) is in the form of the C₂-C₄ hydrocarbons, but the contribution from higher-molecular species is by no means

negligible. Since biomass burning emissions involves both NO_x and NMHC, it may be expected that ozone formation in these plumes is very efficient. As an example of the air pollution chemistry in biomass burning regions the photochemical breakdown of ethene can be considered as a major contributor to the reactive NMHC in fire plumes (van Wilgen *et al.*, 1997). The basic degradation scheme for NMHC's have already been discussed in paragraph 4.2.1, but the oxidation of ethene as an example will be discussed in detail. The lifetime of ethene in the tropical atmosphere is limited to about one day, mostly through reaction with the hydroxyl radical:



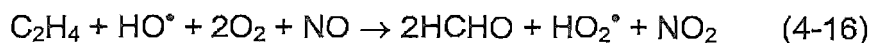
Subsequently, the presence of nitrogen oxides gives rise to ozone formation through the following reactions:



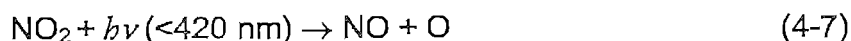
where M is a unreactive molecule in the air that acts to dissipate excess energy. Since NO is recycled in Reaction (4-7) it acts as a catalyst. The hydroxylated alkoxy radical formed in Reaction (4-12) can further react with oxygen or dissociate:



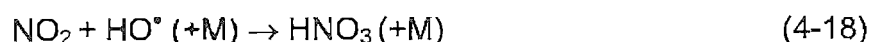
The net result of the above reaction sequence is:



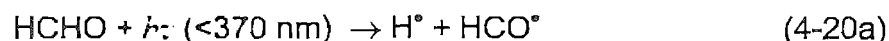
The HO₂[•] radicals produced readily react with NO to form additional ozone:



The NO_x present in the chemical mixture maintains its catalytical role in ozone production until it is transformed into a less reactive form - nitric acid - mostly through reaction with $\text{HO}^\bullet$:



Chemical removal of NO_x may also occur during the night through heterogeneous processes in clouds and aerosol particles (Lelieveld and Crutzen (1990); Dentener and Crutzen (1993)). The formaldehyde formed in Reactions (4-14) and (4-15) photodissociates or reacts with $\text{HO}^\bullet$, which yields additional $\text{HO}_2^\bullet$ and thus ozone:



In addition to this $\text{HO}^\bullet$ initiated reaction sequence leading to ozone production, alkenes also react directly with ozone, which yields an ozonide which rapidly fragments, for example, into formaldehyde. The reaction between ethene (C_2H_4) and ozone (O_3) is



The latter reaction product, a dioxirane (or Criegee intermediate), largely decomposes into CO and H_2O (Finlayson-Pitts and Pitts (1986)). Reactions (4-

23) and (4-24) may also be important at night: in the absence of sunlight the formaldehyde formed can accumulate until the next morning, therefore becoming a readily available source of $\text{HO}_2^\bullet$ and $\text{HO}^\bullet$ radicals which can rapidly initiate ozone production.

The production of oxidized species (for example, CO_2 and NO) dominates in the flaming phase of burning, while emissions of reduced gases (for example, CH_4 , NMHC) become more important in the smouldering phase (van Wilgen *et al.*, 1997). In addition to these reduced gases, a large variety of partially oxidized hydrocarbons (oxygenates) are emitted during the smouldering phase of fires. These volatile organic compounds (VOC's) include alcohols, aldehydes, ketones, carboxylic acids and esters among which species with up to four carbon atoms are the most abundant. Aromatics emissions are also present in biomass burning. Of these substances, benzene and toluene are the most abundant members, which also include polycyclic aromatic hydrocarbons.

Table 4.1 shows the estimated emissions from biomass burning on the Mpumalanga Highveld (Pienaar and Helas, 1996).

A study based on the emissions of VOC and nitrogen oxides from different types of fires was conducted during the SAFARI-92 campaign in southern Africa. Specific biomass plume data was obtained from the SAFARI-92 campaign (Table 4.2). This background plume data was used in the PBM for input data, and the ozone concentrations in biomass burning plumes were modelled under different climatological conditions.

Table 4.1 – Estimated biomass burning emissions on the Mpumalanga Highveld from all sources for South Africa per annum (Helas and Pienaar, 1996).

Activity	CO ₂ /Tg	CO/Tg	CH ₄ /Gg	NO _x /Gg	N ₂ O/Gg
Industrial coal use	239	57.2	2.0	1359	1.9
Domestic coal fires	4.0	161	?	13.1	?
Domestic wood fires	17.9	1687	30.4	49.3	?
All types of vehicles	48	3428	15.9	519	0.82
Veld and bush fires [#]	-	4651	265	30.9	1.32
*Veld and bush fires [#]	64.2	5008(¥1990)	356(¥110)	122(¥38)	-
Sugar cane burning	4.0	94.5	5.4	1.88	0.09

? = value not known; [#]based on an estimated 44.3 Tg dry mass (DM) (=19.9 Tg carbon) burned per year during savanna (23.1 Tg DM), grassland (18.3 Tg DM) and fynbos (2.9 Tg DM); * using averaged emission ratios; ¥for emission ratios measured in SAFARI-92.

The NO_x concentration in Table 4.2 is 40 ppb. The NO_x correlate to a NO₂:NO ratio of 3:1 (JJ Pienaar personal communication, 1999). The alkane concentration of 72 ppb was divided equally between ethane (C₂H₆) and propane (C₃H₈). Ethylene (C₂H₄) and propylene (C₃H₆) shared the alkene concentration of 20 and 19 ppb respectively. The aromatic's class of VOC's was divided between benzene and toluene. The above concentrations were used as input parameters for the PBM in modelling the ozone formation in the biomass plumes.

Table 4.2 – Drakensberg fire data from SAFARI-92 (Koppmann *et al.*, 1998).

Species	Background air data / ppb	Plume data / ppb
NO _x	0.01	40
O ₃	50	0
CO	70	2321
CH ₄	1700	1981
Non Methane Alkanes	-	72
Alkenes	-	39
Aromatics	-	33

*Measured at the source.

Table 4.3 – Biomass burning plume VOC's data SAFARI-92 (von Czapiewski *et al.*, 1998).

Biomass % of Total VOC's			
8%	Aldehydes	Aldehydes % of Total Aldehydes	
7%	Ketones	Asetaldehydes	53%
5%	Furanes	Formaldehydes	15%
2%	Esters	C3	15%
37%	Methane	C4	12%
16%	Alkenes		
10%	Alkanes	Ketones % of Total Ketones	
7%	Aromatics	Acetone	50%
3%	Others	C4	30%
2%	Alkynes	C5	15%
2%	Dienes		
1%	Cyclics		

Table 4.2 and 4.3 were used as input data for the PBM simulations under different seasonal variations.

4.3.1.1 Results

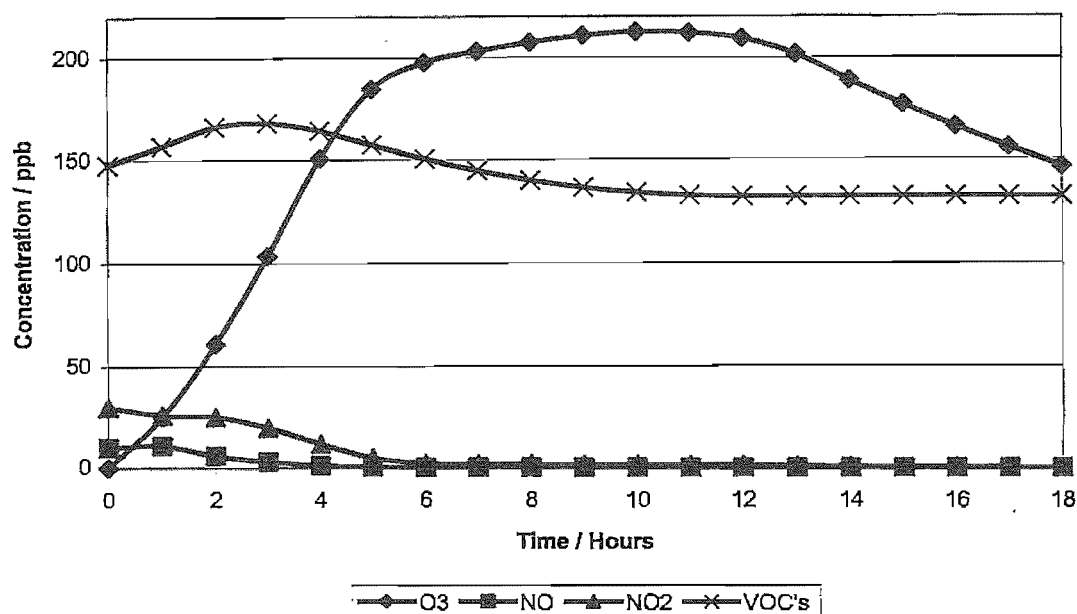


Figure 4.5 – PBM summer conditions simulation, simulation started at 04:00 local time.

Figure 4.5 shows that the ozone concentration increases at a steady rate in the first five hours of the simulation, while the VOC's profile shows decay in the same time period. The modelled ozone reaches a plateau within 6 to 13 hours from the start of the simulation. A maximum concentration of 210 ppb is reported after 10 hours. This is the equivalent of 14:00 (local time) in the simulation. The VOC concentration in Figure 4.5 also increases in the first three hours of the simulation and reaches a maximum concentration of 160 ppb after three hours, before the concentration decays at a steady rate.

NO_x concentration also decays with a steady rate, and after about 4 hours the NO_x concentrations are negligible.

The ozone concentration increase correlate with the increase in solar radiation of the same time period and the rapid decay of the NO_x, presented in Figure 4.6. Figure 4.7 shows the profiles of the free radical catalysed oxidation of the VOC's in the presence of NO_x, and the associated generation of ozone (O₃).

A latitude parameter of -27° was used in all of the simulations, and the solar declination angle was changed from -23° in summer to 23° under winter conditions. This means that the zenith angle changes from 4° in summer to 50° in winter.

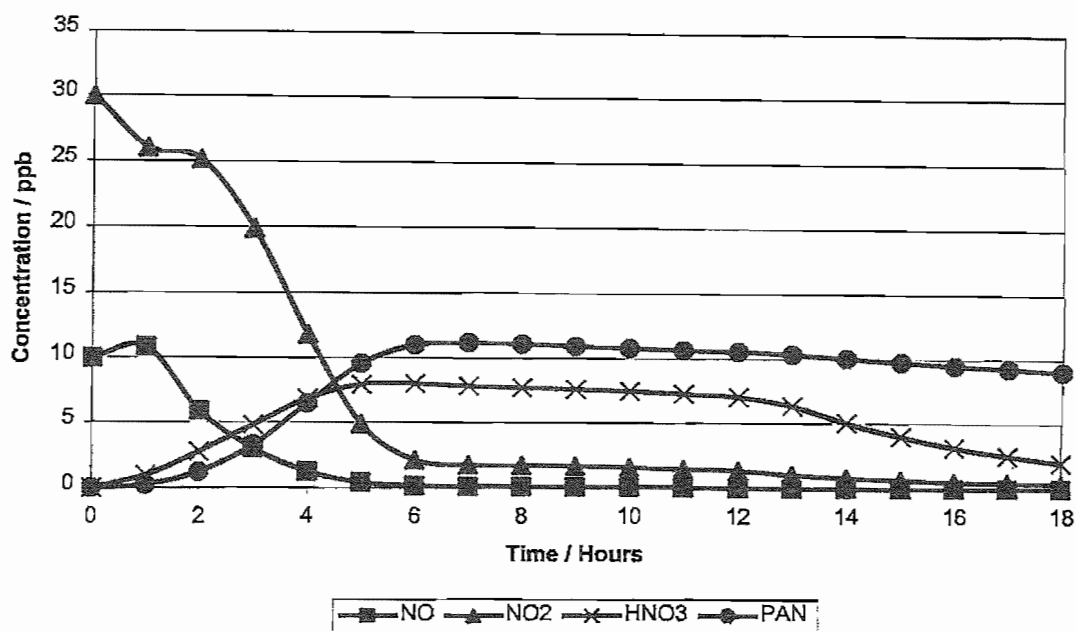


Figure 4.6 – PBM summer conditions simulation, simulation started at 04:00 local time.

The ozone concentration increase during the first five hours correlate with the increase in solar radiation of the same time period, and the rapid decay of NO_x , presented in Figure 4.6. The NO_x concentration decays at a rapid rate over the first five hours, and then decays at a steady rate until it is depleted after about 15 hours. The PAN concentration also increases until it reaches a maximum value on six hours after the simulation started. Subsequent to this increase the PAN concentration decays at a very low rate.

After the oxidation of NO_x species (7 hours), a maximum ozone concentration is reported (Figure 4.5). This maximum ozone level gives rise to elevated levels of $\text{HO}^\bullet$ radicals (Reactions 4-1 and 4-2).

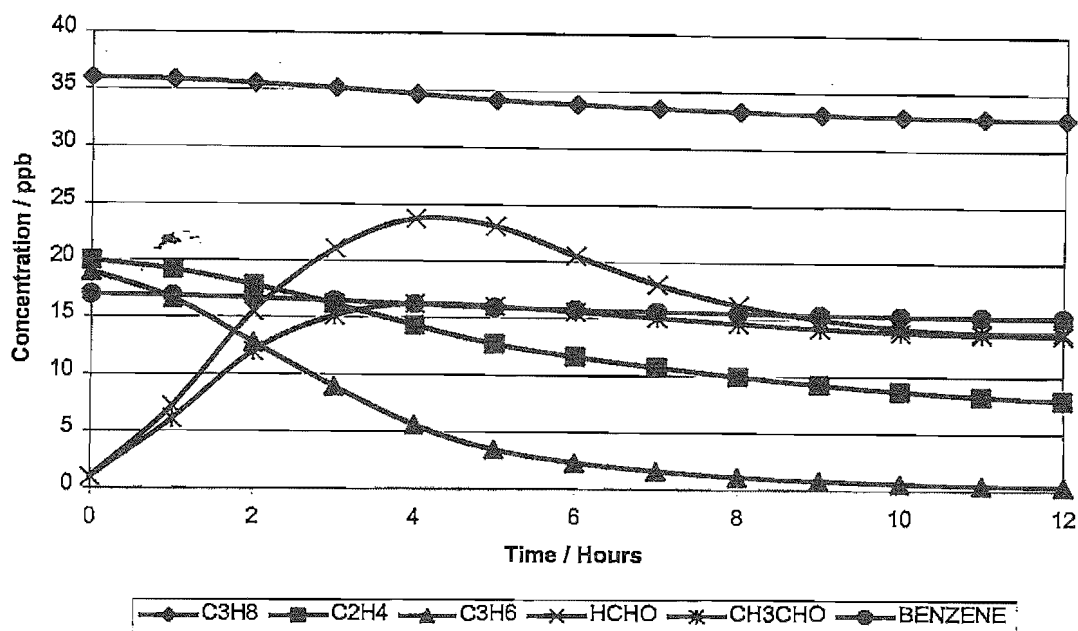


Figure 4.7 – PBM summer conditions simulation, simulation started at 04:00 local time.

Figure 4.7 shows the free radical catalysed oxidation profiles of selected VOC's. The alkanes in the simulation correlates to the tendency of propane, represented in the curve (C_3H_8) in Figure 4.6. The aldehydes or formaldehyde (HCHO) in particular shows that the aldehyde concentration increases to a maximum of 24 ppb on 4 hours after the simulation had started. After this maximum the aldehydes start to decay to a final concentration of 15 ppb after 12 hours. The aromatics (benzene) show little reduction in concentration over the simulated time period, and stay almost constant at about 14 ppb. The alkenes however show a steady rate of decay over the simulated time period.

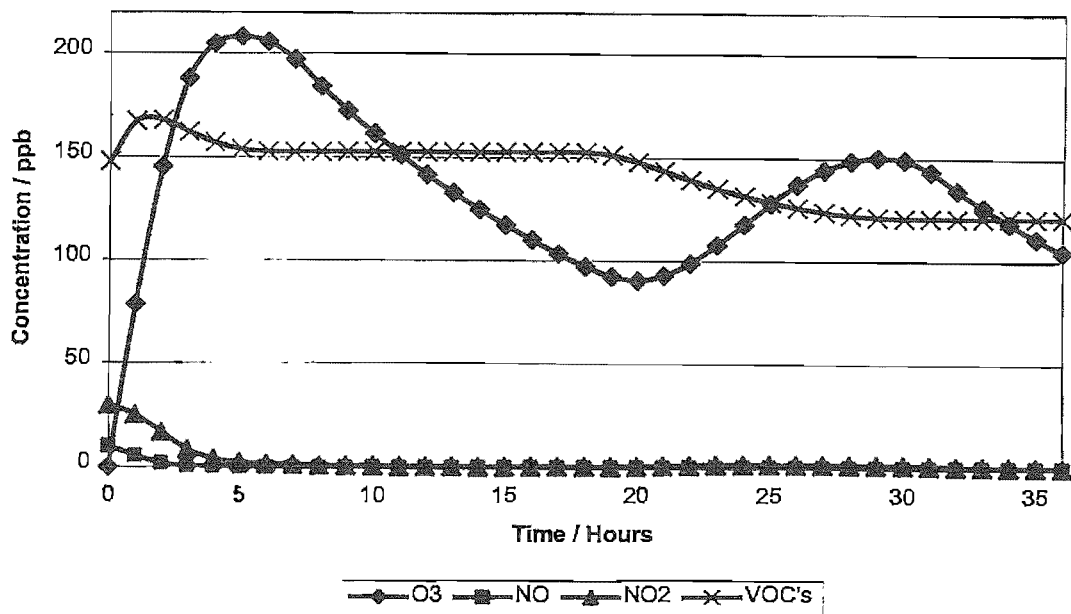


Figure 4.8 – PBM summer conditions simulation, simulation started at 10:00 local time.

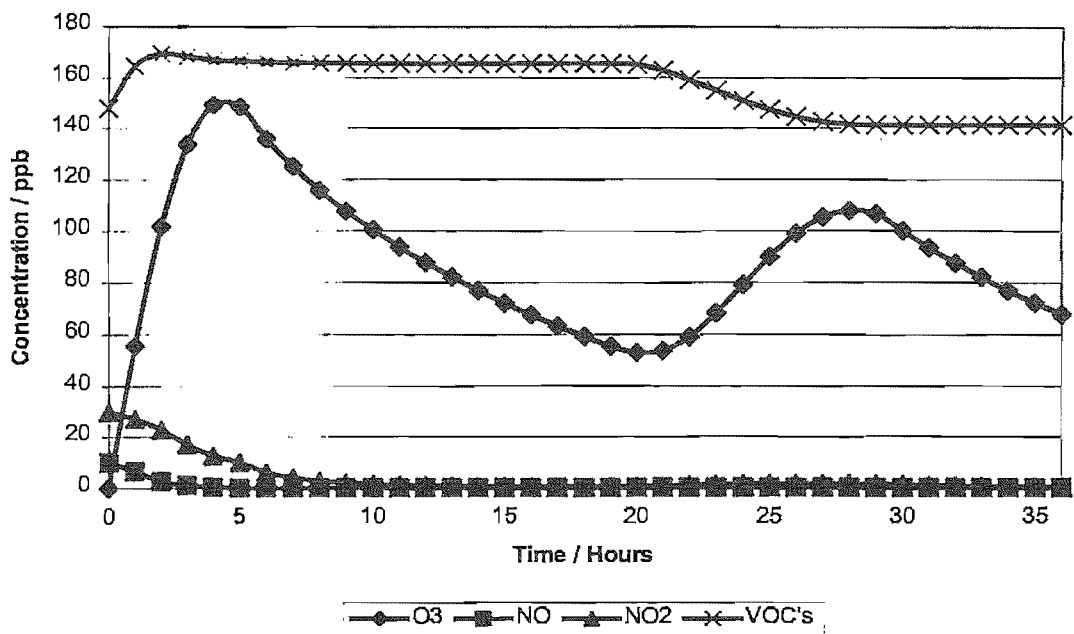


Figure 4.9 – PBM winter conditions simulation, simulation started at 10:00 local time.

Figure 4.8 and 4.9 graphically depicts a simulation started at 10:00 (local time) and ran for 36 hours. The ozone diurnal cycle is clearly visible on both figures, with a maximum of about 210 ppb after 2 hours after maximum solar radiation for the summer conditions. This ozone concentration decayed in the afternoon and

reached a minimum of about 50 ppb in the night, when solar radiation was at a minimum. When the solar radiation rapidly increased the next morning after about 20 hours (08:00 local time) the ozone increased to a maximum of 150 ppb in the case of summer conditions. The winter simulation showed the same tendency but with lower concentrations of ozone, because the mean solar radiation was lower during the winter than the summer season.

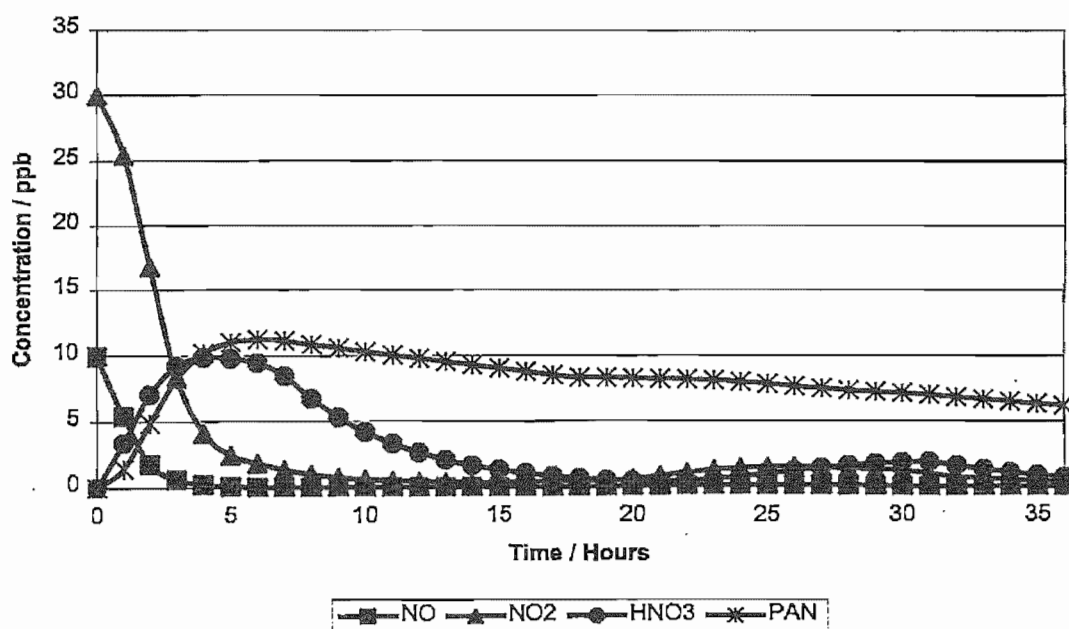


Figure 4.10 – PBM summer conditions simulation, simulation started at 10:00 local time.

The differences in the starting time of the simulations are illustrated by comparing Figure 4.6 with Figure 4.10. It is clear from these two figures that the starting time has an influence on the concentrations of the species. This is due to photochemical reactions been initiated sooner in the biomass plume.

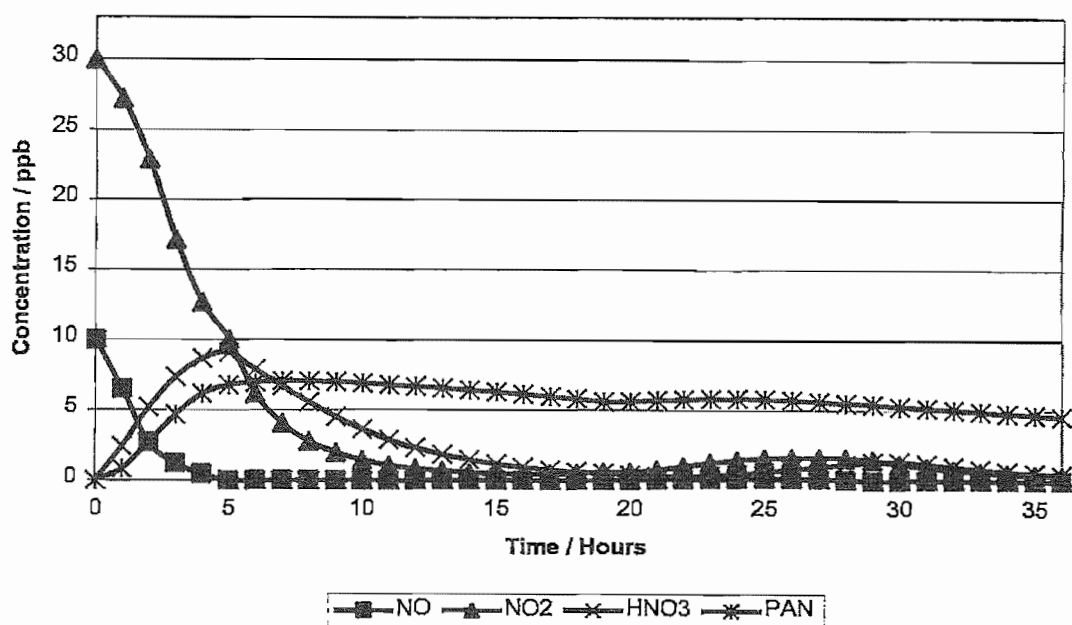


Figure 4.11 – PBM winter conditions simulation, simulation started at 10:00 local time.

Figures 4.10 and 4.11 show the tendency for the oxidation of PAN under summer and winter conditions. The simulation started at 10:00 (local time), and the simulation ran for 36 hours. Figure 4.11 shows that the PAN concentration reached a maximum of 7 ppb in winter while the concentration reached 12 ppb during summer condition. This is the result of lower ozone values for the two seasonal conditions, and thus a lower oxidation potential for winter conditions.

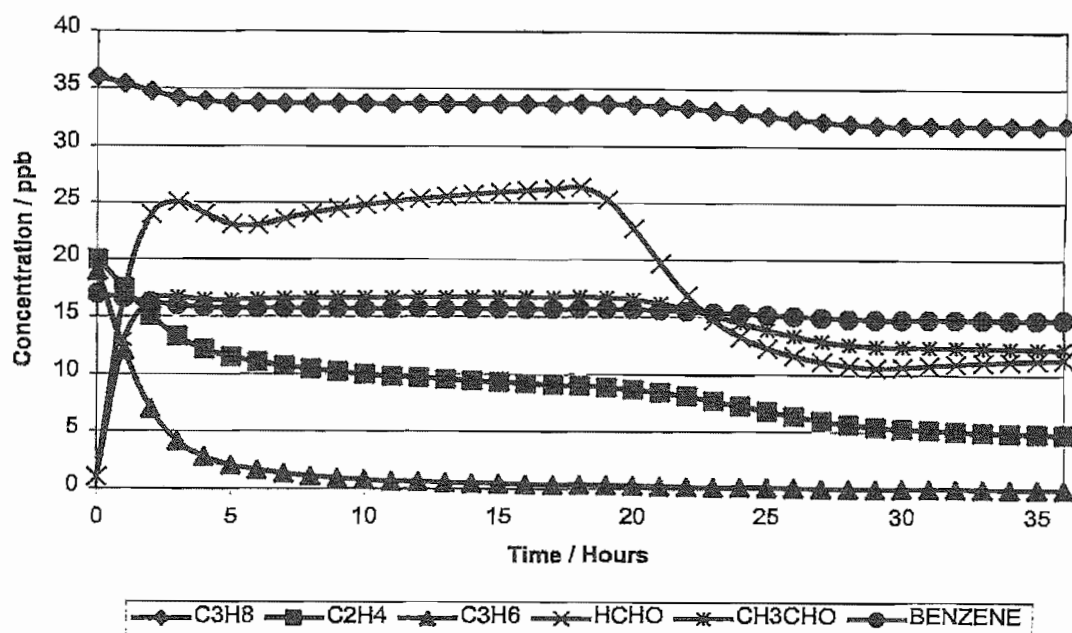


Figure 4.12 – PBM summer conditions simulation, simulation started at 10:00 local time.

Figure 4.12 and 4.13 shows the free radical catalysed oxidation profiles of selected VOC's, under the two seasonal conditions. The simulation started at 10:00 (local time) and ran for 36 hours.

Under these conditions the aldehydes or formaldehyde (HCHO) reached a higher maximum for winter conditions than for summer conditions. HCHO reached a maximum of 27 ppb in summer and 32 ppb under winter conditions.

Again this tendency is related to the lower ozone levels under winter conditions, and thus a lower oxidation capacity for HCHO under these conditions in comparison to the summer conditions.

The aromatic (benzene) concentration showed very little change over the time period, and thus very little oxidation of the aromatics took place.

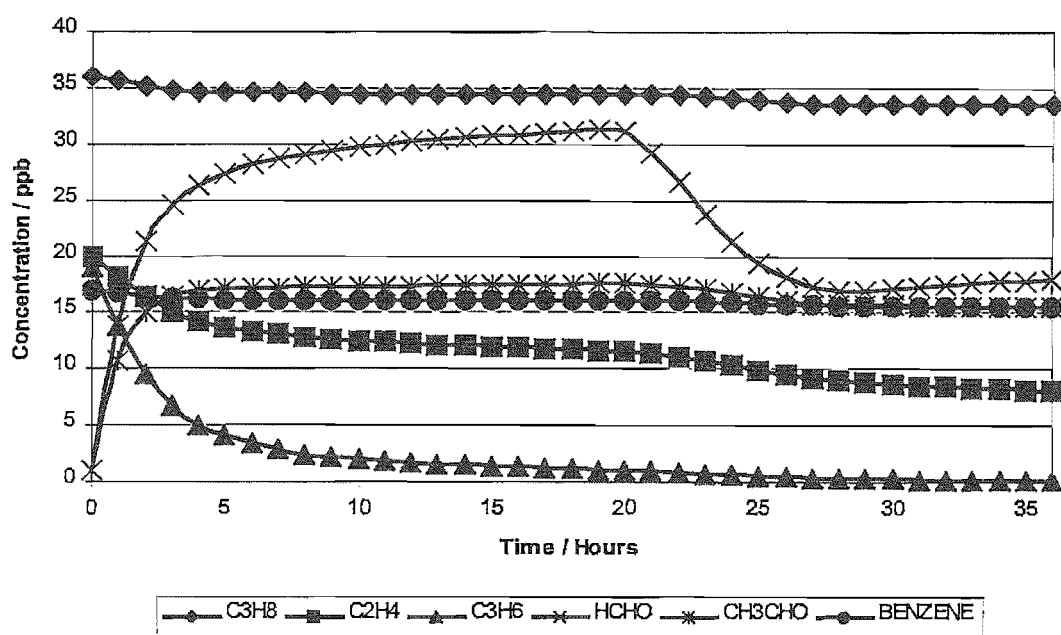


Figure 4.13 – PBM winter conditions simulation, simulation started at 10:00 local time.

The effects of the above reactions and additional ones with NMHCs on ozone build-up in biomass burning plumes can be summarised as follows. An attack of a NMHC molecule by $\text{HO}^\bullet$ yields alkylperoxyl radicals ($\text{RO}_2^\bullet$) in the presence of NO_x . NO-NO_2 conversion takes place through which an ozone molecule is formed without net loss of NO_x . Important additional reaction products are aldehydes (RCHO) and peroxyradicals ($\text{RO}_2^\bullet$). Photodissociation of formaldehydes or their reaction with $\text{HO}^\bullet$ also yields $\text{HO}_2^\bullet$ radicals which contribute to the NO-NO_2 conversion and enhance ozone production. In this NO-NO_2 conversion, $\text{HO}^\bullet$ is regenerated so that the overall reactivity of the reaction mixture is maintained, and the breakdown of NMHC is continued. The chemical destruction of NMHC through aldehyde formation (reactions 4-20 to 4-25) is also a source of CO and, in turn, is not as reactive. As a result of its relatively longer lifetime of several weeks to months it is mixed into the free troposphere where it can contribute to large-scale ozone formation.

The efficiency of ozone formation in the plumes per molecule of NO_x is largest after some dilution has taken place because the ozone yield is a non-linear function of the NO_x concentration, which is largest at relatively low NO_x levels (van Wilgen *et al.*, 1997). Ozone is also depleted by the reaction of NO into NO_2

at high NO levels and HO^{*} is reduced by its reaction with NO₂ (4-19). On the other hand, after several hours the most reactive NMHC's have become depleted (Figure 4.6), so that one can expect the highest ozone production rates after a few hours (Figure 4.6), depending on the rates of dispersion and chemical reactions.

The NO_x:CO emission ratio in biomass fires is used to quantify the efficiency of ozone production in biomass burning plumes. Low NO_x:CO emission ratios in biomass fires reflect relatively low combustion temperatures, and at high latitudes, the low nitrogen content of vegetation reports a positive correlation between O₃ and NO_x in biomass burning plumes, implying that ozone production is NO_x-limited. This NO_x-limitation is also found in photochemical models of plume chemistry, where it is explained by the high NMHC emissions in biomass fires Jacob *et al.* (1992).

4.3.1.2 Conclusions

The results of the modelled biomass plume shows that biomass burnings emissions indeed yield results in high O₃ concentrations as it has been confirmed by measurements during SAFARI '92 (Helas, 1995). It also follows from Figure 4.1 that the biomass plume is NO_x limiting. Due to this fact, VOC's from biomass burning plumes will be transported over long distances. This aspect is enhanced during the winter when the total VOC concentration exceeds ozone concentrations. It should be noted that the starting time of the fire have a significant effect on the concentration time profiles.

4.3.2 Diffusive sources

A diffusive source can be defined as any source, which emit certain pollutants over a wide and not always clearly defined area. These sources may include road services, waste disposal areas and product storage areas to name only a few. Emissions from a large waste disposal area, mainly handling tar, pitch, heavy oils and "gunk" were investigated. These unutilised products are commonly referred to as black products. These products are usually rich in volatile-, semi-volatile- and heavy hydrocarbon species, with BTEX being prominent.

The VOC monitoring results reported in Chapter 3 were intended to validate VOC emissions from diffusive sources in Secunda. The emission data are considered to be confidential and are therefore not given. The same model as it is described in the previous paragraphs was used to model summer and winter ozone formation potential and the chemical transformation rates of selected VOC's (Benzene, Toluene, Xylene, Ethyl-benzene and PAN).

4.3.2.1 Results

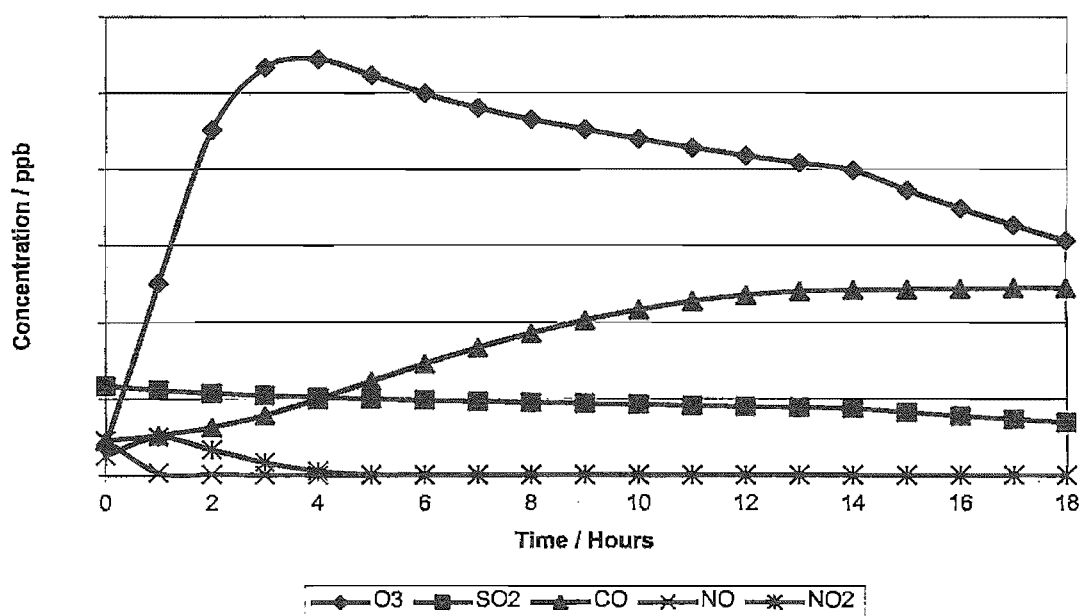


Figure 4.14 – PBM summer conditions simulation, simulation started at 06:00 local time.

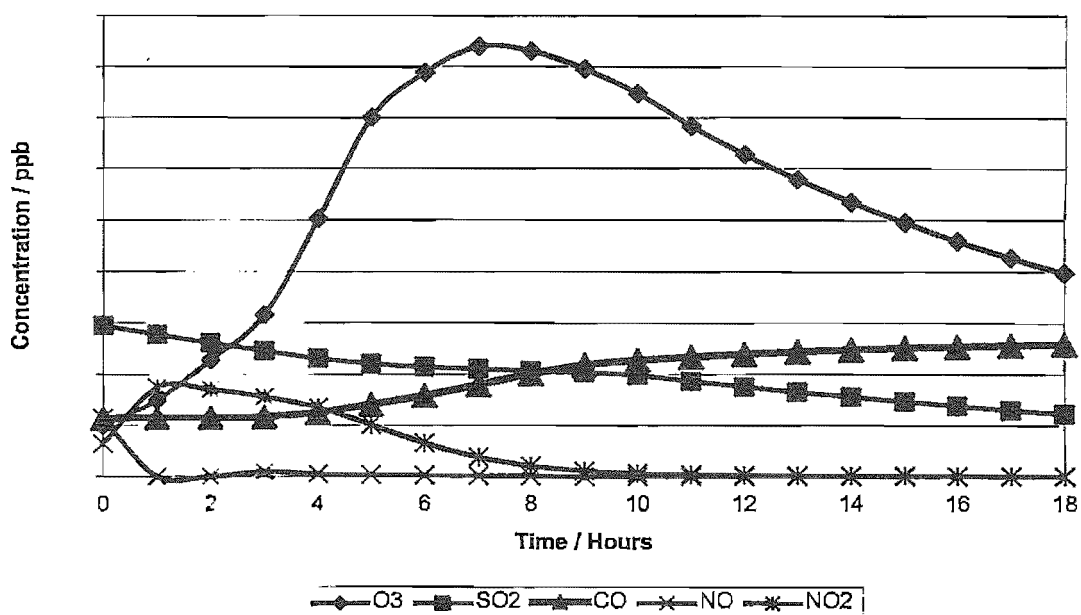


Figure 4.15 – PBM winter conditions simulation, simulation started at 06:00 local time.

The concentration values on the figures are not shown, for reasons of confidentiality.

Figures 4.14 and 4.15 show the summer and winter simulations of the inorganic components. The simulation started at 06:00 (local time) and ran for 18 hours. The difference between the summer and winter season can be differentiated by the ozone concentrations in the two figures. The ozone concentration reached a maximum after four hours during summer simulation, while a much lower maximum concentration could only be achieved after six hours during the winter simulation. This is the result of a lower mean solar radiation during winter months in comparison to the summer months. Also worth mentioning is the time when the ozone reaches the maximum concentration (4 hours – 10:00 local time), against the winter simulation of 7 hours (13:00 local time). Intense solar radiation is thus experienced in a shorter time during the summer season.

The NO concentration decayed rapidly during the first hour of the simulation, because of an oxidation reaction to NO₂ or as part of the ozone forming reaction. After this phase, the NO₂ gets converted back to NO (4-7 and 4-8) in of the ozone forming process. In Figure 4.14 at 4 hours, when the ozone concentration is at a maximum, the NO₂ concentration is depleted.

The CO concentration rised very slowly over the time period, until it remained constant at about 14. hours. This is because CO is an end product of many of the aromatic reactions as it is shown in Appendix A.

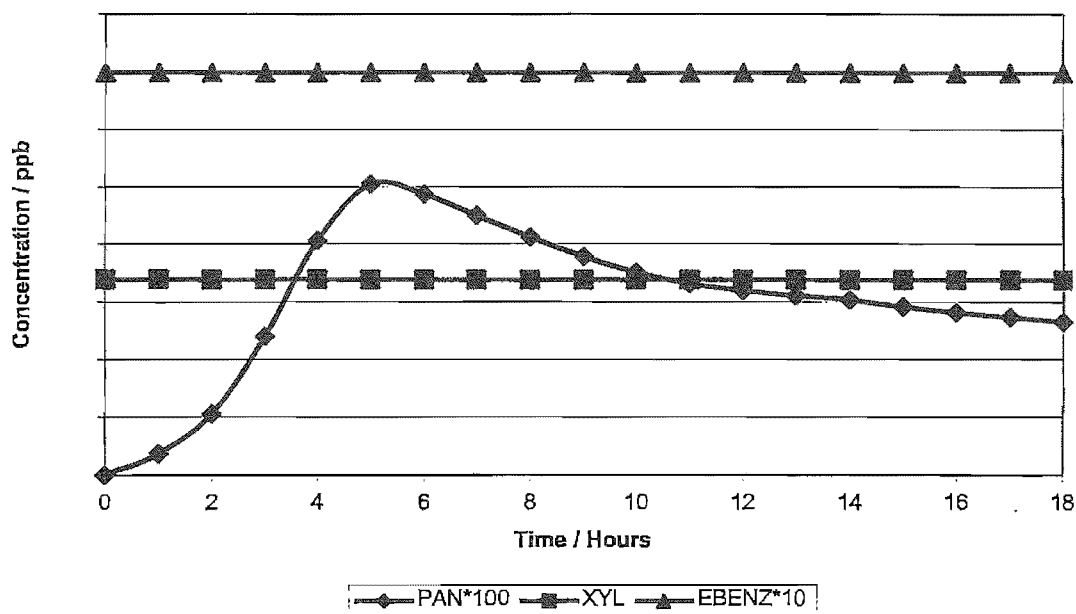


Figure 4.16 – PBM summer conditions simulation, simulation started at 06:00 local time.

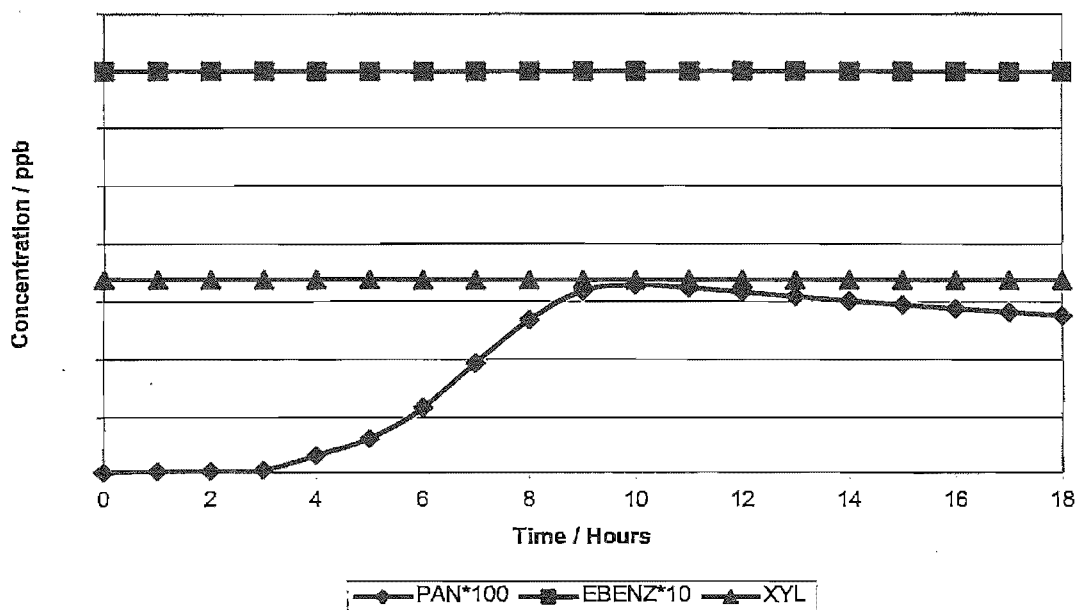


Figure 4.17 – PBM winter conditions simulation, simulation started at 06:00 local time.

Figures 4.16 and 4.17 show the results for the aromatics (Xylene and Ethylbenzene) and PAN during the summer and winter simulation. There was only a slight decrease in the xylene and ethylbenzene concentrations during both of the simulations. The PAN concentration showed a steady increase in both figures, and reached a maximum after five and nine hours respectively during the summer and winter simulation. The PAN reached a much higher concentration during the summer simulation, than during the winter simulation.

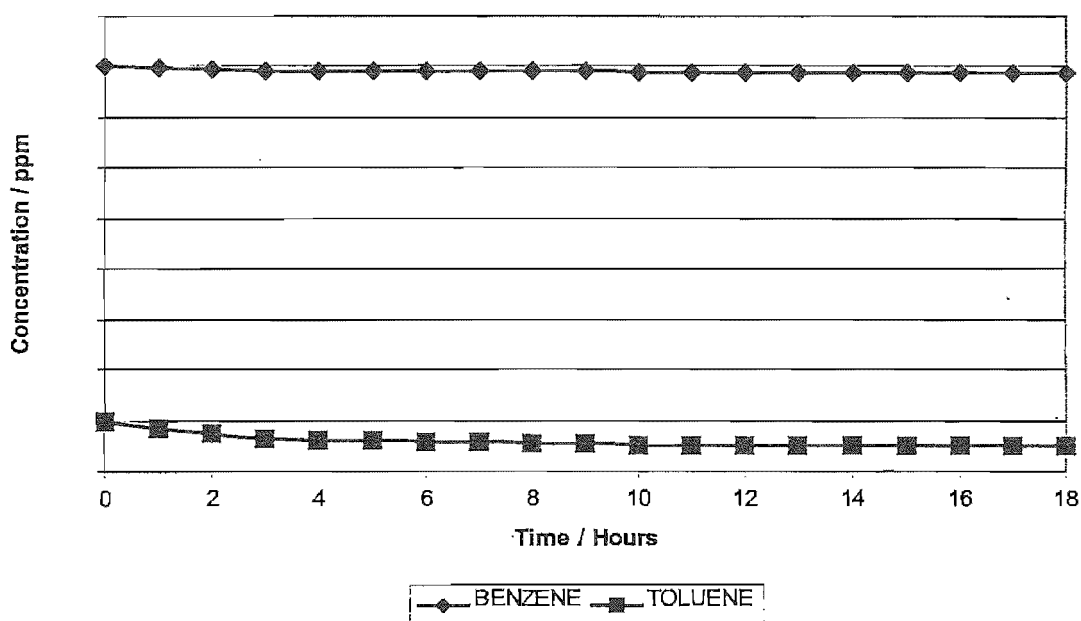


Figure 4.18 – PBM summer conditions simulation, simulation started at 06:00 local time.

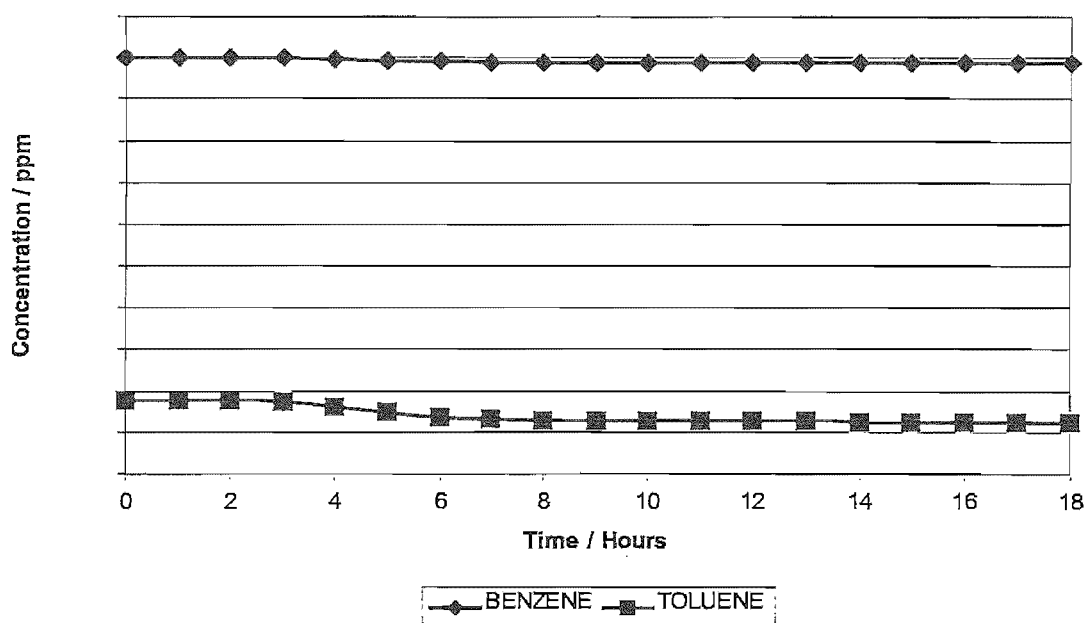


Figure 4.19 – PBM winter conditions simulation, simulation started at 06:00 local time.

Figures 4.18 and 4.19 show the results for benzene and toluene during the two simulations. It should be noted that the ambient concentrations for the species were measured in the vicinity of the source. Benzene and toluene are rather stable (like the previously mentioned aromatics (xylene and ethyl-benzene)). Toluene was a bit more reactive than benzene during the simulated time period. The oxidation of benzene and toluene during the summer conditions showed an immediate decay due to radiation from the sun. Results from the winter conditions shows immediate stability with decay after two hours, when sun radiation took place. Oxidation is also coupled to the ambient NO_x concentration. The NO_x species were depleted after eight hours of simulation. This resulted in the stability of the species after eight hours. The complete degradation mechanisms for benzene and toluene that was used in the PBM, are attached to this dissertation as Appendix A. During the decay of benzene and toluene, large quantities of CO were formed as it is shown in Appendix A. This accounts for the steady increase of CO in Figures 4.14 and 4.15.

4.3.2.2 Conclusions

The results of the modelled diffusive source plume showed that the aromatic compounds are very stable and therefore will the concentration largely depend on meteorological removal processes. High concentrations of these species would be measured at these sites under stable conditions. Temperature variations would also play an important role in the concentration levels at these sites. It also followed from the results that the ozone production in the plumes was NO_x limited.

4.4 VALIDATION OF THE PBM

Validation of the detailed chemical mechanism that was used in the PBM was done by Jenkin *et al.*, 1997 and Derwent *et al.*, 1998. Due to this fact it was decided that the use of the chemical mechanism as defined by Jenkin and Derwent for the degradation of VOC's under southern African conditions would be relevant.

Typical day cycles of ambient species were reported by Calvert *et al.*, 1995. A schematic presentation of these cycles is presented in Figure 4.20.

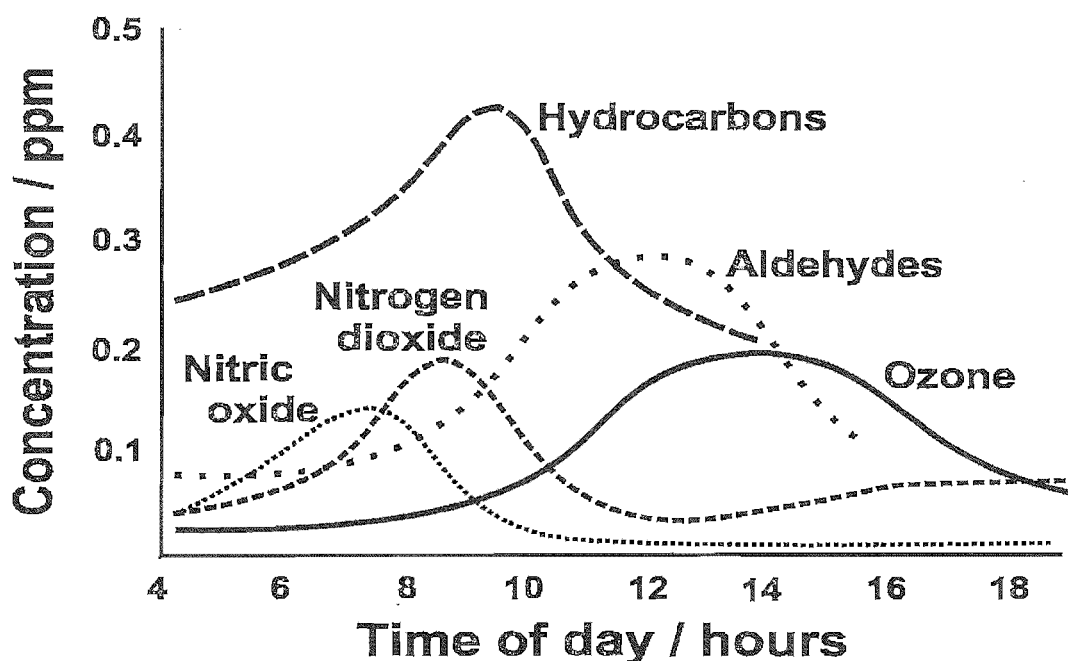


Figure 4.20 – Daily cycles of ambient species (Calvert, 1995).

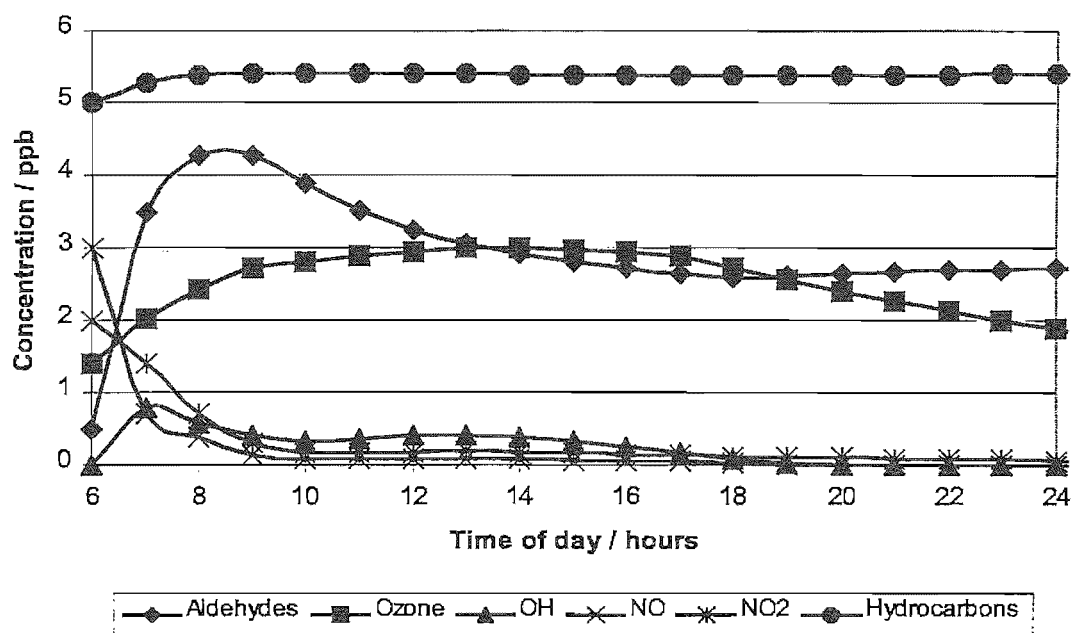


Figure 4.21 – PBM simulation of ambient species, simulation started at 06:00 local time.

Figure 4.21 represents these cycles as simulated by the PBM, under southern African conditions.

Figure 4.20 represents these cycles, which started at 04:00 local time, while Figure 4.21 represents the same simulation started at 06:00 local time. It should be noted that the simulation represented in Figure 4.20 was conducted under European conditions, with less solar radiation and light intensity. Southern African conditions with a high solar radiation will result in rivalry between the photochemical and thermal reactions. Although there is a concentration difference between the two figures, the ratios of production between the different species remains the same. The ozone concentration in Figure 4.21 reached a maximum at 15 hours in comparison to the maximum achieved and represented in Figure 4.20 at 14 hours. The aldehydes reached a maximum concentration before the ozone did in both Figures. The ozone formation process started at 8 hours, following a rapid decline of the nitrous oxide and dioxide species. The high initial concentrations of the NO_x species in Figure 4.21 show that no NO_x species will be formed (such as those in Figure 4.20), but that immediate decay will set in. Figure 4.20 shows low initial NO_x concentrations, with formation occurring when the solar radiation begins.

4.5 CONCLUSIONS

Ozone production in biomass and diffusive petrochemical plumes tends to be initially NMHC limited, shifting to a NO_x limited regime as the plume ages and when NO_x is diluted and chemically destroyed.

The effect of biomass burnings on tropospheric ozone production is driven more by regional-scale production from dispersed biomass burning effluents than by the process of production within concentrated plumes.

Available experimental data sets are hardly sufficient for a conclusive evaluation of diffusive dispersion models, however. A better emission inventory is required for the modelling of petrochemical diffusive plumes.

Considering the validation studies and the results from the simulations, the photochemical box model succeeds in simulating chemical transformations for photochemical species.

CHAPTER 5

TRAJECTORY TRANSFORMATION MODEL

In this Chapter...

An introduction to the trajectory model (Par 5.1) is provided. Par 5.2 points out the various stages in the model development, while Par 5.3 focuses on the modelling results from the trajectory model. Par 5.4 focuses on the validation of the trajectory model. Par 5.5 concludes the chapter by summarizing and pointing out the limitations of the trajectory model. Appendix B contains the complete source code for the model.

5.1 INTRODUCTION

Since 1992 a great deal of research had been undertaken in South Africa on the horizontal and vertical transport of aerosols and trace gases over southern Africa (Tyson *et al.* 1998). This research addresses the need to understand the extent of trace gas transport and deposition over South Africa, its neighbours and other African countries in order to assess the extent of transboundary pollution transport. Air pollutants affect the environment both directly, through wet and dry deposition to exposed surfaces, e.g., acid rain, and indirectly through the effects of trace gases and aerosols on the global climate (Houghton *et al.*, 1996). It is therefore important to understand the relationship between the emission of pollutants from major industrial sources and their distribution over the globe (Andreae, 1995).

The purpose of this trajectory transformation model (TTM) is to explore the transport of trace gases and deposition over the subcontinent from the highveld region, the industrial heartland of South Africa. Deposition of trace gases is a key issue in the transboundary transport of pollution debate. In particular, it is of interest to determine the extent to which industrial pollutants impact on neighbouring and other states.

Forward trajectories have been calculated for the South African Highveld (Piketh *et al*, 1998). Each trajectory was classified to determine patterns of general flow for a period of five years. Transboundary transport has been estimated from the identified classification and estimates of impacts to neighbouring states made annually, seasonally and at different trajectory starting levels (Piketh *et al*, 1998).

Atmospheric trace gases follow the above mentioned trajectories, and are important contributors to global change. Little is known, however, about the increase in atmospheric trace gases since the industrial revolution. South Africa is the largest source of anthropogenic aerosols and trace gases in southern Africa. Sulphur is the most important component of climate forcing aerosols. It manifests in the atmosphere as a secondary pollutant through the oxidation of SO₂ to sulphate (SO₄²⁻) (Warneck, 1988). Sulphate exists in the atmosphere in the accumulation mode of the particle size spectrum (~0.4 µm) and acts to force climate change directly by increasing the amount of short wave radiation reflected back to space, and indirectly by increasing the atmospheric life-time of clouds, thus increasing albedo (Andreae, 1995 and Houghton *et al*, 1996). South Africa emits approximately 730 million kilogram of sulphur into the atmosphere each year (Siversten *et al*, 1995). This represents 0.3% of the total aerosol emissions from all human sources worldwide (Andreae, 1995). The central plateau of the highveld was found to be a major source of trace gases (and of SO₂ in particular), primarily from power plants and the petrochemical and metallurgical industries (Wells *et al*, 1996).

In the 1980s it was thought that transport from the industrial highveld was more or less directly eastward (Tyson *et al*, 1988). Evidence of recirculation of air parcels at a regional scale was reported by Held *et al* (1994). Trajectory analysis conducted for the SAFARI-92 initiative showed that approximately 40% of all air parcels that originate over the subcontinent recirculate in an anticyclonic type pattern before being transported to the Atlantic (18%) and Indian oceans (54%). This is true of all synoptic circulation types (Tyson *et al*, 1996; Tyson, 1997; Tyson and Garstang, 1997). The trajectory climatology conducted by Tyson *et al*. (1996), is representative for the entire sub-region.

Continental high pressure systems are the most common feature of the

atmospheric circulation over southern Africa and may occur up to 80 per cent of the time in winter. The horizontal transport of air associated with these systems is distinctive. Recirculation occurs on scales ranging from hundreds of kilometers around a local source to thousands of kilometers over a number of southern African countries. Transboundary transport is common and recirculation occurs on a massive scale (Tyson et al, 1998).

Direct offshore transport takes place over South Africa, whereas the recirculation coming back towards the land occurs in a stream that re-enters southern African airspace over Mozambique. The aerosol and trace gas transport plumes involved are extremely large. Frequently, they may be more than a thousand kilometres wide and sometimes the juxtaposition of the two transport plumes may be so close as to be contiguous (Tyson et al, 1998).

The trajectory transformation model (TTM) is a box model for computing the horizontal and vertical transport of air parcels on distinctive trajectory patterns over southern Africa, and can be run on a personal computer. The TTM also incorporates dry deposition algorithms for acidification processes.

5.2 MODEL DEVELOPMENT

5.2.1 Trajectory patterns

Five distinctive trajectory patterns were identified and obtained from the Climatological Research Group at Wits (Piketh and Pranglely, 1998). These five categories are shown as a composite diagram in Figure 5.1.

The breadth of the arrows indicates the spatial variation of the transport pathway as an average (no statistical error calculated in terms of spatial domain). The southern African plume was identified as air parcels moving in a northerly direction but remaining below 10°S. The Central African plume, on the other hand, included all trajectories that moved above 10°S. A trajectory was classified as having recirculated once, if it left and returned to southern Africa. According to this study, the Indian Ocean plume consists of all the trajectories that moved quickly in the westerly winds. They may have started to move eastward initially but began to move westward, before leaving South Africa, and continued to do so. The Cape plume consisted of those trajectories whose paths

moved south for as long as they were tracked. Those moving southeastward were placed into the Indian Ocean plume. Each category is shown individually in Figure 5.2.

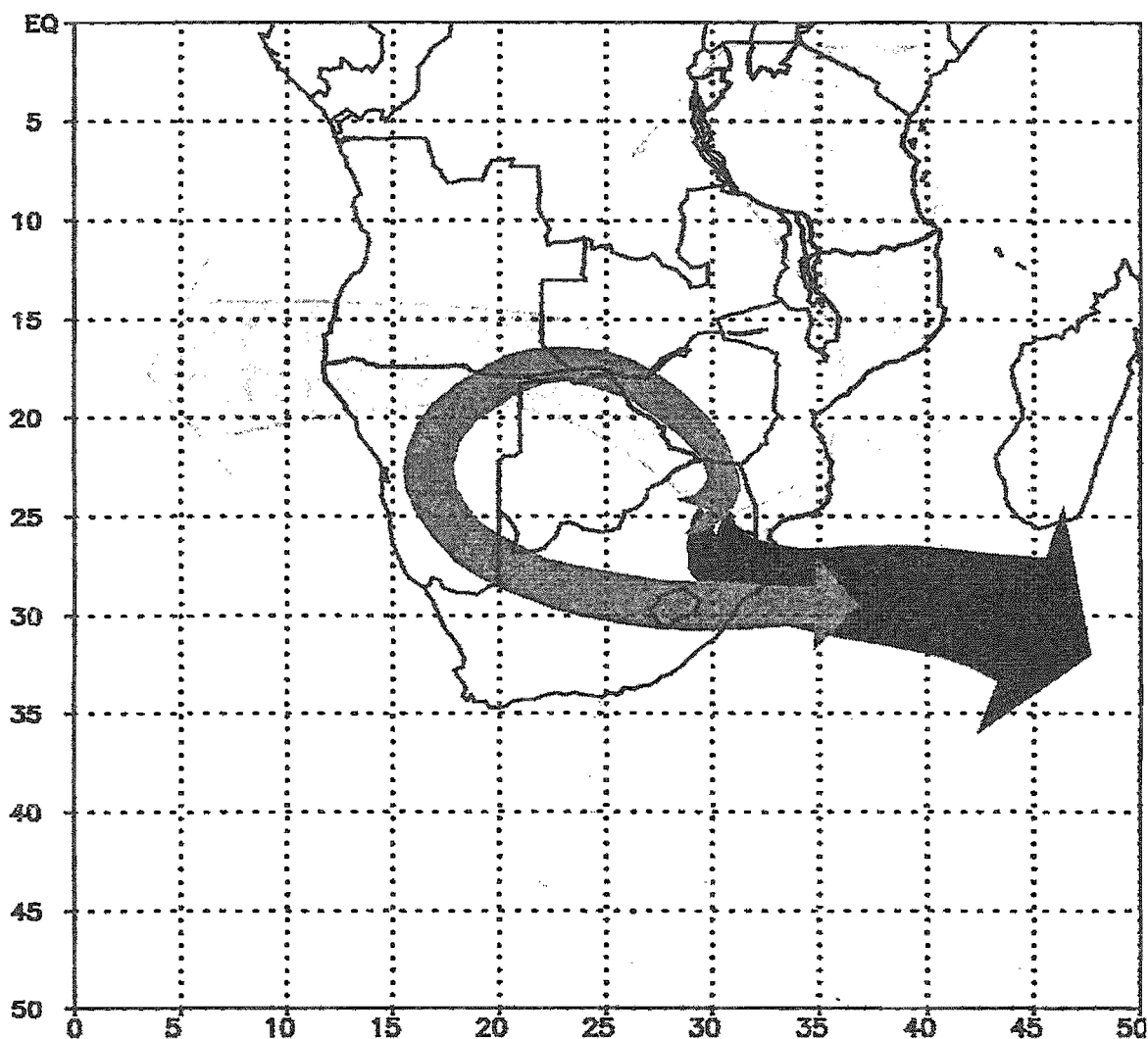
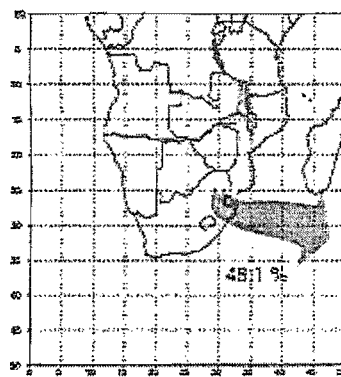
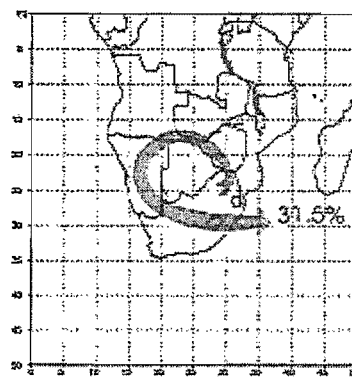


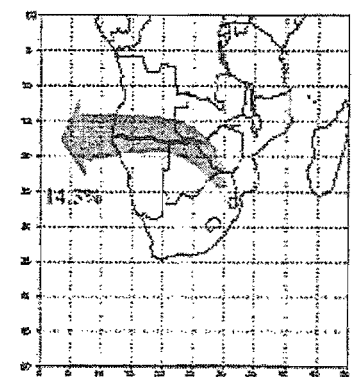
Figure 5.1 - Five transport pathways identified from the forward trajectory analysis for the five-year period 1990-1994. (The shading represents the relative importance of the flow patterns) (Piketh and Pranglely, 1998).



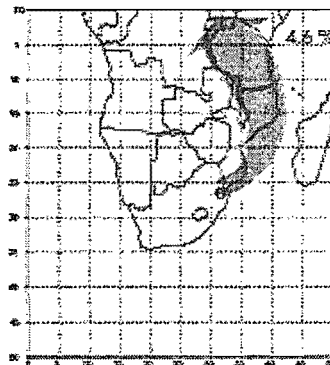
(a) Indian Ocean Plume



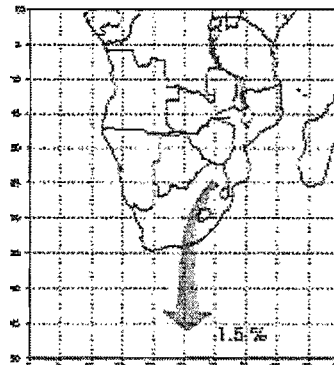
(b) Recirculation



(c) Southern Africa plume



(d) Central African Plume



(e) Cape Plume

Figure 5.2 - Five transport pathways from the industrialised highveld region. Percentages represent the annual percentage of flow for the five-year period (Piketh and Pranglely, 1998).

5.2.1.1 Indian Ocean Plume

Almost 50% of air parcels moved directly off the subcontinent over the Indian ocean (Figure 5.2a). This confirms the direct advection of material off the highveld over the Indian ocean as proposed by Tyson *et al.*, (1988).

5.2.1.2 Recirculation

Recirculation over South Africa occurs 32% of the time from within the Highveld (Figure 5.2b). An air parcel was considered to be recirculating if it showed any tendency to turn back on its initial pathway over southern Africa. The different recirculation patterns occurred at a range of scales as they were described in detail by Garstang *et al* (1996). The vast majority of the recirculating air parcels exited the subcontinent on the east coast of South Africa (Piketh *et al.*, 1998).

5.2.1.3 Southern African Plume

Slightly more than 14% of flow was transported northward but remains below 10 degrees south. This included all flows that remained over southern Africa which, in the main, were ultimately transported towards the west or the Atlantic Ocean. This flow included that which was described by Garstang *et al* (1996) to be transported over the Atlantic ocean and which was termed easterly transport. On average, in view of the southern African climatology this type of flow occurred for 24% of the time from the surface to 800 hPa and for 13% of the time from 700 to 500 hPa for all synoptic circulation types (Tyson *et al*, 1996). The flow typically took between seven and ten days to reach the west coast of southern Africa.

5.2.1.4 Central African Plume

Although the schematic in Figure 5.2d shows flow mainly to the eastern equatorial Africa, the flow also reached the western parts of central Africa. Only 4.5% of the trajectories travelled into central Africa above 10°S. Although as a percentage of the total flow from the highveld this is a relatively low frequency of occurrence it does extend the possible impacts of highveld-generated pollutants over a significantly larger area than any of the other flows.

5.2.1.5 Cape Plume

The least frequent of the transport pathways from the Highveld was the Cape plume (Figure 5.2e). This occurred for only 1.5 % of the time. The transport towards the south off the subcontinent was rapid and rarely exceeded three days. The plumes typically exited the subcontinent at approximately 25°E at a height of about 3000 m (700 hPa). The transport along this pathway was therefore consistently below the level of the 700 hPa absolutely stable layer.

5.2.2 Emission inventory

Most of the sulphur emitted into the southern African atmosphere is derived from fossil burning for power generation and processes of mined ores. The main industrial areas linked to mining of a large variety of minerals can be found along the oldest and most stable geological formation on the earth in southern Africa.

Along this same belt we will find a number of large primary smelters (copper, sink, lead, iron, nickel and many others) and also the largest emitters of air pollutants in southern Africa.

In order to complete the sulphur emission inventory, other industrial sources, domestic use of coal, fuel wood and waste, various oil fired boilers and diesel generators and emissions from traffic must be considered, in addition.

Figure 5.3 shows the major point sources of SO₂ in southern Africa (Sivertsen *et al.*, 1995).

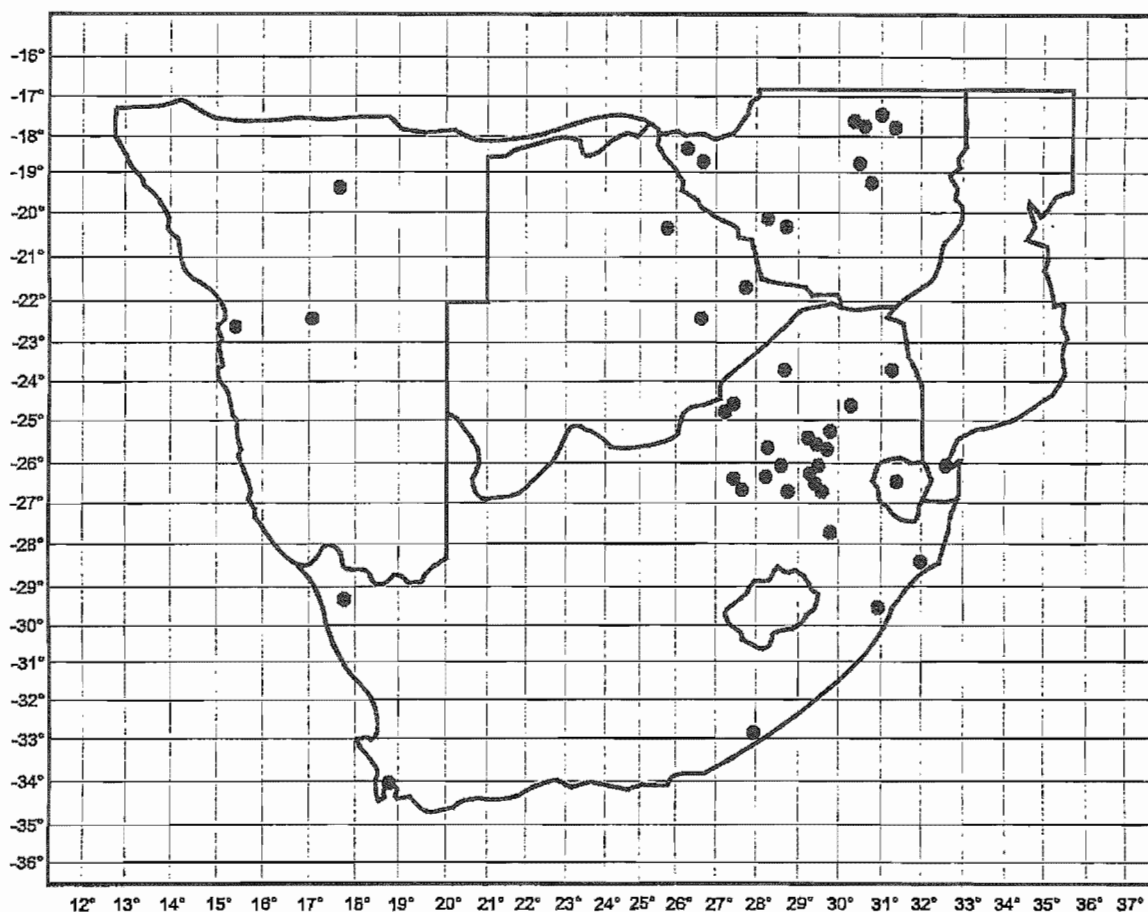


Figure 5.3 – The location of major point sources of SO₂ in Southern Africa (Sivertsen *et al.*, 1995).

The areas with the largest emissions of sulphur are located along an axis from Natal via the Mpumalanga Highveld, through eastern Botswana to western and northern Zimbabwe. Large single sources are also seen in the northern Cape province and in northern Namibia.

The geographical distribution of the total sulphur emissions in southern Africa is presented in a 1x1 deg, latitude-longitude grid system. Each grid square represents about (110 x 110) km² in the northern and (100 x 90) km² in the southern part of the grid. The final distribution presented in Figure 5.4 represents the best estimate of the emissions in 1990/1 (Sivertsen *et al.*, 1995).

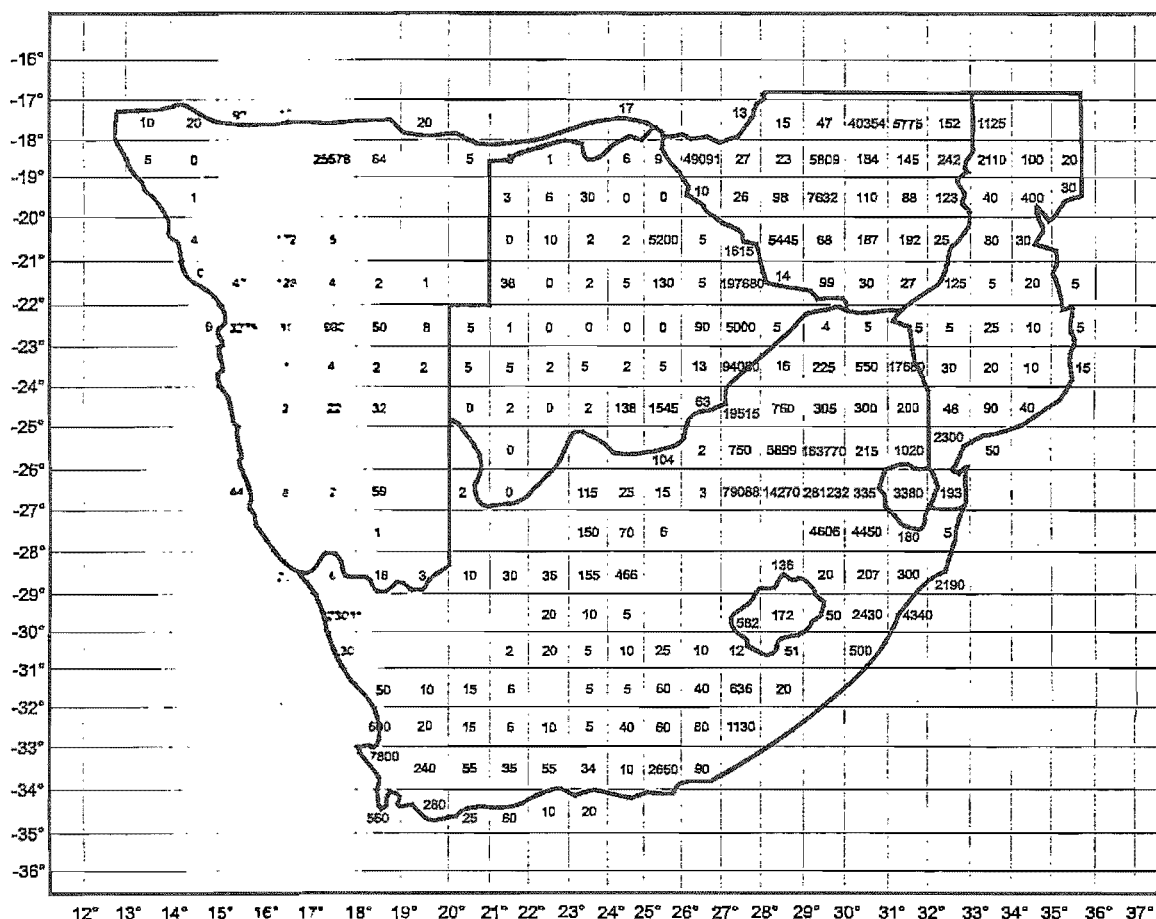


Figure 5.4 – Grid emissions of sulphur (tonnes S/year) for Southern Africa south of the 16 parallel for 1990/91 (Sivertsen *et al.*, 1995).

The trajectories that were obtained were on a 1x1 deg, latitude-longitude grid system in order to correlate with the available SO₂ gridded emission database for South Africa.

Five case study trajectories were obtained from the Climatological Research Group (one example for each of the above mentioned categories). These five trajectories coupled with the emissions database will be used for the path and input for the TTM in this study.

5.2.3 Model description

In order to test the understanding of atmospheric processes, a zero-dimensional box model was designed to evaluate the chemistry along the identified transport pathways.

The model represents a box-shaped parcel of air, which traverses with a specific trajectory over the emissions grid of southern Africa. SO₂ emissions were introduced into the model in accordance with the amount of SO₂, which entered the air parcel from the specific grid cell, under the trajectory. The chemistry within this box, and the concentrations of all the species were modelled throughout this navigation process along the trajectory.

The vertical extent of the box was determined by the depth of the mixing layer (inversion layer). This boundary layer was kept to a constant height of 1000 m. This is typical for southern African conditions (G Held personal communication, 1999). The dimensions of the air parcel were assumed to remain constant for transport period (normally 10 days).

The starting point of all trajectories, and thus the air parcel or box, is Middelburg, South Africa (-25.8°S, 29.3°E) at 12:00 local time. Background concentrations of some of the major, longer-lived species (Table 5.1) and the emissions from the gridded emission database for the specific grid cell are assumed to initialise the model. The background concentrations for specific species in the upper layer are kept constant at these levels. The rate of flow and injection of SO₂ emissions into the box as it follows the trajectory pattern was assumed to be inversely proportional to the speed of the air parcel and the underlying concentration of SO₂ in the grid cell, from the emissions database.

Hourly input into the TTM includes the pressure of the trajectory from which the temperature is derived.

The chemical mechanisms and rate coefficients have been taken from the Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III, from IUPAC's Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (Atkinson *et al.*, 1989).

The TTM contains an extended inorganic chemistry section, and contains 50 inorganic chemistry reactions. This section contains the complete range of sulphur chemistry including H₂S that is unique for southern African conditions.

The chemical change, photolysis and the heterogeneous loss to aerosols in the TTM, were dealt with in the same manner as discussed in paragraph 4.2.2.

5.2.4 Computer implementation

The computer code for the TTM is written in FACSIMILE, previously reported in paragraph 4.2.3.

5.2.5 Trajectory transformation model code

Appendix B contains the facsimile source code for the TTM, which was used in the modelling of the different trajectories. The input files used by the model to simulate the trajectory and emission data are not included in this section of the appendix.

5.3 MODELLING RESULTS

The five trajectory patterns that were used in the model are shown from Figure 5.5 to Figure 5.9. The shaded area represents the trajectory path in each figure. The trajectory starts at grid cell 1, and the numbering is only an identification for the specific grid cells, showing the path of the trajectory and is not proportional to the time (hours) spent in each grid cell.

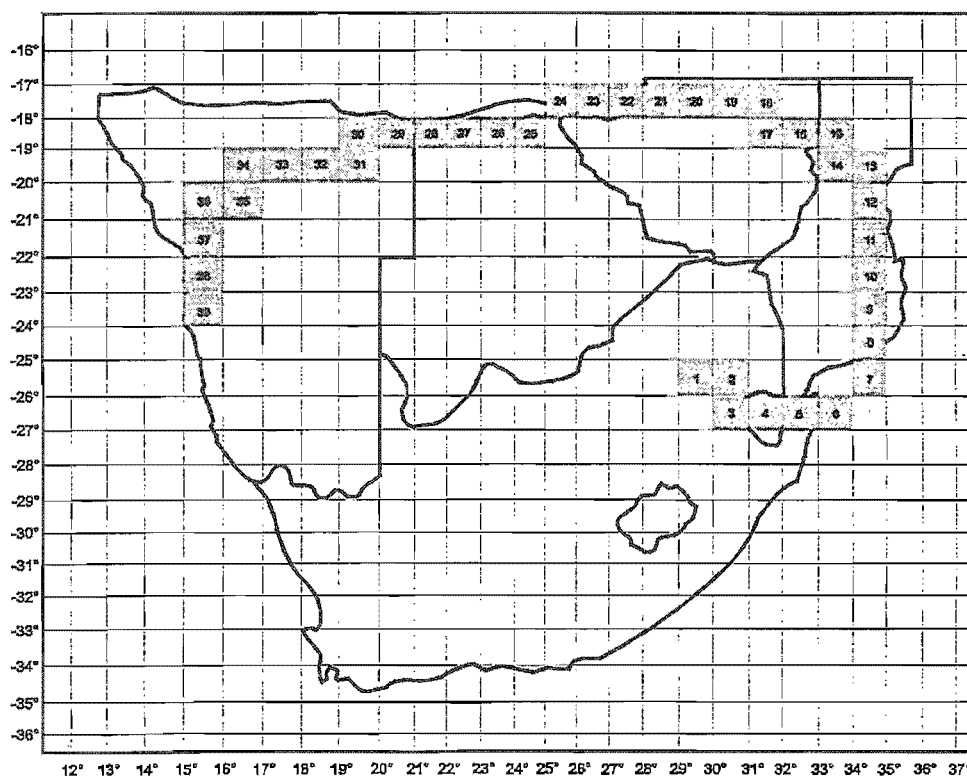


Figure 5.5 - A trajectory pattern started on 10 April 1992. Southern African transport.

Figure 5.5 shows typical southern African transport of the pollutants. The trajectory simulation was followed for 10 days (240 hours) from grid cell 1 to 39.

Table 5.2 shows a summary of the results for the 10 day period.

Table 5.2 - Results from 10 April 1992 simulation.

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
1	-25	29	6	3.27	0.01	2.87
2	-25	30	19	3.06	0.04	8.55
3	-26	30	6	2.57	0.23	2.38
4	-26	31	12	2.42	0.25	4.52
5	-26	32	7	2.22	0.26	2.44
6	-26	33	7	2.02	0.29	2.25
7	-25	34	6	1.88	0.28	1.81
8	-24	34	5	1.78	0.27	1.42
9	-23	34	3	1.70	0.26	0.82
10	-22	34	4	1.63	0.27	1.05
11	-21	34	5	1.55	0.27	1.26
12	-20	34	5	1.47	0.26	1.19
13	-19	34	9	1.38	0.25	2.03
14	-19	33	13	1.25	0.24	2.67
15	-18	33	3	1.23	0.23	0.61
16	-18	32	15	1.22	0.22	2.99
17	-18	31	9	1.12	0.21	1.65
18	-17	31	4	1.24	0.20	0.80
19	-17	30	10	1.86	0.20	2.90
20	-17	29	7	3.76	0.21	3.98
21	-17	28	4	3.81	0.21	2.30
22	-17	27	4	3.65	0.20	2.20
23	-17	26	5	3.46	0.20	2.62
24	-17	25	6	3.23	0.24	2.96
25	-18	24	4	3.05	0.24	1.87
26	-18	23	5	2.90	0.23	2.23

Continue...

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
27	-18	22	4	2.77	0.23	1.70
28	-18	21	6	2.61	0.23	2.42
29	-18	20	7	2.41	0.25	2.62
30	-18	19	2	2.29	0.25	0.71
31	-19	19	3	2.23	0.24	1.04
32	-19	18	5	2.14	0.24	1.67
33	-19	17	7	2.26	0.24	2.46
34	-19	16	3	2.45	0.25	1.15
35	-20	16	4	2.35	0.26	1.47
36	-20	15	4	2.26	0.25	1.41
37	-21	15	6	2.14	0.24	2.01
38	-22	15	5	2.03	0.23	1.59
39	-23	15	1	2.00	0.24	0.31



Figure 5.6 - A trajectory pattern started on 11 April 1992. Transport directly into the Indian ocean.

Table 5.3 - Results from 11 April 1992 simulation.

Grid	Latitude /°	Longitude /°	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
1	-25	29	2	2.92	0.01	0.85
2	-26	29	12	12.51	0.03	21.92
3	-27	29	13	31.34	0.75	60.32
4	-28	29	5	28.77	3.95	22.87
5	-28	30	1	27.73	4.07	4.43
6	-27	30	14	25.70	3.93	57.77
7	-26	31	8	21.98	4.67	29.24
8	-25	31	11	19.63	4.68	36.45
9	-24	31	31	15.02	4.73	82.05
10	-25	31	10	11.30	4.76	21.08
11	-25	32	10	10.10	4.48	19.06
12	-25	33	1	9.47	4.36	1.80
13	-26	33	3	9.19	4.38	5.29
14	-26	34	5	8.65	4.40	8.43
15	-27	34	1	8.31	4.36	1.63
16	-27	35	4	8.09	4.28	6.37
17	-28	35	6	7.66	4.13	9.10
18	-29	36	7	7.10	3.98	9.94
19	-30	36	5	6.51	3.95	6.66
20	-30	37	5	6.11	3.87	6.32
21	-31	37	1	5.91	3.78	1.23

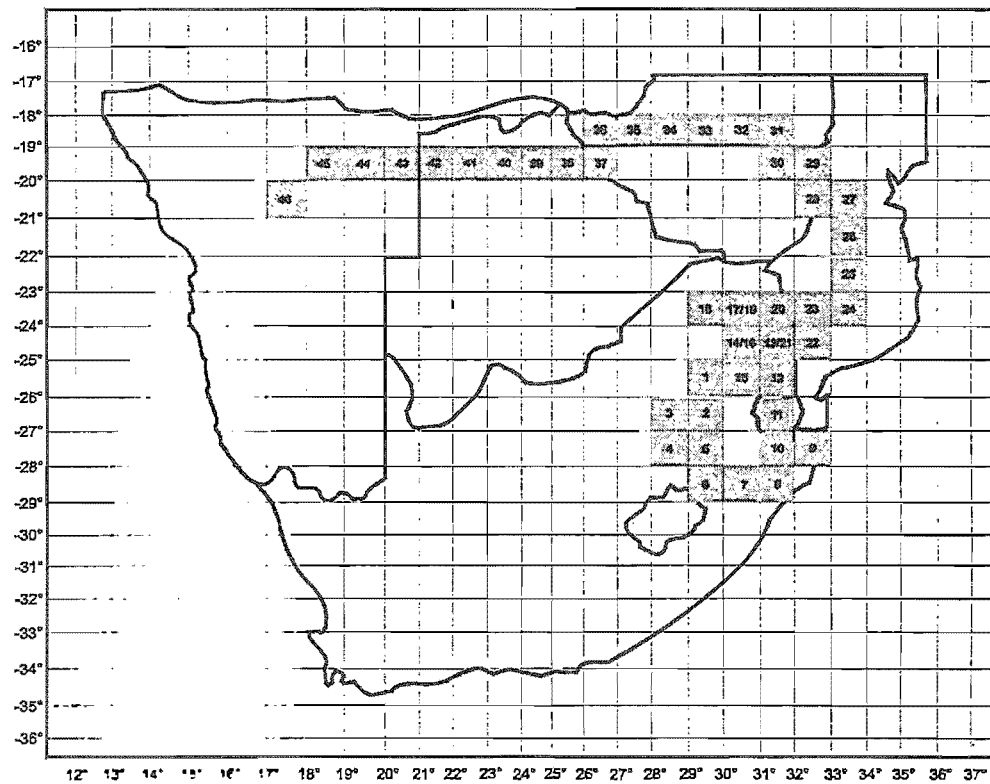


Figure 5.7 - A trajectory pattern on 22 July 1992. Typical Southern African Transport.

Table 5.4 - Results from 22 July 1992 simulation.

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
1	-25	29	8	6.61	0.02	7.73
2	-26	29	6	14.90	0.03	13.05
3	-26	28	3	21.75	0.03	9.52
4	-27	28	5	29.47	0.10	21.53
5	-27	29	3	31.68	1.04	14.16
6	-28	29	5	28.54	2.95	22.23
7	-28	30	7	26.18	3.54	29.10
8	-28	31	9	23.96	3.37	34.37
9	-27	32	6	21.55	3.71	21.00
10	-27	31	1	20.39	3.96	3.36

Continue...

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
11	-26	31	5	19.68	3.94	16.25
12	-25	31	7	18.49	3.78	21.42
13	-24	31	8	16.94	3.69	22.61
14	-24	30	2	15.69	3.91	5.33
15	-25	30	6	14.86	3.96	15.30
16	-24	30	12	13.57	3.74	28.08
17	-23	30	11	12.32	3.77	23.77
18	-23	29	12	10.74	3.62	22.98
19	-23	30	15	9.13	3.57	25.12
20	-23	31	22	9.20	3.38	36.68
21	-24	31	7	9.22	3.27	11.62
22	-24	32	8	8.48	3.13	12.31
23	-23	32	2	7.90	3.15	2.91
24	-23	33	3	7.62	3.17	4.25
25	-22	33	4	7.29	3.13	5.46
26	-21	33	3	7.02	3.05	3.95
27	-20	33	2	6.83	3.00	2.57
28	-20	32	1	6.72	2.96	1.27
29	-19	32	3	6.58	2.92	3.72
30	-19	31	2	6.40	2.87	2.42
31	-18	31	1	6.29	2.85	1.19
32	-18	30	4	6.08	2.85	4.65
33	-18	29	4	5.78	2.85	4.47
34	-18	28	3	5.66	2.81	3.29
35	-18	27	3	5.49	2.75	3.20
36	-18	26	1	5.38	2.71	1.05
37	-19	26	2	5.48	2.68	2.12

Continue...

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
38	-19	25	3	5.90	2.63	3.34
39	-19	24	3	5.71	2.58	3.24
40	-19	23	4	5.46	2.55	4.17
41	-19	22	4	5.16	2.55	3.99
42	-19	21	4	4.90	2.52	3.83
43	-19	20	4	4.69	2.45	3.68
44	-19	19	4	4.49	2.38	3.54
45	-19	18	5	4.27	2.30	4.23
46	-20	17	1	4.01	2.26	0.80

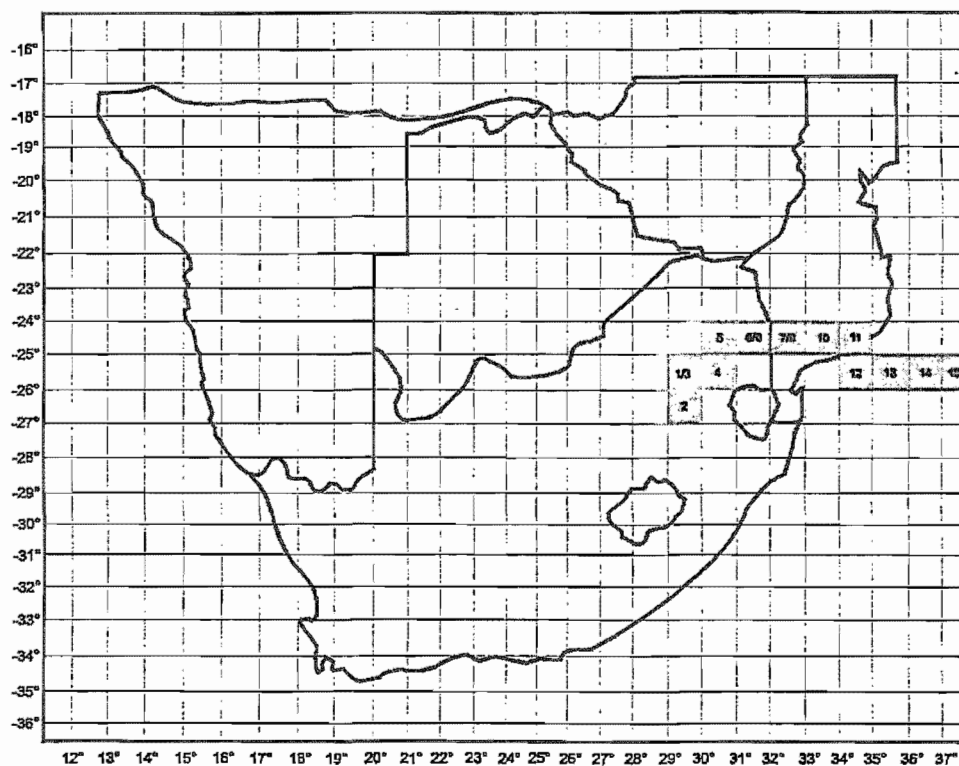


Figure 5.8 – A trajectory pattern on 25 July 1992. Typical Equatorward Transport.

Table 5.5 - Results from 25 July 1992 simulation.

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	SO _x / kg/grid
1	-25	29	1	2.28	0.01	0.33
2	-26	29	14	8.10	0.03	16.57
3	-25	29	5	8.59	0.03	6.27
4	-25	30	5	7.92	0.25	5.89
5	-24	30	22	6.19	0.95	21.86
6	-24	31	7	5.10	1.06	5.92
7	-24	32	5	4.73	1.07	3.96
8	-24	31	15	4.23	1.02	10.72
9	-24	32	7	3.65	1.04	4.43
10	-24	33	4	3.43	1.01	2.39
11	-24	34	2	3.33	0.99	1.16
12	-25	34	2	3.25	0.98	1.14
13	-25	35	3	3.17	0.96	1.66
14	-25	36	3	3.05	0.95	1.61
15	-25	37	2	2.95	0.96	1.05

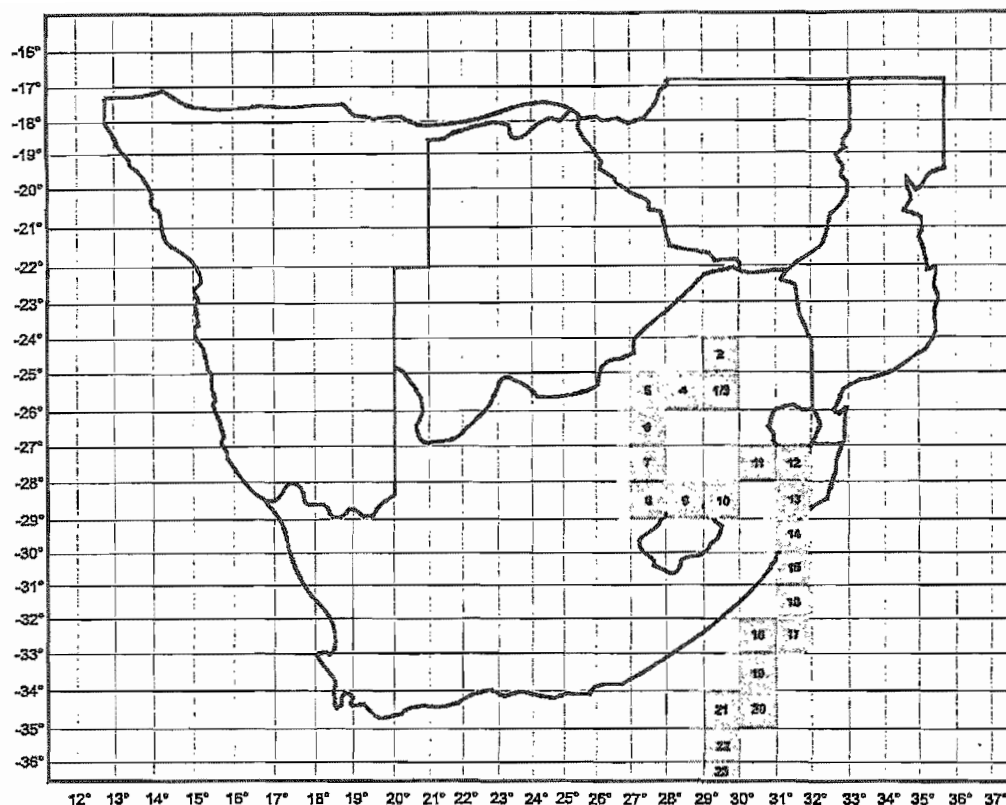


Figure 5.9 – A trajectory pattern on 29 July 1992. South eastern Cape transport.

Table 5.6 - Results from 29 July 1992 simulation.

Grid	Latitude / °	Longitude / °	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
1	-25	29	8	3.29	0.02	3.84
2	-24	29	5	3.22	0.02	2.36
3	-25	29	4	3.08	0.02	1.81
4	-25	28	6	2.93	0.04	2.58
5	-25	27	2	2.84	0.12	0.85
6	-26	27	6	3.06	0.23	2.81
7	-27	27	6	5.35	0.26	4.82
8	-28	27	1	5.50	0.25	0.83
9	-28	28	7	5.30	0.25	5.57
10	-28	29	6	5.01	0.29	4.55

Continue...

Grid	Latitude /°	Longitude /°	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ SO _x / kg/ha
11	-27	30	12	4.71	0.34	8.64
12	-27	31	3	4.44	0.33	2.04
13	-28	31	6	4.22	0.33	3.89
14	-29	31	4	3.96	0.38	2.46
15	-30	31	4	3.87	0.40	2.41
16	-31	31	4	3.73	0.39	2.32
17	-32	31	1	3.63	0.38	0.57
18	-32	30	2	3.57	0.38	1.11
19	-33	30	4	3.46	0.37	2.16
20	-34	30	2	3.34	0.37	1.05
21	-34	29	1	3.28	0.37	0.51
22	-35	29	4	3.16	0.40	2.00
23	-36	29	4	2.99	0.43	1.91

5.4 VALIDATION OF THE TTM

The validation of the TTM was a twofold process, which involved an investigation of the oxidation rate of SO₂ in the box, as well as the validation of the TTM to a trajectory with known ambient concentrations and deposition values, measured over Ben MacDhui (30.5°S, 27.9°E; 3001 m above sea level).

Since it has been showed that the decomposition of SO₂ in the atmosphere follows a simple first order rate law (Seinfeld, 1985). The oxidation rate of the SO₂ in the box model was calculated by using the well-known integrated rate law: $\ln(c_0 - c_t) = -kt$ where c_0 = initial SO₂ concentration (time = 0), c_t = concentration of SO₂ at time t, $-k$ = first order rate constant and t = time. A scenario was simulated with only one initial emission into the box, while the box remained constant on a fixed grid cell to ensure constant photochemical reaction rates.

Figure 5.10 shows a graph of the SO₂ concentration oxidising over time, while Figure 5.11 displays $\ln(c_t - c_0)$ against time.

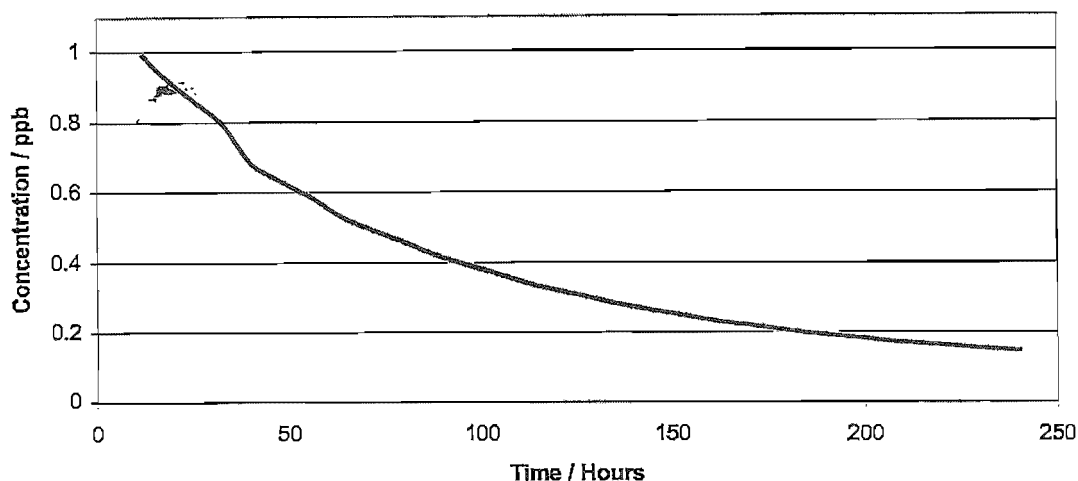


Figure 5.10 – The SO₂ concentration as a function of time.

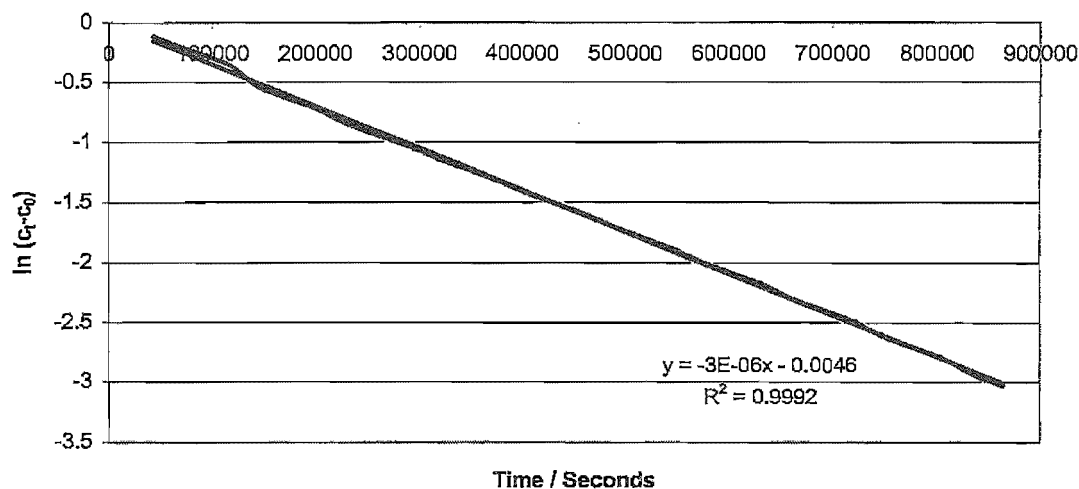


Figure 5.11 – $\ln(c_t - c_0)$ against time.

The wavy nature of the curve at about thirty hours in Figure 5.10 is due to oxidation of SO₂ by photochemical species, which are not constant during day/night cycles.

It follows from the slope in Figure 5.11 that the oxidation of SO₂ in the model results in a decomposition rate of $3 \times 10^{-6} \text{ s}^{-1}$. This is in exact agreement with the oxidation rates of $3 \times 10^{-6} \text{ s}^{-1}$ reported in the Matador's and Fishskip Models (AEA Report, 1997). This translates to a SO₂ chemical conversion ratio of 1.3 % per

hour, which is also in agreement with acceptable values of 1.29% (AEA Report, 1997).

A backward trajectory that could be use for validation purposes was obtained from the Climatological Research Group at Wits. This trajectory was calculated during the BHATTEX (Ben MacDhui High Altitude Trace Gas and Transport Experiment) field campaign and represent a trajectory which transported sulphur for the Mpumalange Highveld region over Ben MacDui, with a path over the ambient monitoring station at Ben MacDhui. Ambient measurements were obtained from the station for the specific plume (Zunckel *et al.*, 1999) and are reported in Table 5.7. Figure 5.12 shows the trajectory pattern.

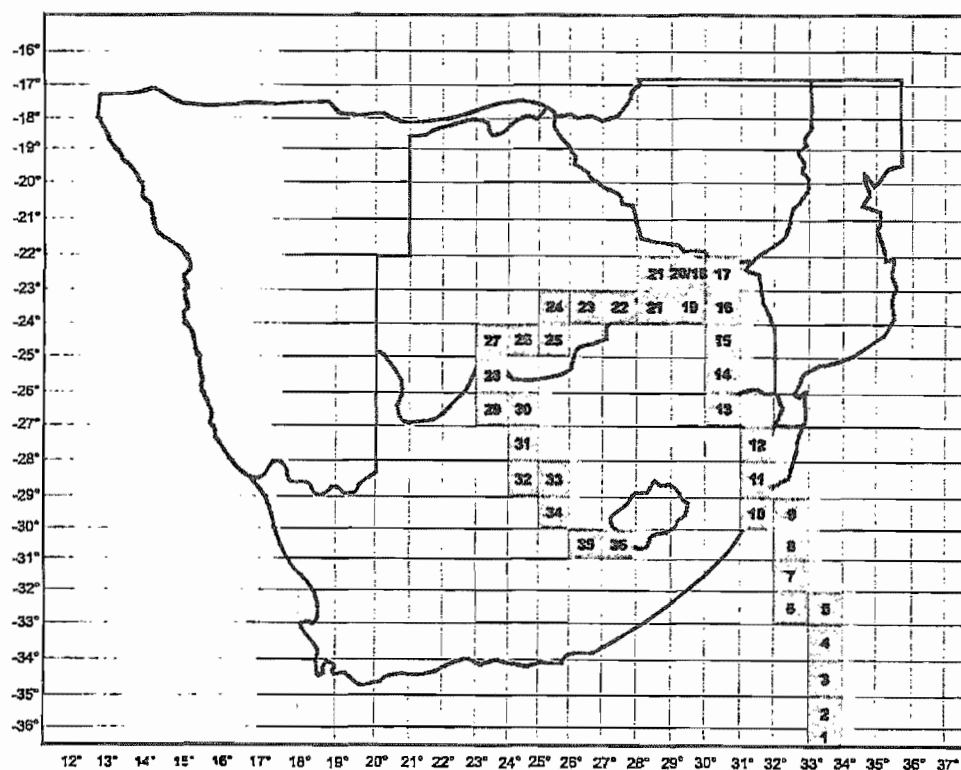


Figure 5.12 – The complete trajectory pattern on 12 March 1996.

Table 5.7 Results from Ben MacDhui (-30°S, 27°E) on 12 March 1996 (Zunckel *et al.*, 1999).

Species	Value
Total elemental sulphur	0.3 $\mu\text{g.m}^{-3}$
Sulphur deposition	1.00 $\text{kg.ha}^{-1}.\text{a}^{-1}$
[SO ₂]	0.85 ppb
[O ₃]	7.6 ppb

According to Zunckel *et al.*, 1999, the results that were obtained (Table 5.7) should be treaded with caution, as the analyser was operating close to its minimum detection limit and the recorded concentrations fell within the manufacturers specified noise limits of 1 ppb ($\pm 2.7 \mu\text{g.m}^{-3}$). Nevertheless, this was the only data available to validate the TTM.

A simulation of the Ben MacDhui trajectory was done with the TTM, starting at 12:00 at -24°S, 30°E.

The trajectory for the simulation is shown in Figure 5.13, while the results are shown in Table 5.9.

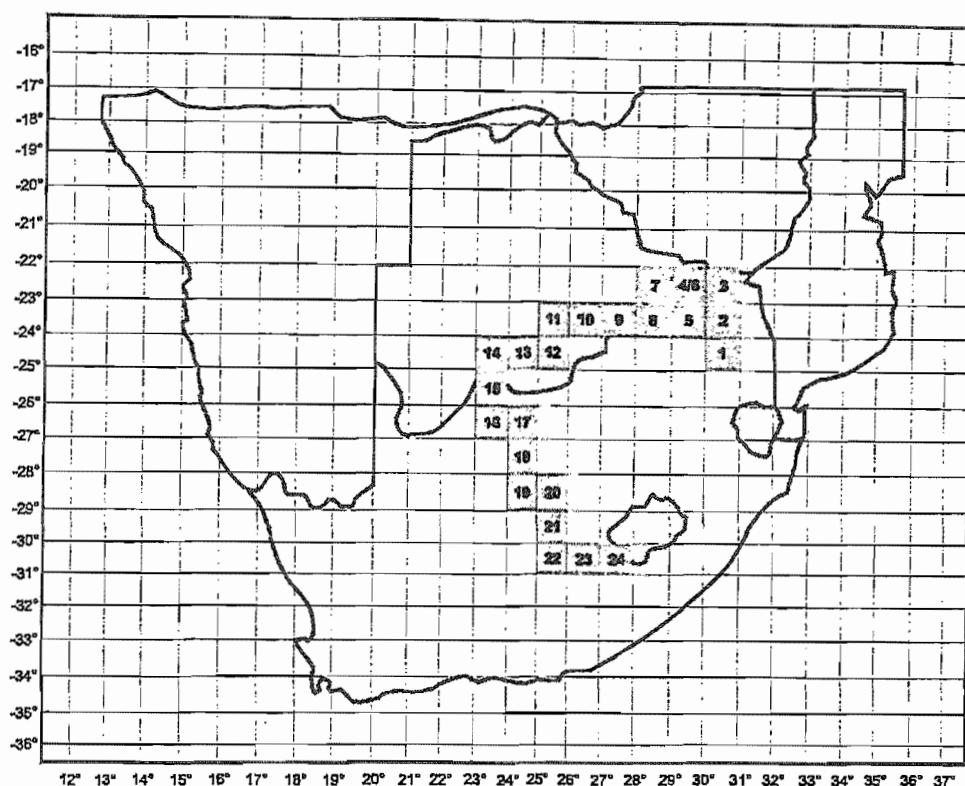


Figure 5.13 – The simulated trajectory pattern on 12 March 1996.

Table 5.8 Results from 12 March 1996 simulation.

Grid	Latitude /°	Longitude /°	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ S / kg ha ⁻¹
1	-24	30	2	0.99	0.00	0.29
2	-23	30	10	1.34	0.01	1.97
3	-22	30	6	1.50	0.01	1.32
4	-22	29	20	1.22	0.10	3.76
5	-23	29	19	0.95	0.15	2.90
6	-22	29	4	0.83	0.15	0.54
7	-22	28	11	0.77	0.15	1.39
8	-23	28	2	0.72	0.15	0.24
9	-23	27	8	0.71	0.15	0.94
10	-23	26	9	1.72	0.14	2.38
11	-23	25	3	2.18	0.14	0.99

Continue...

Grid	Latitude /°	Longitude /°	Time / Hours	[SO ₂] / ppb	[H ₂ SO ₄] / ppb	10 ⁻³ S / kg ha ⁻¹
12	-24	25	6	2.06	0.16	1.89
13	-24	24	8	1.90	0.17	2.34
14	-24	23	1	1.81	0.16	0.28
15	-25	23	10	1.71	0.16	2.65
16	-26	23	11	1.51	0.18	2.61
17	-26	24	2	1.41	0.17	0.44
18	-27	24	9	1.33	0.17	1.89
19	-28	24	2	1.25	0.17	0.40
20	-28	25	2	1.22	0.17	0.39
21	-29	25	5	1.17	0.18	0.94
22	-30	25	1	1.13	0.18	0.18
23	-30	26	11	1.06	0.17	1.89
24	-30	27	7	0.97	0.16	1.10

The simulation showed a SO₂ concentration of 0.97 ppb at Ben MacDhui (grid cell 24), while the total sulphur deposition was calculated at 1.10x10⁻³ kg ha⁻¹ for the seven hours spent in the grid. This 1.10x10⁻³ kg ha⁻¹ for seven hours is equivalent to a deposition value of 1.38 kg ha⁻¹ per annum. This is in excellent agreement with the measured values reported in Table 5.7.

Taking into account the simplicity of the model (e.g. only gas phase reactions are considered, no emission data for species other than SO₂ is available, a very simplistic approach to deposition is followed, etc.) as well as the uncertainties in the empirical (reported) values, the modelled and experimental results are in a surprisingly good agreement.

5.5 CONCLUSIONS

The values obtained from the simulation are slightly higher than the measured values but still in excellent agreement. However, the discrepancies between the measured ambient values and instrumentation detection limits are a matter of concern for the validation process. Nevertheless, the model conforms to these published results.

It follows from the validation results, that realistic SO₂ residence times and chemical conversion rates are obtained from the model. The total sulphur deposition values obtained in Tables 5.2 – 5.6, are also of a realistic magnitude.

FUTURE PERSPECTIVES

In this Chapter...

Shortcomings in this study, and future opportunities in the field of atmospheric transformation modelling, is discussed.

VOC's and their oxidation products are a persistent threat to sustainable development. These compounds have to be fully characterised and sampled under southern African conditions. Only then can their impact on the region be determined.

The sampling of VOC species under different meteorological conditions is still a highly debatable topic. The use of expensive active sampling equipment remains the desired method, but financial constraints especially under southern African conditions path the way for innovative alternative methods of sampling. Further investigations into these alternative sampling techniques still need to be embarked on and possible changes made for local conditions.

The key issue in transboundary transport of air pollutants is the deposition of trace gases. South Africa emits a large number of trace gases into the atmosphere, with transport paths existing over the whole of southern Africa. The deposition ratios for some of these gases have already been determined for South Africa in previous studies (Zunckel, 1999). The extent of the impact of industrial pollutants on neighbouring and other states must, however, still be determined.

It is generally accepted that air pollution models are important tools not only for assessing emission reduction strategies, but also for estimating exposures and for investigating economical aspects of air pollution. Moreover, there is a trend towards the increased role of air pollution models in the decision making process. Models are already available for most of the applications where they might be of use. At the same time the status of model documentation is

considered to be satisfactory.

The trend towards more accurate air pollution models forces the abandonment of the conventional rigid separation of atmospheric processes into individual scales. Multiscale approaches will be indispensable in the future. Nesting techniques are necessary if models which were developed for individual scales are to be combined in order to describe processes extending over several scales.

Future model refinements should be compatible with the needs of model users. Correspondingly, contact and exchange of information between environmental managers and model communities should be established and maintained. One of the objective's of such contact would be to identify needs for specific activities aiming at a further improvement of model documentation and a better assessment of model accuracy. Only with such activities will it be possible to improve the status of model evaluation, which seems to be unsatisfactory at present.

Present models do not include the effect of pollution as corrosion rates on buildings, plant damage and health aspects. Future models will have to include these effects. At this stage the effects of pollution are not sufficiently quantified to allow their incorporation into mathematical models.

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APPENDIX A

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* ***** ;
* AROMATIC VOCs ;
* ***** ;
* ;
* BENZENE ;
* ;
% 3.58D-12*EXP(-280/TEMP) : BENZENE + OH = OXEPIN + HO2 ;
% 9.95D-11 : OXEPIN + OH = MUCONALD1 + HO2 ;
% 9.23D-12 : OXEPIN + NO3 = MUCONALD1 + HNO3 + HO2 ;
% J<61> : OXEPIN = PHENOL ;
% 9.85D-11*0.59 : MUCONALD1 + OH = C6DIALOHO2 ;
% 9.85D-11*0.41 : MUCONALD1 + OH = C6DIALCO3 ;
% KRO2NO*0.902 : C6DIALOHO2 + NO = C6DIALOHO + NO2 ;
% KRO2NO*0.098 : C6DIALOHO2 + NO = C6AL2OHNO3 ;
% KRO2NO3 : C6DIALOHO2 + NO3 = C6DIALOHO + NO2 ;
% KRO2HO2*0.770 : C6DIALOHO2 + HO2 = C6DALOHOOH ;
% 1.42D-12*0.6*RO2 : C6DIALOHO2 = C6DIALOHO ;
% 1.42D-12*0.2*RO2 : C6DIALOHO2 = C6136CO2OH ;
% 1.42D-12*0.2*RO2 : C6DIALOHO2 = C6DIAL23OH ;
% KDEC : C6DIALOHO = MALDIAL + GLYOX + HO2 ;
% KAPNO : C6DIALCO3 + NO = MALDIAL + HO2 + CO + NO2 ;
% KFPAN % KBPAN : C6DIALCO3 + NO2 = C6DIALPAN ;
% KRO2NO3*1.60 : C6DIALCO3+NO3 = MALDIAL + HO2 + CO + NO2 ;
% KAPHO2*0.71 : C6DIALCO3 + HO2 = C6ALCO3H ;
% KAPHO2*0.29 : C6DIALCO3 + HO2 = C6ALCO2H + O3 ;
% 1.00D-11*0.70*RO2 : C6DIALCO3 = MALDIAL + HO2 + CO ;
% 1.00D-11*0.30*RO2 : C6DIALCO3 = C6ALCO2H ;
% 5.20D-11*0.27 : MALDIAL + OH = MALDIALO2 ;
% 5.20D-11*0.73 : MALDIAL + OH = MALDIALCO3 ;
% J<18> : MALDIAL = GLYOX + HO2 + CO + HO2 + CO ;
% J<19> : MALDIAL = GLYOX + HO2 + CO + HO2 + CO ;
% KRO2NO : MALDIALO2 + NO = MALDIALO + NO2 ;
% KRO2NO3 : MALDIALO2 + NO3 = MALDIALO + NO2 ;
% KRO2HO2*0.625 : MALDIALO2 + HO2 = MALDIALOOH ;
% 8.80D-13*0.60*RO2 : MALDIALO2 = MALDIALO ;
% 8.80D-13*0.20*RO2 : MALDIALO2 = HOCOC4DIAL ;
% 8.80D-13*0.20*RO2 : MALDIALO2 = HOHOC4DIAL ;
% KDEC : MALDIALO = GLYOX + GLYOX + HO2 ;
% KAPNO : MALDIALCO3 + NO = GLYOX + HO2 + CO + NO2 ;
% KFPAN % KBPAN : MALDIALCO3 + NO2 = MALDIALPAN ;
% KRO2NO3*1.60 : MALDIALCO3 + NO3 = GLYOX + HO2 + CO + NO2 ;
% KAPHO2*0.71 : MALDIALCO3 + HO2 = MALDALCO3H ;
% KAPHO2*0.29 : MALDIALCO3 + HO2 = MALDALCO2H + O3 ;
% 1.00D-11*0.70*RO2 : MALDIALCO3 = GLYOX + HO2 + CO ;
% 1.00D-11*0.30*RO2 : MALDIALCO3 = MALDALCO2H ;
% J<41> : MALDIALOOH = MALDIALO + OH ;
% J<15>*2 : MALDIALOOH = C32OH13CO + CO + OH + HO2 ;
% 1.90D-12*EXP(190/TEMP) : MALDIALOOH + OH = MALDIALO2 ;
% 1.22D-10 : MALDIALOOH + OH = HOCOC4DIAL + OH ;
% J<34> : HOCOC4DIAL = HCOCOHCO3 + HO2 + CO ;
% J<15> : HOCOC4DIAL = HCOCOHCO3 + HO2 + CO ;
% 3.67D-11 : HOCOC4DIAL + OH = CO2C4DIAL + HO2 ;
% J<34>*2 : CO2C4DIAL = CO + CO + HO2 + HO2 + CO + CO ;
% 2.45D-11 : CO2C4DIAL + OH = CO + CO + CO + CO + HO2 ;
% KAPNO : HCOCOHCO3 + NO = GLYOX + HO2 + NO2 ;
% KFPAN % KBPAN : HCOCOHCO3 + NO2 = HCOCOHCO3 ;
% KRO2NO3*1.60 : HCOCOHCO3 + NO3 = GLYOX + HO2 + NO2 ;

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% KAPHO2 : HCOCOHCO3 + HO2 = HCOCOHCO3H ;
% 1.00D-11*RO2 : HCOCOHCO3 = GLYOX + HO2 ;
% 6.97D-11 : HCOCOHCO3H + OH = GLYOX + CO + NO2 ;
% J<41> : HCOCOHCO3H = GLYOX + HO2 + OH ;
% 7.33D-11 : HCOCOHCO3H + OH = HCOCOHCO3 ;
% J<15>*2 : HOHOC4DIAL = C32OH13CO + HO2 + HO2 + CO ;
% 8.13D-11 : HOHOC4DIAL + OH = HOCOC4DIAL + HO2 ;
% J<15>*2 : C32OH13CO = GLYOX + HO2 + HO2 + CO ;
% 1.36D-10 : C32OH13CO + OH = HCOCOHCO3 ;
% 4.91D-11 : C6AL2OHNO3 + OH = C6136CO2OH + NO2 ;
% J<15> : C6AL2OHNO3=C4DALOHNO3+HO2+CO+HO2+CO ;
% J<41> : C6DALOHOOH = C6DIALOHO + OH ;
% J<15> : C6DALOHOOH = C6DIALOHO + OH ;
% J<18> : C6DALOHOOH=MALDIALOOH+HO2+CO+HO2+CO ;
% J<19> : C6DALOHOOH=MALDIALOOH+HO2+CO+HO2+CO ;
% 1.42D-10 : C6DALOHOOH + OH = C6DIALOHO2 ;
% J<15> : C6136CO2OH = MALDIALCO3 + GLYOX + HO2 ;
% J<22> : C6136CO2OH = MALDIALCO3 + GLYOX + HO2 ;
% J<18> : C6136CO2OH=HOCOC4DIAL+HO2+CO+HO2+CO ;
% J<19> : C6136CO2OH=HOCOC4DIAL+HO2+CO+HO2+CO ;
% 9.64D-11 : C6136CO2OH + OH = C5CO2OHCO3 ;
% J<15> : C6DIAL23OH=HOHOC4DIAL+HO2+CO+HO2+CO ;
% J<18> : C6DIAL23OH=HOHOC4DIAL+HO2+CO+HO2+CO ;
% J<19> : C6DIAL23OH=HOHOC4DIAL+HO2+CO+HO2+CO ;
% 9.65D-11 : C6DIAL23OH + OH = C6136CO2OH + HO2 ;
% 6.50D-11 : C6DIALPAN + OH = MALDIAL + CO + CO + NO2 ;
% J<41> : C6ALCO3H = MALDIAL + HO2 + CO + OH ;
% J<18> : C6ALCO3H=MALDALCO3H + HO2 + CO + HO2 + CO ;
% J<19> : C6ALCO3H=MALDALCO3H + HO2 + CO + HO2 + CO ;
% 6.90D-11 : C6ALCO3H + OH = C6DIALCO3 ;
% J<18> : C6ALCO2H=MALDALCO2H + HO2 + CO + HO2 + CO ;
% J<19> : C6ALCO2H=MALDALCO2H + HO2 + CO + HO2 + CO ;
% 6.50D-11 : C6ALCO2H + OH = MALDIAL + HO2 + CO ;
% 3.70D-11 : MALDIALPAN + OH = GLYOX + CO + CO + NO2 ;
% J<41> : MALDALCO3H = GLYOX + HO2 + CO + OH ;
% J<18> : MALDALCO3H=HCOCO3H + HO2 + CO + HO2 + CO ;
% J<19> : MALDALCO3H=HCOCO3H + HO2 + CO + HO2 + CO ;
% 4.00D-11 : MALDALCO3H + OH = MALDIALCO3 ;
% J<18> : MALDALCO2H=HCOCO2H + HO2 + CO + HO2 + CO ;
% J<19> : MALDALCO2H=HCOCO2H + HO2 + CO + HO2 + CO ;
% 3.70D-11 : MALDALCO2H + OH = GLYOX + HO2 + CO ;
% 2.00D-18 : MALDIAL + O3 = GLYOX + GLYOOA ;
% 1.00D-17*0.5 : MUCONALD1 + O3 = GLYOX + ALVINOOA ;
% 1.00D-17*0.5 : MUCONALD1 + O3 = MALDIAL + GLYOOD ;
% 1.00D-14 : MALDIAL + NO3 = MALDIALCO3 + HNO3 ;
% 1.00D-14 : MUCONALD1 + NO3 = C6DIALCO3 + HNO3 ;
% KAPNO : C5CO2OHCO3+NO=HOCOC4DIAL + HO2 + CO + NO2 ;
% KFPAN % KBPAN : C5CO2OHCO3 + NO2 = C5CO2OHPAN ;
% KRO2NO3*1.60 : C5CO2OHCO3+NO3=HOCOC4DIAL+HO2+CO+NO2 ;
% KAPHO2 : C5CO2OHCO3 + HO2 = C5COOHCO3H ;
% 1.00D-11*RO2 : C5CO2OHCO3 = HOCOC4DIAL + HO2 + CO ;
% 7.66D-11 : C5CO2OHPAN+OH=HOCOC4DIAL+CO+CO+NO2 ;
% 8.01D-11 : C5COOHCO3H + OH = C5CO2OHCO3 ;
% J<41> : C5COOHCO3H = HOCOC4DIAL + HO2 + CO ;
% KDEC*0.24 : ALVINOOA = ALVINOO ;
% KDEC*0.08 : ALVINOOA = GLYOX + CO + OH + HO2 + CO ;
% KDEC*0.34 : ALVINOOA = GLYOX + HO2 + CO + HO2 ;
% KDEC*0.34 : ALVINOOA = ACR ;
% 7.00D-14 : ALVINOO + SO2 = MALDIAL + SO3 ;
% 1.20D-15 : ALVINOO + CO = MALDIAL ;
% 1.00D-14 : ALVINOO + NO = MALDIAL + NO2 ;
% 1.00D-15 : ALVINOO + NO2 = MALDIAL + NO3 ;

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% 6.00D-18*H2O          : ALVINO = MALDIAL + H2O2          ;
% 1.00D-17*H2O          : ALVINO = MALDALCO2H              ;
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* METHYL BENZENE (TOLUENE) ;
* ;
% 1.81D-12*EXP(355/TEMP)*0.10 : TOLUENE + OH = C6H5CH2O2      ;
% 1.81D-12*EXP(355/TEMP)*0.90 : TOLUENE + OH = TOLOXPIN + HO2    ;
% 1.00D-10               : TOLOXPIN + OH = MUCONALD2 + HO2      ;
% 1.00D-11               : TOLOXPIN + NO3 = MUCONALD2 + HNO3 + HO2 ;
% J<61>                   : TOLOXPIN = CRESOL                    ;
% KRO2NO*0.895           : C6H5CH2O2 + NO = C6H5CH2O + NO2     ;
% KRO2NO*0.105           : C6H5CH2O2 + NO = C6H5CH2NO3         ;
% KRO2NO3                 : C6H5CH2O2 + NO3 = C6H5CH2O + NO2     ;
% KRO2HO2*0.820          : C6H5CH2O2 + HO2 = C6H5CH2OOH        ;
% 1.30D-12*0.60*PO2      : C6H5CH2O2 = C6H5CH2O              ;
% 1.30D-12*0.20*PO2      : C6H5CH2O2 = BENZAL                 ;
% 1.30D-12*0.20*PO2      : C6H5CH2O2 = C6H5CH2OH              ;
% 3.70D-14*EXP(-460/TEMP)*O2 : C6H5CH2O = BENZAL + HO2      ;
% J<41>                   : C6H5CH2OOH = C6H5CH2O + OH          ;
% 2.05D-11               : C6H5CH2OOH + OH = BENZAL + OH        ;
% 8.93D-12               : C6H5CH2OH + OH = BENZAL + HO2        ;
% J<53>                   : C6H5CH2NO3 = C6H5CH2O + NO2         ;
% 6.03D-12               : C6H5CH2NO3 + OH = BENZAL + NO2       ;
% 1.10D-10*0.335         : MUCONALD2 + OH = C72COHOAO2          ;
% 1.10D-10*0.325         : MUCONALD2 + OH = C72COHOB02          ;
% 1.10D-10*0.340         : MUCONALD2 + OH = MUCALD2O2          ;
% KAPNO                   : MUCALD2O2+NO = C5DICARB + HO2 + CO + NO2 ;
% KFPAN % KBPAN          : MUCALD2O2 + NO2 = MUCALDNO2          ;
% KRO2NO3*1.60           : MUCALD2O2+NO3=C5DICARB + HO2 + CO + NO2 ;
% KAPHO2*0.71            : MUCALD2O2 + HO2 = MUCALDOOH          ;
% KAPHO2*0.29            : MUCALD2O2 + HO2 = MUCALDOH + O3       ;
% 1.00D-11*0.70*PO2      : MUCALD2O2 = C5DICARB + HO2 + CO      ;
% 1.00D-11*0.30*PO2      : MUCALD2O2 = MUCALDOH          ;
% KRO2NO                  : C72COHOAO2 + NO = C72COHOAO + NO2    ;
% KRO2NO3                 : C72COHOAO2 + NO3 = C72COHOAO + NO2    ;
% KRO2HO2*0.820          : C72COHOAO2 + HO2 = C72COHOAOOH        ;
% 1.40D-12*0.60*PO2      : C72COHOAO2 = C72COHOAO          ;
% 1.40D-12*0.20*PO2      : C72COHOAO2 = C723COHOA          ;
% 1.40D-12*0.20*PO2      : C72COHOAO2 = C72COHOAOH          ;
% KDEC                    : C72COHOAO = MGLYOX + MALDIAL + HO2      ;
% KRO2NO*0.943           : C72COHOB02 + NO = C72COHOB0 + NO2    ;
% KRO2NO*0.057           : C72COHOB02 + NO = C72COHOBNO3        ;
% KRO2NO3                 : C72COHOB02 + NO3 = C72COHOB0 + NO2    ;
% KRO2HO2*0.820          : C72COHOB02 + HO2 = C72COHOB0OH        ;
% 1.40D-12*0.60*PO2      : C72COHOB02 = C72COHOB0          ;
% 1.40D-12*0.20*PO2      : C72COHOB02 = C725COHOB          ;
% 1.40D-12*0.20*PO2      : C72COHOB02 = C72COHOB0H          ;
% KDEC                    : C72COHOB0 = C5DICARB + GLYOX + HO2      ;
% J<18>                   : C5DICARB = MGLYOX + HO2 + CO          ;
% J<19>                   : C5DICARB = MGLYOX + HO2 + CO          ;
% J<24>                   : C5DICARB = GLYOX + CH3CO3 + HO2 + CO    ;
% J<23>                   : C5DICARB = GLYOX + CH3CO3 + HO2 + CO    ;
% 5.58D-11*0.642         : C5DICARB + OH = C5DICARBO2        ;
% 5.58D-11*0.358         : C5DICARB + OH = C5CO14O2          ;
% KAPNO                   : C5CO14O2 + NO = MGLYOX + HO2 + CO + NO2 ;
% KFPAN % KBPAN          : C5CO14O2 + NO2 = C5COO2NO2          ;
% KRO2NO3*1.60           : C5CO14O2 + NO3 = MGLYOX + HO2 + CO + NO2 ;
% KAPHO2*0.71            : C5CO14O2 + HO2 = C5CO14OOH        ;
% KAPHO2*0.29            : C5CO14O2 + HO2 = C5CO14OH + O3       ;
% 1.00D-11*0.70*PO2      : C5CO14O2 = MGLYOX + HO2 + CO      ;
% 1.00D-11*0.30*PO2      : C5CO14O2 = C5CO14OH          ;
% KRO2NO                  : C5DICARBO2 + NO = C5DICARBO + NO2    ;

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% KRO2NO3 : C5DICARBO2 + NO3 = C5DICARBO + NO2 ;
% KRO2HO2*0.706 : C5DICARBO2 + HO2 = C5DICAROOH ;
% 1.40D-12*0.60*RO2 : C5DICARBO2 = C5DICARBO ;
% 1.40D-12*0.20*RO2 : C5DICARBO2 = C5134CO2OH ;
% 1.40D-12*0.20*RO2 : C5DICARBO2 = C514CO23OH ;
% KDEC : C5DICARBO = MGLYOX + GLYOX + HO2 ;
% J<41> : C7COHOAOOH = C72COHOAO + OH ;
% J<22> : C7COHOAOOH = C72COHOAO + OH ;
% J<18> : C7COHOAOOH = C72COHOAO + OH ;
% J<19> : C7COHOAOOH = C72COHOAO + OH ;
% 1.90D-12*EXP(190/TEMP) : C7COHOAOOH + OH = C72COHOAO2 ;
% 8.74D-11 : C7COHOAOOH + OH = C723COHOA + OH ;
% J<35> : C723COHOA = C5134CO2OH + HO2 + CO ;
% 6.44D-11 : C723COHOA + OH = C71456CODB + HO2 ;
% J<18> : C72COHOAOH = C514CO23OH + HO2 + CO ;
% J<19> : C72COHOAOH = C514CO23OH + HO2 + CO ;
% J<22> : C72COHOAOH = C514CO23OH + HO2 + CO ;
% 7.05D-11 : C72COHOAOH + OH = C723COHOA + HO2 ;
% J<15> : C7COHOBNO3=C42COOHNO3 + CH3CO3 + HO2 + CO ;
% J<24> : C7COHOBNO3=C42COOHNO3 + CH3CO3 + HO2 + CO ;
% J<23> : C7COHOBNO3=C42COOHNO3 + CH3CO3 + HO2 + CO ;
% 4.71D-11 : C7COHOBNO3+OH=C5DICARB+GLYOX+NO2+HO2 ;
% J<41> : C7COHOB0OH = C72COHOB0 + OH ;
% J<15> : C7COHOB0OH = C72COHOB0 + OH ;
% J<23> : C7COHOB0OH = C72COHOB0 + OH ;
% J<24> : C7COHOB0OH = C72COHOB0 + OH ;
% 1.90D-12*EXP(190/TEMP) : C7COHOB0OH + OH = C72COHOB02 ;
% 2.02D-10 : C7COHOB0OH + OH = C725COHOB + OH ;
% J<15> : C725COHOB=HOCOC4DIAL + CH3CO3 + HO2 + CO ;
% J<24>*2 : C725COHOB=HOCOC4DIAL + CH3CO3 + HO2 + CO ;
% J<23>*2 : C725COHOB=HOCOC4DIAL + CH3CO3 + HO2 + CO ;
% 9.57D-11 : C725COHOB + OH = C71236CODB + HO2 ;
% J<15> : C72COHOB0H = HOHOC4DIAL + CH3CO3 + HO2 ;
% J<23> : C72COHOB0H = HOHOC4DIAL + CH3CO3 + HO2 ;
% J<24> : C72COHOB0H = HOHOC4DIAL + CH3CO3 + HO2 ;
% 1.14D-10 : C72COHOB0H + OH = C725COHOB + HO2 ;
% J<41> : C5DICAROOH = C5DICARBO + OH ;
% J<15> : C5DICAROOH = C5DICARBO + OH ;
% J<22> : C5DICAROOH = C5DICARBO + OH ;
% 1.90D-12*EXP(190/TEMP) : C5DICAROOH + OH = C5DICARBO2 ;
% 1.21D-10 : C5DICAROOH + OH = C5134CO2OH + OH ;
% J<15> : C5134CO2OH = CO23C3CHO + HO2 + CO ;
% J<35> : C5134CO2OH = CO23C3CHO + HO2 + CO ;
% 7.48D-11 : C5134CO2OH + OH = C54CO + HO2 ;
% J<15> : C514CO23OH = CO2H3CHO + HO2 + CO ;
% J<22> : C514CO23OH = CO2H3CHO + HO2 + CO ;
% 6.26D-11 : C514CO23OH + OH = C5134CO2OH + HO2 ;
% 3.59D-12 : C5CO14OOH + OH = C5CO14O2 ;
% J<41> : C5CO14OOH = MGLYOX + OH + HO2 + CO ;
% 5.44D-11 : C5CO14OH + OH = MGLYOX + HO2 + CO ;
% J<23> : C5CO14OH = CH3CO3 + HCOCO2H + HO2 + CO ;
% J<24> : C5CO14OH = CH3CO3 + HCOCO2H + HO2 + CO ;
% 5.43D-11 : C5COO2NO2 + OH = MGLYOX + CO + CO + NO2 ;
% 5.28D-11 : MUCALDNO2+OH= C5DICARB+CO+CO+NO2 ;
% 5.64D-11 : MUCALDOOH + OH = MUCALD2O2 ;
% J<41> : MUCALDOOH = C5DICARB + OH + HO2 + CO ;
% 5.28D-11 : MUCALDOH + OH = C5DICARB + HO2 + CO ;
% J<23> : MUCALDOH = MALDALCO2H + CH3CO3 + HO2 + CO ;
% J<24> : MUCALDOH = MALDALCO2H + CH3CO3 + HO2 + CO ;
% 2.00D-18*0.5 : C5DICARB + O3 = MGLYOX + GLYOOA ;
% 2.00D-18*0.5 : C5DICARB + O3 = GLYOX + MGLOOB ;
% KDEC*0.18 : MGLOOB = MGLOO ;

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% KDEC*0.57      : MGLOOB = CH3CO3 + CO + OH      ;
% KDEC*0.125     : MGLOOB = CH3CO3 + HO2         ;
% KDEC*0.125     : MGLOOB = CH3CHO              ;
% 2.00D-17*0.25  : MUCONALD2 + O3 = MGLYOX + ALVINOOA ;
% 2.00D-17*0.25  : MUCONALD2 + O3 = MGLOOD + MALDIAL ;
% 2.00D-17*0.25  : MUCONALD2 + O3 = GLYOX + KETVINOOA ;
% 2.00D-17*0.25  : MUCONALD2 + O3 = GLYOOD + C5DICARB ;
% 1.00D-14       : C5DICARB + NO3 = C5CO14O2 + HNO3 ;
% 1.00D-14       : MUCONALD2 + NO3 = MUCALD2O2 + HNO3 ;
% J<18>          : MUCONALD1 = MALDIAL + HO2 + CO + HO2 + CO ;
% J<19>          : MUCONALD1 = C6DIALCO3 + HO2 + CO ;
% J<18>          : C6AL2OHNO3=C4DALOHNO3+HO2+CO+HO2+CO ;
% J<19>          : C6AL2OHNO3=C4DALOHNO3+HO2+CO+HO2+CO ;
% 2.89D-11      : C4DALOHNO3 + OH = HOCOC4DIAL + NO2 ;
% J<15>*2        : C4DALOHNO3 = C32OH13CO + HO2 + CO + NO2 ;
% J<35>          : C71456CODB=CH3CO3+CO+CO+HO2+CO+GLYOX ;
% 1.90D-11      : C71456CODB + OH = C63CDBCO3 ;
% KAPNO          : C63CDBCO3 + NO = C54CO + HO2 + CO + NO2 ;
% KFPAN % KBPAN  : C63CDBCO3 + NO2 = C63CDBPAN ;
% 5.20D-12      : C63CDBPAN + OH = C54CO + CO + CO + NO2 ;
% KRO2NO3*1.60  : C63CDBCO3 + NO3 = C54CO + HO2 + CO + NO2 ;
% KAPHO2         : C63CDBCO3 + HO2 = C6CDBCO3H ;
% 1.00D-11*RO2  : C63CDBCO3 = C54CO + HO2 + CO ;
% J<34>          : C54CO = HO2 + CO + CO + CO + CH3CO3 ;
% J<35>*2        : C54CO = HO2 + CO + CO + CO + CH3CO3 ;
% J<15>*2        : C42COOHNO3 = C32OH13CO + HO2 + CO + NO2 ;
% 1.15D-11      : C42COOHNO3 + OH = HOCOC4DIAL + NO2 ;
% J<34>          : C71236CODB=MGLYOX+HO2+CO+CO+CO+CO+HO2 ;
% J<35>          : C71236CODB=MGLYOX+HO2+CO+CO+CO+CO+HO2 ;
% 4.94D-11      : C71236CODB+OH=MGLYOX+CO+CO+CO+CO+ HO2 ;
% KDEC*0.24      : KETVINOOA = KETVINOO ;
% KDEC*0.08      : KETVINOOA = MGLYOX + CO + OH + HO2 + CO ;
% KDEC*0.34      : KETVINOOA = MGLYOX + HO2 + CO + HO2 ;
% KDEC*0.34      : KETVINOOA = MVK ;
% 7.00D-14      : KETVINOO + SO2 = C5DICARB + SO3 ;
% 1.20D-15      : KETVINOO + CO = C5DICARB ;
% 1.00D-14      : KETVINOO + NO = C5DICARB + NO2 ;
% 1.00D-15      : KETVINOO + NO2 = C5DICARB + NO3 ;
% 6.00D-18*H2O  : KETVINOO = C5DICARB + H2O2 ;
% 1.00D-17*H2O  : KETVINOO = C5CO14OH ;
* ;

```

APPENDIX B

```

* ***** * ;
* * ;
* ONE LAYER PHOTOCHEMICAL AIR POLLUTION TRAJECTORY BOX MODEL * ;
* * ;
* GERHARD FOURIE - ATMOSPHERIC CHEMISTRY RESEARCH GROUP - 2000 * ;
* * ;
* POTCHEFSTROOM UNIVERSITY FOR CHRISTIAN HIGHER EDUCATION * ;
* * ;
* ***** * ;
* ;
* ***** ;
* PARAMETER AND VARIABLE DECLARATION ;
* ***** ;
* ;
* DEFINE PARAMETERS USED IN SIMULATION ;
PARAMETER HOUR DAYTIME DAWN DUSK COSZEN QTVG 1.0
          RH LT ALPHA THSTART HMIX
          PI LHA COSLD COSA ACOSA RADIANT SINLD
          TSTART THSTOP HHMIN HHMAX DEC LAT ;
* ;
PARAMETER KRO2NO KRO2HO2 KAPHO2 KRO2NO3 KNO3AL KDEC KAPNO ;
PARAMETER M O2 N2 H2O K0 KI FC F K1 K2 K3 K4 KMT01 KMT02 ;
PARAMETER KMT03 KMT04 KMT05 KMT06 KMT07 KMT08 KMT09 KMT10 KMT11 ;
PARAMETER KMT12 KMT13 KMT14 KMT15 KMT16 KMT17 KFPAN KBPAN ;
PARAMETER COSX SECX ;
PARAMETER <70> J ;
PARAMETER RO2 RO2FRAC RO2TOT PANTOT HCPOINT KALKOXY ;
PARAMETER KALKPXY ;
PARAMETER TT LAT LON PRES TEMP EMIS Q DAY;
PARAMETER MO3 MSO2 MNO MNO2 MHNO3 MH2O2 MOH MOH2 MCO MTIME;
PARAMETER THNO3 TSO2 TH2SO4 TSO3 DSO2 DH2SO4 DHNO3 DSOX DSO4;
PARAMETER BSO2 1.0 TYD;
* ;
* DECLARE VARIABLES FOR ALL THE SPECIES IN THE BOX ;
VARIABLE
O      O3      O1D      OH      HO2      H2O2      H2      CO CH4
NO     NO2     NO3     N2O5     HONO     HNO3     HO2NO2 NA
SO2    SO3     HSO3     SA      HS      H2S      H2SO4     HSO     SO
HSNO CH3O2 CH3O CH3 HCHO CH3OH CH3NO3
CH3OOH HCH HCHOO CH3O2NO2;
* ;
* ***** ;
* INSTANT ROUTINE ;
* ***** ;
* ;
COMPILE INSTANT;
OPEN 10 "Stream1.out" UNKNOWN ;
OPEN 17 "Stream2.out" UNKNOWN ;
* OPEN FILES TO READ TIME, LATITUDE, LONGITUDE, PRESSURE, ;
* PRESSURE, TEMPERATURE AND EMISSIONS AS INPUT FROM TRAJECTORY ;
OPEN 11 "TIME.DAT";
OPEN 12 "LAT.DAT";
OPEN 13 "LON.DAT";
OPEN 14 "PRES.DAT";
OPEN 15 "TEMP.DAT";
OPEN 16 "EMI.DAT";
**;
```

```

* ;
* ***** ;
*                               INITIAL ROUTINE ;
* ***** ;
* ;
COMPILE INITIAL ;
THSTOP=50400.0 ;
HHMIN=3.0D+4 ;
HHMAX=1.0D+5 ;
* SOLAR DECLINATION ANGLE (DEGREES) ;
* DEC=-23.79 (SUMMER CONDITIONS) ;
* DEC=23.79 (WINTER CONDITIONS) ;
DEC=-23.79 ;
* LATITUDE (DEGREES) ;
READ 12 LAT ;
* DEFINE A VALUE FOR PI ;
PI=4.0*ATAN(1.0D+0) ;
* DEFINE A VALUE FOR RADIAN ;
RADIAN = 180.0/PI ;
* CONVERT LATITUDE AND SOLAR DECLINATION ANGLE DEG TO RAD ;
LAT = LAT/RADIAN ;
DEC = DEC/RADIAN ;
COSLD = COS(LAT)*COS(DEC) ;
SINLD = SIN(LAT)*SIN(DEC) ;
COSA = SINLD/COSLD ;
* IF COSA = NEGATIVE OR POSITIVE JUMP LABEL 5 ;
* IF COSA = 0 NEXT INSTRUCTION ;
IF(COSA)5,*,5 ;
* IF COSA = 0 ;
ACOSA = PI/2.0D0 ;
* JUMP TO LABEL 10 ;
JUMP 10 ;
LABEL 5 ;
ACOSA = ATAN((SQRT(1.0D0-COSA**2))/COSA) ;
IF(ACOSA)*,10,10 ;
ACOSA = ACOSA+PI ;
LABEL 10 ;
DAWNLONLO = (43200.0/PI)*ACOSA ;
DUSK = 86400.0-DAWN ;
THSTART = DAWN+7200.0 ;
DAWN = DAWN-600.0 ;
DUSK = DUSK-600.0 ;
HMIX=1.0E+5 ;
READ 11 TT ;
READ 15 TEMP ;
* START OF SIMULATION (43200 - 12:00) ;
* TIME= 21600 ;
TIME= 43200 ;
HMIX=1.0E+5 ;
* SPECIFY AIR DENSITY (MOLECULES/CM3) ;
M=2.55E+19 ;
* INITIAL CONCENTRATIONS OF THE SPECIES IN THE BOX (BACKGROUND) ;
* ALL CONCENTRATIONS ARE CALCULATED AS A FUNCTION OF AIR DENSITY (M) ;
* PASSIVE SAMPLING DATA - G HELAS ;
O2=0.2095*M ;
N2=0.7809*M ;
NO=8.0D-9*M ;
NO2=3.2D-8*M ;
SO2=1.0D-9*M ;
CO=2.32D-6*M ;
CH4=1.98D-6*M ;
O3=5.0D-8*M ;

```

```

H2=0.5D-6*M ;
H2O2=2.0D-9*M ;
** ;
* ;
* ***** ;
*                               FTIME ROUTINE ;
* ***** ;
* ;
* ROUTINE FTIME CALLED AT EACH TIME STEP TO COMPUTE ;
* FUNCTIONS OF TIME ;
COMPILE FTIME ;
DAYTIME= AMOD(TIME,86400.0) ;
LHA=(1.0+(TIME/4.32D+4))*PI ;
SECX=1.0D+0/(RAMP((COS(LHA)*COSLD)+SINLD)+1.0D-30) ;
COSX=(COS(LHA)*COSLD)+SINLD ;
IF (COSX-1.0E-10) 11,11,* ;
* ;
* **** PHOTOLYSIS PARAMETERS **** * ;
* ;
* IN FORMAT J = L*COSX@M*EXP(-N*SECX) * ;
* ;
J<1>=6.073D-05*(COSX@(1.743))*EXP(-0.474*SECX) ;
J<2>=4.775D-04*(COSX@(0.298))*EXP(-0.080*SECX) ;
J<3>=1.041D-05*(COSX@(0.723))*EXP(-0.279*SECX) ;
J<4>=1.165D-02*(COSX@(0.244))*EXP(-0.267*SECX) ;
J<5>=2.485D-02*(COSX@(0.168))*EXP(-0.108*SECX) ;
J<6>=1.747D-01*(COSX@(0.155))*EXP(-0.125*SECX) ;
J<7>=2.644D-03*(COSX@(0.261))*EXP(-0.288*SECX) ;
J<8>=9.312D-07*(COSX@(1.230))*EXP(-0.307*SECX) ;
J<11>=4.642D-05*(COSX@(0.762))*EXP(-0.353*SECX) ;
J<12>=6.853D-05*(COSX@(0.477))*EXP(-0.323*SECX) ;
J<13>=7.344D-06*(COSX@(1.202))*EXP(-0.417*SECX) ;
J<14>=2.879D-05*(COSX@(1.067))*EXP(-0.358*SECX) ;
J<15>=2.792D-05*(COSX@(0.805))*EXP(-0.338*SECX) ;
J<16>=1.675D-05*(COSX@(0.805))*EXP(-0.338*SECX) ;
J<17>=7.914D-05*(COSX@(0.764))*EXP(-0.364*SECX) ;
J<18>=1.140D-05*(COSX@(0.396))*EXP(-0.298*SECX) ;
J<19>=1.140D-05*(COSX@(0.396))*EXP(-0.298*SECX) ;
J<21>=7.992D-07*(COSX@(1.578))*EXP(-0.271*SECX) ;
J<22>=5.804D-06*(COSX@(1.092))*EXP(-0.377*SECX) ;
J<23>=1.836D-05*(COSX@(0.395))*EXP(-0.296*SECX) ;
J<24>=1.836D-05*(COSX@(0.395))*EXP(-0.296*SECX) ;
J<31>=6.845D-05*(COSX@(0.130))*EXP(-0.201*SECX) ;
J<32>=1.032D-05*(COSX@(0.130))*EXP(-0.201*SECX) ;
J<33>=3.802D-05*(COSX@(0.644))*EXP(-0.312*SECX) ;
J<34>=1.537D-04*(COSX@(0.170))*EXP(-0.208*SECX) ;
J<35>=3.326D-04*(COSX@(0.148))*EXP(-0.215*SECX) ;
J<41>=7.649D-06*(COSX@(0.682))*EXP(-0.279*SECX) ;
J<51>=1.588D-06*(COSX@(1.154))*EXP(-0.318*SECX) ;
* ;
LABEL 10 ;
JUMP 12 ;
LABEL 11 ;
DO 13 FOR #1=0(1)51 ;
J<#1>=1.0E-30 ;
LABEL 13 ;
LABEL 12 ;
* ;
* SET HUMIDITY ;
RH=23.*SIN((7.2722D-5*TIME)+1.1781)+66.5 ;
H2O=6.1078*EXP(-1.0D0*(597.3-0.57*(TEMP-273.16)))*
18./1.986*(1./TEMP-1./273.16))*10./(1.38D-16*TEMP)*RH ;

```

```

*;
* SET THE MIXING HEIGHT AND ITS RATE OF INCREASE IF DESIRED ;
IF(HHMIN) *,*,39 ;
HMIX = HHMAX ;
ALPHA = 0.0 ;
LT=0.0 ;
JUMP 49 ;
*;
LABEL 39 ;
IF(DAYTIME-THSTART) *,40,40 ;
ALPHA = 0.0D+0 ;
HMIX = HHMAX ;
LT=0.0 ;
JUMP 49 ;
*;
LABEL 40 ;
IF(DAYTIME-THSTOP) *,41,41 ;
ALPHA = (HHMAX-HHMIN)/(THSTOP-THSTART) ;
HMIX = HHMAX ;
LT=ALPHA/HMIX ;
JUMP 49 ;
*;
LABEL 41 ;
IF(DAYTIME-DUSK) *,42,42 ;
ALPHA = 0.0D+0 ;
HMIX = HHMAX ;
LT=0.0 ;
JUMP 49 ;
*;
LABEL 42 ;
ALPHA = 0.0D+0 ;
HMIX = HHMAX ;
LT=0.0 ;
*;
LABEL 49 ;
*;
* **** SIMPLE RATE COEFFICIENTS ***** * ;
*;
KRO2NO = 4.10D-12*EXP(180/TEMP) ;
KRO2HO2 = 3.00D-13*EXP(1250/TEMP) ;
KAPHO2 = 4.30D-13*EXP(1040/TEMP) ;
KAPNO = 8.10D-12*EXP(270/TEMP) ;
KRO2NO3 = 2.50D-12 ;
KNO3AL = 1.44D-12*EXP(-1862/TEMP) ;
KDEC = 1.0D+06;
KALKOXY=3.70D-14*EXP(-460/TEMP)*O2 ;
KALKPXY=1.80D-14*EXP(-260/TEMP)*O2 ;
*;
* *** COMPLEX RATE COEFFICIENTS ***** * ;
*;
* KMT01 * ;
K0 = 9.00D-32*((TEMP/300)@-1.5)*M ;
KI = 3.00D-11 ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI))))@2))) ;
KMT01=(K0*KI*F)/(K0+KI) ;
*;
* KMT02 * ;
K0 = 9.00D-32*((TEMP/300)@-2.0)*M ;
KI = 2.20D-11 ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI))))@2))) ;

```

```

KMT02=(K0*KI*F)/(K0+KI) ;
*;
* KMT03 * ;
K0 = 2.70D-30*((TEMP/300)@-3.4)*M ;
KI = 2.00D-12*((TEMP/300)@0.2) ;
FC = (EXP(-TEMP/250) + EXP(-1050/TEMP)) ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT03=(K0*KI*F)/(K0+KI) ;
*;
* KMT04 * ;
K0 = 2.20D-03*((TEMP/300)@-4.4)*EXP(-11080/TEMP)*M ;
KI = 9.70D+14*((TEMP/300)@0.1)*EXP(-11080/TEMP) ;
FC = (EXP(-TEMP/250) + EXP(-1050/TEMP)) ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT04=(K0*KI*F)/(K0+KI) ;
*;
* KMT05 * ;
KMT05 = 1 + (0.6*M)/(2.687D+19*(273/TEMP)) ;
*;
* KMT06 * ;
KMT06 = 1 + 1.40D-21*EXP(2200/TEMP)*H2O ;
*;
* KMT07 * ;
K0 = 7.00D-31*(TEMP/300)@-2.6)*M ;
KI = 3.60D-11*(TEMP/300)@-0.1) ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT07=(K0*KI*F)/(K0+KI) ;
*;
* KMT08 * ;
K0 = 2.50D-30*(TEMP/300)@-4.4)*M ;
KI = 1.60D-11*(TEMP/300)@-1.7) ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT08=(K0*KI*F)/(K0+KI) ;
*;
* KMT09 * ;
K0 = 1.80D-31*(TEMP/300)@-3.2)*M ;
KI = 4.70D-12 ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT09=(K0*KI*F)/(K0+KI) ;
*;
* KMT10 * ;
K0 = 4.10D-05*EXP(-10650/TEMP)*M ;
KI = 5.70D+15*EXP(-11170/TEMP) ;
FC = 0.5 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;
KMT10=(K0*KI*F)/(K0+KI) ;
*;
* KMT11 * ;
K1 = 7.20D-15*EXP(785/TEMP) ;
K3 = 1.90D-33*EXP(725/TEMP) ;
K4 = 4.10D-16*EXP(1440/TEMP) ;
K2 = (K3*M)/(1+((K3*M)/K4)) ;
KMT11 = K1 + K2 ;
*;
* KMT12 * ;
K0 = 3.00D-31*((TEMP/300)@-3.3)*M ;
KI = 1.50D-12 ;
FC = 0.6 ;
F=10@(LOG10(FC)/(1.0+(SIGN(K0-KI)*(ABS(LOG10(K0/KI)))@2))) ;

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% 1.10D-14*EXP(-500/TEMP)      : HO2 + O3 = OH      ;
% 4.80D-11*EXP(250/TEMP)       : OH + HO2 =      ;
% 2.30D-13*KMT06*EXP(600/TEMP) : HO2 + HO2 = H2O2 ;
% 1.70D-33*M*KMT06*EXP(1000/TEMP) : HO2 + HO2 = H2O2 ;
% KMT07                        : OH + NO = HONO      ;
% KMT08                        : OH + NO2 = HNO3      ;
% 2.20D-11                     : OH + NO3 = HO2 + NO2    ;
% 3.50D-12*EXP(250/TEMP)       : HO2 + NO = OH + NO2 ;
% KMT09 % KMT10                : HO2 + NO2 = HO2NO2   ;
% 1.30D-12*EXP(380/TEMP)       : OH + HO2NO2 = NO2   ;
% 3.50D-12                     : HO2 + NO3 = OH + NO2    ;
% 1.80D-11*EXP(-390/TEMP)      : OH + HONO = NO2     ;
% KMT11                        : OH + HNO3 = NO3        ;
% 4.00D-32*EXP(-1000/TEMP)*M   : O + SO2 = SO3       ;
% KMT12                        : OH + SO2 = HSO3        ;
% 1.30D-12*EXP(-330/TEMP)*O2   : HSO3 = HO2 + SO3    ;
% 1.4D-11*EXP(-1920/TEMP)      : O+H2S = OH+HS       ;
% 6.3D-12*EXP(-80/TEMP)        : OH+H2S = H2O+HS     ;
% 3.6D-12                      : HS+O3 = HSO+O2       ;
% 2.7D-11                     : HS+NO = HSNO        ;
% 2.6D-11*EXP(240/TEMP)        : HS+NO2 = HSO+NO     ;
% 1.1D-13                     : HSO+O3 = OH + SO3    ;
% 9.6D-12                     : HSO+NO2 =      ;
% 4.0D-19                     : HS+O2 = OH+SO       ;
% 1.4D-13*EXP(-2275/TEMP)      : SO+O2 = SO2+O       ;
% 4.5D-12*EXP(-1170/TEMP)      : SO+O3 = SO2+O2      ;
% 1.4D-11                     : SO+NO2 = SO2+NO     ;
% 1.0D-19                     : NO3+SO2 = NO2 + SO3  ;
% 1.0D-15                     : NO3+H2S = NO2 + H2O ;
% 2.0D-12                     : SO3 + H2O = H2SO4   ;
* ;
% 7.44D-18*TEMP@2*EXP(-1361/TEMP) : OH + CH4 = CH3O2;
% 3.00D-12*EXP(280/TEMP)          : CH3O2 + NO = CH3O + NO2 ;
% 3.00D-15*EXP(280/TEMP)          : CH3O2 + NO = CH3NO3 ;
% KMT13 % KMT14                  : CH3O2 + NO2 = CH3O2NO2 ;
% KRO2NO3*0.40                  : CH3O2 + NO3 = CH3O + NO2 ;
% 4.10D-13*EXP(790/TEMP)          : CH3O2 + HO2 = CH3OOH ;
% 0.60D-13*EXP(416/TEMP)*RO2     : CH3O2 = CH3O ;
% 0.61D-13*EXP(416/TEMP)*RO2     : CH3O2 = HCHO ;
% 0.61D-13*EXP(416/TEMP)*RO2     : CH3O2 = CH3OH ;
% 7.20D-14*EXP(-1080/TEMP)*O2    : CH3O = HCHO + HO2 ;
% 1.00D-14*EXP(1060/TEMP)        : OH + CH3NO3 = HCHO + NO2 ;
% J<51>                          : CH3NO3 = CH3O + NO2 ;
% 1.90D-12*EXP(190/TEMP)         : OH + CH3OOH = CH3O2 ;
% 1.00D-12*EXP(190/TEMP)         : OH + CH3OOH = HCHO + OH ;
% J<41>                          : CH3OOH = CH3O + OH ;
% 1.20D-14*TEMP*EXP(287/TEMP)    : OH + HCHO = HO2 + CO ;
% J<11>                          : HCHO = CO + HO2 + HO2 ;
% J<12>                          : HCHO = H2 + CO ;
% 5.80D-16                      : NO3 + HCHO = HNO3 + CO + HO2 ;
% 6.01D-18*TEMP@2*EXP(170/TEMP)  : CH3OH + OH = HO2 + HCHO ;
% 5.50D-12*EXP(-2000/TEMP)       : OH + H2 = HO2 ;
* ;
* gas-particle reactions ;
* ;
% 6.00D-06                      : HNO3 = NA ;
% 4.00D-04                      : N2O5 = NA + NA ;
% 1.20D-15*H2O                  : SO3 = SA ;
* ;
* photolysis reactions ;
* ;
% J<1>                          : O3 = O1D ;

```

```

% J<2>                                : O3 = O                                ;
% J<3>                                : H2O2 = OH + OH                            ;
% J<4>                                : NO2 = NO + O                                ;
% J<5>                                : NO3 = NO                                    ;
% J<6>                                : NO3 = NO2 + O                            ;
% J<7>                                : HONO = OH + NO                            ;
% J<8>                                : HNO3 = OH + NO2                            ;
** ;
* ;
* ***** ;
*                                     WHENEVER TIME ROUTINE                        ;
* ***** ;
* ;
* FOR THE VALIDATION THE SIMULATION RUN FOR 240 HOURS ;
WHENEVER
    TIME = 864000 % ;
    TIME = 0 + 3600*240 CALL OUTPUT ;
** ;
* ;
* ***** ;
*                                     GENERAL ROUTINE                            ;
* ***** ;
* ;
* SETRESTARTS 5 ;
SETHMAX 100.0 ;
* ;
* MONITOR 6 ;
* ;
* ***** ;
*                                     OUTPUT ROUTINE                            ;
* ***** ;
* ;
COMPILE OUTPUT ;
* MOLECULES/CM3 TO PPB ;
MO3 = O3/M * 1.0D+9 ;
MSO2 = SO2/M * 1.0D+9 ;
MNO = NO/M * 1.0D+9 ;
MNO2 = NO2/M * 1.0D+9 ;
MHNO3 = HNO3/M * 1.0D+9 ;
MH2O2 = H2O2/M * 1.0D+9 ;
MOH = OH/M * 1.0D+9 ;
MOH2 = OH2/M * 1.0D+9 ;
MCO = CO/M * 1.0D+9 ;
MH2SO4 = H2SO4/M * 1.0D+9 ;
* ;
READ 11 TT ;
READ 12 LAT ;
READ 13 LON ;
READ 14 PRES ;
READ 15 TEMP ;
READ 16 EMIS ;
PI = 4.0*ARTAN(1.0) ;
RADIAN = 180.0/PI ;
DEC=-23.79 ;
LAT = LAT/RADIAN ;
DEC = DEC/RADIAN ;
COSLD = COS(LAT)*COS(DEC) ;
SINLD = SIN(LAT)*SIN(DEC) ;
* ;
* EMISSIONS OF SO2 FROM TRAJECTORY INTO MODEL ;
* DATA IN TONNES SULPHUR / YEAR / GRID (100x100 km) ;
Q = EMIS ;

```

```

* ;
* EMISSIONS PER HOUR ;
Q = Q/8760 ;
* ;
* Q IN MOLE SO2 ;
Q = (Q*2*1.0D+06)/64 ;
* ;
* IDEAL GAS LAW pV = nRT ;
* TOTAL VOLUME OF THE BOX = 1.0D+13 m3 ;
* VOLUME SO2 IN BOX = Q*0.0224 m3 ;
* VOLUME SO2 IN BOX*1.0D+06 = ppm ;
Q = (Q*0.0224*1.0D+06)/1.0D+13 ;
* ;
* Q IN PPM TO PPB ;
Q = Q*1000 ;
* Q IN PPB ;
MSO2 = MSO2+Q ;
* ;
* DEPOSITION OF SELECTED POLLUTANTS (SO2 & H2SO4) ;
* DEPOSITION VELOCITY FOR SO2 = 0.3 CM/S - ZANNETTI/ZUNCKEL/WMO ;
* DEPOSITION VELOCITY FOR SO2 = 0.003 M/S ;
* ATMOS ENVIRON 1999 ;
* WMO REPORT 106 GLOBAL ACID DEPOSITION ASSESSMENT 1997 ;
* DEPOSITION VELOCITY FOR H2SO4 = 0.2 CM/S ;
* DEPOSITION VELOCITY FOR H2SO4 = 0.002 M/S ;
* ;
* DEPOSITION = (MSO2)*(DEPO.VELOCITY IN M/HOUR) ;
TSO2 = MSO2*(0.003*3600) ;
TH2SO4 = MH2SO4*(0.002*3600) ;
DSO2 = TSO2 ;
DH2SO4 = TH2SO4 ;
* ;
* NB HMIX IN METERS ;
MSO2 = MSO2-(TSO2/(HMIX*1.0D-02)) ;
MH2SO4 = MH2SO4-(TH2SO4/(HMIX*1.0D-02)) ;
* ;
* CONVERT DEPOSITION PPB TO ug/m2/hour ;
DSO2 = DSO2/0.375 ;
DH2SO4 = DH2SO4/0.245 ;
* ;
* CONVERT DEPOSITION ug/m2/hour SO2 TO kg/ha/hour SO2 ;
* CONVERT DEPOSITION ug/m2/hour H2SO4 TO kg/ha/hour H2SO4 ;
DSO2 = (DSO2*1.0E-9)*1.0E+04 ;
DH2SO4 = (DH2SO4*1.0E-9)*1.0D+04 ;
* ;
* FROM SO2 & H2SO4 TO TOTAL S in kg/ha/hour ;
DSOX = (DSO2/1.9979) + (DH2SO4/3.0587) ;
* ;
* DIFFUSION OF SELECTED POLLUTANTS FROM THE PLUME ;
MSO2 = (MSO2)+((10*BSO2-2*(MSO2)+BSO2)/(100**2)) ;
* ;
* MTIME IN HOURS FOR OUTPUT;
MTIME = TIME/3600;
* ;
PSTREAM 1;
LAT = LAT*RADIAN ;
PSTREAM 2;
* ;
* CONVERTING SPECIES THAT WAS USED FOR DEPO AND DIFF ;
* FROM PPB BACK TO MOL/CM3 FOR THE REACTIONS;
SO2 = (MSO2*M)/1.0D+9 ;
H2SO4 = (MH2SO4*M)/1.0D+09 ;

```

```

RESTART;
* ;
** ;
* ;
* ***** ;
*                               SETPSTREAM ROUTINES ;
* ***** ;
* ;
SETPSTREAM 1 10 6 ;
MTIME MSO2 DSO2 MH2SO4 DH2SO4;
** ;
* ;
SETPSTREAM 2 17 10 ;
MTIME TT LAT LON MSO2 MH2SO4 DSO2 DH2SO4 DSOX EMIS ;
** ;
* ;
* ***** ;
*                               MODEL INITIALISATION ;
* ***** ;
* ;
BEGIN ;
STOP;

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ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists.
BaP	Benzo[a]pyrene.
BHATTEX	Ben MacDhui High Altitude Trace Gas and Transport Experiment.
BTEX	Benzene, Toluene, Ethylbenzene and Xylene.
CO	Carbon monoxide.
CO ₂	Carbon dioxide.
EPA	Environmental Protection Agency.
GC	Gas Chromatograph.
GPS	Global Positioning System.
HAP	Hazardous air pollutant(s).
IUPAC	International Union of Pure and Applied Chemistry.
MCM	Master Chemical Mechanism.
MS	Mass Spectrometer.
NH ₃	Ammonia.
NMHC	Non-methane hydrocarbons.
NO	Nitrogen oxide.
NO ₂	Nitrogen dioxide.
NO _x	Nitrous oxides.
OEL	Occupational Exposure Levels.
PAH	Polycyclic aromatic hydrocarbon(s).
PAN	Peroxyacetyl nitrate.
PBM	Photochemical Box Model.
PM 10	Particulate Matter with a size distribution smaller than 10 µm.

PM 2.5	Particulate Matter with a size distribution smaller than 2.5 μm .
PPB	Parts per billion (concentration value).
PPM	Parts per million (concentration value).
SO ₂	Sulphur dioxide.
TLV	Threshold Limit Value.
TTM	Trajectory Transformation Model.
VOC	Volatile organic compound(s).
WHO	World Health Organization.
WMO	World Meteorology Organization.