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Volatile organic compounds(VOC's) analysis from Cape Town haze II study

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Declaration

I declare that this Dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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Abstract

A brown haze which builds-up over Cape Town under calm and cold weather conditions causes public concern. The brown haze is thought to be due to the gaseous and particulate emissions from the city, industries, traffic and townships in the Cape Town region. Volatile organic carbon (VOCs) compounds are an important component of the haze layer particularly because of their reactivity. VOCs play an important role in the carbon budget and radiation balance, regional oxidant balance, and in the distribution of ozone and other reactive gases, both at the regional and global scale. In this study the variation in ambient VOC concentrations during brown and non-brown haze days over Cape Town during July and August 2003 were characterised. Ambient air samples were collected in evacuated stainless steel canisters from the South African Weather Service (SAWS) research aircraft (Aerocommander, ZS-JRB) and later analysed by gas chromatography equipped with a flame ionisation detector (GC-FID). Benzene, toluene, ethylbenzene and xylene (BTEX) were the specific VOCs targeted for this study. Comparable meteorology data was also collected to determine the effects of wind fields and atmospheric stability on BTEX concentrations.

Benzene and ethylbenzene were detected as the most abundant VOCs during brown haze days and highly stable conditions, whereas xylenes were significant on non-brown haze days and slightly stable conditions. Toluene concentrations were similar for both brown and non-brown haze days, highlighting the existence of a similar continuous source of this species over Cape Town. The prevailing wind direction was northerly to north westerly during brown haze days. Local BTEX concentrations were examined throughout Cape Town to identify sites with the highest concentrations. On average the highest levels of benzene (138 $\mu g.m^{-3}$), toluene (386 $\mu g.m^{-3}$), ethylbenzene (228 $\mu g.m^{-3}$) and xylene (122 $\mu g.m^{-3}$) were detected in the CBD, Mitchell's Plain (township), Wallacedene and Grassy Park respectively during both brown haze and non-brown haze days throughout Cape Town. Significant BTEX concentrations did not only correspond to brown haze episodes; non-brown haze episodes also showed considerable concentrations. Benzene to toluene (B/T) ratios for all episodes except brown haze afternoons were lower

than 0.3 implicating sources other than vehicle emissions contributing to the levels of the two species. This study identified vehicle emissions and stationary sources such as industries and domestic fuel burning as the primary sources of BTEX compounds over the Cape Town region. Concentrations of these species in this study were relatively high in comparison to typical World Health Organisation guidelines, and are a cause of concern with respect to health risks especially as these values are not taken at the surface where many of the listed emissions occur.

Preface

Volatile organic carbon (VOCs) compounds form an important component of the troposphere because they are highly reactive and are precursors of greenhouse gases such as ozone. Knowledge of their atmospheric transformation processes, with regard to their relationships with oxides of nitrogen, hydroxyl radicals and sunlight, is essential to the understanding of the regional and global atmosphere. Identifying source types and strengths is critical to this understanding and for monitoring and controlling the emissions of VOCs.

Although inadequate scientific data for VOCs exists for South Africa, this study provides baseline data for further studies and modelling of these pollutants throughout the country. The new air quality legislation of South Africa has recently been approved by the national parliament, and it is believed that it will bring about reductions in emissions within a decade provided its enforcements and penalties are observed. The aim of this study is to characterise VOCs (particularly BTEX) from the brown haze layer in the Cape Town region. Specifically, the primary objectives of this study are to:

(a) quantify the ambient concentrations of benzene, toluene, ethylbenzene and xylene (BTEX) compounds over Cape Town;

(b) compare BTEX concentrations from a non-brown haze to a brown haze day;

(c) determine the BTEX concentration variation through the day; and

(d) investigate sources of these BTEX compounds.

The report is divided into four chapters. **Chapter 1** presents the basis of the study giving literature review on previous air pollution and volatile organic carbon

compounds studies undertaken in other countries and related background information. **Chapter 2** outlines the description of VOCs sample collection and data analysis methodologies used in this study. The results are presented and discussed in **Chapter 3**. Results are also compared to those obtained in similar studies worldwide. In **Chapter 4** the key findings are summarised and conclusions are presented.

Sections of this report have been presented at the National Association for Clean Air (NACA) and South African Society for Atmospheric Sciences (SASAS) annual conferences in 2003 and 2004.

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List of Abbreviations

APPA – Atmospheric Pollution Prevention Act
BTEX – Benzene, toluene, ethylbenzene, xylenes
CBD- Central Business District
CRG – Climatology Research Group
CSIR - Council for Scientific and Industrial Research
CTM –Cape Town Metropolitan
DEAT - Department of Environmental Affairs and Tourism
EPA – Environmental Protection Agency
FID – Flame Ionisation Detector
Ft - Feet
GC - Gas Chromatography
HAP – Hazardous Air Pollutants
HNO_3 – Nitric acid
ISO – International Standards Organisation
NACA – National Association for Clean Air
NMHC – Nonmethane hydrocarbons
NO_2 - Nitrogen dioxide
NO_x - Oxides of nitrogen
NRF - National Research Foundation
O_3 – Ozone
OH – Hydroxyl radical
PAN – Peroxyacetyl nitrate
Pb - Lead
PM – Particulate matter
ppb – Parts per billion
R^2 – Correlation coefficient
SAPIA - South African Petroleum Industry Association
SASAS – South African Society for Atmospheric Sciences
SAWS – South African Weather Services
SO_2 – Sulphur dioxide
$Tg.yr^{-1}$ – Terra grams per year
THRIP - Tertiary Human Resource and Industry Programme
UK – United Kingdom
US – United States
UV - Ultraviolet
$\mu g.m^{-3}$ – micro grams per cubic metre
VOCs – Volatile organic carbons
WHO – World Health Organisation

Chapter 1 Overview

Air pollution in South Africa, specifically Cape Town is discussed in detail. Previous studies of volatile organic carbon (VOCs) compounds and their effects on tropospheric chemistry and the global carbon budget are examined. Objectives of this study are outlined in this chapter.

Introduction and Literature Review

Air pollution has played a critical role in human lives and the climate since the early 1950s. During the last millennium industrial revolution increased population growth and urbanisation have been the major determinants in shaping our environmental quality. Scientists also began to understand the cause and atmospheric mechanisms for the formation of Los Angeles photochemical smog during the 1950s. It is now known that surface level ozone and photochemical smog are a worldwide problem at both regional and continental scales (Karnosky *et al.,* 2003). Studies continue on the atmospheric photochemical processes, air pollutant transport, their atmospheric transformations and removal mechanisms in an effort to control and monitor the emissions of primary pollutants. Knowledge of the adverse effects of air pollutants on human health and welfare has improved substantially over the past 20 years. Further studies have also been directed to improve the levels of understanding of the accumulation of persistent inorganic and organic chemicals in the environment and their impacts on sensitive receptors, including humans (Karnosky *et al.,* 2003).

Recent environmental literacy has become an increasingly important factor in our lives, particularly in the developing nations due to their rapid population and industrial growth (Karnosky *et al.,* 2003). Currently the scientific, public and political communities are concerned with the increasing global scale air pollution and the consequent global climate change implications. Human health, environmental impacts,

risk assessment and the associated cost-benefit analyses, including global economy form an essential component in dealing with air pollution issues. Air pollution issues in South Africa were only brought to public attention in the late eighties as a result of concerns expressed over the high emissions from industries in the Highveld region. Most of South Africa's coal is burned on the Highveld in industrial plants such as petrochemical works, smelters, manufacturing plants and power plants (van Tienhoven, 1999). With the rapid increase in industries and population growth in South Africa, an effective control of emissions into the atmosphere is essential.

Methodological and data constraints affect air pollution studies in the African continent. Inadequate quantitative data are available on the extent of air pollution with regard to sources or source types, transport, transformations in the atmosphere, deposition of pollutants and the associated health impacts on a regional and continental scale; despite the good understanding of the controlling mechanisms. In addition, the influence of pollution on regional climate and meteorology also requires extensive attention. Although the research and monitoring of air pollution has been largely fragmented and uncoordinated, a substantial amount of information on air quality has been collected. South Africa is among the top ten countries contributing to the global greenhouse effect, and accounts for the 15% of the greenhouse gas emissions for the African continent (van Tienhoven, 1999).

Brown haze

Haze can be defined as an aerosol that impedes vision and may consist of a combination of water droplets, pollutants and dust. An aerosol is technically defined as a suspension of fine solid or liquid particles in a gas, and is generally considered being a particle that range in size from a few nanometres (nm) to tens of micro-metres (μm) (Seinfeld *et al.,* 1999; Jacobson, 2002). Brown haze formation over cities and surrounding industrial areas is a worldwide phenomenon (Ramanathan *et al.,* 2002). During the 19th and early 20th centuries dramatic smog episodes, known as pea-soupers, associated with the burning of coal became common in many Britain's inner cities leading to a poor air quality. One of the major London smog occurred in December 1892 and lasted for 3 days, resulting in approximately 1000 deaths. A similar episode occurred on the 4th December 1952 and lasted for 5 days and resulted in approximately four thousand deaths. In response to this, the London government passed its first Clean Air Act in 1956, which aimed to control domestic sources of smoke (Air Quality Topics, 2004).

The colour of the brown haze was originally attributed to the blue absorbing gas, nitrogen dioxide (NO_2), until laboratory studies by Charlson and Ahlquist (1969) showed that the wavelength dependence of the extinction coefficient was due to light scattering by atmospheric aerosols and was mostly responsible for a yellow or brown haze (Waggoner *et al.,* 1983). Recent studies by Jacobson (2002) have attributed the reddish brown colour in smog to the presence of NO_2, absorption in the UV and visible by nitrated aromatics and polycyclic aromatic hydrocarbons in aerosol particles, with an occasional and small enhancement by suspended soil and dust. Castro (2001) found that in Mexico City the presence of aerosols in the atmosphere can have a non-negligible effect on the ultraviolet radiation field and hence on the formation of photochemical smog. Studies by Groblicki *et al.* (1981) suggested that most of light absorption in the Denver haze is due to fine elemental carbon in the particulate matter. In Los Angeles

two potential causes of brown-yellow smog colour have been identified as light absorption by gaseous NO_2 and wavelength dependent light scattering by aerosols.

In addition, it was also found that the angle between the observer's line of sight and the sun play an important role in the coloration of the smog layer and it also determines the relative importance of NO_2 and aerosol (Husar and White, 1976). Further studies carried out by Hodkinson (1966) on the optical effects of gaseous NO_2 in the presence and absence of aerosols found that in the absence of aerosols the colour of distant white objects, viewed through NO_2 to resemble that of scotch whisky, while calculations with the presence of aerosols suggests the role of aerosols as to reduce the coloration of smog by the introduction of white air light. Some organic aerosol particles scatter the incoming solar radiation back into space. In so doing, these aerosols reduce the amount of incoming solar energy and consequently cool the Earth's surface (Seinfeld *et al.,* 1999). Observations and numerical models show that UV-scattering particles in the boundary layer accelerate photochemical reactions and smog production, but UV-absorbing aerosols such as mineral dust and soot inhibit smog production (Dickerson *et al.,* 1997). And the results can have major implications for the control of air pollution (Charlson *et al.,* 1992).

Brown haze is a term used to describe a brown coloured smog (extensive contamination by aerosols) found predominantly in the wintertime in the Cape Town and other cities. It occurs mostly from April to September due to strong temperature inversions and windless conditions that prevent pollutants from dispersing upwards or into the sea. This leads to the build-up of pollutants emitted into the atmosphere very close to ground level. (Wicking – Baird *et al.*, 1997; CCT, 2001). The haze extends over most of the Cape Metropolitan Area, and shifts depending on the direction of wind. It is normally most intense in the morning after which it lifts and disperses as the day progresses as a result of the lifting of the inversion layers (Wicking – Baird *et al.*, 1997). It has a strong degrading effect on visibility, which is immediately apparent to the general public and tourists (Wicking – Baird *et al.*, 1997). The haze is also cause for

concern to residents because of health risks that may accompany the visible air pollution. The same conditions that are conducive to the formation of a haze are also conducive to the accumulation of gases, which are invisible that can have unpleasant health and odour effects (Wicking – Baird *et al.*, 1997). Studies by Wicking – Baird *et al.* (1997) indicated that brown haze in the Cape Town region is due to the gaseous and particulate emissions (aerosols) from the city, industries, traffic and townships. Generally, aerosols and gases such as volatile organic carbon compounds (VOCs) that undergo chemical transformations within the haze layer are the most contributory factors to the visibility impairment and are a cause of concern to residents because of their adverse health and environmental impacts. Cape Town brown haze also consists of secondary pollutants such as ozone, peroxyacetylnitrate (PAN) and other organic aerosols derived from the oxidation of VOCs. Chemical transformations of volatile organic carbon compounds into other secondary species have significant influence on the composition and formation of brown haze. As a result, in depth characterisation of these VOCs is essential.

Volatile Organic Carbon Compounds (VOCs)

Volatile organic carbon compound is the word used to denote the entire set of vapour phase atmospheric organics excluding CO and CO_2, with boiling points (1 atm) below 260 ^{0}C (Seinfeld *et al.,* 1999; De Nevers *et al.,* 2000; Hewas *et al.,* 2002) and are classified as hazardous air pollutants (HAPs). They are called organics because they contain the element carbon in their molecular structures. They are described by the United Nations Economic Commission for Europe as all organic compounds of anthropogenic nature other than methane that are capable of producing photochemical oxidants by reactions with oxides of nitrogen (NO_x) in the presence of sunlight (Wicking – Baird *et al.*, 1997; Seinfeld *et al.,* 1999).

VOCs are highly reactive and these reactions have significant consequences for the chemical composition of the atmosphere (Fujita *et al.,* 1995; Andreae and Crutzen,

1997; Derwent; 1999; Kourtidis *et al.,* 1999; Atkinson *et al.,* 2000; Derwent *et al.,* 2000; Na *et al.,* 2000; Fernandes *et al.,* 2002; Hakami *et al.,* 2004). For example, VOCs and NO_x are known precursors of ozone (O_3), a greenhouse gas involved in global warming of the atmosphere (Liu *et al.,* 1987; Warneck, 1988; Seinfeld *et al.,* 1999; De Nevers *et al.,* 2000). Their reactions can also lead to the formation of peroxyacetylnitrate (PAN), which can be transported over long distances, and other oxidants (Finlayson-Pitts and Pitts, 1986; Warneck, 1988; Friedrich and Obermeier, 1999; Kalabokas *et al.,* 2001). Further more, VOCs play an important role in the carbon budget, the radiation balance and the regional oxidant balance, both at the regional and global scale. Characterising VOCs requires the individual chemical compounds that constitute the entire mixture, and not just the total VOCs because of their variability in atmospheric behaviour (Seinfeld *et al.,* 1999).

VOCs play a major role in regulating the oxidation potential of the troposphere. They are unstable, with short lifetimes in the atmosphere and undergo chemical transformation processes (oxidation) resulting in the formation of a variety of secondary pollutants and aerosols in the presence of hydroxyl radicals and light, according to equations 1 to 5. It is well known that reaction with OH radicals is the primary mechanism by which most volatile organic compounds are removed from the atmosphere (Brasseur *et al.,* 1999). BTEX compounds have different reactive properties towards hydroxyl radicals resulting in variations in their atmospheric levels during certain times of the day (Atkinson, 2000).

Accurate kinetic and mechanistic data for reactions of OH radicals with organic compounds are therefore essential to model the contribution of anthropogenic emissions to the formation of smog in urban areas. In the troposphere, photochemical ozone production begins with the attack of parent hydrocarbons (RH) (e.g. volatile organic carbon compound) by tropospheric hydroxyl radicals ($HO^{\cdot}$), in the presence of oxides of nitrogen (NO_x) and light, and proceeds through the following reactions (Jacobson, 2002; Dickerson *et al.,* 1997):

$$RH + HO^{\cdot} \longrightarrow H_2O + R^{\cdot} \quad (1)$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \quad (2)$$

$$RO_2^{\cdot} + NO \longrightarrow RO^{\cdot} + NO_2 \quad (3a)$$

$$RO_2^{\cdot} + NO \longrightarrow RONO_2 \quad (3b)$$

$$NO_2 + h\nu \longrightarrow NO + O \quad (4)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (5)$$

Where $R^{\cdot}$ is an alkyl radical, $RO_2^{\cdot}$ and $RO^{\cdot}$ are its alkylperoxy and alkoxy counterparts respectively, and hν represents a quantum of light from solar radiation. Hydroxyl radicals have strong seasonal concentration dependence, peaking in the summer in temperate and polar regions (Zafonte *et al.,* 1977; Dickerson *et al.,* 1997; Colman *et al.,* 2001; Katzenstein, *et al.,* 2003). The rate of smog production is dependent on the concentrations of these pollutants and the intensity of solar near- UV ($300 < \lambda < 400$ nm) radiation.

Tropospheric ozone produced is a secondary pollutant harmful to both the environment and human life. The types of compounds formed during the process are greatly influenced by the VOC/NO_x ratio. Ozone production is enhanced by high VOC/NO_x levels. At low ratios reactivity of the hydrocarbons and their ability to produce ozone is highly variable. (Dodge 1984; Liu *et al.,* 1987). Reduction in VOCs concentrations causes nitrogen to stay in more stable form like nitric acid (HNO_3), while increasing VOCs favours the formation of more oxidized forms such as PAN (Roselle *et al.,* 1991). Concentrations of volatile organic compounds are indicators of health effects of pollution originating from inefficient combustion. The role that

emissions play in atmospheric chemistry and biogeochemistry especially with regard to production and transport of VOCs and aerosols over southern Africa has drawn the attention of the international research community (Crutzen and Andreae, 1990; Andreae *et al.,* 1992; Stein *et al.,* 2003). In some developed countries, especially United States and Europe, there have been various studies on the nature and ambient concentrations of the aromatic hydrocarbons (Singh *et al.,* 1985; Grosjean *et al.,* 1992; Bowman *et al.,* 1995; Brocco *et al.,* 1997; Grosjean *et al.,* 1999; Skov *et al.,* 2001), for their role as toxic air contaminants and important precursors to the formation of ozone (Carter, 1994; Bowman *et al.,* 1995) and secondary organic aerosols.

Environmental impacts of VOCs

VOCs are important because of their detrimental effects on human health. Typical VOCs examples occurring in the atmosphere that constitute a health risk are benzene, aldehydes, 1,3 butadiene, n-hexene, and some chlorinated hydrocarbons (Wicking – Baird *et al.*, 1997). Benzene guideline exists as 16.25 $\mu g.m^{-3}$ over a 24 hour exposure period according to the World Health Organisation (WHO, 1987). VOCs are emitted from both anthropogenic (industrial processes and motor vehicle exhaust) and biogenic (vegetation and oceans) sources (Rasmussen, 1972; Greenberg and Zimmerman, 1984; Lamb *et al.,* 1995). Biogenic emissions dominate the global budget of VOCs (Fesenfeld *et al.,* 1992; Guenther *et al.,* 1995; John *et al.,* 2002). These VOCs, for example isoprene and mono-terpene are as reactive as or more reactive than anthropogenic VOCs and can also have higher ozone-forming potential (Carter, 1994; Benjamin and Winer, 1998). Even though biogenic VOCs are extremely important this study focuses on anthropogenic VOCs as there have been studies in southern Africa on biogenic emissions, however the anthropogenic data for the region is limited.

Estimates of global anthropogenic non-methane VOCs emissions in 1990 are given in Table 1.1, and the breakdown by chemical compounds is not yet available. Transportation is the largest source of VOCs worldwide, with solvent use following as the second largest source. In South Africa, levels of VOCs also indicate transport as the primary source (559 kilotons yr^{-1}), followed by industrial processes (194 kilotons yr^{-1}), and energy (electricity, industrial, domestic and refineries) (88 kilotons yr^{-1}) (van Tienhoven, 1999).

Table 1.1 Estimated global atmospheric emissions (in Tg yr^{-1}) of non-methane volatile organic compounds (after Seinfeld *et al.,* 1999).

Activity	Emission
FUEL PRODUCTION/DISTRIBUTION	
Petroleum	8
Natural gas	2
Oil refining	5
Gasoline distribution	2.5
FUEL CONSUMPTION	
Coal	3.5
Wood	25
Crop residues (including waste)	14.5
Charcoal	2.5
Dung cakes	3
Road transport	36
Chemical industry	2
Solvent use	20
Uncontrolled waste burning	8
OTHER	10
TOTAL	142

Sources of VOCs

For many years it was thought that VOCs were mainly produced from anthropogenic sources (Lonneman *et al.,* 1978), until the late 1960s that biogenic emissions emerged as another sources. The United States called for a reduction in oxides of nitrogen and anthropogenic VOCs in an attempt to reduce ozone production. It was noticed that no significance reduction in ozone levels were observed and this was the case in other studies. (Trainer *et al.,* 1987). The assumption that anthropogenic VOCs were the principal hydrocarbons, and therefore the main source of ozone was incorrect. The influence of biogenic VOCs on ozone formation can therefore not be underestimated (Chameides *et al.,* 1988).

Anthropogenic VOCs concentration profiles differ from one country to another due to several factors such as legislative control for VOCs, composition of vehicle fuel, differences in heating pattern in residential area and meteorological conditions (Na *et al.,* 2000). Therefore to develop effective strategies on the reduction and control of ambient levels of VOCs, they should be quantified and their major emission sources be identified. In 1998 studies on VOCs emissions in the UK found that 53% came from other sources, 40% from transport, 4% from domestic sources and 3% from industry. In comparison with other pollutants, the monitoring of VOCs in the UK is not yet well developed and there is no long-term database of information (Air Quality Topics, 2004). The automatic hydrocarbon monitoring network is currently monitoring 25 species in urban air on a daily basis. Measurements of speciated VOCs in the urban sites have not been reported so far (Wicking – Baird *et al.*, 1997). Various sources of BTEX ranging from traffic, industrial and domestic emissions are expected in Cape Town. These sources are located mainly in the CBD, residential areas (townships and informal settlements) and highly industrialised areas (Wicking-Baird *et al.,* 1997).

Studies undertaken by Liu *et al.* (2000) presented the first available data and temporal variation of BTEX compounds in China, and showed that concentrations were not only affected by traffic volume and meteorological factors but also by emissions from other sources. Furthermore, laboratory studies conducted by Sigsby *et al.* (1987), found that toluene, ethylbenzene and xylene contents in vehicle exhaust decreased as the driving speed increases. The existing volatile organic carbon compound measurements performed at Cape Town monitoring networks, urban or industrial, are mostly in the form of total non-methane hydrocarbons (NMHC) (CCT, 2001).

All volatile organic carbon compounds are essential; however BTEX compounds are seen as the most common species expected in the Cape Town region due to high fuel concentrations and petrochemical industries. In addition these compounds have implications for the chemistry of the atmosphere and also pose high health risks. Levels of these compounds are thus presumably significant. Other species are not so common in the general atmosphere. This report therefore focuses on the findings from airborne measurements of benzene, toluene, ethylbenzene and xylenes from the second brown haze study in Cape Town.

BTEX Compounds

Benzene

Benzene (C_6H_6) is a clear, colourless liquid with a sweet aromatic odour, a molecular weight of 78.11 g/mol. It can be smelled when it reaches 4792 $\mu g.m^{-3}$ in air (Amoore and Hautala, 1983; ATSDR, 1999). It is formed from both natural such as volcanoes and forest fires and anthropogenic processes. Its vapour form has the melting point of – 5.5 ^{0}C and a boiling point of 80 ^{0}C (Spectrum Chemical Fact Sheet, 2003; EPA, 2004). It is used in motor fuels, in the extraction of oils from seeds and nuts, as a fluid for cleaning, in the printing process and cigarette smoke, in the manufacture of other chemicals such as plastics, resins, nylon, and synthetic fibres, detergents,

explosives, drugs, and dyes. And it is widely used in the United States and ranks in the top 20 chemicals produced (ATSDR, 1997).

Benzene is released when fossil fuels such as wood, coal, and oil are burned. And it is also released when gasoline and diesel evaporate or when it is used in an industrial process. It is found in urban areas at levels between 10 to 64 $\mu g.m^{-3}$ due to greater number of industrial sources such as gas stations and vehicles. In the atmosphere it will exist in vapour phase and react with photochemically produced hydroxyl radicals with a half-life of 13.4 days. In atmospheres polluted with oxides of nitrogen and sulphur dioxide the reaction time is accelerated and the half-life is 4-6 hours; resulting in the production of phenol, nitrophenols, nitrobenzene, formic acid and peroxyacetylnitrate (PAN) as products of photo-oxidation. Benzene is fairly soluble in water and is removed by wet deposition (rain) (Spectrum Chemical Fact Sheet, 2003).

It is known to have both acute (less than 14 days) health effects, such as headache, dizziness, drowsiness and skin, eye and lung irritation; and chronic health effects (longer than 365 days) including cancer, leukaemia, aplastic anaemia, reproductive effects in women, and damage to the immune system health effects. Studies on animals have shown effects when mothers were exposed during pregnancy including low birth weight, delayed bone formation and bone marrow damage. The Maine Department of Environmental Protection (ME DEP) has developed exposure guidelines for benzene as an average of 440 $\mu g.m^{-3}$ over 24 hours exposure and an average of 1.2 $\mu g.m^{-3}$ over one year exposure (EPA, 1992; ATSDR, 1997). The WHO has calculated that over a lifetimes exposure, for every additional $ug.m^{-3}$ of benzene in air, approximately 4 additional cases of leukaemia per million inhabitants can be expected (WHO, 1987).

Toluene

Toluene (C_7H_8) is a clear, colourless liquid with a sweet pungent benzene-like odour, and a molecular weight of 92.13 g/mol. It can be smelled when it reaches 1093 $\mu g.m^{-3}$ in air. It occurs naturally in crude oil fuels (including gasoline and aviation fuels) and in the tolu tree. It is produced during the process of making gasoline and other fuels from crude oil, in the manufacturing of coke from coal and as a by product of styrene (HSDB, 1999). It is a flammable liquid and vapour with a melting point of - 95 ^{0}C, a boiling point of 111 ^{0}C at 760 mm Hg. Toluene vapour is heavier than the air and may spread long distances and can decompose at high temperatures forming toxic gases such as benzaldehyde and cresol. It also has both acute and chronic health effects (EPA, 2004).

Toluene is used in the production of nylon, plastic soda bottles, dyes, explosives, benzene, benzoic acid and many other organic compounds; as a solvent for paints, lacquers, gums, resins and as a gasoline additive. It is also used in making paints, paint thinners, fingernail polish, adhesives, and rubber in some printing and leather tanning processes. It is released into the atmosphere primarily from the volatilisation petroleum fuels and toluene-based solvents and thinners, and from motor vehicle exhaust; and exists as a vapour phase. In the atmosphere it degrades rapidly by the reaction with photochemically produced hydroxyl radicals. Its half-life is 3 hours to some days and it is very effectively washed out by rain (EPA, 1992; Spectrum Chemical Fact Sheet, 2003). EPA has not classified it as a carcinogen and neither human nor animals studies have shown resulting cancer tumours. The Maine Department of Human Services has developed two standards for toluene as an average of 256 $\mu g.m^{-3}$ over 24 hours exposure and an average of 177 $\mu g.m^{-3}$ over one year exposure (EPA, 2004).

Ethylbenzene

Ethylbenzene (C_8H_9) is a colourless liquid with gasoline-like odour and a molecular weight of 106.16 g/mol. It can be smelled when it reaches 10 $\mu g.m^{-3}$ in air (Amoore and Hautala, 1983). It has the boiling point of 136.2 ^{0}C at 760 mm Hg, the melting point of – 95 ^{0}C. It is used in the production of synthetic rubber as a solvent or diluent, as a component of automotive and aviation fuels, in the manufacture of cellulose acetate, and as a precursor to styrene (ATSDR, 1999; Spectrum Chemical Fact Sheet, 2003). It is also known to have both acute (less than 14 days) and chronic health effects.

Information on the development or reproductive effects of ethylbenzene on humans is not available (ATSDR, 1999; HSDB, 1999; US EPA, 1999). Ethylbenzene is not classifiable as a carcinogen to humans by EPA. Ethylbenzene enters the atmosphere from fugitive emissions and exhaust connected with its use in gasoline and exists in vapour phase based on its vapour pressure. More localised emissions include spills from its production and industrial use. It will be removed from the atmosphere by reactions with hydroxyl radicals. Its half-life is 0.5 hours to days, with additional quantities being removed by rain (Spectrum Chemical Fact Sheet, 2003).

Xylene

Xylene (C_8H_{10}) is a clear colourless liquid with a sweet smell, with a molecular weight of 106.17 g/mol, boiling and melting points of 139.3 and – 47.8 ^{0}C respectively. And it can be smelled when it reaches 347 $\mu g.m^{-3}$ (EPA, 1992; Spectrum Chemical Fact Sheet, 2003). It exists in three different forms called isomers namely, meta-, ortho- and para- xylene, meaning that they have the same chemical formula but different chemical structure. The combination of these forms is normally referred to as

xylenes. It occurs naturally in petroleum and coal tar and formed during forest fires (EPA, 1992; EPA, 2004).

Xylene is used in gasoline and aviation fuels, and as a solvent in the printing, rubber and leather industries, as well as an intermediate for dyes and insecticides. Small amounts are found in cigarette smoke. It is one of the most produced chemicals in the United States in terms of volume and ranges from 4 to 382 $\mu g.m^{-3}$ (EPA, 1992; Spectrum Chemical Fact Sheet, 2003.). It is also known to cause both acute (less than 14 days) and chronic health effects. EPA has not classified it as a carcinogen and neither animal nor human studies have shown resultant cancer symptoms. In the atmosphere, it degrades by reactions with photochemically produced hydroxyl radicals and it has a half-life of one hour in summer and 10 hours in winter. The Marine Department of Human Services has developed two guidelines for xylenes as an average of 64 $\mu g.m^{-3}$ over 15 minutes exposure and an average of 295 $\mu g.m^{-3}$ over 24 hours exposure (EPA, 1992; EPA, 2004).

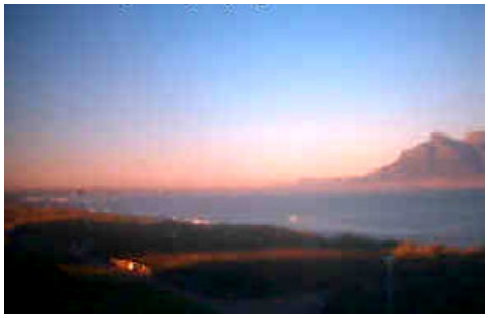
Air Pollution in Cape Town

Cape Town is a city of over 3 million people situated on the southern tip of Africa. Like many other cities in the world the city is faced with deteriorating air quality and this trend could accelerate if corrective action is not taken (CCT, 2001). This is attributed to the combination of its adverse climatic conditions and local topography causing the city to be susceptible to air pollution particularly during autumn and winter (Jury *et al.,* 1992). The city experiences higher pollution levels due to low level temperature inversions trapping pollutants in a mass of stable air. These early morning inversions often coincide with morning peak traffic conditions, causing visible levels of air pollution in the form of a white or brown haze (Wicking – Baird *et al.*, 1997). With the rapid urbanisation and industrialisations in Cape Town, more and more chemicals

are introduced into the atmosphere, and environmental air pollution has attracted increasing public and regulatory concerns (Linde and Ravenscroft, 2003).

Since the late sixties Cape Town has experienced a thick smog over the city thought to be caused by the three power stations in the area, coal-burning locomotives and tugs, industrial incinerators, and heavy fuel burning appliances. The City Council initiated a programme of air pollution control in 1968 that implemented measures terminating the use of coal-burning locomotives and tugs, the closure of two power stations, and enforcement of standards for fuel burning appliances to remedy the situation. This lead to considerable reduction of pollutant levels within a decade. Brown haze emerged as another form of air pollution, leading to the installation of a sophisticated pollution monitoring network targeting pollutants mostly associated with motor vehicles as they were thought to be the major cause of the problem (Wicking – Baird *et al.*, 1997).

Under cold, calm winter mornings and nights, periods of stagnation develop in the region causing pollution levels to rise significantly. This causes a build-up of a brown haze often termed “urban haze” which is usually most intense in the early morning (Figure 1.1) but lifts and disperses as the day progresses (Wicking – Baird *et al.*, 1997; EPA, 2001; Senaratne *et al.,* 2004).



07h30



10h30

Figure 1.1 Brown haze episodes in Cape Town (August 2003). Photograph courtesy of Cape Town air quality website, www.capetownwebcam.com.

Although significant pollutant levels were measured, little was known of the contribution of each potential source to the brown haze and no measurements have been made of the severity of the haze. By daily visual observation of the haze, the City Council was convinced that the haze problem is intensifying and appropriate action needs to be taken (Wicking – Baird *et al.*, 1997). Various sources including industry, road traffic, power generation and the domestic use of fuels by a large sector of the population extensively contribute to the air pollution over Cape Town (Wicking – Baird *et al.*, 1997).

The first brown haze study was carried out by Wicking-Baird, (1997, and the main objective was to determine the contribution of all major sources to the brown haze and obtain a better understanding of the mechanism of haze formation. The study focused mainly on the visibility impairment properties of the haze (Wicking – Baird *et al.*, 1997). Carbonaceous particles of less than 2.5 micron size range, from diesel-powered vehicles exhaust fumes; tyre burning and industry were identified as the primary constituents of the brown haze. While the time evolution and frequency of visible brown haze layers are well known, there are gaps in current knowledge of the exact physical and chemical nature of these particles, and their potential health effects (Wicking – Baird *et al.*, 1997).

The study also indicated that based on the projections of vehicle, population and industry growth, the intensity of the brown haze will increase by 48 % over the next decade resulting in hourly international accepted air pollution health standards being sometimes exceeded on occasions (Linde and Ravenscroft, 2003). Identifying contributions to the haze will therefore specify the most important areas where authorities should focus their activities and will enable the effects of possible measures to be assessed. It also found that the intensity and causes of the brown haze vary with time and location due to uneven distribution of the sources of the haze and different meteorological conditions in various parts of Cape Town (CCT, 2001). The introduction of low-sulphur fuels, and the voluntary phasing in of emission controls on new vehicles as means of improving ambient air quality, necessitate that baseline air quality conditions are established, and that the anticipated benefits of these costly changes be quantified, so that potential improvements can be realistically assessed.

Over the past ten years Cape Town has become an important tourist destination in South Africa, which stimulates the country's economy. The presence of a visible brown haze over the city on many winter days is problematic for the tourist industry as well as being indicative of air quality problems in Cape Town. In an attempt to understand the Cape Town brown haze, a one-month intensive campaign was undertaken during July and August 2003, to accurately characterise the physical and chemical characteristics of the brown haze layer, and to determine its lateral and vertical extent, and potential health effects, especially in disadvantaged residential areas. During the first brown haze study, the extent and impact of the brown haze and fine particle pollution on informal settlement areas was not studied. The objectives of the second brown haze study were therefore to:

1. Characterise brown haze sources and chemical, physical, spatial and temporal profiles (both particulate and gaseous);
2. Identify and quantify the contribution of sources of brown haze;

3. Evaluate impact of brown haze against international health and environmental standards;
4. Provide a baseline measurement to assess the impact of the introduction emission control initiatives (e.g. catalytic converters and low sulphur fuel reformulation); and
5. Based on the above, identify strategies for mitigating measures to control and mitigate brown haze precursors.

Air Pollution Monitoring and Legislation in Cape Town

Monitoring of air quality started in the late fifties with the introduction of the first monitoring station measuring SO_2 and smoke (Wicking – Baird *et al.*, 1997). Before the introduction of the Atmospheric Pollution Prevention Act No. 45 of 1965 (APPA) based on British Clean Air Act, air pollution was controlled reactively by attending to complaints and smoke emissions from factories. Although the Act and regulations initially served well to control smoke and products of combustion as enforced by local authorities, it became outdated and lacked amendment to deal more effectively with the real issues of air quality management. And this is now being addressed at national and local level, with the new air quality legislation being approved by the national parliament (Linde and Ravenscroft, 2003).

In 2001 the City of Cape Town adopted a two-phased approach to update and promulgate its own Air Pollution Control By-law which included the control of air pollution related to nuisance, but the control of VOCs, vehicle emissions and scheduled industries will require broader consultation. The City of Cape Town have implemented an ambient air quality monitoring network consisting of thirteen continuous monitoring stations and thirty eight analysers operating across the 500 km^2 metropolitan areas, to continuously assess real-time concentrations of critical pollutants such as carbon monoxide, carbon dioxide, sulphur dioxide and oxides of nitrogen in the atmosphere, using EPA equivalent methods, with analysis operated in accordance with ISO 17025 guidelines (Linde and Ravenscroft, 2003). Figure 1.2 shows the locations of thirteen continuous air quality monitoring sites in Cape Town. The concentration levels of the following pollutants: lead (Pb), oxides of nitrogen (NO_x), ozone (O_3), particulate matter (PM), and sulphur dioxide (SO_2) are presently being monitored, with volatile organic compounds monitored in specific surveys (CCT, 2001). The study by Wicking-Baird *et al.* (1997) also suggested that air quality monitoring be expanded into informal areas and townships, and a long term consideration should be given to improved diesel, petrol

fuel oil formulation in order to reduce emissions and an integrated air quality management system be developed (Linde and Ravenscroft, 2003; CCT, 2001).

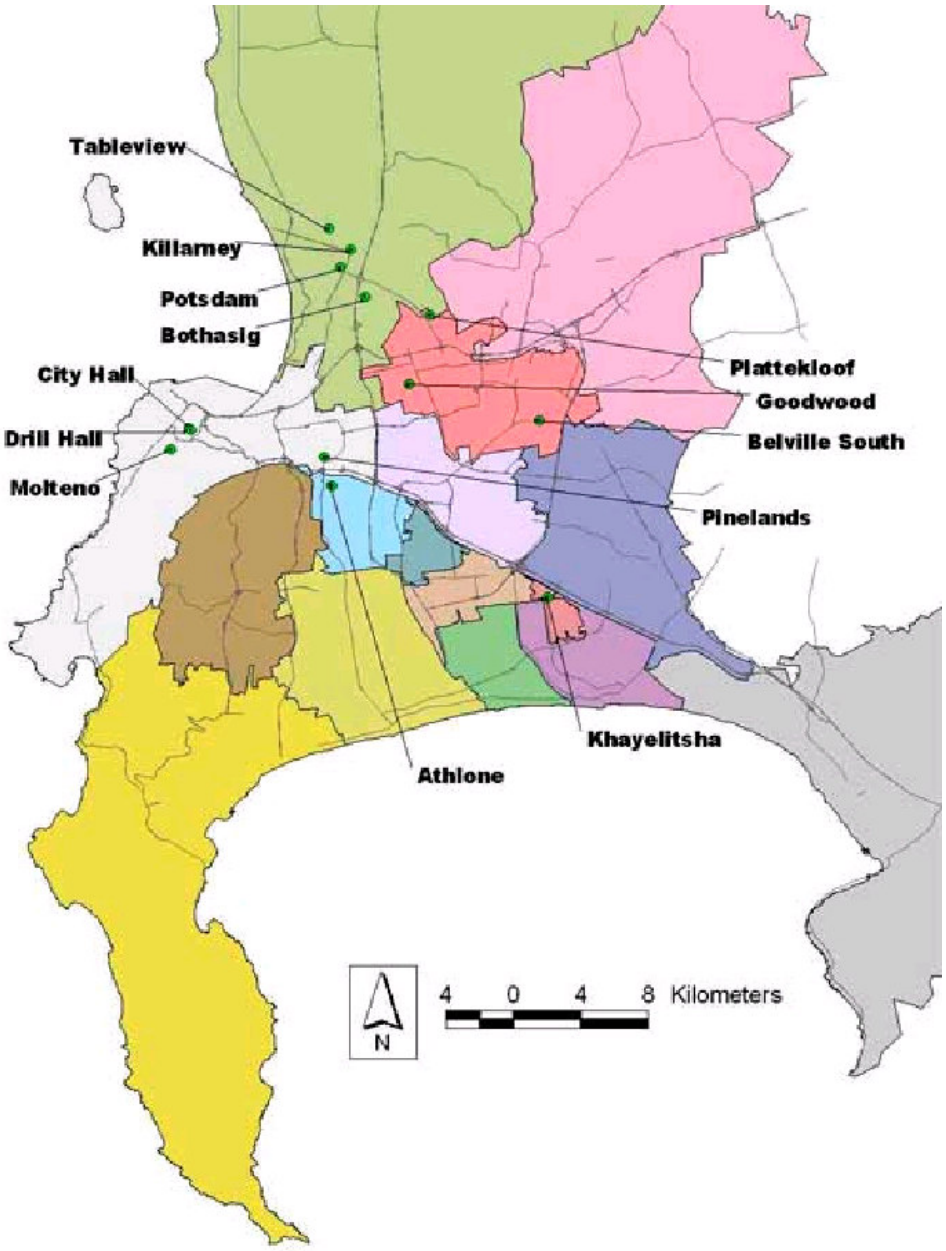


Figure 1.2 Map showing existing air quality monitoring network with 13 sites throughout Cape Town (www.capetownwebcam.com).

Meteorology of Cape Town

Prevailing meteorological conditions are among the single most important influences on the nature of the atmosphere; with regard to air pollution. The South African atmosphere is generally dominated by a high pressure system, which results in clear, sunny skies with gentle winds. Atmospheric pollutants are consequently not at all times readily dispersed, but rather accumulate in the stable boundary layer, which is a problem in winter months when it is dry and stable. The pollutants are transported away from the sources but can also be re-circulated both on a regional and sub-continental scale (Piketh *et al.,* 1998). Under unstable boundary layer conditions, the industrial stack plumes can loop down to ground level, with high ground level concentrations of gases being experienced very close to the source (Turner, 1996).

Cape Town is situated in a Mediterranean climatic zone and experiences complex meteorology. Furthermore, it is the only part of South Africa that receives mostly winter rainfall, due to westerly waves (cold fronts) occurring with a frequency of between 2-8 days during winter (Jury *et al.,* 1992). A total of 11 westerly waves (cold fronts) passed over Cape Town during the campaign, resulting in the effective dilution and dispersion of atmospheric pollutant. Between the passage of cold fronts, influence by atmospheric subsidence driven by the semi permanent Atlantic anticyclone predominates, giving rise to a highly stable atmosphere over Cape Town. These conditions therefore result in ineffective dispersion of emissions to the atmosphere, hence the build-up of pollutants very close to the ground; and brown haze incidents form preferentially on these days. The complex Cape Town meteorology can be summarised by four synoptic maps (Wicking-Baird *et al.,* 1997) for the Southern African subcontinent (Figure 1.3). Summer months are characterised by a high south-easterly air flow (Figure 1.3a) caused by a ridging anticyclone over the south Atlantic. This results in high wind velocity and atmospheric turbulences that dilute and disperse pollutants efficiently. During winter months north-westerly winds predominate (Figure

1.3b) as a result of a pre-frontal system causing low temperatures and overcast conditions.

Figure 1.3c shows continental high pressure conditions that occur mainly in early spring and late winter. These are associated with brown haze episodes in the Cape Town region. According to Jury *et al.* (1992) the atmospheric characteristics that are associated with pollution episodes are local berg winds from northerly to north easterly and a temperature increase of about 11°C from ground level to 500m above the earth's surface. The latter represents temperature inversion conditions in the atmosphere that are generally calm resulting in little dilution of emitted pollutants. The presence of warm berg winds causes dry night-time conditions in the lower atmosphere as a consequence night-time radiative heat loss and sinking motion from the upper atmosphere combine to form a strong ground based inversion.

Figure 1.3d describes stagnant conditions over the region caused by an anti-cyclone resulting in light variable winds and an elevated temperature inversion that lead to pollution episodes as there is insufficient air flow to dilute pollutants. This simply means that pollutants are being emitted into a smaller air mass where the air velocity is insufficient for dilution. This results in higher than normal pollutant concentrations.

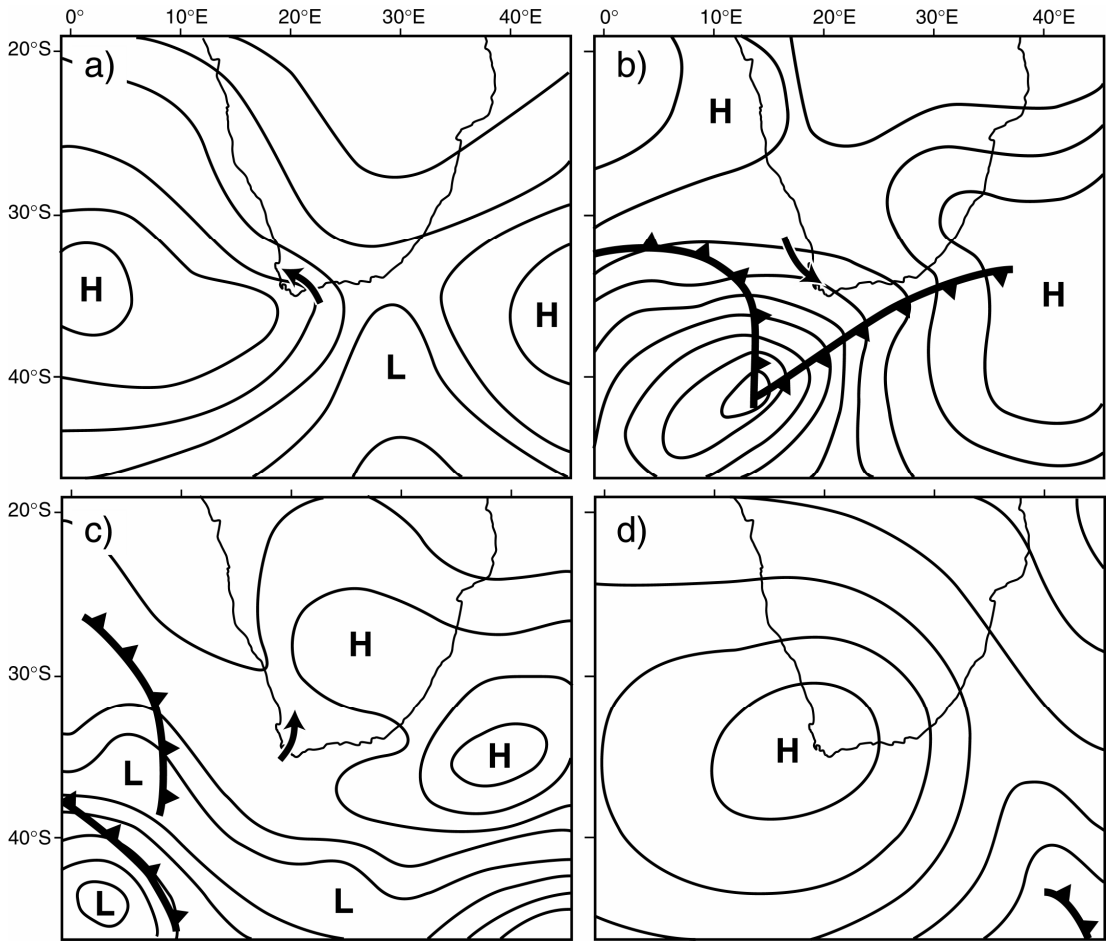


Figure 1.3 Typical synoptic maps for the Southern African subcontinent and resultant surface winds at Cape Town (dark arrows). a) Easterly wave, b) Westerly waves, or cold front, c) Continental high pressure, d) Ridging high pressure (after Wicking-Baird *et al*, 1997).

Study Objectives

The second brown haze study undertaken in July/August 2003 acquired data on meteorological conditions, trace gas pollutants, all volatile organic carbon compounds (VOCs), aerosol chemical composition, aerosol physical properties and optical thickness to extensively characterise the brown haze. Several studies on levels and sources of criteria pollutants have been carried out in Cape Town; however intensive characterisation of volatile organic carbon compounds and their impacts have not been thoroughly investigated. This study only summarises findings from airborne measurements of VOCs especially benzene, toluene, ethylbenzene and xylenes (BTEX) during this study. Specifically, the primary objectives of this study are to:

(a) quantify the ambient concentrations of BTEX compounds over Cape Town,

(b) compare BTEX concentrations from a non-brown haze to a brown haze day,

(c) determine the concentration variation through the day, and

(d) investigate sources of these BTEX compounds.

Chapter 2 Data and Methodology

Sampling of VOCs samples and the analytical techniques used in quantifying the species are discussed. Meteorological data collection technical details are also examined in this chapter.

Sample Collection

Volatile organic compounds samples were collected during flights into evacuated stainless steel canisters to be analysed by gas chromatography in the laboratory. Flights were mostly undertaken during brown and non-brown haze days, as well as mornings and afternoons. The research aircraft was based in Malmesbury, north of Cape Town. Before undertaking the flights, synoptic charts obtained from the South African Weather Service (SAWS) were consulted to establish whether brown haze conditions would occur before a flight plan was drawn up and submitted to Cape Town International Airport for approval. Brown and non-brown haze days were basically distinguished through synoptic conditions and visible inspection. Only six brown haze incidents were identified by the City of Cape Town during the month of August 2003 (Figure 2.1).

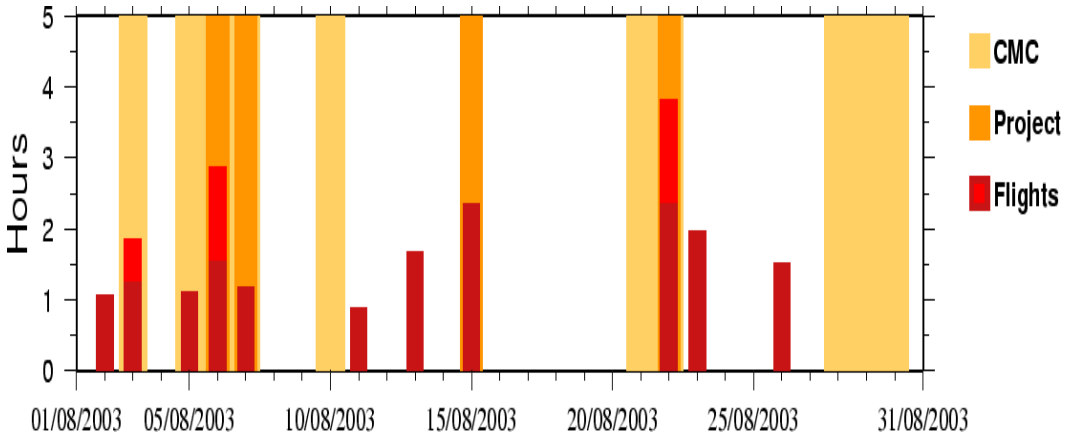


Figure 2.1 Brown haze events identified by the City of Cape Town (CMC) during the Cape Town brown haze intensive field campaign. The shading brown indicates identified brown haze events by the CMC. The orange bars indicate days identified as brown haze days by aircraft team. The red bars indicate the days on which flights were conducted over Cape Town (Piketh *et al.,* 2004).

A total of seventeen flights were conducted over the study period and flight paths are shown in Figure 2.2. Airborne volatile organic carbon compounds samples were collected from the South African Weather Service research aircraft (Aerocommander, ZS-JRB) (Figure 2.3), between 22 July and 28 August 2003 over ground-based sites in Cape Town during the day. Sites were chosen to cover the whole of the Western Cape region, and most importantly the townships and informal settlements.

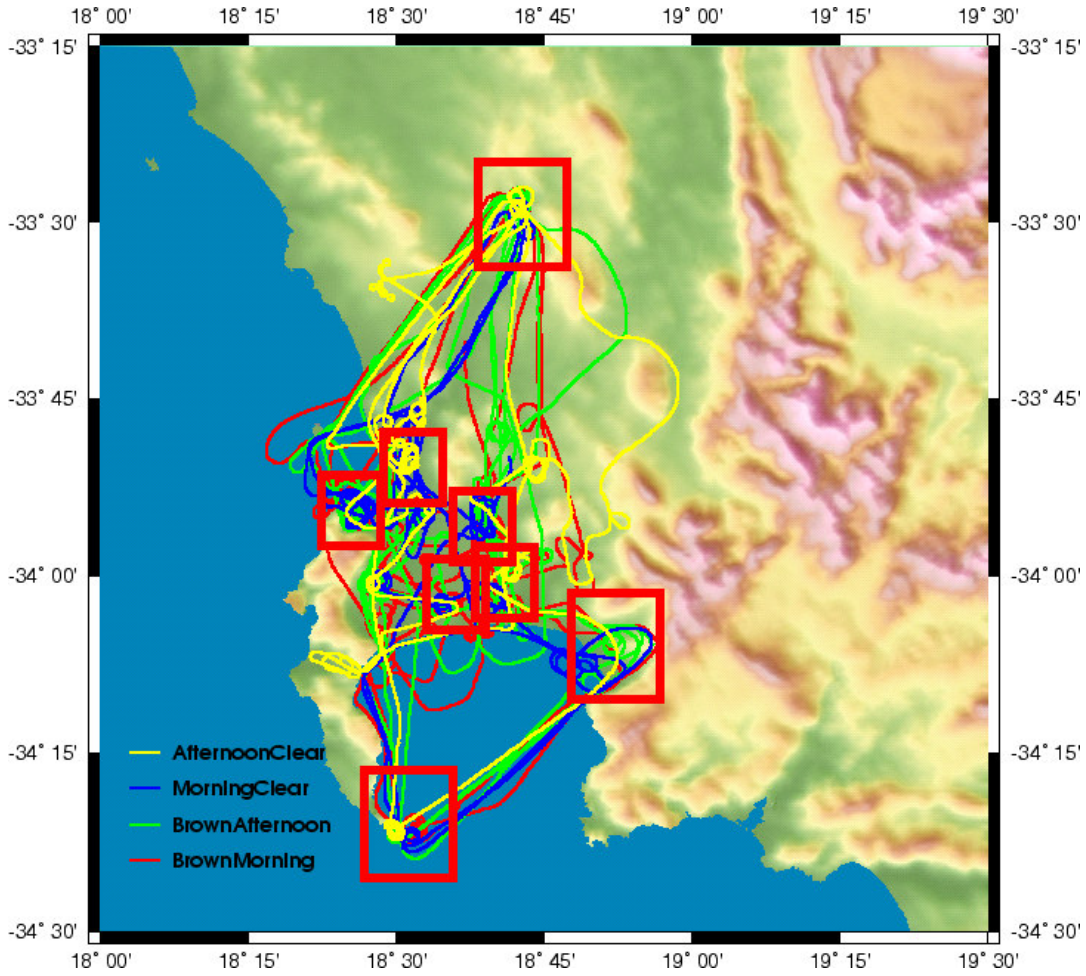


Figure 2.2 Map of Cape Town indicating sites over which airborne VOCs samples were collected. The solid lines show the flight tracks of all the flights stratified into brown haze, non-brown haze days and mornings and afternoon flights. The red boxes define the areas of interest, namely Malmesbury, Cape Town, Tableview, Bellville, Strand, Khayelitsha, Mitchell's Plain and Cape Point (Piketh *et al.,* 2004).

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Figure 2.3 Aerocommander 690A (ZS-JRB) fitted with canisters to collect ambient VOCs samples.

Flights of 1 to 2 hours and were carried out between 500 and 1500 feet, during early in the morning to correspond with the peak traffic, when the brown haze starts to form, and in the afternoon to investigate the temporal transformation of the haze. Sampling was performed predominantly on brown haze days, often after the passage of a cold front with a few flights taken on non-brown haze days. Flights were also done on weekdays and on weekends to examine the influence of traffic to the haze.

The research aircraft had inlet probes on its rooftop for continuous air intake throughout the flights (Figure 2.4). Instantaneous VOC samples were collected into evacuated stainless steel canisters (Figure 2.5) and later analysed by gas chromatography (GC) (SRI Instruments Inc., Las Vegas, NV model 8610C), fitted with a flame ionisation detector (FID) within six hours of sampling. After analysis the canisters were cleaned by simultaneously heating (to 100 ^{0}C) and flushing with zero air for 2 hours. Canisters were then evacuated before the next sampling period.



Figure 2.4 Inlets on the aircraft roof-top.



Figure 2.5 Canisters connected inside the plane for the collection of VOCs samples.

Sample Analysis

Ambient VOCs are present at trace levels (ppb) in the atmosphere; therefore preconcentration traps and valves are normally attached to the GC system in order to detect these low concentrations (Figure 2.6). The GC method used in this study follows that of Greenberg *et al.* (2003) with a few minor modifications (method discussed below in detail). This was the most appropriate method considering the type of GC and traps available at the time. The standard EPA T014A method, which is frequently used, is similar but has three noticeable differences, namely a Nafion drier is used to remove oxygen and water, whereas Greenberg et al's method uses a Tenax trap; the temperature program does not start at sub-ambient temperatures due to the nature of the GC; and the column is slightly different. Furthermore, this method can detect very low concentrations of VOCs. The T014 standard gas was run through the GC using the method described below and all the BTEX compounds could easily be detected and calibrated, thus the method was deemed to be appropriate.

Before sample analysis, zero air and blanks were run to make sure the column and traps are clean and to set the baseline. Between 100 and 400 ml of sample were loaded onto the column at a time. Samples were preconcentrated before being loaded onto the column via two preconcentration traps. Samples were first introduced onto a Tenax TA (60-80 mesh, 2.2 mm I'd x 100 mm length) which was cooled to 0 ^{0}C. The concentrated sample was then transferred (transfer time of 5 minutes) by rapidly heating the trap to 180 ^{0}C, to the second trap, a cryo-focusing trap.

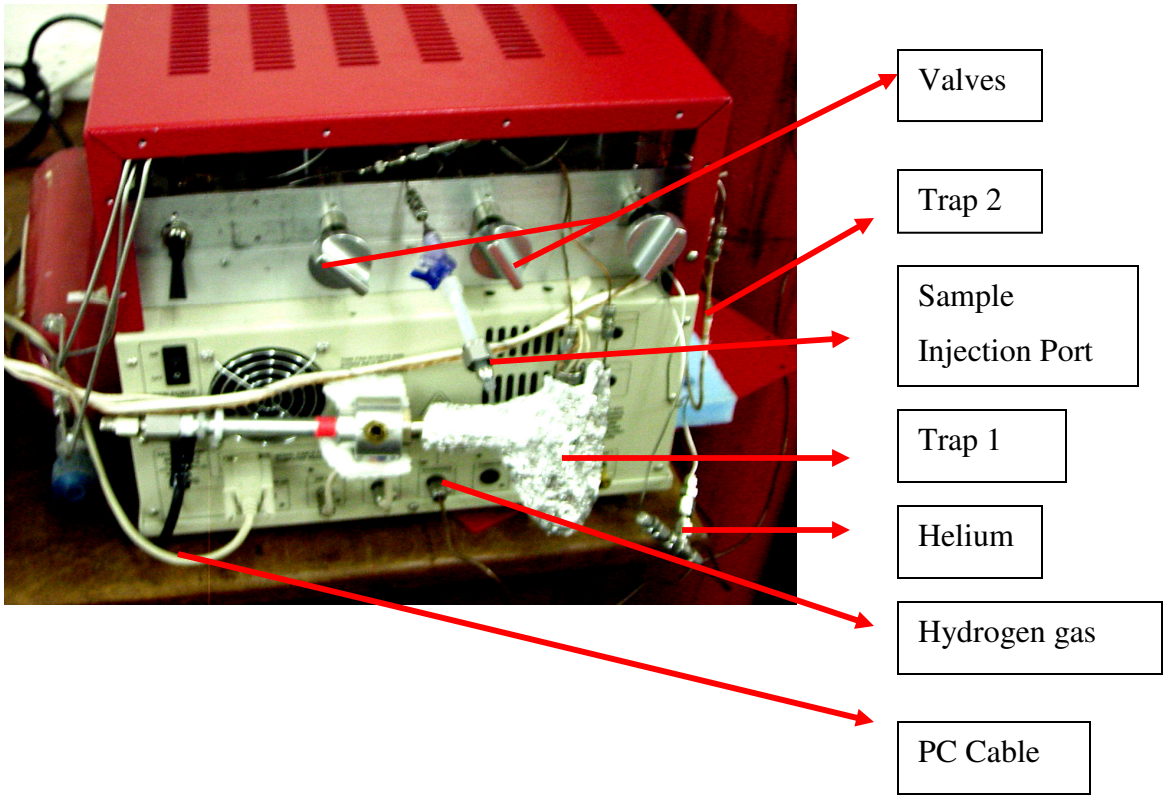


Figure 2.6 The GC-FID used for the determination of VOCs in this project, showing the preconcentration traps.

The second trap was cooled with liquid nitrogen for 5 minutes then heated to 180 ^{0}C to transfer the sample onto the column. Separation was carried out using a MTX-624 (30 m x 0.52 µm x 1.4 µm, Restek Corp., Bellefonte, PA) column with helium (UHP, AFROX, SA) as the carrier gas (flow rate of 5 ml.minute^{-1}) and a temperature program (initial temperature 40 ^{0}C for 5 minutes, increased to 200 ^{0}C at a rate of 15 ^{0}C/min, then hold for 1 minute). The detector was set at 300 ^{0}C. Zero air and blanks were run after analysing all the samples to remove any remaining organic material in the columns and traps respectively.

GC calibration

Calibration curves were determined for the BTEX compounds using a TO14 - 43 compound, 1 ppm standard (Restek, 1 ppm). This was used together with individual concentrated references (99% pure, Restek) for benzene, toluene, ethylbenzene and xylenes (p, m, and o) to determine their retention times. Calibrations were done with 100ml of standards; therefore all samples were scaled to 100ml before applying the calibration curve equations. The concentration of each compound (ppb) was determined from the area of the chromatographic peak (in mV) by using the following equations derived from the calibration curves:

Benzene = Peak area * 0.73137 (1)

Toluene = Peak area * 0.84743 (2)

Ethylbenzene = Peak area * 2.06734 (3)

Xylene = Peak area * 0.76395 (4)

These concentrations were converted to micro grams per cubic metre ($\mu g.m^{-3}$) using the following equation (US EPA, 1999):

Concentration ($\mu g.m^{-3}$) = (ppb x molecular weight of compound) / 24.45 m^3, where 24.45 m^3 is the volume occupied by 1 mol at 25 ^oC and 1 atm. standard pressure.

Meteorological Data Collection

Cape Town's complex meteorology has the most significant influences on the nature of the atmosphere with respect to air pollution. A 10m ground based meteorological station was set up at Goodwood to measure wind speed and direction, solar radiation, temperature, relative humidity, pressure and precipitation at three levels; 5m, 8m and 10m (Figure 2.7). In addition, upper air soundings obtained from Cape Town International Airport were also used to illustrate effects of atmospheric stability on BTEX levels.

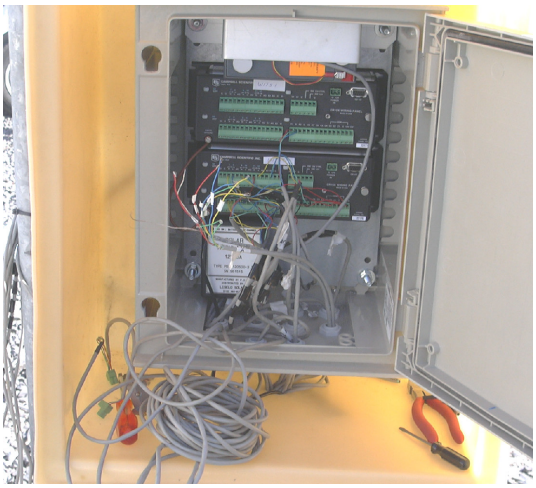
(a)  (b) 

Figure 2.7 (a) Meteorology data logger used to download data on a daily basis; and (b) a 10 m tower with all the equipments connected at Goodwood.

Chapter 3 Results and Discussion

BTEX compounds concentrations on brown and non-brown haze days, diurnal variations as well as possible primary sources are examined. Spatial distribution of these species over Cape Town is presented in this chapter identifying sites with considerable concentrations.

Role of local meteorology

Atmospheric characteristics play an important role in determining the dispersion and accumulation of pollutants in the atmosphere. Between the passages of cold fronts, typically the atmosphere over Cape Town will become highly stable, mostly influenced by atmospheric subsidence driven by the semi permanent Atlantic anticyclone (Jury *et al.,* 1992). These conditions are not conducive to the effective dispersion of emissions to the atmosphere. It is most likely that brown haze incidents will form preferentially on these days. The best manner to evaluate the atmospheric stability is by looking at the daily vertical radiosonde soundings conducted from Cape Town International Airport. The soundings for every day of the campaign have been evaluated. Absolute stability occurs whenever the environmental lapse rate is smaller than or equal to the saturate lapse rate. This will occur in the atmosphere from either atmospheric subsidence or surface cooling during the night. Elevated subsidence in the atmosphere leads to endothermic heating and thus atmospheric stability.

The subsidence stable layers are well defined and easy to identify throughout the atmosphere over Cape Town (Figure 3.1 top and bottom). The most important of these occurs between 900 and 750 hPa. Surface cooling at night is also responsible for the development of absolutely stable layers forming at the surface. These typically take the form of surface inversions. Surface inversions are clearly identifiable over Cape Town on 1, 3, 5, 6, 7, 12, 13, 14, 17, 18, 20, 21, 22, 23, 24, 25, 29, 30, 31 August

2003 (19 days) at midnight. Ten out of the eleven brown haze days identified in Figure 2.1 are associated with surface absolute stability. By midday there is no evidence of any surface stability over Cape Town.

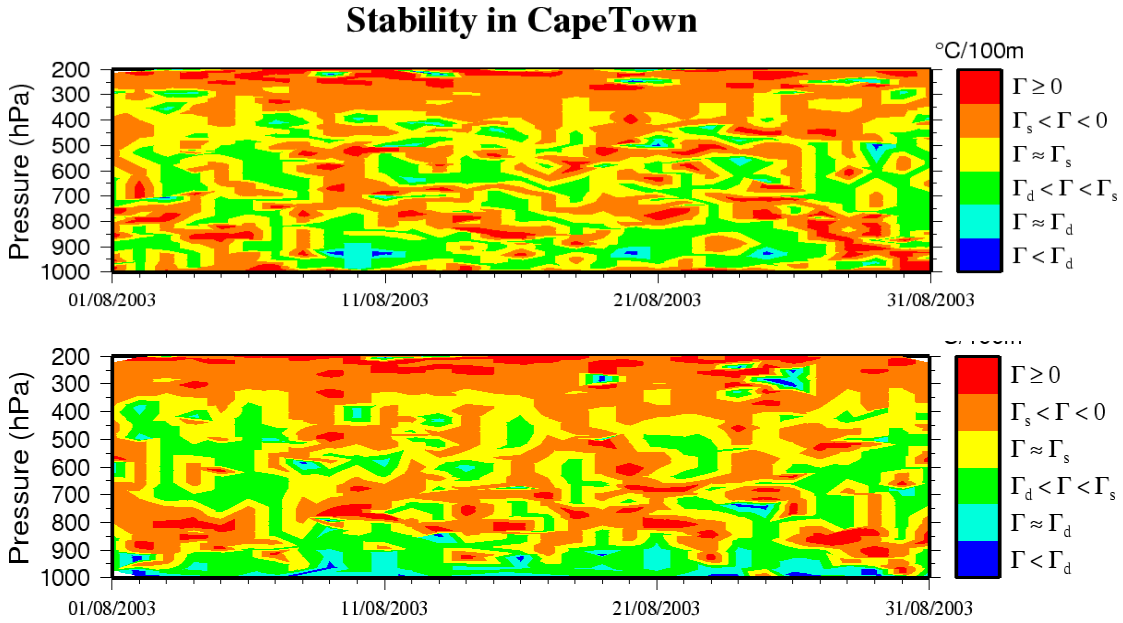


Figure 3.1 Atmospheric stability analyses for August 2003 over Cape Town at midnight (top) and midday (bottom) UTC time. The colour scale gives the stability classification in terms of atmospheric lapse rates. Absolute stability is given by yellow orange and red. Absolute instability is shown by light and dark blue.

Coupled to the synoptic scale circulation at any given site, wind fields also influence BTEX concentrations (Figure 3.2 top and bottom). Brown haze mornings and afternoons has light to moderate south easterly and north easterly winds respectively. Brown and non-brown haze days wind roses however illustrate insignificant differences in wind speeds. The wind speeds are 52 and 55 % in the 2 to 4 ms^{-1} respectively. This can be clearly illustrated by looking at the stability diagrams that highlight the presence of surface inversion layers giving rise to stagnant conditions. Stable layers only form preferentially on brown haze days and are usually associated with light wind speeds.

Light wind speeds result in stagnant conditions that lead to insufficient dispersion and dilution of pollutants. In addition, these surface inversions that trap

pollutants close to the ground. During August 2003 distinctive patterns of wind are discernable at the surface up to 700 hPa both from the midnight and midday soundings (Figure 3.3). On average northerly to north westerly and southerly winds were observed on brown and non-brown haze days respectively. The passage of cold fronts is easily identified by looking at the temperature data over Cape Town for the duration of the study (Figure 3.4).

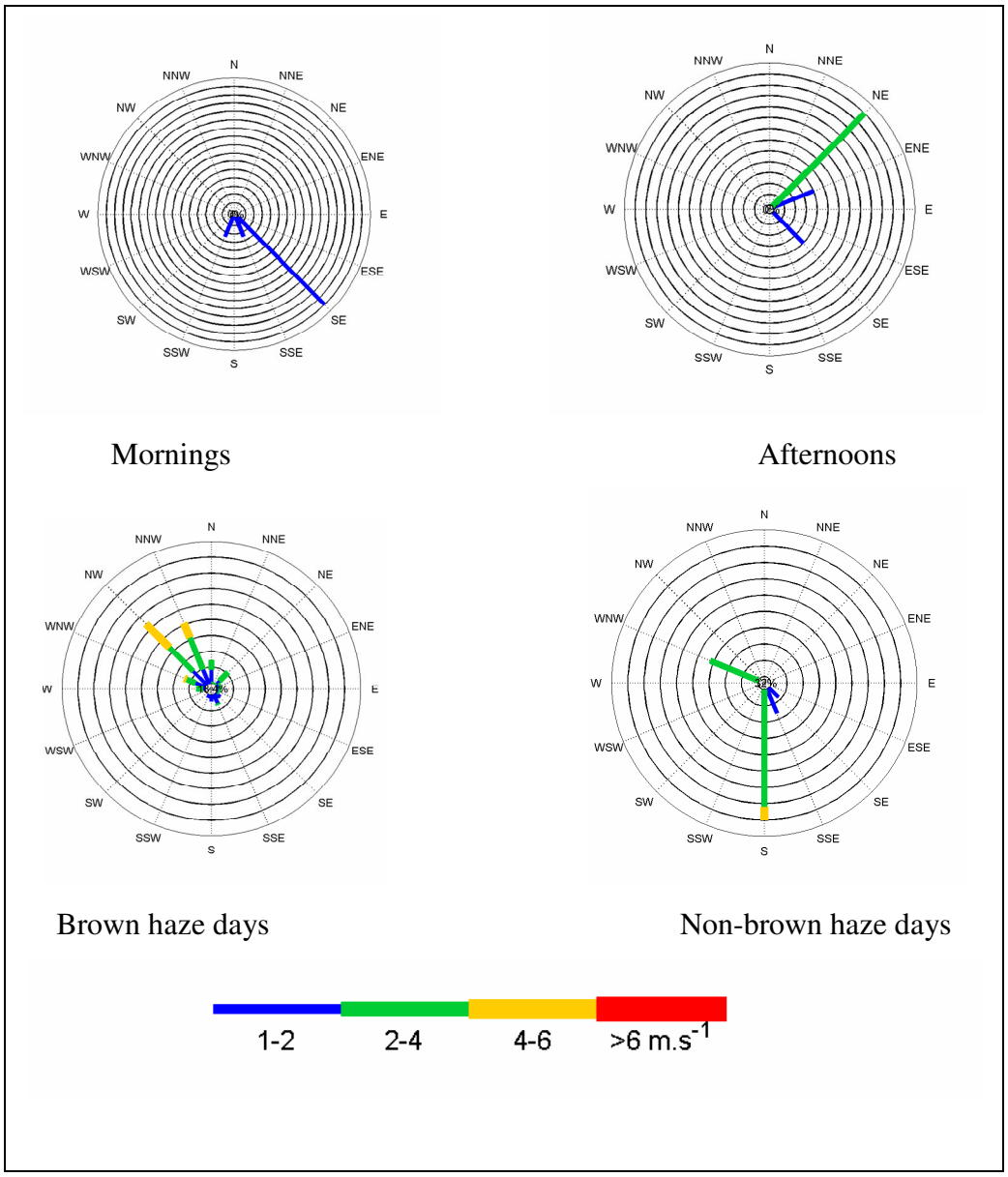


Figure 3.2 Mornings and afternoons, brown and non-brown haze days wind roses for the whole campaign taken from Goodwood meteorology station. The colour scale represents different wind speeds. The arcs represent 5% frequency intervals with average values represented by the dashed polygon (July/August 2003).

The switching between north westerly and southerly flow is associated with the influence of the westerly lows and cold fronts for the most part. In summary, brown haze days are typically characterised by light north westerly winds and surface inversions, whereas non-brown haze days are characterised mainly by southerly winds. In addition it is clear that the strongest surface stability is associated with slight warming at the surface. It is also noticeable that during these periods of warming the boundary layer has a tendency to increase in height slightly. These results in the lifting of temperature inversions and unstable conditions which give rise to improved dispersion and dilution associated with usually insignificant BTEX concentrations being detected over Cape Town. This is caused by the warmer conditions during the daytime.

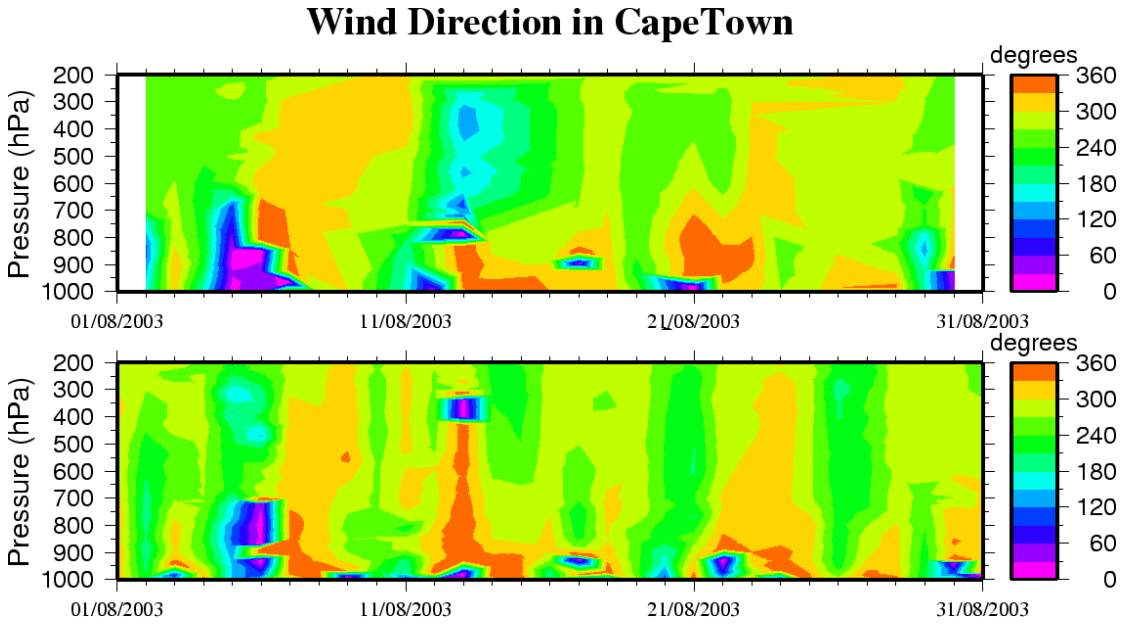


Figure 3.3 Wind directions over Cape Town for the month of August derived from midnight (top) and midday (bottom) sounding at Cape Town International Airport UTC time.

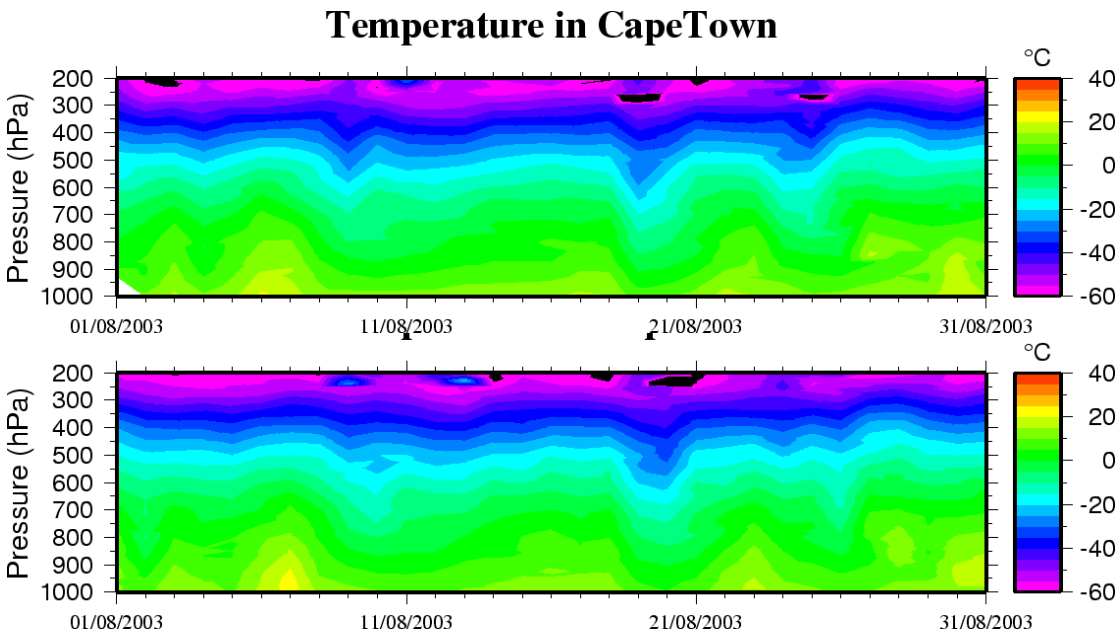


Figure 3.4 Temperature profiles over Cape Town during August 2003. Soundings are taken at Cape Town International airport at midnight (top) and midday (bottom) UTC time.

BTEX Concentrations

Concentrations of most BTEX species were lower on non-brown haze days due to the dilution effect. The maximum concentrations were four to six times higher on brown than non-brown haze days. Average concentrations of BTEX samples collected for the period 31 July to 26 August 2003 are presented in Figure 3.5. Six brown haze episodes (06, 07, 15, 22, 23 and 26 August 2003) were observed during the campaign, and they highlight considerable BTEX concentrations except for the 07 and 15 that show insignificant concentrations. During non-brown haze episodes, 31 July, 03 and 13 August 2003 significant toluene and xylene concentrations were measured.

Benzene, toluene and ethylbenzene are clearly distinct in the morning and afternoon of the 06th August, a brown haze day. The highest toluene average was observed on the 22nd August 2003, which is also a brown haze day. This can be explained by taking into account various factors such as the reaction of BTEX compounds with oxides of nitrogen, times of the flights (some species have short lifetimes in the atmosphere and undergo chemical transformations during certain times of the day), the photochemical oxidation process with hydroxyl radicals, as well as the associated meteorological conditions of Cape Town. In addition, sampling sites, source strength, the amount of NOx available to react with BTEX species and the different meteorological conditions during these days could account for the differences in levels of the all species on the 6th and 22nd brown haze days.

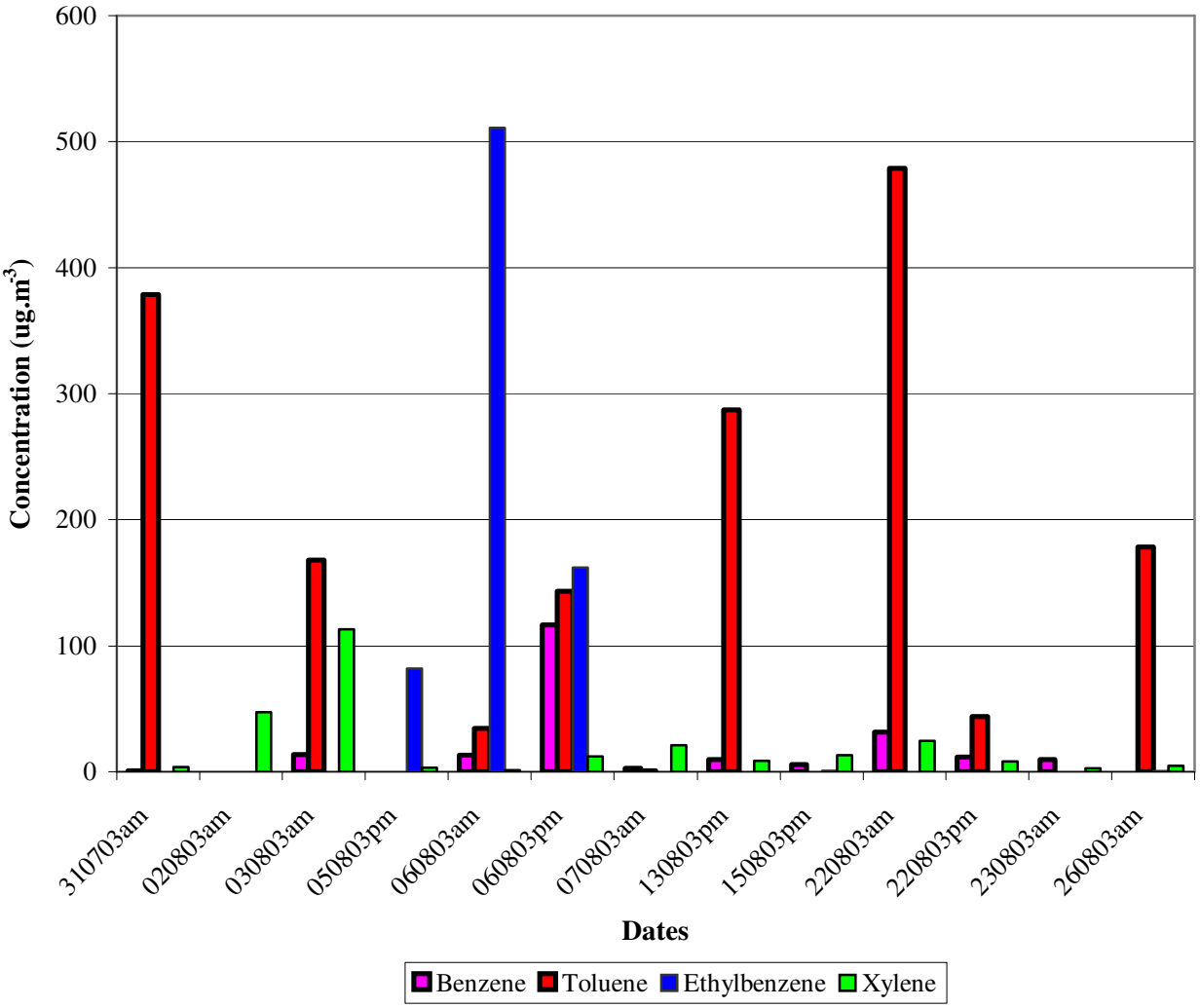


Figure 3.5 Average concentrations of benzene, toluene, ethylbenzene and xylene detected from samples taken between 31 July and 26 August 2003 for all the flights.

Detected mean concentrations and ranges of BTEX for all samples collected during brown haze mornings and afternoons, as well as brown and non-brown haze days are given in table 3.1. Mean concentrations of all BTEX compounds, except xylenes were higher on brown haze relative to non-brown haze days. Significant

concentrations of BTEX except toluene were detected during the afternoons as compared to mornings.

Table 3.1 Detected means and ranges of BTEX compounds in the airborne samples collected over Cape Town (in $\mu g.m^{-3}$) during the campaign. The numbers in parentheses give one standard deviation about the mean.

Episodes	Benzene		Toluene		Ethylbenzene		Xylenes	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
BH days	19.7 (77)	1.6-544.5	96.0 (200)	1.4-1053.1	100.4 (215)	4.1-1060.0	10.8 (12)	0.7-65.4
NBH days	4.5 (9)	7.0-34.2	95.8 (190)	3.9-613.1	19.2 (42)	46.7-150.0	37.4 (53)	0.91-183.4
BH am	13.4 (4)	7.4-18.5	39.5 (42)	1.4-112.8	511.0 (254)	230.0-1060.0	1.6 (1)	0.7-3.7
BH pm	146.0 (266)	7.5-544.5	143.1 (206)	2.2-462.5	162.0 (153)	47.0-430.0	21.0 (18)	1.5-38.0

Key: am = mornings, pm = afternoons, BH = brown haze, NBH = non-brown haze.

Characteristics of observed BTEX concentrations in the mornings and afternoons

Diurnal variations of BTEX compounds indicate differences in concentrations depending on dilution conditions. The increase in benzene concentration on brown haze afternoons can be attributed to its low reactivity with OH radicals and high traffic volumes, which results in its increase as the day progresses. In addition, low benzene (compared to other species) content in petrol fuel coupled with low temperatures in the mornings can also account for its low concentrations during these periods. High toluene concentrations in the afternoons can also be explained by its higher evaporation rate from fuels especially during elevated temperatures. Toluene levels measured in this study especially in the afternoons were much higher than ground-based levels found in cities around the world, for example, ground-based toluene

levels were 33.6, 14.3, 7.2, 8.3, 117.2 and 24.1 μg.m^{-3} in Sydney, Chicago, Edmonton, London, Osaka and Seoul, respectively (Na *et al.,* 2003). Extremely high levels of ethylbenzene in the mornings may be due to inputs from stationary sources such as industry and domestic fuel burning. Ethylbenzene is not abundant in petrol fuel and therefore its presence points to an additional source (Wang *et al.,* 2002). The source is still unidentified and needs further investigation.

Differences between brown and non-brown haze days

BTEX concentrations were different for brown and non-brown haze days. The results indicate that considerable BTEX levels were measured during brown haze days compared to non-brown haze days, except toluene and xylene, which were significant during almost all flights conducted. Benzene and ethylbenzene emerge as the most abundant species on brown haze days. Concentrations of these species were approximately four to five times lower on non-brown haze days possibly due to the dilution effects caused by an increase of the mixing depth that enhance dilutions during non-brown haze days, as well as the existence of sources of unequal strengths (Na *et al.,* 2003).

However this is not the case with toluene, given that equal mean concentrations were observed during both brown and non-brown haze days. This might be a highlight of the existence of a similar continuous source over Cape Town during these episodes. The results also highlight that not only brown haze episodes result in high BTEX concentrations. For instance vehicle and industrial emissions are not only observed during brown haze days, but also occur on non-brown haze days. . Better dilution conditions of benzene and ethylbenzene during non-brown haze days can account for their lower levels measured compared to brown haze days.

Effect of BTEX lifetimes on concentrations

Atmospheric removal of BTEX compounds varies due to their different reaction rates with OH radicals. This can be attributed to the chemistry of the species, source strengths, dilution and meteorological conditions. The lifetimes of benzene, toluene, ethylbenzene and m-xylenes are 22, 4.7, 3.9 and 1.2 hours respectively, at 10^7 molecules/cm^3 OH radical (Wang *et al.,* 2002). The relatively longer lifetime of benzene indicates that it has lower reactivity towards OH radicals and is more stable in the atmosphere. The chemical removal of toluene in ambient air is therefore much higher than that of benzene due to its important reaction rates with OH radicals, owing to its low lifetime in the atmosphere (Field *et al.,* 1992). Xylenes are therefore considered the most reactive species compared to the rest of the species. This together with source strengths therefore accounts for the low xylenes levels observed during all episodes because most of it reacts very quickly in the atmosphere to form other secondary species (Hsieh and Tsai, 2003).

Cross Correlations of BTEX

Table 3.2 summarises BTEX mutual linear correlation coefficients for brown haze mornings and afternoons, as well as brown and non-brown haze days to investigate if the species were emitted from similar sources. Noticeably, BTEX compounds were insignificantly correlated on brown and non-brown haze days implying different sources of these species during these periods. The good correlation among benzene, toluene and ethylbenzene on brown haze afternoons indicates that they came predominantly from a single source, most possibly traffic or industrial related emissions, or both (B/T: 0.75 and B/E: 0.95). Additionally, this difference is might be due to morning and afternoon differences and the reactive properties of the species. Careful examination revealed that there were site-specific BTEX patterns, implying possibly different sources in different sites especially for benzene and

ethylbenzene. During non-brown haze days even toluene had poor correlation with other species. In urban air, BTEX compounds are typically related to emissions from gasoline vehicles and stations (i.e. evaporation) (McClenny *et al*., 1989; Cohen *et al*., 1991; Jose *et al*., 1998).

Table 3.2 Summary of BTEX correlation coefficients (R^2) for brown haze, non brown haze, mornings, afternoons, and brown haze and morning against non-brown haze and afternoon respectively.

Compound	benzene	toluene	ethylbenzene	xylenes
Brown haze				
benzene	1.00	-	-	-
toluene	0.09	1.00	-	-
ethylbenzene	0.06	0.005	1.00	-
xylenes	0.06	0.03	0.07	1.00
Non-brown haze				
benzene	1.00	-	-	-
toluene	0.02	1.00	-	-
ethylbenzene	0.06	0.06	1.00	-
xylenes	0.19	0.02	0.10	1.00
Mornings				
benzene	1.00	-	-	-
toluene	0.03	1.00	-	-
ethylbenzene	0.02	0.08	1.00	-
xylenes	0.02	0.01	0.34	1.00
Afternoons				
benzene	1.00	-	-	-
toluene	0.75	1.00	-	-
ethylbenzene	0.95	0.59	1.00	-
xylenes	0.13	0.60	0.03	1.00
Mornings vs. Afternoons				
benzene	0.23	-	-	-
toluene	0.18	0.14	-	-
ethylbenzene	0.05	0.23	0.05	-
xylenes	0.12	0.03	0.31	0.02
Brown haze vs. non-brown haze				
benzene	0.03	-	-	-
toluene	0.13	0.04	-	-
ethylbenzene	0.02	0.001	0.18	-
xylenes	0.09	0.001	0.001	0.002

Relationships between BTEX compounds over Cape Town

BTEX ratios for all episodes were calculated to identify possible sources of the species over Cape Town (Table 3.3). These ratios highlight various sources of BTEX during the study periods. Values of benzene to toluene (B/T) ratio for other cities vary between 0.3 and 0.5 when associated with mobile sources (Brocco *et al.,* 1997; Gee and Sollars, 1998). For all episodes except brown haze afternoons B/T ratio was lower than 0.3 implicating sources other than vehicle emissions contributing to the levels of the two species. In some Asian cities, such as Bangkok (Thailand) and Manila (Philippines), this ratio was reported to be lower, around 0.1, due to high aromatic content in fuels used and increased production of toluene by automobile engines in these countries (Gee and Sollars, 1998). The High B/T ratio (1.02) in the afternoons indicates that there is also input from other stationary sources for benzene such as industries and domestic fuel burning; and the low dissipation of emissions and photochemical smog.

Benzene to toluene ratio is expected to increase with time after release into the environment due to the low lifetime of toluene coupled with the continuous accumulation of benzene throughout the day (Chattopadhyay *et al.,* 1997). In Calcutta and Bombay, India this ratio is surprisingly high, always > 1, due to high inputs from stationary sources such as domestic coal burning and industrial emissions (Chattopadhyay *et al.,* 1997; Mohan Rao *et al.,* 1997). Gee and Sollars (1998) also suggested that either there were large additional sources of toluene during these periods or there were vehicle maintenance conditions as well as differences in the fuels or vehicles used. This diurnal B/T relationships should be explored further in future studies.

Table 3.3 Summary of average B: T: E: X ratios for mornings, afternoons, brown and non-brown haze days.

	Brown haze days				**Non-brown haze days**			
Compound	B	T	E	X	B	T	E	X
Benzene	1	0.21	0.20	1.83	1	0.05	0.23	0.12
Toluene		1	0.96	8.73		1	5.00	2.57
Ethylbenzene			1	9.13			1	0.51
Xylene				1				1
	Mornings				**Afternoons**			
	B	T	E	X	B	T	E	X
Benzene	1	0.14	0.03	8.38	1	1.02	0.90	6.95
Toluene		1	0.09	24.90		1	0.88	6.81
Ethylbenzene			1	319.0			1	7.71
Xylene				1				1

Xylene to ethylbenzene (X/E) ratio is a useful tool to estimate the photochemical age of the air mass (Ho *et al.,* 2004). Diurnal variations of X/E were observed for brown haze days with very low ratios in the mornings (0.003) indicating an aged air parcel. Non-brown haze days showed higher X/E ratio indicating that the freshly emitted xylene during these periods decayed at different rates in the atmosphere (Ho *et al.,* 2004). In addition, X/E for brown haze days was much lower (0.11) than that on non-brown haze days (1.95). Generally speaking, the X/E ratio in the afternoons is also very low possibly due to reaction or degradation of the more reactive isomers of xylene (Monod *et al.,* 2001).

Table 3.4 summarises various ratios and the expected source that caused them for all episodes averaged in the Cape Town region. Previous studies indicating motor vehicle emissions found B/E ratios typically < 5 and T/E ratios < 6 (Lonneman *et al.,* 1986; Doskey *et al.,* 1992; Haszpra and Szilagyi, 1994; Chang *et al.,* 1996). In this study the above ratios were found to be within the aforementioned ranges during all episodes. On average, overall ratios highlight vehicle emissions as the single prominent source of BTEX compounds throughout Cape Town.

Table 3.4 Comparisons of various ratios and the expected source of the species found in other studies with the average ratios obtained in the Cape Town region for all episodes (Gee and Sollars, 1998; Wang, *et al.,* 2002).

Species	**Ratio**	**Source Type**	**Average Ratio for Cape Town**
Benzene/Toluene	<0.3 0.3 – 0.5 > 0.5	Stationary Motor vehicle Stationary	0.36
Benzene/Ethylbenzene	< 5 > 5	Motor vehicle Stationary	0.34
Toluene/Ethylbenzene	< 6 > 6	Motor vehicle Stationary	1.73
Xylene/Ethylbenzene	Low High	Aged parcel Freshly emitted parcel	0.55

Spatial distribution of BTEX over Cape Town

BTEX concentrations vary significantly over Cape Town for the period of 31 July to 26 August 2003 (Figure 3.6). On average the highest levels of benzene (138 $\mu g.m^{-3}$), toluene (386 $\mu g.m^{-3}$), ethylbenzene (228 $\mu g.m^{-3}$) and xylene (122 $\mu g.m^{-3}$) were detected in north east over the Central Business District (CBD), Mitchell's Plain (township), Wallacedene and Grassy Park respectively during both brown and non-brown haze days. Most townships and informal settlements are characterised by a lot of poorly maintained vehicles and tyre burning that can be highlighted as potential sources of higher toluene concentrations in Mitchell's Plain. The high benzene and toluene levels at Ysterplaat can be attributed to the fact that it is located within the Cape Town CBD, where there is high traffic density that results in significant

concentrations. High levels of ethylbenzene at Wallacedene, Table view, Waterfront and Wynberg; and xylene at Grassy Park can be attributed primarily to stationary sources such as industries, since most of the industrial areas are concentrated at these sites.

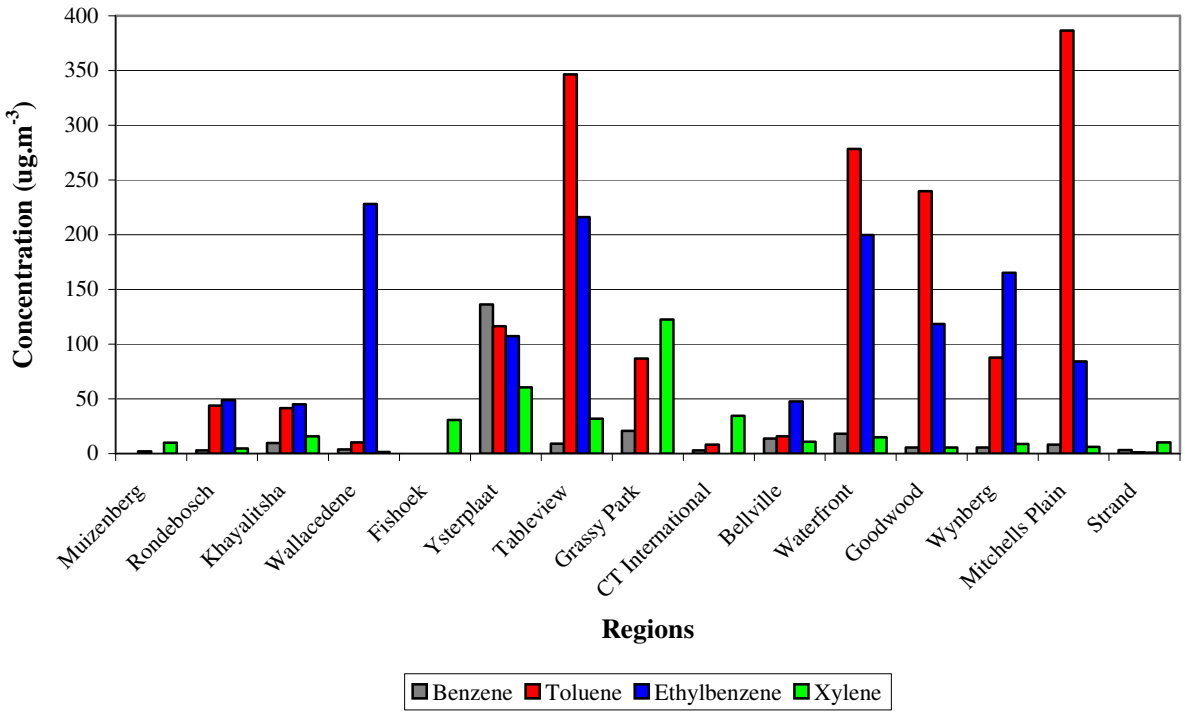


Figure 3.6 Regional BTEX concentrations over Cape Town for both brown and non-brown haze days throughout the campaign.

The low benzene concentration detected in Waterfront, situated close to CBD with large number of cars can be attributed the possibility of better ventilation around this area than elsewhere. Table view is among the highly industrialised sites in Cape Town, the higher toluene concentrations can be attributed to solvents used in petrochemical and other manufacturing industries. Summarised spatial distribution for the whole campaign of all BTEX compounds over Cape Town is illustrated in figure 3.7.

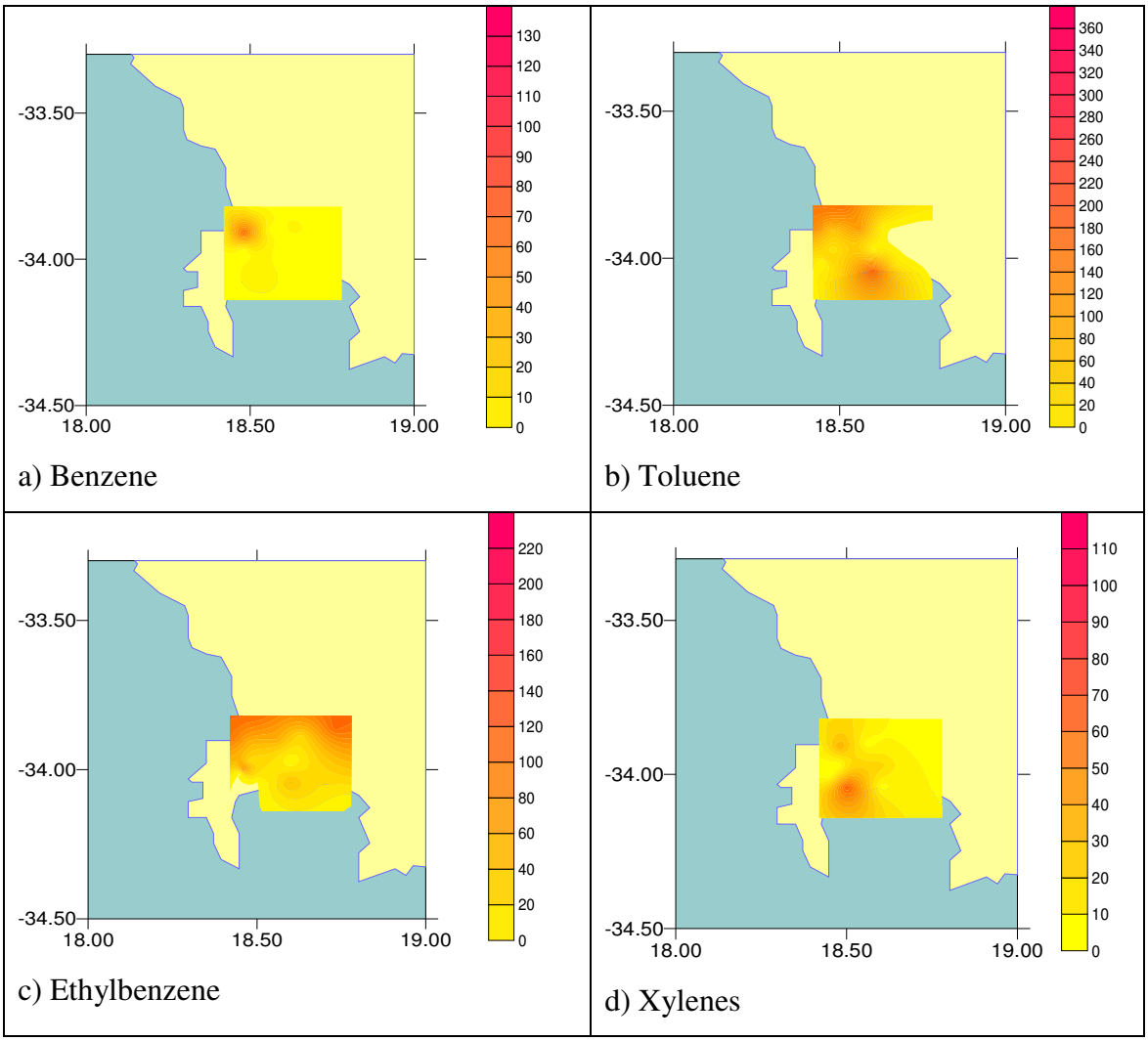


Figure 3.7 Spatial distributions of BTEX compounds over Cape Town during August 2003, to illustrate areas where different compounds are high and low (in $\mu g.m^{-3}$). Red and yellow indicate high and low concentrations respectively.

BTEX concentrations comparisons with international guidelines

Comparisons of Cape Town BTEX levels with the World Health Organisation (WHO) guidelines are given in table 3.5. These levels cannot be compared directly with typical guidelines and standards of BTEX compounds worldwide due to the fact that the standards are based on ground-based measurements. BTEX emissions sources are mainly ground-based and this study performed at measurements above the ground,

where some of these species might have been diluted or reacted to form other species. In addition, the difference in time intervals, that is a 10 second data collected during the campaign compared to 1, 8 or 24 hours averaged guidelines, makes it impractical for direct comparisons to be made (Table 3.5). Nonetheless it can be highlighted that airborne levels of BTEX over Cape Town were much higher when compared to those reported in other North American and European cities (Singh *et al.,* 1985; Finlayson-Pitts and Pitts, 1986; Edgerton *et al.,* 1989; Scheff and Wadden, 1993; Jose *at al.,* 1998.). In China, the highest ground-based benzene and toluene levels were 185 $\mu g.m^{-3}$ and 314 $\mu g.m^{-3}$ respectively (Wang *et al.,* 2002).

From the higher BTEX concentrations detected in this study, it cannot be safely concluded that Cape Town experiences high levels of these species at ground level. Similar airborne studies on SO_2 and O_3 have shown strong gradients in SO_2 and O_3 concentrations with increasing height. If so, it could be that BTEX concentrations measured aloft are higher than the surface, therefore indicating the need for appropriate action to remedy this situation. However, convincing conclusions cannot be made based on these airborne measurements only. Further studies on ground-based levels can be essential in order to make appropriate conclusions.

In Europe, the annual average ambient concentrations of benzene over cities are between 1 and 50 $\mu g.m^{-3}$. The highest values are almost always associated with high traffic densities (Skov *et al.,* 2001). Ambient standard for benzene in Brazil is 10 $\mu g.m^{-3}$, while in Europe, regulatory limits are between 10 – 16 $\mu g.m^{-3}$, a value that will be reduced to ~ 3 $\mu g.m^{-3}$ in the future with the increased use of catalyst-equipped cars (Gee and Sollars, 1998; Fernandes *et al.,* 1999). In the UK the ambient standard for benzene is 16 $\mu g.m^{-3}$ as an annual rolling mean, reducing to 3.24 $\mu g.m^{-3}$ in the future (Gee and Sollars,1998). The World Health Organisation (WHO) has estimated that a life time exposure of 1 $\mu g.m^{-3}$ of benzene leads to about six cases of leukaemia per 1 million inhabitants (WHO, 1987).

Table 3.5 Comparison between BTEX detected compounds concentrations (in $\mu g.m^{-3}$) in Cape Town and WHO guidelines over 24 hours exposure period (EPA, 2001).

Compound	Guideline	Cape Town
Benzene	16	138
Toluene	256	386
Ethylbenzene	-	228
Xylenes	295	122

All BTEX species, except xylene are higher than the recommended WHO guidelines and are a cause of concern with respect to health, especially as these values are not taken at the surface where many of the listed emissions occur. In South Africa only guidelines for the total ambient volatile organic carbon compounds exist as 400 ppb over one hour average period, and not for the individual VOCs species (DEAT, 1999). In addition, direct comparisons of the reported concentrations with other cities is therefore difficult due to the differences in several factors such as sampling site, sampling periods, sample number, meteorological conditions and the main city's activities as well as differences associated with vehicles, such as vehicle fuel composition.

These results however provide baseline levels of airborne BTEX compounds over Cape Town at very low altitudes (500 to 1500 ft). BTEX concentrations were found to vary greatly, even over relatively short periods monitored for both brown and non-brown haze days. This is associated with sample number, where the samples are taken (some samples are of background air and some over specific sources) and the complex meteorological conditions in Cape Town.

Chapter 4 Summary and Conclusions

Benzene, toluene, ethylbenzene and xylene concentrations were measured over Cape Town during brown and non-brown haze days. Substantial BTEX levels were measured during brown haze days compared to non-brown haze days, except toluene and xylene, which were significant during all flights conducted. Toluene concentrations were equal during both brown and non-brown haze days highlighting the existence of a similar continuous source of this species. All BTEX levels were high during brown haze mornings except ethylbenzene, which is significant in the afternoons. These can be attributed to the differences in sampling sites (terrain characteristics), source strengths and the dilution conditions during these periods. The dominant wind direction during brown haze days was north westerly, at the maximum speeds of 4 $m.s^{-1}$.

Spatially, significant BTEX concentrations were detected over north east of the city (CBD), townships and informal settlements, and highly industrialised areas respectively. Domestic burning in townships and informal settlements clearly produce significant concentrations of BTEX relative to the surroundings. Except for brown haze mornings, benzene-to-toluene ratios do not indicate vehicle emissions to be the only possible predominant source in Cape Town during all brown haze episodes despite low benzene levels in proportion to other VOCs. Averaged overall BTEX ratios however identify vehicle emissions as the single most prominent source of these species throughout the Cape Town region during both brown and non-brown haze episodes. Levels obtained indicate that there is high variability in VOC concentrations indicating specific sources.

Cross correlations of these species also confirm the insignificant relationship between brown and non-brown haze days sources of BTEX over the region. There is a

clear relationship between BTEX species during brown haze afternoons, indicating similar source during these periods. The diurnal variations of BTEX concentrations may be affected by three factors: (1) variations of BTEX source strengths; (2) variations of atmospheric mixing pattern such as enhancement of vertical mixing through the increased convection during the day (Cheng *et al.,* 1997); and (3) diurnal abundance of OH radical and, thus the degree of photochemical activities. Sources of BTEX compounds vary significantly for selected sites over the study area and are present in considerable concentrations, and their nature and potential impact need further assessment. Traffic and industrial emissions as well as domestic fuel burning were identified as the primary sources of BTEX compounds over the Cape Town region. To extensively understand the significance of these VOCs , their levels should be measured and addressed at ground level as one of the strategies for mitigating and controlling these pollutants, coupled with detailed evaluation of their health impacts; and this information be made available to the public.

In general, BTEX concentrations measured were relatively high in comparison with those previously found on ground-based measurements of urban areas in other countries. Average levels of 5 $\mu g.m^{-3}$ or less for benzene are typical in the UK and US (NETCEN, 1995; USEPA, 1995). Elevated BTEX concentrations do not only correspond to brown haze days but non-brown haze days also showed sizeable concentrations. This can be explained by comprehensively modelling the general atmospheric chemistry of these VOCs and their relationships with oxides of nitrogen and hydroxyl radicals. The levels measured in this study, although conducted over a short period, are considered to be sufficiently high to represent a degree of risk to the local population. However, levels found in this study cannot be directly compared to typical ground-based guidelines and standards because they were not measured at the surface where most of the emissions occur. Based on the BTEX concentrations detected in this study, it cannot be safely concluded that Cape Town experiences high levels of these species at ground level. Similar airborne studies on SO_2 and O_3 have shown strong gradients in SO_2 and O_3 concentrations with increasing height. If so, it could be that BTEX concentrations measured aloft are higher than the surface,

therefore indicating the need for appropriate action to remedy this situation. However, convincing conclusions cannot be made based on these airborne measurements only. . Detailed ground-based BTEX compounds characterisation would be essential to better quantify these VOCs.

This is some of the first regional VOC data obtained in South Africa and it provides some baseline values to assess the introduction of emission control initiatives. The sample size should be increased in the future to obtain better average values with lower standard deviations. This data will also provide information to the authorities about the areas to focus more attention when monitoring and assessing BTEX species in the Cape Town region.

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