IDENTIFICATION AND COMPARISON OF THE VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN AMBIENT AIR IN THE CAPE TOWN METROPOLIS AND THE VAAL TRIANGLE

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M.Sc.

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LIST OF ABBREVIATIONS

ABC	Asian brown clouds
AGL	Above ground level
AHCs	Anthropogenic (man-made) hydrocarbons
ASL	Above sea level
BVOCs	Biogenic volatile organic compounds
BVOVs	Biologiese vlutige organiese verbindings
CBD	Central business district
CFC	Chlorofluorocarbons
CFCs	Chlorofluorocarbons
$cm^3.min^{-1}$	cubic centimetre per minute
CMA	Cape metropolitan area
CMC	Cape Town Metropolitan Council
CO	Carbon monoxide
CO_2	Carbon dioxide
COC	Chain-of-custody
CSIR	Council for Scientific and Industrial Research
DEAT	Department of Environmental Affairs and Tourism
DEC	New York State Department of Environmental Conservation
$dm^3.g^{-1}$	cubic decimetre per gram
$dm^3.min^{-1}$	cubic decimetre per minute
EC	European Community
EPA	Environmental Protection Agency
ESCOM	Electricity Supply Commission
GAW	Global Atmospheric Watch
GC	Gas chromatograph
GC/MS	Gas chromatography coupled with mass spectrometry
HCs	Hydrocarbons
$HO^{\bullet}$	Hydroxyl radicals
km	kilometre
KWe	Koolwaterstowwe
MS	Mass spectrometer
MTBE	Methyl tert-butyl ether
NATREF	National Petroleum Refiners of South Africa
NHCs	Natural hydrocarbons
NHD	n-Hexadecane

NIST	National Institute for Standards and Technology
NMHCs	Nonmethane hydrocarbons
NMTOC	Nonmethane total organic compounds
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen
O_3	Ozone
PAH	Polyaromatic hydrocarbons
PAN	Peroxyacetyl nitrate
PDMS	Poly (dimethylsiloxane)
PIXE	Particle induced x-ray emission
$PM_{10/2.5}$	Particulate matter: diameter of ≥10 µm or diameter of ≥ 2.5 µm
ppb	parts per billion
ppm	Parts per million
ppt	parts per trillion
$R^{\bullet}$	Organic radicals
$R_2O^{\bullet}$	Peroxyradicals
RH	Reactive volatile organic compound
SASOL	South African Coal, Oil and Gas Corporation
SEM	Standard error of means
SFME	Soliede fase mikro-ekstraksie
SO_2	Sulphur dioxide
SOA	Secondary organic aerosols
SPME	Solid phase micro-extraction
STASSA	Statistics South Africa
TACs	Toxic air contaminants
TCA	Trichloric acid
THCs	Total hydrocarbons
tpa	tons per annum
TRS	Total reduced sulphurs
TSP	Total suspended particulate matter
TVOCs	Total volatile organic compounds
UK	United Kingdom
USA	United States of America
US-EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
VOVs	Vlugtige organiese verbindings

WHO	World Heath Organisation

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ABSTRACT

The growing concern for environmental problems underlines the importance of correctly predicting the fate of pollutants released into the environment. In the case of VOCs, this is a complex task due to the large number of VOCs with different reactivity's present in ambient air (Atkinson, 1990).

In Cape Town and the Vaal Triangle brown haze layers develops in ambient air during windless days in the wintertime. This leads to the build-up of pollutants emitted into the atmosphere. The haze is usually most intense in the early mornings, gradually dispersing during the day. The aim of the study was the identification, quantification and comparison of VOCs in Cape Town and the Vaal Triangle.

Different sampling techniques have been used during intensive field campaigns in Cape Town and the Vaal Triangle. Three different sampling techniques were used, namely: 6 litre TO canisters, Carbotrap^{TM} 300 tubes and 75 mm Carboxen-PDMS SPME fibres. Samples were also taken at different altitudes in the lower troposphere, because the pollution layers are formed at different altitudes. Background corrections were also carried out.

A Supelco (Cat no: 41900-U) calibration standard, was used as external standard. Samples were analysed by a Hewlett Packard Agilent 6890 gas chromatograph (GC) and Micromass Autospec-TOF mass spectrometer (MS) according to the EPA TO-14a compendium method. The samples were concentrated on a Perkin-Elmer Turbo matrix thermal desorber. A temperature program was used and VOCs not present in the Supelco standard were identified using the MS data system library (NIST). SMPE was only used as a qualitative comparison to the other techniques.

A large number of VOCs were identified and quantified at ground level and at different altitudes in ambient air in both Cape Town and in the Vaal Triangle region. The aim was identifying and quantifying manmade emissions. The

total VOC profile may differ from these since oxygenated species have not been focussed on.

In the Cape Town study more unsaturated VOCs and longer chain HCs were detected during the night than during the day. The number of ketones present also seemed to be higher during the day. In the city centre and Khayelitsha a wide range of halogenated hydrocarbons was detected at ground level. Chlorinated HCs do not take part in photochemical reactions and the concentrations of these VOCs did not to change very much in the day and night samples. It appeared that the concentration of the VOCs at different altitudes in some cases differ significantly. This correlated with the brown haze that forms visible layers and it seemed that the concentration of VOCs in layers differ. The VOCs found at ground level were in most cases related to petroleum products while the VOCs detected at higher altitudes are compounds that remained in the atmosphere and can be transferred from their source over great distances, or photochemical products.

In the Vaal Triangle study a very wide variety of VOCs that included a large range of halogenated VOCs were detected. The north-east wind prevailing on the day of sampling diluted the VOCs sampled in the Vaal Triangle.

The comparison of the two study regions showed that in both regions the toluene had the highest concentrations of all the measured VOCs. The reported daytime benzene concentrations at Goodwood, Table View and the city centre and the nighttime levels in Khayelitsha exceeded 1.6 ppb ($5\ \mu g.m^{-3}$). The low benzene concentration levels in the Vaal Triangle are mainly due to the wind diluting pollution at the time of sampling. A wider variety of VOCs were detected in the Vaal Triangle than in Cape Town. Pollutants detected in the Vaal Triangle had very low concentrations, mostly even below the detection limits. This was due to the strong wind that is typical for August in the Vaal Triangle. BVOCs were detected in both regions. In both areas the influence of photochemical processes is evident and secondary products of photochemical reactions were found. A large range of halogenated VOCs was found in the ground level samples in the Vaal

Triangle and at higher altitudes in the Cape region. Halogenated VOCs were also detected in the city centre in Cape Town and in Khayelitsha. In both regions a large range of complex benzene derivates were found.

The comparison of the values obtained using canisters and the Carbotrap^{TM} 300 tubes showed differences that cannot be explained unambiguously. VOCs sampled with SPME correlated with the above-mentioned techniques but the identification of the unknown compounds was much easier in samples taken with the SPME than with the other techniques used. SPME proved to be a handy "screening" tool for the identification of VOCs.

A comparison of the two different regions investigated gave insight into the concentrations and the fate of VOCs on a regional and global scale in South Africa. It followed from the results reported in this study that VOC emissions in Cape Town and in the Vaal Triangle would most definitely play a significant role in the formation of photochemical smog.

OPSOMMING

Wêreldwyd is groeiende kommer oor die impak van lugbesoedeling op die omgewing. Die probleem word vererger deur VOVs, 'n groot groep chemiese verbindings met verskillende reaktiwiteite in die lug (Atkinson, 1990).

'n Bruin dynserigheid ontwikkel gedurende windstil dae in die winter in Kaapstad en oor die Vaaldriehoek. Konsentrasie-vlakke van besoedelstowwe in die lug verhoog, omdat die wind dit nie versprei nie. Die dynserigheid is meer intens vroeg in die oggend en verminder deur die loop van die dag. Die doel van die studie was die identifisering, kwantifisering en vergelyking van VOVs in Kaapstad met die wat in die Vaaldriehoek voorkom.

Drie verskillende monsterneemtegnieke is gebruik in veldstudies in Kaapstad en die Vaaldriehoek, t.w.: 6 liter TO gassilinders, Carbotrap^{TM} 300 buise and 75 mm Carboxen-PDMS SFME vesels. Monsters is ook geneem op verskillende hoogtes bo seespieël, omdat die dynserigheid soms lae vorm. Agtergrond monsters is ook in alle gevalle geneem.

'n Supelco (Cat no: 41900-U) kalibrasie standaard, is as eksterne standard gebruik. Monsters is geanaliseer met 'n Hewlett Packhard Agilent 6890 gaschromatograaf (GC) en 'n Micromass Autospec-TOF massaspektrometer (MS) volgens die EPA TO-14a metode. Die monsters is gekonsentreer op 'n Perkin-Elmer Turbo matriks termiese desorbeerder. 'n Temperatuurprogram is gebruik en VOVs wat nie in die Supelco standaard teenwoordig is nie, is geïdentifiseer met die MS-datasisteembiblioteek. SFME is slegs gebruik as 'n kwalitatiewe vergelyking met die ander tegnieke.

'n Groot aantal VOVs is geidentifiseer en gekwantifiseer op grondvlak en op verskillende hoogtes bo seespieël in die Kaapstad- en die Vaaldriehoek-areas. Die doel van die studie was die identifisering en kwantifisering van mensgemaakte VOVs. Die geheelbeeld van VOVs-konsentrasies mag verskil omdat daar nie op geoksideerde spesies gefokus is nie.

In Kaapstad is meer onversadigde VOVs en langer ketting KWe waargeneem gedurende die nag. Die verskeidenheid ketone waargeneem was ook hoër gedurende die dag. In die middestad en Khayelitsha is 'n wye verskeidenheid gehalogeneerde koolwaterstowwe op grondvlak waargeneem. Gechlorineerde KWe word nie fotochemies vernietig nie en die vlakke van hierdie VOVs het nie baie verander van die nag na die dag nie. Dit lyk of die konsentrasies van die VOVs op verskillende hoogtes merkbaar verskil, dit korreleer met die verskynsel dat die bruin dynserigheid lae vorm en dit wil voorkom of die konsentrasies van die VOVs in die lae ook merkbaar verskil. Die grondvlak-monsters het hoofsaaklik petroleumverwante VOVs bevat, terwyl die VOVs op verskillende hoogte verbindings is wat stabiel is en oor groot afstande vervoer kan word, of die produkte van fotochemiese reaksies is.

In die hoogs ge-industrialiseerde Vaaldriehoek is 'n wye verskeidenheid VOVs, wat 'n groot aantal gechlorineerde VOVs insluit waargeneem. Konsentrasies van die VOVs in die Vaaldriehoek is verlaag deur 'n noordooste-wind wat tydens die monsterneming gewaai het.

'n Vergelyking van die twee studie-areas toon dat tolueen die VOV met die hoogste konsentrasie was. Die benseenvlakke gedurende die dag in Goodwood, Table View en die middestad en die vlakke gedurende die nag in Khayelitsha was hoër as 1.6 ppb (5 $\mu g.m^{-3}$). Die lae benseenkonsentrasies in die Vaaldriehoek was as gevolg van verdunning deur die wind, tydens die monsterneming. 'n Groter verskeidenheid VOVs is in die Vaaldriehoek waargeneem. Besoedelstowwe in die Vaaldriehoek het lae konsentrasie vlakke getoon, meestal onder die deteksie limiete van die metode. Dit was as gevolg van die tipiese Augustuswinde in die Vaaldriehoek. BVOVs is in beide gebiede waargeneem. In beide areas was die effek van fotochemiese reaksies duidelik waarneembaar en die sekondêre produkte van die reaksies is in die monsters gevind. 'n Groot verskeidenheid gehalogeneerde VOVs is op grondvlak in die Vaaldriehoek en op verskillende hoogtes bo seespieël gevind. Gehalogeneerde VOVs is waargeneem in die middestad van

Kaapstad en in Khayelitsha. In biede areas is 'n groot verskeidenheid benseenkomplekse gevind.

Die vergelyking van die konsentrasievlakke van die gassilinders en die Carbotrap™ 300 buise toon verskille, wat nie onomwonde verklaar kon word nie. VOV-monsters wat met die SFME geneem is korreleer goed met bogenoemde tegnieke, maar dit was makliker om die onbekende VOVs te identifiseer in die SFME-monsters. SFME is 'n handige "sifting" tegniek vir die identifisering van VOVs.

'n Vergelyking van die twee areas het tot 'n beter begrip van die konsentrasies en die lot van VOVs op 'n plaaslike en landswye skaal in Suid-Afrika gelei. Dit blyk uit die resultate dat VOV emissies in Kaapstad en die Vaaldriehoek 'n betekenisvolle rol speel in die vorming van fotochemiese rookmis.

CHAPTER 1

INTRODUCTION AND PROBLEM STATEMENT

This chapter...

The relevancy (Par. 1.1) and the background (Par. 1.2) of the study as well as the problem statement (Par. 1.3) provide the motivation and objectives for identifying and comparing VOCs in ambient air in Cape Town and the Vaal Triangle (Par. 1.4). The possible benefits of the study are given in Par. 1.5. The chapter is concluded (Par. 1.6) by a short summary of the analytical techniques that will be used to meet the objectives.

1.1 RELEVANCY OF THE STUDY

Air pollution is not only a local problem but is of worldwide concern (Elsom, 1987). Atmospheric pollution is caused by the emission of contaminants produced naturally, as well as by human activities. Some of these substances become harmful when they reach certain concentration levels or when reactions take place that lead to the formation of more harmful compounds (Gammage & Kay, 1987). Human activities, primarily the combustion of coal, oil and natural gas, are important contributors to air pollution (especially hydrocarbon emissions), which can even lead to global climate changes. The air in industrialised metropolises contains mixtures of substances originating from various industrial processes, internal combustion engines and anthropogenic processes. South Africa has a high unemployment rate as well as an ever-increasing population that makes sustainable development an even more complex problem.

Legislation and monitoring of pollution in South Africa have historically been focussed on primary and secondary inorganic pollutants such as sulphur dioxide (SO_2), ozone (O_3), and the oxides of nitrogen (NO_x). Worldwide,

however, people have become more concerned about the total effect of air pollution on human health and the environment and since the late 1990s more emphasis has been placed on the role and contribution of volatile organic compounds (VOCs) (Commission of European Communities, 1998). The increased focus on VOCs in ambient air pollution is mainly due to enhancements in the monitoring methodology of these compounds and the proven health impacts of these pollutants. The monitoring of VOCs, especially benzene, has therefore been included in recent legislation in European countries (Commission of European Communities, 1998). The growing concern for environmental problems underlines the importance of correctly predicting the fate of pollutants released into the environment. In the case of VOCs, this is a complex task due to a large number of VOCs with different reactivities present in ambient air (Atkinson, 1990).

1.2 BACKGROUND TO THE STUDY

The formation of a brown haze due to urban air pollution is a common phenomenon in many industrialised cities worldwide. Los Angeles's smog is one of the earliest examples known. It has recently been recognised that the chemical composition of these haze episodes are not all the same and large international projects like ABC (Asian Brown Clouds) have been initiated to determine the exact nature of these haze clouds.

Increasing industrialisation has increased the release of volatile organic compounds (VOCs) into the ambient air due to rapidly increasing industrial emissions. These trace gasses have relatively long lifetimes in the atmosphere and have a local as well as distant impact. VOCs consist of a wide range of different compounds; these include alkenes, alkanes, oxidated hydrocarbons, carbonic acids, ethers, esters, ketones, and polyaromatic hydrocarbons (PAHs). The different VOCs released into the ambient air can react at different rates with ozone (O_3), hydroxyl radical ($HO^{\cdot}$) and NO_x in the presence of sunlight to form secondary VOCs and O_3. Although VOCs are usually found as trace gasses, the concentrations of VOCs in ambient air are of concern because:

1. VOC pollution leads to the formation of O_3 (see Par. 2.4.1) that could indirectly affect human and plant material.
2. Some of the VOCs are carcinogenic and can affect human health (see Par. 2.5.7).
3. Halogenated VOCs can react with stratospheric O_3 that could lead to climate changes.
4. Climatic changes can also occur due to VOC emissions that inevitably increase the concentration CO_2 in the atmosphere.

1.3 PROBLEM STATEMENT

Cape Town in South Africa is known for its scenic beauty, but by the late sixties, the region was beginning to experience thick smog on certain windless days from March to August during the winter. Strong temperature inversions lead to build-up of pollutants emitted into the atmosphere that formed a brown haze. The haze consists of a white to brown layer, which covers most of the Cape Peninsula and Cape Flats. In 1968 the Cape Town Metropolitan Council (CMC) initiated a program of air pollution control (Wicking-Baird *et al.*, 1997). In the mid-eighties local authorities began the installation of monitoring systems in Cape Town to monitor the brown haze.

In the Vaal Triangle industrial growth and urbanisation are the major contributors of air pollution. This region is a highly developed industrial, mining and residential metropolis in South Africa, but it also has serious smoke pollution problem from non-electrified informal settlements. Air pollution leads to poor visibility and brown haze formation especially during windless days in the winter. During the winter the air pollution is even further intensified when strong temperature inversions trap the air pollutants and, being at a lower altitude than the Witwatersrand, results in the draining of air pollutants under a catabatic flow regime (Van Graan *et al.*, 1992). It is therefore not surprising that the impact of the air quality in the Vaal Triangle on the health of the population is of great concern to the residents of the region.

In both regions studied the brown haze is most intense during windless, early winter mornings, gradually dispersing during the day. Cape Town is situated in a winter rainfall region next to the cold Atlantic Ocean and the warmer Indian Ocean, so that the fluctuation in temperature from the night to the day is not very high.

The Vaal Triangle is situated in the highveld in a summer rainfall region and has a multitude of industries, mines and cultivated agricultural land. All these, including veld fires and incomplete burning of coal contribute to the formation of the brown haze. The dry winter months are subjected to strong temperature inversions and long cold winters, so that local air quality is likely to be affected by stable climatic conditions that hamper pollution dispersion and dry conditions that promote dust formation. The temperature fluctuations between nights and days are thus rather extreme.

1.4 OBJECTIVES OF THE STUDY

This study is aimed at providing scientific data that can assist in solving problems related to industrial emissions, human health, optimum economical growth and the atmosphere. The objectives of this study are therefore:

1. the identification, quantification and comparison of man-made VOCs found in ambient air during the winter months when brown haze pollution layers are noticeable in both the Cape Town metropolis and in the Vaal Triangle;
2. to compare different sampling (TO-canisters, Carbotrap^{TM} 300 tubes and solid phase micro-extraction (SPME)) techniques for assessing VOCs in urban air;
3. to provide information on which air quality policies can be based in order to assist local governments in drawing up an air emission inventory for the particular metropolitan; and
4. to compare the two different regions in order to also provide more insight into the concentration and the fate of VOCs on a regional and global scale.

1.5 SIGNIFICANCE OF THE STUDY

The project is unique in the respect that the man-made VOCs in the ambient air in these two regions have never been compared before. The analytical techniques used have also never been compared under the prevailing conditions.

Knowledge of the VOCs present in the brown haze would:

1. Assist the local councils as well as industries in their aim for maximum economical growth without compromising the health of residents.
2. Assist local councils and industries in identifying possible shortcomings in their policies and improving the quality of air by reducing the intensity of the brown haze that has a negative impact on tourism and public health.
3. Generate new knowledge, which might also result in more cost-effective techniques for monitoring air pollution included in future air quality guidelines for South Africa.

1.6 MEETING THE OBJECTIVES

Three different analytical techniques for monitoring VOCs in urban air will be used during intensive field campaigns in Cape Town and the Vaal Triangle, namely: 6 litre TO canisters, Carbotrap™ 300 tubes and 75 mm Carboxen-PDMS solid phase micro-extraction (SPME) fibres. Sampling with canisters and with tubes are both carried out using United States Environmental Protection Agency (US-EPA) accredited methods. Since the absorption rate and stability of the compounds on the SPME fibres differ, it will only be used as a qualitative comparison to the other techniques. The pollution layers are formed at different altitudes above ground level so that samples will be taken at ground level as well as at different altitudes (in the brown haze layers) using a suitably equipped small aircraft.

CHAPTER 2

LITERATURE SURVEY

This chapter...

The chapter summarises the current knowledge about VOCs in ambient air. The literature survey starts with defining air pollution (Par 2.1) and describes the different types of air pollution (Par. 2.2 and Par. 2.3). Photochemical oxidants are discussed in Par. 2.4. The sources (Par. 2.5.3), the reactions (Par. 2.5.4.1), the products (Par. 2.5.4.2), the sinks (Par. 2.5.5), the tropospheric lifetimes (Par. 2.5.6), the health effects (Par. 2.5.7) and the levels worldwide of volatile organic compounds (VOCs) and halogenated hydrocarbons are described in Par. 2.5. Par. 2.6 concentrates on the sampling techniques for VOCs, while Par. 2.7 indicates the climatic factors that might affect the VOC-levels in South Africa. Par. 2.8 and Par. 2.9 focus on previous or related studies of the brown haze in Cape Town and the Vaal Triangle, respectively.

2.1 DEFINING ATMOSPHERIC POLLUTION

Elsom (1987) defined pollution as the presence in the atmosphere of compounds or energy in such large amounts and over such duration liable to cause harm to human, plant, or animal life, or damage to human-made materials and structures, or changes to the weather and climate, or interference with the comfortable enjoyment of life or property or other human activity. Although natural air pollution has occurred through the ages (see Par. 2.2.1), humans have increased the intensity and the frequency of some of these natural occurring atmospheric compounds (Wayne, 1985). This type of pollution is known as anthropogenic pollution (Godish, 1991).

TYPES OF AIR POLLUTION

2.1.1 Natural air pollution

Natural air pollution has occurred through the ages as a result of volcanic disruptions, dust storms, decomposition of animal and plant material, emission from the surface of the sea, wind, erosion of soil, natural fires, pollen, mould spores and vegetation (Wayne, 1985; Godish, 1991). Biogenic volatile organic compounds (BVOCs) may consist of compounds such as methanol, ethanol, acetone, propanal, hexanol, isoprene, camphene, limonene, pinene, terpene (Geron *et al.,* 2006; Chameides *et al.,* 1988). BVOCs are the products of biogenic (biological processes) or geogenic (geochemical) processes (Godish, 1991) and make up 90% of the global VOC budget (Guether *et al.*, 1996). Godish (1991) estimates the BVOC emissions are between 3.3 to 6.6 x 10^7 tons per year. Benjamin *et al.* (1997) estimated that the BVOCs measured in the California South Coast Basin represent approximately 9% of the total volatile organic compounds (TVOCs) emissions for a summer day. In general natural hydrocarbons (NHCs) react faster than anthropogenic hydrocarbons (AHCs) (Chameides *et al.,* 1998). BVOCs such as isoprene and monoterpene are a factor of three more reactive than a weighted average of VOCs emitted by motor vehicle exhaust (Carter, 1994) 90% of the global VOC budget is biogenic (Guenther *et al.*, 1996). Thus NHCs can have a significant effect even though the concentrations are lower than AHCs (Chameides *et al.,* 1988).

2.1.2 Anthropogenic (man-made) air pollution

In the early 1900s most people considered air pollution as suspended particulate matter (soot, smoke) and sulphur dioxide. These are waste products produced mainly by domestic heating, a wide range of industrial plants, and power plants. Towards the end of the twentieth century, the term, "air pollution" had increased to include a large number of pollutants (Elsom, 1987). The tremendous increase in the use of petroleum products, particularly in petroleum-powered motor vehicles, introduced several new

pollutants (WHO, 1972). Exhaust emissions lead to oxides of nitrogen (NO_x), carbon monoxide (CO), hydrocarbons (HCs), that add to the pollution in urban areas. Photochemical reactions (see Par. 2.4) form secondary pollutants (or photochemical oxidants) from the emissions of the oxides of nitrogen and HCs in the presence of sunlight (Elsom, 1987). Anthropogenic air pollution has been and continues to be viewed as a serious problem. The danger of man-made pollution lies in the fact that potentially harmful pollutants in high concentrations are produced in environments where human health and welfare is the most likely to be affected (Godish, 1991). Künzil *et al.* (2000) concluded that air pollution caused 6% of the total annual mortality in Austria, Switzerland and France. About half of the mortality caused by air pollution was attributed to motorised traffic.

2.2 COMMON TYPES OF POLLUTION

Air pollution has traditionally been classified in different categories and these are discussed separately in this section.

2.3.1 Smog

"Smog" originally referred to a mixture of smoke and fog. Smog is caused by vast quantities of pollutants being emitted from industrial and domestic sources during periods when meteorological conditions fail to disperse the pollution. Elsom (1996) distinguishes between summer and winter smog. Summer smog occurs on warm sunny days when the wind is calm or light and photochemical activity encourages ozone formation (see Par. 2.4). During winter when cold, anticyclonic conditions prevail, smog is characterised by calm or light winds and below-freezing point temperatures. These conditions restrict the mixing depth due to a stable or inversion atmospheric lapse rate so that little dispersal and dilution of pollutants occurs, causing pollution concentrations to build up to high levels (Elsom, 1987). During winter smog, hourly and daily concentrations of benzene, CO, nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and suspended particles reach many times their average winter values (Elsom, 1996). Smog is considered as being a chemical 'soup' that might effect human health and consists of: sulphur

oxides, (SO_2) (see Par. 2.3.3), fine particulate matter, $PM_{10/2.5}$ (see Par. 2.3.4), oxides of nitrogen (NO_x) (see Par. 2.4), volatile organic compounds (VOCs) (see Par. 2.4 and Par. 2.5), CO (see Par. 2.4.) ground level ozone (O_3) (see Par. 2.4.1), and totally reduced sulphurs (TRS) (Simpson, 2003). The ambient air quality standards for these photochemical compounds for South Africa are given in Table 2.1.

Table 2.1: Ambient air quality standards in South Africa (SA, 2005)

	NO (ppb)	NO_2 (ppb)	NO_x (ppb)	PM_{10} ($\mu g.m^{-3}$)	SO_2 (ppb)	O_3 (ppb)	CO (ppb)
Instantaneous peak	900	500	1 400		600	0.25	
Annual average	150	50	200	60	30		
1 Month average	200	80	300		50		
Max. 24 hour average	300	100	400	180	100		
Max. 8 hour average							9
Max. 1 hour average	600	200	800		300	0.12	35

Although stable weather conditions can cause pollution levels to increase, smog will only form if pollutant emissions are high to start with (Elsom, 1996). According to Elsom (1996) the following factors can all contribute to the build up of higher pollution levels:

Sub-freezing temperatures

An increase in energy consumption for heating will increase emissions from fuels burned for domestic heating. An increase in emission from vehicles also occurs, as the engines take longer to reach optimum efficiency, leading to an increase in the emission of CO and HCs.

High temperature

Increased evaporation of VOCs. Light wind and low atmospheric mixing altitudes produce a reduced volume of air in which pollutants are dispersed and diluted. High temperature also leads so larger atmospheric mixing volumes, driven by convection.

Low temperatures

Low temperatures combined with mist, fog or particulate matter increase the possibility for some chemical reactions too occur. Low temperatures also reduce the boundary layer height.

Location of an urban area

Where an urban area is located in a basin or a valley, the slopes of the valley act like the sides of a box and a temperature inversion may form the box lid, trapping the pollutants. Anticyclonic conditions let cold air drain down the valley sides, cooling the valley bottom and increase the inversion.

Coastal conditions

Circulation patterns in coastal air develop as a result of the difference in the heating and cooling of land and water surfaces. When skies are clear and prevailing winds are light, land surfaces heat more rapidly than water (Godish, 1991). Land and sea breeze circulation can then play a part in aggravating coastal smog. At night an offshore breeze sweeps the pollutants out to sea but an onshore wind brings them back during the day. In the case of photochemical pollution the precursor emissions, which lead to ozone formation, may be transported by the land breeze out to sea at night. The next day, after photochemical reactions have converted the precursor emissions into ozone over the sea, the ozone might be brought back onshore (Elsom, 1996).

2.3.2 Haze

Haze is caused (EPA, 1998) when sunlight encounters tiny pollution particles (see Par. 2.3.4) in the air. Although Godish (1991), Barrie (1986) and Kemf (1984) distinguished between smog and haze, Elsom (1996) used them as synonyms. Godish (1991) refers to haze as a reduction in visibility that is not as intense as smog. He describes smog as a marked visibility reduction over cities or large metropolitan areas, while haze refers to a wide-scale low-level pollution that causes a reduction in visibility (Godish, 1991).

The fine particle matter in haze absorbs some of the light or scatters the light. The higher the concentration of the pollution the more absorption and scattering occurs, which reduce the visibility and the colour observed. Particles can obscure the landscape, blocking out distant scenery or buildings. Depending on the type of particles present, the haze can appear to be yellowish-brown or even white.

The transporting of sulphates, nitrates and HCs over long distances results in regional hazes developing, which reduces visibility in areas distant from the emission sources of these secondary pollutants (Godish, 1991). Haze can restrict the horizontal visibility range between three and eight kilometres and may be extended over an area equal in size to the North America continent (Barrie, 1986; Kemf, 1984).

Wolff and co-workers (1981) determined that combustion sources account for more that 80% of the fine particulate matter and the visual range reduction in the Denver brown haze. In 1996 the data Schwartz and his co-workers collected suggest that the increase in daily mortality in 17 cities is specifically associated with combustion-related particles. Although their study excluded the contribution of SO_2 and O_3 to these deaths, they did not address the contribution of other gaseous pollutants (such as NO_2, that is known to cause breathing disorders) that could also be present in the brown haze layer.

2.3.3 Sulphur dioxide (SO_2)

Combustion of coal and oil can lead to the formation of sulphur dioxide (SO_2), a colourless gas. Sulphur dioxide can lead to chronic respiratory diseases, it can also photochemically or catalytically react with other pollutants to form sulphur trioxide, sulphuric acid and sulphates (Elsom, 1987). Sulphur trioxide is converted in the presence of water to sulphuric acid (H_2SO_4), which can deteriorate limestone and sandstone and cause acid rain.

2.3.4 Particulate matter (PM_{10}, $PM_{2.5}$)

Particulate matter (PM) or particulates is a range of solids or liquids dispersed into air (Elsom, 1987), grouped according to the size of the particle: PM_{10} (particulates with a diameter of 10 μm or less) contributes to premature soiling of buildings and plays a role in damage to human health. PM_{10}-particulates are deposited in the back of the throat, once there, they are moved along and eventually expelled. $PM_{2.5}$ (particulates with a diameter of 2.5 μm or less) often carry an acidic package (sulphuric or nitric). These small particles can penetrate deep into the lungs and can be absorbed into the blood stream (Simpson, 2003) so that health effects are mostly related to $PM_{2.5}$ contaminants. Other particulate matter include PM_1 and $PM_{0.1}$.

2.3 PHOTOCHEMICAL OXIDANTS

Photochemical oxidants are secondary pollutants produced by the action of sunlight on an atmosphere containing reactive hydrocarbons and oxides of nitrogen (WHO, 1972). In addition to the production of oxidants, photochemical reactions produce a large number of new HCs and oxy-hydrocarbon species. These secondary products may comprise as much as 95% of the total HCs present in a severe smog episode (Godish, 1991). According to Elsom (1996), this is more likely to occur during warm, sunny, stable days during summer.

The precursors of photochemical oxidants are:

Nitrogen oxides (NO_x)

Bacteria, lightning and volcanoes naturally produce NO_x. The combustion of fossil fuels is the major source of man-made NO_x emissions (Elsom, 1987). NO_x-species are defined as a wide range of nitrogen containing compounds, these include NO, NO_2, nitrate radical (NO_3·), N_2O_5, HNO_2 and HNO_3 and are formed by dissociation of nitrogen (N_2) followed by oxidation of N_2O and ammonia (NH_3) (Wofsy & McElroy, 1974). Motor vehicles contribute 5 - 10% of nitrogen dioxide (NO_2), while the rest depends on the availability of O_3

(Elsom, 1996). Ozone photochemically reacts with nitric oxide to form nitrous dioxide. During this photochemical reaction, nitrous dioxide can act as an oxidising agent, but it can also cause respiratory diseases (Elsom, 1996). The only known way by which ozone is formed is by the photolysis of NO_3 (Pienaar & Helas, 1996). The NO_3 can react with aldehydes to proceed via abstraction of aldeyde H-atom to form acyl radicals (Jenkin *et al.*, 1997).

Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are part of a very large and complex group of air pollutants. Volatile organic compounds contribute to the formation of O_3 during photochemical reactions (Elsom, 1996). Since this study is focussed on VOCs in two metropolitan areas in South Africa, VOCs will be discussed in more detail in Par. 2.5.

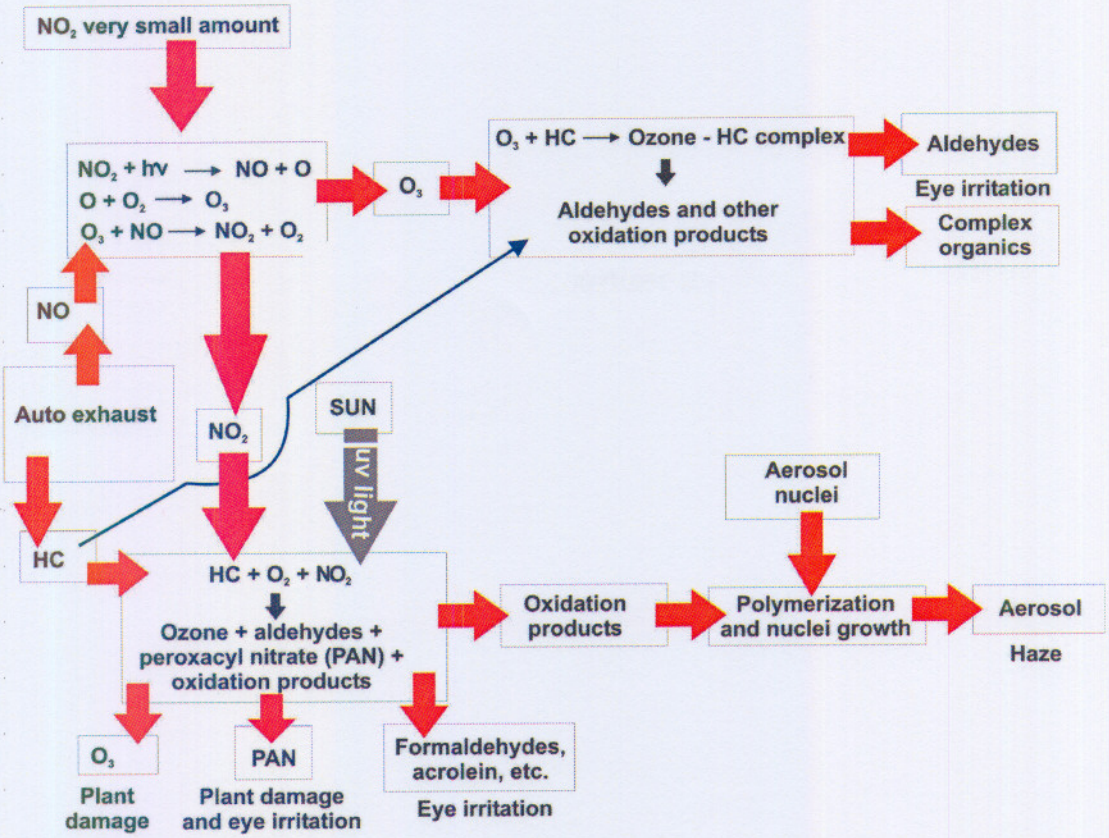
Carbon monoxide (CO)

Petroleum-powered vehicles are an important source of carbon monoxide (CO) emissions. The incomplete combustion of carbon-based fuels contributes more than 90% of CO in most urban areas (Elsom, 1996), but domestic fuel burning also contributes significantly to CO emissions. Carbon monoxide is characteristic of residential coal combustion, because ineffective combustion of domestic fuels will result in higher CO emissions. Carbon monoxide is also released from the industrial sector. Volatile organic compounds are progressively oxidized to CO and CO_2 over periods of hours to weeks.

2.4.1 Formation of ozone

Ozone is formed as a secondary pollutant by photochemical reactions in the atmosphere due to VOCs and NO_x pollution. The chemistry of O_3 is complex and in some cases non-linear. Low VOC/NO_x ratios or VOC-limited conditions can increase the formation of O_3, while high VOC/NO_x ratio or NO_x-limiting conditions can have the opposite effect. The complex series of photochemical reactions produces various oxidants, the most important being ozone and peroxyacetyl nitrate (PAN) as indicated in Figure 2.1.

Figure 2.1: Photochemical processes associated with ozone (adapted from Elsom, 1987)



Although HO·-pathways are the main reaction pathways for the oxidation of VOC, it is excluded in Figure 2.1. Ozonolysis is the reaction of ozone and a VOC to produce an oxygenated VOC and a HO•. The atmospheric chemistry of the tropospheric formation of ozone is complex. A short summary according to the National Research Council (1991), gives the following steps: The reactive VOCs (RH), react with hydroxyl radicals (HO·) leading to the formation organic radicals (R·):

$$RH + HO\cdot \rightarrow R\cdot + H_2O \qquad (2.1)$$

(Additional reaction of some RH species with ozone and the nitrate radical NO_3, could also be significant). Organic radicals (R·) combine with the

molecular oxygen to form peroxy radicals ($R_2O\cdot$), a process that usually requires an inert third body, M (e.g. N_2 or O_2):

$$R\cdot + O_2 \xrightarrow{M} R_2O\cdot \qquad (2.2)$$

Peroxy radicals ($R_2O\cdot$) react with NO to form NO_2:

$$R_2O\cdot + NO \rightarrow NO_2 + RO\cdot \qquad (2.3)$$

NO_2 is photochemically dissociated by solar radiation to release ground state oxygen atoms, $O(^3P)$, and form NO:

$$NO_2 + h\nu\ (< 400nm) \rightarrow NO + O(^3P) \qquad (2.4)$$

($h\nu$ = photon of light, represents the energy from solar radiation. It is the product of Planck's constant h, and the frequency ν, of the electromagnetic wave of solar radiation).

Finally, oxygen atoms combine with molecular O_2, in the presence of a third body to form O_3:

$$O(^3P) + O_2 \xrightarrow{M} O_3 + M_2O\cdot \qquad (2.5)$$

This process is a chain reaction: O_3 is photochemically dissociated by near-ultraviolet solar radiation to form an excited oxygen atom, $O(^1D)$:

$$O_3 + h\nu\ (< 315nm) \rightarrow O_2 + O(^1D) \qquad (2.6)$$

which, in turn, can react with water vapour (H_2O) to form two $HO\cdot$ radicals:

$$O(^1D) + H_2O \rightarrow 2HO\cdot \qquad (2.7)$$

The resulting $HO\cdot$ radicals drive the chain process. Reactions initiated by $RO\cdot$ radicals can lead to the production of $HO\cdot$ in the presence of NO. With

enough VOCs and NO_x in the atmosphere, this can lead to an increased concentration of ozone in the troposphere (National Research Council, 1991).

2.5 VOLATILE ORGANIC COMPOUNDS AND HALOGENATED HYDROCARBON COMPOUNDS

2.5.1 Definition of volatile organic compounds

Hydrocarbons (HCs) represent a wide range of organic compounds consisting primarily of hydrogen and carbon atoms. HCs can react with other substances such as nitrogen, oxygen, halogens and sulphur, or even metals to form a very wide variety of HC derivatives. HCs as such are chemically inert under most circumstances. HCs found in polluted air include compounds such as esters, ketones, aldehydes, alcohols, ethers and organic acids.

Volatile organic compounds (VOCs) are the collective name for a large group of compounds sufficiently volatile to exist as a vapour in ambient air. The properties of these compounds can vary widely, making it a very complex group of compounds.

According to the United Nations Economic Commission for Europe: VOCs are "all organic compounds of anthropogenic nature other than methane that are capable of producing photochemical oxidants by reactions with oxides of nitrogen in the presence of sunlight" (Hoskins, 1995). The VOCs have a boiling point range with a lower limit between 50 - 100 °C and an upper limit between 240 - 260 °C, where the higher values refer to polar compounds (Gammage & Kaye, 1987). VOCs have vapour pressures greater than ~1 mm Hg at ambient temperatures and exist entirely in the vapour phase.

2.5.2. Definition of halogenated hydrocarbons

Halogenated hydrocarbons as a group are unique because of their environmental impact and persistence. They include volatile compounds

used as solvents such as methyl chloride, carbon tetrachloride, trichloroethylene, perchloroethylene and tetrachloroethylene. Halogenated hydrocarbons also include chlorofluorocarbons (CFCs), which is a very stable group of VOCs that pose a threat to the ozone layer because they behave as greenhouse gasses. The most common atmospheric CFC contaminants are trichlorofluoromethane, dichlorodifluoromethane and chlorotrifluoromethane. Because VOCs have very long atmospheric lifetimes, the CFC concentration in the atmosphere increases with time. For trichlorofluoromethane and dichlorodifluoromethane the atmospheric lifetimes are in the order of 75 and 111 years (Godish, 1991).

Halogenated hydrocarbons do not correlate well with vehicle emissions, because motor vehicle emissions emit significantly higher quantities of hydrocarbons than halogenated hydrocarbons (Mohammed *et al.*, 2002).

2.5.3 Sources of VOCs

Hydrocarbons and their oxygenated derivatives are important pollutants because of their role in atmospheric photochemistry. They are emitted from a variety of sources.

Natural sources

Sources include emanations from plant and animal decomposition, emission of volatile oils from plant surfaces, biological decomposition and emission of volatile fossil fuel deposits (see Par. 2.2.1). USA emissions of natural HCs, including methane, have been estimated to be in excess of 7×10^7 tons per year (Godish, 1991).

Man-made (Anthropogenic) sources

Worldwide emissions of hydrocarbons are estimated at 9×10^7 tons per year (Godish, 1991). Globally man-made emissions represent only about 5% of the total HC emissions (Godish, 1991). According to Pankow *et al.* (2003) the concentrations of certain VOCs increase significantly with an increase in

urbanisation. VOCs that exhibit this phenomenon include chloroform, toluene, C_2, C_3 and C_4-benzenes and methyl tert-butyl ether (MTBE).

Industrial sources

Industries producing paint, chemical production processes, waste treatment and disposal and solvent usage are all possible sources of hydrocarbon emissions.

Vehicle emission sources

Hydrocarbon emissions from motor vehicles result from evaporation losses and incomplete combustion processes. Petroleum sources and to a lesser extent diesel sources are important sources of VOCs and tend to overwhelm the contribution of other industrial sources (EPA, 1998). Chang *et al.* (1999) measured 156 individual VOCs from vehicle exhaust emissions. According to Godish (1991) light-duty motor vehicles account for 75% of mobile sources in the USA.

Hydrocarbons emitted in the atmosphere are oxidised (combining with oxygen) to form a variety of oxygenated derivatives or oxy-hydrocarbons. Oxy-hydrocarbons in exhaust emissions include a wide variety of organic chemical species, such as ethers, ketones, aldehydes, alcohols, and acids. Formaldehyde and other aldehydes are the major by-products of combustion processes. Significant amounts of aldehydes occur in motor vehicle exhaust emissions. Aldehyde levels in the atmosphere may be elevated as a result of source emissions and photochemical reactions in the atmosphere (see Par. 2.4.1). Peak levels occur near the solar noon, indicating their significant dependence on atmospheric photochemistry (Godish, 1991). According to Winebrake *et al.* (2001) mobile sources are among the major contributors of benzene, 1,3-butadiene, acetaldehyde and formaldehyde.

Since fuels are distributed from the producer to the user, evaporative processes are also responsible for the emission of large amounts of aromatic hydrocarbons in the atmosphere. Van der Westhuizen *et al.* (2004) determined that South African vehicles exceeded the allowed fuel loss level

set by the EPA 10 to 50 times higher than vehicles equipped with pollution control devices. They calculated that 97 million litres of petrol were lost in South Africa due to evaporation during 2000. This is probably due to the fact that South Africa has no emission legislation for HC emissions from vehicles. Vehicles in South Africa are not equipped with evaporative emission control devices as found in the rest of the developed world. In South Africa fuel specifications have not tended to lower vapour pressure to reduce the evaporative potential of fuels (Van der Westhuizen *et al.*, 2004). Vehicles in South Africa are also considerably older than those found in other developed countries (Van der Westhuizen *et al.*, 2004).

Domestic coal and wood burning

The inefficient burning of coal may be an important source of VOCs. Some urban areas in South Africa are not electrified. Paraffin and wood are mainly used for cooking and heating in most informal settlements in the Western Cape (see Par. 2.8.2.2). In the Vaal Triangle, paraffin and coal is used for the same purposes especially during the winter (see Par. 2.9.4.3). The highly inefficient combustion of coal or biomass fuels and the fact that these emissions are released less than two metres above ground level within residential areas means the exposure of people to these emissions can be extremely high (Mage *et al.*, 1996).

Holzinger *et al.* (2001) found that biomass burning dominates the emission of hydrocarbons during the dry season in Venezuela and this leads to higher concentrations of benzene during the dry season, while the toluene levels were lower during the dry season.

Indoor sources of VOCs

Prior to 1970, the common belief was that outdoor sources (industrial and motor vehicles emissions) were the primary contributors of VOCs in indoor environments. Gas chromatography coupled with mass spectrometry (GC/MS), enabled people to measure trace amounts of VOCs in indoor environments (Gammage & Kaye, 1987). Fisher *et al.* (2000) determined

that benzene and TVOCs were almost 100% higher in homes nearer to high density traffic roads than homes further away from them.

Sources of indoor VOCs include building material, furnishing, dry-cleaned clothes, cigarettes, gasoline, cleaners, moth crystals, hot showers and printed materials. Indoor concentration of VOCs are often two or more orders of magnitude higher than the outdoor levels (Gammage & Kaye, 1987).

Marine environments and the formation of VOCs

The emissions from marine environments could be the predominant factor affecting ambient levels of certain halogenated hydrocarbons (see Par. 2.5.2). Marine algae form chloroform (Yung *et al.*, 1975) and its concentration increases near large bodies of salt water (Mohammed *et al.*, 2002). Over 90% of chloromethane in air is from natural sources, such as biogenic production by marine phytoplankton (ATSDR, 1995).

2.5.4 Gas phase tropospheric chemistry of VOCs in ambient air

As stated in Par. 2.5.1, VOCs can react with substances to form a wide variety of derivates, but the VOCs differ in reactivity and the products formed.

2.5.4.1 Reactions of VOCs

The gas phase oxidation of VOCs in the troposphere proceeds via a complex mechanism leading firstly to the production of a variety of first generation oxidised organic products (Atkinson, 1990; Jenkin *et al.*, 1996). The products of these mechanisms are either of the same carbon number as the parent VOC or have a lower carbon number if a fragmentation process has occurred. Those of the same carbon number as the parent VOC, are invariably less volatile than the parent compound, because they are of a higher molecular mass and contain one or more polar functional groups. According to Güsten, (1985) free radicals oxidize hydrocarbon molecules to form consecutive chains of photochemical reactions. These chain reactions can be classified as follows:

Chain initiation: The reaction of photons with free radicals as source are mainly the primary process. They include:

$$NO_2 + h\nu \rightarrow NO\cdot + O\cdot \quad (2.8)$$

$$HONO + h\nu \rightarrow HO\cdot + NO\cdot \quad (2.9)$$

$$HCHO + h\nu \rightarrow H\cdot + HCO\cdot \quad (2.10)$$

$$H_3CCHO + h\nu \rightarrow CH_3\cdot + CHO\cdot \quad (2.11)$$

$$O_3 + h\nu \rightarrow O[^1D] + O_2 \quad (2.12)$$

Chain propagation: These reactions produce no net gain or loss of radicals. They occur when some of the inorganic radicals produce organic radicals.

$$HO\cdot + RH \rightarrow \cdot R + H_2O \quad (2.13)$$

$$\cdot R + O_2 \rightarrow \cdot RO_2 \quad (2.14)$$

An attack by a $HO\cdot$ radical is the first step in the oxidation process of the various classes of hydrocarbons. Molecular oxygen contributes to the formation of peroxy radicals.

$$\cdot R + O_2 \rightarrow \cdot RO_2 \quad (2.15)$$

$$\cdot RO + O_2 \rightarrow HO_2\cdot + R'CHO \text{ (aldehyde or ketone)} \quad (2.16)$$

Chain branching: These reaction steps lead to a net increase in radical species for example:

$$O + \text{hydrocarbon} \rightarrow \text{products} + \text{radicals}$$

More than one radical is formed. In polluted air, a very small fraction of ground-state oxygen produced in the reaction

$$NO_2 + h\nu \rightarrow NO\cdot + O\cdot \quad (2.17)$$

does not form ozone,

$$O[^3P] + O_2 (+M) \rightarrow O_3 (+ M) (M = N_2 \text{ or } O_2), \quad (2.18)$$

but react with unsaturated hydrocarbons, in particular olefins

$$O[^3P] + R_1,R_2C{=}CR_3,R_4 \rightarrow [\text{adduct}] \rightarrow R_2,R_3,R_4\text{-}C^{\cdot} + R_1\text{-}C^{\cdot}{=}O \quad (2.19).$$

Depending on the chemical structure of R_1 - R_4, the fission of the olefin- $O[^3P]$-adduct may result in other radicals. When the oxidation of unsaturated hydrocarbons proceeds, the oxygen atoms may react with their oxidation products, e.g. aldehydes formed in the oxidation processes:

$$O[^3P] + RCHO \rightarrow [\text{adduct}] \rightarrow OH^{\cdot} + R\text{-}C^{\cdot}{=}O \quad (2.20)$$

In any event, the result of branching is the formation of two or more free radicals in a single process.

Chain termination: This is the removal of the free radicals from the highly reactive mixture by the formation of more stable end products (see Par. 2.5.4.2) such as aldehydes, ketones, PAN, nitric and nitrous acids (Güsten, 1985).

2.5.4.2 Products of gas phase oxidation of VOCs

The following oxidation products of VOCs have been identified:

Alkyl radicals

In 1990, Atkins determined that the initial reaction of organic compounds with $HO^{\cdot}$ and $NO_3^{\cdot}$ lead to the formation of alkyl radicals. Alkanes react with $HO^{\cdot}$ and $NO_3^{\cdot}$ by H-atom abstraction, while alkenes react with $HO^{\cdot}$ and $NO_3^{\cdot}$ by radical addition to the double bond. For aromatic hydrocarbons the reaction with the $HO^{\cdot}$ leads to the formation of benzyl and hydroxycyclohexadienyl and

methyl-substituted hydroxycyclohexadienyl radicals. (Toluene for instance, would form benzaldehyde.)

Peroxyacetyl nitrate (PAN)

Peroxyacetyl nitrate ($CH_3COO_2NO_2$) is the main compound of a family of nitrogenous compounds produced in polluted urban atmosphere by photochemical smog (Güsten, 1985) when a VOC radical combines with a NO_x-species.

Aldehydes and ketones

The major products of HC oxidation in urban smog are aldehydes and ketones. They form from most types of HCs either by reaction with HO· or with O_3. The formation of aldehydes by the reactions of alkenes with O_3 tends to occur later in the day as ozone concentrations increase. Reactions of HCs with HO· can occur throughout the day. In addition aldehydes and ketones are emitted to the atmosphere as combustion products and by chemical industries in the region. Typical aldehydes formed include formaldehyde (emission exceeding the concentration of the other aldehydes), acetaldehyde, propanal, n-butanal and benzaldehyde. Higher-molecular mass aldehydes are photo-oxidized to lower-molecular weight aldehydes (Güsten, 1985). Acetaldehyde and formaldehyde are formed during the incomplete combustion of HC-based fuels. In addition, they can form as a secondary pollutant in the atmosphere (Winebrake *et al.*, 2001).

Carbon monoxide (CO)

CO is typically found in smog (see Par. 2.4). Although 90% of CO is contributed by petroleum-driven vehicles (Elsom, 1996), VOCs are progressively oxidized to CO and carbon dioxide (CO_2) over periods of hours to weeks.

The rate of oxidation of VOCs initiated by these routes, is more rapid during the summertime due to higher solar intensity. The levels of HO· and O_3 are higher, and therefore secondary aerosol formation resulting from the oxidation

of VOCs contributes to the photochemical haze observed during summertime pollution episodes (Jenkin *et al.*, 1997).

Certain VOCs are more likely to contribute to aerosol formation by the virtue of their general high reactivity, and the types of oxidation products formed (Jenkin *et al.*, 1997).

2.5.5 Sinks of VOCs

The most important sink of HCs is photochemical reactions (see Par. 2.4.1), which convert HCs to CO_2 and H_2O or to soluble condensable products. Among the most common condensed products are dicarboxylic acids, a major component of photochemical aerosols. Secondary organic aerosols (SOA) are formed from organic gases consumed by photo-dissociation or reactions with $HO^{\cdot}$, O_3 or NO_3. According to Takekawa *et al.* (2003) higher SOA yields are found at lower temperatures. These SOAs are removed from the atmosphere by dry and wet deposition processes (Godish, 1991).

HCs remain in the atmosphere for long periods of time because most have a low photochemical reaction rate and either positively or weakly correlate with temperature (Mohammed *et al.*, 2002). The degradation of chlorinated hydrocarbons leads to the release of Cl-radicals (Fabian, 1985). These radicals can react rapidly with most organic compounds, but can also react with O_3 (Jenkin *et al.*, 1997).

Methyl chloride and methyl chloroform react with $HO^{\cdot}$ and are largely removed by tropospheric $HO^{\cdot}$-reactions (Fabian, 1986). Khalil and Rasmussen (1983) consider photochemical reactions as a possible source to remove chloroform from the atmosphere and they determined that at least 60% of the annual removal of chloroform is due to reactions with $HO^{\cdot}$.

2.5.6 Tropospheric lifetimes of VOCs and halogenated hydrocarbons

Table 2.4 gives an indication of the tropospheric lifetimes of selected VOCs due to photolysis and reactions with HO· and NO_3 radicals and ozone according to Calvert *et al.* (2002).

Table 2.2: Tropospheric lifetimes of selected VOCs due to photolysis and reactions with HO· and NO_3 radicals and O_3 (Calvert *et al.*, 2002)

Compound	HO·	NO_3	O_3	hν
Methane	~ 12 years	> 120 years	> 4 500 years	
Ethane	60 days	> 12 years	> 4 500 years	
Propane	13 days	> 2.5 years	> 4 500 years	
n-Butane	6.1 days	~ 2.5 years	> 4 500 years	
n-Octane	1.8 days	260 days	> 4 500 years	
Ethene	1.8 days	225 days	9.7 days	
Propene	7.0 hours	4.9 days	1.5 days	
Isopropene	1.8 hours	50 min	1.2 days	
α-Pinene	3.4 hours	5 min	1.0 days	
Acetylene	19 days	≥ 2.5 years	5.8 years	
Formaldehyde	1.6 days	77 days	> 4.5 years	
Acetaldehyde	1.0 day	17 days	> 4.5 years	4 hours
Acetone	68 days		> 4.5 years	15 days
Methyl ethyl ketone	13.4 days		> 4.5 years	
Methylglyoxal	10.8 hours		> 4.5 years	2 hours
Methanol	17 days	> 77 days		
Ethanol	47 days	> 51 days		
Methyl-t-buthylether	5.5 days			
Benzene	12.5 days	> 6 years	> 4.5 years	
Toluene	2.6 days	1.9 years	> 4.5 years	
m-Xylene	7.8 hr	200 days	> 4.5 years	
Biogenic VOCs				
Isoprene	1.8 hr	1.2 days	1.7 day	
d-Limonene	1.1 hr	1.9 hr	53 min	

Most of the commercially important chlorinated hydrocarbons have relatively long lifetimes in the atmosphere and are comparatively stable compounds. Dichloromethane and tetrachloroethene have shorter lifetimes, so that they decompose rapidly in the troposphere (Fabian, 1985). Methyl chloride, CFC-12, CFC-11, carbon tetrachloride and CFC-22 contain 88% of organically bounded chloride found in the atmosphere. The remaining 12% is held by the other halogenated hydrocarbons (Fabian, 1985).

Table 2.3: Tropospheric lifetimes of selected halogenated hydrocarbons

Halogenated VOC	Lifetime	Reference
Methyl chloride	2-3 years	Fabian *et al.*, 1985
Chloroform	> 6 months	Khalil & Rasmussen, 1983
	4 – 7.2 months	Fabian *et al.*, 1985
Methyl chloroform	5.7 – 10 years	Fabian *et al.*, 1985
Carbon tetrachloride	60 - 100 years	Fabian *et al.*, 1985
	Tens to hundreds of years	Mohammed *et al.*, 2002
Methyl bromide	1.7 years	Fabian *et al.*, 1985

2.5.7 Health effects of VOCs

VOCs include a wide range of substances with diverse health effects. Some VOCs are known as strong irritants, some affect the central nervous system and some are known animal carcinogens (Lippman, 1992). The concentrations of most VOCs in the atmosphere are far too low to be a potential health risk. Compounds that can have a potential health risk include: benzene, aldehydes, 1,3-butadiene, n-hexane and some chlorinated hydrocarbons (see Table 2.4). Benzene (see Par. 2.5.9) is a well-known carcinogen associated with leukaemia. Benzene is associated primarily with the production, distribution and marketing of gasoline.

Table 2.4: Summary of harmful VOCs (WHO, 1987)

VOC	Possible health effects on people
Acetonitrile	Carcinogen
Benzene	Carcinogen
Carbon disulfide	Degeneration of the brain tissue.
1,2-Dichloroethane	Headaches, dizziness, weakness, vomiting, unconsciousness. Death often follows.
Dichloromethane	Affects nervous system and elevate CO levels in blood. Carcinogen of animals. Evidence in humans is inadequate.
Formaldehyde	Irritation of eyes, nose and throat. Carcinogen of animals. Evidence in humans is inadequate.
Styrene	Irritation of mucous membranes and eyes. Weakness, dizziness.
Tetrachloroethylene	Mutagen.
Toluene	Fatigue, confusion, lack of coordination, impairment of reaction time and perceptual speed.
Trichloroethylene	Skin and eye irritation.
Vinyl chloride	Carcinogen

According to Table 2.4 some of these VOCs are not only toxic but are known carcinogens. Table 2.5 summarises the VOCs that are on the toxic air contaminants list (TACs) as carcinogenic compounds together with the unit cancer risk for each VOC.

Table 2.5: VOCs that appear on the toxic air contaminants list as carcinogenic compounds (Woodruff, 1990)

VOC	Unit cancer risk $(\mu g.m^{-3})^{-1}$	Unit cancer risk $(ppb)^{-1}$
1,3-Butadiene	1.7×10^{-4}	3.7×10^{-4}
Ethylene oxide	8.8×10^{-5}	1.6×10^{-4}
Vinyl chloride	7.8×10^{-5}	2.0×10^{-4}
Ethylene dibromide	7.1×10^{-4}	5.5×10^{-4}
Carbon tetrachloride	4.2×10^{-5}	2.6×10^{-4}
Benzene	2.9×10^{-5}	9.3×10^{-5}
Ethylene dichloride	2.2×10^{-5}	8.9×10^{-5}
Perchloroethylene*	8.0×10^{-6}	5.4×10^{-5}
*Risk is under review at Office of Environmental Health Hazard Assessment		
Formaldehyde	6.0×10^{-6}	7.0×10^{-6}
Chloroform	5.3×10^{-6}	2.6×10^{-5}
Trichloroethylene	2.0×10^{-6}	1.1×10^{-5}
Methyl chloride	1.0×10^{-6}	3.5×10^{-6}

(*Unit cancer risk is the increased risk of cancer if exposed to a VOC)

2.5.8 VOC levels worldwide

The concentration levels of VOCs differ from place to place, due to different factors. For instance the concentration of ethanol in São Paulo is well above the levels available for US cities due to the high percentage use of alcohol-based fuels (Colón *et al.*, 2001). Table 2.6 gives a comparison of different VOC concentrations measured worldwide.

Table 2.6: Summary of VOC concentrations (ppb) in the ambient air in cities from around the globe

	Osaka City-	Mexico City	*Sydney Harbour	São Paulo		*Baltimore	Athens
Reference	Tsujino & Kuwata, 1993	Zielinska *et al.*, 2001	Duffy & Nelson, 1996	Colón *et al.*, 2001		Vukovich, 2000	Moschonas & Glavas, 1996
				Canister	Tube		
Ethane			44.1			6.9	
Ethylene (ethane)	23.3		150.3			3.69	
Methanol				10.6	1.9		
Ethanol				141.0	90.0		
Ethane + acetylene	24.3						
Propane	8.9		67.4			5.31	
Propylene	6.1					1.87	3.9
Propene			83.2			3.79	
Methylene chloride				0.5	0.6		
Ethyne (acetylene)			173.5			2.49	
i-Butane	5.1		31.3			3.49	1.1
i-Butene + 1-butene	3.6					0.41	0.9
n-Butane	11.0		45.8	6.9		1.84	2.1
Trans-2-butene	1.1					0.52	0.4
1-Butene			12.2				
I-Butene (2-methylpropene)			20.0			0.41	
Cis-2-Butene	0.9		6.6			0.32	
3-Methyl-1-butene	0.2						
i-Pentane	10.6					8.4	11.7
1-Pentene	0.4						0.4
2-Methyl-1-butene	0.7						0.4
n-Pentane	7.7			7.2		3.28	4.2
1,3-Pentadiene							0.2
1,1-Dimethyl-cyclopropane							0.7
Trans-2-pentene	0.7						
Cis-2-Pentene	0.3					0.33	
2-Methyl-2-butene	0.5						1.4
2,2-Dimethylbutane							0.8
Cyclopentane	0.4		2.3			0.46	0.2
1-Ethyl-1-methyl-cyclopropane							0.1
2,3-Dimethylbutane	0.8					0.92	0.6
2-Methylpentane	3.9		21.0			2.35	3.33
3-Methylpentane	3.1		13.1			1.85	2.3
1-Hexene							0.2
n-Hexane	5.5		12.6	2.0		2.30	1.6
2-Methyl-2-pentane							0.3
Cis/Trans-3-methyl-2-pentene							0.2
Trans-3-hexene							0.2
Cis-3-Methyl-2-pentene							0.3
Methylcyclopentane	1.7					0.92	0.7
2,4-Dimethylpentane	0.3		2.5			0.56	
Freon-12		0.45					
Vinyl chloride		0.01					
Freon-11		0.23					
Freon-113		0.08					
Chloroform		0.01					
Benzene	5.1		45.4	2.6	2.5	2.27	5.0
Cyclohexane	0.8					0.38	0.3

Table 2.6: *(Continued)*

	Osaka City-	Mexico City	*Sydney Harbour	São Paulo		*Baltimore	Athens
Reference	Tsujino & Kuwata, 1993	Zielinska *et al.*, 2001	Duffy & Nelson, 1996	Colón *et al.*, 2001		Vukovich, 2000	Moschonas & Glavas, 1996
				Canister	Tube		
1,1,2-Trichloroethane		0.00		0.2	0.2		
2-Methylhexane	1.5					0.96	1.8
2,3-Dimethylpentane	0.6					0.84	0.3
3-Methylhexane	1.7					1.45	3.5
1,2-Dichloroethane		0.01					
n-Heptane	2.0		4.6	1.2		1.35	2.4
Methylcyclohexane	0.7					0.92	1.8
Toluene	31.1		68.6	9.0	15.1	7.09	14.3
2-Methylheptane	0.6					0.37	2.3
4-Methylheptane	0.3						
3-Methylheptane	0.7					0.42	0.8
n-Octane	0.6		2.0	1.0			0.6
Ethylbenzene	3.8		8.6	2.0	3.5	1.24	2.7
p-Xylene	2.3						
m-Xylene	5.4		31.3	4.6	7.8	3.72	12.1
Styrene				0.7	1.6	0.53	
o-Xylene	2.8		11.7		2.4	1.39	3.7
n-Nonane	0.7			0.5		0.57	1.7
2,3,7-Trimethyl-octane							0.9
Isopropylbenzene	0.1					0.2	1.1
m-Ethyltoluene	2.0		7.2			1.11	
p-Ethyltoluene	1.1					0.41	
o-Ethyltoluene	0.7		2.0				
1,3,5-Trimethylbenzene	1.2		2.2		0.7	0.67	9.2
1,2,4-Trimethylbenzene	2.9		6.3		2.3	5.35	3.9
n-Decane	0.9			0.3		0.91	
1-Ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene							9.5
3-Methyl-nonane							1.0
1-Ethyl-2-methylbenzene							2.2
1,2,3-Trimethylbenzene	0.6					1.17	3.3
1,4-Dichlorobenzene		0.04		0.0	0.0		
1,2-Dichlorobenzene		0.01					
n-Undecane	0.4			0.2		0.86	3.1
1-Methyl-3-propylbenzene							1.3
2-Diethylbenzene							2.3
1-Methyl-2-propylbenzene							0.4
2-Ethyl-1,4-dimethylbenzene							1.8

(*Where more than one result were available for a site, the average concentration for a compound was calculated. Measurements in 1996 were before serious efforts to reduce VOCs)

2.5.9 Standards/guidelines for benzene

Due to the adverse health effects of the air pollutants mentioned in Par. 2.5.7, certain ambient air quality standards/guidelines have been set to protect the general public against these adverse effects (EPA, 1998). The United States Environmental Protection Agency (US-EPA) and World Heath Organisation (WHO) are the two primary bodies that publish air quality standards/guidelines for VOCs. Guidelines are the concentrations of pollutants that are recommended not to be exceeded in the interest of public health, while standard pollutant levels can, by law, only be exceeded a set number of times over a given period of time.

It is assumed that future air quality legislation in South Africa will require the measurement and monitoring of ambient benzene levels. Benzene is a carcinogen (see Table 2.4 and Table 2.5); exposure to it is interpreted in terms of chronic exposure. It is accepted that benzene is a genotoxic carcinogen and that therefore no absolutely safe exposure level can be defined. Absorption of benzene occurs through inhalation, ingestion and through the skin. Ingested benzene is assumed to be fully absorbed so that the concentration of benzene in the blood is in direct equilibrium with the benzene in the expired air. The half-life of benzene in humans is in the order of 1 to 2 days (Lippman, 1992).

Sources of benzene in urban air

Anthropogenic sources produce 90% of the benzene in the atmosphere (Commission of European Communities, 1998). Emissions of benzene to the atmosphere are mainly due to combustion processes for energy production (including motor vehicles) and domestic heating. The worldwide industrial production of benzene is in the order of 15 million tons per year. For the period 1991 to 1993 the European production of benzene, excluding benzene in petrol was 5.5 million tons (Commission of European Communities, 1998). Benzene is present in petroleum products such as vehicle fuels, crude oil, and is a significant component of gasoline. Evaporation of ambient gasoline

during refuelling and vehicle emissions remains a substantial source of community exposure to benzene.

Sinks of benzene

Benzene is removed slowly from the atmosphere by reactions with $HO^{\cdot}$, NO_3 or O_3. The dispersion of benzene is dependent on wind speed and wind direction, solar radiation, and temperature (Commission of European Communities, 1998). The lifetime of benzene with respect to $HO^{\cdot}$ attack is calculated between 9 days (Finlayson-Pitts & Pitts, 1986), 12.5 days (Calvert *et al.*, 2002) and 12 days (Seinfeld & Pandis, 1998). If NO_3 is the only oxidant of benzene the lifetime of benzene is calculated to be $\geq$ 235 days (Finlayson-Pitts & Pitts, 1986) and 6 years (Calvert *et al.*, 2002) and if O_3 is the oxidant, the lifetime of benzene is calculated to be $\geq$ 470 days (Finlayson-Pitts & Pitts, 1986) and 4.5 years (Calvert *et al.*, 2002).

Standards/guidelines in other countries

The annual standard for benzene in the Netherlands and Germany is 3 ppb; the United Kingdom (UK) government suggested a running annual standard of 5 ppb (Elsom, 1996). The USA observed exposure is 4.7 ppb and the WHO observed exposure is 6.4 ppb benzene. Benzene levels below 3.13 ppb, the average value for long-term exposure, correspond to typical urban and suburban concentrations and would be acceptable in the general residential context. The WHO has listed average background levels of benzene between 1.5 – 6.4 ppb (WHO, 1987). The European Community (EC) has recently promulgated a limit value for annual average benzene concentrations of 5 $\mu g.m^{-3}$ (1.6 ppb), to be met by 1 January 2010. In the interim, the limit (including a margin of tolerance) is set at 10 $\mu g.m^{-3}$ (3.2 ppb).

The data in Table 2.7 give a comparison of different benzene levels in different cities around the globe.

Table 2.7: Comparison of mean benzene concentrations (ppb) at different cities around the globe

City	Concentration (ppb)	Sampling time	Reference
Athens (Greece)	5.0	June 1993, May, July 1994	Moschonas & Glavas, 1996
Osaka City Centre	5.1		Tsujino & Kuwata, 1993
Birmingham	1.02	1996	Derwent *et al.*, 2000
Cardiff	1.21	1996	Derwent *et al.*, 2000
Leeds	1.04	1996	Derwent *et al.*, 2000
Edinburgh	0.7	1996	Derwent *et al.*, 2000
Harwell	0.38	1996	Derwent *et al.*, 2000
Bristol	1.22	1996	Derwent *et al.*, 2000
London Eltham	1.06	1996	Derwent *et al.*, 2000
Middlesborough	1.01	1996	Derwent *et al.*, 2000
Belfast	0.92	1996	Derwent *et al.*, 2000
Southampton	1.92	1996	Derwent *et al.*, 2000
UC London	1.87	1996	Derwent *et al.*, 2000
Liverpool	0.89	1996	Derwent *et al.*, 2000
Baltimore- (mean weekday time)	2.27	Aug 1994 Jul, Aug 1996 Jun, Jul, Aug 1997	Vukovich, 2000.
São Paulo	2.6 (canister)	Nov 1998	Colón *et al.*, 2001
	2.5 (tube)	Nov 1998	Colón *et al.*, 2001
Mexico city	1.7		Bravo *et al.*, 2002
Toulouse	0.69	Spring and summer 1999	Simon *et al.*, 2004
Caracas (Venezuela)	4.45	1995-1995	Gee & Sollars, 1998
Quito (Ecuador)	1.57		Gee & Sollars, 1998
Santiago (Chile)	4.64		Gee & Sollars, 1998
São Paulo (Brazil)	5.23		Gee & Sollars, 1998
Bangkok (Thailand)	5.70		Gee & Sollars, 1998
Manila (Philippines)	3.95		Gee & Sollars, 1998
Copenhagen	6.2	Feb 1994 – March 1995	Hansen & Palmgren, 1996
Copenhagen	2.19	Aug 1997 - June 1999	Palmgren *et al.*, 2001
Izmir, Turkey	14.55	Aug - Sep 1998	Muezzinoglu *et al.*, 2001
Rome	11.13	1994	Brocco *et al.*, 1997

Future legislation for the annual average benzene level in South Africa

It is assumed that future air quality legislation in South Africa, will propose an annual average concentration of 1.6 ppb benzene.

2.6 SAMPLING TECHNIQUES FOR VOCs

The sampling and analysis of organic compounds in air remains a challenge and the sampling of air is probably one of the most difficult activities to undertake. Due to the fact that air is compressible, a volume of air sampled

must include the sample pressure, temperature and volume (Harrington, 2003). Various techniques are used to measure VOCs in ambient air. Off-line methods of field sampling include the following:

1. Sampling bags (Tedlar bags),
2. Evacuated stainless steel canisters (see Par. 2.6.2) that can be used as passive samplers or with pumps to overpressure
3. Tubes consists of solid absorbents like Tenax® and/or activated carbon (see Par. 2.6.3)
4. Filter/foam combinations
5. Passive sampling (e.g. disks, tubes and canisters)

Sample types can differ in relative humidity and concentration of VOCs. The two basic types of air samples consist of:

1. *Source samples*: Samples taken at the source, for instance, at a landfill, a combustion stack or an incinerator.
2. *Ambient samples*: Samples are taken adjacent to the source of VOCs, in areas where humans are affected. The VOCs are usually diluted and the concentrations of ambient samples are generally lower than those of the source samples (Harrington, 2003).

2.6.1 Recommended methods for the analysis of VOCs

The US-EPA describes validated methods for the sampling and analysis of compounds in ambient air. The selected (see Table 2.8) and preferred methods depend on the sampling techniques (canisters, tubes or Tedlar bags), the analytes of interest and analytical testing equipment.

Table 2.8: List of the sampling techniques with the recommended analysing methods for VOCs (Harrington, 2003)

Sampling technique	Analysing method
Tenax tubes	TO-1, CLP (tube method)
Carbon molecular sieve	TO-2
Multi-bed tubes	TO-17
SUMMA® Canister	TO-14, CLP, TO-15 (canister method)
VOST tube	5040 / 5041
Tedlar bags	TO-14 (modified by user)

Hazardous volatile organics can be sampled either with adsorbent tubes (TO-17) or with passivated stainless steel canisters (TO-14A & TO-15). Analysis of these samples can be achieved by pre-concentration and thermal desorption followed by GC/MS techniques. These methods are able to identify and quantify more than 40 hazardous volatile organic compounds at sub part per billion concentration levels in ambient air (Jordaan *et al.*, 2002).

2.6.2 Air sampling with canisters

The EPA TO-14 (EPA, 1997) method is also known as "determination of volatile organic compounds in ambient air using TO polished canisters sampling and gas chromatographic analysis" in the EPA *Compendium of methods for the determination of toxic organic compounds in ambient air.* The method involves the sampling of VOCs in evacuated stainless steel canisters where samples can be stored for up to 30 days.

SUMMA canisters are specially treated stainless steel containers (see Fig. 2.2) used for collecting VOCs in air. The SUMMA passivation process involves special polishing and deactivating procedures. The canister interior is specially prepared using an electro-polishing or similar process to clean the surface and reduce the number of active adsorption sites. The result is a coating of the canister's interior with chrome-nickel oxide (Harrington, 2003).

Figure 2.2: A TO canister with inlet and flow regulator (Photo: Jordaan, 2003)

Before sampling is carried out, a canister must be cleaned properly and evacuated using a proper vacuum pump. The final pressure in the evacuated canister must be well below atmospheric pressure (Harrington, 2003).

Ambient air samples are taken either actively or passively.

1. *Active sampling*: Samples are pumped into an evacuated canister. The flow rates of the air samples pumped into a canister are controlled by the pumping system so that the volume of air sampled is determined by the pumping rate and time. It must however, be taken into account that the sampling pump can emit HCs or organic solvents that can contaminate the sample.
2. *Passive sampling*: When a valve of an evacuated canister is opened, air flows into the canister. A calibrated mass flow controller can control the air flow rate into a canister, so that the sample can be taken for a

specified time period (e.g. 8 or 12 hours). With passive sampling, canisters are not allowed to fill up to ambient pressure. At ambient pressure any change in pressure will cause air to flow into or out of the canister and a representative sample will not be taken (Harrington, 2003).

At the end of the sampling period, the canister is sealed and transported to a laboratory for determination of target VOCs (McClenny *et al.*, 1991). Preconcentration of VOCs, is followed by chromatographic separation of individual VOCs on a high-resolution, fused-silica capillary column and subsequent analysis by mass spectrometry (McClenny *et al.*, 1991).

A passivated canister is an ideal container for volatile and non-polar species (Camel & Caude, 1995) and it provides an accurate representation of the air under investigation. According to Brymer *et al.* (1996) canisters are suitable for collection and storage of samples in the part per billion (ppb) range including alkanes, alkenes, alkynes, aldehydes, ketones, alcohols, aromatic and sulphur-containing compounds. Canisters have undergone extensive evaluation and are now accepted as the most appropriate method for the sampling of hazardous volatile, organic air compounds in ambient air, as specified in the US-EPA method TO-14A (Jordaan *et al.*, 2002).

The effect of water on the canister

If the water vapour pressure inside the canister exceeds the saturation vapour pressure during sampling, the water vapour is condensed on the canister wall. When a sample is subsequently extracted for analysis, the first samples will have a lower humidity that the original samples. This is due to the mixing ratio of water vapour and air, which has been reduced by the amount of water on the wall of the canister (McClenny *et al.*, 1999).

Humidification of the air stream that goes into the canister is necessary to prevent non-polar VOC losses. Water vapour is beneficial in maintaining sample integrity by occupying active adsorption sites on the canister surface. Since "real" air samples generally contain water molecules orders of

magnitude (6 to 7) higher than the analytes in the ppb range, this mechanism is rather effective (McClenny *et al.*, 1991).

Storage of canisters

Zielinska *et al.* (1996) found that the losses due to storage of canisters are not constant. In one canister they found that the concentration of VOCs decreased during the first three months and then remained relatively constant, while in another canister the concentration dropped after four months but the total loss was smaller than that of the first canister. For C_5 - C_9 hydrocarbons the general drop was 20%. They also reported that the behaviour of higher molecular mass hydrocarbons or more polar compounds is affected by the history of the canisters, their cleanliness, age and quality (Zielinska *et al.*, 1996).

Effect of Nafion® dryer

Zielinska *et al.* (1996) found that the Nafion® dryer (used to remove moisture prior to cryogenic concentration of canister samples) was found to lower the measured concentrations of alkanes, olefins and aromatics collected with canisters and to introduce contaminants into the system. It also lowered the nonmethane hydrocarbons (NMHCs) with 10 - 20%.

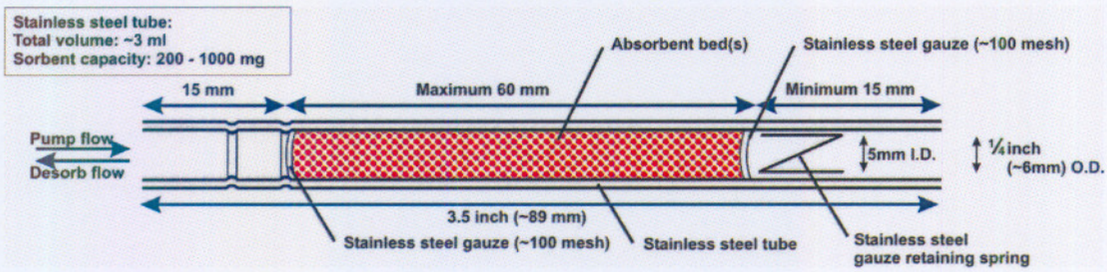
2.6.3 Sampling with adsorbent tubes

The US-EPA Method TO-17 (1997) prescribes the use of adsorbent tubes to adsorb specific VOC species in air samples onto selected adsorbent materials. Trapping air directly onto portable adsorbent tubes avoids the high cost disadvantages of canisters.

The air is drawn through a tube by a pump and the VOCs are adsorbed on the adsorbent. Tubes will not trap all components passing through the tube. Adsorbents are optimised to retain VOCs and not all the components (like N_2, CO_2, O_2, Ar, H_2O) of air. If too much air is passed through the tube, some of the organic components can be passed through the adsorbent. This happens if the concentration of the VOC is to high and the adsorption of the packing

material is exceeded. If these "breakthroughs" occur, analytes are lost (Harrington, 2003). TO17 give safe sampling volumes.

Figure 2.3: The construction of a stainless steel tube used for sampling air samples (adapted from Woolfenden, 1997)



Tubes also referred to as cartridges or traps, are filled with an absorbent material such as Tenax®, Tenax/charcoal or a carbon molecular sieve. Single-bed sorbent tubes are used in routine analysis, while multi-bed tubes are only recommended for monitoring unknown atmospheres or wide volatility range sets of target analytes. If target analytes cover a wide volatility range, tubes are packed with a series of discrete beds of sorbents of increasing strength. Alternatively, a train of single sorbent tubes may be coupled together in series. Taking volatility range, sorbent stability and artefact formation into consideration, a selection of four sorbents will cover most of the VOCs present in air monitoring applications;

1. Tenax-graphitised (GR) form (a weak hydrophobic adsorbent)
2. Carbotrap of Carbopack B (a medium strength hydrophobic adsorbent)
3. Spherocarb (a strong less hydrophobic adsorbent)
4. Carboxen 1 000 of Carbosieve III (a strong less hydrophobic adsorbent)

Table 2.9: Guidelines for sorbent selection (EPA, 1997)

Sample tube sorbent	Volatility range	Examples of VOCs
Carbopack C / Carbotrap C	n-C_8 to n-C_{20}	Alkyl benzene and aliphatic compounds.
Tenax TA /Tenax GR	n-C_7 to n-C_{30}	Aromatics except benzene, Non-polar components, vapor phase PAHs.
Carbotrap / Carbopack B	n-C_5 to n-C_{14}	Wide range of VOCs inc., ketones, aldehydes and all non-polar compounds.
Chromosorb 102 / 106		Suits a wide range of VOCs: oxygenated compounds. Halogenated hydrocarbons less volatile than methylene chloride.
Porapack Q / N	n-C_5 to n-C_{12}	Suits a wide range of VOCs: oxygenated compounds. Porapack N specifically used for nitriles, acrylonitrile.
Spherocarb*	n-C_3 to n-C_8	Very volatile VOCs, volatile polar VOCs.
Carbosieve SIII* / Carboxen 1000*		Ultra volatile compounds: C_3 and C_4 hydrocarbons, volatile haloforms and freons
Molecular sieve**		1,3-butadiene and nitrous oxide.
Charcoal*		Rarely used for thermal desorption due to metal degradation.

* Sampling volumes must be reduced at high relative humidity. Sorbent retains water.

** Do not use in high relative humidity. Hydrophilic sorbents.

Selecting the correct adsorbent material (see Table 2.9) for a particular application is important in order to eliminate:

- breakthrough during sampling;
- formation of artefacts;
- analyte losses during thermal desorption.

The most suitable adsorbent material for a particular analyte will give a retention volume for that compound that is more than 100 $dm^3.g^{-1}$ adsorbent. The correct selection of adsorbent material, leads to the use of a relatively small quantity of adsorbent (200 - 500 mg), which can be thermally desorbed efficiently. This also decreases the possibility of artefact interference and improves quantitative recovery of analytes.

Treatment of tube-samplers

Before tubes are sent in the field for sampling, they must be conditioned to remove any VOCs, the ends of the tubes must be capped securely, and packed in proper containers, to prevent any contamination (Harrington, 2003).

Flow rate of tube-samplers

Roche *et al.* (1999) studied benzene take-up rates of Perkin-Elmer diffusion samplers with Tenax TA as adsorbent. They reported that uptake rates of benzene might be substantially higher during the sampling due to diffusion, especially at low exposure doses. Pump flow rates should therefore not fall below 5 $cm^3.min^{-1}$ in order to minimise errors due to ingress of VOCs via diffusion (Woolfenden, 1997). Natural diffusion of VOCs occurs at a rate equivalent to a flow of approximately 3 - 5 $cm^3.min^{-1}$. If a low pump flow rate is used, ingress by diffusion will result in significant positive errors.

Once a tube sample has been taken, it is placed in a clean airtight container and shipped to the laboratory for analysis. Alternately, the ends of the tube can be capped with airtight fittings, and the capped tube can be sent for analysis (Harrington, 2003).

Storage of tubes after sampling but before analysis

Zielinska *et al.* (1996) determined that the initial drop in Tenax values is probably less significant than the drop in canisters. Tubes can be stored for longer times than canisters without changes in VOCs concentrations.

Analysing tube samples

The tube is thermally desorbed into a GC/MS system and the VOC concentrations are determined. The low ambient VOC concentrations retained on adsorbent tubes necessitate the need to pre-concentrate the air sample before introduction to the GC/MS analytical system. The pre-concentration takes the form of a cold trap or a capillary cryo-focusing device to concentrate the VOCs contained in a specific volume of air. The tube undergo a two-stage desorbing from the tube to a secondary trap (where the temperature can increase quicker) so that the VOC concentration would

typically be to a final sampling volume of 2 000 cm^3. Thermal desorption is then used to transfer the concentrated VOCs from the cold trap to the gas chromatograph for separation (Jordaan *et al.*, 2002).

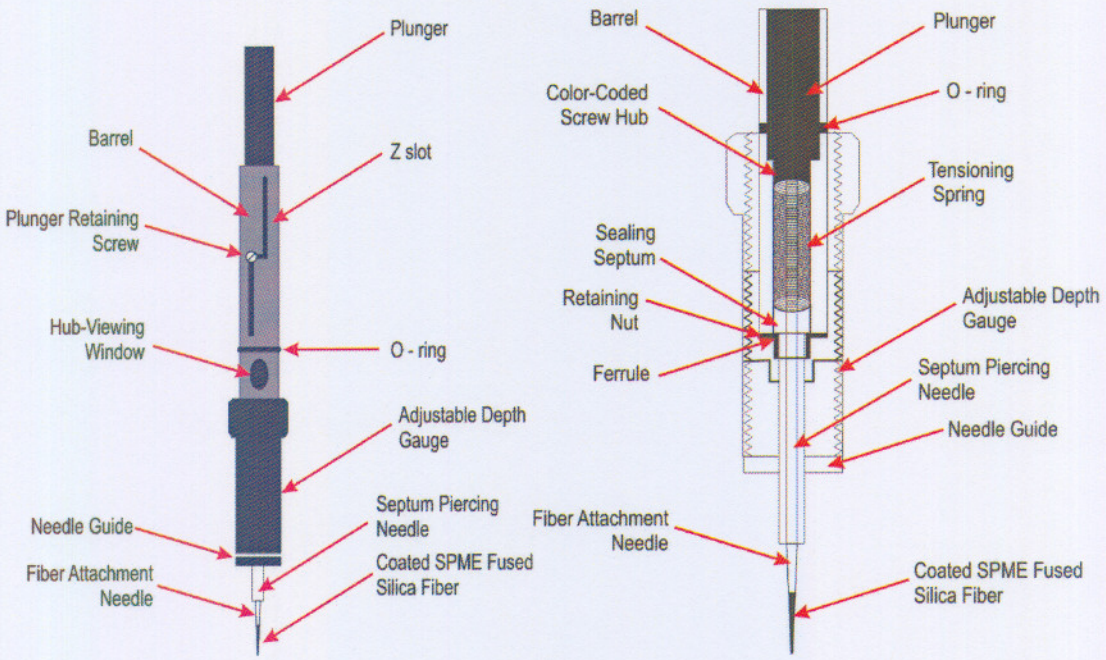
Effect of humidity on tubes

According to the EPA (1997) Carbotrap™ tubes are relatively unaffected by humidity. Charcoal exhibits some water retention and if the humidity is high (>90%) sampling volumes must be reduced. Zeolite molecular sieves are very hydrophilic and can only be used in a high humidity atmosphere if they are fitted with silicone caps. It is also important that tubes are not kept at temperatures lower than ambient temperature at the start of sampling, or condensation will retain water on the tube.

2.6.4 Solid phase micro-extraction (SPME)

Solid phase micro-extraction (SPME) is a simple alternative to the techniques mentioned above (see Par. 2.6.1 – 2.6.3). SPME is fast, inexpensive and can be automated easily. This technique is based on chemically modified fused-silica fibres. Optical fibres are used because they are inexpensive and are made of chemically inert fused silica, the same material that is used to make capillary GC (gas chromatographic) columns. They have a small diameter that allows convenient introduction into chromatographic injectors. Fibres coated with polymers such as poly(dimethylsiloxane) of various thicknesses are available commercially and can be used directly for extractions (Louch *et al.*, 1992).

Figure 2.4: Diagram of a SPME-holder to illustrate the construction of the manual fibre-holder and a sectional view when the fibre is exposed to air (adapted from Sulpelco, 1998)



The fibre is supported in a syringe to allow it to be handled easily and to protect the fibre during penetration of the GC septum. The SPME process consists of a few simple steps.

1. The fibre, with immobilised organic film, is exposed to the air sample (Peñalver *et al.*, 1999). Equilibrium is established between the fibre and the sample when the organic components are extracted from the sample into the stationary phase.
2. The fibre is then inserted directly into a conventional gas chromatographic injection port.
3. The organic compounds are thermally desorbed and analysed. A linear relationship is expected between the amount absorbed by the fibre and concentration in solution.
4. Calibration of SPME can cause a problem.

Table 2.10: Advantages and disadvantages of SPME (Namieśnik *et al.*, 2000)

Advantages	**Disadvantages**
No need for GC modifications.	The fibre is very fragile.
Compatibility for different GC-injection ports: split less, on-column (if equipped with independent heating system), programmed temperature vaporiser.	A small sample and/or if the partition coefficient is high, the sample can be analysed only once.
Automated sampling and sample injections are available.	High molecular mass compounds cannot be analysed on a GC.
Relative good precision and wide linear range even for complex matrixes.	Difficulty of selecting fibre coating to match the polarity of the analytes.
Eliminating sample clean-up and sample preparation.	Variation of parameters can affect the precision.
Gas, liquid and solid (head space sampling) applications.	
Short sampling time.	
Applicable for a wide spectrum of analytes in different matrixes.	
Gas, liquid and solid (head space sampling) applications.	
Easy field sampling.	

Increasing the amount of analyte absorbed on the fibres

The principle of "like dissolves likes" can be applied for SPME fibre coatings, so the choice of the most suitable fibre is very important. The selectivity of the coating for the analyte can be improved by modifying the chemical structure of the polymer. (If polar liquids are coated onto the fibre, more polar compounds can be analysed at low concentrations.) Table 2.11 gives a summary of the different coatings that are available for SPME GC-applications.

Table 2.11: Summary of the different fibre coatings for VOC-determination commercially available for SPME GC-applications (Sulpelco, 1996)

Applications	Abbreviate	Fibre coating	Thickness of coat (µm)	Phase	Maximum Temperature (° C)
BTEX, PAHs, VOCs, Non-polar organic compounds	PDMS	Poly(dimethyl siloxane)	100	Non-bonded	280
			30	Non-bonded	280
			7	Bonded	340
Low molecular weight VOCs and HCs	Carboxen-PDMS	Carboxen-(polydimethyl siloxane)	75	Partially cross-linked	320
Aromatic HCs, small VOCs, air analysis, PAHs	PDMS-DVB	Poly(dimethyl siloxane divinyl) benzene	65	Partially cross-linked	270
Polar organic compounds, triazines, phenols	PA	Polyacrylate	85		320
Polar organic compounds such as alcohols, PAHs	CW-DVB	Carbowax-divinyl benzene	65		265

Absorption time

The amount absorbed by the stationary phase is primarily affected by three factors:

1. the distribution constant,
2. the volume of the stationary phase,
3. whether the solution is stirred or not (Arthur & Pawliszyn, 1990).

Eq. 2.21 describes this relationship mathematically,

$$n_s = KV_sC_{aq} \qquad (2.21)$$

where the number of moles of analyte absorbed into the stationary phase, n_s, is proportional to the distribution constant, K, the volume of the stationary phase, V_s, and the concentration of the water, C_{aq}.

Detection limits

Llompart *et al.* (1998) determined that the detection limits were in the lower ppb level.

Canister-based sampling of air samples with SPME

Chai and Pawliszyn (1995) inserted SPME-fibres into TO-treated stainless steel canisters under atmospheric pressure and sampled from the canisters. The sampling area was the narrow space between the valve and a septum placed on the top cap of the canister. Because the valve provided only a very small hole to the canister outlet, a period of at least 1 hour was required for equilibrium before sampling with SPME. Chai and Pawliszyn (1995) also reported that equilibrium time could be decreased if either a pump was used to flush the system or, preferably, if the inlet was better designed.

Alternatively, Martos and Pawliszyn, (1997) focussed on controlled static sampling conditions in gas sampling bulbs and stainless steel canisters. Under static conditions, the analytes were absorbed onto the SPME, eventually reaching equilibrium. The time to reach equilibrium depends on the kinetics of the overall process of the analyte uptake of the fibre, which is based in part on the rate of the analyte diffusion in the air and the distribution coefficient of the analyte between the air and SPME. The ideal air system for SPME is when a constant flow rate of gas mixture containing an unchanging concentration of the analytes of interest passes over the SPME sampling device. In static sampling, the system virtually eliminates the wall effect of the sampling vessel and presents a continual concentration of analytes to the SPME.

Stability of SPME in the storage of air samples

Chai and Pawliszyn (1995) found that the analytes in air samples on the fibre were relatively stable when a sample fibre was withdrawn into the syringe needle with no plug on the needle tip for a time span of 2 minutes between sampling and desorbing the analytes. Longer storage time gave a significant concentration drop for all target compounds, especially for highly volatile compounds. Benzene and toluene can be stored up to 2 days if the fibre is kept on dry ice (± - 70 °C).

The combined use of SPME and passivated containers appears to be a successful method when a longer storage time (up to two weeks) is required. Further research is required to find a better solution to the problem of long-term storage for less volatile compounds. Less volatile analytes will remain stable in the coating of the canister for several days (Chai & Pawliszyn, 1995).

Temperature dependents

The effect of temperature on the gaseous sampling is complex. It appears that the temperature can cause the amount of analytes in an air sample absorbed on the SPME-coating to fluctuate significantly. The amount of analytes absorbed by the coating increases approximately 20% on average when the environmental temperature drops by 10 °C (Chai & Pawliszyn, 1995). The temperature effect occurs because the partition coefficient between the fibre coating and gaseous phase is temperature dependent (Arthur *et al.*, 1992). Temperature could also affect the rate of diffusion through the gas. At lower temperatures a slower diffusion rate would increase equilibration times and could cause an apparently lower concentration value as the equilibrium value would not have been reached within the normal sampling time (Chai & Pawliszyn, 1995).

The effect of temperature change on the distribution constant can be conveniently predicted since log K_f is linearly related to T^{-1} and the heat of vaporization of the pure solute, ΔH^V:

$$\log_{10} K_f = \frac{\Delta H^V}{2.303\,RT} + \left[\log_{10}\left(\frac{RT}{\gamma i p^*}\right) - \frac{\Delta H^V}{2.303\,RT^*}\right] \quad (2.22)$$

where p^* is the analyte vapour pressure at a known temperature T^* for a pure solute and γ_i is the activity coefficient of the solute in the coating. K_f can be calculated for given extraction conditions by measuring the temperature of the sample and knowing the heat of vaporization for the target compound (Pawliszyn, 1997).

Humidity

The relative humidity has a significant influence on the accuracy of SPME analyses because the analyte molecules can associate with the water present in the gas phase, consequently the amount of analyte molecules absorbed on the fibre is decreased (Chai & Pawliszyn, 1995). A relative humidity of 75% can reduce the amount of VOC extracted at room temperature with SPME by 10% (Chai & Pawliszyn, 1995).

Gaseous samples with an unknown humidity should be analysed using internal standards. If the humidity is known, an external standard should be used with the same humidity level or the response should be calibrated (Chai & Pawliszyn, 1995).

SPME and real air samples

Analysis of BTEX-compounds in ambient air using automated SPME has shown to be fast and efficient (Thomas *et al.*, 1996). Llompart *et al.* (1998) could detect BTEX, propylbenzene, butylbenzene and naphthalene and lighter PAHs with a 100 µm PDMS SPME fibre.

2.6.5 Comparison of sampling techniques

Table 2.12: Comparison of the advantages and disadvantages of canisters and tubes

Sampling technique	Advantages	Disadvantages
Canisters	Suitable for a broad range of VOCs.	Adsorption or decomposition of compounds.
	Good quality assurance and quality control.	Complex analysing apparatus needed.
	Applicable for non-polar compounds.	Time-consuming clean-up and cleaning procedures.
	Multiple analyses of the sample can be performed per canister.	Bulky and expensive to transport.
	Sampling is simple.	
	Air samples are collected without any breakthrough of compounds.	
	No degradation of the trapping material takes place.	
Tubes	Convenient, small, portable and low cost.	Contamination of adsorbent.
	No reconditioning needed after desorption step.	Not suitable for C_2s.
	Comprehensive data base and proven technology.	Desorption of some VOCs are difficult.
	Suitable for a wide range of VOCs.	Only one analysis per tube, if the sample is not split.

Zielinska *et al.* (1996) compared parallel runs with stainless steel SUMMA^{TM} – polished canisters with Tenax-TA solid adsorbent cartridges. They found that the canister samples were not very different between two runs with different ratios of heavy duty diesel, while the corresponding Tenax samples showed

dramatic differences in the intensities of the C_9 - C_{18} hydrocarbon peaks. They found that the Tenax/canister concentration ratio for most C_8 - C_{10} compounds was around 1, although this ratio increased substantially for compounds eluting after C_{10}, when the Tenax concentrations found were much higher than those of the canisters. They found that the C_8 - C_{10} compounds were more stable in the Tenax cartridge than in the canister. They argued that it is probably due to some heavier compounds absorbed onto the canister walls upon storage, or/and were desorbed non-quantitatively from the freeze-out loop during preconcentration for the GC analysis.

Colón *et al.* (2001) found a difference in the concentrations of VOCs if canister and adsorbent tubes where compared. According to them the standard error of means (SEM) for the canisters is smaller than those for the tube data, indicating the probability of better precision using canisters. They found that if they allow for the SEM, the data means of methyl chloride, benzene, trichloroethene, toluene, butanal and nonanal are essentially equivalent but not for the remaining aldehydes.

McClenny *et al.* (2002) compared canisters and tubes consisting of Carboxen and graphitic carbon, when spiked with ozone. They found a major disagreement (for n-aldehydes) between the methods. The autoGC preconcentration had strong positive artifacts, while the canister and the tubes showed negative artifacts.

In a study in New York where SUMMA canisters and Carbotrap 300 tubes were compared, the comparison between the canister and the tubes was found to be quite good. The results of the adsorption tubes indicated markedly lower levels than those of the canisters. It was reported that the canister sampling followed by cryogenic analysis has higher precision than the tube sampling. Differences in the concentrations are due to different sampling handling techniques (e.g. the used of a Nafion® dryer) and real time analysis (DEC, 2000).

Comparison of tubes and automated instruments

Skov *et al.* (2001) found a good agreement between benzene measured by a Tenax® TA/Carbopac B tube (Perkin-Elmer) pumped during sampling and an automated BTEX monitor. When the results obtained from Perkin-Elmer diffusion tubes and the automated benzene, toluene, ethylbenzene and xylene isomers (BTEX) monitor are compared, the diffusive sampler measured 20% higher values.

Wideqvist (2003) also compared Tenax TA and Carbopack B tubes with an automatic BTEX instrument and found the Tenax TA showed about 30% higher benzene levels than the BTEX instrument.

2.7 CLIMATIC FACTORS INFLUENCING VOLATILE ORGANIC CONCENTRATIONS IN SOUTH AFRICA

2.7.1 Meteorological conditions in South Africa

Figure 2.5: Synoptic weather map for a typical day in the summertime (Van Heerden & Hurry, 1987)

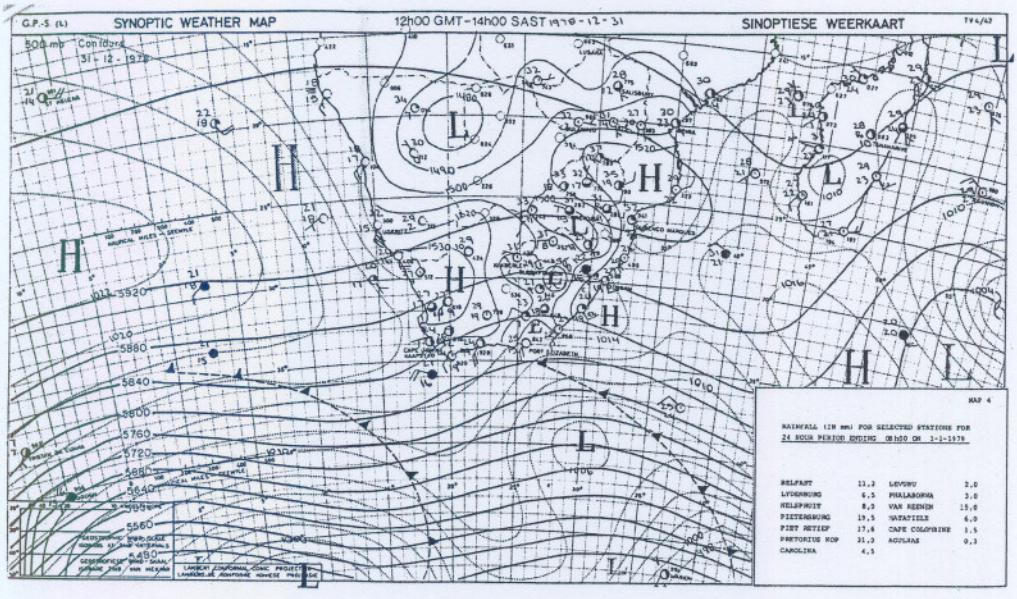
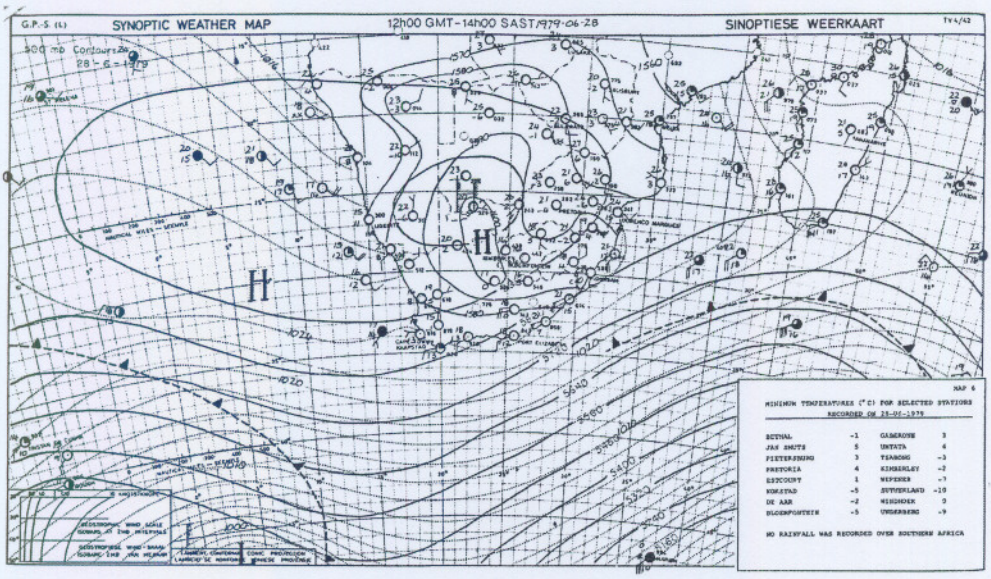


Figure 2.6: Synoptic weather map for a typical day in wintertime (Van Heerden & Hurry, 1987)



Anticyclonic conditions generally prevail during the winter over southern Africa (see Figure 2.6); calm or light winds, low nocturnal temperatures and a restricted mixing depth due to the stability of the atmosphere are characteristic. The pollution concentration may build up to high levels because little dispersion or dilution of the atmosphere occurs. Polluted air masses from urban and industrial areas affect suburban and rural areas in the direction of the prevailing wind over considerable distances (Oosthuizen *et al.*, 1998).

Possibly due to the lower mixing heights during the season, certain researchers have noted an increase in the concentrations of benzene and toluene during the winter (Pankow *et al.*, 2003; Brocco *et al.*, 1997) although other researchers have measured higher ratios in the summer than the winter (Ho *et al.*, 2004).

Sunlight

South Africa is renowned for its sunshine. Photochemical reactions (see Par. 2.4) form secondary pollutants when the sun shines. Clouds decrease photochemical activity and the formation of secondary pollutants, while solar

radiation and high temperatures accelerate this formation (Kassomenos *et al.*, 2003).

Topography

In Cape Town the low-level intense inversion of winter anticyclones form a "lid" and the mountains surrounding the city can form the sides of a "box" into which massive quantities of pollutants can be deposited (see Par. 2.3.1). With moisture added to the atmosphere by combustion processes and the sea, the availability of vast quantities of condensation nuclei in the form of suspended particulates, and low temperatures that increase the relative humidity, fog formation is encouraged (Elsom, 1987). This "lid" prevents the denser, cooler air underneath it from rising through it. The pollutants trapped below this layer are confined to a smaller volume beneath the inversion layer and this results in much higher ground-level concentrations (Finlayson-Pitts & Pitts, 1986).

Humidity

Cape Town is in a winter rainfall area and is a coastal town, which means that the humidity during the winter is usually higher than that of the Vaal Triangle. The Vaal Triangle is inland and typically has clear, cloudless, windless days during the winter. Clear days have much more warming and more variable temperature profiles while cloudy days have higher humidities, although some clear days can also have high humidities, especially in Cape Town. Chung *et al.* (2003) found higher VOC concentrations on clear days than on cloudy days. Clouds capture the more soluble VOCs, which are oxidized to material.

2.8 BROWN HAZE IN CAPE TOWN

The Cape Town brown haze develops from March to August during the winter on certain windless days. The haze has a strong degrading effect on visibility - this is immediately apparent to the tourist and the general public. It is of great concern that the brown haze might have a negative influence on tourism in the area. In addition, this has an impact on the flora of the Cape metropolitan area (CMA), which is unique in itself.

Figure 2.7: Typical brown haze in Cape Town (Photo: Muller, 2006)

Eastward movement of an intense, synoptic anticyclone initiates brown haze episodes over the Cape Town area (Jury *et al.*, 1990). A day before the brown haze episode occurs, the 859 hPa geopotential height typically increases to 1600 gpm. The north-easterly mountain winds dry out the boundary layer and a nocturnal radiation inversion forms a mean temperature of 11 °C that extends from the surface layer to 500 m above the surface. Thermal and gradient winds tend to cancel out the provision for low net transport rates for near-surface emissions (Jury *et al.*, 1990). The haze is usually most intense in the early mornings, gradually dispersing during the day (Linde, H. Personal communication, 23 July 2003). These climatic conditions often coincide with early morning traffic patterns, causing visible levels of air pollution in the form of a white to brown layer, which covers most of the Cape Peninsula and Cape Flats (Wicking-Baird *et al.*, 1997).

In a study to determine the PM_{10} levels in the brown haze in Cape Town, Wicking-Baird *et al.* (1996) found that the PM_{10} concentration usually increases from about six o'clock in the morning. According to these authors this is due to the increase in human activity, e.g. people going to their daily work and industry starting up. These emissions are concentrated by ground based temperature inversions reducing the volume into which pollutants are emitted. The peak then gradually tails off, and the inversion layer lifts or disperses. This is aided by the heat of the sun or surface wind action

decreasing the concentration of pollutants. Another peak, which occurs later in the evening, coincides with human activity after working hours and inversion layer formation after dark.

2.8.1 Meteorology of Cape Town

The location of Cape Town plays a key role in its susceptibility to the formation of smog. Land and sea breezes can play a significant role in the formation of coastal city smog (see Par. 2.3.1). The mountains also play a role in trapping the pollutants in the city basin. The Cape Metropolis is in the unique situation that it has mountains and sea on the western side, False Bay to the south and mountains ranges to the east, and the Atlantic Ocean to the north-west. The slopes of the mountains can act as the sides of a temperature inversion box that traps pollutants (see Par. 2.3.1).

2.8.2 Sources of VOCs in brown haze in Cape Town

A variety of sources can contribute to the VOC concentrations in the Cape Town area. Industries such as Kynoch and Caltex are possible contributing sources (see Table 2.13), as well as diesel and petroleum combustion (see Par. 2.8.2.1), wood and grass fires (see Par. 2.8.2.2), certain marine organisms (see Par. 2.8.2.3), and coal- and oil-fired boilers.

2.8.2.1 Road traffic and motor vehicle emission sources

An increase in the population, urban sprawl and poor public transport all lead to more vehicles on the roads and an increase in the emissions due to the combustion of petroleum and diesel. Vehicle numbers have increased by 80% in the CMA in the last 20 years (Wicking-Baird *et al.*, 1997). Petroleum industries such as Caltex Petroleum and oil refineries also increase the possibility of petroleum evaporation (see Par. 2.5.3). A further reason for concern is the fact that maximum guideline limits for nitrogen oxides (NO_x), sulphur oxides (SO_x) and particulate matter (PM_{10} and $PM_{2.5}$) are approached or exceeded with increasing frequency (Wicking-Baird *et al.*, 1997).

2.8.2.2 Domestic paraffin, coal, wood and grass burning

Paraffin, wood, coal and animal dung is widely used for cooking and heating in the majority of the informal settlements in the Western Cape. (Approximately 14% of households in the CMA do not have electricity). According to Statistics South Africa (STASSA) 122 768 households in Cape Town used paraffin for cooking, 18 592 used gas, 2 732 used wood, 1 702 used coal and 2 450 used animal dung. While 141 137 used paraffin for heating, 17 126 used wood, 9 129 used gas, 1 921 used coal and 1 057 used animal dung during 2001 (statssa, 2001). The inefficient burning of these carbon hydrates for fuel may be an important source of VOCs (see Par 2.5.3).

Wood

Wicking-Baird *et al.* (1997) determined that Port Jackson and Rooikrantz wood contains high mass fractions for chlorine, organic and elemental carbon. Although grass burning is more a summer phenomenon the burning profile of grass according to Wicking-Baird *et al.* (1997) is very similar to the wood burning profiles (see Par. 2.5.3).

2.8.2.3 Marine environments and the formation of VOCs

The emissions from marine environments may be the predominant factor affecting ambient levels of certain halogenated hydrocarbons (see Par. 2.5.3).

2.8.3 Previous studies

X-ray emission spectroscopy was used during the winter period in 1992 in an attempt to determine the common pollutant elements in the brown haze. The most common pollutant elements found were Al, Si, P, S, Cl, K, Ca, Ti, Fe, Cu, Zn and Pb (Pineda & De Villiers, 1995). This study was carried out only on inorganic compounds and no measurement of organic compounds was carried out.

During the period from July 1995 to June 1996, Wicking-Baird *et al.* (1997) used $PM_{2.5}$ samplers at the city centre, Goodwood, Table View and Wynberg. A single sample was taken at Gugulethu. Possible sources (see Table 2.13) included in their model were various soils, road dust, sea salt, coal-fired boilers, oil-fired boilers, Caltex oil and gas-fired equipment, Caltex's fluidised catalytic cracker unit, Kynoch's ammonium nitrate emissions, diesel combustion, petrol combustion, wood fires, grass fires and tyre burning. Secondary sources for sulphates, nitrates and carbon were also taken into account. It was found during the year that the nitrogen dioxide levels were exceeded during most of the brown haze episodes, sulphur dioxides were seldom exceeded and PM_{10} was never exceeded. They concluded that Cape Town experienced strong pollution episodes only a few hours per day on certain days of the year. Visibility and pollution levels can be compared with some of the worst polluted cities in the world during these brown haze occasions, but this is not sustained. For this reason daily and annual air pollution standards are seldom exceeded. They concluded that the contribution of the various sources of brown haze were as given in Table 2.13, if they used the chemical mass balance model, (an accepted source apportionment tool of the United States Environmental Agency):

Table 2.13: A summary of the source percentage contribution to the brown haze from the results of the Cape Town brown haze study (Wicking-Baird *et al.*, 1997)

	$PM_{2.5}$ apportionment	**Visibility apportionment**
Diesel	42%	48%
Petrol	25%	17%
Wood	14%	11%
Unknown	8%	9%
Boilers	6%	13%
Soil dust	3%	1%
Sea salt	2%	1%

According to the brown haze study by Wicking-Baird *et al.* (1997) the major source of brown haze in the Cape Town area is diesel vehicles, petrol vehicles, wood burning and industrial boilers also playing a significant role. An unknown source also exists, which comprises mostly of organic carbon. According to these researchers it is likely that a significant portion of this organic carbon is derived from industrial emissions or that it is some carbon contribution caused by the formation of secondary organic carbon in the atmosphere.

From October 1994 to September 1995 the Council for Scientific and Industrial Research (CSIR) conducted a steering air quality project in the Milnerton and surrounding areas to determine the air quality. According to this project they concluded that a number of VOCs were detected but only benzene levels presented an unacceptable health risk.

During 1997 the CSIR undertook a project on behalf of the Department of Environmental Affairs and Tourism (DEAT) to quantify atmospheric volatile organic compounds (VOCs) in the major metropolitan areas in South Africa, using passive samplers. In this study it was found that the mean TVOC concentrations in Cape Town was significantly higher than those in Johannesburg and Durban (Oosthuizen *et al.*, 1998). According to Oosthuizen *et al.* (1998) mean TVOC concentrations for the industrial area as well as the Cape Town central business district (CBD) and residential areas may cause detrimental health effects such as breathing problems and other forms of lung irritation.

Table 2.14: Previous VOC studies done in Cape Town (Results in ppm except for TVOC that is expressed in $\mu g.m^{-3}$)

	Terblanche *et al.*, 1996		**Oosthuizen *et al.*, 1998**	
Study period	**1/10/1994 – 30/09/1995**		**Spring 1997**	
Sampling point	**Table View**	**Goodwood**	**Table View**	**City Hall**
Benzene	0.72 - 2.10 Average: 1.22	0.85 - 3.8 Average: 1.69	Below detection limits	0.09
Toluene	0.35 - 3.14 Average: 1.4	0.58 - 4.23 Average: 1.9	1.5	8.34
Xylene	0.21 - 2.38 Average: 0.8	0.34 - 4.34 Average: 1.9	1.2	7.95
Heptane	0.25 - 3.43 Average: 1.0	0.35 - 4.59 Average: 1.4	0.69	1.3
Trimethylbenzene	0.20 - 1.5 Average: 1.0	0.20 - 1.1 Average: 1.4	0.58	4.63
TVOCs	10.5 - 62.5 Average: 34.89 $\mu g.m^{-3}$	42.1 - 110.5 Average: 38.05 $\mu g.m^{-3}$	Not measured	Not measured

2.9 BROWN HAZE IN THE VAAL TRIANGLE

The Vaal Triangle is a highly industrialised region situated about 50 km south-south-west of Johannesburg in the provinces of Gauteng and the Free State. The Vaal Triangle is approximately 4 729 ft ASL in the west and 5 038 ft ASL in the east. The average high at Vanderbijlpark is 4884 ft ASL. The Vaal Triangle is situated in the Highveld region of South Africa, covering an estimated area of 4 000 km^2.

The name "Vaal Triangle" was originally allocated to the towns Vanderbijlpark (Emfuleni), Sasolburg (Metsimaholo) and Vereeniging (Kopanong) (about 50 km south of Johannesburg), which formed a triangle spread across the Vaal river, with Vereeniging and Vanderbijlpark being on the north of the Vaal river, in Gauteng, and Sasolburg south of the river in the Free State Province. Meyerton which is situated just north-east of Vereeniging, was eventually regarded as an inherent part of the Vaal Triangle. The residential areas

Boipatong and Bophelong (situated within the municipal boundary of Vanderbijlpark), Evaton, Orange Farm, Sebokeng, Sharpeville (in Vereeniging), Zamdela (in Sasolburg) are all included in the Vaal Triangle, as are residential areas Rust-ter-Vaal and Roshnee, which are both situated in the municipal area of Vereeniging.

According to the 2001 census, the population in the Vaal Triangle was an estimated total of 938 082 (statssa, 2001).

2.9.1 Meteorology of the Vaal Triangle

During the dry winter period stable atmospheric conditions prevent the removal of pollution from the region and are combined with dry conditions that promote dust formation. The winter months in the area are subjected to strong temperature inversions and long cold spells. This results in pollution layers covering the Vaal Triangle region, especially in the early mornings and evenings. Smoke formed at low levels is trapped and reaches high concentration levels in this area.

The Vaal Triangle is at a lower altitude than the Witwatersrand. Under the influence of a catabatic flow regime, the smoke originating from Johannesburg and surrounding areas are drained into the Vaal basis from outside the region (Van Graan *et al.*, 1992).

2.9.2 Pollution in the Vaal Triangle

The Vaal Triangle is one of the most polluted areas in South Africa. Studies in the past (see Par. 2.9.5) indicated the occurrence of elevated concentrations of certain hazardous air pollutants such as SO_2, O_3, NO_x and particulate matter. In an article Tempelhoff (2004) stated that in the Vaal Triangle at least 25 premature babies died, 78 750 working hours were lost, 24 000 people suffered from bronchitis, 6 000 people were ill due to the emissions from coal and 15 700 were ill due to the emissions from industries during 2003.

Air quality of the Vaal Triangle is considered to be poor as a result of the multitude of industrial pollution sources, mining and dust from cultivated agricultural land. Possible sources of pollution include: industries, agricultural activity, domestic emissions, veld fires, unpaved roads, vehicle emissions, ash dumps, landfill and waste incineration, power stations, mines, material stockpiles and pollutants from outside the region. Table 2.15 gives an indication of the estimated tons per annum (tpa) emissions of VOCs in the Vaal Triangle.

Table 2.15: Estimated emissions of VOCs (tpa) in the Vaal Triangle (Scorgie, 2004) (Data not available for all the compounds at all the sources)

	Household burning	Fuel emissions	Biomass burning	Industries and mining	Energy generation
Benzene	23	76			
TVOCs	1242			44647	366
CO	3070	36885	5090	1909	111124
THC		5868	431		
1,3-Butadiene		60			
NMHC			243		
Methane		173	188		
Formaldehyde		40			
Acetaldehyde		21			

(TVOCs = Total volatile organic compounds, CO = Carbon monoxide, THC = Total hydrocarbons, NMHC = Nonmethane hydrocarbons)

2.9.3 Brown haze in the Vaal Triangle

Figure 2.8: Typical brown haze in Vereeniging on the morning of 20 August 2004 (Photo: Author)

Brown haze in the Vaal Triangle varies from a white, light yellow to light brown layer in the vicinity of Sasolburg, to a light brown to blue-purple layer over Vanderbijlpark. Brown haze consists of a single or multiple bands at different altitudes. The problem is more intense during windless conditions in winter, especially from early evenings till early mornings. Occasionally these layers do not dilute or diffuse till mid-morning. During the winter these layers form much nearer to ground level than during the summer.

In the summer, layers are formed that are clearly visible from long distances. These layers are generally not so intense because the wind dilutes and transports them. The solid particles suspended in the air at ground level is also much more intense during winter evenings than during the rest of the year. These solid particles lead to the reduction in visibility due to the scattering of light.

2.9.4 Sources of VOCs in brown haze in the Vaal Triangle

2.9.4.1 Industries

A wide range of industries is situated in the industrial areas of the Vaal Triangle. Industrial activities include: metallurgical industries, open-cast coal mines, chemical manufacturing plants, coal-fired power generation utilities, steel processing industries and fuel processing plants. These industries include Mittal, NATREF, Sasol Polymers, Omnia Fertilisers, Sasol Midlands, and ESCOM's Lethabo power plant.

2.9.4.2 Road traffic and motor vehicle emission sources

Emissions from vehicles are important sources of VOCs (see Par. 2.5.3). Scorgie (1994) determined the estimated vehicle emissions in the Vaal Triangle based on fuel sales for 2001. These values are given in Table 2.16.

Table 2.16: Estimated vehicle emissions for the Vaal Triangle (tpa) (Scorgie, 2004)

	Source			
	Emissions from diesel-driven vehicles (tpa)	Emissions from petrol-driven vehicles (tpa)		Total emissions from vehicles (tpa)
		Non-catalytic converter equipped vehicles	Catalytic converter equipped vehicles	
THCs	518	5197	152.4	5868
CO	2001	34204	679.5	36885
CO_2	421667	436738	45306.6	903712
CH_4	41	126	6.6	173
NMTOC	478	3938	112.4	4529
1,3-Butadiene	3	57	0.0	60
Benzene	1	70.3	4.5	76
Formaldehyde	4	35	0.6	40
Acetaldehyde	5	15	1.0	21

(THCs = Total hydrocarbons, CO = Carbon monoxide, CO_2 = Carbon dioxide, NMTOC = Nonmethane total organic compounds)

2.9.4.3 Domestic paraffin, coal, wood and grass burning

The incomplete burning of coal (see Par. 2.5.3) and other substances (tyres, plastic, etc) for heating (especially during winter) also contribute to the brown haze formation in informal settlements where houses or shacks have no electricity. Smoke from coal burning forms a dense layer that covers vast areas of the Vaal Triangle especially during windless conditions. The problem is increased due to the continued urbanisation of the population in the expanding non-electrified residential towns. The low-income population is increasing dramatically in the inner core zone of the Pretoria-Witwatersrand-Vaal Triangle region (Geyer, 2002).

Paraffin

During 2001, 1 296 households in Metsimaholo, 5 179 in Emfuleni, 391 in Midvaal and 3 809 in Lesedi used paraffin for cooking. Additionally 9 207 households in Metsimaholo, 21 912 in Emfuleni, 1 865 in Midvaal and 5 570 in Lesedi used paraffin for heating in 2001 (statssa, 2001).

Coal

Paraffin and coal are the primary forms of domestic fuel in the townships. Due to the coal mines operating in the region, coal is relatively inexpensive and is an easily accessible source of energy for non-electrified houses. Coal is used in an estimated 140 000 households in Boipatong, Bophelong, Evaton, Orange Farm, Sebokeng, Sharpeville and Zamdela; this consumes 145146 tons (Scorgie, 2004) of coal per annum. According to STASSA 1 296 households in Metsimaholo, 5 179 in Emfuleni, 391 in Midvaal and 3 809 in Lesedi used coal for cooking in 2001. In 2001, 9 207 households in Metsimaholo, 21 912 in Emfuleni, 1 865 in Midvaal and 5 570 in Lesedi used coal for heating (statssa, 2001).

The Lethabo power station (south of Vereeniging) uses 15 million tons of coal per annum (Scorgie, 2004) to supply 194 508 households in the Vaal Triangle with electricity for cooking and heating (statssa, 2001).

Although Zhang and Smith (1999) determined that coal produces less carbonyl emissions than kerosene, coal has been identified as the single most significant contributor of respiratory diseases in children 8 to 12 years in Sebokeng (Terblanche *et al.,* 1995).

Wood

In 2001, 858 households in Metsimaholo, 1 037 in Emfuleni, 813 in Midvaal and 812 in Lesedi used wood for cooking, whilst 1 694 households in Metsimaholo, 2 562 in Emfuleni, 2 482 in Midvaal and 1 096 in Lesedi used wood for heating and cooking (statssa, 2001).

Scorgie (2004) determines that 23 359 tons of wood per annum is consumes in the Vaal Triangle. McDonald *et al. (*2000) determined that 5 to 22 $g.kg^{-1}$ volatile organic compounds are emitted from wood burned. This means that the burning of wood releases between 116.795 and 513.898 tpa of VOCs in the Vaal Triangle.

According to Scorgie (2004) 50% of the carbon are HCs from the emissions of wood burning in South Africa. Some of the hydrocarbons emitted when wood is burned are: 1,3-butadiene, butanone, 3-butene-2-one, 3-methyl-3-butene-2-one, methanol, chloromethane, isoprene, α/β-pinene, 1-methyl-7-isopropylphenanthrene, 1,7-dimethylphenanthrene, benzene, toluene, xylene, methyl chloride and methyl chloroform (Scorgie, 2004).

Veld fires

Veld fires (mainly grass fires), during the winter months when the grass is dry, are common phenomena in this region. The short burning period releases VOCs at ground level. According to Van Nierop (1995) veld fires make a negligible contribution to the total emissions and contribute only 1% of the area source of total suspended particulate matter (TSP) and 3% of the PM_{10}, but the emitted emissions are higher locally, so that the local dose is high. The estimated methane emissions due to biomass burning in the Vaal Triangle is 188 tpa and for NMHC it is estimated at 243 tpa (Scorgie, 2004).

2.9.4.4 Landfills

The following VOCs were routinely measured at various local landfills: toluene, ethylbenzene, xylene, carbon tetrachloride, methylene chloride, benzene, acetone, chlorobenzene, styrene, nonane, decane, undecane, dodecane, naphthalene, ethylene dichloride, tetrachloroethylene, trichloroethylene and chloroform. This is due to the burning of local waste and refuse at municipal landfills and ash dumps (Sorgie, 2004).

2.9.5 Related studies

From 1982 to 1984 particle induced x-ray emission (PIXE) was used to analyse the air in Soweto (Formenti *et al.*, 1998). Although the results may differ from that of the Vaal Triangle, they could provide an indication of the contribution of coal burning in townships. In this study it was found that between 40% and 50% of aerosol matter originated from coal emissions, while 18 to 22% originated from road dust.

Previous studies in the Vaal Triangle concentrated on SO_2, O_3, NO_x and particulate matter. It is only recently that the contribution of VOCs was taken into account. According to van Zyl (1994) the average winter (April to September) particulate matter concentration from 1977 to 1992 in Vanderbijlpark varied between about 32 and 54 $\mu g.m^{-3}$.

In 1992 Van Nierop undertook an investigation on the suspended particulates with an aerodynamic diameter of less than 10 micron in emissions in the ambient air pollution in the Vaal Triangle. It was found that the largest contribution of dust originates from roads, followed by the primary iron and steel industry.

Van Nierop (1995) determined that a total of 137 180 tons of total suspended particulate matter (TSP) and 55 852 tons of PM_{10} were emitted into the atmosphere in the Vaal Triangle during 1992. He determined that 58% of the

TSP and 61% of the PM_{10} were emitted by industrial sources. The domestic fuel combustion contribute 5% of the area source TSP (Van Nierop, 1995). Coal combustion is the largest contributor of domestic fuel combustion emissions, contributing 84% of domestic fuel combustion TSP emissions and 69% of PM_{10}. He found that Evaton was the largest single residential area contributing to domestic fuel combustion emissions, which contributes 40% of the domestic fuel combustion TSP emissions and 38% of the PM_{10}. He concluded that the townships that burn more wood have emissions with larger PM_{10} fractions than those of townships that burn less wood and the contribution of the domestic coal combustion to total emissions is unexpectedly low.

According to a study conducted by Reddy (1995) it was found that arc furnace sources are contributing between 11 and 26% of the airborne particulate matter in the Vaal Triangle. Soil dust contributes between 0 and 35% and domestic coal fire emissions peak in mid-winter at 30%. Reddy observed a definite seasonal influence on source contribution. Coal fire emissions peak in June and July when ambient temperatures are at the lowest. Contributions during April, May and the end of August are less than 10%.

Reddy and his co-workers (1996) did a study for the period mid-April 1994 to mid-April 1995 using PM_{10} ambient samplers in the central business areas of Vereeniging, Vanderbijlpark and Sasolburg. They found high gravimetric loading during cold dry periods (late April to September) and low gravimetric loading during warm and wet periods (November to early April).

Table 2.17: Percentage contribution and the mean PM_{10} source apportionment results in the Vaal Triangle for the period 22 April 1994 to 21 April 1995 (Reddy *et al.*, 1996)

	Vereeniging	Vanderbijlpark	Sasolburg
Domestic coal combustion	23%	25%	22%
Soil dust	21%	22%	20%
Ammonium sulphate	22%	24%	28%
Iron arc furnace emission	15%	14%	10%
Power station fly-ash	8%	5%	13%
Sinter plant emissions	6%	7%	5%
Coking furnace emissions	3%	2%	1%
Petrol vehicle emissions	2%	1%	1%
Fe-Mn plant emissions	<1%	-------	<1%
Mean PM_{10} concentration	70 $\mu g.m^{-3}$	58 $\mu g.m^{-3}$	57 $\mu g.m^{-3}$

During 1997 the CSIR undertook a study on behalf of the Department of Environmental Affairs to quantify atmospheric VOCs in the major metropolitan areas in South Africa, using passive samplers. Although the Vaal Triangle was not included in this study, Johannesburg, 50 km north of the Vaal Triangle, was. The lowest TVOCs were found in Johannesburg. In this study it was found that industry was the main contributor to TVOCs. The authors stated that although the main source is industry, the compounds found are typically those from exhaust fumes of motor vehicles (Oosthuizen *et al.*, 1998).

Sasol Infrachem has been monitoring thirty-nine VOCs and (especially BTEX-compounds) since September 2001. Volatile organic species are sampled with canisters for eight-hour periods at different sampling sites in Sasolburg, Vaalpark and Zamdela. The US-EPA method TO-14A (EPA, 1997) (see Par. 2.6.2) is used to analyse these samples. Analysis of the samples is done at the North-West University, Potchefstroom.

From November 2001 till April 2002 Van der Walt and co-workers (2004) undertook a study to compare the levels of BTEX in the Vaal Triangle and in

Potchefstroom (a rural area). The US-EPA methods TO-14A (EPA, 1997), TO-15 (EPA, 1997) and TO-17 (EPA, 1997) were used. Samples at 8 sites over an 8-hour averaging period were collected. The levels of toluene, ethylbenzene, and xylenes were within the range of background concentrations.

Table 2.18: A summary of the monthly average benzene concentration levels obtained in the Vaal Triangle and Potchefstroom (Van der Walt *et al.*, 2004)

	Vaal Triangle (ppb)	**Potchefstroom (ppb)**
Electrified residential	1.9 - 2.4	0.3
Semi-electrified residential	5.6	0.4
Non-electrified residential	1.9	0.4
Industrial area	3.9 – 11.3	

According to Van der Walt *et al.* (2004) the industrial areas showed higher concentrations of VOCs, but the pollution impact remained small. Although the concentrations in the Vaal Triangle in residential areas are similar to suburban concentrations elsewhere in the world, a semi-electrified site has the highest average monthly benzene concentration of 5.6 ppb. This level is still below the WHO level of 6.4 ppb.

2.10 CONCLUSIONS FROM LITERATURE

From the preceding discussion of the current literature it is clear that:

1. VOCs are playing an important role in photochemical reactions and are playing a major role in air quality and safety in general.
2. There are different sampling techniques for VOCs available, each with its own set of advantages and limitations.
3. Many uncertainties regarding VOCs still exist.
4. Results from different studies vary and many discrepancies cannot yet be fully explained.

In comparison to other pollutants, the monitoring of VOCs (and in particular benzene) in South Africa is not yet well documented and there is no long-term database of information. There is no information available that has been published on VOCs present in brown haze in South Africa. The objectives of this study (Par. 1.4) are therefore to widen the current knowledge base of VOCs in ambient air in South Africa. This study is therefore set out to quantify VOCs and to determine the concentration levels of certain VOCs in the ambient air in South Africa using different sampling techniques.

CHAPTER 3

EXPERIMENTAL METHOD

This chapter...

The chapter starts with the description of the preparation of the canisters, tubes and SPME used (Par. 3.1). The sampling in Cape Town (Par. 3.2.1), the meteorological data (Par. 3.2.2) and the analysis of the Cape Town samples are described (Par. 3.2.3). Next, the sampling in Vaal Triangle (Par. 3.2.4) and the meteorological data (Par. 3.2.5) are given. Finally, the analysis of the Vaal Triangle samples is described (Par. 3.2.6).

It follows from the literature study in Chapter 2 that different techniques are available to sample VOCs in ambient air. The sampling and analysis techniques for each of the procedures chosen are described in this chapter.

3.1 PREPARATION OF CANISTERS, TUBES AND SPME SAMPLERS

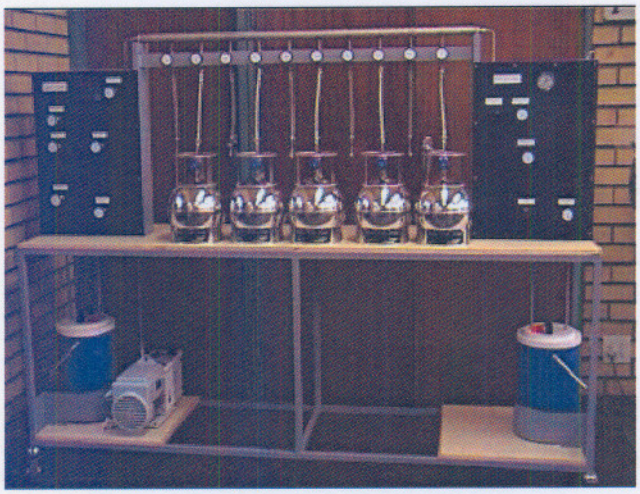
3.1.1 Canister preparation

All the canisters were tested for possible leakages. Canisters were filled with zero air. The initial pressure of all the canisters was measured and the final pressures were also measured after 24 hours. If the pressure varied by more than 13.8 kPa the canister had a leakage. (Canisters with leakages were not considered suitable for sampling.)

The canisters that passed the leakage test were cleaned as prescribed by the TO-14A (see Par. 2.6.2) clean-up procedure (EPA, 1997). For this process a special automated canister cleaning system was used (see Fig. 3.1). Liquid nitrogen (used as the cryogen) was added to both the zero air trap and the vacuum pump. The canisters were connected to the cleaning system and

evacuated to below 0.05 mm Hg for at least an hour. After this, zero air was used to pressurise the canisters with humid zero air. The cleaning cycle was continued consisting of several flushing and evacuation cycles at room temperature with humidified zero air. The final vacuum pressures of the canisters were between -25 and -30 mm Hg or less. Finally, sampler flow rates were set and checked for accuracy.

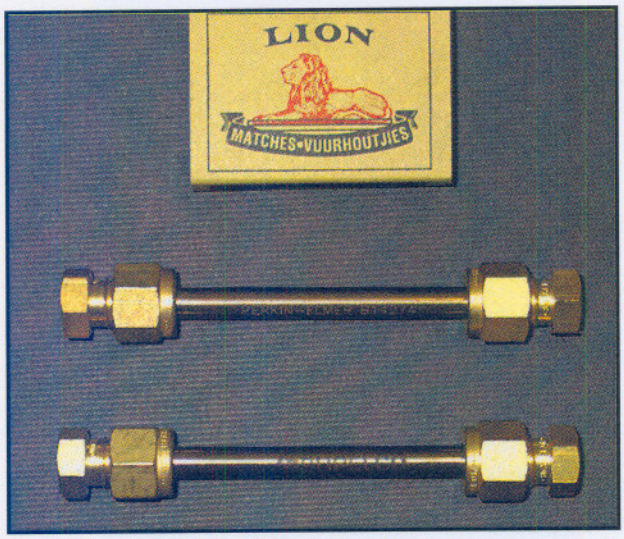
Figure 3.1: The automated canister cleaning system as used for cleaning canisters in this study (Photo: Jordaan, 2003)



3.1.2 Tube preparation

As described in Par. 2.6.3 adsorbent tubes can be used to sample VOCs according to the US-EPA Method TO-17 (EPA, 1997). Before shipping, all tubes (see Fig. 3.2) were preconditioned with helium for 30 minutes at 350 °C at a flow rate of 50 $cm^3.min^{-1}$ to remove any possible impurities. Tests were carried out to certify that the tubes are clean. Processed tubes were sealed with Swagelok fittings and individually wrapped in aluminium foil. The tubes were kept below -18 °C during shipping.

Figure 3.2: The Carbotrap^{TM} 300 tubes used in this study (Photo: Jordaan, 2003)



3.1.3 SPME preparation

Two types of SPME fibrews were used field and manual samplers. Before use, SPME fibres (See Fig. 2.4) were conditioned for 1 hour in a gas chromatograph (GC) at 250 °C. Following this, the fibres were retracted into the SPME sampler and the metal part was sealed off with a septum. SPME samplers were kept sealed at -18 °C until they were used.

3.2 SAMPLING DETAILS

The sites in Cape Town were selected to get a representative cross-section of the whole Cape Metropolis area (see Fig. 3.3). Different areas such as the central business districts (city hall), residential areas (Goodwood and Table View) and informal settlements (Khayelitsha) were included in ground level sampling. VOCs were sampled for the study at ground level at the following sites: Residential areas: Goodwood and Table View,

Informal settlement: Khayelitsha,

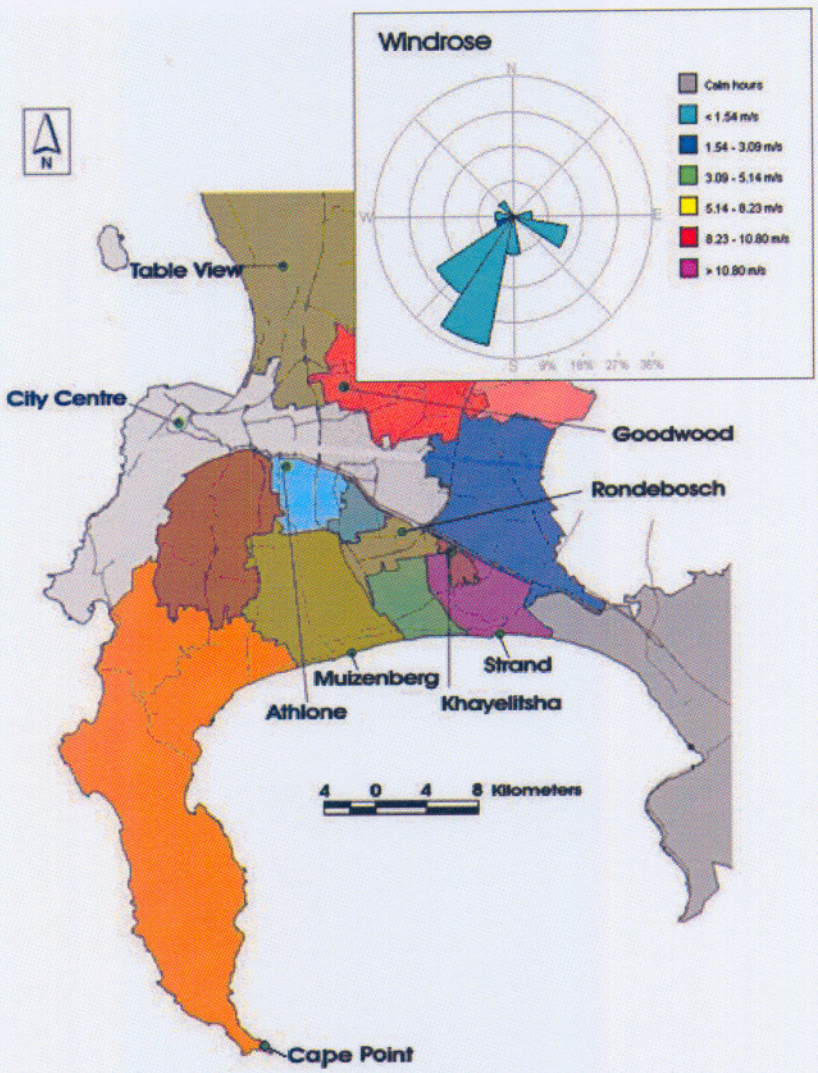
Central business district: City centre (city hall)

Background: Global Atmospheric Watch (GAW) station at Cape Point.

Samples were also taken at 1 000 and 1 500 ft AGL. The flights heights were chosen to characterise the top of the inversion layer and the VOCs just below

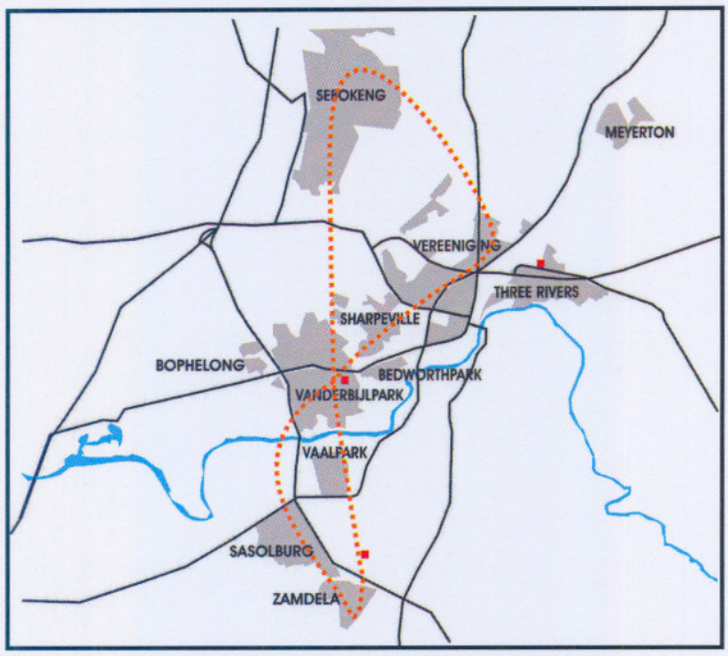
the top of the mixing layer. The residential areas of Rondebosch, Muizenberg and Strand were covered during flight sampling.

Figure 3.3: Map of Cape Town indicating the different air quality monitoring stations of the Cape Town metropolitan council (CMC) as well as the wind rose for the sampling period



The site selections in the Vaal Triangle were done to get a selection of different possible sources of VOCs. The three major towns (Vereeniging, Vanderbijlpark and Sasolburg) were included in ground-level sampling. These sites were chosen so that VOCs from different sources such as road-traffic, industry and informal settlement (Zamdela) would be covered. Samples were also taken at 616, 1 116, 1 616 and 2 616 ft AGL.

Figure 3.4: Map of the Vaal Triangle indicating the flying route for the sampling period and the different air quality monitoring stations



(Ground samples were taken at Three Rivers (Vereeniging) and (SW5) Vanderbijlpark and a sampling point between an informal settlement (Zamdela) and the industrial area in Sasolburg)

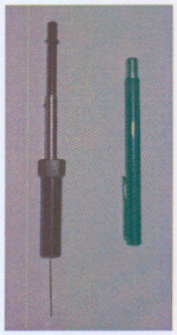
3.2.1 Sampling in Cape Town

Different sampling techniques were used during an intensive field campaign in the Cape Town area. This study was carried out during July 2003 in an attempt to identify and quantify the temporal and spatial distribution of VOCs in the Cape Metropolis. Sampling in Cape Town was done during the night of 28 July 2003 and during the day of 29 July 2003, for eight-hour intervals. This represents typical day and night conditions during the winter season. The 29th of July 2003 was characterised by a moderate brown haze cloud in the early morning. Three different sampling techniques were used, namely: 6 litre TO canisters, Carbotrap^{TM} 300 tubes and 75 mm Carboxen-PDMS SPME fibres. The typical brown haze forms in layers at different levels above ground level (Linde, H., Personal communication, 23 July 2003). In order to take this into account, samples were taken at altitudes of 1 000 and 1 500 ft AGL using a fully equipped research aircraft (Aero Commander 690A), operated by the South African Weather Services. The samples on board the Aero

Commander were taken for shorter time intervals between 10 to 14 minutes using a specially designed continuous sequential tube sampler (see Fig. 3.5c) fitted with 12 standard Perkin Elmer adsorbent sampling tubes as well as 6 litre canisters fitted with variable flow controllers. The continuous sampler sucked the air into specific tubes for the time interval, before switching to the next tube.

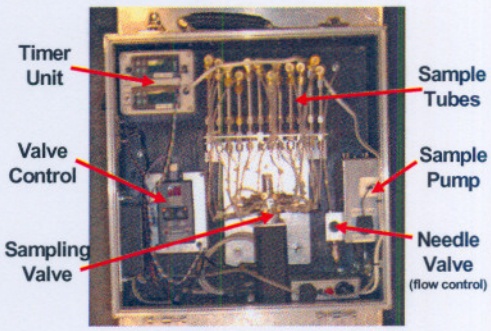
Figure 3.5: The sampling devices used in the Cape Town study (Photo: Jordaan, 2003)

a. SPME



b. Canister

c. Sampler used on board the 690A



Samples were taken at five different sites during the night of the 28th July 2003 and the day of the 29th July 2003 (see Fig. 3.3).

Background samples, data comparison and corrections

Cape Point (see Fig. 3.3) is the most southern tip of Africa and the wind direction is predominantly in a south-westerly direction towards South Africa. We can thus assume that VOCs measured at Cape Point are originating from the Atlantic Ocean. We can further assume that this air should be relatively pollution free compared to air from inland regions. For this study the air sampled at Cape Point was characterised as "clean background marine air" in terms of the CO and Radon 222 levels measured on the 28th and 29th July 2003 (Brunke, E., Personal communication, 10 March 2004).

Background corrections were also carried out at the different sites by placing sealed canisters and sealed tubes at these sites. During the analysis of the different samples, the VOC concentration in the laboratory air was also

analysed for background correction purposes. Duplicate tube samples were collected at the Goodwood site using different flow rates to check the impact on the found concentrations.

Samples taken at 1 000 and 1 500 ft above sea level

Canister and tube samples were taken at 1 000 ft AGL from Rondebosch to Goodwood, Rondebosch to Muizenberg and Muizenberg to Strand (see Fig. 3.3). Samples were taken at 1 500 ft AGL from Rondebosch to Goodwood, Rondebosch to Muizenberg to Strand and Malmesbury to Goodwood. The flight path also covered sections from Malmesbury to Muizenberg, Rondebosch and over Khayelitsha (see Fig. 3.3).

3.2.2 Meteorological data for the sampling period at Cape Town

The Cape Town metropolitan council (CMC) made the meteorological data for Cape Town from the 28th – 29th July 2003 available (Ravenscroft, 2006).

Table 3.1: Meteorological conditions at Cape Town for the period 28 - 29 July 2003

Date and time	Temperature/°C	General
28 - 29 July 2003 (18:00 - 02:00)	11.8 – 15.2 Average: 14.8	*Ground level wind*: Light south-westerly breeze (<1.5 m.s^{-1}) *O_3-levels*: 1-10 ppb; Average: 3.5 ppb *Relative humidity*: 82-87; Average 84.8
29 July 2003 (06:00 - 14:00)	11.9 – 26.9 Average: 18.1	*Ground level wind:* Light south-westerly breeze (<1.5 m.s^{-1}) *O_3-levels*: 2-35 ppb; Average: 17 ppb *Relative humidity*: 26-84; Average 58.8

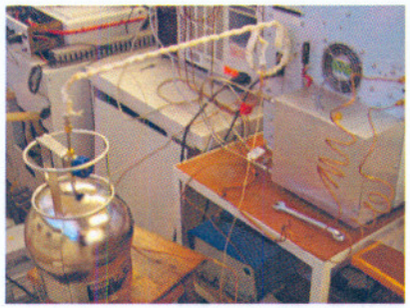
The canister valves were closed after the air samples were collected. The chain-of-custody (COC) forms were completed for every canister and the canisters were transported to the laboratory.

3.2.3 Analysis of samples

A suitable calibration standard obtained from Supelco (Cat no: 41900-U) containing 39 VOCs (100 ppb) was used as an external standard.

Samples were analysed as follows: water vapour in the canisters was reduced in the gas stream by a Nafion® dryer. VOCs were then pre-concentrated by collection with Peltier (electronic) in a cryogenically cooled trap (see Fig. 3.6). Liquid CO_2 were used to cool the GC-oven.

Figure 3.6: Connections used to introduce the sample from the canister to the thermal desorber system before the analyses of canisters (Photo: Jordaan, 2003)



The cryogen was removed and the sample was let into a Perkin-Elmer Turbo matrix thermal desorber. The VOCs collected were revolatilised and compounds were separated by a Hewlett Packard Agilent 6890 gas chromatograph (GC). The GC oven program was started at -10 °C (4 minutes hold) by using liquid carbon dioxide. The temperature was increased at a rate of 7 °C.min^{-1} up to 250 °C and held for 10 minutes at this value. The column used was a Perkin Elmer PE-1 60 m, 320 µm id, 1 µm film thickness. The detector used to identify the different compounds was a Micromass Autospec-TOF mass spectrometer (MS) set up to the prescribed EPA TO-14A compendium method. The detection limit of this procedure is about 200 ppt.

VOCs in the external calibration standard provided retention times that were converted to the scan numbers. The scan numbers were used to identify VOCs in samples. The identification was confirmed using the MS-spectra of

the compound. VOCs not present in the Supelco standard were identified using the MS data system library (NIST), that consists of a library of about 35 000 compounds. Since the adsorption rate and stability of all the compounds on the SMPE fibres are unknown, it was only used as a qualitative comparison to the other techniques.

The Supelco standard was used in the following way to quantify VOCs present in the standard and the samples. Firstly, a response factor (R_f) for the VOCs in the standard was calculated using the following formula:

$$R_f = \frac{area\ of\ VOC\ in\ standard}{concentration\ of\ VOC_{standard}\ (ppm) \times time\ (min) \times flow\ rate\ (cm^3.min^{-1})} \quad (3.1)$$

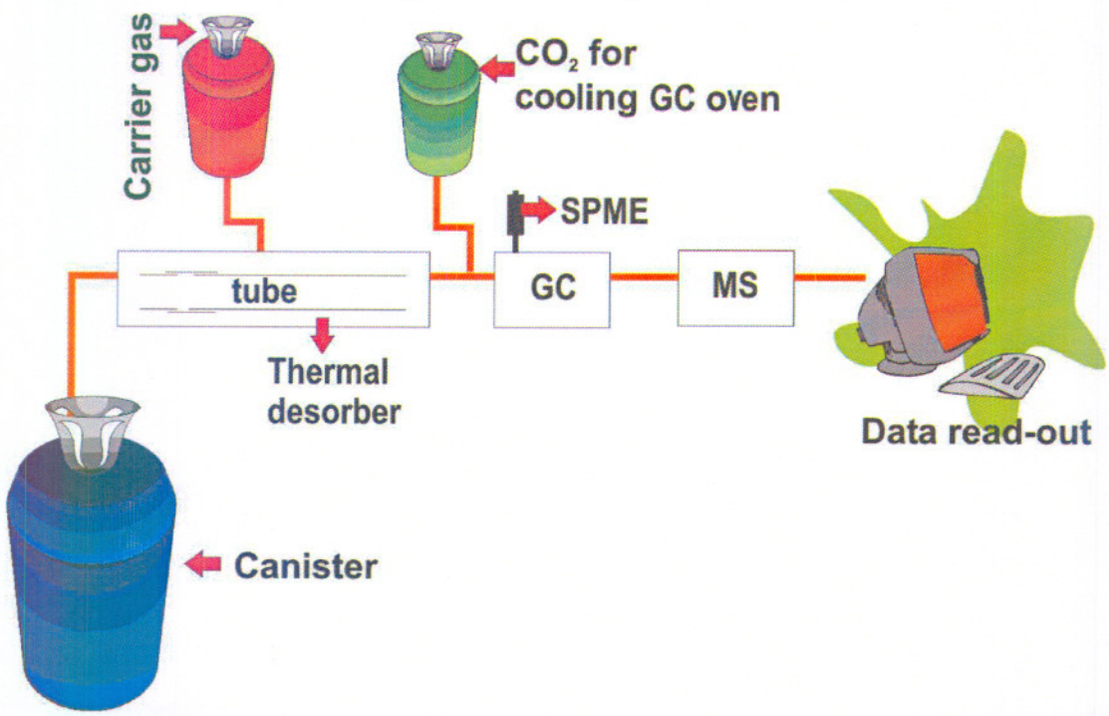
The concentration of the VOC in the sample was then calculated:

$$C_{unknown\ (ppm)} = \frac{dilution\ factor\ (only\ for\ canisters) \times area\ of\ VOC\ in\ sample}{time\ (min) \times flow\ rate\ (cm^3.min^{-1}) \times R_f} \quad (3.2)$$

The abundance in arbitrary units of the VOC in the sample that could not be quantified was calculated as follows:

$$Abundance\ in\ arbitray\ units = Peak\ area\ x\ time\ (min)\ x\ flow\ rate(cm^3.min^{-1}) \quad (3.3)$$

Figure 3.7: Schematic diagram of the analysis of the samples



3.2.4 Sampling in the Vaal Triangle

TO canisters, Carbotrap^{TM} 300 tubes and Carboxen-PDMS SPME samplers were used during an extensive field sampling survey in the Vaal Triangle. This was undertaken during August 2004.

Ground samples

Samples were taken at three different ground sites. The site selection was done in order to obtain a representative cross-section sampling of towns in the Vaal Triangle covering the region where the air samples were taken. Residential areas (Three Rivers in Vereeniging and SW5 in Vanderbijlpark) were included in the ground samples taken, as well as a sampling point used by Sasol Infrachem in Sasolburg. This site is situated between the industrial sites and Zamdela (an informal settlement).

Samples were taken on the 18th August 2004 for an 8-hour period (06:00 - 14:00) at Sasolburg (canisters and SPME), on 18 – 19 August 2004 for a 24-hour period (06:00 - 06:00) at Sasolburg (only canisters) and on 20 August 2004 for an 8-hour period (06:00 - 14:00) at Vereeniging (canisters and SPME) and Vanderbijlpark (canisters, tubes and SPME). These represent typical day conditions experienced during late winter and early spring season. Typically, the 20th of August was characterised by a very light brown haze cloud in the early morning.

Samples at different altitudes

On the 20th August 2004 samples were also taken in the lower troposphere at altitudes of 5 500, 6 000, 6 500 and 7 500 ft ASL using a suitable equipped aircraft (Cessna 182) to obtain a vertical profile of VOCs in this region. The samples taken on board the aircraft were for shorter time intervals, i.e. between 10 - 14 minutes. Sampling was done using a specially designed continuous sequential tube sampler fitted with 12 standard Perkin Elmer (Carbotrap 300) adsorbent sampling tubes (see Fig. 3.6) as well as 6 litre canisters fitted with a variable flow controller.

Background sample, data comparison and corrections

Background corrections were carried out (at Vanderbijlpark and Sasolburg) by placing canisters and tubes at these sites. During analysis of the different samples, the VOC concentration in the laboratory air was also analysed for background correction purposes. Duplicate tube samples were collected at the Vanderbijlpark and Sasolburg sites using different flow rates to check the impact thereof on the reported concentrations.

Samples taken at 616, 1 116, 1 616, 2 616 ft above ground level

Canister and tube samples were taken at 616 ft AGL covering the area from Zamdela, over Sasolburg, to Vanderbijlpark and then to Vereeniging up to Sebokeng (see Fig. 3.4). The aeroplane was then turned around and measurements were taken at the next selected altitude.

3.2.5 Meteorological data for the sampling period at the Vaal Triangle

Meteorological data for the Vaal Triangle from the 18th – 20th August 2004 were monitored and made available by the South African Weather Bureau and Sasol Infrachem. Temperatures were measured at all the sites.

Table 3.2: Meteorological conditions for the Vaal Triangle during the sampling period 18 – 20 August 2004

	Vereeniging **6:00 – 14:00** **20 August 2004**	***Vanderbijlpark*** **6:00 – 14:00** **20 August 2004**	***Sasolburg*** **6:00 – 14:00** **18 August 2004**	***Sasolburg*** **6:00 – 6:00** **18,19 August 2004**	***Sasolburg*** **6:00 – 14:00** **20 August 2004**
Temperature / °C	9.5 – 25.0	8.5 – 24.0	9.1 – 19.4 Average: 13.2	8.4 – 19.65 Average: 13.6	7.8 – 24.0 Average: 18.0
Wind at ground level	Strong north-west breeze. Cloudless.	Strong north-west breeze. Cloudless.	South-east Average speed: 4.7 m.s^{-1}	South-east Average speed: 4.2 m.s^{-1}	South-east Average speed: 5.6 m.s^{-1}
Humidity	Cloudless.	Cloudless.	Almost cloudless. Fog from 6:15 – 6:30	Almost cloudless. Fog from 6:15 – 6:30 on the 18th August 2004	Cloudless.
O_3 (ppb)	Not available.	Not available.	15.0 – 49.7 Average: 32.2	3.24 – 53.0 Average: 23.5	2.44 – 65.6 Average: 38.5
Brown haze	Slightly visible.	Almost not visible.	Strong brown haze layer visible.	Strong brown haze layer visible on 18 August 2004.	Slightly visible.

(Sasol Infrachem (Van der Walt, 2004) made the results for Sasolburg available. Results for Vereeniging and Vanderbijlpark were obtained from SA Weather Bureau)

3.2.6 Analysis of samples

All samples were analysed using the identical method as for the samples taken during the Cape Town study (see Par. 3.2.3).

CHAPTER 4

RESULTS OF THE CAPE TOWN FIELD STUDY

This chapter...

The results of the VOCs sampled in different regions in Cape Town are given and discussed in this chapter. The layout of the chapter is as follows:

1. *Concentrations of other gaseous pollutants monitored at the sampling sites during the campaign.*
2. *The ground level results: The VOCs monitored at the residential areas of Goodwood (Par. 4.1) and Table View (Par. 4.2) are given, followed by the results for city centre (Par. 4.3) and Khayelitsha (Par. 4.4).*
3. *A comparison of the quantifiable VOCs detected in the ground level samples is given in Par. 4.5.*
4. *A comparison of the VOCs detected in the ground level samples not in the calibration standard are given in Par. 4.6.*
5. *The comparison of VOCs sampled at different altitudes is given in Par. 4.7.*

As discussed in Par. 3.2.1, TO Canisters, Carbotrap™ 300 tubes and SPME-fibres were used to take 8-hour integrated samples of VOCs during the night of the 28th July 2003 (18:00 - 02:00) and during the day of the 29th July 2003 (06:00 - 14:00) in the Cape Town field study. Ground level samples were taken at Goodwood, Table View, the city centre and at Khayelitsha (see Fig. 3.3). Samples were also taken at different altitudes on the 29th July 2003 in the lower troposphere over the Cape Town area.

The Cape Town Metropolitan Council (CMC) (Ravenscroft, 2003) made the monitoring data in Table 4.1 available. These data were obtained at the different sites on the night of the 28th July 2003 (18:00 - 02:00) and during the day of the 29th July 2003 (06:00 - 14:00). NO, NO_2, NO_x in combination with VOCs can lead to the photochemical formation of ozone (see Par. 2.4).

Ozone can also react with some VOCs (see Par 2.4.1) to result in the formation of oxygenated products. Furthermore SO_2 (see Par. 2.3.3), PM_{10} (see Par. 2.3.4) NO_x and CO (see Par. 2.4) are compounds typically associated with brown haze (see Par. 2.3.1 and Par. 2.3.2) and photochemical pollution (see Par. 2.4).

The CMC made the data in Table 3.1 and Table 4.1 (Ravenscroft, 2003) available for the sampling period (Ravenscroft, 2003) and for interpretation purposes (Ravenscroft, G., Personal communication, 10 April 2006).

Table 4.1: Concentrations of atmospheric compounds monitored during the night of the 28th July 2003 (18:00 - 02:00) and during the day of the 29th July 2003 (06:00 - 14:00) (Ravenscroft, 2003)

	NO (ppb)		NO_2 (ppb)		NO_x (ppb)		SO_2 (ppb)		CO (ppb)		O_3 (ppb)		PM_{10} ($\mu g.cm^{-3}$)	
	N	D	N	D	N	D	N	D	N	D	N	D	N	D
Goodwood														
H	214	377	26.5	45.7	81.9	399.0	8.5	25.2	2537	7296	2.6	18	61.9	132.4
L	10.7	11.2	16.5	13.3	33.5	25.5	1.3	1.7	1553	884	0.5	1.0	39.3	16.5
A	31.4	141.9	22.2	23.8	54.7	166.7	3.8	10.5	1922.7	3373.4	1.1	8.7	48.9	50.2
Table View														
H	21.1	26.3	28.0	18.5	38.2	38.6	21	8.9					63.0	73.0
L	3.30	4.89	13.6	8.94	14.3	10.7	0.15	0.0					25.0	23.0
A	10.5	15.6	22.1	13.8	29.6	26.3	8.1	2.02	NM	NM	NM	NM	49.6	44.7
City centre														
H	189	962	37.2	96.3	213	1032	9.5	45	4525	13981				
L	27.7	136	15.4	25.5	43.6	173	0.38	6.8	325	2480				
A	101.8	476.0	24.6	62.82	124	536.5	4.45	24.9	2324	7162.6	NM	NM	NM	NM
Khayelitsha														
H													162.1	101.8
L													38.9	37.8
A	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	91.22	57.8

(N = Nighttime, D = Daytime, H = Highest concentration measured during the time period, L = Lowest concentration measured during the time period, A = average concentration for the time period, NM = not monitored at this site)

The data from the CMC (Ravenscroft, 2003) showed that the 28th July 2003 was a cold day with a maximum temperature of 15 °C at midday (see Table 3.1). The CMC confirmed high NO and low O_3 concentrations during the day of 28th July 2003. These concentrations persisted from the day of the 28th July 2003 into the sampling time of the night of the 28th July 2003.

From the information in Table 3.1 the maximum temperature for the 29th July 2003 was 26.9 °C. The CMC reported a slow increase of the O_3 levels during

the day of 29th July 2003 at remote sites, away from the city centre and precursor gasses (Ravenscroft, G., Personal communication, 10 April 2006).

Oxides of nitrogen

It follows from the data in Table 4.1 that for the Goodwood site NO and NO_x levels measured increased from night to day. NO_2 levels did not reflect the same higher values.

In Table View the NO levels did not fluctuate appreciably from night to day, but even the average daytime levels were almost half the nighttime levels measured in Goodwood. At the Table View site, the NO_2 levels decreased from night to day, the NO_x levels did not change significantly.

The levels of NO during daytime at Goodwood were found to be almost ten times higher than that of Table View. The nighttime results of the levels of NO and NO_x in Goodwood were again found to be significantly higher (almost double and up to three times) than that of Table View. Interestingly though, it was found that the average NO_2 levels (for Goodwood and Table View) at night were almost identical.

From Table 4.1 the NO (only the daytime), NO_2 and NO_x levels measured at the city centre were the highest of all the sites measured. NO increased more than four times from nighttime to daytime, NO_2 was found to be almost three times higher during the day than during the night and NO_x four and a half times higher during the day than during the night.

Sulphur dioxide (SO_2)

From the SO_2-data in Table 4.1 it can be concluded that SO_2 levels increased from night to day at the Goodwood-site and that SO_2 are five times higher at Goodwood than the Table View area during the daytime. SO_2 levels at Table View during the night were found to be four times higher than during the day and were the highest of all the stations measured. A fertilizer factory situated near Table View might be the source of the increased SO_2 levels at this site

during the night. At the city centre, SO_2 was almost six times higher during the day than during the night.

Carbon monoxide (CO)

The data in Table 4.1 indicated that the city centre had higher CO-levels than the residential areas (Goodwood). At the city centre CO are three times higher during the day than during the night, the average CO levels increased from night to day in Goodwood. The increased CO levels during the day are probably due to an increase in traffic in daytime.

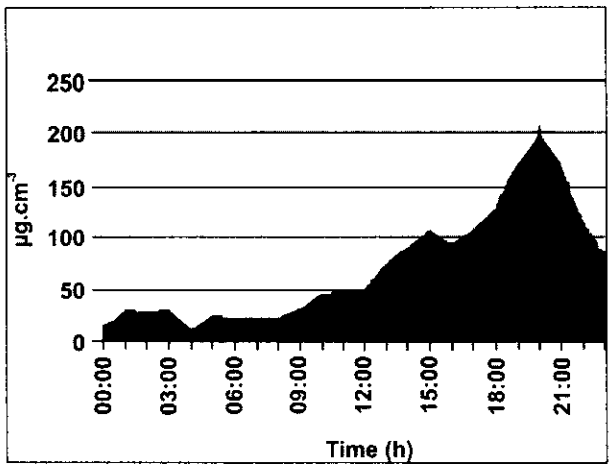
Ozone (O_3)

The ozone levels in Goodwood increased almost 8 times from the night to the day. According to Loewenheim (1988) stable conditions during the winter in Cape Town lead to the increase of precursor levels. He also determined that low O_3 levels occurred during bad weather and winter months. The O_3 levels during the sampling time in Cape Town were much lower than experienced in the Vaal Triangle (see Table 3.2).

Particulate matter (PM_{10})

It follows from the data in Table 4.1 that the PM_{10} levels for Khayelitsha were the highest of all the sites measured. The PM_{10} levels in Khayelitsha showed a significant increase during the nighttime due to the open fires used for cooking and heating compared to the day (see Figure 4.1). The PM_{10}-levels for Khayelitsha during the day were found to be slightly higher than that measured at Goodwood. The nighttime levels for PM_{10} in Khayelitsha were double the level of Table View during the day.

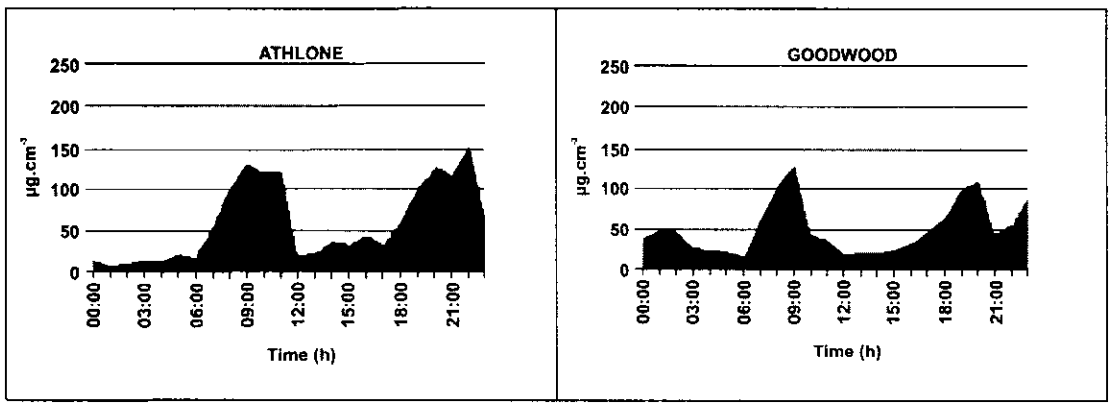
Figure 4.1: Hourly measurements for Khayelitsha on the 28th July 2003 for a 24-hour period (0:00 - 24:00)(CMC, 2003a)



The CMC reported a PM_{10} episode (when the PM_{10} levels exceeded the allowed UK daily average guideline of 50 $\mu g.cm^{-3}$) on 28th July 2003 at Khayelitsha. The PM_{10} levels stayed high for the remainder of the night (CMC, 2003a).

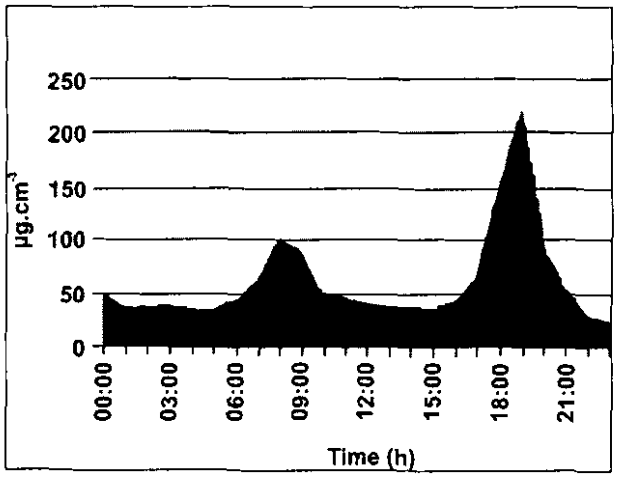
The CMC (2003b) confirmed another PM_{10} episode (when the levels exceeded the allowed UK daily average guideline of 50 $\mu g.cm^{-3}$) on the 29th July 2003 at Khayelitsha, Goodwood and at Athlone (a sampling site used by CMC; no samples for this study were taken there. Athlone is south-east from Goodwood and east from the city centre).

Figure 4.2: Comparison of the hourly measurements for Athlone and Goodwood on the 29th July 2003 for a 24-hour period (00:00 - 24:00)(CMC, 2003b)



From Figure 4.2 it can be seen that the Athlone site reported two PM_{10}-peaks from 09:00 - 12:00 and again from 18:00 - 24:00. The Goodwood site (that is downwind from Athlone) also reported a PM_{10}-episode consisting of two peaks, these PM_{10} peaks correspond with those experienced in Athlone (CMC, 2003b). The increase in PM_{10} levels measured in Goodwood is due to an early morning temperature inversion and domestic fires in Athlone (CMC, 2003b).

Figure 4.3: Hourly measurements for Khayelitsha on the 29th July 2003 for a 24-hour period (0:00 - 24:00)(CMC, 2003b)



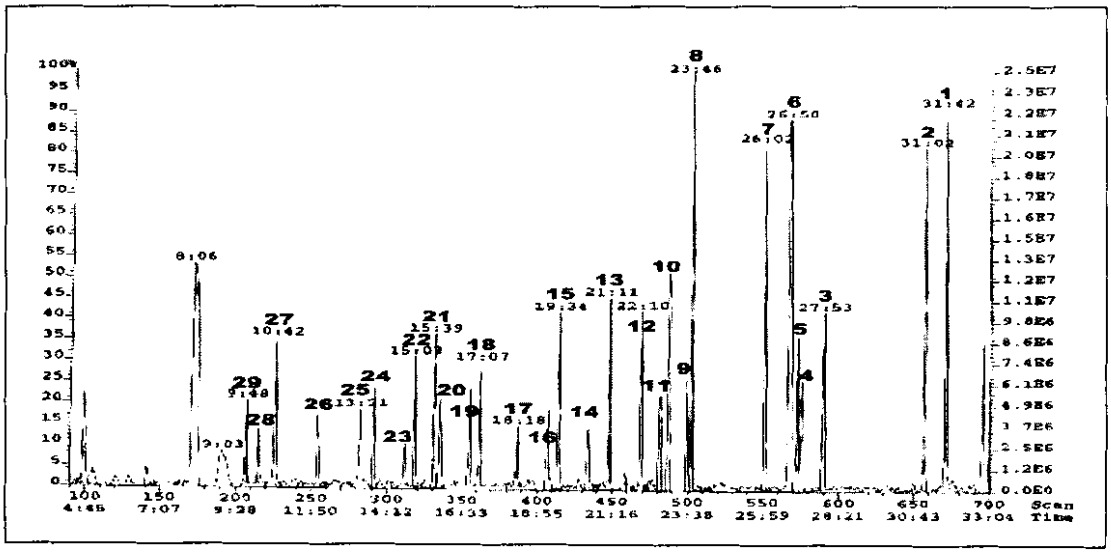
On the 29th July 2003 the PM_{10} levels in Khayelitsha started at a high level and had two distinct peaks (one in the morning – corresponding with the peak traffic hours and one in the afternoon – corresponding with domestic fires).

4.1 GOODWOOD

Goodwood is a residential area and as mentioned it was downwind from Athlone during the sampling period (see Fig. 3.4). This site is about 500 m from a frequently used road, two major motorways (the N7 and N1) and the R102 with a high traffic density, is near the Goodwood site. At the Goodwood site, canister, tube and SPME samples were taken.

Figure 4.4: Comparison of the chromatograms of samples collected at Goodwood on 29th July 2003 (integrated 8-hour average, 06:00 – 14:00)

(a) Chromatogram of calibration standard consisting of 39 VOC compounds of interest; benzene (22), toluene (15), ethylbenzene (11), p+m-xylene (9), styrene (10), o-xylene (8), 1,3,5-trimethylbenzene (7), 1,2,4-trimethylbenzene (6), 1,2-dichlorobenzene (3)



(b) Chromatogram of the Carboxen-PDMS SPME fibre

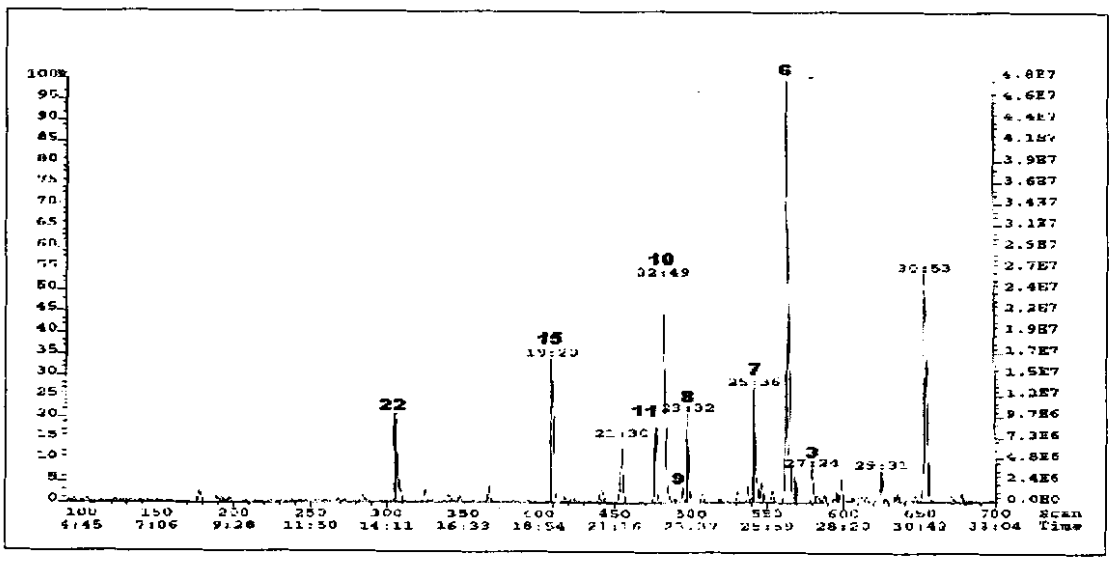
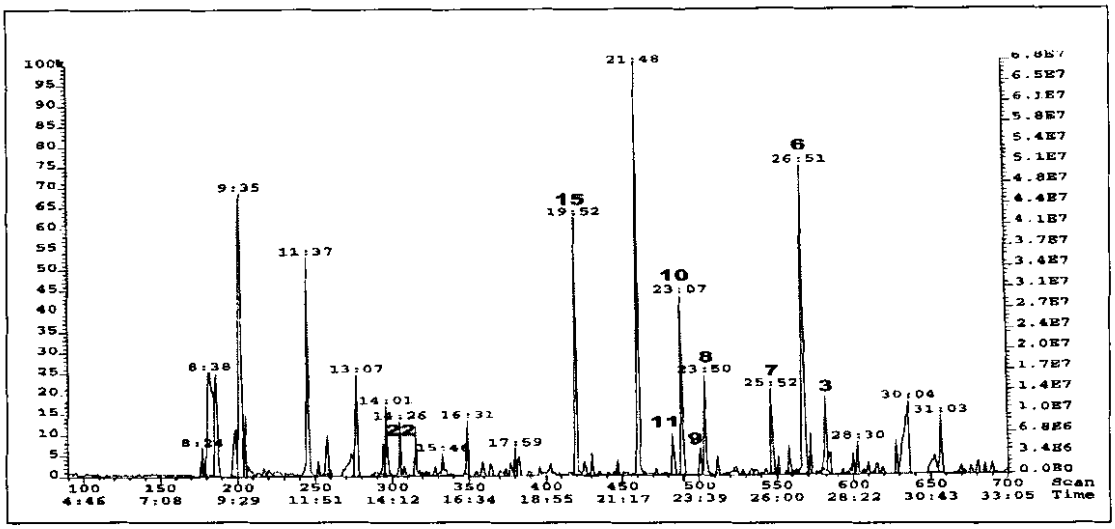
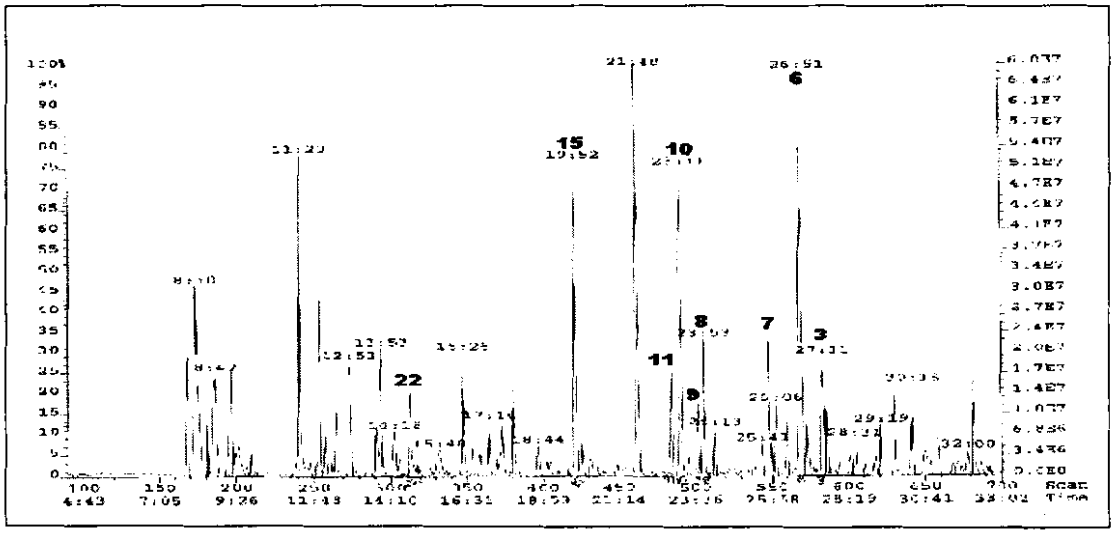


Figure 4.4: *(continued)*

(c) Chromatogram of the Carbotrap^{TM} 300 adsorption tube operated at a flow rate of 4 $cm^3.min^{-1}$



(d) Chromatogram of the Carbotrap^{TM} 300 adsorption tube operated at a flow rate of 16 $cm^3.min^{-1}$



4.1.1 Goodwood nighttime samples

Table 4.2: Concentration (ppb) of selected volatile organic compounds at the Goodwood site during the night

	◦Tube	•Tube	▫Canister
Benzene	0.85	2.89	0.75
1,1,2-Trichloroethane	0.48	3.54	—
Toluene	2.70	13.9	7.72
Ethylbenzene	2.05	5.98	4.22
p-Xylene	2.97	8.34	4.12
m-Xylene	2.97	8.34	4.11
Styrene	0.36	5.34	—
1,3,5-Trimethylbenzene	0.25	2.88	—
1,2,4-Trimethylbenzene	0.20	0.90	1.43
1,2-Dichlorobenzene	6.22	20.2	11.0

(*Nighttime sample: 28th – 29th July 2003 from 18:00 – 02:00)

(**◦ = Flow rate: 16 $cm^3.min^{-1}$, • = Flow rate: 4 $cm^3.min^{-1}$, ▫ = Flow rate: 12.6 $cm^3.min^{-1}$, — = Not detected)

It is clear from the data in Table 4.2 that the flow rate of the tube sampler is critical in terms of the reported concentrations. The concentration in the Carbotrap™ 300 tube with a flow rate of 16 $cm^3.min^{-1}$ correlated better with the canister than the Carbotrap™ 300 tube with a flow rate of 4 $cm^3.min^{-1}$. Comparison between the concentrations of certain VOCs measured by using Carbotrap™ 300 tubes (with a flow rate of 16 $cm^3.min^{-1}$) and the canisters were found to be within reasonable limits. The substantial variance between the values of the VOCs like 1,1,2-trichoroethane, not detected in the canister sample, could not be explained. A positive artefact due to a too low flow rate is however clearly evident by comparing the two sets of the tube sampler results.

A number of species not included in the Sulpelco standard were also observed in both tube and canister samples. Since no calibration standard for these compounds is available, these compounds could not be quantified. The

MS NIST library database was used to identify the compounds not included in the Supelco standard. These compounds are presented with similar observations at other sites in Table 4.7.

4.1.2 Goodwood daytime samples

Table 4.3: Concentrations (ppb) of selected volatile organic compounds at the Goodwood site during the day

	°Tube	•Tube	□Canister	×Carboxen SPME
Methylene chloride	—	—	3.58	—
Chloroform	1.40	11.8	2.95	—
Benzene	4.49	6.40	5.58	D
Toluene	10.7	23.2	4.16	D
Ethylbenzene	6.05	8.25	2.06	D
p-Xylene	9.99	16.8	2.63	D
m-Xylene	9.99	16.8	2.63	D
Styrene	0.73	3.17	0.84	D
o-Xylene	0.68	0.70	—	D
1,3,5-Trimethylbenzene	0.73	0.85	—	D
1,2,4-Trimethylbenzene	6.08	9.46	7.61	—
1,2-Dichlorobenzene	4.22	7.71	—	D

(*Daytime sample: 29th July 2003 from 06:00 – 14:00)

(**° = Flow rate: 16 $cm^3.min^{-1}$, • = Flow rate: 4 $cm^3.min^{-1}$, □ = Flow rate: 12.6 $cm^3.min^{-1}$, × = exposed for 8 h, not used for quantification, — = Not detected, D = Detected)

As was observed in Table 4.2, the data in Table 4.3 showed positive artefacts at low flow rates for the tube sampler. Reasonable correlation exists between the canisters and the tube operated at higher flow rates, but in this case the concentrations of the VOCs obtained from the canister samplers are lower than those reported from the tube sampler. The data in Table 4.3 indicated that the concentration of benzene correlated with the samples taken with Carboxen SPME, the Carbotrap™ 300 tubes and the canisters.

The results of the tubes operating at 16 $cm^3.min^{-1}$ and the canisters sampled during the day compared better than the tubes and the canisters sampled during the night at the same site. According to Woolfenden (1997) pump flow rates above 5 - 10 $cm^3.min^{-1}$ should be used for tubes to minimise errors due to ingress of VOCs via diffusion. In this study, the tube samplers were connected to the manifold of a standard air quality monitoring station by a long thin Teflon tube to exclude any possible diffusion errors.

VOCs not present in the Supelco standard were also detected in samples taken at Goodwood during the day (29th July 2003), however, as mentioned in Par. 4.1.1, since no calibration standard for these compounds was available, these were not quantified. These compounds are listed in Table 4.7.

The chromatograms of samples from the SPME fibre also did not show peaks for all the compounds detected in the chromatograms from the tube and canister samples. This can possibly be ascribed to the adsorption characteristics of the SPME fibres. The MS-spectra obtained from the chromatograms from the SPME were, however, easier to interpret, because there were less background interferences in these spectra than in the spectra from the tubes.

4.1.3 Comparison of results obtained at Goodwood during night and day

By comparing the data in Table 4.2, and Table 4.3 it was evident that in general at these sites, the concentrations of most of the VOCs are lower during the night than during the day. As stated, Goodwood experienced a PM_{10} episode on 29th July 2003, and the concentration levels of all the atmospheric pollutants (see Table 4.1) were higher during the day than the night. The largest contributor for the increase in VOC concentrations at Goodwood was that this site was downwind from Athlone. The increase in VOCs might also have been due to the fact that the traffic intensity increases during the day in a residential area. Varshney and Padhy (1998) found that in

Delhi, India the TVOCs peaks at 09:00, which coincided with the peak-hour traffic in the city.

4.2 TABLE VIEW

Table View is a residential area. The site is located a few metres from an infrequently used road and is situated about one kilometre from the sea and about two kilometres north-west of the petrochemical storage tanks of the Caltex petrochemical refinery and Kynoch, a fertiliser factory.

At the Table View site only canister-samples were taken, since only a limited number of tubes were available.

Table 4.4: Concentrations (ppb) of selected volatile organic compounds at the Table View site

	▫Canister (Night)	▫Canister (Day)
Methylene chloride	0.69	—
Chloroform	—	0.21
Benzene	1.39	1.94
Toluene	2.34	0.81
Ethylbenzene	1.53	—
p-Xylene	1.40	—
m-Xylene	1.40	—
Styrene	0.95	—
o-Xylene	0.43	0.23
1,1,2,2-Tetrachloroethane	0.43	0.23
1,2,4-Trimethylbenzene	3.49	2.75
1,2-Dichlorobenzene	3.14	—

(*Nighttime sample: 28th - 29th July 2003 from 18:00 – 02:00, Daytime sample: 29th July 2003 from 06:00 – 14:00)
(**▫ = Flow rate: 12.6 $cm^3.min^{-1}$, — = Not detected)

Table View showed the lowest measured ground levels for benzene during the sampling time. This site was ± 13.5 km downwind from the city centre

(see Fig. 3.3), but Table Bay lies between these two sites. Keen (1979) concluded that sea-breezes (see Par. 2.3.1), as a result of cooling and heating of water and land, are important to circulation patterns in Cape Town. This could cause the dilution of VOCs originating from the city centre.

At this site a number of compounds not in the Sulpelco-standard were identified and are given in Table 4.7.

4.2.1 Comparison of night- and daytime samples at Table View

The total number of VOCs detected in the daytime sample as well as the concentrations of the individual VOCs were slightly lower than those measured during the nights. This is probably due to increased mixing processes during the day. During the day the average ozone concentration (measured at Goodwood) was found to be 8.7 ppb, while it was only 1.1 ppb during the night; this is probably due to an increase in photochemical reactions during the daytime. Although NO levels increased from night to day at the Table View site (see Table 4.1), NO_2 levels decreased and NO_x levels did not fluctuate significantly. Photochemical reactions could occur under these conditions in the presence of sunlight to produce ozone.

Methylene chloride, ethylbenzene, p-, m- and o-xylene and 1,2-dichlorobenzene were found in the nighttime sample but not in the daytime sample, while chloroform was detected in the daytime sample but not in the nighttime sample.

4.3 CITY CENTRE

Samples were taken at the city hall in the central business district (CBD) of Cape Town. It is to be expected that the major contributor of VOCs in this area should be emissions from traffic. Only canister samples were taken at this site due to the limited number of tubes.

Table 4.5: Concentrations (ppb) of selected volatile organic compound concentrations at the city centre site

	▫Canister (Night)	▫Canister (Day)
1,2-Dichloroethane	—	4.77
Benzene	0.93	2.06
1,2-Dichloropropane	—	3.27
Trichloroethylene	0.90	2.00
Toluene	9.26	10.4
Ethylbenzene	5.86	5.10
p-Xylene	2.51	2.41
m-Xylene	2.50	2.41
Styrene	4.78	4.59
o-Xylene	1.28	0.89
1,1,2,2-Tetrachloroethane	1.28	0.89
1,3,5-Trimethylbenzene	1.86	0.92
1,2,4-Trimethylbenzene	4.30	4.90
1,4-Dichlorobenzene	5.75	4.99
1,2,4-Trichlorobenzene	1.20	0.98
Hexachloro-1,3-butadiene	1.43	1.50

(*Nighttime sample: 28th - 29th July 2003 from 18:00 – 02:00, Daytime sample: 29th July 2003 from 06:00 – 14:00)
(*▫ = Flow rate: 12.6 $cm^3.min^{-1}$, — = Not detected)

The HCs found in these samples are mostly associated with combustion emissions from petrol and diesel vehicles. One of the reasons for the similar day- and nighttime hydrocarbon levels may probably be the active nightlife (constant traffic density) or weak removal processes at the city centre. As stated in the discussion on Table 4.1, CO was found to be higher during the day than during the night. This indicated that the traffic volume must have been higher during the day than the night. The NO concentration also increased two and a half times from night to day, NO_2 was almost three times higher during the day than the night and NO_x four times higher during the day than during the night (see Table 4.1). This data indicated a definite increase in the emissions from traffic during the day at this site. The similar night and

day VOC concentrations may be due to the longer atmospheric lifetimes of these compounds under the prevailing conditions. In the city centre the high buildings restricted the dispersion of the VOCs. Because VOCs are not vertically removed, the night and day levels of benzene, toluene, ethylbenzene, p-, m- and o-xylene and 1,2,4-trimethylbenzene do not fluctuate appreciably.

According to Dewulf and Langhove (1997) trichloroethylene has a relatively short atmospheric lifetime and at very remote continental sites the concentrations were found to be lower than the average 64 - 159 ppt, found for most continental sites. In this study the levels (see Table 4.5) measured during the day were found to be double that of the night. This is probably due to the use of trichloroethylene during the day by industries, which close down during the night.

VOCs not present in the Supelco standard were also detected in samples taken at the city centre during both night and day sampling periods. These VOCs were not quantified, but are compared with other similar results in Table 4.7.

4.4 KHAYELITSHA

Khayelitsha is an informal settlement. The sampling site is situated about 8 km south-east of the Cape Town international airport. This is an non-electrified area where paraffin and wood are the main sources of energy (see Par. 2.8.2.2). As mentioned previously PM_{10} episodes due to domestic fires were experienced during the sampling time (CMC, 2003a; CMC, 2003b).

Canister samples were taken at ground level. Special permission was granted to undertake a low level flight so that canister samples were taken at an altitude of 500 ft above ground level (AGL).

Table 4.6: Concentrations (ppb) of selected volatile organic compound concentrations at the Khayelitsha site

	□Canister (Night)	□Canister (Day)	◇Canister (500 ft AGL)
Freon -113	B	—	—
Chloroform	0.96	1.34	1.37
Benzene	1.58	0.81	—
Carbon tetrachloride	B	B	—
Trichloroethylene	2.29	0.80	—
Toluene	4.80	2.96	0.27
Tetrachloroethylene	0.72	0.62	—
Chlorobenzene	—	—	0.93
Ethylbenzene	2.95	1.97	—
p-Xylene	0.71	2.46	—
m-Xylene	0.70	2.45	—
Styrene	0.51	—	—
o-Xylene	0.60	0.51	—
1,1,2,2-Tetrachloroethane	0.60	0.51	—
1,3,5-Trimethylbenzene	0.87	0.74	—
1,2,4-Trimethylbenzene	0.92	4.10	—
1,3-Dichlorobenzene	0.29	0.90	0.11
1,2-Dichlorobenzene	—	1.05	—

(*Nighttime sample: 28th - 29th July 2003 from 18:00 – 02:00, Daytime sample: 29th July 2003 from 06:00 – 14:00, Air sample: 29th July 2003 - 10 minutes at 500 ft)

(**□ = Flow rate: 12.6 $cm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

The nighttime VOC values in general were higher than the daytime's. The only VOC detected in the daytime samples and not the nighttime samples on ground level was 1,2-dichlorobenzene.

While benzene, trichloroethylene, toluene, tetrachloroethylene, ethylbenzene, o-xylene, 1,1,2,2-tetrachloroethane and 1,3,5-trimethylbenzene have higher levels at night, the other compounds p- and m-xylene, 1,2,4-trimethylbenzene and 1,3-dichlorobenzene had higher levels during the day than during the night. Styrene was only detected in the night sample.

This was the only site where carbon tetrachloride was detected (in both the day and night sample), although it was below the stated detection limit of the analytical method. Chloroform was detected in the night sample as well as in

the day sample. The concentration levels in the ground sample and the sample taken at 500 ft AGL correlated with each other. Chlorobenzene was detected in the sample taken at 500 ft AGL but not in the sample taken at ground level - this probably indicated a remote source.

The increase in the benzene levels found during nighttime is most probably linked to the following factors:

1. The concentration of people in the township increases during the night as the people move back from the central business districts to their homes. The higher concentration of people at night as well as the heating and cooking methods used in such an environment will contribute to the higher concentrations of certain pollutants during the night.
2. Traffic from the highways surrounding Khayelitsha will contribute to the VOCs measured at this site.
3. The concentration of benzene is reduced during the day due to better dispersion processes, since the estimated lifetime of benzene is in the order of days (see Par. 2.5.9).

VOCs not quantified are again given in Table 4.7.

VOCs sampled at an altitude of 500 ft AGL above Khayalitsha identified using the MS NIST library database included: acetone, propane, butanal, propanal, 2-butanone, 3-methylbutanal, hexanal, 3-methylheptane, 1-dodecane and 1,1,3,1-terphenyl. These also included aldehydes and ketones as possible products of VOCs in photochemical reactions.

4.5 COMPARISON OF VOCs DETECTED IN THE GROUND LEVEL (CONCENTRATIONS) NOT QUANTIFIED

As already stated in Par. 4.1 – 4.4 a large number of species not included in the Sulpelco standard were also observed in the tube, canister and SPME samples at ground level, however since no calibration standard was available, these compounds could not quantified (see Table 4.7). The compounds

found were identified using the MS NIST library database. Instead of the retention times, the scan numbers are given in Table 4.7. It was simpler to rather compare scan numbers than retention times.

Table 4.7: Volatile organic compounds not quantifiable on ground level in Cape Town (Abundances in arbitrary units)

		Goodwood			Goodwood				Table View		City centre		Khayelitsha	
		Night			Day				N	Day	Night	Day	Night	Day
Scan	VOC	○ T	● T	□ C	○ T	● T	□ C	× S	□ C	□ C	□ C	□ C	□ C	□ C
58	Butane	–	–	34.0	–	–	36.0	–	–	24.5	–	12.0	48.00	24.0
100	Acetic acid	–	–	–	–	–	–	–	–	–	–	1.23	–	0.50
121	Isopropylamine	–	–	–	–	–	–	–	–	–	–	–	–	15.3
174	2-Methylbutane	78	109	–	208	187	190	–	–	–	–	68	90	–
178	Acetone	–	–	–	–	60.1	49.5	D	–	–	–	–	56.3	–
188	1-Pentene	–	1263	700	105	198	124	D	380	–	278	–	–	–
195	3-Methylbutane	–	175	–	136	–	–	–	–	–	–	157	–	–
197	Pentane	331	763	365	356	386	400	D	–	200	425	782	198	158
202	2-Methyl-1,3-butadiene	–	–	–	–	188	–	–	440	–	–	–	176	–
226	2-Methylbutene	27.3	54.0		14.6	16,7	–	–	11.2	4.03	33.5	17,2	65.0	–
229	2,2-Dimethylbutane	–	11.2	–	–	–	–	–	–	–	–	–	8.06	–
232	Not identified conclusively	–	–	–	–	–	2.45	D	–	–	–	1.34	5.22	0.34
232	1-Chloropentane	–	–	–	–	–	–	–	–	–	–	–	5.23	–
233	2,2-Dimethylbutanone	–	–	–	–	–	–	–	–	–	–	–	4.37	2.21
235	1,2-Dimethylcis-cyclopentane	–	–	–	–	–	–	–	–	–	–	–	1.45	–
236	Not identified conclusively	1.34	3.54	–	2.04	2.15	–	D	–	–	–	–	5.09	–
239	Not identified conclusively	–	–	–	–	–	–	–	2.11	–	–	–	–	
248	2-Methylbutane	–	29.8	13.2	1872	1069	2001	D	–	–	–	999	874	–
252	Cyclopentanone	–	13.5	–	–	–	–	–	7.64	–	–	–	6.41	–
255	2,2-Dimethylbutane	–	–	–	–	–	–	–	–	–	–	–	4.73	–
257	2,3-Dimethylbutane	–	–	–	–	15.4	–	D	–	–	–	11.5	9.78	–
259	Not identified conclusively	–	–	0.57	1.26	1.77	1.99	–	–	–	–	–	–	
265	2-Methyl-1-butene	–	–	–	–	4.55	–	D	–	–	–	–	–	–
265	2-Butanone	–	–	16.3	–	–	–	–	–	7.32	–	22.3	–	64.2
279	Cyclopentane /1-Hexene	–	–	–	22.7	36.4	–	D	11.4	–	–	18.4	–	9.34
280	3-Butanone	–	–	–	–	–	–	–	–	–	–	–	–	2.43
281	Cyclopentamine	–	1.34	0.36	0.26	–	0.54	D	–	–	–	–	–	–
283	3-Methylpentane	105	–	98.0	–	–	–	–	–	–	–	–	124	98.5
288	2-Butanol	57.3	82.8	–	–	–	–	–	14.6	–	–	27.6	–	–
290	2-Methyl-furan	–	286	–	–	–	–	–	–	–	–	–	789	–
301	Hexane	1486	980	1365	–	–	–	–	–	–	659	2086	789d	650
311	Methylcyclopentane	–	180	–	307	–	287	D	–	198	–	315	298	367
315	Ethyl ester formic acid	–	–	–	–	–	–	D	–	–	–	–	–	0.76
318	Not identified conclusively	3.52	8.99	–	1.03	2.01	–	–	–	–	–	–	5.23	
327	Methylcyclopentane	–	–	–	1.35	–	–	D	–	–	–	–	–	–
330	Cyclohexane	402	450	–	12.8	16.4	9.12	D	–	4.12	–	6.12	–	–
339	2-Propenylester-formic acid	37.8	–	–	–	–	–	–	–	–	–	–	–	–
340	2-Methyl-1-pentene	–	–	–	–	–	25.4	–	–	–	–	–	61.3	–
343	Cyclopentone	–	–	–	5.32	–	–	–	19.5	52.6	–	–	78.5	–
347	2-Methylhexane	–	–	–	–	–	18.3	–	12.4	–	–	–	14.5	–
349	3-Methylhexane	–	–	–	–	–	22.4	–	15.3	–	–	–	–	8.43
350	2,3-Dimethylpentane	–	–	–	–	–	–	–	–	–	–	–	7.84	–
354	5-Methyl-2-decene	–	–	–	–	–	–	–	5.23d	–	–	–	–	–
354	6-Methyl-3-undcane	–	–	–	56.3	75.4	63.2	D	22.6	–	–	74.4	–	–
357	Not identified conclusively	7.89	13.4		5.43	5.42		D	–	–	–	–	–	–
363	Heptane	–	179	132	102	89.5	98.4		–	–	–	432	–	–
365	3-Butenylbenzene	–	–	–	22.4	–	–	D	–	–	–	–	–	–
370	3,3-Dimethyl-2-butanone	–	–	–	–	–	–	–	–	–	–	–	22.4	–
372	6-Methyl-3-undecene	–	–	–	67.4	–	–	–	–	–	–	–	–	–
372	1-(Ethyloxy)-2-methylpropane	–	–	–	–	–	–	–	–	–	–	23.7	–	–

Table 4.7: *(Continued)*

		Goodwood			Goodwood				Table View		City centre		Khayelitsha	
		Night			Day				N	Day	Night	Day	Night	Day
Scan	VOC	○ T	● T	□ C	○ T	● T	□ C	× S	□ C	□ C	□ C	□ C	□ C	□ C
376	2-Heptene	–	–	–	–	–	13.2	D	–	–	31.4	22.4	24.5	–
380	Not identified conclusively	314	71.3	–	206	37.2	–	D	–	–	–	–	13.4	–
382	5-Methyl-2-hexene	12.4	27.4	–	8.41	–	–	D	8.41	5.61	–	–	–	–
392	Methyl-isobutylketone	–	–	19.5	4.32	–	3.21	D	–	–		–	–	5.62
396	4-Methyl-3-penten-2-one	862	773	812	85.4	47.6	–	–	–	–	–	–	–	–
396	2-Methylheptane	–	13.4	–	–	–	–	–	–	–	15.4	20.7	12.4	–
408	3-Methylheptane	–	18.4	20.4	–	–	–	–	–	–	–	–	16.5	22.7
425	Not identified conclusively	442	885	–	71.6	40.8		D	–	–	–	–	–	–
428	1-H-tetrazol-5-amine	–	–	–	–	–	–	–	–	–	–	–	71.5	–
430	Not identified conclusively	65.1	99.2			365	–	–	–	–	–	–	–	–
437	1-Octene	275	–	–	289	253	276	–	–	–	–	–	–	–
445	Octane	22.4	34.6	18.4	38.2	47.4	–	D	–	20.1	57.96	–	33.2	–
450	3-Methyloctane	–	–	–	46.3	–	–	–	–	–	–	–	12.4	–
464	1,4-Dichlorobenzene	–	–	–	112 3	–	–	–	–	–	–	–	878	–
473	1,3-Dimethylbenzene	–	231	442	897	656	–	D	–	–	–	–	678	–
487	1,2-Dimethylbenzene	–	–	–	–	–	–	–	–		342	218	915	–
491	1,4-Dimethylbenzene	–	–	–	–	–		–	–	54.3	–	–	920	–
492	2-Heptanone	–	–	–	–	–	–	–	–	–	–	34.8	–	–
503	1-Ethyl-3,5-dimethylbenzene	54.7	80.7	23.7	–	–	–	–	–	–	–	–	42.7	–
511	Nonane	114	101	120	–	69.5	54.2	D	–	–	–	80.2	135	118
527	2-Methylpyridazine	–	–	–	–	–	–	–	–	–	–	58.7d	–	–
529	Not identified conclusively	–	–	–	–	21.7	–	–	25.8	–	–	–	29.7	–
530	Methyl-carbamic acid	–	41.7	–	–	–	–	–	–	–	–	–	–	56.7
534	3-Methylpyridazine	50.6	49.6	–	62.7	77.7	–	–	–	–	–	–	–	–
535	Benzaldehyde	–	–	–	–	–	–	–	–	–	48.5	–	–	–
537	1,3-Hydoxethone	15.8	17.9	–	–	–	–	–	–	–	–	–	–	–
541	Isopropylbenzene	44.3	34.1	–	62.7	51.4	d	D	–	–	–	21.9	25.8	–
543	Not identified conclusively	54.4	78.4	–	100	79	–	D	–	–	–	68.9	–	–
546	Methyl-carbamic acid	668	987	23.7	–	–	–	–	41.9	–	–	–	67.9	–
549	1-Ethyl-3-methylbenzene	–	–	–	212	–	200	–	–	–	–	–	414	173
558	1-Ethyl-2-methylbenzene	–	–	–	–	64.5	–	–	–	–	–	111	85.7	–
552	1,2,4-Trimethylbenzene	584	142	66.2	115	57.9	118	D	62.4	–	–	222	–	–
566	1,3,4-Trimethylbenzene	684	–	92.5	–	56.6	–	–	–	–	–	210	–	198
572	Not identified conclusively	539	214	129	98.6	124	100	D	67.9	–	–	–	–	–
573	Undecane	–	56.3	48.9	–	78.2	–	–	–	–	–	–	80.5	95.6d
575	1,3-Dichlorobenzene	–	–	565	412	–	–	–	–	–	–	–	–	–
577	Decane	18.8	21.9	24.7	34.5	28.6	d	D	–	–	–	79.4	55.2	63.1
583	1,4-Dimethylbenzene	–	882	752	–	453	456	D	–	–	–	–	612	–
585	2-Ethyl-1,4-dimethylbenzene	74.3	258	83.0	–	–	41.6	D	–	–	–	–	124	63.9
587	2,6,10,14-Tetramethylhexane	–	–	–	–	–	–	–	–	–	–	–	68.9	–
588	4-Methyldecane	–	–	–	–	–	–	–	–	–	–	–	52.7	–
593	Limonene	–	–	–	60.1	–	–	D	–	–	–	–	–	–
601	1-Ethyl-2,4-dimethylbenzene	525	149	117	–	85.8	–	–	–	–	–	–	163	–
603	1,2-Diethylbenzene	598	140	–	112	–	–	D	–	–	–	–	119	98.2
604	1-Methyl-2-propylbenzene	–	47.5	–		–	23.4	–	–	–	–	–	–	25.9
609	1,3-Diethylbenzene	712	–	98.0	117	–	–	D	–	–	–	–	124	78.4
607	1-Methylpropylbenzene	–	52.7	–	–	–	–	D	–	–	–	–	–	–
620	1-Ethyl-2,4-dimethylbenzene	28.9	34.9	9.34	–	22.6	6.34	D	–	–	–	–	38.7	–
625	2-Ethyl-1,4-dimethylbenzene	72.6	–	–	–	–	–	–	–	–	–	–	95.4	12.3
629	Not identified conclusively	–	–	–	–	–	–	–		–	67.4	–	55.4	32.1
630	Tridecane	33.7	–	–	–	–	–	–	–	–	–	–	–	12.1
641	1,2,4,5-Tetramethylbenzene	76.9	80.4	12.3	–	9.84	–	D	–	–	–	–	112.6	98.4
663	1-Amine-3,5-dimethylbenzene	11.4	9.83	–		–	–	–	–	–	–	–	–	–
671	1,2,4-Trichlorobenzene	98.4	17.5	12.2	–	–	–	D	–	9.84	–	7.98	–	–
675	No tidentified conclusively	6.73	7.53	9.43	–	–	–	–	–	–	–	–	–	–
676	Naphtalene	–	–	–	–	4.32	–	D	–	–	–	–	33.9	–
681	Dodecane	989	195	789	–	–	–	–	762	–	–	–	–	136
680	1,3,5-Trimethyloctane	–	–	114	–	98.4	76.4	D	–	–	–	–	117	127
683	1,4-Diethylbenzene	–	115	121	224	362	356	–	–	–	–	654	–	–

Table 4.7: *(Continued)*

		Goodwood			Goodwood				Table View		City centre		Khayelitsha	
		Night			Day				N	Day	Night	Day	Night	Day
Scan	VOC	○ T	● T	□ C	○ T	● T	□ C	× S	□ C	□ C	□ C	□ C	□ C	□ C
687	1-(2-naphthalenylmethyl)-naphthalene	–	–	–	–	–	–	D	–	–	–	–	–	–
691	6-Methyl-octadecane	24.6	–	–	27.9	–	–	–	–	–	67.9	–	–	–
700	1-Chloro-8-heptadecene	–	98.2	76.2	–	–	–	–	–	–	–	–	74.3	–
714	Not identified conclusively	34.1	49.2	–	–	–	–	–	–	–	–	–	–	–
722	Not identified conclusively	21.7	32.5	–	–	–	–	–	–	–	–	–	–	15.7
731	1-Methylnaphtalene	9.43	–	–	–	–	–	–	–	–	–	–	–	6.78
734	Not identified conclusively	–	108	–	–	–	–	–	–	–	–	–	112	134
732	Tetradecane	–	37.6	–	–	–	–	–	–	–	–	–	65.4	84.2
743	Not identified conclusively	–	24.3	–	–	–	–	–	–	–	–	–	–	–
749	1,2,3,4-Tetrachlorobenzene	–	–	–	–	–	–	–	–	–	–	–	–	112
761	Hexadecene	23.4	41.5	36.2	–	–	–	–	–	–	–	–	–	–
768	Hexadecane	–	30.8	–	–	–	–	–	–	–	–	–	–	186
799	Pentadecane	–	–	–	–	–	–	–	304	–	–	–	–	–
801	2-Butyl-1-octanol	–	–	–	9.87	–	–	–	–	–	–	–	–	6.89
809	2,3-Dihydro-1-methylindene	–	–	–	–	–	–	–	–	–	–	–	13.7	–
811	1,1,3,4-tetrachloro-1,2,2,3,4,4-hexafluorobutane	–	–	–	–	–	–	–	–	–	–	–	11.9	–
828	Diethylphtalate	–	–	7.91	–	–	–	D	2.12	–	–	–	8.91	4.31

(*Nighttime sample: 28th - 29th July 2003 from 18:00 – 02:00, Daytime sample: 29th July 2003 from 06:00 – 14:00)
(**○T = Tube samplers with flow rate: 16 $cm^3.min^{-1}$, •T = Tube sampler with a flow rate: 4 $cm^3.min^{-1}$, □C = Canister samplers with flow rate: 12.6 $cm^3.min^{-1}$, ×S = SPME exposed for 8 h, — = Not detected, D = Detected)

From a comparison of the different ground level samples from Table 4.7 the following observations were made:

Goodwood

It appeared that some of the VOCs found in the Goodwood samples are associated with petrol and diesel and the combustion products of these fuels. A large number of species found in the Goodwood samples was detected only in the Goodwood and Khayelitsha samples, and not in the Table View or the city centre samples. These VOCs probably originated in Athlone and were transported towards Goodwood. In the Goodwood day sample, the only PAH compound found was (1-(2-naphthalenylmethyl)-naphthalene).

Table View

This was the site where the lowest levels of different VOCs were detected. This correlates with the data in Table 4.1 – where Table View had relatively lower levels of other pollutants (NO and NO_x) compared to the other sites in this study. In the night samples more unsaturated VOCs were detected than in the daytime samples, these compounds are probably oxidised by O_3 and photo-oxidants during the day. The night samples also contained a longer

chain hydrocarbon (e.g. 4-ethyl-1-methylbenzene); this is probably reduced to a shorter chain compound (1,4-dimethylbenzene) during the day by means of photochemical reactions.

City centre

The following compounds detected in the night sample but not included in the Supelco standard were identified by using the MS NIST library database: 1-pentene, pentane, 2-methylbutane, hexane, heptane, 2-heptene, 3-methylheptane, octane, 1,2-dimethylbenzene, benzaldehyde, decane, undecane and 6-methyl-octadecane. In the day samples the following VOCs were detected but could not be quantified: butane, acetic acid, 2-methylbutane, 3-methylbutane, pentane, 2-methylbutene, 2-methylbutane, 2,3-dimethylbutane, 2-butanone, cyclopentane, 2-butanol, hexane, methylcyclopentane, cyclohexane, 3-methyl-3-undecane, heptane, 1-(ethyloxy)-2-methylpropane, 2-heptene, 2-methylheptane, 2-heptanone, 2-methylpyridazine, nonane, isopropyl benzene, 1-ethyl-2-methylbenzene, decane, 1,2,4,-triethylbenzene, 1,3,4,-triethylbenzene, decane, 1,2,4-trichlorobenzene and 1,4-dimethylbenzene. The number of carbonyl groups detected in the daytime samples, supported the idea that carbonyls originate due to photochemical reactions.

Khayelitsha

The night sample at this site contained more VOCs than the day sample. These samples contained a large number of complex VOCs not detected at other sites, which included the two PAHs naphthalene and 1-methylnaphtalene. The VOCs detected in the nighttime samples were associated with domestic fires for heating and cooking.

Volatile organic species

The following lists give a summary of the VOCs that could not be quantified at the different ground level samples from Table 4.7:

1. A large number of alkanes were found at all the sites. Pentane was detected in all the samples except in the sample taken at Table View during the night.
2. The following alkenes were detected in samples: 2-methylbutene, 1-pentene, 2-methyl-1-butene, hexane, 2-methyl-1-pentene, 5-methyl-2-decene, 2-heptene, 1-octene, 5-methyl-2-hexene, 2-methyl-3-undecene, 6-methyl-3-undecene and 2,3-dihydro-1-methylindene. Although some were found in the day samples, most of these VOCs were detected in the night samples. This can probably be explained by the fact that alkenes contain reactive double bonds that are more likely to react with radicals during the daytime.
3. Although this study did not concentrate on BVOCs, typical BVOCs detected included isoprene (2-methyl-1,3-butadiene) in the night sample taken at Khayelitsha and limonene in Goodwood.
4. Halogenated hydrocarbons included: 1-chloropentane, 1,4-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, 1-chloro-8-heptadecene, 1,2,3,4-tetrachlorobenzene and 1,1,3,4-tetrachloro-1,2,2,3,4,4-hexafluorobutane. (See the back trajectory analysis plot – Appendix 1)
5. 2-Butanol and 2-butyl-1-octanol represent the alcohols detected in samples. Alcohols form HO· radicals that can take part in photochemical reactions.
6. A number of benzene compounds were also detected in these samples, these included methyl-, ethyl- and chlorine-containing benzenes.
7. Acetic acid, 2-propenylester-formic acid and methyl-carbamic acid were detected in the Khayelitsha daytime sample. The SPME sample showed the presence of an ethyl ester formic acid in the Goodwood daytime sample.
8. Diethylphtalate was detected in the samples from Goodwood, Table View and Khayelitsha.

9. 2-Methylpyridazine and 3-methylpyridazine were both detected in some samples.
10. Nitrogen-containing VOCs included: isopropyl amine, 1-H-tetrazol-5-amine, cyclopentamine and 1-amine-3,5-dimethylbenzene
11. The following ketones were detected: acetone, 2,2-dimethylbutone, cyclopentanone, 2-butanone, 3-butanone, cyclopentone, 1,3-hydoxethone, 3,3-dimethyl-2-butanone, methyl-isobutylketone, 4-methyl-3-penten-2-one and 2-heptanone.

4.6 COMPARISON OF RESULTS AT GROUND LEVEL IN THE DIFFERENT AREAS IN CAPE TOWN

4.6.1 Residential areas

1,3,5-Triethylbenzene, ethylbenzene, p- + m-xylene, styrene, 1,2-dichlorobenzene were detected in the daytime sample taken at Goodwood but not in the daytime sample taken at Table View. Methylene chloride was detected in the nighttime sample in Table View but not in the Goodwood night sample indicating a marine influence at Table View.

The nighttime benzene levels at the Table View site (also a residential area but in close vicinity of petrochemical storage tanks) were very low if compared to the levels of Goodwood, due to the prevailing meteorological conditions at the time of sampling. As stated the south-east wind transported pollution on 29th July 2003 from Athlone towards Goodwood. This correlates with data in Table 4.1 that indicates that NO_x, SO_2 and PM_{10} concentrations were higher than Table View during the sampling period. It also correlated with the data that indicated that the concentration levels of NO_x, SO_2 and PM_{10}, chloroform, toluene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene in the Goodwood-site increased from the night to the day.

These results can be partly explained by the prevailing meteorological conditions and geographical position of this site at the time of sampling. As stated in Par. 4.1 it must be noted that the traffic highways N7, N1 and the

R102 pass near the Goodwood site. The VOCs found in Goodwood, thus originated from domestic fires as well as traffic. The increased daytime benzene levels can thus probably be explained by these traffic emissions.

4.6.2 Residential areas compared to the city centre

1,2-Dichloroethane, 1,2-dichloropropane and trichloroethylene were detected in the daytime samples taken at the city centre but not in any of the samples taken at the residential areas. While 1,4-dichlorobenzene, 1,2,4-trichlorobenzene and hexachloro-1,3-butadiene were detected in both the night and the day samples taken at the city centre, these VOCs were not detected in the samples taken at the residential areas. In general, more chlorine-containing compounds were found in the city centre samples than in the samples from the residential areas.

According to Mohamed *et al.* (2002) methyl chloride is the highest at locations close to large bodies of salt water, due to biogenic production of marine phytoplankton. Methylene chloride was detected in the daytime sample from Goodwood (only in the canister) and in the nighttime sample taken at Table View. This result can most probably be explained by the fact that the wind was blowing during the night from the sea towards the land and towards the Table View site. Under the prevailing wind conditions the distance from the sea to the land is further for the Goodwood site than for the Table View site.

Dewulf and Langehove (1997) determined that chloroform concentrations measured over remote open seas normally range from 8.8 to 45 ppt range, while chloroform measured at remote coastal sites were 19 to 875 ppt. These values were found to be high in comparison with remote non-coastal sites. It was suggested that both natural biotic or abiotic sources contribute to the formation of chloroform. Results from this study indicated that chloroform originates not only from the sea but also from inland sources. Chloroform was detected during the day at both residential sites, but not at the city centre. If the concentrations of chloroform are only due to sources from the sea the concentrations should then have been higher during the night when the wind

direction is from the sea towards the land and not as found in this study. This unfortunately does not explain why it was not detected at the city centre. Khalil and Rasmussen (1983) measured chloroform 1 000 km from the nearest anthropogenic source. If long-range transportation is the only reason for increased chloroform levels kilometres downwind of sources (Godish, 1991) then the day and the night levels should correlate with each other. A more reasonable explanation could probably be the evaporation of chloroform from certain industries. These industries are probably closed down during the night, so that the chloroform concentration is diluted during the night. Nighttime is generally cooler than the daytime and the evaporation rates at night are lower than during the day.

The main sources of VOCs in the city centre appeared to be motor vehicle emissions, industries and the ocean.

4.6.3 Residential areas compared to informal settlements

As stated in Par. 4.5, in Khayelitsha a wide range of different VOCs was detected. A comparison of the types and concentrations of VOCs found in residential areas and in Khayelitsha indicated that there is a better agreement with Goodwood, than with Table View. The main source of pollution in Khayelitsha is the inefficient burning of paraffin, wood and coal. The main source of VOCs in Table View is emissions from motor vehicles. In Goodwood it was domestic fires from Athlone and traffic sources. Carbon tetrachloride, trichloroethylene, tetrachloroethylene and 1,3-dichlorobenzene were detected during the night and the day at Khayelitsha but not at any of the residential areas. Freon-113, although below the detection limit of the method, was also detected at Khayelitsha but not at any of the other residential areas.

4.6.4 An informal settlement compared to the city centre

Both the city centre and Khayelitsha have higher levels of chlorine containing compounds than the residential areas. The following VOCs were detected at Khayelitsha but not at the city centre: freon-113, chloroform, carbon tetrachloride, tetrachloroethylene, 1,3- and 1,2-dichlorobenzene. 1,2-Dichloroethane, 1,2-dichloropropane, 1,4-dichlorobenzene and hexachloro-1,3-butadiene were detected at the city centre during the day, but not at Khayelitsha.

4.7 RESULTS FOR DIFFERENT ALTITUDES OVER THE CAPE TOWN REGION

The samples taken at different altitudes were for shorter time intervals (10 - 14 minutes) than the samples taken at ground level (8 hours). Higher flow rates (0.23 $dm^{-3}.min^{-1}$) were used so that volumes between 2.3 – 3,2 dm^3 were sampled during the flights on 29th July 2003.

The results in this section will be presented and discussed in the following way: The results of samples taken at 1 000 (Par. 4.7.1) and 1 500 ft AGL (Par. 4.7.2) will be discussed separately. The results of VOCs that could not be quantified will be given for each flight level. The VOCs sampled at different altitudes will be compared in Par. 4.7.3, initially flights from Rondebosch to Muizenberg and Strand at different altitudes followed by flights around Goodwood at different altitudes.

4.7.1 Samples taken at 1 000 ft above ground level

VOCs found in the canister and tubes at 1 000 ft AGL are given in Table 4.8.

Table 4.8: Concentrations (ppb) of selected VOCs sampled at 1 000 ft AGL

	Rondebosch to Muizenberg to Strand		Rondebosch to Goodwood	
	◆ Tube	◇ Canister	◆ Tube	◇ Canister
Freon-12	B	—	—	—
Chloroethane	—	—	1.38	—
Methylene chloride	1.12	—	—	—
Freon-13	—	—	0.20	—
Chloroform	0.45	0.38	0.52	0.28
Cis-1,2-Dichloroethylene	—	—	1.12	—
1,2 - Dichloroethane	—	—	—	2.51
1,1,1-Trichloroethane	0.85	0.54	—	1.10
Benzene	—	—	0.82	0.57
1,2-Dichloropropane	—	—	—	0.61
Trichloroethylene	—	—	24.7	—
Cis-1,3-Dichloropropene	—	—	—	1.12
Toluene	0.72	0.62	80.7	31.4
Ethylbenzene	0.71	0.62	—	0.43
Styrene	2.09	—	—	—
1,2,4-Trimethylbenzene	—	4.26	17.3	4.73
1,3-Dichlorobenzene	—	—	0.35	—

(*Samples taken on 29th July 2003 for 10 - 14 minutes)

(◆ = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

At 1 000 ft AGL from Rondebosch to Goodwood a very strong peak from 1-butanol was found in the tube sample that probably originated from a single source. This might also have resulted in the very high concentration of trichloroethylene, toluene (80.7 ppb) and 1,2,4- trimethylbenzene found in the tube sample. The 1-butanol peak in this sample was so intense; it overlapped the benzene and carbon tetrachloride peaks in the GC trace in such a way that it masked the peaks of these compounds.

Table 4.9: Volatile organic compounds not quantifiable sampled at 1 000 ft AGL (Abundances are in arbitrary units)

		Rondebosch to Muizenberg to Strand		Rondebosch to Goodwood	
Scan	VOC	◆ Tube	◇ Canister	◆ Tube	◇ Canister
116	Not identified conclusively	—	—	0.18	—
150	Not identified conclusively	—	—	—	62.13
159	1-Butene	—	—	—	15.7
165	Not identified conclusively	—	—	—	23.4
170	Not identified conclusively	—	—	—	19.4
178	Acetone	—	—	0.27	—
205	Metoxy-ethene	—	—	—	17.4
262	2-Methylbutene	—	—	—	22.8
266	Hexane	63.4	—	102	111
271	2-Butanone	—	—	64.3	—
318	Not identified conclusively	—	—	—	11.4
347	Hexanol	18.9	—	—	—
349	1-Butanol	—	—	9648	8321
438	2-Hexanol	—	—	—	68.4
465	Butyl ester acetic acid	25.6	—	—	—
446	2,2,5-Trimethylhexene	—	—	—	16.8
481	Ethylcyclohexane	—	—	—	14.2
500	1-Chloropentane	212	—	—	—
553	6-Dimethyl-5-hepten-2-one	78.2	—	—	—
561	Propylbenzene	—	—	—	72.9
563	1-Methyl-1H-tetrazole	7.32	—	—	—
574	Decane	—	—	—	50.2
747	Not identified conclusively	—	—	—	20.1

(*Samples taken on 29th July 2003 for 10 - 14 minutes)

(** ◆ = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, D = VOC was detected, but could not be quantified.)

A number of VOCs present in the GC chromatograms could not be identified conclusively. As stated a very intense 1-butanol peak was observed on the flight from Rondebosch to Goodwood.

4.7.2 Samples taken at 1 500 ft above ground level

Table 4.10: Concentrations (ppb) of selected VOCs sampled at 1 500 ft AGL

	Take off to Muizenberg	Rondebosch to Muizenberg to Strand		Rondebosch to Goodwood		Malmesbury to Goodwood
	*Tube	*Tube	◇Canister	*Tube	◇Canister	*Tube
Methylene chloride	—	0.65	0.25	0.45	—	—
Freon-113	B	B	—	—	—	—
Chloroform	0.21	0.20	0.47	0.28	0.41	B
1,1,1-Trichloroethane	—	—	—	—	0.46	—
Benzene	—	0.66	0.40	0.72	0.51	0.61
Toluene	—	11.5	2.23	6.56	2.25	2.94
Styrene	—	0.94	—	—	—	—
1,2,4-Trimethylbenzene	8.2	4.78	2.51	7.01	2.68	—
1,3-Dichlorobenzene	—	0.46	0.67	—	—	—

(*Samples taken on 29th July 2003 for 10 - 14 minutes)

(*** = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

Toluene and 1,2,4-trimethylbenzene were found to be present in the analysis of the laboratory blank taken before the analysis of the tube sampled during the Rondebosch, Muizenberg and Strand flight. Although the value of the laboratory blank was subtracted, the concentration of toluene in the tube remained much higher than the toluene in the canister. This is probably due to the fact that toluene has a tendency to remain in the sampling system. The sample taken at Malmesbury (a rural area 50 km to the north of Cape Town) contained less man-made VOCs than those from Rondebosch to Goodwood or to Muizenberg. Chloroform levels in these samples seemed to correlate well.

Table 4.11: Volatile organic compounds not quantifiable sampled at 1 500 ft AGL (Abundances in arbitrary units)

		Take off to Muizenberg	Rondebosch to Muizenberg to Strand		Rondebosch to Goodwood		Malmesbury to Goodwood
Scan	VOC	*Tube	*Tube	◇Canister	*Tube	◇Canister	*Tube
82	Not identified conclusively	11.3	—	—	—	—	—
116	Not identified conclusively	—	—	21.3	—	62.8	—
130	Not identified conclusively	—	—	—	—	—	27.8
150	1-Butene	—	11.8	—	9.21	—	—
159	1-Butane	—	74.8	—	133	—	58.2
165	Not identified conclusively	—	—	—	—	—	57.9
178	Acetone	—	—	—	—	124	—
192	Pentene	58.3	—	—	—	—	—
201	2-Methylbutanone	76.8	—	—	114	—	43.2
246	Pentane	124	—	—	62.1	—	32.4
249	Hexane	—	—	—	—	—	247
255	2,2-Dimethylbutane	—	—	43.9	—	—	—
260	2-Methylbutene	—	—	—	—	79.4	—
271	2-Butanone	—	—	22.8	—	78.3	—
340	2-Methyl-1-pentene	—	—	—	73.6	—	—
349	1-Butanol	—	—	—	230	—	—
353	3-Methylhexane	—	82.1	—	—	—	—
364	Heptane	72.8	52.1	—	60.4	—	—
413	Not identified conclusively	—	—	—	—	114	—
437	Phenol	—	—	—	—	54.4	—
465	Butyl ester acetic acid	113	109	—	—	—	—
573	Ether/alcohol	—	—	62.5	—	—	—
588	4-Methyldecane	16.8	—	—	32.1	—	—
621	Nonanal	—	221	—	—	—	—
656	2-Ethylhexanoic acid	—	84.9	—	—	—	—
701	Not identified conclusively	—	35.9	—	—	—	—
741	Dodecane	—	32.1	—	—	—	—
766	Not identified conclusively	—	—	27.4	—	—	—
809	2-Methylpiperazine	12.1	—	—	—	—	—
826	Diethyl phthalate	—	2.13	—	3.13	—	—

(*Samples taken on 29th July 2003 for 10 - 14 minutes)

(* = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, D = VOC was detected, but could not be quantified.)

As with Table 4.9 a number of VOCs present in the GC chromatograms that could not be identified conclusively are given. These compounds do not correlate well with the MS-NIST library fits.

4.7.3 Comparison of results obtained at different altitudes

Table 4.12: Concentrations (ppb) of selected VOCs at different altitudes on flights from Rondebosch to Muizenberg to the Strand

	1 000 ft		1 500 ft	
	*Tube	◇Canister	*Tube	◇Canister
Freon-12	B	—	—	—
Methylene chloride	1.12	—	0.65	0.25
Freon-113	—	—	B	—
Chloroform	0.45	0.38	0.47	0.20
1,1,1-Trichloroethane	0.85	0.54	—	—
Benzene	—	—	0.66	0.40
Toluene	0.72	0.62	11.5	2.23
Ethylbenzene	0.71	0.62	—	—
Styrene	2.09	—	0.94	—
1,2,4-Trimethylbenzene	—	4.26	4.78	2.51
1,3-Dichlorobenzene	—	—	0.46	0.67

(*Samples taken on 29th July 2003 for 10 - 14 minutes)

(** = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

The sudden increase in toluene levels in the tube at 1 500 ft is probably due to the tendency of toluene to remain in the sampling system. Although 1,2,4-trimethylbenzene was not detected at 1 000 ft with the tube, the other results indicated that the level remained constant at the different levels.

At 1 000 ft the following VOCs not detected at 1 500 ft were found; hexanol, 1-chloropentane, 6-dimethyl-5-hepten-2-one and 1-methyl-1-H-tetrazole. The following VOCs were detected at 1 500 ft but not at 1 000 ft: acetone, 1-butene, 1-butane, 2-butane, heptane, nonanal, 2-ethylhexanoic acid dodecane and diethyl phthalate. Butyl ester acetic acid was the only VOC that could not be quantified but identified in both layers.

It can be concluded from Table 4.11 (and from the VOCs not quantified) that the concentrations of the VOCs at different altitudes differ significantly. This correlated with the brown haze found in layers and it appeared that the concentrations of the VOCs in these layers are different.

Table 4.13: Concentrations (ppb) of selected VOCs on ground level in Goodwood and at different altitudes on flights from Rondebosch to Goodwood

	Ground level (Goodwood)			1 000 ft		1 500 ft	
	○Tube	●Tube	□Canister	◆Tube	◇Canister	◆Tube	◇Canister
Chloroethane	—	—	—	1.38	—	—	—
Methylene chloride	—	—	3.58	—	—	0.45	—
Freon-13	—	—	—	0.20	—	—	—
Cis-1,2-Dichloroethylene	—	—	—	1.12	—	—	—
Chloroform	1.40	11.8	2.95	—	0.52	0.28	0.41
Cis-1,2-dichloroethylene	—	—	—	1.12	—	—	—
1,2 - Dichloroethane	—	—	—	—	2.51	—	—
1,1,1-Trichloroethane	—	—	—	—	1.10	—	0.46
Benzene	4.49	6.40	5.58	0.82	0.57	0.72	0.51
1,2-Dichloropropane	—	—	—	—	0.61	—	—
Trichloroethylene	—	—	—	24.7	—	—	—
Cis-1,3-Dichloropropene	—	—	—	—	1.12	—	—
Toluene	10.7	23.2	4.16	80.7	31.4	6.56	2.25
Ethylbenzene	6.05	8.25	2.06	—	0.43	—	—
p-Xylene	9.99	16.8	2.63	—	—	—	—
m-Xylene	9.99	16.8	2.63	—	—	—	—
Styrene	0.73	3.17	0.84	—	—	—	—
o-Xylene	0.68	0.70	—	—	—	—	—
1,3,5-Trimethylbenzene	0.73	0.85	—	—	—	—	—
1,2,4-Trimethylbenzene	6.08	9.46	7.61	17.3	4.73	7.01	2.68
1,3-Dichlorobenzene	—	—	—	0.35	—	—	—
1,2-Dichlorobenzene	4.22	7.71	—	—	—	—	—

(*Ground samples taken on 29th July 2003: 6:00 – 14:00, Flight samples taken on 29th July 2003 10 – 14 minutes)
(**○ = Flow rate: 16 $cm^3.min^{-1}$, • = Flow rate: 4 $cm^3.min^{-1}$, □ = Flow rate: 12.6 $cm^3.min^{-1}$, • = Flow rate: 0.23 $dm^3.min^{-1}$, ◇ = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

In Table 4.13 it is important to note that the sampling time and the flow rate for the different sampling techniques were not the same. As stated in the discussion on Table 4.8, a very strong 1-butanol peak masked the benzene peak at 1 000 ft AGL. The VOC concentrations found at 1 000 ft AGL markedly differed from those observed at ground level. The concentration of toluene and 1,2,4-trimethylbenzene was found to be much higher at 1 000 ft

than at 1 500 ft AGL. At ground level VOCs from petroleum products were detected in samples as well as VOCs originated from domestic burning in Athlone. Results in Table 4.7 and Table 4.13 showed a considerably higher concentration of compounds containing chlorine than samples taken at ground level. Halogenated hydrocarbons have longer lifetimes in the atmosphere, because they are not highly susceptible to photochemical reactions.

VOCs typically associated with petroleum products like xylene and styrene were found at ground level. It also appeared that the concentrations of the more stable chlorinated hydrocarbons are higher at higher altitudes than at ground level. This correlated with the fact that halogenated hydrocarbons are not easily photochemically destroyed.

Methylene chloride was detected at Goodwood in the canister sample and again at 1 500 ft but not at 1 000 ft, illustrating the layering of compounds in different pollution layers.

4.8 COMPARISON OF THIS STUDY WITH OTHER STUDIES

In the study by Oosthuizen *et al.* (1998), toluene was found to have the highest concentration of all the VOCs measured in Cape Town. According to Oosthuizen *et al.* (1998) industry contributed 66% of the total toluene concentration found. In the study by Oosthuizen *et al.* (1998) 1,2,4-trimethylbenzene was found to be the compound with the second-highest index value (after toluene). This was linked mostly to industrial activities (73%) with a smaller contribution from townships (Oosthuizen *et al.*, 1998).

In this study toluene was also found to have the highest concentration and 1,2,4-trimethylbenzene also found the VOC with the second highest concentration of all the VOCs measured in Cape Town.

At higher altitudes the VOCs are either the products of photochemical reactions or more stable VOCs that remained in the atmosphere and can be

transferred from their source over great distances. VOCs found at 1 000 ft and 1 500 ft included acetone, 1-butene, pentane, 2-butanone, 1-butanol and butyl ether acetic acid. The VOCs detected at 1 000 ft that could not be quantified unambiguously included compounds such as methoxy-ethene, 2-methylbutene, hexanol, 2-hexanol, 2,2,5-trimethylhexane, ethylcylohexane and 1-propylbenzene. VOCs detected only at 1 500 ft include 2-methylbutanone, hexane and diethyl phthalate. It was also noted that compounds containing alcohol and ketone-groups were found in higher concentrations at higher altitudes than at ground level.

Benzene is the only VOC included as a criteria pollutant to be monitored in future air quality legislation in South Africa. The spatial and temporal distribution of benzene during the sampling period is therefore of special interest and presented in Table 4.14.

Table 4.14: Comparison of the spatial and temporal distribution of benzene (ppb) using TO canisters with previous studies (using passive samplers)

	This study		Previous studies	
Site	**Nighttime 28th July 2003**	**Daytime 29th July 2003**	**Oct 1994 – Sep 1995**	**Spring 1997**
Cape Point	0.00	0.00	NM	NM
Goodwood	0.75 (0.85*)	5.58 (4.49*)	1.69	NM
Table View	1.39	1.94	1.22	B
City centre	0.93	2.06	NM	0.09
Khayelitsha	1.58	0.81	NM	NM
			Terblanche *et al.*, 1996	Oosthuizen *et al.*, 1998

(* Results from Carbotrap™ 300 tubes, NM = Not measured at the site, B = VOC was detected, but the concentration was below the detection limit of the analytical method)

Terblanche *et al.* (1996) raised concern about the levels of benzene in 1996. The levels at Goodwood and the city centre were even higher than the average values reported in earlier studies by Terblanche *et al.* (1996) and Oosthuizen *et al.* (1998). This is possibly due to an increase in the number of vehicle users in Cape Town and the meteorological conditions during this sampling period.

As stated in Par. 4.6.1 benzene levels at the Goodwood site were much higher than those at any of the other sampling sites. The reported daytime values at Goodwood, Table View and the city centre and the nighttime levels in Khayelitsha exceeded the suggested future air quality annual average target value of 1.6 ppb (5 $\mu g.m^{-3}$). The nighttime benzene levels at the Table View site (also a residential area) but in close vicinity of petrochemical storage tanks) were very low mainly due to the prevailing meteorological conditions at the time of sampling. The day- and nighttime benzene levels at the city centre were very similar during day and night, probably reflecting the active nightlife (constant traffic density) or poor dispersion characteristics at the city centre.

The highest benzene level reported in this study (5.58 ppb) was higher than that reported (Derwent *et al.,* 2000) for Birmingham (1.02 ppb), Cardiff (1.21 ppb) and Leeds (1.94), reported by Vukovich (2000) for Baltimore (2.27 ppb) but similar to that reported by Lewis *et al.,* (1999) for Atlanta (7.66 and 4.00 ppb).

It can be concluded from the results reported in this study that VOC emissions in Cape Town most definitely play a significant role in the brown haze formation in this region, but is also not the only contributing factor. A complete summary of the conclusions of the Cape Town results is given in Chapter 6.

CHAPTER 5

RESULTS OF THE VAAL TRIANGLE FIELD STUDY

This chapter...

The results of the VOCs sampled in towns in the Vaal Triangle are given and discussed in this chapter. The ground level results of the residential areas of Vereeniging, Vanderbijlpark and Sasolburg are given (Par. 5.1) followed by (Par. 5.2) the results taken at different altitudes by using a small aircraft. The chapter is concluded by a discussion of the comparison of the different VOCs detected at ground level and at higher altitudes (Par. 5.3).

Samples were taken on the 18th August 2004 for an 8-hour period (06:00 - 14:00) at Sasolburg, on 18th – 19th August 2004 for a 24-hour period (06:00 - 06:00) at Sasolburg and on 20th August 2004 for an 8-hour period (06:00 - 14:00) at Vereeniging and Vanderbijlpark. On 20th August 2004 samples were also taken at shorter time intervals in the lower troposphere by using a small aircraft to obtain a vertical profile of VOCs in this region (see Par. 3.2.4). August is generally a very windy month in the Vaal Triangle and basically signals the end of the highly polluted winter months. During the sampling time, the Vereeniging site was downwind from a major road passing through the town. The sampling site at Vanderbijlpark was upwind from a major road and an informal settlement (Sharpeville) during the sampling time. According to Table 3.2, an increase in the daily temperatures was already observed and a strong north-west breeze was blowing in Vereeniging and Vanderbijlpark, while Sasolburg experienced a south-east wind during the sampling periods.

Sasol Infrachem made the data in Table 5.1 available (Van der Walt, 2004). These data were collected at the Leitrum and Power Station 2 sites (two sites in Sasol Infrachem) on the 18th August 2004 for an 8-hour period (06:00 -

14:00), on 18th – 19th August 2004 for a 24-hour period (06:00 - 06:00) and on 20th August 2004 for an 8-hour period (06:00 - 14:00). The Power Station 2-site is 4.3 km south-west from the Leitrum site (see Fig. 3.4).

Table 5.1: Concentrations of air pollutants measured by active samplers for the period 18 – 20 August 2004 at Sasolburg (Van der Walt, 2004)

	Leitrum				Power Station 2			
	NO_2 (ppb)	Xylene (ppb)	Benzene (ppb)	PM_{10} ($\mu g.m^{-3}$)	CH_4 (ppb)	SO_2 (ppb)	NMHCs (ppb)	Solar radiation ($Watt.m^{-2}$)
For 8-hour period (06:00 – 14:00) on 18th August 2004								
H	28.9	1.5	4.6	13.1	2.39	31.0	0.2	527.3
L	9.90	0.5	0.2	1.1	2.03	6.50	0.1	13.5
A	17.0	0.8	1.6	9.8	2.32	13.80	0.1	275.7
For 24-hour period (06:00) on 18th August 2004 till (06:00) on 19th August 2004								
H	54.9	1.9	5.0	62.16	2.73	31.05	0.6	527.3
L	6.60	0.4	0.2	1.09	2.03	2.32	0.1	13.1
A	29.3	1.0	2.1	11.7	2.45	8.89	0.3	146.5
For 8-hour period (06:00 – 14:00) on 20th August 2004								
H	29.2	1.21	4.18	121.2	2.98	81.7	0.5	828.0
L	8.20	0.1	0.10	3.40	2.40	3.90	0.2	13.74
A	9.80	0.3	0.60	59.4	2.69	25.1	0.3	515.1

(Data: Sasol Infrachem (Van der Walt, 2004)

(H = Highest concentration measured during the sampling time, L = Lowest concentration measured during the sampling time, A = average concentration for the sampling time, NMHCs = Exclude methanes, but include all other HC)

The Power Station 2 site is 4.3 km south-west from the Leitrum site. The CO concentrations for August were not available. SO_2, NO_x, PM_{10} and CO are compounds typically associated with brown haze (see Par. 2.3.2) and photochemical pollution (see Par. 2.4). The solar radiation gives an indication of the possibility of photochemical reactions occurring. Under the prevailing wind conditions the wind were from a south-east direction towards this site, so that it was from an rural area.

Oxides of nitrogen

The only NO_x measured was NO_2. For all three sampling times, the highest concentrations of NO_2 were measured between 11:00 and 14:00. The concentration levels decreased later in the afternoon and during the night. The highest level of 54.9 ppb measured during the sampling time was still below the highest level of 96.3 ppb measured at the city centre in Cape Town.

Ozone (O_3)

The O_3 levels for Sasolburg are given in Table 3.2. As mentioned in Par. 2.4.1 NO reacts with O_3 to form NO_2. The O_3 levels (45.0 ppb) in the Vaal Triangle were much higher than the levels measured during the sampling period in the CMC.

Sulphur dioxide (SO_2)

The highest level of 81.7 ppb is much higher than the highest level (45.0 ppb) measured at the city centre in Cape Town. This high volume can most probably be linked to the many coal industries and the use of coal for domestic heating in the Vaal Triangle.

Volatile organic compounds (VOCs) measured with automated instruments

The benzene, toluene and xylene monitored are typical VOCs linked to vehicle emissions and are measured by dedicated instruments at Sasol Infrachem. The NMHCs included benzene and toluene.

PM_{10}

PM_{10} episodes were experienced in Sasolburg (Leitrum-site) for the 24 h period 19 – 20 August 2004 (06:00 - 06:00) and again for the 24 h period 20 – 21 August 2004 (06:00 - 06:00). These PM_{10} levels peaked between 08:00 - 09:00 and again from 19:00 - 24:00 and remained high for the night.

5.1 GROUND LEVEL VOCs IN THE VAAL TRIANGLE REGION

VOCs were sampled on ground level in the Vaal Triangle using Carbotrap™ 300 tubes at different flow rates, canisters and SPME. (As stated in Par. 2.9,

the Vaal Triangle is approximately 4 729 ft ASL in the west and 5 038 ft ASL in the east.) The results are given in Table 5.2.

Table 5.2: Concentrations (ppb) of selected VOCs sampled at different ground-level sites in the Vaal Triangle

	Vereeniging		Vanderbijlpark				Sasolburg		
	□C	×S	□C	•T	○T	×S	△C	□C	×S
Sampling time (h)	**8**	**8**	**8**	**8**	**8**	**8**	**8**	**24**	**8**
Freon-12	B	—	—	B	D	—	—	—	—
Chloroethane	—	—	—	0.53	0.20	D	—	—	—
Freon-114	B	—	B	B	B	—	—	—	—
1,1-Dichloroethene	—	—	—	—	—	—	0.58	—	—
Methylene chloride	B	D	0.35	0.20	—	D	—	0.20	D
Freon-113	—	—	B	B	B	—	—	B	—
1,1-Dichloroethane	B	D	B	—	—	D	0.58	—	—
Cis-1,2-Dichloroethylene	3.87	—	—	—	—	—	—	B	—
Chloroform	0.26	D	0.21	B	0.23	D	0.78	B	D
1,2-Dichloroethane	0.43	—	B	2.06	0.50	—	B	—	—
1,1,1-Trichloroethane	B	D	B	0.92	0.20	D	—	—	—
Benzene	B	D	B	0.91	0.38	D	0.20	B	D
Carbon Tetrachloride	B	—	B	0.69	0.20	—	B	—	—
1,2-Dichloropropane	—	—	B	1.15	0.30	—	B	—	—
Trichloroethylene	—	—	B	0.83	0.36	D	B	B	D
Cis-1,3-Dichloropropene	D	—	B	1.36	0.36	—	B	—	—
1,1,2-Trichloroethane	—	—	B	0.83	0.22	D	—	—	—
Toluene	0.24	D	0.40	0.48	0.60	D	0.40	B	D
1,2-Dibromoethane	B	—	B	1.14	0.31	—	—	B	—
Tetrachloroethylene	B	—	B	0.39	B	D	—	B	D
Chlorobenzene	B	—	B	0.44	B	—	B	—	D
Ethylbenzene	B	—	B	0.44	0.25	D	B	—	D
p-Xylene	B	D	0.39	B	B	D	B	B	D
m-Xylene	B	D	0.39	B	B	D	B	B	D
Styrene	B	—	B	—	—	D	B	—	D
o-Xylene	B	D	B	0.25	B	D	B	—	—
1,1,2,2-Tetrachloroethane	B	—	B	0.25	B	—	B	—	—
1,3,5-Trimethylbenzene	B	—	B	0.37	B	D	B	—	D
1,2,4-Trimethylbenzene	0.54	D	0.53	—	B	D	B	0.63	D
1,3-Dichlorobenzene	0.48	D	0.30	0.49	B	D	—	0.64	—
1,4-Dichlorobenzene	0.29	D	0.22	0.39	B	—	B	B	—
1,2-Dichlorobenzene	0.26	D	B	0.59	B	—	B	B	D
1,2,4-Trichlorobenzene	0.24	D	B	B	B	D	B	0.48	D
Hexachloro-1,3-Butadiene	B	—	—	—	—	—	0.20	D	—

(*Samples were taken on the 18th August 2004 for an 8 h period from 06:00 -14:00 at Sasolburg, on 18th August 2004 – 19th August 2004 for a 24 h period from 06:00 - 06:00 at Sasolburg and on 20th August 2004 for an 8 h period from 06:00 - 14:00 at Vereeniging and Vanderbijlpark)

(**○T = Tube samplers with flow rate: 16 $cm^3.min^{-1}$, •T = Tube sampler with a flow rate: 4 $cm^3.min^{-1}$, □C = Canister samplers with flow rate: 12.6 $cm^3.min^{-1}$, △C = Canister samplers with flow rate: 3.2 $cm^3.min^{-1}$, ×S = SPME exposed for 8 h, not used for quantification, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method, D = Detected)

A larger range of VOCs was detected at every site in the Vaal Triangle than at any site in the Cape Town area, even at very low concentrations and sometimes even below the detection limits. The wide range of VOCs is due the fact that the Vaal Triangle is a highly industrialised area. A large number of the VOCs detected were chlorinated.

By comparing the data from the different sites in Table 5.2 it follows that a large number of VOCs were present at all the sites at rather low concentration levels (some even below the detection limits of 0.2 ppb of the method). The VOC with the highest concentration was cis-1,2-dichloroethylene in the Vereeniging region. The lower concentrations can be explained by the favourable dispersion conditions that existed at the time of sampling. The wind speed and direction given in Table 3.2 support the fact that these strong removal processes could have lead to lower concentrations due to dilution.

It follows from the data in Table 5.1 that the average xylene concentration was 1.0 ppb and the benzene concentration 2.1 ppb for the 24-hour period from 06:00 on 18th August till 06:00 on the 19th August 2004 by using active samplers. The average xylene and benzene levels sampled with the canister were below the detection limits of the method for the same 24-hour period (see Table 5.2). From the data in Table 5.1 it follows that the average xylene concentration was 0.8 ppb and the average benzene concentration was 1.6 ppb for the 8-hour period from 06:00 – 14:00 on the 18th August 2004. The canisters (see Table 5.2) gave average xylene and benzene values below 0.2 ppb for the same 8-hour period. That means that the benzene concentration was at least 8 times higher measured with the auto GC than in the canister for the 8-hour period. Although McClenny *et al.* (2002) determined that auto GC samplers gave positive artefacts, and canister and tubes negative artefacts, the auto GC sampler used in this study is situated at the Leitrum station while the canister sample was taken at Power Station 2. No direct correlation could thus be made although it is reasonable to conclude that the observations may support that made by McClenny *et al.* (2002).

5.1.1 Comparison of samples taken with canisters at different towns in Vaal Triangle region

Cis-1,2-dichloroethylene was found only above the detection limits in Vereeniging although it was also detected in Sasolburg. Chloroethane and 1,1,2-trichloroethane were only detected in Vanderbijlpark. 1,1-Dichloroethene above the detection limits was detected only in Sasolburg. Chloroform, toluene, 1,4-dichlorobenzene 1,2-dichlorobenzene, 1,2,4-trichlorobenzene and BTEX compounds were detected at all three sites measured. Benzene levels measured in the Vaal Triangle were below the proposed legislation levels (see Par. 2.5.9).

Ethylbenzene and p-, m- and o-xylene measured at Vereeniging and Sasolburg were below the detection limits.

5.1.2 Comparison of samples taken with carboxen SPME at different towns in the Vaal Triangle

Eight-hour SPME samples were taken at all three sampling sites. The SPME proved to be able to detect the BTEX compounds as well as other compounds not present in the standards used. As in the Cape Town study (Par. 4.1.2), a very good correlation existed between the VOCs sampled with the SPME fibres, the tubes and canisters. As stated (see Par. 2.6.4) the adsorption characteristics of the SPME-fibre determined the VOCs sampled with the fibre. As with the Cape Town study (see Par. 4.1.2) the MS-spectra obtained from the chromatograms from the SPME were easier to interpret than those of the corresponding tube samples.

5.1.3 Comparison of samples taken with canisters and tubes at Vanderbijlpark

In Table 5.2 the concentrations of VOCs sampled with tubes at a 4 $cm^3.min^{-1}$ flow rate gave positive artefacts compared to the tubes sampled at a 16 $cm^3.min^{-1}$ flow rate. These results correlate with the Cape Town results (see

Table 4.2 and Table 4.3). It follows from these results that the effective control of the flow rate for tube sampling is critical and a flow rate higher than 4 $cm^3.min^{-1}$ is required to minimize the effect of positive artefacts.

As in the Cape Town study there was a good correlation between the canister results and the tubes sampled at a flow rate of 16 $cm^3.min^{-1}$.

Colón *et al.* (2001) found that the standard error of the mean (SEM) for canisters is appreciably smaller than that for tubes, indicating that the precision of canisters is better. If they include SEM, the data means are essentially equivalent for methyl chloride, benzene, trichlororethene, toluene, butanal and nonanal.

5.1.4 Compounds detected at ground level not included in the Sulpelco standard

A large number of species not included in the Sulpelco standard were also observed in the tube, canister and SPME samples at ground level, however since no calibration standard was available, these were not quantified (see Table 5.3). These compounds were identified using the MS NIST library database. Instead of using the retention times, the scan numbers are given in Table 5.3 since it was easier to compare scan numbers than retention times.

Table 5.3: Volatile organic compound not quantifiable sampled on ground level in the Vaal Triangle (Abundances in arbitrary units)

		Vereeniging		Vanderbijlpark				Sasolburg		
		□C	×S	□C	•T	○T	×S	△C	□C	×S
Sampling time (h)		**8**	**8**	**8**	**8**	**8**	**8**	**8**	**24**	**8**
Scan	**VOC**									
100	Acetic acid	—	D	—	11.45	—	D	—	—	D
174	Propane	215	D	413	—	—	—	314	—	—
174	2-Methylbutane	—	—	—	115	—	—	—	—	—
178	Acetone	5.16	D	2.34	3.15	3.84	D	17.8	8.41	D
188	1-Pentene	—	—	11.9	—	21.6	—	—	14.5	D
194	2-Methyl-1-butene	—	—	17.5	—	10.3	—	—	—	D
197	Pentane	22.8	D	17.9	29.4	10.4	D	13.8	—	D
202	2-Methyl-1,3-butadiene	—	—	23.6	17.4	13.4	D	—	—	—
206	2-Pentene	—	—	—	—	11.4	—	—	—	—
250	2-Chlorohexane	—	—	98	—	104	—	—	—	—
257	2,3-Dimethylbutane	—	—	—	—	80.9	—	—	—	—
261	2-Methylpentane	—	—	71.5	98.4	103	D	514	—	D
265	2-Methyl-1-butene	8.41	D	11.8	9.7	—	—	—	—	—
265	2-Butanone	0.34	D	—	—	552	—	342	—	D
266	2-Methylpropanol	—	—	—	—	56.6	—	—	—	—
274	Hexanal	—	D	—	—	—	D	65.4	—	D
279	Cyclopentane /1-Hexene	—	—	49.5	64.9	52.8	—	—	—	—
289	Cis-2-penten-1-ol	—	—	1.16	—	75.4	D	—	—	D
301	Hexane	—	D	29.3	35.4	36.4	D	69.5	37.5	D
303	1,4-Butanediol	—	—	—	—	—	—	7.81	—	—
309	Cis-2-Hexene	—	—	—	—	4.74	—	—	—	—
311	Methylcyclopentane	—	—	—	—	4.53	—	—	—	—
336	2,4-Dimethylpentane	—	—	—	—	2.28	—	1.19	—	D
345	Butyrolacetone	—	—	—	—	—	—	9.23	—	D
347	2-Methylhexane	0.48	D	8.34	9.43	6.25	D	—	—	—
352	3-Methylbutanal	—	—	—	—	—	—	9.76	—	—
357	Not identified conclusively	—	—	—	0.98	1.65	—	—	—	—
363	Heptane	9.11	D	—	11.4	7.14	D	23.1	—	D
372	1-(Ethyloxy)-2-methylpropane	—	—	7.89	4.21	—	D	—	—	D
376	2-Heptene	—	—	—	—	—	—	—	—	D
380	Not identified conclusively	4.23	D	—	—	—	—	0.81	—	D
288	Methylcyclohexane	—	D	—	—	—	—	1.34	—	D
382	5-Methyl-2-hexene	—	—	—	—	—	—	—	—	D
390	Pyridine	—	D	—	—	—	D	—	—	D
396	4-Methyl-3-penten-2-one	—	—	—	5.76	4.35	—	7.43	—	D
404	4-Methylpentane	—	D	—	—	—	D	—	—	—
408	3-Methylheptane	—	D	—	—	3.87	—	—	—	—
421	1-Pentanol	—	—	—	1.23	0.98	—	—	—	D
424	Butyl ester acetic acid	—	D	—	—	—	—	—	—	D
430	Dihydro-5-methyl-2-(3H)-furanone	1.23	—	—	—	—	—	2.24	—	—
437	1-Octene	—	—	—	3.52	4.60	—	—	—	—
443	Butylacetate	—	—	—	3.52	3.80	—	—	—	—
445	Octane	0.93	D	—	—	5.40	D	2.31	—	D

Table 5.3: *(Continued)*

		Vereeniging		Vanderbijlpark				Sasolburg		
		□C	×S	□C	•T	○T	×S	△C	□C	×S
Sampling time (h)		**8**	**8**	**8**	**8**	**8**	**8**	**8**	**24**	**8**
Scan	VOC									
455	2,4-Dimethyl-1-heptane	—	D	—	—	—	—	—	—	—
459	1,2-Dichloro-3-nitrobenzene	12.63	—	22.6	—	—	D	—	—	—
487	1,2-Dimethylbenzene	—	D	—	87.2	92.3	—	—	—	D
489	Bromoform	—	D	—	—	—	—	—	—	D
494	1,3,5,7-Cycloteratraene	—	—	—	—	37.1	D	27.1	—	D
499	Heptanal	—	—	—	—	—	—	D	—	—
511	Nonane	44.8	D	—	—	47.0	D	50.4	29.3	D
519	1-Bromo-2-fluoro-benzene	0.62	—	0.31	—	0.88	—	—	—	D
528	1-Tetradecanol	—	—	—	—	—	—	11.2	—	D
534	Phenol / 3-methylpyridazine	—	—	—	—	4.18	—	—	—	—
535	Benzaldehyde	7.89	D	5.69	—	3.96	D	11.4	12.5	D
542	Propylbenzene	4.79	D	—	—	4.49	D	—	—	D
545	Phenol	7.42	D	21.6	—	39.6	D	—	—	D
546	(1-Methylethyl)-benzene	24.5	D	29.8	—	45.9	D	60.7	—	D
552	2-Methylnonane	—	D	—	—	4.35	D	3.65	—	D
557	3-Methylnonane	—	—	—	—	—	D	—	—	D
558	1-Ethyl-2-methylbenzene	—	D	—	—	—	—	—	—	—
558	1,2,3-Trimethylbenzene	69.8	D	—	—	47.0	—	13.4	—	D
563	Octanal	12.7	D	—	—	52.2	—	33.2	—	—
577	Decane	—	D	—	—	—	D	9.65	—	D
579	Not identified conclusively	—	—	—	—	—	—	—	—	D
585	2-Ethyl-1,4-dimethylbenzene	0.12	D	3.18	—	46.9	D	17.8	—	D
588	4-Methyldecane	—	D	—	—	—	—	—	—	D
592	Limonene	—	D	—	21.5	41.2	D	—	—	D
600	1-Methyl-4-propylbenzene	—	D	—	—	43.7	D	—	—	D
603	1,2-Diethylbenzene	—	—	—	—	49.3	D	—	—	D
608	4-Methyldecane	—	D	—	—	—	D	65.2	—	D
609	2-Octen-1-ol	22.4	—	0.19	—	40.7	D	12.4	—	D
611	1-Methyl-1-propylbenzene	—	D	—	—	—	D	—	—	D
615	3-Methyldecane	—	—	—	—	—	D	—	—	D
620	Dimethylstyrene	—	D	—	—	—	—	—	—	—
620	1-Ethyl-2,4-dimethylbenzene	—	—	29.6	—	44.8	—	—	—	—
622	Nonanal	36.2	D	65.7	94.5	78.3	D	90.4	—	D
629	Undecane	—	—	—	—	44.1	D	—	—	D
630	Tridecane	—	—	—	—	40.9	D	12.9	13.4	D
635	2-Ethylhexanoic acid	—	—	—	—	—	—	—	—	D
641	4-Chloro-octane	12.7	—	—	—	—	—	—	—	D
641	1,2,4,5-Tetramethylbenzene	—	—	—	—	42.0	—	—	—	D
649	Benzoic acid	—	—	—	—	—	—	13.8	—	—

Table 5.3: *(Continued)*

		Vereeniging		Vanderbijlpark				Sasolburg		
		□C	×S	□C	•T	○T	×S	△C	□C	×S
Sampling time (h)		**8**	**8**	**8**	**8**	**8**	**8**	**8**	**24**	**8**
Scan	VOC									
655	Ethylester heptanoic acid	—	—	—	—	—	—	—	—	D
658	Dodecanal	—	—	—	—	61.8	D	—	—	—
663	1-Amine-3,5-dimethylbenzene	—	—	—	—	—	—	—	—	D
665	2-Methyl-undecane	—	—	—	—	—	—	—	—	D
676	Trans-2-undecanal	—	—	—	—	—	—	63.5	—	—
676	2,4,6,8-Tetramethyl-1-undecene	124	D	—	—	132	D	—	—	—
681	Dodecane	—	D	—	—	—	D	12.6	—	—
683	2-Iodine-2-methyl-butane	—	—	—	—	—	D	—	—	D
691	6-Methyl-octadecane	—	—	—	—	—	—	—	—	D
732	Tetradecane	—	—	—	—	—	D	—	—	D
749	1,2,3,4-Tetrachlorobenzene	—	—	—	—	—	—	—	—	D
761	Hexadecene	—	—	—	—	—	—	—	—	D
768	Hexadecane	—	D	44.8	—	—	—	—	—	—
775	Cyclododecane	—	—	—	—	—	—	23.7	—	—
782	3,7-Dimethyl-2,6-octadien-1-ol-acetate	—	—	—	—	—	—	—	—	—
799	Pentadecane	—	—	13.4	—	—	—	—	—	D
801	2-Butyl-1-octanol	—	—	—	—	—	—	17.8	—	D
805	2-Methylpirazine	—	—	—	—	—	D	19.7	—	D
828	Diethylphtalate	—	D	—	—	—	—	16.5	D	—
848	2,6-Bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	—	—	—	—	—	D	—	—	D
856	Dibuthylphthalate	—	D	—	—	—	D	—	—	—

(*Samples were taken on the 18th August 2004 for an 8 h period from 06:00 -14:00 at Sasolburg, on 18th August 2004 – 19th August 2004 for a 24 h period from 06:00 - 06:00 at Sasolburg and on 20th August 2004 for an 8 h period from 06:00 - 14:00 at Vereeniging and Vanderbijlpark)

(**○T = Tube samplers with flow rate: 16 $cm^3.min^{-1}$, •T = Tube sampler with a flow rate: 4 $cm^3.min^{-1}$, □C = Canister samplers with flow rate: 12.6 $cm^3.min^{-1}$, △C = Canister samplers with flow rate: 3.2 $cm^3.min^{-1}$, ×S = SPME exposed for 8 h, not used for quantification, — = Not detected, D = Detected)

From Table 5.3 it appeared that the compounds found at ground level consisted mainly of alkynes, alkenes, alkanes and benzene related compounds. Dihydro-5-methyl-2-(3H)-furanone was only detected in the canister samples, while other compounds like cis-2-hexene, methylcyclopentane, 1-octene, butylacetate were only detected in the tube samples. By using the SPME the following compounds were detected: trichloroethylene, pyridine, 4-methylpentane, butylester acetic acid, 2,4-dimethyl-1-heptane, bromoform, 1-ethyl-2-methylbenzene, 4-methyldecane

and dimethylstyrene which were not detected in the samples of the other sampling techniques.

Products due to photochemical reactions of primary VOCs have been detected in many of the samples. The ketones present in many samples are an indication of photochemical reactions. According to Atkinson (1990) aliphatic aldehydes and ketones were formed as the intermediate "stable" chemical products of a wide variety of organic compounds. The following ketones were detected in the samples taken at the different towns in the Vaal Triangle: acetone, 2-butanone, butyrolacetone, 4-methyl-3-penten-2-one, dihydro-5-methyl-2-(3H)-furanone and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione. Many oxygenated VOCs have an industrial origin (solvent etc.) inaddition to be a secondary emission this is particulary the case for acetone. The following aldehydes were detected: benzaldehyde, hexanal, 3-methylbutanal, heptanal, octanal, nonanal, dodecanal and trans-2-undecanal. These compounds are all likely to be the result of photochemical reactions. Atkinson (1990) indicated that benzaldehyde forms from toluene in the presence of NO.

The 8-hour and 24-hour canister samples taken at Sasolburg gave some interesting results - significantly more VOCs were detected during the 8-hour sampling time from 06:00 – 14:00 than over a 24-hour period. The 8 hours in question were during daytime when photochemical reactions are more likely to occur. This correlates with Godish (1991) who stated that secondary photochemical products might comprise as much as 95% of the total HC compounds present in a severe smog episode. Although ketones such as acetone and benzaldehyde were detected in both samples, certain ketones such as 2-butanone, butyrolacetone, 4-methyl-3-penten-2-one, dihydro-5-methyl-2-(3H)-furanone, were only found in the 8-hour sample.

5.2 RESULTS FOR DIFFERENT ALTITUDES OVER THE VAAL TRIANGLE

In Par. 3.2.4 it was stated that samples were taken during flights at different altitudes on 20th August 2004, over the Vaal Triangle. Samples were taken at

616, 1 116, 1 616 and 2 616 ft AGL in the Vaal Triangle and at 2 616 ft on the return flight to Potchefstroom. Firstly, the quantifiable VOCs (Table 5.4) and then those that could not be quantified (Table 5.5) are given and discussed.

5.2.1 Concentrations of VOCs taken at different altitudes over the Vaal Triangle

Table 5.4: Concentrations (ppb) of selected VOCs sampled at different altitudes over the Vaal Triangle

	Flight path								
	Zamdela to Vereeniging		Sebokeng to Zamdela	Zamdela to Sebokeng		Sebokeng to Vereeniging		Back to Potchefstroom	
Height AGL (ft)	**616**		**1 116**	**1 616**		**2 616**		**2 616**	
VOC	◇C	◆T	◇C	◇C	◆T	◇C	◆T	◇C	◆T
Freon-11	0.23	—	B	0.22	—	—	—	B	—
1,1-Dichloroethene	B	—	—	B	—	—	8.51	—	—
Methylene chloride	0.27	1.69	B	0.45	1.90	1.50	1.66	0.20	—
Freon-113	B	—	—	B	—	—	0.21	B	—
Chloroform	0.61	1.51	0.57	0.46	2.30	0.39	1.42	0.56	3.47
1,2-Dichloroethane	0.48	2.66	0.41	B	0.20	0.20	1.82	0.27	—
Benzene	0.38	0.47	1.13	0.66	0.89	0.92	1.19	0.79	0.97
Carbon tetrachloride	—	B	—	—	—	B	B	B	B
1,2-Dichloropropane	—	—	—	B	—	0.37	—	—	—
Trichloroethylene	5.14	—	2.23	4.26	—	1.86	—	2.10	—
Cis-1,3-Dichloropropene	—	—	—	—	—	B	—	—	—
Toluene	6.18	14.8	2.46	4.40	9.52	5.30	10.9	2.20	7.82
1,2-Dibromoethane	—	—	—	—	—	D	7.24	B	0.87
Tetrachloroethylene	—	—	—	—	—	0.41	—	B	—
Chlorobenzene	—	—	—	—	—	B	—	B	—
Ethylbenzene	B	3.44	B	—	1.18	B	1.19	B	1.40
p-Xylene	B	0.36	B	B	1.89	B	1.98	B	1.18
m-Xylene	B	0.36	B	B	1.89	B	1.98	B	1.18
Styrene	—	1.14	—	B	0.74	0.22	0.71	—	0.75
o-Xylene	B	1.54	B	—	0.69	B	0.70	B	B
1,1,2,2-Tetrachloroethane	B	—	B	—	—	B	0.52	—	—
1,3,5-Trimethylbenzene	0.20	0.26	B	B	2.83	—	2.78	B	B
1,2,4-Trimethylbenzene	B	1.27	0.57	—	2.83	1.09	3.38	B	1.36
1,3-Dichlorobenzene	—	—	B	—	0.85	B	—	B	2.27
1,4-Dichlorobenzene	—	—	5.02	—	—	0.49	—	B	—
1,2-Dichlorobenzene	—	—	—	—	—	0.44	—	B	—
1,2,4-Trichlorobenzene	—	—	B	—	—	—	—	B	—

(*Samples were taken on the 20th August 2004 for a 10 - 14 min period between 07:10 – 09:21)

(***◆T = Flow rate: 0.23 $dm^3.min^{-1}$, ◇C = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, B = VOC was detected, but the concentration was below 0.2 ppb – the detection limit of the analytical method)

(***◆Average ground level at Vanderbijlpark = 4 884 ft AGL)

The concentration of the VOCs measured by using tubes appeared to be higher than those measured by using the canisters. In Table 2.6 Colón *et al.* (2001) also recorded higher values for toluene, ethyl benzene, styrene and p- and m-xylene in tube samples when compared with canister samples.

Similar to the Cape Town study (see Par. 4.7), it seemed that the pollutants measured at higher altitudes are mostly compounds that are more resistant to photochemical reactions and secondary products of photochemical reactions. Samples taken at higher altitudes have higher amounts of chlorine containing HC-compounds than the samples taken at ground level. According to Mohammed *et al.* (2002) halogenated HCs are more resistant to photochemical reactions and thus have longer lifetimes in the atmosphere than HC. It is also possible that these VOCs were transferred over long distances from their source. (See the
jectory analysis plot – Appendix 2).

According to these results the concentration distribution of the pollutants over the Vaal Triangle at higher altitudes exhibit the following distribution patterns:

1. Chloroform and 1,2-dichloroethane had the highest concentrations at 5 500 ft. The concentrations then slowly decreased at higher altitudes. Both these halogenated hydrocarbons have long lifetimes in the atmosphere. They are diffusing from the source and are stable in the air and can travel over long distances.
2. Trichloroethylene were found in pollution layers, high concentrations were found at 5 500 ft, decreased at 6 000 ft, increased again and then decreased again.
3. The p- and m-xylene levels also fluctuate; this can be due to the formation of pollution layers at certain levels and the diffusion of higher concentrations to lower concentrations in these layers.
4. The levels of trichloroethylene and toluene were found to be significantly higher at higher altitudes than on ground level. Toluene, although short-lived had the highest concentration of all the VOCs measured! The concentration of trichloroethylene and toluene were higher than the concentration of most measured pollutants (except for

1,4-dichlorobenzene at 6 000 ft, 1,2-dichloroethane at 5 500 ft – measured with the tube and ethylbenzene at 5 500 ft in the tube). The concentration of toluene seemed to be high at 5 500 ft., decreasing and increasing again with an increase in altitude. This possibly indicated that these pollutants have been trapped earlier in a pollution layer and are not due to ground level emissions on that specific morning, or that stack emissions may cause pollution at higher altitudes to differ from pollution at ground level.

5. The following compounds appeared to be in higher concentration levels at higher altitudes, some of the pollutants were only detected at 7 500 ft: 1,1-dichloroethene, freon-113, 1,2-dichloropropane, 1,2-dibromoethane, tetrachloroethylene, 1,1,2,2-tetrachloroethane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2-dichlorobenzene. VOC emissions from high industrial stacks in this region may cause higher concentrations at higher altitudes than found at ground level.

The concentration of toluene and 1,3-dichlorobenzene were found to be high on the return flight from the Vaal Triangle to Potchefstroom. The fact that certain compounds were sampled on the way back to Potchefstroom gave an indication that these compounds are relatively stable in the atmosphere and are transported over long distances from their sources.

5.2.2 Compounds sampled at higher altitudes not included in the Sulpelco standard

At higher altitudes a large number of species not included in the Sulpelco standard were also observed, these compounds could not be quantified (see Table 5.5). The MS NIST library database was used to identify these VOCs. The results are given in Table 5.5.

Table 5.5: Volatile organic compounds not quantifiable at different altitudes over the Vaal Triangle (Abundances in arbitrary units)

		Flight path								
		Zamdela to Vereeniging		Sebokeng to Zamdela	Zamdela to Sebokeng		Sebokeng to Vereeniging		Back to Potchefstroom	
Height AGL (ft)		**616**		**1 116**	**1 616**		**2 616**		**2 616**	
Scan	**VOC**	◇C	•T	◇C	◇C	•T	◇C	•T	◇C	•T
174	Propane	—	—	212	20.3	11.2	—	—	—	—
194	2-Methyl-1-butene	—	—	—	—	22.4	—	—	—	—
197	Butane	—	—	67.4	275	312	—	—	—	—
202	2-Methyl-1,3-butadiene	—	—	78.9	60.4	65.2	41.4	22.1	13.6	—
229	2,2-Dimethylbutane	—	—	78.3	—	—	62.1	60.4	—	—
245	2-Methylbutane	12.6	38.9	—	—	67.2	—	—	—	—
246	Pentane	688	700	—	—	48.0	—	—	—	—
250	2-Chlorohexane	67.4	76.5	—	—	112	—	89.4	—	—
257	2,3-Dimethylbutane	78.2	65.4	—	102	98.2	—	34	—	—
261	2-Methylpentane	—	—	—	27.8	11.2	—	7.6	5.4	—
265	2-Butanone	23.7	41.0	—	65.4	57.7	—	—	—	—
271	2,3-Methylpentane	—	—	3.41	—	—	—	—	—	—
274	Hexanal	—	—	59.0	40.9	44.7	—	28.7	16.5	15.6
275	Dimethylhydrazone	—	—	—	—	—	—	15.7	—	—
279	Cyclopentane	—	—	—	—	11.4	—	9.48	—	—
285	2.3-Dimethylbutane	383	400	—	—	—	—	—	—	—
288	2-Methylpentane	208	198	—	—	—	—	—	—	—
289	Cis-2-penten-1-ol	—	—	—	—	9.23	—	—	—	—
301	Hexane	—	—	—	—	—	—	—	16.8	17.4
309	Cis-2-Hexene	—	2.71	—	—	—	—	—	—	—
314	2,4-Dimethylpentane	185	—	—	—	4.32	3.98	3.71	1.76	1.76
322	Not identified conclusively	—	—	—	2.32	1.21	—	—	—	—
325	2,2,3-Trimethylbutane	—	—	—	—	—	—	—	14.5	12.4
345	Butyrolacetone	54.4	67.4	22.1	11.4	—	—	—	9.41	—
347	2-Methylhexane	225	—	—	—	288	6.31	17.9	1.76	1.86
352	3-Methylbutanal	—	—	316	—	212	—	—	—	—
363	Heptane	—	—	—	—	—	—	11.5	—	—
366	2,2,3,3-Tetramethylbutane	—	—	—	—	187	—	—	—	—
396	4-Methyl-3-penten-2-one	—	—	—	—	671	—	—	—	—
397	2,5-Dimethylhexane	17.8	28.4	9.63	8.74	9.74	4.11	398	2.76	3.11
399	2,4-Dimethylhexane	—	12.1	—	—	3.76	—	—	—	—
410	2,3,4-Trimethylpentane	—	18.6	223	423	458	10.4	9.87	5.43	2.31
418	2,3-Dimethylhexane	21.4	—	17.43	16.2	31.8	—	8.17	6.72	4.12
421	1-Pentanol	—	—	—	25.7	31.7	—	—	—	—
423	2,5-Dimethyloctane	6.78	—	—	—	3.54	0.88	1.16	2.11	—
425	Diethylmethylpentane	43.1	—	—	—	27.9	—	30.8	—	—
428	2-Methyl-2H-tetrazole	—	—	—	—	20.8	—	—	—	—
430	Dihydro-5-methyl-2-(3H)-furanone	47.8	56.3	—	—	44.4	—	22.1	—	—
434	2,2-Dimethyl-hexane	—	—	—	—	80.9	—	23.6	—	—
439	2,2,4-Trimethylhexane	22.6	29.7	—	—	—	—	—	—	—
445	Octane	—	—	—	—	7.26	—	—	—	—
446	2,2,5-trimethylhexane	12.5	15.7	—	—	—	—	—	—	—
453	2,3-Dimethylpentane	—	—	—	—	2.31	—	—	—	—

Table 5.5: *(Continued)*

		Flight path								
		Zamdela to Vereeniging		Sebokeng to Zamdela	Zamdela to Sebokeng		Sebokeng to Vereeniging		Back to Potchefstroom	
Height AGL (ft)		**616**		**1 116**	**1 616**		**2 616**		**2 616**	
Scan	**VOC**	◇C	•T	◇C	◇C	•T	◇C	•T	◇C	•T
459	1,2-Dichloro-3-nitrobenzene	—	—	11.6	16.8	—	—	—	12.4	—
511	Nonane	—	—	34.6	—	—	—	26.1	13.6	—
519	1-Bromo-2-fluoro-benzene	—	—	19.5	—	17.2	—	—	8.27	—
524	2,5,6-Trimethyloctane	6.71	—	—	—	2.34	2.64	—	—	—
528	1-Tetradecanol	—	—	—	—	0.99	—	—	—	—
542	Propylbenzene	—	—	2.13	—	—	1.13	2.03	2.05	—
546	(1-Methylethyl)-benzene	—	—	3.67	6.11	5.67	—	2.13	3.13	—
549	1-Ethyl-3-methylbenzene	—	—	—	—	4.31	—	—	1.21	—
552	2-Methylnonane	—	—	—	—	92.8	41.2	41.2	—	—
557	3-Methylnonane	—	—	—	—	—	—	2.31	3.13	—
558	1,2,3-Trimethylbenzene	—	—	34.2	8.21	7.36	5.31	4.31	—	—
563	Octanal	—	–	—	62.8	70.5	—	33.6	13.6	—
573	Undecane	—	—	—	—	28.4	—	—	8.63	—
579	Not identified conclusively	—	—	—	—	2.76	5.67	7.89	—	—
585	2-Ethyl-1,4-dimethylbenzene	—	—	7.31	—	3.21	—	1.21	0.91	—
591	6-Methyl-octadene	10.4	14.3	—	—	2.13	—	—	—	—
593	Limonene	—	—	—	—	2.13	—	1.76	—	—
594	Indane	63.4	—	—	—	—	—	8.41	—	2.13
600	1-Methyl-4-propylbenzene	45.7	50.8	—	—	21.2	14.2	—	8.43	6.72
603	1,2-Diethylbenzene	55.1	49.2	—	—	2.12	3.12	2.16	2.32	—
607	6-Hepten-1-ol	—	65.1	—	—	23.8	—	22.4	—	—
609	2-Octen-1-ol	—	—	—	—	16.8	—	13.4	—	—
615	3-Methyldecane	—	—	—	—	3.12	—	3.12	—	—
620	1-Ethyl-2,4-dimethylbenzene	—	—	6.21	—	23.6	—	—	—	—
622	Nonanal	112	120	—	—	299	—	315	112	127
622	Trichlorobenzene	—	—	9.12	12.15	—	—	—	—	—
630	Tridecane	—	—	—	—	—	—	—	3.54	4.76
632	Not identified conclusively	0.92	1.34	—	—	—	—	—	—	—
635	2-Ethylhexanoic acid	—	—	—	—	—	—	12.4	—	—
649	Benzoic acid	—	—	—	—	6.79	—	—	—	—
652	Not identified conclusively	—	—	—	—	—	—	2.34	—	—
658	Dodecanal	—	—	44.5	—	12.5	7.43	—	3.12	5.12
661	Not identified conclusively	3.75	4.02	—	—	—	—	2.56	—	—
665	2-Methyl-undecane	2.31	—	—	—	—	—	—	—	—
676	Trans-2-undecanal	74.2	88.9	115.9	—	—	—	11.4	8.47	112
676	2,4,6,8-Tetramethyl-1-undecene	—	—	—	—	329	—	—	—	—
713	1,1-{1-(2,2-dimethylbutyl)-1,3-propanediyl}bis-cyclohexane	9.43	7.27	—	—	3.12	—	5.46	—	—
729	Not identified conclusively	—	—	7.54	—	—	—	—	3.21	—
732	Tetradecane	—	2.13	—	—	1.96	—	2.14	—	—

Table 5.5: *(Continued)*

		Flight path								
		Zamdela to Vereeniging		Sebokeng to Zamdela	Zamdela to Sebokeng		Sebokeng to Vereeniging		Back to Potchefstroom	
Height AGL (ft)		**616**		**1 116**	**1 616**		**2 616**		**2 616**	
Scan	VOC	◇C	*T	◇C	◇C	*T	◇C	*T	◇C	*T
749	1,2,3,4-Tetra-chlorobenzene	—	—	—	—	2.13	—	—	—	3.14
751	Not identified conclusively	11.5	14.6	—	—	—	—	—	—	—
768	Hexadecene	—	—	—	—	12.1	—	19.4	—	8.70
776	6,10-Dimethyl-5,9-undecadien-2-one	14.8	19.5	—	—	—	—	11.4	—	—
782	3,7-Dimethyl-2,6-octadien-1-ol-acetate	—	—	—	—	8.94	—	18.9	—	6.45
803	1,1-{1-(2,2-dimethylbutyl)-1,3-propanediyl}bis-cyclohexane	—	—	4,53	—	2.43	—	4.51	—	3.67
815	Not identified conclusively	7.89	9.16	—	—	—	—	—	—	—
828	Diethylphthalate	—	—	—	—	—	—	14.7	—	—
856	Dibutylphthalte	—	—	—	—	—	—	2.31	—	—

(*Samples were taken on the 20th August 2004 for a 10 - 14 min period between 07:10 – 09:21)

(**◆T = Flow rate: 0.23 $dm^3.min^{-1}$, ◇C = Flow rate: 0.6 $dm^3.min^{-1}$, — = Not detected, D = Detected)

(***◆Average ground level at Vanderbijlpark = 4 884 ft AGL)

According to the chromatograms on which the results in Table 5.5 are based, some large peaks were observed for some of these VOC compounds sampled at higher altitudes. In general it appeared that the VOCs are found in pollution layers in which emissions are trapped.

The chromatogram peak of 2,5-dimethylhexane appeared to be much higher than that of the 2,4-dimethylhexane peak; the higher concentration is probably because 2,5-dimethylhexane is more stable under atmospheric conditions than 2,4-dimethylhexane.

Again, as with the ground samples, possible products of photochemical reactions have been detected. The ketones present were: 2-butanone, dimethylhydrazone, butyrolacetone, 4-methyl-3-penten-2-one, dihydro-5-methyl-2-(3H)-furanone and 6,10-dimethyl-5,9-undecadien-2-one. The following aldehydes were detected in the samples: benzaldehyde, hexanal, 3-methylbutanal, octanal, nonanal, dodecanal and trans-2-undecanal.

5.3 COMPARISON OF VOCs SAMPLED AT GROUND LEVEL AND AT HIGHER ALTITUDES IN THE VAAL TRIANGLE REGION

According to the results in Tables 5.2 to 5.5, the concentration distribution of the VOCs over the Vaal Triangle showed different distribution patterns than those observed in the Cape Town study. The VOCs quantified displayed the following patterns:

1. VOCs detected only in ground level samples. These included: chloroethane, 1,1-dichloroethane, cis-1,2-dichloroethylene, 1,1,2-trichloroethane and hexachloro-1,3-butadiene.
2. Freon-11 was the only VOC not detected in the ground level samples but detected in samples at higher altitudes. This indicated a distant source for this CFC - possessing a longer lifetime.
3. VOCs with higher concentrations in the ground level samples than the samples at higher altitudes. This also indicated that the VOCs must have been released at ground level, pointing that the source of pollution must be in the Vaal Triangle. These VOCs included carbon tetrachloride and 1,2-dichloropropane that are diluted by diffusion at higher altitudes and 1,3-propene that is likely to be destroyed photochemically.
4. VOCs detected at higher concentrations at higher altitudes. These are VOCs that are more stable in the air and less easily destroyed photochemically. These include chloroform, benzene and trichloroethylene. Some of these VOCs might have distant sources. 1,2-Dibromoethane was detected in the samples from Vanderbijlpark, at 7 500 ft (at concentrations higher than at ground level) and on the flight back to Potchefstroom. Other VOCs at higher levels at higher altitudes included toluene, 1,1,2,2,-tetrachloroethane, 1,3,5-trimethylbenzene (lifetime = 6 hours), 1,2,4-trimethylbenzene (lifetime = 10 hours) and 1,4-dichlorobenzene.

In Tables 5.3 and 5.5 VOCs (not quantified) are given, - as previously mentioned no standards were available to quantify these VOCs. It is

therefore not possible to determine if they have concentration gradients at different altitudes.

5.3.1 VOCs detected only in ground level samples in the Vaal Triangle

Certain VOCs were detected only in the ground level samples in the Vaal Triangle were quantified and included the following halogenated HCs: freon-12, chloroethane, freon-114, 1,1-dichloroethane, cis-1,2-dichloroethylene, 1,1,-trichloroethane and hexachloro-1,3-butadiene. The VOCs not in the external standard, and thus could not be quantified, include:

VOCs sampled with canisters but not with other techniques

In the ground samples 1,4-butanediol and heptanal were detected only in canisters samples.

VOCs sampled with tubes but not with other techniques

The tube sampled 2-methylbutane, 2-pentene, 2-methylpropanol, methylcyclopentane, 1-octene, and phenol / 3-methylpyridazine which were not found in the ground samples of the other techniques.

VOCs sampled with SPME but not with other techniques

The SPME as a sampling technique was the only technique that sampled a large range of VOCs. The tube and/or the canisters might also have sampled some of these VOCs – but the peaks were smaller than the baseline drift in the chromatograms. Except for pyridine and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione these VOCs include:

1. Alkanes such as, 4-methylpentane, 3-methylheptane, 2,4-dimethyl-1-heptane and 4-methyldecane.
2. Alkenes such as, 2-heptene, 5-methyl-2-hexene and hexadecane.
3. Bromoform, 4-chloro-octane, 1,2-dichlorobenzene and 2-iodine-2-methyl-butane are all halogenated hydrocarbons.
4. Complex benzene compounds detected in the samples include 1-methyl-1-propylbenzene, dimethylstyrene and 1,2,4,5-tetramethylbenzene.

5. Butyl ester acetic acid and ethylester heptanoic acid are both organic acids.

VOCs sampled with canisters and tubes but not with SPME

The tubes and the canisters sampled cyclopentane and/or 1-hexene and 1-ethyl-2,4-dimethylbenzene.

VOCs sampled with canisters and SPME but not with tubes

SPME and canisters both sampled methylcyclohexane, decane, 4-methyldecane, dodecane, cyclododecane, pentadecane, 2-butyl-1-octanol and 2-methylpirazine.

VOCs sampled with tubes and SPME but not with canisters

Although acetic acid, butyl acetate, 1,2-dimethylbenzene, undecane were sampled with the SPME and tubes - the canisters did not sample these VOCs.

VOCs sampled with canisters, tubes and with SPME

Acetone, 1-pentene, 2-methyl-1-butene, 1-(ethyloxy)-2-methylpropane, 1,3,5,7-cycloteratraene, benzaldehyde, phenol, (1-methylethyl)-benzene, nonanal were sampled with all three techniques.

The VOCs detected in ground level samples must be compounds originated near the source of pollution and must have either short atmospheric lifetimes or they could be the first products of a photochemical step. The following ketones and aliphatic aldehydes (typical of photochemical reactions) detected only in ground level samples included acetone, benzaldehyde, heptanal and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

5.3.2 VOCs sampled only at higher altitudes over the Vaal Triangle area

The following compounds were detected only in samples taken at higher altitudes. The origin of these detected compounds can be either secondary pollutants or these VOCs were transported from outside the Vaal Triangle and have longer half-lifetimes. Freon-11 was the only quantifiable VOC detected

in samples taken at higher altitudes but not in the ground samples. A large range of VOCs, not in the standards, was detected in samples, these VOCs include:

VOCs sampled with canisters but not tubes

At higher altitudes 2,3-methylpentane was sampled only with canisters.

VOCs sampled with tubes but not with canisters

The tubes sampled dimethylhydrazone, 2,2,3,3-tetramethylbutane, 2-methyl-2H-tetrazole, 2,2-dimethylhexane, 2,3-dimethylpentane, 1-tetradecanol, 6-hepten-1-ol.

VOCs sampled with canisters and tubes at higher altitudes

A large range of VOCs was sampled with both canisters and tubes. These VOCs are butane, 2,2-dimethylbutane, 2,2,3-trimethylbutane, 2,4-dimethylhexane, 2,3,4-trimethylpentane, 2,4-dimethylhexane, 2,5-dimethyloctane, 2,2,4-trimethylhexane, 2,2,5-trimethylhexane, 2,5,6-trimethyloctane, 1-ethyl-3-methylbenzene, indane, 1,1-{1-(2,2-dimethylbutyl)-1,3-propanediyl}bis-cyclohexane and 6,10-dimethyl-5,9-undecadien-2-one.

VOCs sampled only at higher altitudes must be either secondary pollutants formed during photochemical reactions or have remained in the air for a time and since emission moved some distance. Ketones found only at higher altitudes were: dimethylhydrazone and 6,10-dimethyl-5,9-undecadien-2-one. Aldehydes were only detected in samples taken at higher altitudes but not in samples taken at ground level.

5.3.3 VOCs detected in ground level samples and in samples at higher altitudes over the Vaal Triangle

Certain VOCs detected in ground level samples and in samples taken at higher altitudes must be more stable and have longer lifetimes in the atmosphere. These VOCs include:

1. Alkanes such as: Propane, pentane, 2,3-dimethylbutane, 2-methylpentane, hexane, 2,4-dimethylpentane, 2-methylhexane,

heptane, octane, nonane, 2-methylnonane, 3-methylnonane, 4-methyldecane, 3-methyldecane, tridecane, dodecanal, 2-methyl-undecane, trans-2-undecanal, tetradecane and hexadecane.

2. In comparison with alkanes the alkenes are much more likely to react with radicals in the air. Not surprising is that only cis-2-hexene and 2,4,6,8-tetramethyl-1-undecene were detected in ground level samples and in samples taken at higher altitudes.
3. Halogenated hydrocarbons such as 2-chloro-hexane, 1,2-dichloro-3-nitrobenzene and 1-bromo-2-fluoro-benzene were detected in samples on the ground and at higher altitudes.
4. Cis-2-penten-1-ol, 1-pentanol, 1-tetradecanol and 2-octen-1-ol were alcohols detected in samples. The most important way for atmospheric loss of alcohols is the HO· that is formed and which can take part in photochemical reactions.
5. The more complex benzene compounds that are probably more stable in atmospheric conditions and do not take part in reactions or are destroyed during photochemical reactions include: propylbenzene, 1-ethyl-2-methylbenzene, 1,2,3-trimethylbenzene, 2-ethyl-1,4-dimethylbenzene, 1-methyl-4-propylbenzene, 1,2-diethylbenzene, 1-ethyl-2,4-dimethylbenzene and 1,2,3,4-tetrachlorobenzene.
6. The BVOC limonene is most likely to have its origin in plant species. Yassaa *et al.* (1999) detected limonene, due to biogenic emissions of trees sited near their sampling site. Guenther *et al.* (1996) detected d-limonene as a monoterpene emission from plant species found in the Southern African savannah.
7. The only conjugated alkene detected in ground level samples and in samples taken at higher altitudes was 2-methyl-1,3-butadiene, also known as isoprene. According to Seinfeld and Pandis (1998) this is the most important BVOC in the atmosphere. Ground samples also contained 1,1,2,3,4,4-hexachloro-1,3-butadiene and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohaxadiene.
8. Organic acids included 2-ethylhexanoic acid and benzoic acid. According to Atkins (1990) the logical way of removing formic and acetic acid is the reaction with the HO·. For formic and acetic acids

these processes are very slow so that the major processes for removing these compounds from the gas phase would be wet or dry deposition (Atkins, 1990). The dry deposit is due to adsorption, - these processes can probably remove other acids from the atmosphere as well.

9. Ester species measured included 3,7-dimethyl-2,6-octadien-1-ol-acetate and the two phthalate species diethylphthalate and dibutylphthalate.
10. Proof of photochemical reactions includes the formation of 2-butanone, butyrolacetone, 4-methyl-3-penten-2-one and dihydro-5-methyl-2-(3H)-furanone. The following aldehydes were detected in samples, hexanal, 3-methylbutanal, octanal, nonanal, dodecanal and trans-2-undecanal, at ground level as well as at higher altitudes. Of these compounds at least butyrolacetone is an intermediate "stable" chemical compound and the product of atmospheric degradation of a wide variety of organic compounds.
11. On ground level benzene, above the detection limits, was only reported in Vanderbijlpark. Although benzene was detected in samples at higher altitudes the concentrations were still below the proposed new air quality bill.

5.4 COMPARISON OF THIS STUDY WITH OTHER STUDIES

As stated in Par. 2.9.5 Van der Walt and his co-workers (2004) determined the monthly average benzene levels in the Vaal Triangle from November 2001 till April 2002.

Table 5.6: Comparison of benzene levels in the Vaal Triangle (ppb) using TO canisters to a previous study

This study		Van der Walt *et al.*, 2004	
18, 19, 20 August 2004		**Monthly average 2001 - 2002**	
Sampled at:	**Concentration (ppb)**	**Sampled at:**	**Concentration (ppb)**
#Vereeniging	B	#Electrified residential:	1.9 - 2.4
#Vanderbijlpark	B		
+Sebokeng to Zamdela	1.13	#Semi-electrified:	5.6
*Zamdela to Sebokeng	B	#Non-electrified:	1.9
#Sasolburg	0.2	#Industrial area:	3.9 – 11.3

(# = Ground level sample, + = sampled at 6 000 ft ASL, * = = sampled at 6 500 ft ASL, B = Benzene was detected, but the concentration was below 0.2 ppb – the detection limit of the instrument)

Benzene levels in this study were found to be much lower than the monthly averages measured by Van der Walt *et al.* (2004). This is probably due to the prevailing wind at the sampling time. Van der Walt *et al.* (2004) determined that industrial areas showed the highest concentrations of benzene. In this study, samples taken at flights over informal settlements showed higher concentrations of benzene than the ground samples at the industries.

The levels of benzene measured during this study in Vanderbijlpark correlated with the concentrations in Birmingham (1.02 ppb), Leeds (1.04 ppb) and London (1.06 ppb) found by Derwent *et al.* (2000). The concentration levels were much lower than the levels in Izmir (14.55 ppb) measured by Muezzinoglu *et al.* (2001) and the 11.13 ppb measured in Rome by Brocco *et al.* (1997).

5.5 CONCLUSIONS

From the results presented in this chapter it clearly follows that atmospheric VOCs include a very large range of compounds. Many of these compounds could not be quantified due to the absence of suitable standards. A need clearly exists to develop methods by which more of these compounds can be quantified. Similarly, the impact on health and the environment of many of these compounds are known and more impact-related research is needed.

CHAPTER 6

COMPARISONS AND CONCLUSIONS

This chapter...

Firstly, errors and uncertainties are evaluated and validated in Par. 6.1. A summary of the final results for Cape Town (Par. 6.2) and the Vaal Triangle is given (Par. 6.3), and compared (Par. 6.4). The study is further critically evaluated in terms of the goals stated at the outset of the study and the results obtained (Par. 6.5). Future challenges identified during the project are also pointed out (Par. 6.6).

6.1 VALIDATION OF PARAMETERS

Errors and uncertainties as well as variations were found between the results obtained with the tubes and canisters. The reliability of the analytical methods used to quantify the VOCs had to be validated, especially because the concentrations of VOCs measured with the tubes differed from those of the canister samples. The accuracy (how close the measured values found were to the true values) and precision (how close were results obtained in exactly the same way) for the analytical methods were determined.

6.1.1 Possible changes in the external calibration

This study was carried out over a period of more than a year. Supelco recommend that the external calibration standard Supelco (Cat no: 41900-U) should not be used for a period longer than a year to exclude the possible decrease in the concentration of VOCs with time. The concentrations of the VOCs in the standard are between 0.99 and 1.05 ppm. The levels of VOCs detected in the ambient samples were in the ppb range.

Two different calibration standards (one used in 2005 and one used in 2006) were injected into the system during January 2006, using the same set of conditions. A laboratory blank was also analysed. The individual areas of 39 VOCs obtained from the two calibration standards were compared in the following manner:

1. The areas measured in the laboratory blank that correlated with the retention times of the VOCs in the calibration standard were subtracted from the areas of the VOCs in the two calibrations standards. These areas were used to obtain the absolute difference between the two calibration standards.
2. It was assumed that the concentrations of the VOCs in the new standard was correct and had not changed.
3. Absolute differences between the peak areas for each individual VOC in the two calibration standards were obtained.

$$\textit{Absolute difference} = |\ \textit{Area in new calibration standard} - \textit{area in old calibration standard}\ | \quad (6.1)$$

4. The response factor (R_f) for each individual VOC was calculated using the following formula.

$$R_f = \frac{\textit{area of VOC in the new standard}}{\textit{concentration of VOC}_{(standard)}\ (ppm) \times \textit{time (min)} \times \textit{flow rate}\ (cm^3.min^{-1})} \quad (6.2)$$

5. The difference in the concentration of VOCs between the old and the new calibration standard was then calculated and given in Table 6.1:

$$C_{(ppb)} = \frac{\textit{absolute difference (From 6.1)}}{\textit{time (min)} \times \textit{flow rate}\ (cm^3.min^{-1}) \times R_f} \times 1000 \quad (6.3)$$

Table 6.1: Changes in the concentrations (x 10^{-3} ppb) of VOCs in the calibration standard over a one-year period

VOC in Supelco standard	Difference in concentration (x 10^{-3} ppb) between the old and the new calibration standard
Freon-12	0.39
Chloromethane	1.80
Freon-114	0.13
Vinyl Chloride	3.45
Bromomethane	1.99
Chloroethane	3.28
Freon-11	1.89
1,1-Dichloroethene	1.11
Methylene chloride	3.14
Freon-113	0.41
1,1-Dichloroethane	0.99
Cis-1,2-Dichloroethylene	1.40
Chloroform	0.33
1,2-Dichloroethane	3.38
1,1,1-Trichloroethane	0.25
Benzene	0.10
Carbon Tetrachloride	0.86
1,2-Dichloropropane	2.73
Trichloroethylene	2.50
Cis-1,3-Dichloropropene	3.79
Trans-1,3-Dichloropropene	0.37
1,1,2-Trichloroethane	1.73
Toluene	0.52
1,2-Dibromoethane	3.04
Tetrachloroethylene	1.50
Chlorobenzene	1.16
Ethylbenzene	0.13
p-Xylene	0.59
m-Xylene	0.59
Styrene	0.45
o-Xylene	0.73
1,1,2,2-Tetrachloroethane	0.73
1,3,5-Trimethylbenzene	0.86
1,2,4-Trimethylbenzene	0.87
1,3-Dichlorobenzene	1.19
1,4-Dichlorobenzene	0.98
1,2-Dichlorobenzene	1.70
1,2,4-Trichlorobenzene	1.26
Hexachloro-1,3-butadiene	2.28

From Table 6.1 it appeared that the concentrations in the calibration standard changed so little that its contribution to possible variations in the reported results can be ignored. It also appeared that the chlorine containing

compounds are more susceptible to deterioration than the other VOCs, but even those changes were insignificant. CFC's are very stable as expected.

6.1.2 Validation of canister results

The validation of canister results was done by injecting the Supelco standard (Cat no: 41900-U) containing 39 VOCs, with known concentrations (± 100 ppb) into a canister. The standard was taken from vacuum to 40 psi, without dilution, into the canister. Three replicate samples were taken and treated in the same way as the unknown samples. This was done as follows:

1. The average peak area for each individual VOC was calculated. This was done by adding all three the peak areas (from the three replicates) for each VOC together and dividing by three. The average peak areas were assumed to be the correct areas.

$$Average\ peak\ area = \frac{sum\ total\ of\ all\ three\ peak\ areas\ for\ a\ specific\ VOC}{3} \qquad (6.4)$$

2. The absolute error in terms of areas for every peak in all three replicates was calculated. This gave an indication of how much the individual peak area differed from the corrected area (average area) of each VOC.

$$Absolute\ error\ for\ each\ individual\ VOC = \frac{area\ of\ individual\ peak - average\ peak\ area\ (from\ 6.4)}{average\ peak\ area} \qquad (6.5)$$

The average error (as an indication of accuracy) in terms of area for each individual VOC was calculated by using Excel and is given in Table 6.2.

$$Average\ error\ in\ areas\ for\ each\ VOC = \frac{sum\ total\ of\ absolute\ errors\ for\ an\ individual\ VOC}{total\ of\ three\ replicates} \qquad (6.6)$$

3. The response factor (R_f) for each individual VOC was calculated using the following formula:

$$R_f = \frac{\text{average peak area for each individual VOC (from 6.4)}}{\text{concentration of VOC}_{standard}\ (ppm) \times \text{time (min)} \times \text{flow rate } (cm^3 . min^{-1})} \quad (6.7)$$

4. The average error of the areas was then converted to the average error in terms of the concentration (in ppb) for each individual VOC and given in Table 6.2:

$$\text{Average error in } C_{(ppb)} = \frac{\text{average error for each VOC (from 6.6)}}{\text{time (min)} \times \text{flow rate } (cm^3 min) \times R_f \text{ (from 6.7)}} \times 100 \quad (6.8)$$

5. The standard deviation (as a measurement of precision) of the area for each individual VOC was calculated by using Excel. The assumption was made that the average areas (see Formula 6.4) of the replicate samples were the correct areas.
6. The standard deviation of the areas was then converted to the standard deviation in terms of the concentration (in ppb) for each individual VOC and given in Table 6.2:

$$\text{Standard devaition in } C_{(ppb)} = \frac{\text{standard deviation in area for the individual VOC}}{\text{time (min)} \times \text{flow rate } (cm^3\ min^{-1}) \times R_f \text{ (from 6.7)}} \times 100 \quad (6.9)$$

6.1.3 Validation of tube results

Validation of the tube results was done by injecting a known volume of the Supelco standard (Cat no: 41900-U) containing 39 VOCs, with known concentration, (± 100 ppb) into a previously cleaned tube. The tube was then analysed. This was repeated four times. Four replicate samples were used to carry out the calculations. Formulae 6.4 – 6.9 were used in a similar way for the calculations of the absolute error and the standard deviation in the tubes as well as in the canisters. For the tubes four replicate samples were

taken, and not three as in the case of the canisters. The results are given in Table 6.2.

Table 6.2: Comparison of the standard deviation (x 10^{-3} ppb) and the average error (x 10^{-4} ppb) for canisters and tubes

VOCs in Supelco standard	Concentration in the standard (x 10^{-3} ppb)	Replicate samples taken from canisters		Replicate samples taken from tubes	
		Average error (x 10^{-4} ppb)	Standard deviation (x 10^{-3} ppb)	Average error (x 10^{-4} ppb)	Standard deviation (x 10^{-3} ppb)
Freon-12	1.01	5.66	0.94	5.98	52.7
Chloromethane	1.00	1.36	1.19	4.52	28.7
Freon-114	1.02	0.14	0.17	3.38	10.6
Vinyl Chloride	1.02	0.45	0.05	23.9	61.3
Bromomethane	1.03	0.89	0.11	9.38	42.2
Chloroethane	1.03	5.35	0.20	7.08	20.2
Freon-11	0.99	0.17	0.07	9.08	132
1,1-Dichloroethene	1.03	5.14	1.10	4.40	42.5
Methylene chloride	1.03	10.0	0.53	3.33	15.2
Freon-113	1.03	0.24	0.36	4.49	125
1,1-Dichloroethane	1.03	0.73	0.10	3.66	30.0
Cis-1,2-Dichloroethylene	1.03	0.51	0.08	4.16	44.4
Chloroform	1.02	1.32	0.30	6.53	62.0
1,2-Dichloroethane	1.03	3.91	0.25	6.49	46.6
1,1,1-Trichloroethane	1.03	0.95	0.43	9.51	155
Benzene	1.03	2.01	0.40	4.35	63.4
Carbon Tetrachloride	1.00	1.25	0.32	1.70	24.6
1,2-Dichloropropane	1.02	2.11	0.26	3.19	32.6
Trichloroethylene	1.03	0.48	1.17	37.0	65.8
Cis-1,3-Dichloropropene	0.99	4.07	0.42	5.99	34.3
Trans-1,3-Dichloropropene	1.03	4.98	0.54	8.12	43.0
1,1,2-Trichloroethane	1.05	1.27	0.44	2.93	57.5
Toluene	1.02	3.17	1.01	11.6	169
1,2-Dibromoethane	1.04	5.60	0.87	4.91	52.1
Tetrachloroethylene	1.01	0.60	0.29	2.58	74.1
Chlorobenzene	1.02	2.73	1.19	3.43	63.3
Ethylbenzene	1.01	2.36	1.32	2.73	68.0
p-Xylene	1.01	0.78	0.81	1.46	58.7
m-Xylene	1.01	0.78	0.81	1.46	58.7
Styrene	1.00	1.95	0.87	3.40	68.9
o-Xylene	1.02	0.57	0.72	1.89	74.6
1,1,2,2-Tetrachloroethane	1.02	0.57	0.72	1.89	74.6
1,3,5-Trimethylbenzene	1.02	1.61	0.97	1.28	30.8
1,2,4-Trimethylbenzene	1.01	1.85	1.24	3.51	70.6
1,3-Dichlorobenzene	1.00	1.32	1.00	4.04	106
1,4-Dichlorobenzene	1.01	3.12	3.24	4.13	106
1,2-Dichlorobenzene	0.99	2.51	2.02	5.77	119
1,2,4-Trichlorobenzene	0.96	9.81	2.87	52.2	181
Hexachloro-1,3-butadiene	0.98	4.09	2.68	17.1	134

From data in Table 6.2 it can be concluded that the standard deviation and the absolute error in both the canisters and the tubes are so small, they can be safely ignored.

6.2 SUMMARY OF CONCLUSIONS FOR THE CAPE TOWN STUDY

Conclusions for Cape Town include:

1. During the night more unsaturated VOCs were detected than during the day. These compounds are probably removed by photochemical reactions during daytime.
2. The night samples also contained longer chain HCs; these are probably reduced to shorter chain compounds by photochemical reactions during the day.
3. The number of ketones present also seemed to be higher during the day than the night; they are probably the products of photochemical reactions.
4. The city centre and Khayelitsha were the only ground level sites where a wide range of halogenated hydrocarbons was detected on ground level, most probably indicating the burning of halogenated materials for heating and cooking.
5. Concentrations of chlorinated hydrocarbons seem not to change very much in the day and night samples. This correlated with the fact that they are not taking part in photochemical reactions at an observable rate.
6. It appeared that the concentration of the VOCs at different altitudes in some cases differ significantly. This correlated with the brown haze that forms visible layers and it seemed that the concentration of VOCs in layers differed.
7. The VOCs found on ground level are in most cases related to petroleum products. At higher altitudes the VOCs were either the products of photochemical reactions or more stable VOCs that remained in the atmosphere and can be transferred from their source over great distances.

6.3 SUMMARY OF CONCLUSIONS FOR THE VAAL TRIANGLE STUDY

Conclusions for the Vaal Triangle include:

1. A wide variety of pollutants were detected at each site in the Vaal Triangle. The wide range can be ascribed to the fact that the Vaal Triangle is a highly industrialised area with many different types of industries.
2. The Vaal Triangle is a highly polluted area especially during the wintertime. The north-east wind prevailing on the day of sampling diluted the VOCs sampled in the Vaal Triangle.
3. The BVOCs detected (although BVOCs were not the main focus of the study) include: isoprene (2-methyl-1,3-butadiene) and limonene.
4. The possibility for photochemical reactions to occur in the presence of sunlight and higher concentrations of O_3 and NO_2 in this region give a unique opportunity to investigate the formation of photochemical products higher during daytime.
5. A large range of halogenated VOCs was found in the Vaal Triangle. According to Bruckmann and Kersten (1988), halogenated hydrocarbons are typically found in industrial areas and the results found seem to support this statement.

6.4 COMPARISON OF CAPE TOWN AND THE VAAL TRIANGLE

A comparison of the VOCs sampled in Cape Town and the VOCs sampled in the Vaal Triangle include:

1. In both regions the toluene had higher concentrations in the samples at higher altitudes than the ground samples. In both regions toluene was the VOC with the highest concentration of all the measured VOCs. This correlates with the study of Oosthuizen *et al.* (1998) where toluene was found to have the highest concentration of all measured VOCs in the major metropolitan areas in South Africa.
2. The reported daytime benzene concentrations at Goodwood, Table View and the city centre and the nighttime levels in Khayelitsha

exceeded the annual average target value of 1.6 ppb (5 $\mu g.m^{-3}$). (It is assumed that future air quality legislation in South Africa will propose an annual average value of 1.6 ppb.) The low benzene concentration levels in the Vaal Triangle are mainly due to the wind diluting pollution at the time of sampling. Benzene was detected in samples at higher altitudes but the concentrations found were still below the proposed new air quality guideline.

3. A wider variety of VOCs were detected in the Vaal Triangle than in Cape Town. This may be due to the fact that the Vaal Triangle is a highly industrialised area and pollution is not only from domestic wood burning for household purposes and motor vehicles.
4. Pollutants detected at each site in the Vaal Triangle had very low concentrations, mostly even below the detection limits. The lower concentrations of the VOCs found in the Vaal Triangle compared to the Cape Town study may be due to the strong winds that are typical for August in the Vaal Triangle.
5. The BVOCs were detected in both regions and include well-known compounds such as: isoprene (2-methyl-1,3-butadiene) and limonene.
6. The concentration of O_3 in the Vaal Triangle was much higher than in Cape Town. The average O_3 levels in Cape Town for July is much higher than the levels measured during the sampling time (Brunke, E., Personal communication, 10 March 2004). The NO_2 levels measured at the city centre in Cape Town were much higher than levels measured in the Vaal Triangle. In both areas the influence of photochemical processes is evident and secondary products of photochemical reactions were found.
7. A large range of halogenated VOCs was found in the ground level samples in the Vaal Triangle. Industrial areas generally have elevated halogenated hydrocarbons (Bruckmann & Kersten, 1988). Halogenated hydrocarbons were detected at higher altitudes in the Cape region and in the Vaal Triangle. Halogenated VOCs were also detected in the city centre in Cape Town and in Khayelitsha.

8. In both regions a large range of complex benzene derivates were found. In most cases these derivates contained methyl-, ethyl-, or halogen substitutions.
9. The identification of the unknown compounds was much easier in samples taken with the SPME than the other techniques used, because the spectra had less background noise.

6.5 COMPARISON WITH OTHER STUDIES

In Table 2.6 a list of similar studies at ground level is given. If the canister results from this study at ground level are compared with the data in Table 2.6, the following conclusions can be made:

1. The detection limit of the analytical methods used in this study was 0.2 ppb. In Table 2.6 some researchers measured concentration levels lower than this, using different detectors than the MS used in this study.
2. Some researchers have quantified compounds detected in this study but not quantified due to absence in the calibration standard.
3. The chloroform measured by Zielinska *et al.* (2001) in Mexico City was much lower than the average value sampled in the Cape Town or the Vaal Triangle.
4. The benzene level of 5.58 ppb measured at Goodwood is very similar to the level in Athens (Moschonas & Glavas, 1996) and Osaka (Tsujino & Kuwata, 1993), but much lower than the 45.5 ppb sampled in Sydney harbour by Duffy and Nelson in 1996.
5. The highest concentration of toluene sampled during the day at the city centre (10.4 ppb) and the 7.72 ppb (sampled at Goodwood during the night) correlates with the toluene (9.0 ppb) that Colón *et al.* (2001) sampled in São Paulo and the average of 7.09 ppb sampled by Vukovich, (2000) in Baltimore. These values are much higher than the concentration levels in Vanderbijlpark (0.40 ppb) or Sasolburg (0.40 ppb).
6. The ethylbenzene levels of 5.86 and 5.10 ppb measured in the city centre are lower than ethyl benzene levels measured in Sydney

Harbour (8.6 ppb) by Duffy and Nelson (1996). This is higher than the samples taken in Athens (Moschonas & Glavas, 1996), Baltimore (Vukovich, 2000) or Osaka (Tsujino & Kuwata, 1993).

7. For p- and m-xylene the average of 4.12 ppb correlates with the concentration level of 4.6 ppb sampled in a canister in São Paulo by Colón *et al.* (2001).
8. The styrene measured in the city centre during the night and the day (4.78 and 4.59 ppb, respectively) was much higher than the levels measured by Vukovich (2000) and Colón *et al.* (2001).
9. The concentration of 1,2,4-trimethylbenzene in Khayelitsha (4.10 ppb), the night sample at the city centre (4.30 ppb), the day sample at the city centre (4.90 ppb) correlate with the 3.9 ppb measured in Athens (Moschonas & Glavas, 1996). Again the concentrations in the Vaal Triangle were much lower (0.53 ppb in Vereeniging, 0.53 ppb in Vanderbijlpark and 0.63 ppb in Sasolburg).

6.6 PROJECT EVALUATION

The objectives and the goals for this study were stated in Chapter 1. The main goal of the study was the identification, quantification and comparison of VOCs in Cape Town and the Vaal Triangle. A larger number VOCs could be identified and quantified at ground level and at different altitudes in ambient air in both Cape Town and in the Vaal Triangle region. The techniques employed were aimed at identifying and quantifying man-made emissions. The total VOC profile may differ from these since oxygenated species have not been focussed on.

Comparing the values obtained using canisters with the Carbotrap^{TM} 300 tubes showed differences that cannot be explained unambiguously. VOCs sampled with SPME correlated with the above-mentioned techniques and proved to be a handy screening tool in the identifying of VOCs.

A comparison of the two different regions investigated gave more insight into the concentrations and the fate of VOCs on a regional and global scale in

South Africa. It followed from the results reported in this study that VOC emissions in Cape Town and in the Vaal Triangle would most definitely play a significant role in the formation of photochemical smog. Photochemical reactions remove certain VOCs but lead to the formation of secondary VOCs (see Par. 2.5.4.1).

6.6 FUTURE STUDIES

This was the first study aimed at identifying and quantifying as many VOCs as possible in ambient air in these two regions. The following uncertainties and issues that must be addressed follow from this study.

1. A study over a longer period of time, including the summer and winter seasons, would probably give more information about the origin and removal of the wide range of VOCs found.
2. The significantly larger range of chlorinated HC in the Vaal Triangle is interesting and needs further investigation. Weissflog *et al.*, (2004) reported high concentrations of the secondary VOC TCA (trichloric acid) in the Vaal Triangle that can have a negative impact on plant growth.
3. The discrepancies between the concentrations of VOC sampled with tubes and canisters need further investigation. In some cases the differences found were indeed very large.
4. The contribution of the emissions of commercial aircraft from the Cape Town International Airport and the effect of these VOC emissions on Cape Town and in particular the pollution in Khayelitsha also needs to be investigated.
5. No results of the VOC contribution of the ever-increasing marine-traffic in the Cape Town harbour have been published and this unique source may be of great interest.
6. Biomass burning processes in both the CMC and the Vaal Triangle needs to be more fully quantified and potential health implications assessed.

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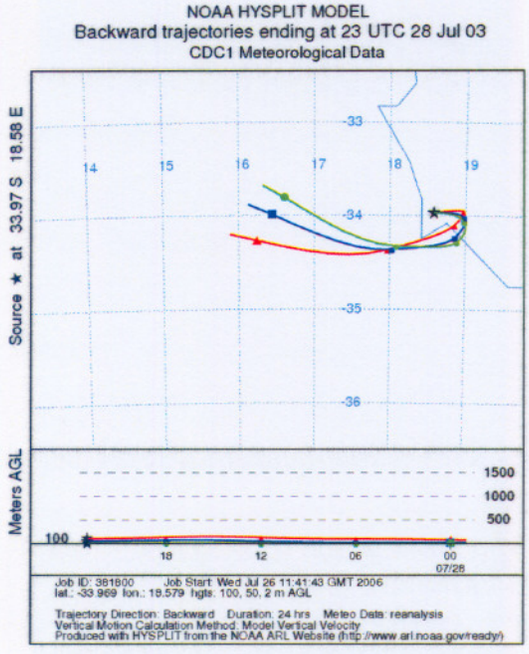
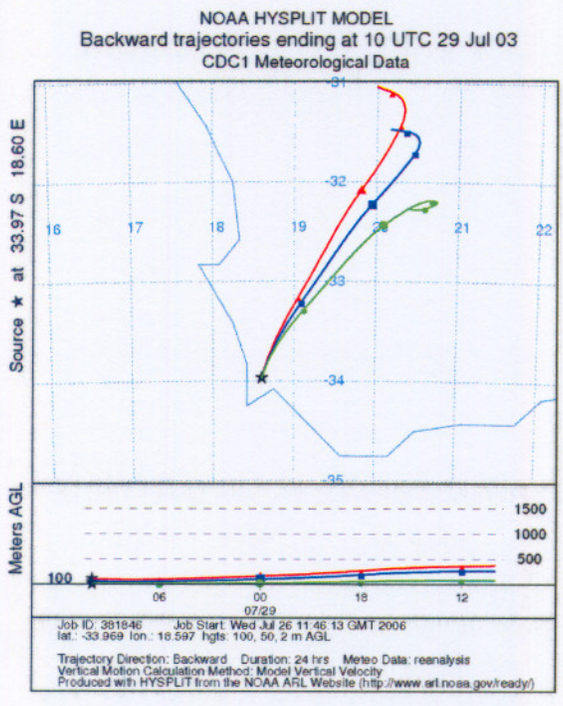
APPENDIX 1

BACK TRAJECTORIES FOR CAPE TOWN USING THE NOAA HYSPLIT MODEL

Back trajectory for the night of 28th July 2003



Back trajectory for the night of 29th July 2003



APPENDIX 2

BACK TRAJECTORIES FOR THE VAAL TRIANGLE USING THE NOAA HYSPLIT MODEL

Back trajectory for the night of 20th August 2004