THE IMPACT OF HYDROCARBON EMISSIONS ON REGIONAL AIR QUALITY IN A SOUTH AFRICAN METROPOLITAN AREA

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LIST OF ABBREVIATIONS

AGL	Above ground level
ASL	Above sea level
BTEX	Benzene, Toluene, Xylene and Ethylbenzene
BVOCs	Biogenic volatile organic compounds
CBD	Central business district
CO	Carbon monoxide
CO_2	Carbon dioxide
COC	Chain-of-custody
DEAT	Department of Environmental Affairs and Tourism
EPA	Environmental Protection Agency
GC	Gas chromatograph
GC/MS	Gas chromatography coupled with mass spectrometry
HAPs	Hazardous Air Pollutants
HC's	Hydrocarbons
$HO^{\bullet}$	Hydroxyl radicals
IPCC	Intergovernmental Panel on Climate Change
km	Kilometres
LED_{10}	Lethal exposure dose resulting in a 10% population mortality
MDL	Minimum Detection Limit
MOE	Margin of Tolerance
MS	Mass spectrometer
NASA	National Aeronautics and Space Administration
NAQMA	National Air Quality Management Act
NMHC	Nonmethane hydrocarbon
NMTOC	Nonmethane total organic compounds
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen
NOAA	National Oceanic and Atmospheric Administration
O_3	Ozone
ORAC	Organics by Real-time Airborne Chromatography
PAH	Polyaromatic hydrocarbons
PAN	Peroxyacetyl nitrate
PBL	Planetary Boundary Layer

$PM_{10/2.5}$	Particulate matter: diameter of ≥10 μm or diameter of ≥ 2.5 μm
POCP	Photochemical Ozone Creation Potential
POD	Point of Departure
ppbv	parts per billion per volume
pptv	parts per trillion per volume
$R^{\bullet}$	Organic radicals
$R_2O^{\bullet}$	Peroxyradicals
RH	Reactive volatile organic compound
SAWS	South African Weather Service
SO_2	Sulphur dioxide
SOA	Secondary organic aerosols
TACs	Toxic air contaminants
TAPM	The Air Pollution Model
THCs	Total hydrocarbons
tpa	tons per annum
TVOCs	Total volatile organic compounds
UK	United Kingdom
USA	United States of America
US-EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
WHO	World Health Organisation

ABSTRACT

The understanding of the source, transport, fate and impact of anthropogenic emissions is critical if the management of air pollution is to be effective in improving and sustaining acceptable air quality in a given area. In an attempt to improve the current lack of information pertaining to volatile organic compounds (VOC) and specifically benzene, toluene, xylene and ethylbenzene (BTEX), a study was conducted in the metropolitan area of Sasolburg, an industrial town approximately 70 kilometres south of Johannesburg, South Africa. The study aimed to assess the ambient BTEX levels in Sasolburg, comparing results with the Mpumalanga Highveld area and a non-industrial city, Potchefstroom. A number of chromatographic systems, including *in situ* analyses utilising an Organic Real-time Airborne Chromatograph (ORAC), passive samplers and stainless steel canisters were employed during the six-year study period. The ubiquitous nature of BTEX species in the Sasolburg, Potchefstroom and Mpumalanga Highveld areas is shown. The influence of meteorological conditions coupled to the characteristic of the pollution sources has been highlighted. The similarities in ambient levels observed in the study area and the United Kingdom have been shown. The benzene-health impact study undertaken in the Sasolburg and Potchefstroom areas has highlighted the serious challenges faced by the Sasolburg area during the period 2000 to 2004. The reduction in ambient benzene levels in 2006 at all three monitoring sites, most-notably a reduction of more than 100% at Zamdela, a residential area close to the industrial centre, is shown. The subsequent reduction in community exposure due to lower ambient benzene levels, brought about by the switching of coal to natural gas as feedstock by the petrochemical industry in Sasolburg, is demonstrated by benchmarking the study-area benzene levels with similar sites internationally.

OPSOMMING

'n Deeglike begrip van die bron, vervoer, transformasie en impak van atmosferiese besoedelstowwe is krities noodsaaklik indien bestuursmaatreëls, gemik op die verbetering en handhawing van aanvaarbare lugkwaliteit, hul doelwitte wil bereik in 'n gegewe area. Ten einde bestaande leemtes in kennis rakende vlugtige koolwaterstowwe en meer spesifiek benseen, tolueen, xylene en etiel-benseen (BTEX) aan te spreek, is 'n studie geloods in Sasolburg, 'n metropolitaanse stad geleë 70 kilometer suid van Johannesburg, Suid-Afrika. Tydens die studie is gepoog om die atmosferiese vlakke van BTEX te bepaal in Sasolburg en dit te vergelyk met resultate verkry in die Mpumalanga Hoëveld--area en die stad van Potchefstroom – 'n stad gekenmerk aan 'n gebrek aan groot industrieë. Tydens die ses-jaarlange studie is van verskeie chromatografiese stelsels gebruik gemaak, insluitende die *in situ* analisering van BTEX verbindings deur middel van 'n mobiele organiese intydse chromatograaf (Organic Real-time Airborne Chromatograph (ORAC)), 'n passiewe monsternemer en gepassiveerde vlekvrye staalkannetjies (canisters). Die studie het aangetoon dat BTEX alomteenwoordig was in die Sasolburg-, Mpumalanga- en Potchefstroom studie-areas. Die studie het aangetoon dat plaaslike meteorologie gekoppel aan bron karakteristieke belangrike faktore is in die bepaling van troposferiese benseenvlakke. Die studie het aangetoon dat benseenvlakke in die Sasolburg-area gunstig vergelyk met vlakke waargeneem in die Verenigde Koninkryk. Die Sasolburg benseengesondheidsimpakstudie het aangetoon dat die Sasolburg-gemeenskap se blootstelling vir die periode 2000 tot 2004 onaanvaarbaar was. Die daaropvolgende vermindering in benseenvlakke nà die omskakeling in 2006 van steenkool na natuurlike gas as primêre grondstof by 'n petrochemiese industrie, is aangetoon. Die dramatiese vermindering in benseenvlakke en dus blootstelling van die gemeenskappe by al drie die moniteringstasies en meer spesifiek 'n vermindering van meer as 100% in Zamdela ('n residensiële area geleë naby die industriële area) is aangetoon deur waargenome benseen vlakke te vergelyk met eenderse internasionale areas.

CHAPTER 1

MOTIVATION AND OBJECTIVES

In this Chapter...

The motivation and relevance of the study in the South African context are outlined (Par 1.1) and the project scope and goals discussed (Par 1.2).

1.1 PROJECT MOTIVATION AND RELEVANCE

> *"Everyone has the right to an environment that is not harmful to his or her health and well-being"*

This phrase, taken from the South African Constitution, is increasingly being heard throughout South Africa as the focus on protecting our health and preserving our environment becomes more prominent.

The atmosphere we live in is designed to sustain life as we know it. Therefore, any changes in the atmosphere will directly influence the behaviour and existence of the species it sustains.

South Africa realised this basic requirement and included it in its Constitution, thereby highlighting a clean, healthy environment as a basic human right. Environmental legislation aims to ensure compliance to this basic right. South Africa has been lacking sound, enforceable air quality legislation. The Air Pollution Prevention Act of 1965 was outdated and needed to be replaced by new legislation that could protect the environment and those living in it.

The Ministry of Environmental Affairs and Tourism was tasked to rectify this situation, an endeavour which was embarked on in 2002. This resulted in the establishment of the National Air Quality Management Act of 2004 (NAQMA); an act that clearly highlighted the importance of ambient Air Shed management by all tiers of government in order to reach air quality objectives. The act focuses primarily on the improvement of air quality by means of strict ambient air standards, thereby ensuring that the basic rights embedded in the Constitution are met.

The introduction of the new legislation (NAQMA) brought with it the realisation that ambient air quality monitoring in specifically heavily impacted areas was not sufficient to demonstrate compliance to proposed ambient air quality standards (Zunckel *et.al.*, 2006). Previous legislation focused on inorganic pollutants, excluding volatile organic species. This shortcoming has been rectified with the inclusion of benzene as part of the criteria pollutants.

The Vaal Triangle south of Johannesburg is considered the industrial heartland of South Africa. The area currently exceeds certain of the proposed ambient air quality standards, which resulted in the minister declaring the Vaal Triangle an air-pollution priority area. This declaration is seen as an intervention by National Government to ensure compliance with the Constitution, and involves the establishment of regional air quality improvement plans aimed at bringing the area to within compliance.

The lack of comprehensive air quality standards for hazardous volatile organic pollutants, specifically benzene, has resulted in an overall absence of information pertaining to Volatile Organic Compounds (VOCs) species in South Africa.

1.2 RESEARCH OBJECTIVES

Given the lack of information described in Paragraph 1.1, accompanied by the recognition that information on ambient aromatic hydrocarbon concentration levels is extremely limited, the following objectives for this study have been defined:

- Determine the lower tropospheric benzene, toluene, xylene and ethylbenzene (BTEX) concentration profile over Sasolburg and the South African Highveld area. Compare these *findings with* ground-level observations made in the Sasolburg area. This study will aim to assess the severity of BTEX pollution in the study area.

- Compile a ground-level BTEX concentration profile for the Sasolburg area. Priority would be given to benzene due to the species' inclusion in the national ambient air quality standards. During the study, the impact of fuel switching at a major petrochemical plant in the area from coal to natural gas on ambient BTEX levels is also investigated.
- Assess the potential direct health impacts associated with ambient benzene levels utilising passive sampling data at selected sites in Sasolburg and conduct a control study as part of the assessment. Potchefstroom was chosen, since this area is normally not influenced by industrial activity.
- Assess the risks associated with the observed BTEX levels in the Sasolburg area. The relative contribution of ambient BTEX in Ozone and Secondary Organic Pollutant (SOA) formation over the study area will be discussed.

As a collective result of these activities, a BTEX impact assessment for the Sasolburg area will be conducted for the first time. By achieving these objectives, a comprehensive overview of BTEX species on a temporal and spatial resolution will be obtained. The impact and effectiveness of mitigation measures at source will also be evaluated. Moreover, the study will contribute to the scientific understanding of the processes and factors influencing ambient air quality in a heavily impacted industrial area of South Africa.

CHAPTER 2

LITERATURE REVIEW

In this Chapter...

This chapter aims to provide an overview of literature relevant to the understanding of the study. It also aims to provide a background of air pollution, (Par 2.1) followed by a detailed discussion on ambient volatile organic pollution (Par 2.2). Aspects addressed include sources, transportation, quantification, chemistry and impact. Paragraph 2.3 aims to conclude the literature review findings.

2.1 BACKGROUND TO AIR POLLUTION

2.1.1 Structure of the Atmosphere

The earth's atmosphere consists of five distinct layers. The lower regions (up to 50 kilometres from the earth's surface) consist of the troposphere and stratosphere, while the mesosphere, thermosphere and exosphere are considered the upper regions of the atmosphere. Each of these layers has unique characteristics governed by changes in temperature and pressure as altitude increases (Seinfeld *et al.*, 1998).

Figure 2.1 illustrates that pressure and density decrease exponentially with increasing altitude. This results in the majority of the atmosphere, in terms of mass, residing close to the surface of the planet (Wayne, 2000). Subsequently, more than 99 % of the atmospheric composition exists within the troposphere and stratosphere and therefore where the majority of atmospheric chemistry occurs. The troposphere, as the name suggests (tropos meaning turning), is the layer in the atmosphere where constant mixing, turbulence and change are observed. The importance of this layer is even further highlighted, considering the fact that almost the entire mass of anthropogenic emissions gets released into the lower troposphere from where the pollutants are transported. Aviation, in contrast to most other anthropogenic sources, however, gives rise to significant emission into the upper troposphere (12 000 meter) from where pollutants can be transported over huge distances, thereby amplifying the impact of aircraft emissions globally (Jamin *et al.*, 2004).

The troposphere can be divided into two distinct layers. The first layer, known as the planetary boundary layer (PBL), extends from the earth's surface to a height of between 100 and 3000 meters depending on the prevailing weather conditions. The planetary boundary layer is indicated by the abbreviation PBL in Figure 2.1. The PBL is the lowest layer in the troposphere where wind is influenced by friction. During the cooler evenings the PBL is lower, while during the day-time the PBL layer will expand as the temperature rises, resulting in better convective mixing due to stronger winds associated with this rise in temperature. The PBL expansion and therefore better mixing will result in lower observed ground-level pollution concentrations as the day progresses. The second layer of the troposphere is called the free troposphere, indicated by FT in Figure 2.1. The free troposphere, in contrast, does not experience turbulence and mixing to the same degree as within the PBL. More significant is the fact that the free troposphere experiences lower temperatures and water vapour concentration, thereby promoting long-range transport of pollutants (see Paragraph 2.2.3).

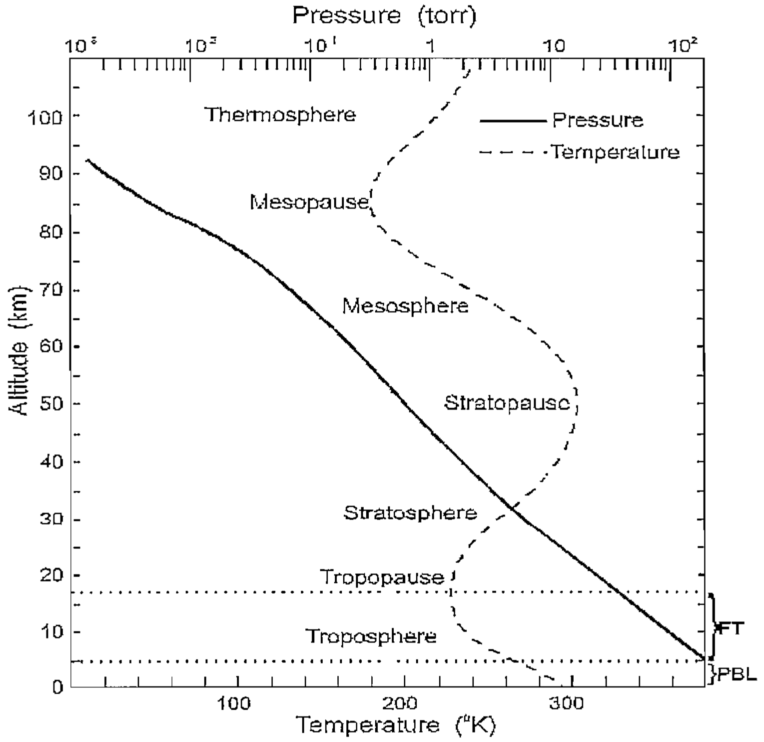


Figure 2.1: Pressure and temperature gradients against altitude in the atmosphere (Wayne, 2000)

2.1.2 Definition of Air Pollution

Elsom (1987) defines air pollution as "the presence in the atmosphere of compounds and energy in such large amounts and over such duration liable to cause harm". Alloway *et al.* (1997) brings the human dimension into the definition by saying that air pollution is "the introduction by man into the environment, substances or energy liable to cause hazards to human health, harm to living sources and ecological systems, damage to structures or amenity or interference with legitimate uses of the environment".

2.1.3 Origin of Air Pollutants

Although Alloway *et al.* (1997) highlighted the impact of human activity on the environment, air pollution includes both man-made and natural sources of pollution (Godish, 1991). Pollution emanating from both these sources is considered substantial, resulting in numerous atmospheric processes taking place, among others acid deposition, climate change and stratospheric ozone depletion (Atkinson, 1990).

Biogenic (natural) sources of pollution include, among others, volcanoes, oceans, swamps, vegetation and natural biomass burning (Wayne, 1985). Non-methane hydrocarbons (NMHCs) emitted into the atmosphere result in, among others, photochemical oxidant formation and acid deposition (Guenther *et al.* 1996). Moreover, Guenther *et al.* (1995) have shown that NMHCs from vegetation are contributing more that 90% of the total global NMHC emission budget of 1150 Tg C being released into the atmosphere. The predominant biogenic NMHC sources are isoprene and monoterpenes contributing 44% and 11% respectively to the total. These biogenic species have been shown to significantly influence the photochemical processes occurring in the atmospheric boundary layer (Simon *et al.,* 2006). The oxidation of these biogenic NMHCs, notably isoprene and monoterpenes, leads to the formation of Secondary Organic Aerosols (SOA) and ozone, which in turn results in, among others, poor visibility and radiative scattering (Pressly *et al.*, 2004).

Anthropogenic (man-made) sources originate from industrial, agricultural and mining activities, to name a few. Anthropogenic emissions may be released from area, point or mobile sources. Area sources include emissions from miscellaneous sources such as buildings, railroads and domestic fuel use for heating and cooking purposes. Mobile sources include both on- and off-road vehicles, while point sources are categorised as large industrial facilities (Scorecard: Pollution Information site, 2005). Emissions associated with combustion equipment include NO_X, SO_X, CO and CO_2, while transport emissions include volatile organic compounds, lead and particulates to name a few.

Anthropogenic emissions are considered more detrimental from a human health perspective, since emission sources are usually in close proximity to human activity (Godish, 1991).

2.1.4 Types of Air Pollutants

The United States Environmental Protection Agency (US-EPA) has classified and managed anthropogenic air pollutants due to its significant impact on community health. According to the US-EPA, all air pollutants can be classified as either criteria- or hazardous air pollutants.

2.1.4.1 *Criteria pollutants*

Criteria pollutants include carbon monoxide, lead, nitrogen oxides, ozone, particulate matter, and sulphur dioxide. The compounds are frequently found in ambient air and are therefore heavily regulated to prevent harm (US-EPA, 2007). The most important species under South African conditions are discussed in more detail.

- Carbon Monoxide (CO).

  Carbon monoxide is associated with the incomplete combustion of carbon-based fuel. This incomplete combustion contributes in excess of 90% to the total CO levels in urban areas (Elsom, 1996). Contributions from residential coal burning and industries are, however, also significant.

Terblanche *et al.* (1996) have indicated that ambient CO emanating from domestic coal burning in South Africa exceeds the local and USA health standards. Carbon monoxide plays a major role in ozone formation and therefore the oxidation potential of the atmosphere according to the following equation:

$$\begin{array}{ll}
 & CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet} \\
 & H^{\bullet} + O_2\ (+M) \rightarrow HO^{\bullet}_2\ (+M) \\
 & HO^{\bullet}_2 + NO \rightarrow HO^{\bullet} + NO_2 \\
 & NO_2 + h\nu(\leq 430\text{nm}) \rightarrow NO + O \\
 & O + O_2\ (+M) \rightarrow O_3\ (+M) \\
\hline
\text{net:} & CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \\
\hline
\end{array}$$

- Nitrogen Oxides (NO_X)

The most important nitrogen species present in the atmosphere are nitrogen oxide (NO), nitrous oxide (N_2O), nitrogen dioxide (NO_2), nitric acid (HNO_3) and ammonia (NH_3). NO_X is commonly considered the sum of NO and NO_2 (Seinfeld and Pandis, 1998). Nitrogen dioxide (NO_2) is the most prominent species in the atmosphere. Emissions of nitrogen species are dominated by the combustion of fossils fuels. The reaction of nitrogen oxides with volatile organic species in the atmosphere results in the formation of ozone (Elsom, 1996).

The transport of nitrogen species by means of the formation of peroxyacetyl nitrate (PAN) is significant and plays an important role in global transport of pollution. PAN transported into the upper troposphere (free troposphere), where temperatures are much colder and water vapour less abundant (see Paragraph 2.1.1), does not undergo dissociation to form nitrogen dioxide. This results in the transport of PAN over vast distances before reaching the lower troposphere. Only when PAN reaches these lower levels can it successfully dissociate to form nitrogen dioxide again (Seinfeld, 1998). This phenomena result in NO_X species becoming a regional, national and global pollutant.

The photolysis of NO_2 is a key reaction in tropospheric chemical processes (Blacet, 1995) (See Paragraph 2.2.3).

- Ozone (O_3)

The formation of ozone has been discussed in the previous section dealing with nitrogen oxides. Photolysis reactions of ozone (O_3) are considered to be the initiator of atmospheric oxidation reactions, since hydroxyl radicals ($HO^\bullet$) are formed (Seinfeld & Pandis, 1998). The concentration of the $HO^\bullet$ radical in the atmosphere is crucial in determining hydrocarbon reaction rates (Atkinson, 2000). This is especially relevant for this study, since the reaction time will determine the residence time in the atmosphere.

- Particulate Matter (PM)

Seinfeld and Pandis (1998) have defined particles as pollutants emanating from natural sources such as dust, sea spray, and anthropogenic activities such as the combustion of fuels. Moreover, they define an aerosol as "a suspension of fine solid or liquid particles in a gas". Particulate matter is usually classified according to particle size. Particulate matter with a cross section diameter smaller that 1 micron is considered as the fine fraction of PM, while particles having a diameter > 1 micron are considered the coarse fraction. The origin of the coarse fraction is mainly associated with mechanical processes such as mineral dust and sea spray, as well as the interaction of secondary aerosol with primary particles. Fine particles may be primary in nature such as diesel soot or may develop from gaseous precursors or via condensation on particulates or nucleation (Perez *et al.*, 2008). The oxidation of primary pollutants, noticeably hydrocarbons both anthropogenic and biogenic, plays an important role in secondary organic aerosol (SOA) formation in the troposphere and therefore the abundance of tropospheric fine particulate matter (Kleindienst *et al.*, 2007). See Paragraph 2.2.3 for a more detailed discussion of the influence of aromatic hydrocarbons on SOA abundance in the troposphere. Particulate matter with a cross section diameter smaller than 10 microns (PM_{10}), 2.5 microns ($PM_{2.5}$) and especially 1 micron and smaller are considered *important* due to its health impacts. Particles with such a small diameter have the capability to penetrate deep into lung tissue and either remain in the lung, or get absorbed into the blood stream. SOAs formed during tropospheric oxidation processes also play an important role in the earth's atmosphere by scattering or absorbing solar radiation. These effects will be discussed in more detail in Paragraph 2.1.7.4.

- Sulphur Dioxide (SO_2)

Sulphur dioxide is formed during the combustion of sulphur-containing fuels such as diesel and coal, and is known to cause respiratory diseases such as asthma in children. Sulphur dioxide, along with NO_X, is considered the predominant precursor to acid deposition (US-EPA, 2007).

2.1.4.2 *Hazardous air pollutants*

Hazardous Air Pollutants (HAPs) include 189 species according to the US-EPA (Kelly *et al.*, 2007). A pollutant is considered as being hazardous if it has the capability to cause serious damage to the living environment. HAPs species, among others, include benzene, 1,3-butadiene, vinyl chloride, mercury and asbestos (Kelly *et al.*, 2007). The hazardous volatile organic compounds, specifically benzene, toluene, xylene and ethylbenzene, will be discussed in more detail in Paragraph 2.2.

2.1.5 Source Quantification of Air Pollutants

A source emission inventory forms the foundation of any sound air quality management system (Held *et al., 1996)*. Source identification and quantification form the backbone of dispersion and transformation models, as well as that of any risk assessment. In order to quantify the emissions from a given source, the emission rates need to be determined. Several acceptable methods exist to determine these emission rates and are summarised below (Ramon *et al.*, 1995).

- Stack monitoring

Stack monitoring is the most reliable, although costly, method to quantify the emission rate from a selected pollution source. Stack monitoring may comprise of a grab sample taken during a specific plant condition, or continuous sampling over a selected period. Major emission sources are usually earmarked for stack monitoring, specifically due to the high cost associated with the technique.

- Emission factors

Due to the high cost associated with stack monitoring, certain international agencies, such as the United States Environmental Protection Agency (US-EPA) conduct stack testing on several processes to determine an emission rate based on a specific operation unit basis. Emission factors tend to be conservative due to the fact that tests are usually carried out on old, less efficient units. Emission factors are usually expressed as grams or kilograms per tonne of feedstock (for example coal).

- Material balance

The quantity of a compound exiting from a piece of equipment can be estimated by adding the amount entering the unit plus the amount formed in the process minus the amount accumulating in it or converted to another compound. If not a product, the material may have an exiting pathway such as water, solid or air. The amount being released into the atmosphere can then be determined by subtracting the material exiting as a liquid or waste from the total material used in the process.

- Engineering equations

Engineering equations aim to estimate emissions based on the volatility of compounds under different conditions. The emission rate determined in this fashion is defensible, although it represents a theoretical presentation of an actual process or condition.

2.1.6 Dispersion of Air Pollution

The meteorological conditions at a site determine the dispersion of pollutants in the atmosphere (Pasquill & Smith, 1983; Godish, 1991). The severity of pollution accumulation or dispersion in the atmosphere is dependent on the magnitude of thermal and mechanical turbulence within the earth's boundary layer. Dispersion includes both a vertical and horizontal component of motion. The stability of the atmosphere and the depth of the surface-mixing layer define the vertical component. The horizontal dispersion of pollution is primarily a function of the wind field, atmospheric stability and height of emission. The wind speed determines the distance of downwind transport as well as the rate of dilution as a result of plume 'stretching'. The generation of mechanical turbulence is similarly a function of the wind speed, in combination with the surface roughness. The wind direction, and the variability in wind direction, determine the general path pollutants will follow, and the extent of cross-wind spreading (Shaw & Munn, 1971; Pasquill & Smith, 1983; Oke, 1990).

2.1.7 Major Global Air Pollutant Impacts

Air pollution has impacted on the earth and its inhabitants over many centuries, and this impact mainly depends on the physical and chemical properties of the pollutant. These properties define the dispersion potential based on chemical reactivity, as well as the retention time in living tissue. Some of the most prominent effects or impacts due to air pollution are summarised below.

2.1.7.1 Impact on Human Health

In 1992, the World Bank estimated that more than 3 billion people in developing countries are exposed to unacceptable levels of air pollutants (World Bank, 1992). The 1952 Great London Smog, which resulted in more than 4000 deaths, can be considered the turning point in the way the world approaches air pollution (HMSO, 1954). Epidemiological research has found that there is a defined correlation between air pollution and human effects, including respiratory illnesses and even death (Bates, 1992). Air pollution in

Austria, France and Switzerland annually causes more than 40 000 deaths, of which almost half can be attributed to emissions from motorised traffic (Kunzil *et al.*, 2000). The World Health Organization (WHO, 2002) has estimated that the in-door use of solid fuels in developing countries is the eighth leading health risk worldwide. A brief summary of the most prevalent inorganic air pollutants and their risks are given below. Volatile organic pollutants, including the BTEX species, are discussed in Paragraph 2.2.5, since these species are the focus point of this study.

- Ozone

Acute exposure to ozone results in decreased pulmonary function and the capacity to exercise in healthy people as well at those with chronic air way diseases such as asthma (Spengler *et al.*, 2006). Ozone induced health effects are dependant on dose and concentration of ozone deposited in the lung as well as the person's ventilation rate and duration of exposure.

- Sulphur dioxide

Sulphur dioxide, mainly formed during the combustion of fossil fuels, can be linked to the formation of acid aerosols and particles, which may lead to a range of health impacts. These health impacts include, among others, short-term respiratory morbidity and mortality, and bronchoconstriction in adults and adults with asthma (Horstman *et al.*, 1986).

- Nitrogen dioxide

Nitrogen dioxide is mainly formed during the combustion of fossil fuels. There is sound evidence that suggests that children with asthma or atopy, as well as female adults, are more sensitive to the respiratory effects of NO_2. Indoor NO_2 exposure in turn may also enhance asthmatic attacks to inhaled allergens (Strand *et al.*, 1997). The acidic nature of NO_2 makes it capable of causing damage to the respiratory system, which in turn may lead to respiratory symptoms in patients with asthma (Tunnicliffe *et al.*, 1994).

- Carbon monoxide

Carbon monoxide is mainly formed during the incomplete combustion of fossil fuels. CO has the ability to impair haemoglobin's capacity to bind oxygen, resulting in nausea, headaches, fatigue and, with high exposures, death (Weaver *et al.*, 2002).

- Particulate matter

Particulate matter can be associated with primary emissions or can be formed from gaseous precursors to form secondary aerosols (see Paragraph 2.1.4.1). The adverse effects of particulate matter are dependant on the deposition rate in the respiratory track, followed by the ability of the respiratory tree to remove the pollutant. This process is directly linked to the size of the matter inhaled. Coarse particles tend to deposit in the nasal, pharyngeal and laryngeal regions of the track. Fine and ultra-fine particulates, however, are deposited in the tracheobronchial region and alveoli, amplifying these smaller fraction's health effects. The large surface areas of these smaller particles also result in better adsorption of toxic species onto these particles such as polycyclic aromatics resulting in aggravated respiratory diseases (Weisel *et al.*, 2002).

2.1.7.2 Impact on Crops and Vegetation

The negative impact of air pollution on vegetation and more specifically crops is well known. Phytotoxic pollutants such as nitrogen oxides (NO_X), sulphur dioxide, ozone and highly volatile C2-chlorohydrocarbons have been proven to impact severely on global crop production yields (Weissflog *et al.*, 2001). Tetrachloroethene (TECE) and Trichloroethene (TCE), emitted during industrial combustion processes and biomass burning, have been shown to be responsible for the production of Trichloroacetic acid (TCA) by means of chemical transformation in the atmosphere (Sidebottom & Franklin, 1996). TCA was used in the 1950s as a very effective herbicide due to its phototoxic properties (Matolcsy *et al.*, 1988). The importance of understanding the effect of air pollution on crops becomes increasingly important as global food demand increases. Recent studies (McFrederick *et al.*, 2008) have shown that floral hydrocarbons providing important signals to pollinators are destroyed in areas where high levels of ozone occur, resulting in poor pollination and therefore potentially poorer crop yield. Studies conducted by Cape (2003) have indicated that Bean (*P. vulgaris*) plants are sensitive to volatile organic pollution, leading to reduced harvested pod weights. He did, however, indicate as well that plants in general show a wide range of tolerance to airborne VOCs.

Studies conducted in Italy (Nali *et al.*, 2002) have indicated significant crop losses due to air pollution in corn and soybean, resulting in an estimated loss of revenue exceeding 8 million Euro. Studies conducted in Malaysia have shown ozone induced crop losses to range between 1.6% and 5% in 2000 (Ishii *et al.*, 2007).

2.1.7.3 Acid Deposition

Sulphur dioxide and nitrogen dioxide present in the atmosphere undergo oxidation in gaseous and aqueous phases to form sulphates and nitrates. These reactions ultimately result in the formation of acidic gases in the troposphere. Once formed, these secondary pollutants return to the surface by means of dry- or wet deposition processes (Seinfeld & Pandis, 1998). Acid deposition has been linked to soil and surface water degradation, crop damage, acidification of lakes, as well as concrete corrosion (buildings) to name a few.

2.1.7.4 Climate Change

Human activity is influencing the earth's climate (IPCC, 2002). Greenhouse gases, including among others, methane and carbon dioxide, are changing the radiative properties of the earth, resulting in the earth's temperature slowly rising. The impact on sea levels, crop production and weather patterns is significant and alarming (IPCC, 2002). Figure 2.2 indicates the relevant contribution to radiative forcing of anthropogenic pollutants. The net positive impact of ozone on the radiative forcing resulting in atmospheric heating is indicated. This is in contrast to particulate matter which gives rise to cooling.

The importance of volatile organic pollutants in determining the concentration of tropospheric ozone, resulting in a net heating effect opposed to the cooling effect brought about by secondary organic aerosol formation during the oxidation of VOCs is highlighted in Figure 2. 2 (IPCC, 2007).

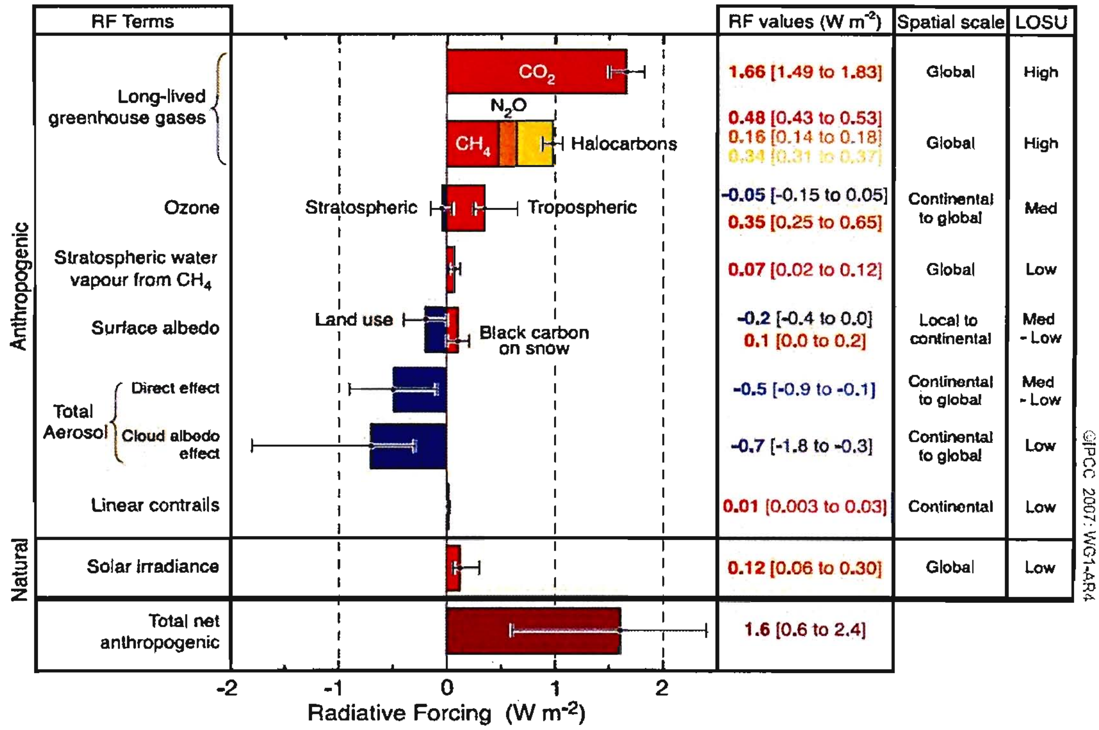


Figure 2.2: Illustration of the global radiative forcing in 2005 associated with atmospheric species, with respect to 1750 (IPCC, 2007)

2.1.7.5 Stratospheric Ozone Depletion

Stratospheric ozone concentrations are declining due to the use of halocarbons that react with stratospheric ozone (Seinfeld & Pandis, 1998). Stratospheric ozone serves as an ultraviolet barrier protecting the earth from high energy ultraviolet radiation. Although halocarbons have been banned in most countries, the problem still exists, with NASA reporting in September 2000 a record Antarctic ozone "hole" size of 28.3 million square kilometres (Barry *et al.*, 2006). Indications from NASA satellites have shown that the average size of the ozone hole has stabilised compared to the last 15 years (Hansen, 2007).

2.2 AMBIENT VOLATILE ORGANIC COMPOUNDS

2.2.1 Definition of Ambient Volatile Organic Compounds

Volatile organic compounds (VOCs) are air pollutants found in the lower and upper troposphere, urban and rural areas, as well as industrial areas. Organic compounds are considered VOCs when its vapour pressure at room temperature is less than 101.3 kPa, but greater than 0.13 kPa (Derwent, 1995).

The United Nations Economic Commission for Europe defines Volatile Organic Compounds as "all organic compounds of anthropogenic nature other than methane that are capable of producing photochemical oxidants by reaction with oxides of nitrogen in the presence of sunlight" (Hoskins, 1995).

2.2.2 Sources of Volatile Organic Pollutants

Volatile organic pollutants are emitted from a variety of sources. These sources may be natural or anthropogenic in nature.

Natural sources may include decomposition of biomass, livestock and forests. Globally, the natural emission of volatile organic pollutants is significant compared to anthropogenic emissions (Godish, 1991). In Paragraph 2.1.3 the importance of biogenic NMHC is highlighted. It was indicated that 90% of all NMHC originated from biogenic sources, with isoprene and monoterpene dominating biogenic NMHC emissions. Biogenic VOC releases from South African vegetation is estimated to be 80 Tg C per annum (Zunckel *et al.*, 2007), highlighting the importance of biogenic VOC species in lower tropospheric processes over southern Africa. Biogenic VOC species, especially isoprene, are much more reactive as an ozone precursor than anthropogenic generated VOC species and therefore also play a major role in industrial areas where anthropogenic sources may be high (Atkinson, 2000). The major sources of isoprene are deciduous trees, resulting in high concentrations of isoprene over forested areas (Apel *et al.*, 2002). Other sources of isoprene include marine phytoplankton and seawood. Isoprene emissions from savannah areas have been calculated to dominate the biogenic VOC emissions over southern Africa, with an estimated 59 Tg C being released annually compared to 7.2 Tg C per annum of monoterpenes (Zunckel *et al.*, 2007).

Globally, monoterpene emissions are dominated by α-pinene (50%). Other monoterpenes emitted include d3-carene, d-limonene, camphene, myrcene, sabinene, b-phellandrene and p-cymene (Geron *et al.*, 2000).

Marine associated VOC species are estimated to contribute only 0.2% to the global biogenic VOC budget. These VOC species do, however, have a significant impact on the marine atmospheric boundary layer chemistry (Plass *et al.*, 1992; Donahue & Prinn, 1990).

Flowering plants have been shown to emit linalool ($C_{10}H_{18}O$), b-myrcene ($C_{10}H_{16}$) and b-ocimene ($C_{10}H_{16}$) (Wright & Smith, 2004). These species act as signals to pollinators such as bees and moths. Compounds also emitted by plants include alkanes, alkenes, alcohols, ethers, esters, aldehydes and ketones, among others (Guenther *et al.*, 2000).

Anthropogenic emissions of hydrocarbons are estimated to contribute about 10% of the total hydrocarbon emissions (Zunckel *et al.*, 2007). Sources of hydrocarbons include industrial, vehicle- and indoor emissions as well as emissions associated with domestic fuel combustion.

Industrial sources include paint production, solvent use, refining, chemical processing and waste treatment and disposal to name a few.

Winebrake *et al.* (2001) have shown that benzene, 1,3-butadiene, acetaldehyde and formaldehyde are major pollutants associated with mobile emission sources. Godish (1991) indicated that 75% of mobile source emissions in the USA can be attributed to light-duty motors.

Emissions from motor vehicles can be divided into two categories, exhaust (tailpipe) emissions (13%) and evaporative emissions (31%) (Van der Westhuizen *et al.,* 2004).

Products of combustion associated with tailpipe emissions include oxygenated derivatives or oxy-hydrocarbons. Species released include *aldehydes,* ketones, alcohols, ethers and acids. Aldehyde emissions associated with tailpipe emissions from motor vehicles are significant.

Van der Westhuizen *et al.* (2004) have shown that evaporation of fuel due to the transportation and storage thereof resulted in 97 million litres of petrol being released into the atmosphere in South Africa alone. Important species released during evaporation include benzene, toluene, 1,3-butadiene and xylene.

Harmse (2002) has indicated that road transport and solvent use dominate VOC emissions in South Africa. Table 2.1 summarises the emission sources and estimated percentage contribution. Source contributions of anthropogenic sources in the Sasolburg area (study area) are given in Paragraph 2.2.7.

Table 2.1: Estimated source contributions to VOC emissions in South Africa (Harmse, 2002) (Actual tonnages have up to date not been estimated)

Emission Source	% of Total VOC Releases
Road Transport	33.0
Other Mobile Sources and Machinery	3.0
Commercial & Residential Combustion	3.0
Industrial Combustion	0.5
Public Power Generation	0.5
Refinery, Chemical Production Processes	6.0
Distribution of Fossil Fuel	6.0
Waste Treatment and Disposal	1.0
Solvent Use	25.0
Agriculture	4.0
Natural Sources	18.0

2.2.3 Atmospheric Chemistry of Volatile Organic Compounds

Atmospheric VOCs play a major role in ozone formation as well as the subsequent formation of secondary aerosols (Atkinson, 2000). It will be shown that, by altering the tropospheric ozone concentration, almost all tropospheric chemical processes are impacted upon.

2.2.3.1 Formation of Atmospheric Oxidants

Sunlight plays a central role in many atmospheric reactions. The gas-phase chemistry of the troposphere involves the oxidation of organic molecules in the presence of nitrogen oxides and sunlight. A vast number of atmospheric species are capable of absorbing solar radiation. Radical-chain oxidation processes are, however, mainly photolytically initiated by ozone (O_3), nitrogen dioxide (NO_2) and formaldehyde (HCHO).

Although present at concentration levels of only a few parts per billion or less, it was recognised that the photolysis of NO_2 is a vital reaction in tropospheric chemical process (Blacet, 1995).

$$NO_2 + h\nu\ (\leq 430\text{nm}) \rightarrow NO + O(^3P) \qquad [1]$$

The photo-dissociation of NO_2 to NO and $O(^3P)$ (one of the electronically excited states of an oxygen atom) is followed by a reaction with an oxygen molecule (O_2) resulting in the formation of ozone.

$$O\ (^3P) + O_2\ (+\ M) \rightarrow O_3\ (+\ M) \qquad [2]$$

where M = a third molecule, mostly N_2 or O_2, which absorbs the excess vibrational energy and thereby stabilising the O_3 molecule formed. The rate constant for both the reaction with N_2 and O_2 is given as 5.4×10^{-36} cm^3 $molecule^{-1}s^{-1}$ and 6.0×10^{-36} cm^3 $molecule^{-1}s^{-1}$, respectively. In a clean and "natural" atmosphere, the O_3 formed will react with NO to regenerate NO_2.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad [3]$$

In a "clean" atmosphere, a steady state ozone concentration will be maintained, which is proportional to the photolysis rate of NO_2 (Reaction 1) and the rate at which NO_2 is regenerated in Reaction 3 (Curtzen, 1973).

$$[O_3] = {}^{\{[NO_2]j_{NO2}\}}/_{k_3[NO]}$$

j_{NO2} is defined as the photolysis rate coefficient (photolysis frequency) for NO_2.

Despite low steady state tropospheric ozone concentrations in "clean" atmospheres, ozone plays a vital role in atmospheric oxidation reactions. Atmospheric oxidation reactions are considered to be initiated by the photolysis of ozone (O_3) (Seinfeld & Pandis, 1998).

$$O_3 + h\nu (< 315\text{nm}) \rightarrow O_2 + O\,(^1D) \qquad [4]$$

The singlet oxygen atoms $O(^1D)$ that are produced react with water (H_2O) to generate two hydroxyl radicals (radicals (indicated by $^\bullet$) = molecules or ions with unpaired electrons). The production of $O(^1D)$ is governed by the photolysis rate coefficient $j_{O(1D)}$. Approximately 10% of the $O(^1D)$ atoms react with water to form hydroxyl radicals (Seinfeld & Pandis, 1998). This relates to approximately 0.2 $HO^\bullet$ radicals from each $O(^1D)$ formed at 298 K and 50% relative humidity (Atkinson, 2000). The formation of $HO^\bullet$ in the free troposphere is therefore dependant on the availability of water vapour. Humidity levels decrease with altitude resulting in very dry conditions in the upper troposphere (low reactivity) and varying reactivity in the free troposphere depending on the water vapour concentration and any given point.

$$O\,(^1D) + H_2O \rightarrow 2HO^\bullet \qquad [5]$$

Even though the photolysis of ozone is considered the principal source of hydroxyl radicals ($HO^\bullet$) in the lower troposphere, $HO^\bullet$ can also be formed during the photolysis of nitrous acid, formaldehyde and carbonyls, as well as the night time reaction of ozone with alkenes (Atkinson, 2000).

The hydroxyl radical ($HO^\bullet$) is non-reactive towards N_2 and O_2 and will in most cases survive collisions with these molecules. The hydroxyl radical ($HO^\bullet$) is, however, highly reactive towards other atmospheric trace species such as hydrocarbons (RCH), carbon monoxide (CO) and aldehydes (RCHO) (Levy, 1971). It has been suggested that approximately 70% of the hydroxyl radicals react with CO to produce carbon dioxide (CO_2), and the rest with methane to produce water and a methyl radical ($CH^\bullet_3$) in a clean atmosphere, mainly due to the elevated levels of these species in the troposphere (Pienaar & Helas, 1996).

$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet}$ [6]

$CH_4 + HO^{\bullet} \rightarrow H_2O + CH^{\bullet}_3$ [7]

The hydrogen ($H^{\bullet}$) and $CH^{\bullet}_3$ radicals react with O_2 to produce hydroperoxy- ($HO^{\bullet}_2$) and methylperoxy ($CH_3O^{\bullet}_2$) radicals.

$H^{\bullet} + O_2 \rightarrow HO^{\bullet}_2$ [8]

$CH^{\bullet}_3 + O_2 \rightarrow CH_3O^{\bullet}_2$ [9]

In the absence of sunlight (e.g. during night-time) the direct reaction between NO_2 and O_3 to produce the nitrate radical ($NO^{\bullet}_3$) is of great importance.

$NO_2 + O_3 \rightarrow NO^{\bullet}_3 + O_2$ [10]

During day-time, $NO^{\bullet}_3$ radicals rapidly photolyse to NO and NO_2.

Due to the following relatively rapid equilibrium:

$NO_2 + NO^{\bullet}_3 \leftrightarrow N_2O_5$ [11]

dinitrogenpentoxide (N_2O_5) acts as a reservoir for the $NO^{\bullet}_3$ radical, which enhances the role of $NO^{\bullet}_3$ during night-time oxidation processes.

In view of the above mentioned processes, tropospheric O_3 thus ultimately "controls" the chemical oxidation potential of the troposphere.

2.2.3.2 *Oxidation of volatile organic compounds*

It follows from reaction [6] and [7] that the oxidation of VOCs is directly linked to the formation, as well as the destruction of ozone. The complete cycle for the oxidation of CO (Reaction [6]) is given by Curtzen (1973):

$$\begin{array}{llr}
 & CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet} & [6] \\
 & H^{\bullet} + O_2 (+M) \rightarrow HO^{\bullet}_2 (+M) & [8] \\
 & HO^{\bullet}_2 + NO \rightarrow HO^{\bullet} + NO_2 & \\
 & NO_2 + h\nu (\leq 430nm) \rightarrow NO + O & [1] \\
 & \underline{O + O_2 (+M) \rightarrow O_3 (+M)} & [2] \\
\hline
\text{net:} & CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 &
\end{array}$$

The overall reaction scheme for the oxidation of methane (Reaction [7]) is given by:

$CH_4 + HO^{\bullet} \rightarrow CH_3^{\bullet} + H_2O$ [7]

$CH^{\bullet}_3 + O_2\ (+M) \rightarrow CH_3O^{\bullet}_2\ (+M)$ [9]

$CH_3O^{\bullet}_2 + NO \rightarrow CH_3O^{\bullet} + NO_2$

$CH_3O^{\bullet} + O_2 \rightarrow HCHO + HO^{\bullet}_2$

$HO^{\bullet}_2 + NO \rightarrow HO^{\bullet} + NO_2$

$2(NO_2 + h\nu(\leq 430\text{nm}) \rightarrow NO + O)$ [1]

$(2O + O_2\ (+M) \rightarrow O_3\ (+M))$ [2]

net: $CH_4 + 4O_2 + 2h\nu \rightarrow HCHO + 2O_3 + H_2O$

It follows from these two reaction schemes that the oxidation of CO and CH_4 leads to the formation of ozone. In general, the oxidation of all other VOCs (e.g. hydrocarbons (RH)) can result in the formation of ozone. The net result, however, strongly depends on the relative ratio and reactivity of species involved in the process. In NO poor environments, the oxidation of CO for instance, can lead to the destruction of O_3 due to the fact that $HO^{\bullet}_2$ radicals then react with O_3 instead of NO as indicated in the following reaction scheme:

$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet}$ [6]

$H^{\bullet} + O_2\ (+M) \rightarrow HO^{\bullet}_2\ (+M)$ [8]

$HO^{\bullet}_2 + O_3 \rightarrow HO^{\bullet} + 2O_2$

net: $CO + 2O_3 \rightarrow CO_2 + O_2$

The dependence on tropospheric NO concentration levels to determine the net photochemical formation of ozone or photochemical ozone loss is therefore clear and is determined by the rate of the reaction between the $HO^{\bullet}_2$ radical with NO:

$$HO^{\bullet}_2 + NO \rightarrow HO^{\bullet} + NO_2$$

versus the self reaction of $HO^{\bullet}_2$

$$HO^{\bullet}_2 + HO^{\bullet}_2 \rightarrow H_2O_2 + O_2$$

and

$$HO^{\bullet}_2 + O_3 \rightarrow HO^{\bullet} + 2O_2$$

The oxidation of RH and interaction of intermediate products with NO can also lead to the formation of peroxyacyl nitrates ($R'C(O)O_2NO_2$).

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$$
$$R^{\bullet} + O_2 \rightarrow RO^{\bullet}_2$$
$$RO^{\bullet}_2 + NO \rightarrow NO_2 + RO^{\bullet}$$
$$RO^{\bullet} + O_2 \rightarrow R'CHO + HO^{\bullet}_2$$
$$HO^{\bullet}_2 + NO \rightarrow NO_2 + HO^{\bullet}$$
$$R'CHO + HO^{\bullet} \rightarrow R'C^{\bullet}O + H_2O$$
$$R'C^{\bullet}O + O_2 \rightarrow R'C(O)O^{\bullet}_2$$
$$R'C(O)O^{\bullet}_2 + NO_2\ (+ M) \leftrightarrow R'C(O)O_2NO_2\ (+ M).$$

An understanding of the key role that the photolysis of ozone as initiator of atmospheric chemistry plays, brings with it the realisation that nitrogen dioxide must be considered to be the precursor of all tropospheric chemistry. Nevertheless, one would expect nitrogen dioxide pollution and therefore the oxidation potential of the troposphere to be a regional phenomenon given the relative short atmospheric lifetime of nitrogen dioxide (<2 days) (Helas *et al.*, 1981). However, the peroxyacyl nitrate species acts as a reservoir for NO_X thereby extending the atmospheric lifetime of NO_X. Considering R' = CH_3, then the peroxyacyl species is known as peroxyacetyl nitrate ($CH_3CO{\cdot}O_2NO_2$) or PAN as it is commonly known.

$$CH_3CO{\cdot}O^{\bullet}_2 + NO_2 \leftrightarrow CH_3CO{\cdot}O_2NO_2$$

The formation of PAN in the troposphere is of importance, since it promotes the long-range transport of nitrogen dioxide. PAN is in equilibrium with its precursors and will therefore be stable at lower temperatures such as experienced above the earth's boundary layer resulting in the long-range transport of PAN (Singh *et al.*, 1986). If the meteorology is favourable, the air stream will transport the PAN closer to the surface where the temperature is higher and the equilibrium is shifted towards NO_2, resulting in its release into the lower troposphere where it can undergo photolysis.

The complexity of atmospheric chemistry in urban and rural areas compared to “pristine” environments is amplified, due to the presence among others, of many VOCs of different classes (such as alkanes, alkenes and aromatic etc.), with different reactivity and different molecular mixing ratios. Considering only the reactions of the three main oxidants ($HO^{\bullet}$,O_3 and $NO^{\bullet}_3$) with VOC compounds, the first reaction step generally involves either H-atom abstraction of the most weakly bound hydrogen atom in the RH molecule, or additional reactions in the case of alkenes and conjugated aromatic compounds. A much generalised reaction is given in Figure 2.3.

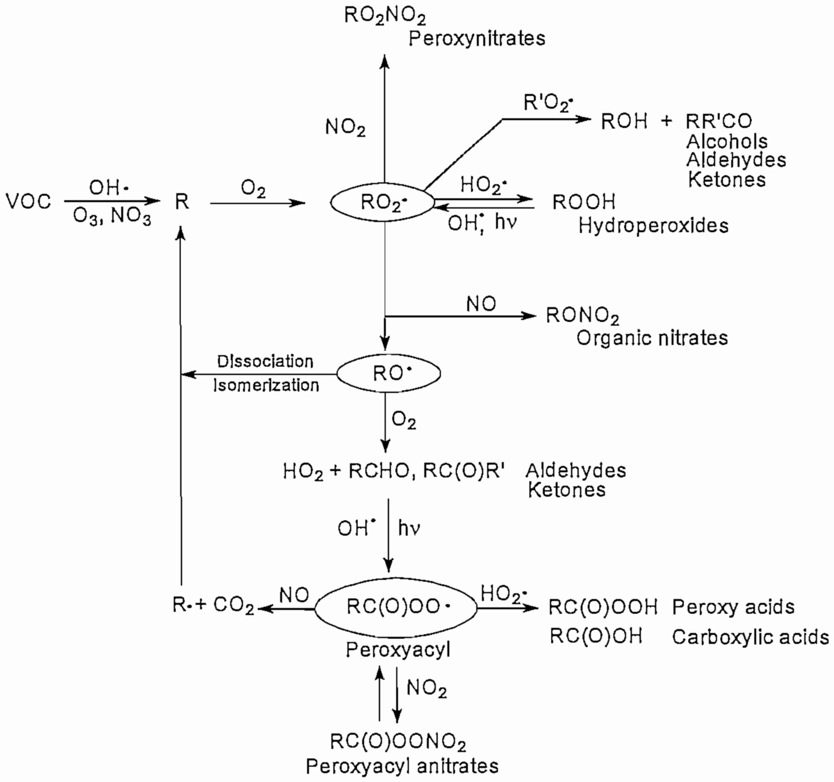


Figure 2.3: Organic radicals and products in the photo-oxidation of an organic molecule (Seinfeld & Pandis, 1998)

The reaction of cyclohexene with ozone (Figure 2.4) has been investigated in a series of smog chamber studies and serves as a prime example (Seinfeld & Pandis, 1998). Aromatic hydrocarbons undergo similar reactions leading to the formation of secondary organic aerosols (Atkinson, 2000).

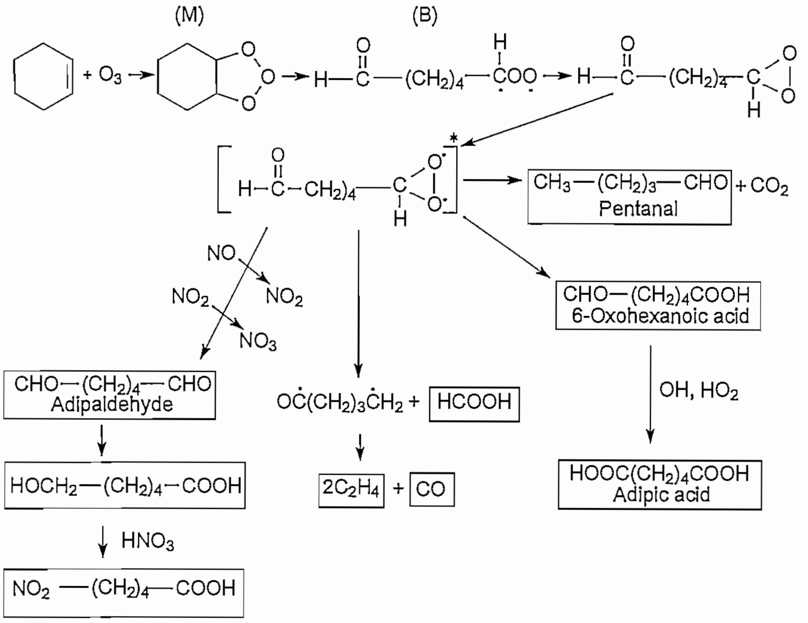


Figure 2.4: The reaction of cyclohexene with ozone (Seinfeld & Pandis, 1998)

Due to the large differences in reactivities, it has become the custom to calculate the so-called ozone forming potential of VOCs. The $HO^{\bullet}$ chain length due to a particular VOC/NO_x ratio is also of great interest as it largely determines the atmospheric oxidation rate. The dependency of ozone formation on initial VOC and NO_x concentrations is illustrated by means of ozone isopleths. Figure 2.5 illustrates a generic ozone isopleth. A prominent feature of the ozone isopleths is the so-called ozone ridge line that divides areas of low VOC-to-NO_X ratios (above the ozone ridge line), with areas of high VOC-to-NO_X (below the ridge line). By utilising this ridge, the maximum ozone concentration at a given VOC concentration can be obtained by varying the NO_X concentration. Therefore, if the NO_X deviates from this line (lower or higher concentrations) the maximum ozone concentration will decrease. In principal therefore, *the area below* the ozone ridge line is considered NO_X-limited (high VOC-to-NO_X ratio), while the area above the line is VOC-limited (low VOC-to-NO_X ratio). Therefore, in an environment with low VOC concentration levels the availability of VOCs will determine the maximum ozone formation at any given NO_X concentration (VOC limited).

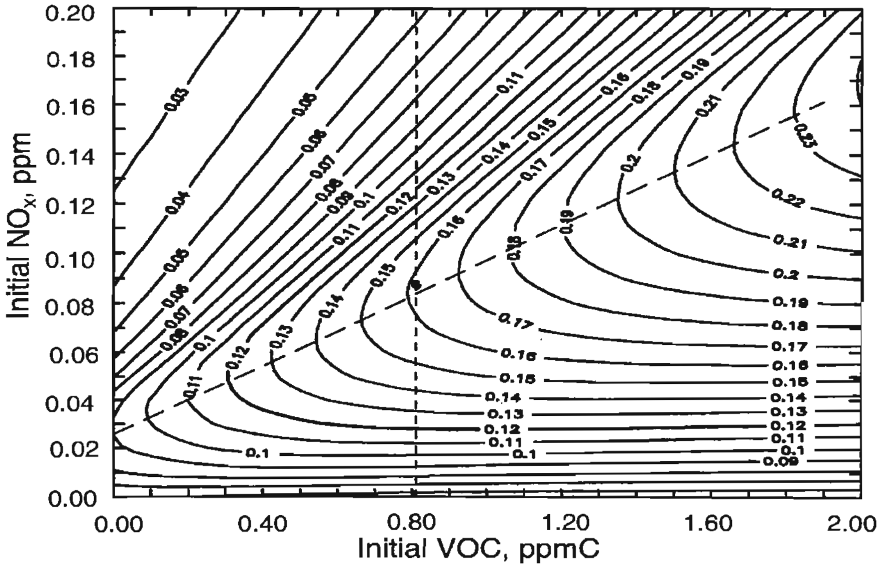


Figure 2.5: Generic ozone isopleth indicating the initial VOC and NOx dependency on ozone formation (Seinfeld & Pandis, 1998)

In order to assess the impact of VOC species on ozone formation, the Photochemical Ozone Creation Potential (POCPs) for several VOC species has been established (Derwent *et al.*, 1998). Table 2.2 summarises POCP values for selected hydrocarbons. POCP for a specific VOC is determined by assessing the effect of incremental changes in ozone formation due to a change in the specific VOC concentration relative to the change in ozone formation of the reference VOC concentration (ethylene):

*POCPi = ((ozone increment with ith VOC) / (ozone increment with ethylene)) *100*

Table 2.2: POCP values for selected organic compounds relative to ethylene (Derwent *et al.*, 1998)

Species	POCP
Ethylene	100.0
Chloroform	2.3
Benzene	21.8
Toluene	63.7
Ethylbenzene	7.3
o-Xylene	105.0
Styrene	14.2
1,3,5-Trimethylbenzene	138.1
1,2,4-Trimethylbenzene	127.8
methane	0.6

Aromatic hydrocarbons contribute between approximately 20% and 30% of the total volatile organic compounds in the urban environment (Calvert *et al.*, 2003). Biogenic and anthropogenic aromatic VOC species oxidation results in the formation of ozone and semi-volatile hydrocarbon species, which then undergo a process of partitioning into the condense phase to form secondary organic aerosols (SOA). Not all VOC species form SOA under atmospheric conditions, since the vapour pressure of the products formed during VOC oxidation is too high. The ability of a VOC to produce aerosols depends on the abundance of the species, its chemical reactivity and finally the vapour pressure of the product of oxidation (Seinfeld & Pandis, 1998). It is therefore clear, based on these factors, that the lower carbon alkanes and alkenes will not readily form SOA due to the high vapour pressures associated with its products of oxidation. Anthropogenic hydrocarbon emissions are estimated to contribute only 10% to the global SOA budget (Tsigaridis & Kanakidou, 2003). Recent studies conducted by Henze *et al.*(2008) have indicated that aromatic VOC and specifically benzene is playing a bigger role in SOA formation than was previously suggested. Henze (2008) has also indicated that benzene oxidation to form SOA is significantly enhanced in areas with low NO_X concentrations compared to a high NO_X environment. These findings are significant given the slow oxidation rate of benzene with the hydroxyl radical, leading to longer residence times compared to other aromatic species such as toluene. This finding indicates that SOA formation associated with benzene will take place more rapidly in cleaner environments (rural areas) where NO_X

concentrations are lower and sufficient benzene molecules exist due to its longer lifetime. This finding has resulted in benzene being considered the most important aromatic species with regard to the global formation of SOA. Studies conducted by Ng *et al.* (2007) have indicated SOA yields from the oxidation of xylene under low-NO_X conditions to be between 35% and 37%, toluene 29% and 31% and benzene 37%. SOAs formed during the oxidation of VOCs have been shown to be di- or poly-functional substituted alkane derivatives, di-carboxylic acids, poly-substituted phenols and nitro-aromatics from aromatic hydrocarbons, among others (Seinfeld & Pandis, 1998).

2.2.4 Quantification of VOCs in the Atmosphere

The identification of the correct method for sampling and analysis of volatile organic compounds in ambient air is crucial if sound information on a specific area is to be obtained. The final decision is based on certain criteria, as well as available methods or technologies. These methods include the following (Harrington, 2003):

- Passivated canisters
- Tubes containing absorbents
- Diffusive (passive) sampling
- On-line sampling
- Sampling bags (Tedlar bags)

Selection of the correct sampling strategy depends upon several factors. These include the nature of the analytes of interest, local environmental considerations, pollutant concentrations, and the specific type of data required, i.e. "snap shot (grab)" sampling, time weighted average measurements or continuous twenty-four hour pollution profiling. Three standard methods are described by the US-EPA. These methods involve using passivated stainless steel canisters or adsorbent tubes (United States Environmental Protection Agency, 1997). A third technique involving diffuse samplers can also be used. Although not part of the EPA suite of monitoring methods, it has been found to be an accurate, cost-effective alternative (IVL, 1998).

- *Passivated canisters*

TO-Cans are ideal containers for sampling non-polar compounds and have the advantage that they provide an accurate representation of the air under investigation (Camel & Caude, 1995). Canisters (Figure 2.6) have undergone extensive evaluation, and are now accepted as the appropriate method for the sampling of forty hazardous volatile organic air compounds in ambient air, specified in the US-EPA method TO-14A (United States Environmental Protection Agency (US-EPA, 1997)). Low ambient volatile organic compound (VOC) concentrations necessitate the need to pre-concentrate the air sample before injection into the gas chromatograph/mass spectrometry analytical system. This pre-concentration step includes a cold trap, or a capillary cryo-focusing device to concentrate the VOCs contained in a specific volume of air.

Figure 2.6: A 6-litre TO-Can air sampling canister utilised in sampling for VOCs according to the EPA compendium method TO-14a

Depending on the VOC concentrations and the sampling method used, pre-concentration would typically amount to a final sampling volume of 1000 ml. Thermal desorption is then used to transfer the concentrated VOCs from the cold trap to the gas chromatograph for separation. The Turbo Matrix thermal desorber from Perkin-Elmer, equipped with an electronically cooled trap, provides an ideal interface for canister analysis. Figure 2.7 is an illustration of the system operation.

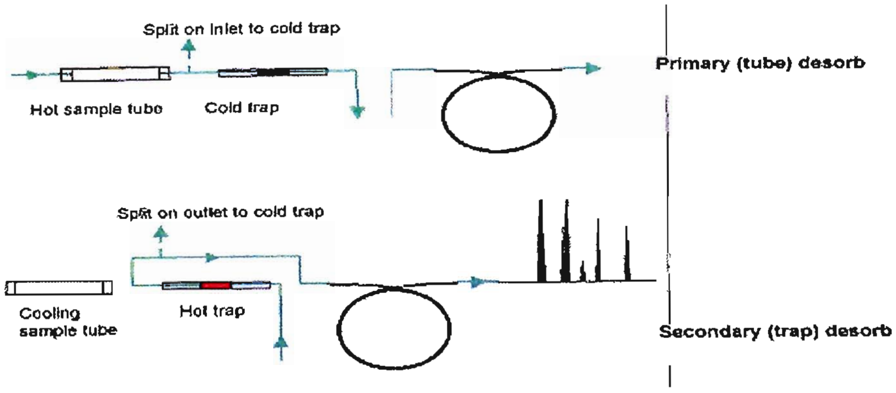


Figure 2.7: The two-stage transfer of canister air samples to the gas chromatograph using a Turbo Matrix thermal desorber

As with any method, advantages and disadvantages exist with the use of a specific analytical method.The advantages and disadvantages of canisters are summarised in Table 2.3.

Table 2.3: Advantages and disadvantages of US-EPA compendium method (TO-14A)

Advantages	**Disadvantages**
Best method for broad spectrum speciation of unknown trace volatile organics	Sample components may be adsorbed or decompose through interaction with container walls
No artefact build-up	Need complex sampling apparatus
Validated for non-polar compounds	Require stringent cleaning procedures
No breakthrough of compounds	Bulky and expensive to transport
Simple to use as a grab sampler	Sampling method is expensive
Good quality assurance and quality control database	Limited to non-polar compounds due to use of permeation type dryer
Simple sampling approach	
Multiple analyses possible per canister	

- *Adsorbent tubes*

The US-EPA prescribes the use of adsorbent tubes to adsorb specific VOC species in ambient air onto selected adsorbent materials (Method TO-17) (1997). Trapping air directly onto portable adsorbent tubes avoids the cost disadvantages of canisters. However, care needs to be taken when selecting an appropriate adsorbent material for a particular application in order to eliminate the risk of:

- breakthrough during sampling;
- artefact formation; and
- analyte losses during thermal desorption.

Tubes suitable for thermal desorption with the Turbo Matrix thermal desorber from Perkin-Elmer are shown in Figure 2.8.

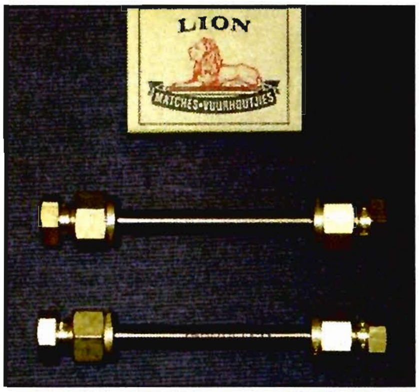


Figure 2.8: Stainless steel adsorbent tubes utilised in the EPA TO-17 compendium method

It is known that adsorbent material should not be recommended for a particular analyte if the retention volume for that compound is significantly less than 100 l/g adsorbent.

Therefore, the correct selection of adsorbent strength for the analytes of interest, facilitates the use of a relatively small quantity of adsorbent (200-500 mg), which can be efficiently desorbed thermally. This has helped to overcome concerns relating to artefact interference and quantitative recovery of analytes.

VOCs retained on adsorbent tubes cannot be transferred directly into the gas chromatograph analytical system without a refocusing step. The desorption process is too slow for effective capillary chromatography. Pre-concentration of the analytes onto the cold trap is required (Figure 2.7). Advantages and disadvantages of adsorbent tubes are shown in Table 2.4.

Table 2.4: Advantages and disadvantages of sample tubes: US-EPA method (TO-17)

Advantages	**Disadvantages**
Convenient, small, portable and cost advantages in sampling equipment	Contamination of adsorbent can be a problem
No reconditioning needed after desorption	Not suitable for C_2s
A comprehensive database and proven technology	Desorption of some VOCs is difficult
Suitable for a wide analyte range	Analysis cannot be repeated

- *Passive Samplers*

The applicability of active sampling techniques in large-scale field monitoring is doubtful due to the excessive cost involved. The maintenance, calibration and purchase of expensive equipment can be a costly venture. Availability of power and the security at sampling sites are major problems in some monitoring situations (Fung *et al.*, 1985).

A passive sampler is a cost effective alternative to active sampling for VOCs in ambient and indoor environments. Passive samplers are used as personnel monitors in industrial hygiene applications in place of the adsorbent tube/pump (active sampling) method. Investigations into the chronic health effects of VOCs may require longer sampler exposure duration than the typical <12 hours used for active VOC sampling (Cohen *et al.*, 1990).

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

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

The diffusive sampling technique is reliable. Figure 2.9 below shows the correlation between a diffusive and an active sampler for benzene, toluene, ethylbenzene and xylene (all three isomers of xylene included), collectively known as BTEX (IVL, 1998).

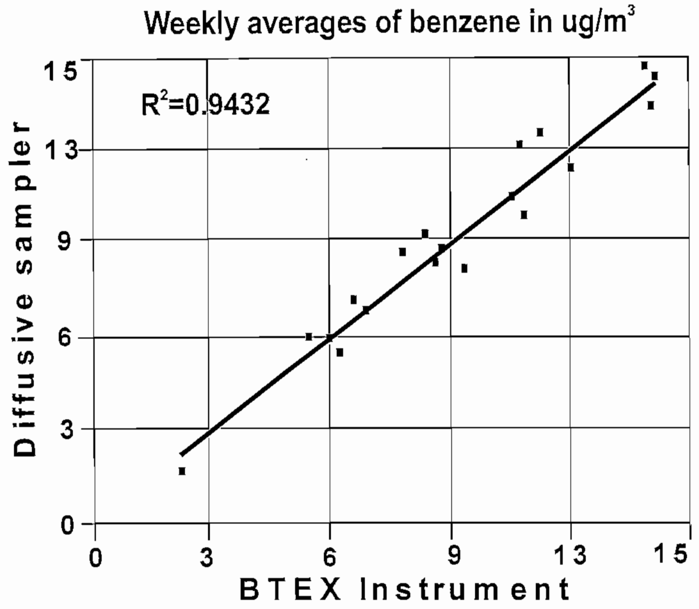


Figure 2.9: Comparison between weekly averages of benzene obtained using diffusive samplers (Tenax) and weekly averages calculated from a parallel BTEX (active sampling) instrument (IVL, 1998). Units of axes are µg/m^3

The major disadvantage associated with the use of a passive sampler in VOC sampling in ambient air is the relatively long sampling period required to collect sufficient material for analysis. Studies that employ active sampling to collect VOCs typically use flow rates in the range of 100 to 150 cm^3 min^{-1}. Thus, it may take longer to collect the same amount of a given compound with passive sampling as in the case with active sampling.

2.2.5 Health Risks Associated with Aromatic Volatile Organic Pollutants

In Paragraph 2.2.3 the oxidation of hydrocarbon species by the hydroxyl radicals (HO$^\bullet$) to form ozone and secondary organic aerosols (SOAs) has been discussed. The health impacts associated with these secondary air pollutants have been summarised in Paragraph 2.1.7.1.

Hydrocarbons have been known to have severe direct impacts on human health. Table 2.5 summarises the direct impacts of some of the hydrocarbon species on human health (WHO, 1987).

Table 2.5: Summary of health effects associated with selected VOCs (WHO, 1987)

VOC	Health effects associated with selected VOCs
Acetonitrile	Carcinogen
Benzene	Carcinogen
Carbon disulfide	Degeneration of the brain tissue
1,2-Dichloroethane	Dizziness, weakness, vomiting, unconsciousness. Death often follows.
Dichloromethane	Carcinogen of animals. Evidence in humans is inadequate. Affects nervous system and elevates CO levels in blood.
Formaldehyde	Carcinogen of animals. Evidence in humans is inadequate. Irritation of eyes, nose and throat.
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

Given the fact that the focus of this study is on BTEX, a synopsis of the direct health impacts of the species is given below.

Benzene

Humans are exposed to benzene in a diversity of environments both at work and at home. Benzene has been widely accepted to cause numerous effects including human non-lymphocytic leukaemia by inhalation (IARC, 1982). Table 2.6 indicates the estimated relative risks of leukaemia derived from the proportional hazards dose-response model according to estimated cumulative exposure (ppm-years).

Table 2.6: Estimated relative risks of leukaemia derived from the proportional hazards dose-response model according to estimated cumulative exposure (ppm-years)

Investigators	**Estimated cumulative exposure in ppm-yrs**			
	4.5	**45**	**90**	**450**
Rinsky *et al.*, 1981, 1987	1.02	1.19	1.41	5.5
Crump and Allen, 1984	1.00	1.04	1.07	1.43
Paustenbach *et al.*, 1993	1.01	1.07	1.14	1.96

- **Toluene**

Inhalation of toluene is the main route of exposure. Uptake of toluene results in accumulation in adipose tissue as well as the adrenal glands, kidney, liver and the brain. Toluene–induced neuro-toxicity has been documented in humans. Under acute exposure toluene exposure results in CNS narcosis. It was shown that environmental exposure did not have any effects on the kidneys, liver or cardiovascular system (WHO, 1987). Table 2.7 summarises the dose-response pattern for acute exposure to toluene in humans.

Table 2.7: Summary of dose-response pattern for acute exposure to toluene in humans (WHO, 1987; Calabrese & Kenyon, 1991)

Exposure levels (ppm)	**Health effects**
10 000 – 30 000	Onset of narcosis within a few minutes; longer exposures may be lethal.
>4 000	Likely to cause rapid impairment of reaction time and coordination; narcosis and death possible with exposures exceeding one hour.
1 500	Probably not lethal for exposure periods of up to eight hours.
300 – 800	Obvious incoordination expected during exposure periods of up to 8 hours. Severe fatigue, pronounced nausea, confusion, lack of self-control and staggering gait may be observed.
100 - 300	Detectable signs of incoordination, muscle weakness and confusion expected during exposure periods of up to 8 hours.
50 – 100	Subjective complaints, e.g. fatigue, headache and sleepiness, but probably no observable impairment of reaction time or coordination. Eye and nose irritation is detectable, also borderline impairment of some cognitive functions.
>37 ppm	Probably noticeable to most humans

- **Xylene**

The atmosphere is the most likely route of exposure from the isomers of xylene. Xylene isomers are readily adsorbed after inhalation and can cross the placenta (WHO, 1993). It is stored in the adipose tissue in humans and animals. Human carcinogen data is currently unavailable for xylene. The most mutagenicity studies also respond negatively (IRIS, 2001). Fetotoxic effects include delayed development, decreased foetal weight and altered enzyme activities.

- **Ethylbenzene**

Ethylbenzene vapour is easily absorbed. Storage in human fat has been reported, as well as crossing of the placenta barrier. Lungs and the central nervous system are target organs during acute high-level exposure. Systemic toxicity of ethylbenzene to humans is lacking (Calabrese & Kenyon, 1991). Table 2.8 summarises the guidelines for risk assessment of these pollutants.

Table 2.8: Summary of guidelines for risk assessment (Van Niekerk & Fourie, 2001)

Compound	**WHO**		**USA**		
	Guideline	**Averaging time**	**Guideline**	**Averaging time**	**US-EPA/AALG**
Benzene	$14.0 - 23.9 \times 10^{-3}$ ppm^{-1}	Annual unit risk	$7.1 - 25.0 \times 10^{-3}$ ppm^{-1}	Annual unit risk	US-EPA
Ethylbenzene	22 mg/m^3	1 week	1 mg/m^3	RfC	US-EPA
Toluene	260 µg/m^3	1 week	0.4 mg/m^3	RfC	US-EPA
Xylene	4 800 µg/m^3	24 hours	xylenes: 1.2 ppm (5.2 mg/m^3):	8-hour TWA	AALG

*AALG: Provisional ambient air quality goal, derived by Calabrese and Kenyon (1991)
*TWA: Time weighted average

2.2.6 Aromatic Ambient Volatile Organic Compounds: Global Perspective

This section will strive to summarise findings pertaining to volatile organic pollutant species in ambient air focusing on benzene, toluene, xylene and ethylbenzene. Table 2.9 summarises the observed VOC concentrations obtained during several international studies:

Table 2.9: Summary of selected ambient VOC concentrations (ppbv) observed during international studies

	Osaka City	**Mexico City**	**Sydney Harbour**	**Baltimore**	**Athens**
Reference	**Tsujino & Kuwata, 1993**	**Zielinska *et al.*, 2001**	**Duffy & Nelson, 1996**	**Vukovich, 2000**	**Moschonas & Glavas, 1996**
Chloroform		0.01			
Benzene	5.1		45.4	2.27	5.0
Toluene	31.1		68.6	7.09	14.3
Ethylbenzene	3.8		8.6	1.24	2.7
p-Xylene	2.3		31.3	3.72	12.1
m-Xylene	5.4				
Styrene				0.53	
o-Xylene	2.8		11.7	1.39	3.7
1,3,5-Trimethylbenzene	1.2		2.2	0.67	9.2
1,2,4-Trimethylbenzene	2.9		6.3	5.35	3.9
n-Decane	0.9			0.91	
1,2,3-Trimethylbenzene	0.6			1.17	3.3
1,4-Dichlorobenzene		0.04			
1,2-Dichlorobenzene		0.01			

The tropospheric concentration of benzene is determined by meteorological conditions, source strength and chemical reaction rates.

International studies have indicated that annual ambient benzene levels are in the order of 0.4 to 14 ppbv (Moschonas & Glavas,(1996); Tsujino & Kuwata (1993); Derwent *et al.* (2000); Simon *et al.* (2001); Gee & Sollars (1998) and Brocco *et al.* (1997)), while concentrations in close proximity of a source, such as a petrol station may be several hundred ppb (WHO, 1987). The Monitoring of Atmospheric Concentrations of benzene in European Towns and Homes (MACBETH, 1996), has highlighted that indoor concentrations of hydrocarbon species are higher than outdoor levels. The study has indicated that the average pollution levels in European homes were 1.5 times the urban levels. The Commission of European Communities (1998) has indicated that anthropogenic sources produce 90% of the VOCs present in the urban atmosphere in Europe.

In order to understand these findings, a study of the reactivity needs to be made. Benzene removal in the atmosphere is mainly dependant on hydroxyl radical reactions. The rate constant for benzene has been shown to be 1.23 $x10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1990). Therefore, given a 24-hour average hydroxyl radical concentration of 1×10^6 $mol.cm^{-3}$ being representative for the troposphere, a nine-day lifetime for benzene can be assumed. This relatively long lifetime will therefore result in benzene playing an important role in regional air pollution, since nine days would be sufficient to transport benzene over long distances. $NO^{\bullet}_3$ oxidation of benzene will result in an atmospheric lifetime of more than 235 days (Finlayson-Pitts and Pits, 1986), while O_3 oxidation will give rise to a lifetime in excess of 470 days (Finlayson-Pitts and Pits, 1986).

Urban ethylbenzene ambient concentrations world-wide is estimated to be in the region of 1 to 100 $\mu g/m^3$, toluene 2 to 200 $\mu g/m^3$ and xylene 3 to 390 $\mu g/m^3$ (WHO, 1993).

The atmospheric lifetime of benzene (9.4 days) is much longer compared to that of toluene (1.9 days) and xylene (5.9-10.1 hours) (Atkinson, 1990). These variations in atmospheric lifetimes between the BTEX compounds allow scientists to determine the probable source, as well as the age of the pollution plume, based on the ratio of the compounds (Holzinger *et al.*, 2001). Xylene, toluene and ethylbenzene will react faster with $HO^{\bullet}$ than benzene, thereby increasing the ratio. Therefore, the higher the benzene:toluene concentration ratio, the older the air mass and the more distant the source. This method and its limitations have been studied by Parrish *et al.* (2007). The fact that the impact of dilution on both species can be discarded by utilising this method, since both species undergo similar dilution affects, is highlighted. However, the influence of atmospheric mixing and the impact of background levels on the species ratio under investigation cannot be discarded. This is especially true for species with long atmospheric life-times such as benzene. The long residence time of these species will ultimately lead to significant background concentrations of the species, resulting in atmospheric mixing and distorted species ratios.

Studies conducted in Venezuela (Holzinger *et al.*, 2001) and the United States of America (Mohamed *et al.*, 2002), have indicated that BTEX compound concentrations in summer tend to be lower than in winter months. These higher concentrations of hydrocarbons in winter months correlate favourably with the effect of photochemical reactions, known to consume hydrocarbons in the summer months (Hagerman *et al.*, 1997). The Venezuela study (Hollinger *et al.*, 2001) has also indicated that rural sites tend to have much higher benzene:toluene and benzene:xylene concentration ratios, indicating that aged polluted air masses affect these rural areas. The study also indicated that favourable correlations between the BTEX compounds ($R^2 = 0.6$) can be used as an indication that these compounds are associated with the same primary source. Similar relationships were found during the Pakistan study (Barletta *et al.*, 2002), where a benzene:toluene correlation of 0.97 indicated a strong single source influence. Rural diurnal variations in benzene, toluene and xylene were shown to be negligible. This was characteristic of compounds having low deposition rates and removed mainly by $HO^{\bullet}$. The study postulated that a lack of diurnal variation indicated the absence of local sources in an area.

A benzene:toluene concentration ratio of 2 has been shown to be closely related to biomass burning, while benzene:xylene concentration ratios of 2.7 have been associated with biomass burning (Holzinger, 2001).

Studies conducted in Pakistan (Barletta *et al.*, 2002) have indicated a decrease in hydrocarbon concentrations in the early afternoon with maximums recorded in the early mornings and late afternoons. Low level inversion during night-time was postulated as the reason for higher observed hydrocarbon concentrations at night, while the daytime boundary layer expansion gave rise to lower observed concentrations in the daytime (Barletta *et al.*, 2002).

Additional studies by Hebb *et al.* (2000) have indicated that the benzene:toluene concentration ratio for non-catalytic cars was 0.4, while cars equipped with converters showed a ratio of 2 (Hebb *et al.*, 2000). Brocco *et al.* (1996) have indicated that the mean distribution of anthropogenic volatile organic compounds in Rome is 12.6% benzene, 35.4% toluene and the remaining VOCs 42%.

Studies in the United Kingdom (Derwent *et al.*, 2000) have indicated that hydrocarbon:benzene concentrations in the UK compare very favourably with ratios determined in Europe, including Athens (Moschanos & Glavas, 1996), Hamburg (Bruckmann *et al.*, 1988) and Australasia (Duffy & Nelson, 1996). Table 2.10 indicates the concentration ratios relative to benzene with their standard deviation for the UK hydrocarbon network (Derwent *et al.*, 2000). These findings, discussed in this paragraph, will be compared to the observations in the Sasolburg and Potchefstroom areas (Chapters 3 and 4).

Table 2.10: Hydrocarbon concentration ratios relative to benzene with their standard deviation for the UK hydrocarbon network ((Derwent *et al.*, 2000)

Concentration Ratio	Mean	Standard Deviation
ethylbenzene:benzene	0.40	0.05
toluene:benzene	2.07	0.12
m+p Xylene:benzene	1.27	0.10
o-Xylene:benzene	0.46	0.04

Burger *et al.* (2002) conducted a study in the greater Johannesburg area as part of the National Standard setting process. Burger's study aimed to determine the impact of heavy traffic density on ambient VOC emissions. The study indicated very high levels of benzene and toluene. Table 2.11 indicates the results Burger obtained. The ratio between benzene and toluene was shown to be 1.07.

Table 2.11: Aromatic hydrocarbon levels observed in the greater Johannesburg area next to a high density freeway, utilising canisters (Burger *et al.*, 2002)

Compound	Concentration (ppbv)	
	Average	Maximum
Benzene	9.8	21.6
Toluene	9.2	19.8
Ethylbenzene	1.9	4.3
p-Xylene	3.0	5.8
m-Xylene	3.0	5.8
o-Xylene	1.1	2.2

2.2.7 Volatile Organic Compounds: Study Area Perspective

Industry in South Africa depends heavily on coal as a primary energy source. Coal utilisation in South Africa is mainly associated with electricity generation and gasification to produce hydrocarbon-based feedstock and liquid fuels. The environmental burden associated with coal utilisation in South Africa is becoming increasingly more noticeable as demand keeps on increasing (Terblanche, 1995). This is especially true in the heavily industrialised areas of South Africa including Cape Town, Durban, Richards Bay and the Vaal Triangle. The Vaal Triangle is situated approximately 60 kilometres south of Johannesburg. The Vaal Triangle covers an estimated 4000 km^2. Figure 2.10 is a map of Southern Africa indicating the position of the Vaal Triangle.

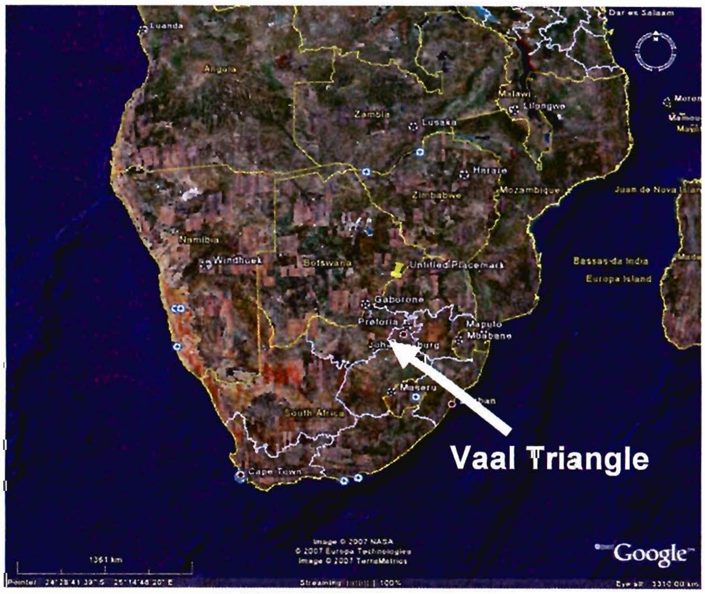


Figure 2.10: Position of the Vaal Triangle in South Africa (google.earth.com)

The Vaal Triangle, situated in the Highveld region of South Africa, experiences stable meteorological conditions in the dry, cold winter months resulting in air pollutants being trapped during this period.

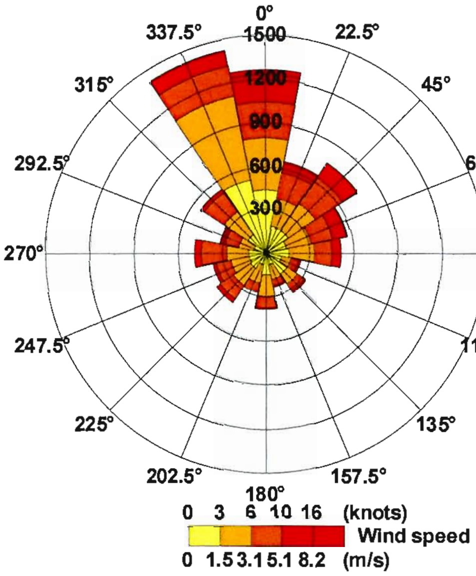
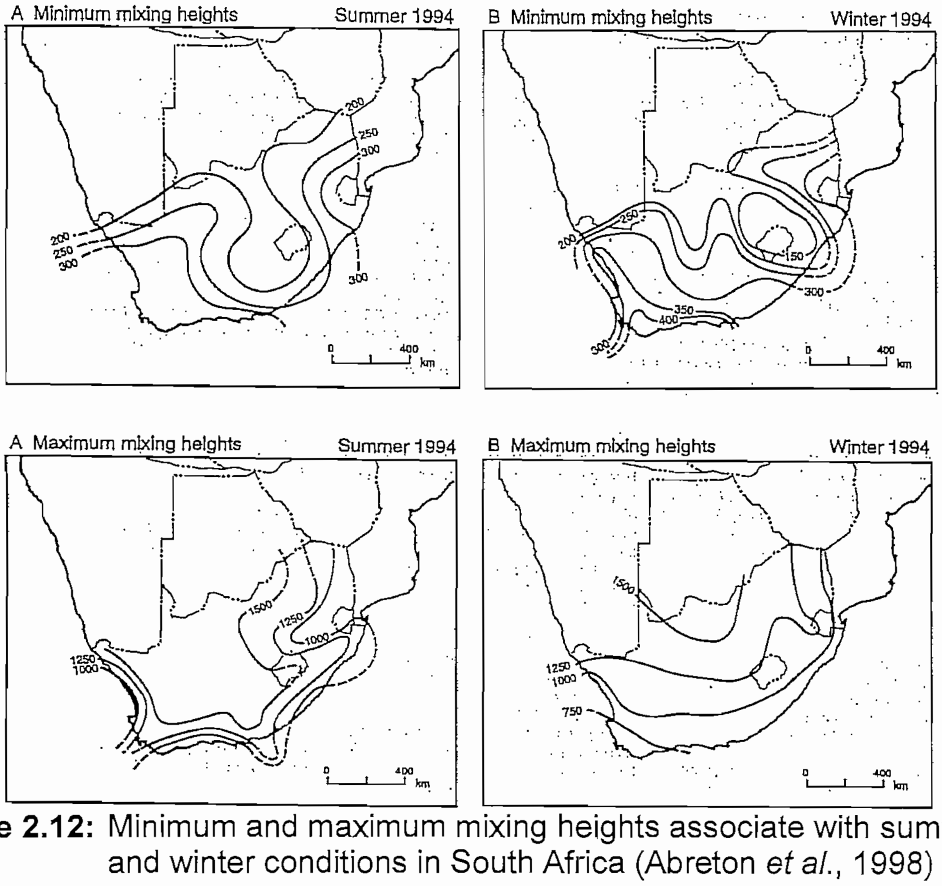


Figure 2.11: Windrose indicating the annual wind direction and wind speed experienced during 2002 at the Vereeniging SAWS station

The 2002 wind field over the region (Figure 2.11) generally reflects the synoptic scale circulation. The flow field is dominated by north-westerly to north-easterly winds due to the anticyclonic circulation, which dominates the region throughout much of the year. During winter months (July to August), the northward shift of the high-pressure belt and the enhanced influence of westerly wave disturbances (e.g. cold fronts) give rise to an increase in the frequency of south-westerly winds. Summer months are characterised by the weakening and southward shift of the anticyclonic belt, which allows tropical easterly flow to resume its influence over the region. An increase in the frequency of north-easterly winds during summer months (December to February), and the continued prevalence of north-westerly and northerly airflow, reflects the combined influence of anticyclonic subsidence and tropical easterly wave systems.

During the daytime, the atmospheric boundary layer is characterised by thermal turbulence due to the heating of the earth's surface and the extension of the mixing layer to the lowest elevated inversion. Radiative flux divergence during the night usually results in the establishment of ground-based inversions and the erosion of the mixing layer. Surface-based inversions may reach depths of 200 to 400 m in the study region. The mixing layer at the study site ranges in depth from near ground level (i.e. only a stable or neutral layer exists) during nighttimes to the base of the lowest level elevated inversion during unstable, daytime conditions.

Figure 2.12 indicates the mean minimum and maximum mixing heights for both summer and winter conditions. The low mean minimum mixing height in winter, 150m-300m, explains the entrainment of pollutants over the Highveld area in winter. Being at a lower altitude than the Witwatersrand, pollution originating from the Greater Johannesburg area is drained into the Vaal.


A Minimum mixing heights Summer 1994

B Minimum mixing heights Winter 1994

A Maximum mixing heights Summer 1994

B Maximum mixing heights Winter 1994

Figure 2.12: Minimum and maximum mixing heights associate with summer and winter conditions in South Africa (Abreton *et al.*, 1998)

The Vaal Triangle houses several industries contributing significantly to the pollution load in the area. Sources contributing to this pollution load in the area include veld fires in winter, domestic coal burning, vehicles, and wind-blown dust. A map of the Vaal Triangle is shown in Figure 2.13. The line running through the map indicates the Vaal River.

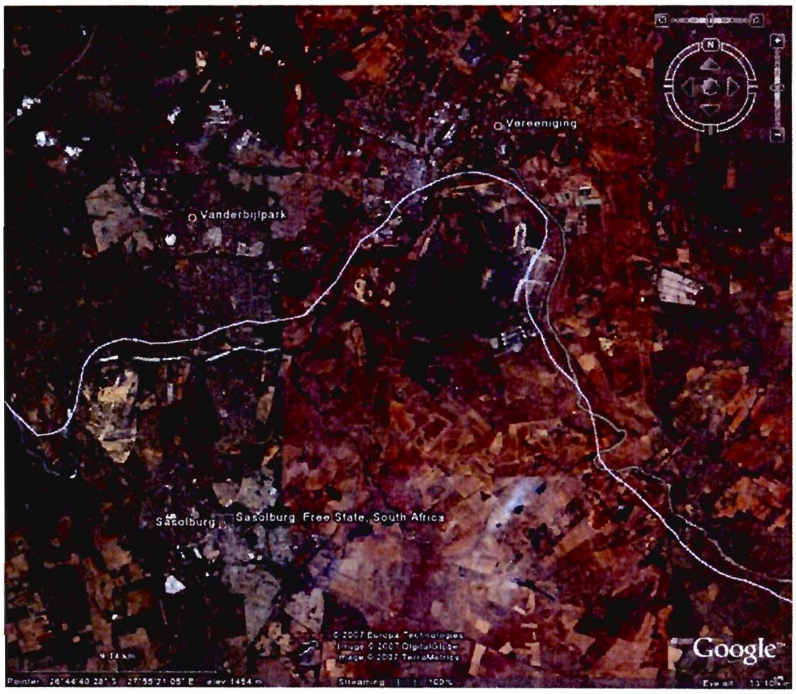


Figure 2.13: Map of the Vaal Triangle indicating the three cities, Vanderbijlpark, Sasolburg and Vereeniging making up the Vaal Triangle (google.earth.com)

Volatile organic compound emissions in the Vaal Triangle are estimated to be 46200 tonnes per annum, with industries accounting for 44 647 tonnes, household burning 1240 tonnes and energy generation 360 tonnes (Scorgie, 2004). Table 2.12 provides a summary of the anthropogenic sources responsible for VOC emissions in the Vaal Triangle according to Scorgie (2004).

Table 2.12: Estimated emissions of VOCs (tonnes per annum) in the Vaal Triangle (Scorgie, 2004)

	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 = non-methane hydrocarbons)

According to Scorgie (2004), more than 1.5 million tonnes of coal is combusted in residential homes in the Vaal Triangle.

In Paragraph 2.2.3.2, the importance of ozone was discussed. It has also been shown that the photolysis of ozone during the daytime plays an important role in determining the oxidation potential of the region. Figure 2.14 indicates the measured ozone levels over southern Africa (Zunckel *et al.*, 2004). It is clear from these findings that southern Africa experiences a mean ozone average maximum in September to November. The existence of semi-permanent stable layers, coupled to recirculation over the source areas that promote long-term transport and therefore ozone formation, has been postulated as a plausible reason for the elevated ozone levels over the region during that time (Cosijn & Tyson, 1996).

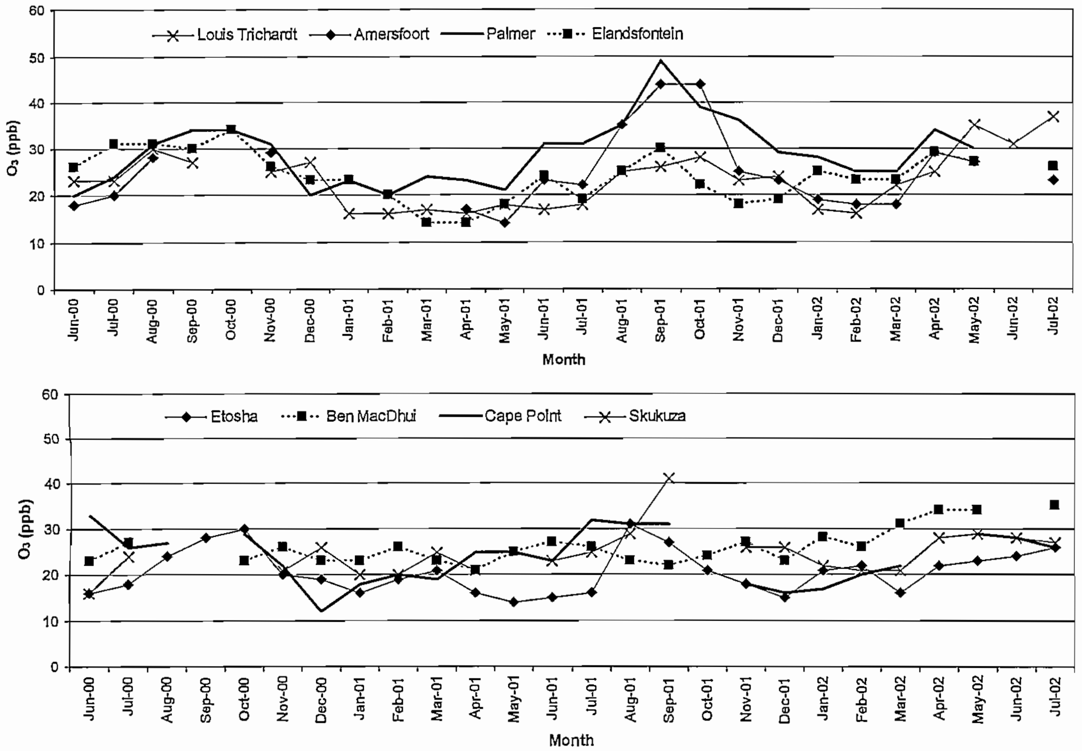


Figure 2.14: Mean monthly ozone concentrations in ppb over southern Africa for the period June 2000 to July 2002

2.3 CONCLUDING REMARKS

In this chapter, the fundamentals of air pollution were discussed. The sources, quantification, distribution and impact were discussed in detail. Hydrocarbons and specifically aromatic ambient volatile organic pollutants were entertained. Emphasis was placed on benzene, toluene, xylene and ethylbenzene. World trends, specifically with regard to spatial and seasonal concentration changes, were explored as well as the impacts these compounds may have on human health and ozone, and SOA formation. The lack of information pertaining to hydrocarbons in South Africa and specifically in the study area (Vaal Triangle) was highlighted. Chapter 3 deals with the initial screening study conducted in the greater Sasolburg and Mpumalanga Highveld area.

CHAPTER 3

AROMATIC HYDROCARBON SCREENING STUDY

In this Chapter...

This chapter describes the process followed to assess the severity of aromatic volatile organic compound pollution in the study area (Par 3.1). The lower tropospheric and ground-level concentration profiles over the Highveld and study area are discussed in Paragraph 3.2. Conclusions are given in Paragraph 3.3.

3.1 EXPERIMENTAL APPROACH

3.1.1 Instrumentation

An airborne gas chromatographic system prototype for use on the UKMO C-130 aircraft has been constructed at the University of Leeds for in-flight analysis of non-methane hydrocarbons (Whalley *et al.*, 2004). This ORAC (Organics by Real-time Airborne Chromatograph) is a unique instrument with sample acquisition and analysis cycles every 5 minutes and a detection limit of less than 50 pptv. Its response to a variety of different species has been characterised, with the focus on hydrocarbons containing 5 to 8 carbon atoms (C5-C8). The airborne gas chromatographic system has the capability to trap, pre-concentrate, separate and detect BTEX (Benzene, Toluene, Ethylbenzene and Xylene) species. Figures 3.1 and 3.2 are pictures of the ORAC that were used in the screening study.

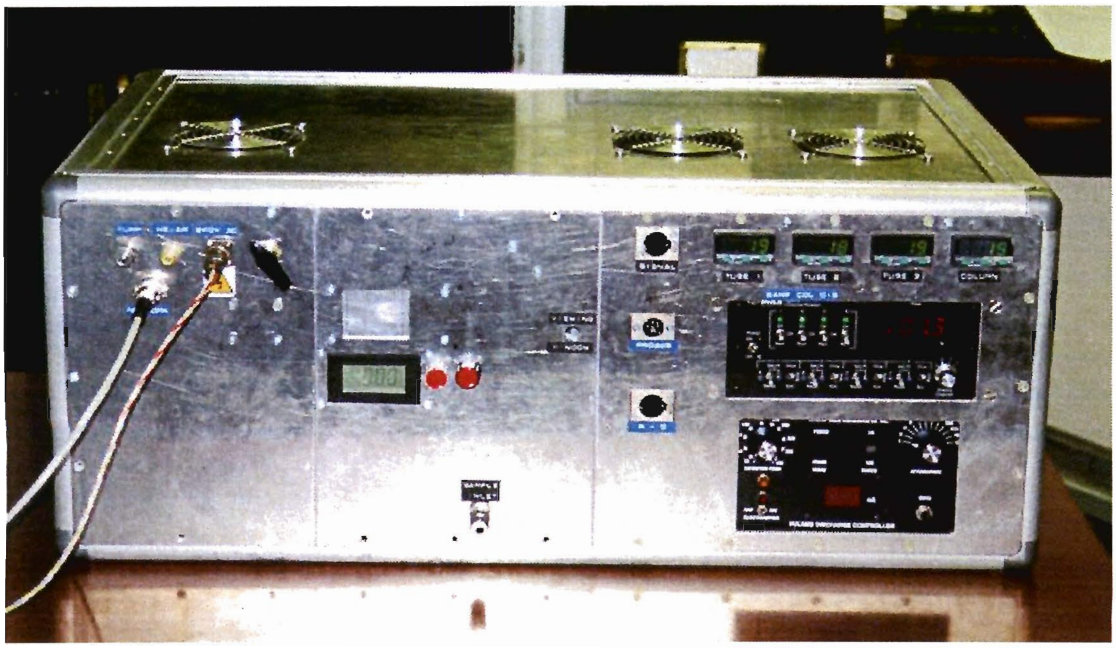


Figure 3.1: The ORAC from Leeds University (Whalley *et al*., 2004)

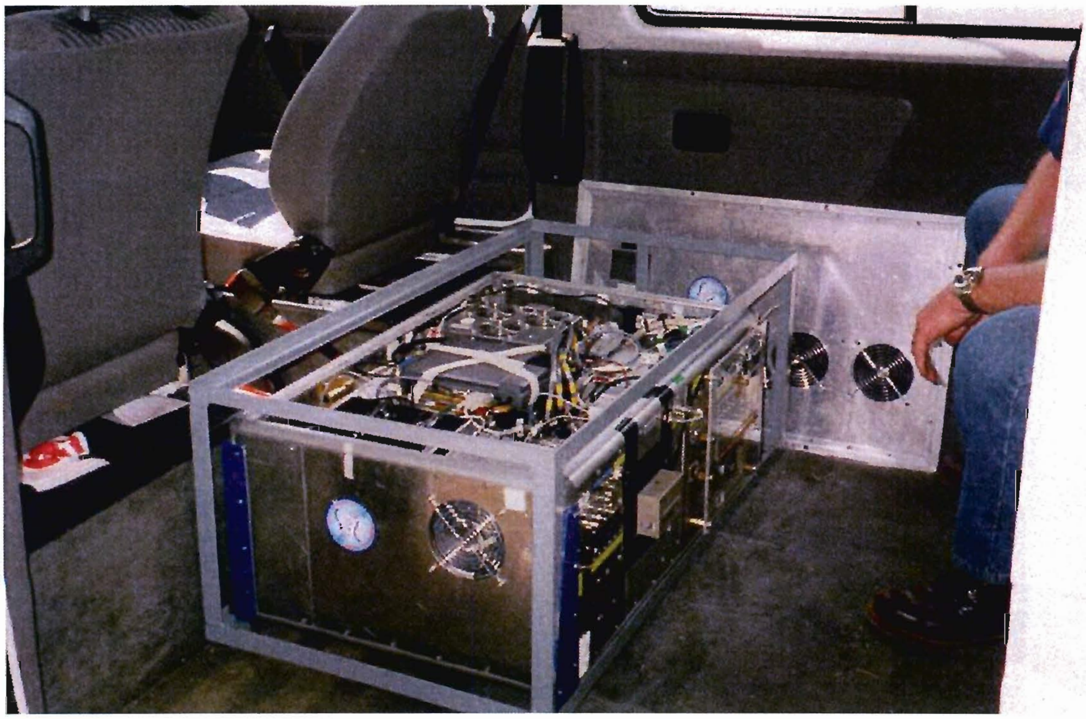


Figure 3.2: An inside view of the ORAC (Whalley *et al*., 2004)

3.1.2 Methodology

3.1.2.1 Lower Tropospheric Concentration Profile Study

In order to determine the lower tropospheric concentration profile of volatile organic air pollutants, an aeroplane sampling study was embarked upon. The ORAC was mounted in the South African Weather Service's Aerocommander 690A for the in-flight sampling. Figure 3.3 is a picture of the Aerocommander that was used in the sampling of the plumes, while Figure 3.4 shows how the ORAC was mounted in the aeroplane.

Figure 3.3: The Aerocommander 690A used for sampling (note inlet on aircraft nose)

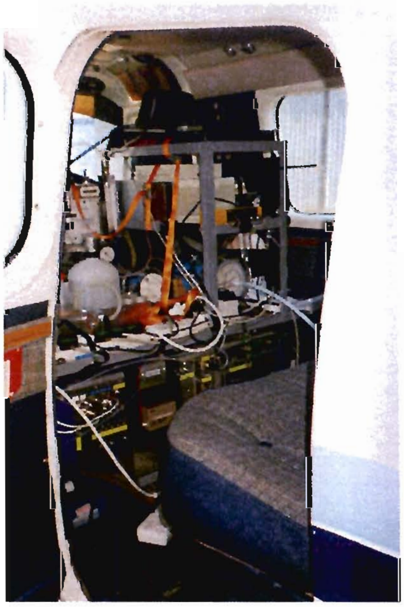


Figure 3.4: The ORAC and other instrumentation inside the Aerocommander 690A

The flight paths used during the campaign are shown in Figure 3.5. The flight plan included the Sasolburg study area (black line), as well as the Mpumalanga Highveld Area (red line). In Paragraph 2.2.7, minimum mean mixing heights according to D'Abreton *et al.* (1998) for the South African Highveld area was shown (see Figure 2.11). These predicted mixing heights were used to determine the feasible flying altitude for the campaign. The TAPM (The Air Pollution Model), a PC-based, nestable, prognostic meteorological and air pollution model, was used to establish the theoretical mixing heights during the Mpumalanga Highveld sampling campaign, since actual measurements could not be undertaken (Hurley, 2002). Meteorological conditions, specifically wind speed and wind directions, were obtained from the South Africa Weather Services.

The Highveld area is host to large energy- and petrochemical facilities, savannah planes and substantial forest areas. The area has been chosen for comparative reasons due to similar meteorological conditions prevailing and the presence of large industries. Nelspruit Airport was used as the operational base.

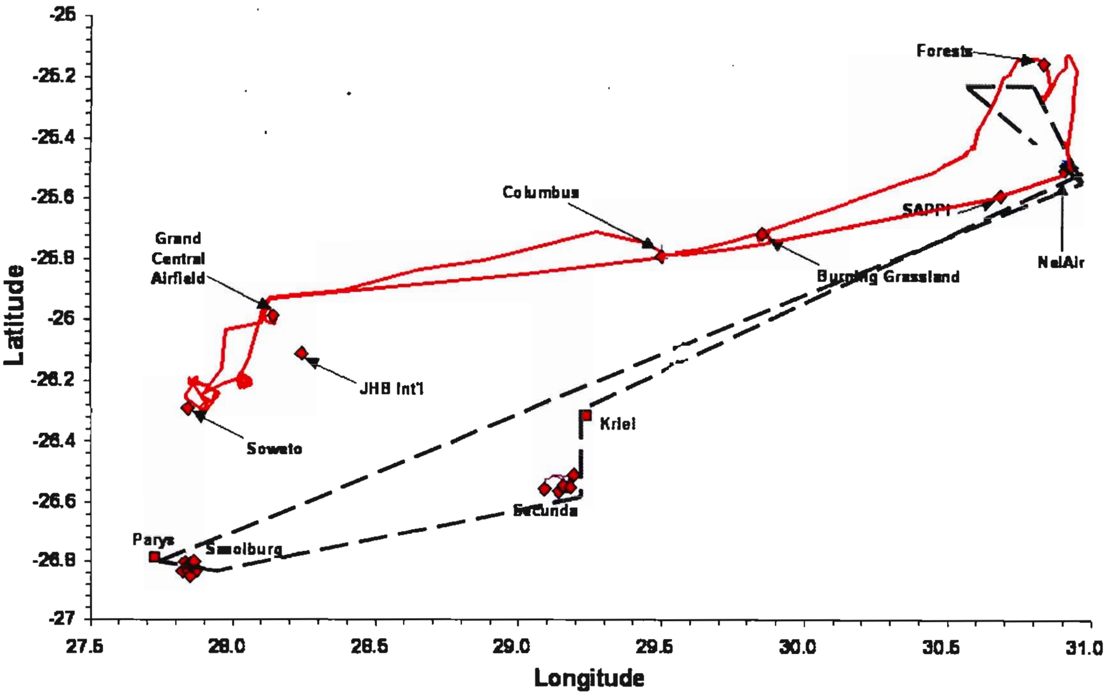


Figure 3.5: Flight path used during the Sasolburg (black line) and Mpumalanga Highveld (red line) sampling campaign

The Mpumalanga Highveld flight plan involved flying over a paper mill, a large veld fire and the outskirts of Johannesburg and Soweto before refuelling at Grand Central. The afternoon flight included flying over a Ferro-alloy industrial site and the Mpumalanga forest area before returning to Nelspruit.

Plume sampling formed the basis of the Sasolburg in-flight campaign. The Sasolburg (study area) flight included areas of the Mpumalanga Highveld. The impact from a very large petrochemical facility utilising coal, similar to what is found in the Sasolburg area and several large coal-fired electricity generators (power plants) were assessed during this study. The advantage of including these large sources situated in Mpumalanga (outside the study area) was that a better understanding of the species' and concentration profile associated with these facilities could be obtained.

3.1.2.2 *Sasolburg Ground Level Concentration Profile*

During the ground level ambient concentration assessment, the ORAC was mounted in a vehicle. Figures 3.6 and 3.7 are pictures of the ORAC in the vehicle used for the ground-level monitoring.

Figure 3.6: The vehicle fitted with the ORAC and other instruments used for the measurement of the ground-level VOC species

Figure 3.7: The ORAC and other instruments inside the vehicle

In order to screen the level of impact of aromatic hydrocarbon pollution in the area, three residential sites and one industrial site were chosen. Figure 3.8 shows a map of the Sasolburg area, highlighting the sampling positions and positioning of dominant sources in the study area. Site selection aimed to include the predominant emission profiles for the area. Residential site 1 is surrounded by homes mainly using coal as primary energy source. The site is also down-wind from most sources given the prevailing wind direction. Residential site 2 is in close proximity to an industry, a residential site mainly utilising electricity (70% of the time) and a filling station. Residential site 3 is situated in an electrified suburb not in close proximity to any industry. The industrial site is next to a refinery and power generation facility utilising coal.

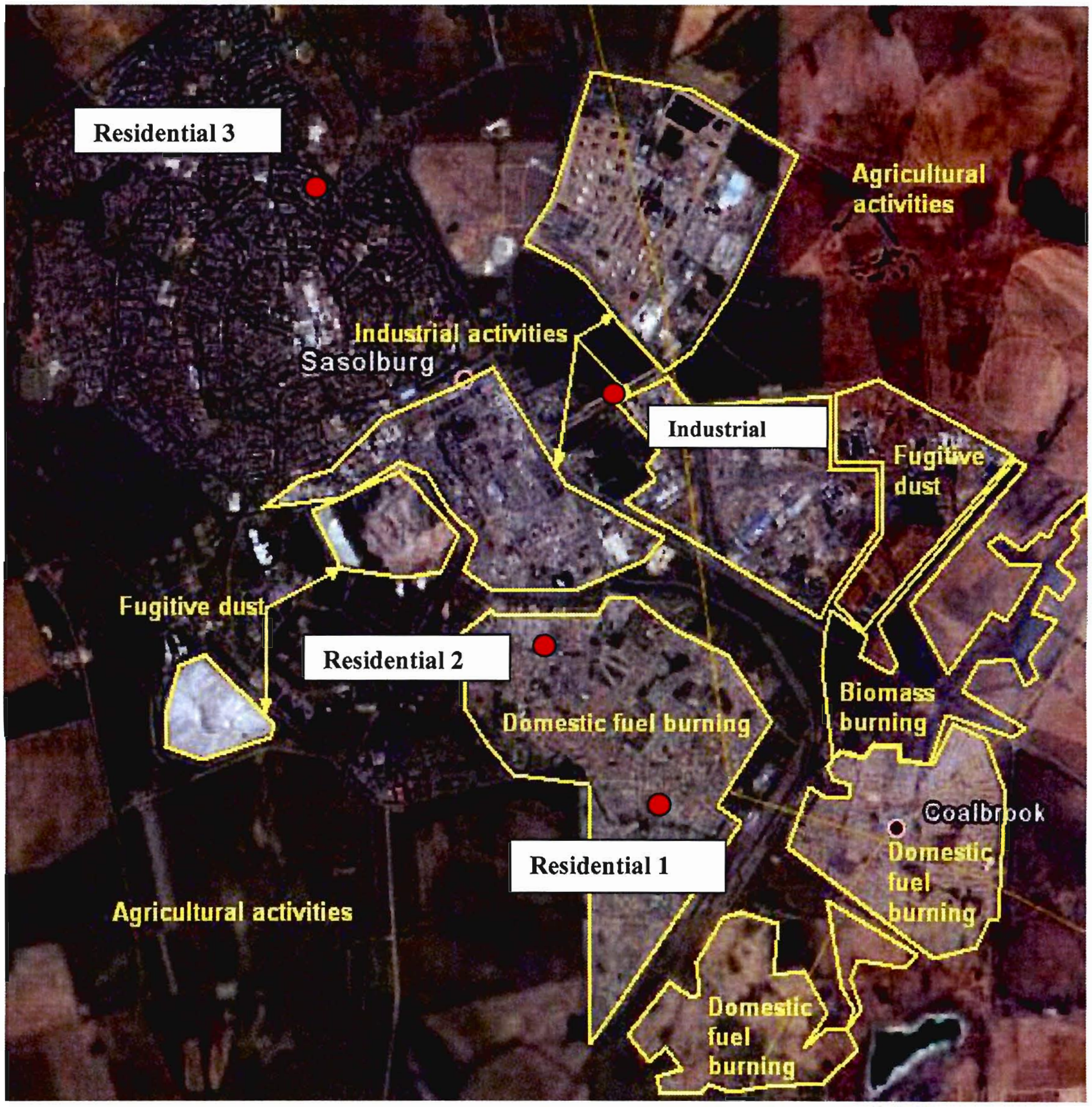


Figure 3.8: Layout of the ground-level sampling sites used in the screening study, as well as the position of prominent source in the area (Map adapted from the Vaal Triangle Air Quality Management Baseline Assessment Report, 2007)

3.2 RESULTS

The results obtained from the in-flight and ground level experiments are discussed in this section. Figure 3.9 shows the frequently observed brown layer over the Highveld of South Africa.

Figure 3.9: Typical brown layer over the Highveld area, during the early morning in South Africa

3.2.1 Tropospheric Concentration Profile Study

3.2.1.1 Mpumalanga Highveld in-flight study results

The prevailing meteorological conditions at each of the sources are indicated in Table 3.1, while Figure 3.10 graphically illustrates the results showing the concentration levels as well as the possible sources contributing, based on visual observations during the Mpumalanga Highveld in-flight sampling campaign. The flight altitudes and estimated atmospheric mixing heights are also included.

Table 3.1: Meteorological conditions experienced during the Mpumalanga Highveld Campaign at each of the sites

Position	Wind speed ($m.s^{-1}$)	Wind Direction (Degrees)	Temperature (°C)
SAPPI	3.9	230	27.1
Biomass Burning	5.3	239	21.4
Soweto	6.1	251	21.8
Columbus	5.6	245	22.9
Forest	2.3	243	23.6

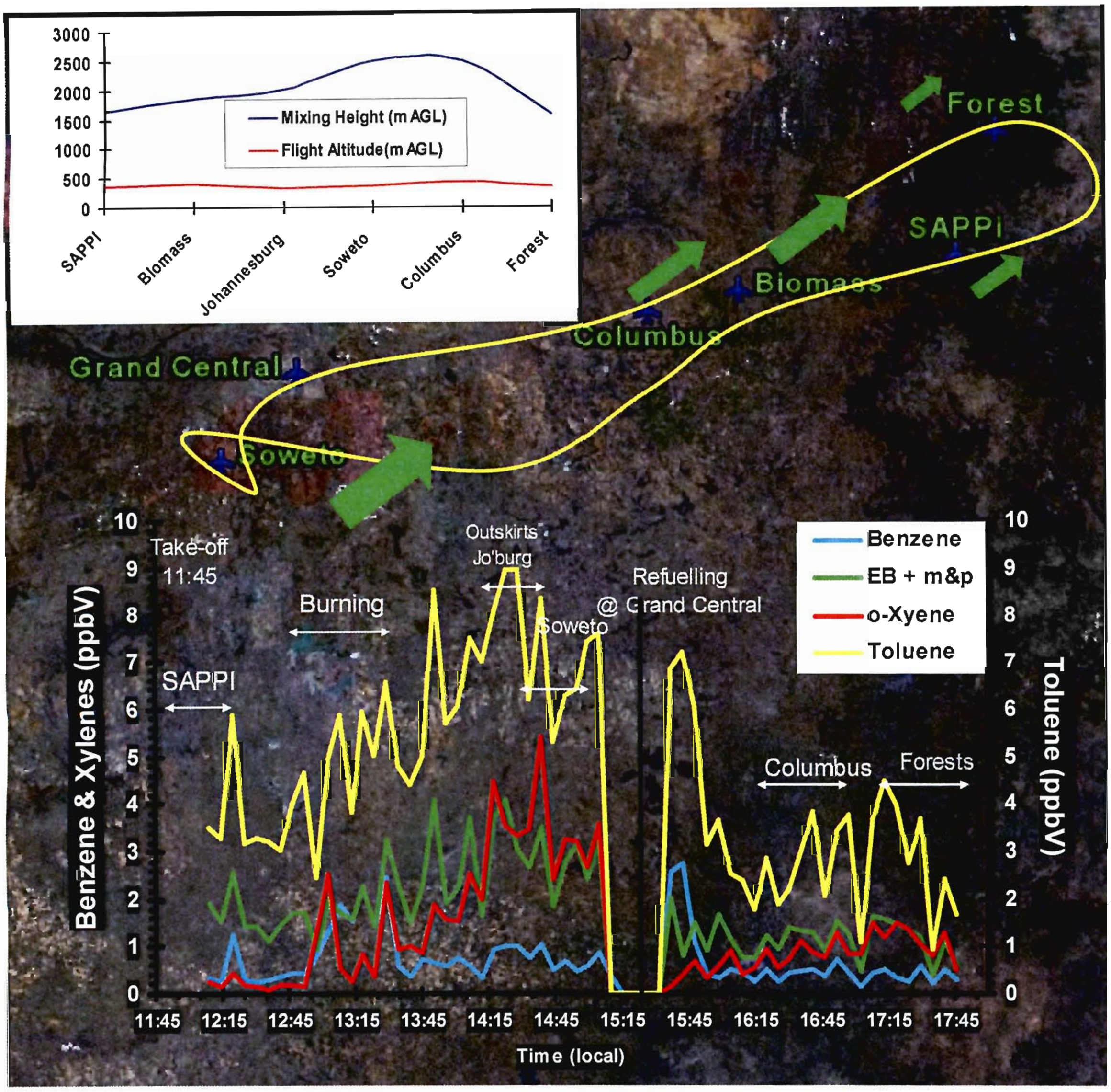


Figure 3.10: VOC results obtained during the Mpumalanga Highveld sampling campaign. Flight altitude and atmospheric mixing height are also indicated. Green arrows indicate mean wind direction and wind speed (size of arrow) during flight

Higher than expected ambient temperatures prevailing on the day of the campaign as well as a relatively high mixing layer promoted the dispersion of pollutants. This was amplified by the fact that sampling only commenced later in the day, minimising entrainment caused by low-level inversion, which tends to dominate during the winter months. All these factors point towards the observations being somewhat lower than the daily peak loadings. A persistent wind blowing from a south-westerly direction also promoted the movement of air from Johannesburg over the eastern Mpumalanga Highveld. The

Johannesburg area experiences severe residential coal burning during the winter months as well as vehicle emissions associated with dense vehicle populations. Large petrochemical industries residing to the south-west of the eastern Mpumalanga Highveld also contributed to the advection of pollution plumes over the area. Biomass burning was observed during the sampling campaign. Widespread biomass burning common to this area during the winter months is expected to influence background concentrations of hydrocarbons in the area. The ubiquitous nature of BTEX during the sampling campaign holds testimony to the impact of biomass burning on hydrocarbon levels in this area.

The findings highlighting the mean, maximum and minimum BTEX levels measured during the study are summarised in Table 3.2. The results indicated that toluene was the most prominent detected VOC species in the Highveld troposphere; while benzene levels were found to be the lowest during the flight (see Figure 3.10). Observed levels in Johannesburg and Soweto were found to be substantially higher than over the eastern Mpumalanga Highveld area (>8 ppbv). The relatively high vehicle density, residential coal burning and high levels of industrial activity in the Johannesburg area are seen as factors giving rise to these levels. Elevated BTEX levels (> 3 ppbv) were experienced over the forest area. No prominent sources, except continuous biomass burning during this period, exist in close proximity to the forest area (< 50 km) that could give rise to the levels experienced during the campaign. Biomass burning, however, was not expected to increase background BTEX levels to this extent, prompting an investigation into plausible factors leading to these observed levels.

Table 3.2: Summary of VOC levels observed over the Mpumalanga Highveld area (number of observations = 60, altitude sampled approximately 6500 ft. ASL)

	Benzene / ppbv	Toluene / ppbv	Ethyl Benzene + m,p-Xylene / ppbv	o-Xylene / ppbv
Average	1.41	5.31	2.02	1.05
Maximum	15.97	19.10	5.23	5.41
Minimum	0.15	0.94	0.40	0.08

In order to assess these findings, statistical analysis involving covariance and correlation calculations was used to investigate the relationship between benzene and toluene in the study area. As discussed in Paragraph 2.2.6, the correlation between species can be use as a tool to determine how strongly pairs of variables are related, with a strong correlation indicating similarities in origin between the two species. However, since the atmospheric lifetimes of toluene and benzene differ significantly, covariance analysis on the normalised values was conducted in parallel. This would allow predictions to be made regarding the interdependence of these two species (how the two species vary in relationship to each other) and therefore a possible mutual source. Values for covariance analysis purposes were normalised by dividing the benzene and toluene values with the maximum benzene and toluene concentration levels observed at each of the sources (waypoints) respectively. Table 3.3 summarises the findings of the statistical analysis undertaken.

Table 3.3: Summary of the covariance and correlation between toluene and benzene during the in-flight Mpumalanga Highveld BTEX campaign

Data Set	Benzene:Toluene Covariance (cov(b,t))	Benzene:Toluene Correlation (r^2)
SAPPI	4.5×10^{-2}	0.98
Biomass Burning	3.8×10^{-2}	0.75
Soweto	1.9×10^{-2}	0.68
Columbus	2.8×10^{-2}	0.86
Forest Area	4.6×10^{-2}	0.70

Following the statistical analysis of the benzene and toluene data set for each of the sources (waypoints), it becomes clear that a relatively strong benzene, toluene correlation over SAPPI and Columbus compared to Soweto exists. The covariance analysis indicated that benzene and toluene levels observed over SAPPI and the Forest are most likely to be interdependent. The level of covariance between benzene and toluene over the area experiencing biomass burning was also found to be significant compared to observations over Soweto. This was expected, given the diversity of sources over Soweto and Johannesburg as described earlier.

In light of the perceived interdependence between benzene and toluene over the eastern Mpumalanga Highveld area, an assessment of prevailing meteorology, especially wind direction and known BTEX sources in the Mpumalanga Highveld area was done.

In Paragraph 3.1.2 mention was made of prominent coal-fired electricity generating facilities and a large petrochemical plant situated to the south-west of the impacted areas. Given that the prevailing wind direction was from the south-west, coupled to relatively high mixing heights experienced during the study, it became clear that these sources may have played a significant role in the levels of BTEX experienced at Columbus, SAPPI and the forest area. However, the strong covariance and correlation, compared to values calculated for Soweto, between benzene and toluene over these areas indicate the possible influence of a strong source on the eastern Mpumalanga Highveld region. Coal fired electricity generation is known to produce substantial amounts of inorganic pollutants such as sulphur dioxide, oxides of nitrogen and carbon dioxide. Although hydrocarbons are emitted from these facilities, it is generally accepted to be a low emitter due to the high carbon to carbon dioxide conversion efficiency associated with the introduction of excessive air into the boiler. Petrochemical industries, however, are known to produce and emit hydrocarbons to a much greater extent compared to power plants. Given the position of the plant, coupled with the fact that emissions are released into the atmosphere at heights exceeding 250 meters, it became evident that this facility may be responsible for the levels observed at SAPPI and the forest area. During the Sasolburg campaign, plume studies were undertaken at both the coal-fired electricity generation plants and the petrochemical facility situated in Secunda. The assessment of BTEX levels in these plumes and the covariance between the benzene and toluene would give an indication of the impact these sources might have had on the levels observed at SAPPI and the forest area. This will be discussed in more detail in Paragraph 3.2.1.2.

3.2.1.2 Sasolburg in-flight Study Results

The Sasolburg in-flight study, including the south-westerly Mpumalanga region, was undertaken on the morning of 29 August 2000, between 8:00 am and 10:00 am. During this time, mixing heights were shown to be very low, thereby promoting entrainment of low-level emissions near the surface (see Figure 3.11). This resulted in poor visibility prevailing on the day of sampling. Table 3.4 indicates the meteorological condition encountered during the Sasolburg in-flight sampling study.

Table 3.4: Meteorological conditions experienced at each site during the actual sample-taking period during the Sasolburg in-flight study (29 August 2000)

Position	**Wind speed ($m.s^{-1}$)**	**Wind Direction (Degrees)**	**Temperature (°C)**
Secunda	3.6	230	8.5
Sasolburg	3.3	72	15.3

Low mixing heights (>200 meters AGL) during the early periods of sampling over the Mpumalanga area resulted in vertical mixing being kept to a minimum, thereby making plume sampling more accurate, since the influence of lower-level emissions were kept to the minimum.

The findings, showing the concentration levels observed, wind direction as well as theoretical mixing heights at each of the sampling sites during the campaign are graphically illustrated in Figure 3.11.

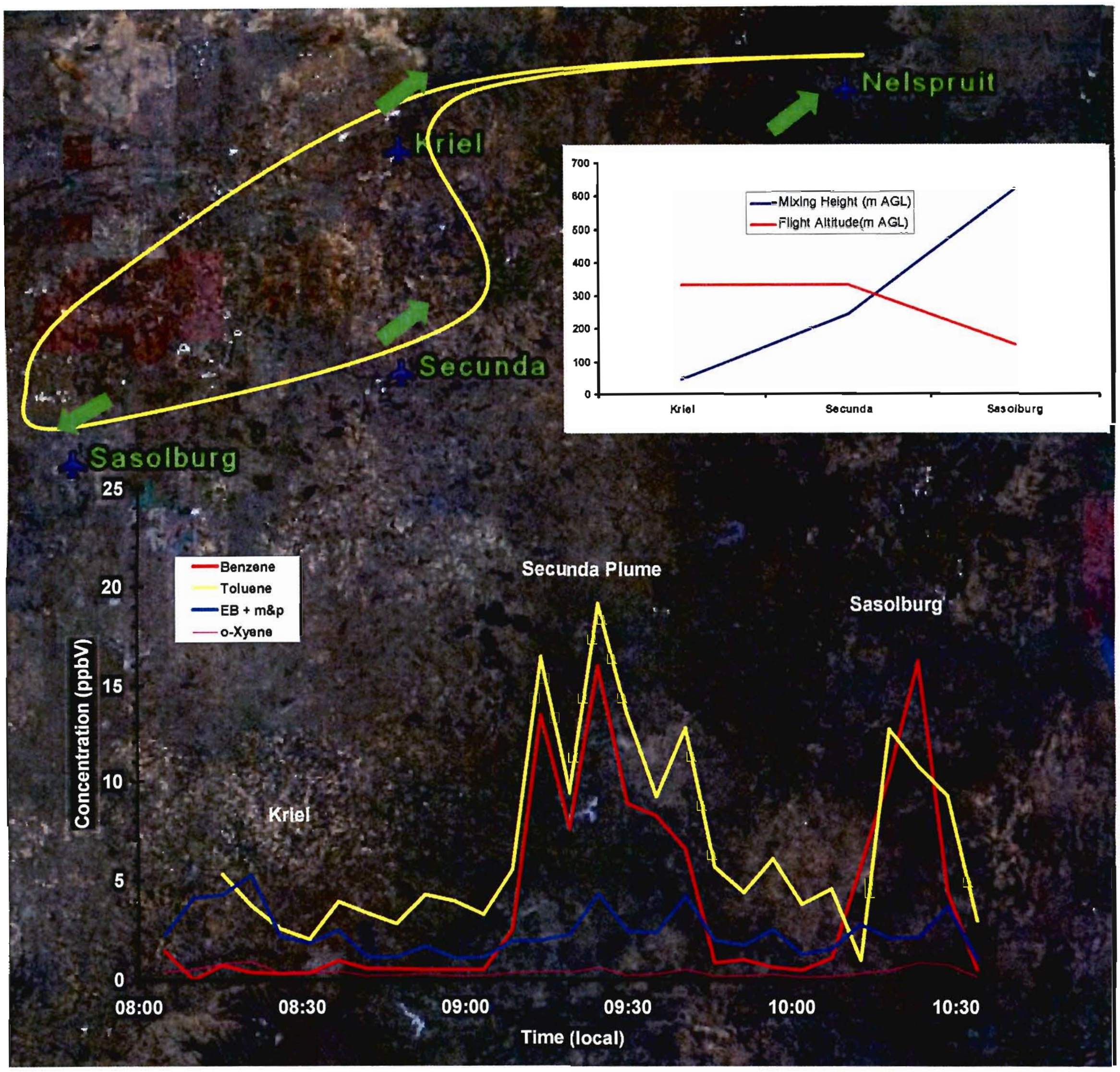


Figure 3.11: Graph depicting the flight results obtained during the study area experiment. The flight included a section of the Highveld area (Power Station and Chemical facility on the Highveld). Flight altitude and atmospheric mixing height is also indicated. Green arrows indicate prevailing wind direction and wind speed (size of arrow) during sampling

The plume study undertaken in the Mpumalanga area has shown that significant levels of BTEX are present in the plume of the petrochemical facility situated in Secunda (see Table 3.5 and Figure 3.11).

Table 3.5: BTEX results obtained during Secunda plume sampling (Altitude 6500 ft ASL)

Sample Time	Benzene / ppbV	Toluene / ppbV	Ethyl Benzene + M,P-Xylene / ppbV	O-Xylene / ppbV
9:14	13.38	16.40	1.95	0.35
9:19	7.55	9.40	2.24	0.35
9:24	15.97	19.10	4.29	0.60
9:30	8.86	13.42	2.41	0.20
9:35	8.24	9.22	2.37	0.27
9:40	6.56	12.72	4.17	0.51

Statistical analysis, utilising correlation and covariance calculations, has shown the benzene:toluene covariance and correlation (r^2) in the plume to be 4×10^{-2} and 0.88, respectively. These levels compare remarkably well with covariance and correlation figures calculated for benzene and toluene at SAPPI, the biomass burning site and the forest area (see Paragraph 3.2.1.1). Considering the much lower levels of BTEX observed in the Kriel pollution plume (power plant) and the prevailing wind direction, it can be deduced that elevated levels observed over the eastern Mpumalanga Highveld area during the Highveld campaign (Paragraph 3.2.1.1) are attributable to emissions from the petrochemical facility.

Plume BTEX levels associated with a petrochemical facility in the Sasolburg area are summarised in Table 3.6. Maximum BTEX levels were found to be similar to values experienced in Secunda. The interdependence of benzene and toluene was also found to be significant, based on a benzene:toluene covariance and correlation (r^2) of 1.2×10^{-1} and 0.66, respectively. Fluctuations in BTEX concentration levels measured can be attributed to periods where sample taking occurred outside the industrial plume.

Table 3.6: Plume BTEX results obtained during Sasolburg (study area) sampling period (Altitude 5700 ft ASL)

Sample Time	Benzene ppbV	Toluene ppbV	Ethyl Benzene + M,P-Xylene /ppbV	O-Xylene ppbV
10:12	5.64	0.97	2.75	0.29
10:17	10.25	12.65	2.06	0.45
10:23	16.20	10.73	2.10	0.83
10:28	4.40	9.26	3.65	0.72
10:33	0.49	2.95	1.00	0.10

The extent of BTEX concentration levels in the Sasolburg petrochemical pollution plume, coupled with relatively low altitude atmospheric release (<100 meters AGL) brings with it the realisation that this plume may have a significant impact on ground-level BTEX levels, especially during periods of stable atmospheric conditions. The following section will discuss the findings made during the ground-level BTEX monitoring campaign.

3.2.2 Ground-level Concentration profile over the Sasolburg Area

The prevailing meteorological conditions during the ground-level BTEX measurement campaign are indicated in Table 3.7

Table 3.7: Meteorological conditions during the ground-level campaign in Sasolburg

Date & Time	Temperature °C	Wind Direction ° From	Wind Speed $m.s^{-1}$
2/9/2000 0:00	8.1	340	2.7
2/9/2000 1:00	7.3	350	2.7
2/9/2000 2:00	7.2	350	2.4
2/9/2000 3:00	7.3	360	1.6
2/9/2000 4:00	6.9	360	1.6
2/9/2000 5:00	7.4	340	2.3
2/9/2000 6:00	8.3	350	2.3
2/9/2000 7:00	15.9	10	1.3
2/9/2000 8:00	23.8	20	2.3
2/9/2000 9:00	26	360	5.2
2/9/2000 10:00	26.7	340	6.8
2/9/2000 11:00	27.4	340	8
2/9/2000 12:00	28	340	8.8
2/9/2000 13:00	28.1	330	7.8
2/9/2000 14:00	27.8	320	7.7
2/9/2000 15:00	27.2	310	6.3
2/9/2000 16:00	26.1	320	5.3
2/9/2000 17:00	24.2	320	4

Meteorological conditions during the sampling period were characterised by light north to north-westerly winds, becoming moderate in the early afternoon. Early morning visibility was poor, indicating entrainment of pollutant during night-time. Temperatures were cool in the morning reaching a high of 28 °C at noon. The theoretical mixing height during the study obtained from the TAPM model grows rapidly from less than 200 m soon after sunrise to a maximum of about 1800 m in the early afternoon, followed by a rapid decrease as surface heating decreases (Figure 3.12).

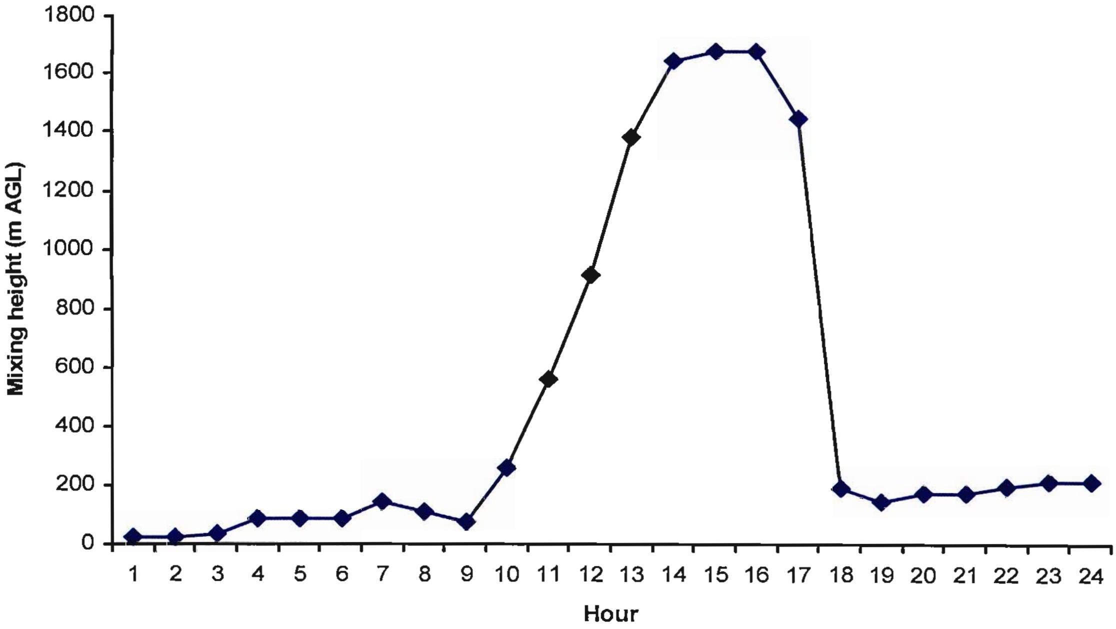
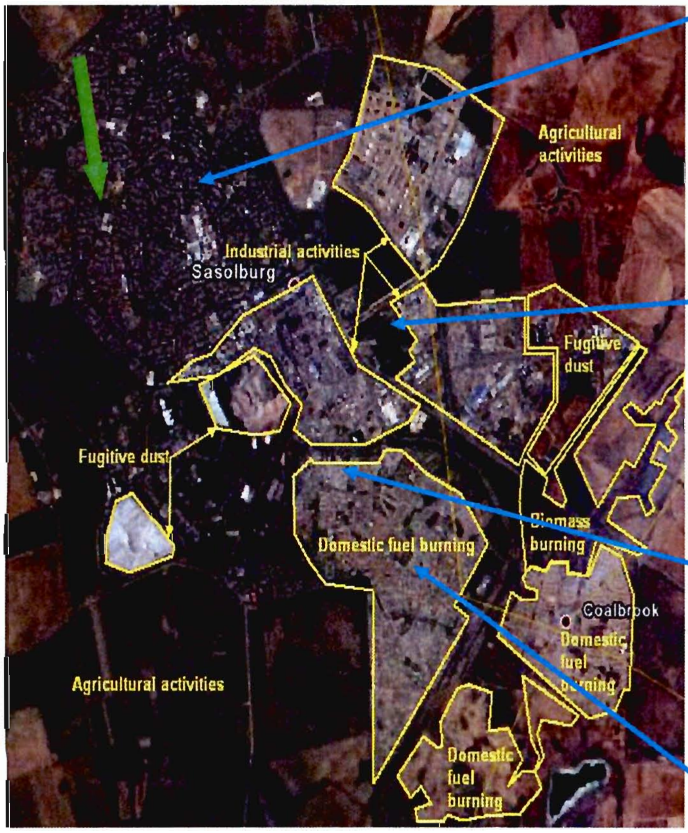


Figure 3.12: Theoretical mixing height evolution during the Sasolburg ground-level BTEX study

The mean and maximum BTEX concentration levels measured during the Sasolburg campaign, as well as the time of sampling and position of each site are grahically depicted in Figure 3.13. Ground-level BTEX concentrations were found to be extremenly high, exceeding the proposed South African standard of 1.6 ppbv. Although a limited amount of sites were chosen, data gathered did indicate a tendency towards elevated BTEX levels close to the industrial and residential coal burning areas (Residential site 1, 2). Residential site 2 experienced the highest BTEX levels during the study. A strong influence from a petrochemical facility situated in close proximity to the sampling site (< 100 meters) seems plausible. The prevailing wind direction from the north, resulting in air mass transport from the industrial facility supports this finding. Residentail site 1, situated to the south of the industrial facility, experienced similar BTEX pollution loads due to the prevailing meteorological conditions.

The lowest mean BTEX concentration levels were measured at Residential site 3. The fact that this site is situated upwind from the chemical facility during the study, supported by a sharp increase in the wind velocity as the day progresses, may have contributed to these lower levels.



11: 32 am

Residential Site 3	**Mean**	**Maks**
Benzene (ppbv)	1.0	6.4
Toluene (ppbv)	3.3	7.5
Ethyl Benzene & m,p-Xylene (ppbv)	1.1	2.6
o-Xylene (ppbv)	1.2	9.2

08:25 am

Industrial Site	**Mean**	**Maks**
Benzene (ppbv)	3.3	5.6
Toluene (ppbv)	4.0	6.3
Ethyl Benzene & m,p-Xylene (ppbv)	0.8	1.3
o-Xylene (ppbv)	7.7	8.5

07:32 am

Residential Site 2	**Mean**	**Maks**
Benzene (ppbv)	10.4	18.1
Toluene (ppbv)	8.8	15.6
Ethyl Benzene & m,p-Xylene (ppbv)	1.2	2.3
o-Xylene (ppbv)	8.3	10.6

06:25 am

Residential Site 1	**Mean**	**Maks**
Benzene (ppbv)	4.0	6.6
Toluene (ppbv)	6.7	25.0
Ethyl Benzene & m,p-Xylene (ppbv)	1.2	3.7
o-Xylene (ppbv)	5.5	11.6

Figure 3.13: Mean and maximum ground-level BTEX concentration levels in the Sasolburg area. Position of sites and time of sampling also indicated. Green arrow indicates prevailing wind direction

Although BTEX levels were found to be lower at Residential site 3, compared to the other sites, maximum levels measured were considered high and unacceptable in light of the proposed ambient standard of 1.6 ppbv. In an attempt to understand the circumstances leading to these elevated levels, backtrajectory modeling utilising the NOAA Hysplit model was conducted (Figure 3.14). Model results indicated both low and high elevation air movement from the north and north-east over the study area. This air movement, given the prevailing conditions, would result in the transport of polluted air originating from Johannesburg to the Sasolburg area during the night, thereby contributing to the pollution load over the study area.

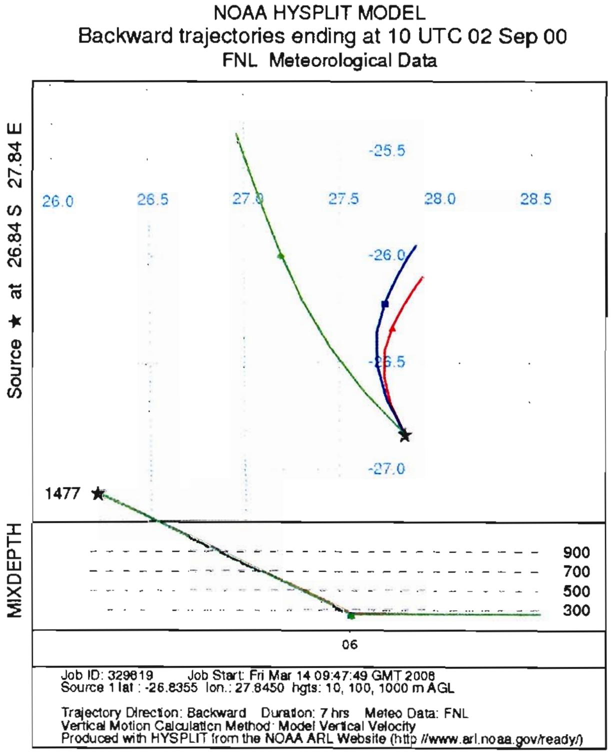


Figure 3.14: Backward trajectory estimation indicating airflow patterns over the Sasolburg area utilising the NOAA Hysplit Model

However, given the extent of pollution emanating from the industrial facilties situated in Sasolburg (see Table 3.6 and Figure 3.11), a more plausible scenario would be the entrainment of emitted BTEX species from the industrial facility during the night, when erosion of the mixing layer occurs, followed by the establishment of strong low-level surface inversion. The validity of this scenario is strenghtened by considering the prominent role of industry in the area source inventory. Paragraph 2.2.7 indicated that 46 000 tonnes of volatile organic compounds are released in the Vaal Triangle, of which industry contributes in excess of 90%. Unfortunately, a complete inventory was not available. Only the contributions of residential coal burning (23 tonnes yr^{-1}) and transport (76 tonnes yr^{-1}) were available.

3.3 CONCLUSION

The BTEX screening study has brought with it the realisation that the understanding of the sources, transport and fate of BTEX in the Sasolburg area was lacking, making the management of these ambient species in the study area extremely difficult. The study highlighted that ambient BTEX levels were at dangerous levels, with benzene exceeding the proposed ambient standard of 1.6 ppbv at all the monitoring sites. Comparison of the ratio between benzene and toluene in background air strongly suggests that strong sources of benzene exist in the region and the relative abundance of benzene compared to toluene only falls to typical industrial/urban levels when such air is mixed into the air masses. In-flight studies undertaken over the Mpumalanga Highveld and the Sasolburg area highlighted the impact of industrial emissions on ambient BTEX levels in the region. The elevated levels measured in the study area, accompanied by our lack of understanding regarding the sources contributing to the observed ambient levels therefore necessitated further research on BTEX pollution and its possible impact on the region.

CHAPTER 4

ASSESSMENT OF SELECTED VOLATILE ORGANIC SPECIES IN THE SASOLBURG AREA

In this Chapter...

This chapter will describe the methodology used to determine the ambient concentration of benzene, toluene, ethylbenzene and xylene (BTEX) in the Sasolburg area (Par 4.1). The results obtained during a 10-month BTEX sampling campaign that was started in 2002 in the Sasolburg Area are discussed. The results obtained during a study that aimed to assess the validity of the 2002 data as a fair representation of the BTEX situation in the study area in 2003 are also shown. The effect of changes in source characterisation on ambient BTEX concentration profiles in the Sasolburg area is discussed by investigating the results obtained during a 2006 sampling campaign at three of the four residential sites chosen for the 2002 and 2003 studies (Par 4.2). Conclusions based on the findings are given in Paragraph 4.3.

4.1 EXPERIMENTAL PROCEDURE

4.1.1 Sampling Procedure

A screening process indicated that the most feasible and practical methodology to follow was the United States Environmental Protection Agency's compendium method TO-14A (US-EPA, 1997). This method utilises polished six-litre stainless steel containers. Figure 4.1 shows the canister containing a critical orifice (flow controller) to regulate the air flow, and therefore the sampling time, into the canister.

Figure 4.1: TO-14A specially prepared canister fitted with an eight-hour flow controller valve to enable eight hours of integrated sampling

Four sampling sites were chosen in the Sasolburg Area for the 2002 sampling campaign. In order to assess whether the data obtained in 2002 could be regarded as being representative, a comparative study was undertaken in 2003.

The strategy was to use existing inorganic ambient pollution information for the area to determine sampling sites with the highest probability of experiencing elevated levels of the selected hydrocarbons. Site selection aimed to include the predominant emission profiles for the area.

The Primary school site is situated at a primary school in an electrified residential area. The site is in close proximity to the Sasolburg Central Business District (CBD), as well as the industrial centre. The Zamdela station is in close proximity to an industry, a residential area mainly utilising electricity (70% of the time) and a filling station. The Zamdela station is also situated down-wind from most localised sources given the prevailing wind direction (north-west). Vaalpark is situated in an electrified suburb not in close proximity to any industry. The industrial site is next to a refinery and power generation facility utilising coal.

A laboratory and field blank were also taken during every sampling exercise. Sample duration for the canister samples was eight hours, conducted every Thursday commencing at 7:00am over a period of ten months (2002). October and December were not included due to the unavailability of analytical facilities over those periods. Figure 4.2 indicates the sampling positions of the four sites during the 2002 and 2003 study (blue dots), in relation to the four sites chosen to conduct the screening study discussed in Chapter 3 (red dots) (see Figure 2.7 and Figure 2.8 for further detailed maps of the site in relation to South Africa).

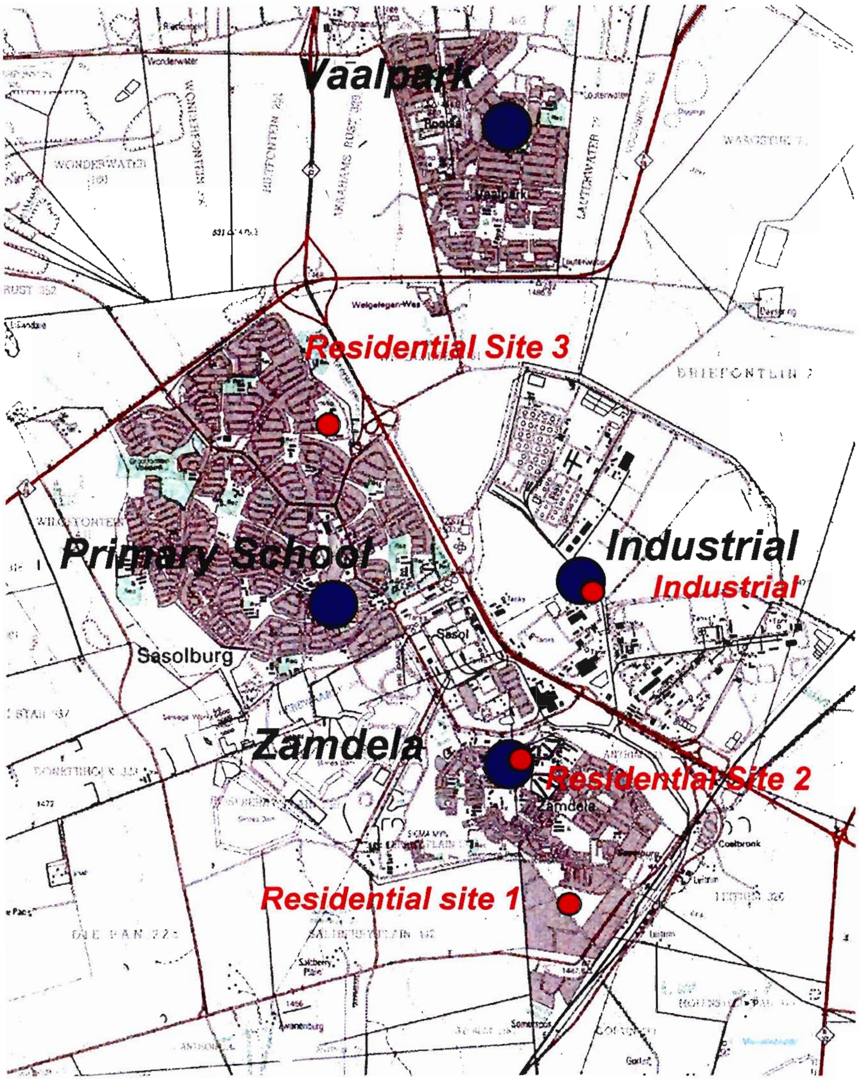


Figure 4.2: Map indicating the four VOC sampling sites in 2002 and 2003 in the Sasolburg area (blue dots), compared to the sampling sites used during the screening study (red dots) (see Chapter 3)

A study aimed at determining the effect of changes in source characterisation on ambient BTEX concentration profiles in the Sasolburg area was prompted by drastic changes in the source profile within the study area. The changes involved fuel switching at a large petrochemical facility from coal gasification to natural gas reforming. Coal gasification results in the production of significant amounts of tar and sludge containing BTEX. These tar and sludge streams need to be treated, stored or disposed of, which resulted in significant BTEX emissions at ground level. Pollution emanating from point sources associated with the cleaning of the gas streams after gasification also resulted in BTEX being emitted into the atmosphere at heights ranging from 5 -100 meters above ground level. The change to natural gas would result in the closing down of coal gasification in the Sasolburg area. The effect of these changes was envisaged to have a significant impact on the BTEX emission profile established in 2002 and 2003.

The same residential sites used in 2002 and 2003 were chosen for the 2006 study. The industrial site was not included since the impact on the community formed the basis for this study. It was furthermore decided to conduct 24-hour sampling, since night-time effects could not be assessed utilising the 8-hour sampling regime. Figure 4.3 indicates the position of the three residential sampling sites within the Sasolburg area.

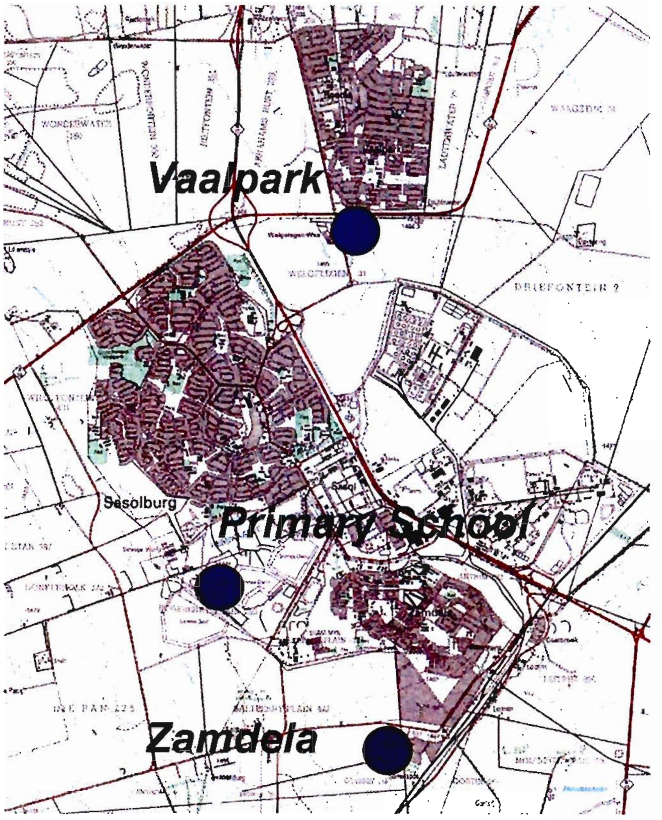


Figure 4.3: Map indicating the three BTEX sampling sites *in 2006 in* the Sasolburg area

4.1.2 Analytical Procedures

Analyses of the samples were undertaken within 72 hours after sampling. Pre-concentration, utilising a cryogenic trap, including water removal by means of a Nafion dryer, of the air samples was done on a Perkin-Elmer Turbo Matrix pre-concentrator and thermal desorber. Figure 4.4 is a photo of the analytical facility.

Figure 4.4: Analytical facility used in determining the concentration of VOC species present in the Sasolburg area using GC-FID/MS

Prior to analysis, the GC instruments were purged with humidified zero air (<0.2 ppbv of the targeted VOCs) to clean the system.

An external calibration standard obtained from Supelco (Cat no: 41900 – U) containing known concentrations of the target compounds was used. Calibration was followed by purging with humidified zero air to ensure that no possible carryover has taken place. Figure 4.5 is a typical chromatogram emanating from the analytical facility. Although several species have been detected, the focus of this study was to investigate the presence of benzene, toluene, xylene and ethylbenzene species due to their current and future inclusion in national ambient standards.

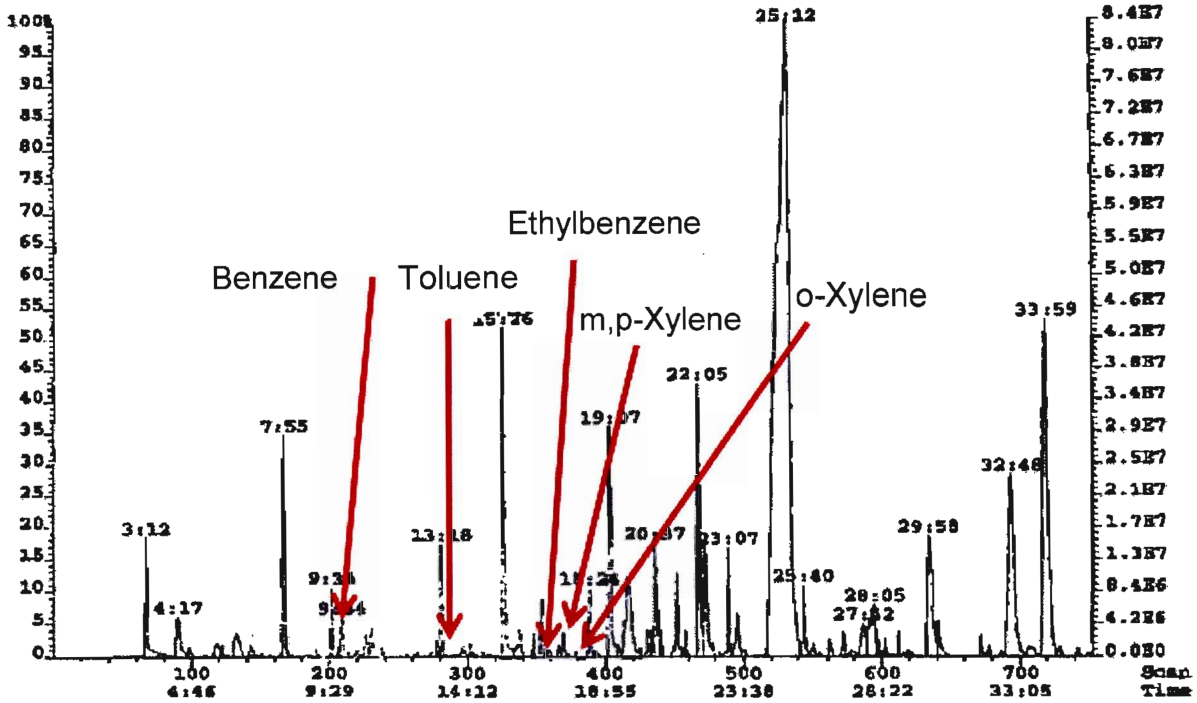


Figure 4.5: Typical GC chromatogram indicating the species of interest as well as the concentration levels observed (benzene 0.7 ppbv, toluene 0.45 ppbv, ethylbenzene 0.08 ppvb , m,p- xylene 0.09 ppbv and o-xylene 0.07 ppbv)

During the study, mass spectrometry was used for peak identification of target species. Once the peak identification was successfully carried out, routine analyses only made use of flame ionisation for quantification based on the retention time information gained from the MS. Emphasis was placed on the BTEX species.

During the analysis, the trapped VOC species were re-volatilised, prior to injection into the GC. The temperature of the GC oven started at -10 degrees Celsius and was taken up to 250 degrees Celsius for 10 minutes, at a rate of 7 degrees per minute.

In order to separate the compounds, a Perkin Elmer PE -1 60 m, 320 micrometer id, 1 micrometer film thickness column was used.

By adopting US-EPA compendium method TO-14A, an unambiguous detection limit of between 0.1 – 25 ppbv, with a minimum detection limit (MDL) of at least 0.1 ppbv could be obtained.

Figure 4.6 illustrates the US-EPA compendium method process followed to prepare the instrument prior to analysis.

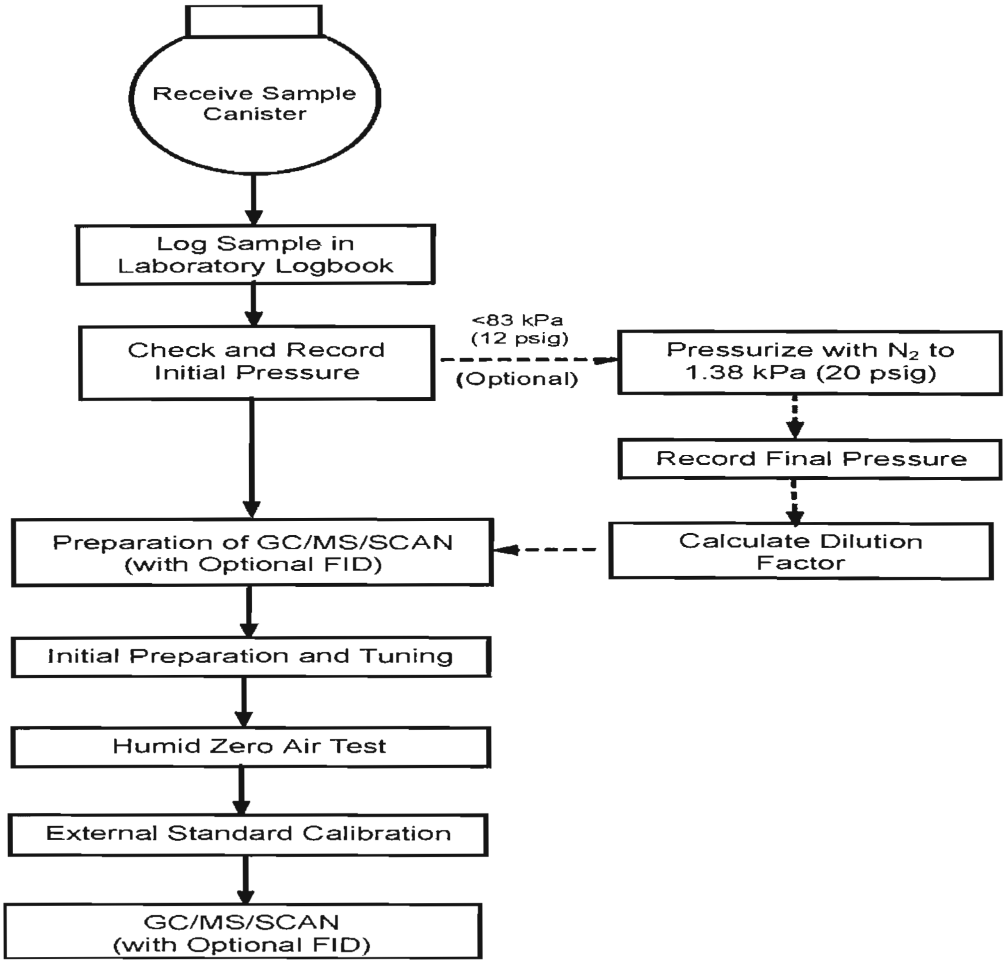


Figure 4.6: Flowchart of GC/MS analytical system preparation (US-EPA Compendium Method TO -14A)

4.1.3 Quality Control and Quality Assurance

Quality assurance is the means to attain sound results. To obtain verified results, the sampling system (canister) and the analytical instrument (GC/MS) performance criteria need to be validated. The actions that need to be taken to meet the criteria are summarised in Table 4.1.

Table 4.1: Sampling- and GC/MS system performance criteria

Sampling system	GC/MS system performance criteria
▪ Pre- and post-sampling measurements with a certified mass flow controller for flow verification. Utilising canisters, a manual flow controller supplied with calibrated orifice is used.	▪ The GC/MS system to be certified clean (<0.1 ppbv of targeted VOCs) prior to sample analysis.
▪ All canisters to be pressure tested to 207 ± 14 kPa (30 ± 2 psig) over a period of 24 hours.	▪ Daily tuning of the GC/MS system with 4-bromofluoro benzene (4-BFB) ensuring it meets the key ions and ion abundance criteria.
▪ All canisters to be certified clean (<0.2 ppbv of the targeted VOCs).	▪ Both an initial and multipoint humid external calibration and a daily calibration of the GC/MS analytical system.
▪ All sampling systems to pass an initial humidified calibration gas certification with a percentage recovery greater than 90.	

4.2 RESULTS

4.2.1 2002 BTEX Sampling Campaign

Table 4.2 indicates the observed ambient temperatures during 2002. Figure 4.7 indicates the prevailing wind direction and speed.

Table 4.2: Monthly maximum, mean and minimum ambient temperatures experienced over the study area in 2002

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Maximum	29.4	27.8	28.1	26.7	21.7	17.4	18.5	22.4	24.5	28.4	28.8	27.6
Mean	22.3	21.6	20.8	18.3	13.1	10.2	9.3	15.0	16.6	20.3	20.9	21.6
Minimum	15.2	15.5	13.4	9.8	4.5	2.9	0.1	7.6	8.8	12.1	12.9	15.5

The temperature profile illustrates the large difference in winter and summer temperatures over the study area. The large temperature gradient between minimum and maximum temperatures is also significant. As discussed in Chapter 2, these cold winter months are associated with persistent low-level surface inversion, which clearly lead to entrainment of pollutants and therefore higher winter pollution levels. It is clear from Figure 4.7 that the prevailing wind direction is from the north-west, accompanied by light to moderate wind speeds rarely exceeding 30 kilometres hour^{-1}.

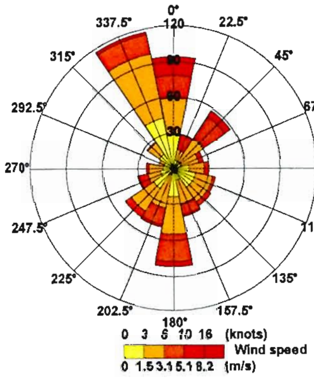


Figure 4.7: Prevailing wind direction and wind speed over the study area during the 2002 sampling campaign

Utilising the NOAA Hysplit back trajectory model, air mass movement over the region was simulated. Figure 4.8 graphically presents the flow of air during the sampling period utilising back trajectory modelling. Back trajectory modelling clearly indicated that the majority of air flow (air mass transfer) at both low (10 meters) and slightly elevated (500 meters) altitudes was from the north-west (Johannesburg). The modelling results have confirmed meteorological coupling between Johannesburg and the study area, thereby indicating that drainage from Johannesburg (Witwatersrand) into the Vaal basin may play a role in the levels of pollution observed in the study area (See Paragraph 2.2.7).

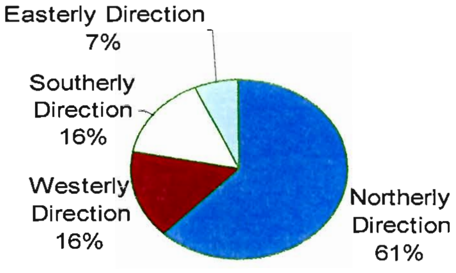


Figure 4.8: Graph indicating the estimated flow patterns over the region during 2002, utilising NOAA Hysplit back trajectory modelling

Table 4.3 indicates the most prevalent pollutant species measured during the 2002 sampling campaign. The study clearly indicated that benzene, toluene, xylene and ethylbenzene are ubiquitous in the study area. Styrene and halogenated hydrocarbons have also been found to be frequently present in the study area during the 2002 study. The relatively stable nature of halogenated hydrocarbons and therefore long lifetimes, noticeably methylene chloride (2-3 years), chloroform (> 6months) and carbon tetrachloride (60-100 years), would result in these species being ubiquitous in ambient air.

Table 4.3: Summary of the most prevalent VOC species identified over a 10-month canister sampling programme in the Sasolburg Area (Jan 2002 - Nov 2002). Number of samples = 140

VOC Species	Max 8 hr [ppbv]	Annual 8hr Mean [ppbv]
Methylene Chloride	11.8	0.4
Chloroform	10.0	0.2
1,2-Dichloroethane	1.7	<0.1
Benzene	16.9	1.8
Carbon Tetrachloride	2.6	<0.1
Trichloroethylene	2.4	<0.1
Toluene	19.9	1.9
Tetrachloroethylene	0.9	<0.1
Ethylbenzene	2.9	0.8
Xylene	8.9	1.7
Styrene	25.9	0.9
1,3,5-Trimethylbenzene	8.8	0.1
1,2,4-Trimethylbenzene	7.1	0.6

The maximum benzene and toluene concentration levels observed over the study area were 16.9 ppbv and 19.9 ppbv, respectively. Ethylbenzene and xylene maximum levels were 2.9 ppbv and 8.9 ppbv, respectively.

Table 4.4 depicts the meteorological conditions that prevailed during periods of maximum observed ambient BTEX concentration levels.

Table 4.4: Table indicating prevailing meteorological conditions during maximum BTEX concentration episodes

Species	Maximum Concentration ppb	Date	Wind Direction	Wind Speed m/s
Benzene	16.9	July '02	N - NNW	0.9
Toluene	19.9	June '02	N - NNW	0.7
Xylene	8.9	Aug '02	N - NW	1.9
Ethylbenzene	2.9	June '02	N - NNW	2.9

The low wind speeds linked to stable winter conditions and strong low level inversion would result in pollution being trapped over the region resulting in these maximum levels being recorded. The prevailing wind direction during these episodes was from the north-west. Given the wind direction, the impact of external sources to the region may be considered to be significant. The low wind speeds and stable conditions during the winter months over the Highveld area are, however, expected to limit the impact of these external sources due to poor dispersion.

The mean annual benzene level over the study area was 1.8 ppbv. This is considered problematic given a proposed benzene standard for South Africa of 1.6 ppbv (5 µg.m^{-3}). This reconfirmed the findings of the 2000 study, which indicated that benzene levels in the Sasolburg area are elevated and cause for concern (see Figure 3.13).

Figures 4.9 to Figure 4.12 graphically depict the BTEX time series during the 2002 study at the four ambient measurement stations.

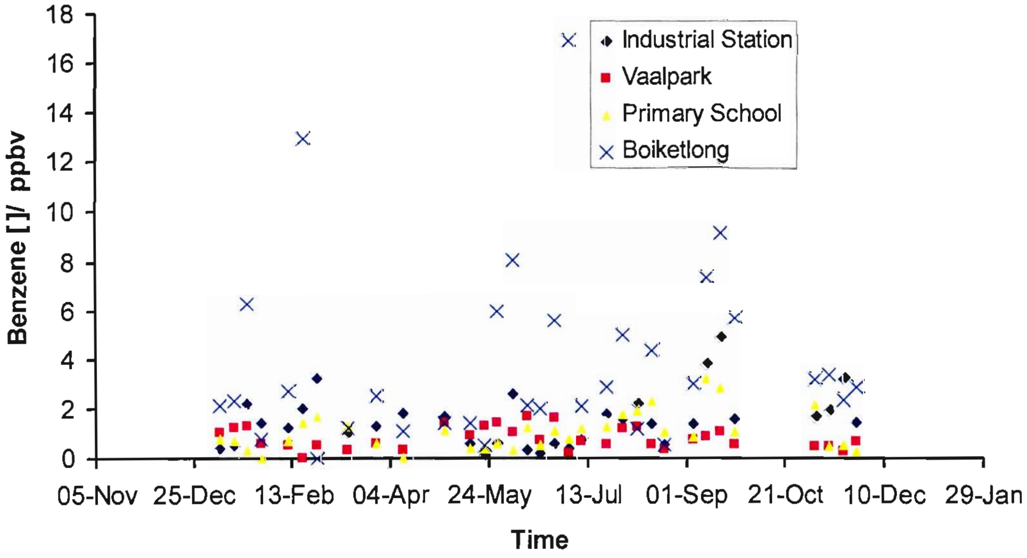


Figure 4.9: Benzene time-series observed during 2002 at the four ambient BTEX stations in the Sasolburg area (see Figure 4.2)

The benzene time series indicate distinctive concentration peaks throughout the year (Figure 4.9). The Zamdela station experienced the highest mean concentrations over the study area.

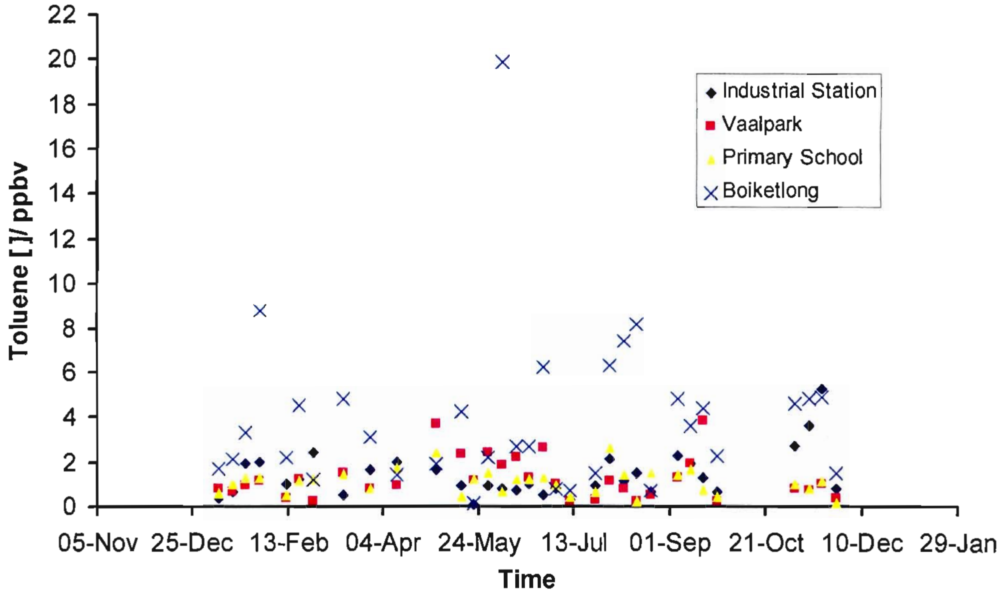


Figure 4.10: Toluene time-series observed during 2002 at the four ambient BTEX stations in the Sasolburg area

The toluene time series also indicated periods of high concentrations in winter (Figure 4.10). The toluene peaks seem to show good correlation with benzene. The highest average toluene values were reported at Zamdela.

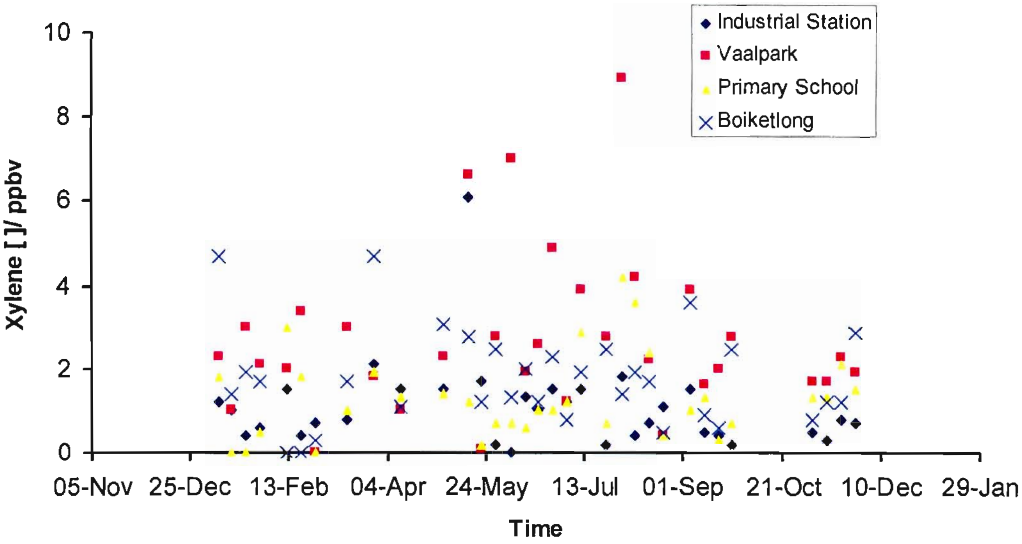


Figure 4.11: Xylene time-series observed during 2002 at the four ambient BTEX stations in the Sasolburg area

Measured Xylene and ethylbenzene levels at the Vaalpark and Primary school sites seem to be higher compared to the Industrial and Zamdela sites (see Figure 4.11 and 4.12).

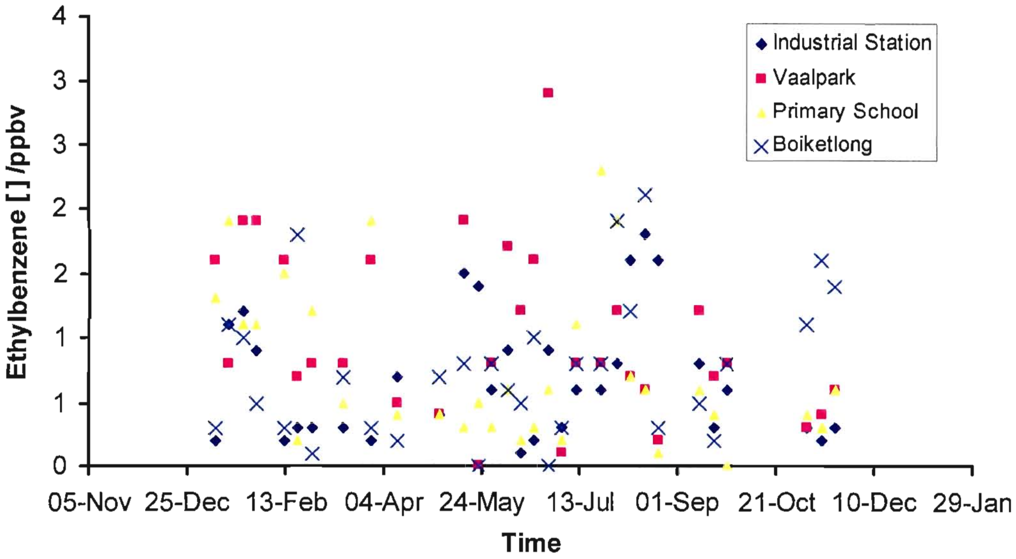


Figure 4.12: Ethylbenzene time-series observed during 2002 at the four ambient BTEX stations in the Sasolburg area

The existence of a seasonal trend in BTEX concentration levels over the study area has been derived from the 2002 data set (see Figure 4.9 to 4.12). Figure 4.13 graphically depicts this trend observed during the 2002 study period. It is clear that mean BTEX concentration levels increase during the winter months.

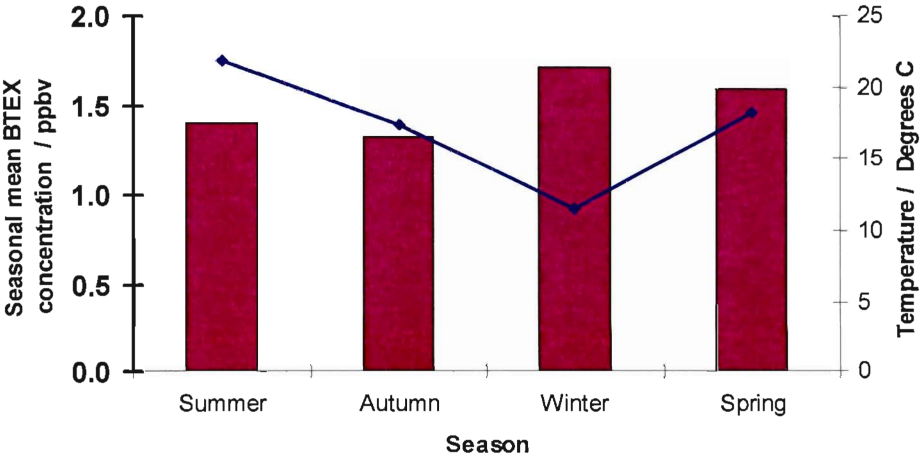


Figure 4.13: Seasonal mean BTEX concentration profiles over the Sasolburg area during 2002. Mean ambient temperatures are also shown.

Previous studies (see Paragraph 2.2.6) have shown that seasonal differences in the oxidation potential may result in higher pollution levels over an area. BTEX species are predominantly oxidised by hydroxyl radicals ($HO^{\bullet}$) in the troposphere. The formation of $HO^{\bullet}$ during the day-time is predominantly determined by radiation flux strength, the overhead ozone column, the local ozone concentration and the percentage water vapour. The photolysis of the ozone results in the formation of electronically excited $O(^1D)$ atoms. These excited atoms are, however, readily quenched to the ground state $O(^3P)$. The number of $O(^1D)$ available to react with water, therefore determines the $HO^{\bullet}$ production rate. The concentration of $O(^1D)$ is determined by the photolysis rate coefficient $jO(^1D)$. Figure 4.14 indicates the difference in $jO(^1D)$ during summer and winter conditions over the study area. The radiative transfer model TUV version 4.1a (Madronich and Flocke, 1998) was used to assess the relative changes in the photolysis rate coefficient $jO(^1D)$.

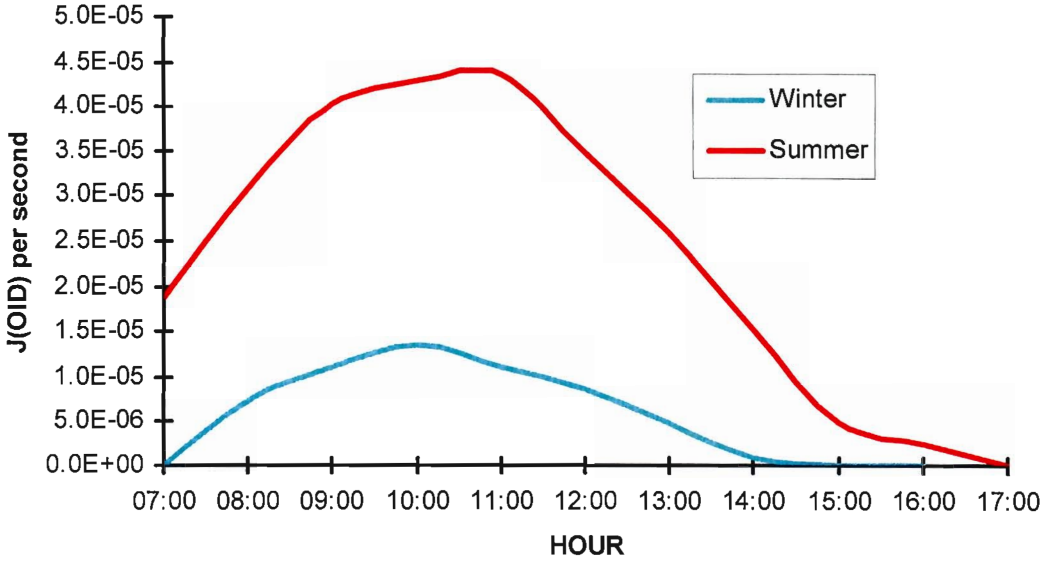


Figure 4.14: Seasonal differences in the photolysis coefficient (frequency) $j(O^1D)$

It is clear from Figure 4.14 that there is a significant difference between the summer and winter photolysis frequency $j(O^1D)$. This is attributed to a decrease in the radiative flux strength during the winter months. Assuming that the photolysis of ozone dominates $HO^{\bullet}$ production in the study area a decline in the rate of O^1D atom formation and therefore a subsequent decrease in the production rate of $HO^{\bullet}$ is to be expected.

The HO• concentration in the troposphere and therefore the BTEX oxidation potential is determined by the relationship between HO• sources and sinks. In an NO_X enriched environment O_3 is formed and the HO• recycled, while in low-NO_X environments O_3 is destroyed and the HO• decreases rapidly. Given the extent of NO_X sources in the study area (see Figure 4.15) an NO_X enriched environment can be assumed, thereby sustaining ground level O_3 concentration levels. In these NO_X enriched environments, an increase in reactive carbon compounds such as ethylbenzene and xylene will not lead to the perturbation of the HO• system, since the HO• consumed will be recycled and more HO• will be formed due to enhanced O_3 formation.

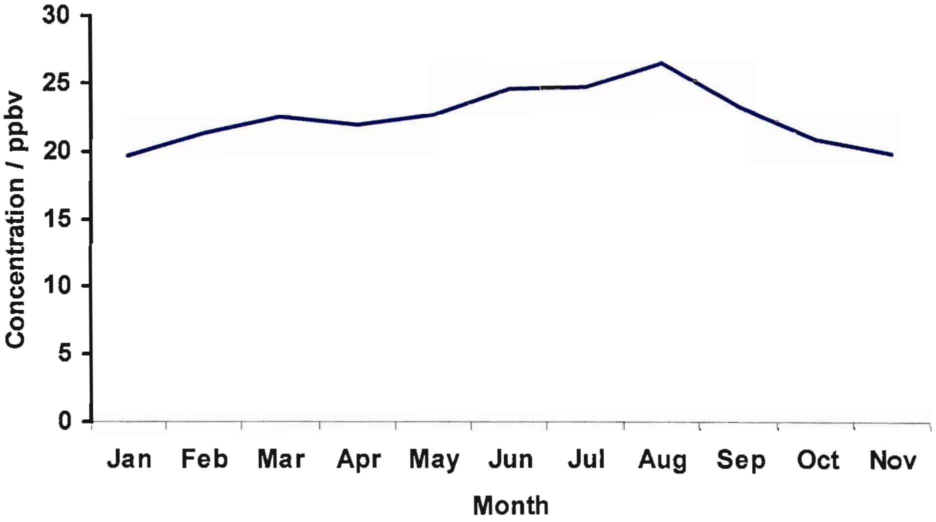


Figure 4.15: Monthly mean NO_X concentration levels (ppbv) observed during 2002

Figure 4.16 indicates the monthly mean ground level ozone concentration over the study area during 2002. The ozone data clearly indicates an increase in ozone concentration levels during the late winter and early spring periods, with a maximum experienced during September. This finding is consistent with similar findings made in the South African Highveld area (see Paragraph 2.2.7, Figure 2.14).

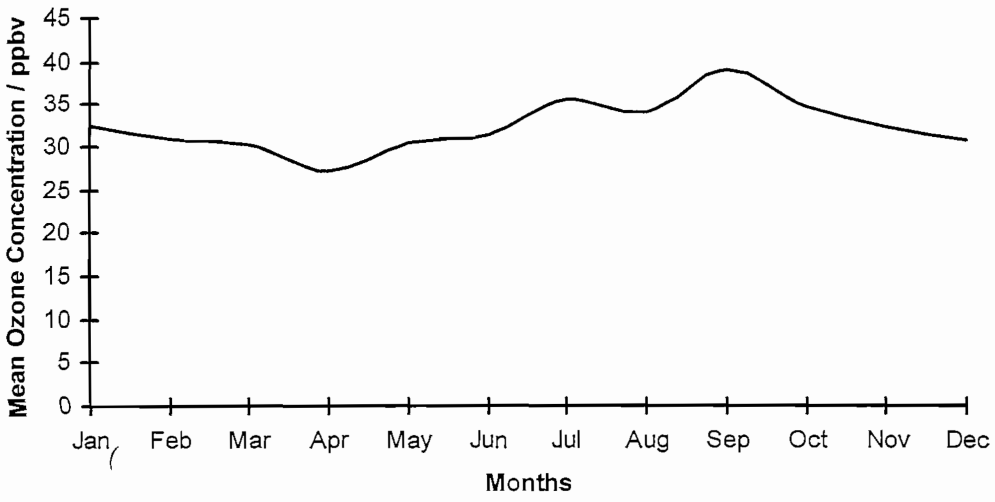


Figure 4.16: Ozone and solar radiation profiles over the Sasolburg area during the 10-month sampling campaign (2002)

The difference between winter and summer ozone concentrations was shown to be between 5-10 ppbv. The higher O_3 concentrations observed during the winter months can be attributed to the recirculation of pollutants over the source area (Sasolburg) coupled with the existence of semi-permanent stable layers that promote the long-range transport and therefore ozone formation over the region (see Paragraph 2.2.7).

During the winter months, biogenic VOC emission rates in the study area are limited, while industrial sources remain constant. BTEX emissions associated with veld fires and residential coal burning, however, increases. It is expected that the net increase in the BTEX flux rate during winter would be small due to the overwhelming contribution from industry (see Paragraph 2.2.7).

As indicated earlier, the production rate of O^1D decreases in winter and subsequently the production rate of the $HO^\bullet$. Considering the loss rate to be constant during the two seasons, a net reduction in BTEX oxidation during the winter months can be assumed due to lower $HO^\bullet$ concentrations. The significance of this reduction in $HO^\bullet$ concentration is, however, expected to be small, considering the strong influence of unique meteorological conditions over the study area (See Paragraph 2.2.7). The impact brought about by a decrease in $HO^\bullet$ is even smaller considering the long atmospheric lifetime of BTEX species, notably benzene (>9 days). Higher mean winter BTEX concentration levels compared to summer conditions can therefore be attributed to meteorological conditions during winter months promoting the entrainment of pollutants over the area. The site-specific BTEX profile for each of the four measurement stations is indicated in Table 4.5. The characteristics of each of the sampling sites have been discussed in Paragraph 3.1.2 and Paragraph 4.1.1.

Table 4.5: Monthly average BTEX concentration (ppbv) obtained at the four stations situated in the Sasolburg area during the 2002 study period (number of observations = 140)

Species	J	F	M	A	M	J	J	A	S	O	N	D	Ave
PRIMARY SCHOOL													
Benzene	0.5	1.3	1.0	0.1	0.6	0.8	1.1	1.8	2.0	na	0.9	na	1.0 ± 06
Toluene	1.1	0.9	1.1	1.7	1.4	1.1	0.7	1.4	1.0	na	0.8	na	1.1 ± 0.3
Xylene	0.6	1.6	1.5	1.3	0.9	0.8	1.6	2.7	0.8	na	1.6	na	1.3 ± 0.6
Ethylbenzene	1.4	1.0	1.2	0.4	0.4	0.4	1.2	0.8	0.5	na	0.4	na	0.7 ± 0.4
VAALPARK													
Benzene	1.0	0.3	0.5	0.3	1.3	1.3	0.5	0.9	0.9	na	0.5	na	0.8 ± 0.4
Toluene	0.8	0.6	1.1	0.9	2.4	2.0	0.5	0.7	1.8	na	0.7	na	1.2 ± 0.6
Xylene	2.1	1.8	2.4	1.0	2.9	4.1	2.6	3.9	2.6	na	1.9	na	2.5 ± 0.9
Ethylbenzene	1.5	1.0	1.2	0.5	1.0	1.9	0.6	0.7	0.9	na	0.4	na	1.0 ± 0.5
ZAMDELA													
Benzene	2.9	5.2	1.9	1.1	2.3	4.5	7.3	2.8	6.3	na	3.0	na	3.7 ± 2.0
Toluene	4.0	2.6	4.0	1.4	2.1	7.9	1.0	5.7	3.8	na	3.9	na	3.6 ± 2.1
Xylene	2.4	0.2	3.2	1.1	2.4	1.7	1.7	1.4	1.9	na	1.5	na	1.8 ± 0.8
Ethylbenzene	0.7	0.7	0.5	0.2	0.8	0.5	0.6	1.4	0.5	na	1.4	na	0.7 ± 0.4
INDUSTRIAL													
Benzene	1.1	2.1	1.2	1.8	0.8	0.9	1.0	1.5	2.2	na	2.1	na	1.5 ± 0.5
Toluene	1.2	1.5	1.1	2.0	0.9	0.8	0.7	1.3	1.5	na	3.1	na	1.4 ± 0.7
Xylene	0.8	0.9	1.5	1.5	2.4	1.0	1.0	1.0	0.7	na	0.6	na	1.1 ± 0.5
Ethylbenzene	0.9	0.3	0.3	0.7	1.0	0.5	0.5	1.5	0.6	na	0.3	na	0.6 ± 0.4

The Sasolburg area can be considered small, with the measurement sites situated in close proximity to each other (<4 km apart). Therefore, considering the prevailing meteorology, a widespread uniform airflow over all the sampling sites can be expected and therefore similar BTEX concentration levels. Differences in BTEX levels observed between the four stations must therefore be attributed to emission sources in close proximity to the specific site.

Table 4.6 indicates the percentage (%) of benzene and toluene data above the 50% and 90% percentile at each of the sites. It follows from Table 4.7 that Zamdela has the greatest percentage of data over the 90% and 50% percentile followed by the Industrial site, Primary school and Vaalpark.

The influence and position of BTEX sources relative to each of these site are postulated as the reason for these distinctive differences in observed BTEX levels between the sites.

Table 4.6: Table indicating the percentage of benzene and toluene data over the 50% and 90% percentile for each of the sites, respectively

	Benzene		**Toluene**	
	% of data >90 percentile	% of data > 50 percentile	% of data >90 percentile	% of data > 50 percentile
Vaalpark	5	0	0	11
Primary School	7	0	0	10
Zamdela	19	8	9	28
Industry	14	2	<1	12

Figure 4.17 is a map of the Sasolburg area indicating the position of the BTEX sites relative to possible sources. The Primary school site is situated in a residential area, approximately one kilometre west of a petrochemical plant (industrial centre). Vehicle emissions are considered small, with slight increases in traffic volumes in the early mornings. A waste site handling tar sludge is situated less than a kilometre south of the Primary school. Industrial pollution down-wash is also known to have an impact on this area if easterly winds prevail. This site is therefore impacted on by both ground-level and elevated pollution sources.

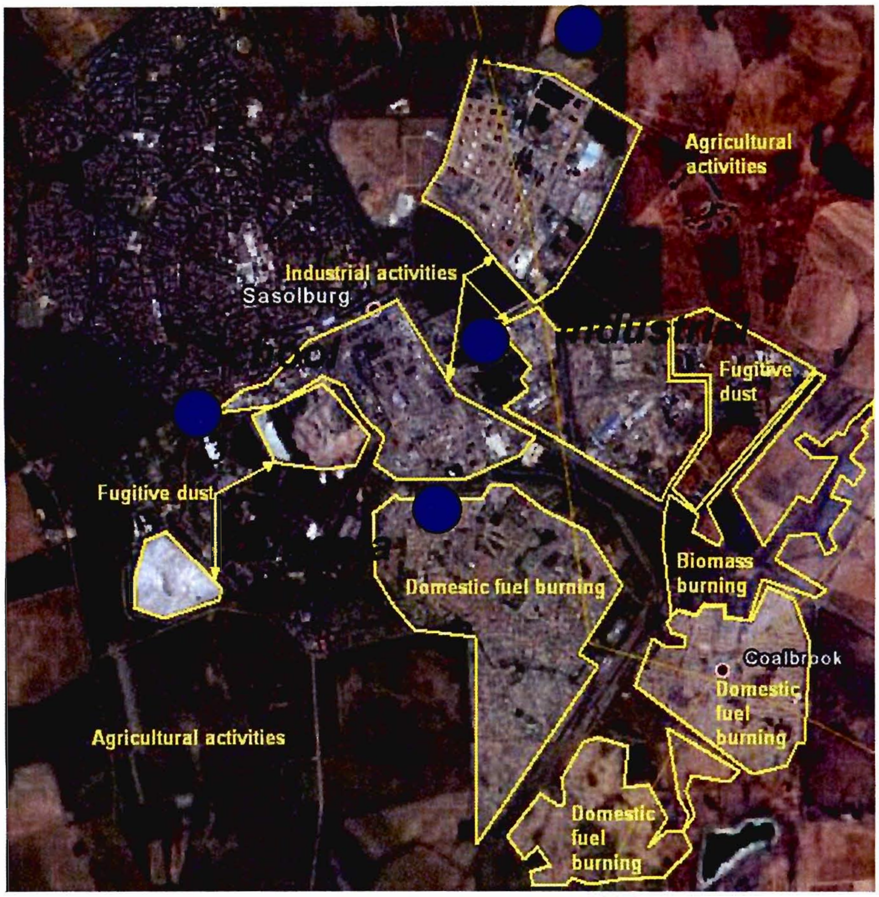


Figure 4.17: Source position in relation to sampling sites during the 2002 BTEX sampling campaign

In order to assess the impact from the predominant ground-level source (tar pits) the impact of temperature on benzene and toluene levels at this site has been determined. Figure 4.18 depicts the temperature dependence at the site.

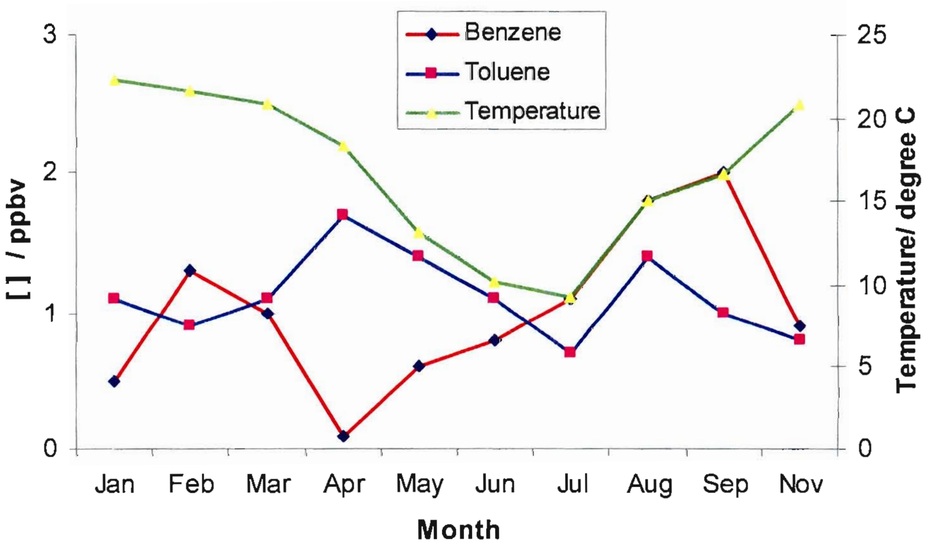


Figure 4.18: Impact of temperature on benzene and toluene concentration levels at the Primary school site during 2002

The temperature profile at the Primary school site has clearly indicated a decrease in benzene and toluene levels during the cooler months of the year, with maximum levels occurring during the warmer months. This finding indicates a possible influence from the waste disposal site, since evaporation would be at its lowest during the winter compared to high evaporation rates during summer.

The Vaalpark site is situated to the north of Sasolburg in an electrified residential area. Vehicle density is known to be low. It is therefore clear that given the position of the Vaalpark site, local meteorological conditions would have an impact on BTEX concentration levels measured at this site. It has been shown previously in the chapter that winter conditions may lead to entrainment of pollutants over the area, while warmer conditions prevailing during summer would promote the dispersion of these pollutants. Figure 4.19 graphically depicts the impact of ambient temperature on benzene and toluene concentration levels at the Vaalpark site.

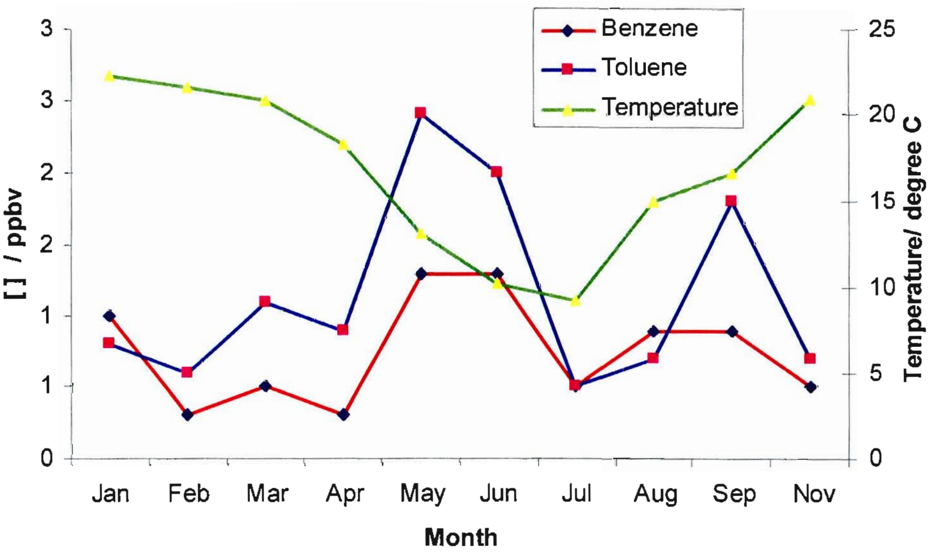


Figure 4.19: Impact of ambient temperature on benzene and toluene concentration levels at the Vaalpark site during 2002

Benzene and toluene levels measured at Vaalpark clearly indicate a strong seasonal trend, with maximum levels recorded during the winter months. The entrainment of pollutants associated with low level surface inversion in winter is therefore postulated to be the predominant factor governing ambient BTEX levels in Vaalpark. The Vaalpark site experienced the lowest mean benzene level of all four sites (20% lower compared to the Primary school site).

The Zamdela site is situated to the north of the industrial centre and directly adjacent to a petrochemical facility (< 100 meters). To the south significant residential coal burning, especially during the winter months, prevails. Situated to the west of the site is a filling station (<500 meters), while to the east fertiliser and polymer industries dominate the source profile. Given a prevailing wind direction from the north-west a significant industrial influence is expected. Low-level emissions emanating from industrial tar separating units will result in increased ambient BTEX levels during summer conditions, while industrial plume down-wash and entrainment of pollution caused by persistent strong surface inversion will increase winter BTEX levels. Figure 4.20 graphically depicts the impact of ambient temperature on benzene and toluene concentration levels at the Zamdela site.

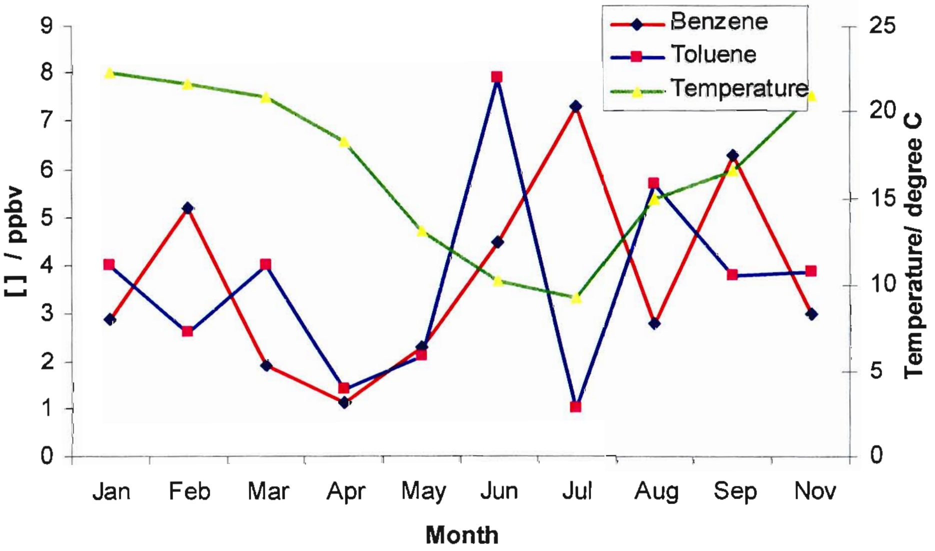


Figure 4.20: Impact of ambient temperature on benzene and toluene concentration levels at the Zamdela site during 2002

Maximum benzene and toluene ambient concentration levels were measured at Zamdela. The mean ambient benzene concentration level was calculated to be 370% and 460% higher compared to the Primary school and Vaalpark sites, respectively. Maximum benzene and toluene levels were observed in winter, while summer levels frequently exceeded 2 ppbv. The close proximity of an industrial source (<100 meters) to the sampling site brought with it significantly higher BTEX levels compared to the Vaalpark site. The percentage of data points measured at the Zamdela site that were higher than then 90% percentile (see Table 4.7), linked to extremely high benzene levels (>7 ppbv compared to a proposed ambient standard of 1.6 ppbv) is indicative of the profound impact that these sources are having on measured BTEX concentration levels in this area.

The Industrial site is situated in the middle of the industrial centre. A petrochemical facility, a crude oil refinery and a coal-fired steam facility surrounds this station. The close proximity of these sources (<500 meters) should result in significant levels of BTEX being observed. Moreover, the presence of both low-level and elevated emission sources in the area, may result in significant levels (>1.6 ppbv) being observed throughout the year. Figure 4.21 graphically depicts the impact of ambient temperature on benzene and toluene concentration levels at the Zamdela site.

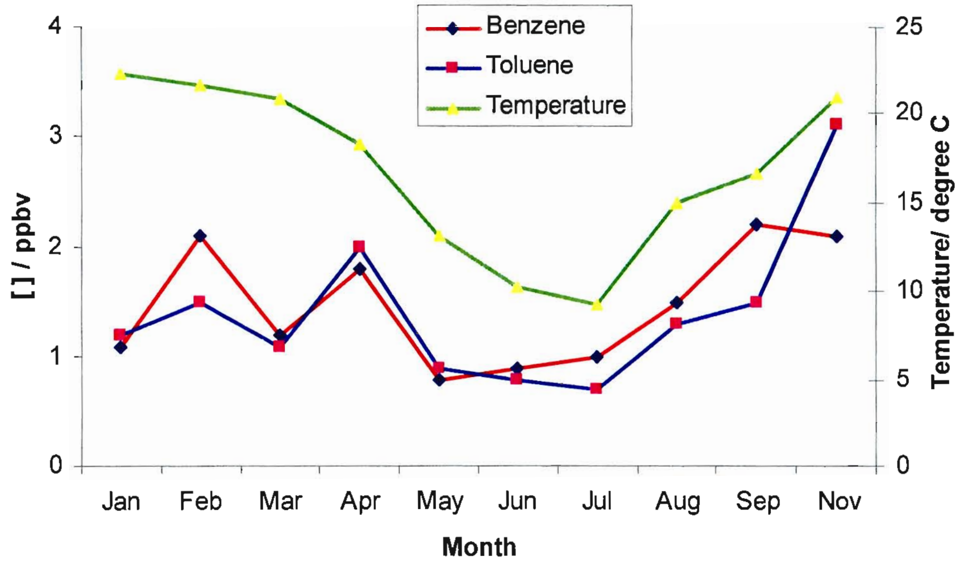


Figure 4.21: Impact of ambient temperature on benzene and toluene concentration levels at the Industrial site during 2002

The industrial station has recorded the second highest mean benzene level during the study period. The mean ambient benzene levels were calculated to be 187% and 150% higher compared to the Vaalpark and Primary school sites, respectively. Ambient levels were found to move in a narrow band between 1ppbv and 2 ppbv, with a marginal decrease during the winter months. The influence of low-level emissions on this site seems therefore realistic, since evaporation would decrease in winter. A similar trend was observed at the Primary school site, were the impact of a waste disposal site was postulated as the reason for the observed lower concentration levels during the winter period.

The influence of low-level surface inversion during the winter months on observed pollution levels has been discussed. The influence of temperature on observed BTEX levels at the different sites has been shown. Wind direction and wind speed also play an important role in determining pollution levels at different sampling sites. Figure 4.22 and Figure 4.23 indicate the relationship between wind speed on observed ambient benzene and toluene concentration levels, respectively.

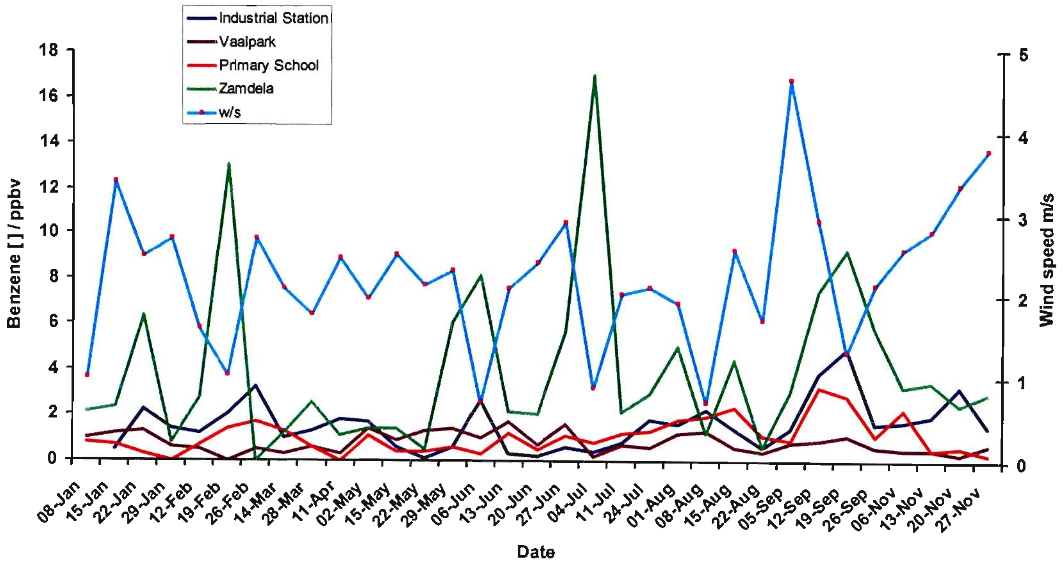


Figure 4.22: Relationship between wind speed and benzene concentration at the sampling sites during 2002

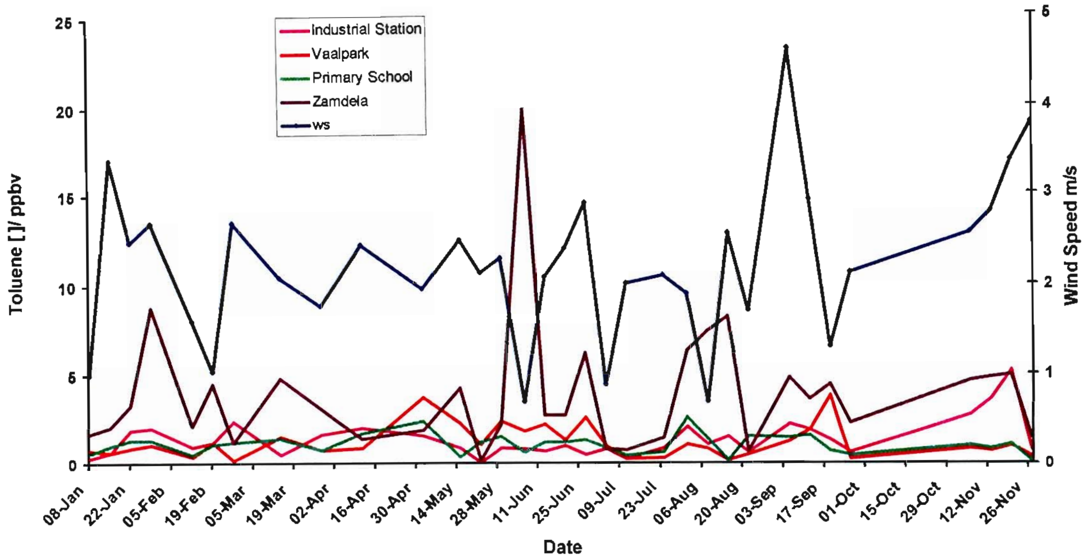


Figure 4.23: Relationship between wind speed and toluene concentration at the sampling sites during 2002

A negative correlation between wind speed and concentration has been observed during this study. Figure 4.22 and Figure 4.23 clearly indicate that calm conditions (<3 m.s^{-1}) have resulted in the highest observed benzene and toluene levels. These calm conditions prevent effective transport and therefore dilution leading to the build-up of benzene and toluene levels over the study area. Table 4.5 indicates that the maximum observed BTEX levels were accompanied by persistent north-westerly winds not exceeding 3 m/s . These conditions prevent the sufficient transport of pollutants thereby reducing the impact of sources outside the study area (>50 kilometres).

Taking into account the oxidation potential of the region, the meteorological conditions and the position of sources in relation to the sampling sites, it becomes clear that industrial pollution sources residing in the study area are having a profound impact on local ambient BTEX concentration levels. The impact of these sources is amplified by the entrainment of industrial pollution during the winter months, and recirculation of pollution over the study area.

4.2.2 2003 BTEX Sampling Campaign

In order to show that the data set obtained for the period January 2002 - November 2002, is a true reflection of the ambient BTEX concentration levels in the Sasolburg area, a comparative study was embarked on in 2003. The results are shown in Table 4.7.

Figure 4.24 shows the prevailing wind direction and wind speed during the 2003 sampling campaign. It is clear from the wind rose that the prevailing wind direction and wind speed compare favourably with conditions experienced in 2002, with north-westerly winds continuing to dominate.

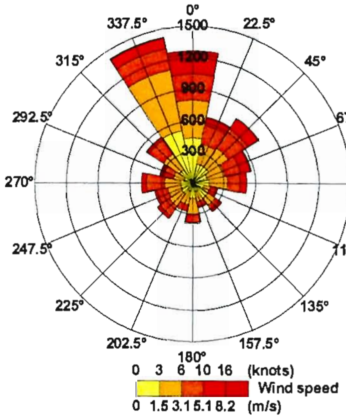


Figure 4.24: Prevailing wind direction and speed over the study area during the 2003 sampling campaign

Table 4.7: Monthly BTEX average (ppbv) obtained at the four stations situated in the Sasolburg area during the 2003 study period (number of observations = 233). Average BTEX concentration levels measured during 2002 are also included for comparative reasons

Species	J	F	M	A	M	J	J	A	S	O	N	D	Ave. 2003	Ave. 2002
PRIMARY SCHOOL														
Benzene	0.6	1.5	1.1	0.1	0.7	0.9	1.2	2.0	2.3	0.8	1.0	1.2	1.1 ± 0.6	1.0 ± 06
Toluene	1.2	1.0	1.2	1.9	1.6	1.2	0.8	1.6	1.1	1.3	0.9	0.9	1.2 ± 0.3	1.1 ± 0.3
Xylene	0.7	1.8	1.7	1.5	1.0	0.9	1.8	3.0	0.9	1.2	1.8	1.6	1.5 ± 0.6	1.3 ± 0.6
Ethylbenzene	1.6	1.1	1.4	0.5	0.5	0.5	1.4	0.9	0.6	0.9	0.5	0.9	0.9 ± 0.4	0.7 ± 0.4
VAALPARK														
Benzene	0.9	0.3	0.4	0.3	1.1	1.1	0.4	0.8	0.8	0.6	0.4	1.3	0.7 ± 0.3	0.8 ± 0.4
Toluene	0.7	0.5	0.9	0.8	2.0	1.7	0.4	0.6	1.5	1.1	0.6	1.5	1.0 ± 0.5	1.2 ± 0.6
Xylene	1.8	1.5	2.0	0.9	2.5	3.5	2.2	3.3	2.2	1.5	1.6	3.0	2.2 ± 0.8	2.5 ± 0.9
Ethylbenzene	1.3	0.9	1.0	0.4	0.9	1.6	0.5	0.6	0.8	0.7	0.3	1.0	0.8 ± 0.4	1.0 ± 0.5
ZAMDELA														
Benzene	2.0	3.6	1.3	0.8	1.6	3.2	5.1	2.0	4.4	1.2	2.1	0.9	2.4 ± 1.4	3.7 ± 2.0
Toluene	2.8	1.8	2.8	1.0	1.5	5.5	0.7	4.0	2.7	0.8	2.7	1.3	2.3 ± 1.4	3.6 ± 2.1
Xylene	1.7	0.1	2.2	0.8	1.7	1.2	1.2	1.0	1.3	3.0	1.1	1.6	1.4 ± 0.7	1.8 ± 0.8
Ethylbenzene	0.5	0.5	0.4	0.1	0.6	0.4	0.4	1.0	0.4	1.0	1.0	0.8	0.6 ± 0.3	0.7 ± 0.4
INDUSTRIAL														
Benzene	1.3	2.5	1.4	2.2	1.0	1.1	1.2	1.8	2.6	2.0	2.5	1.9	1.8 ± 0.6	1.5 ± 0.5
Toluene	1.4	1.8	1.3	2.4	1.1	1.0	0.8	1.6	1.8	2.5	3.7	2.0	1.8 ± 0.8	1.4 ± 0.7
Xylene	1.0	1.1	1.8	1.8	2.9	1.2	1.2	1.2	0.8	1.3	0.7	1.2	1.3 ± 0.6	1.1 ± 0.5
Ethylbenzene	1.1	0.4	0.4	0.8	1.2	0.6	0.6	1.8	0.7	0.9	0.4	1.0	0.8 ± 0.4	0.6 ± 0.4

It is clear from Table 4.7 that the 2003 BTEX concentration profiles at the four stations compare favourably with 2002. The 2003 data showed a slight decrease with BTEX concentrations on average being 13% lower than the previous sampling period. The mean benzene concentration at Zamdela is the exception with a 33% lower benzene average in 2003 compared to 2002. However, when comparing the species averages over the two periods, it becomes clear that the 2002 data set can be considered representative of the BTEX ambient profile over the Sasolburg area.

4.2.3 2006 BTEX Sampling Campaign

Figure 4.25 shows the prevailing wind directions and wind speed observed during the 2006 sampling campaign. Results obtained during the 2006 campaign are shown in Figure 4.26 to Figure 4.29.

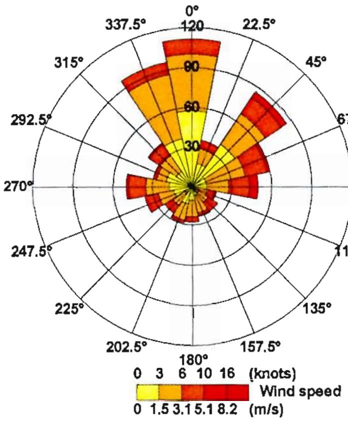


Figure 4.25: Prevailing wind direction and speed over the study area during the 2006 sampling campaign

Figure 4.26 depicting the benzene time series over the 11-month period has shown that Zamdela experiences the highest benzene concentration of all three sites. 24-hour canister sampling was conducted during the 2006 survey and a higher BTEX concentration, compared to 2002, would have been expected due to the impact of night-time inversion trapping pollutants close to the surface. However, the introduction of natural gas as a substitute for coal in a petrochemical facility has brought with it substantial reductions (± 80%) in especially elevated hydrocarbon emissions from this industry. The reasons for this dramatic decrease were discussed in Paragraph 4.1.1. These lower emissions would therefore have a marked impact on the ambient concentrations observed in the study area. The Primary school (A.J. Jacobs) experienced episodes of elevated benzene levels in 2006. In 2002, emissions associated with the evaporation of BTEX from a waste disposal site (tar pits), situated in close proximity to the Primary school, were suggested as the reason for the observed BTEX concentration levels. The introduction of natural gas would, however, drastically reduce the impact of this source, since tar production associated with gasification would have ceased leaving only weather tar exposed to the elements. Significant efforts to rehabilitate these tar pits have started in 2005. During this period fresh tar is brought to the surface resulting in an increase in BTEX emissions. This could explain the findings made during 2006.

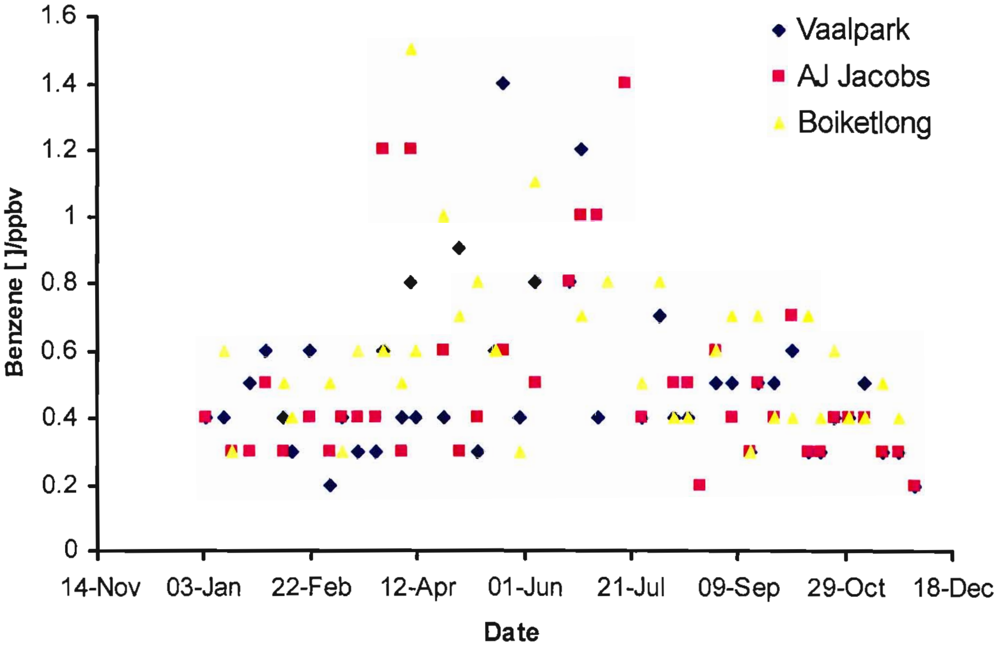


Figure 4.26: Benzene time-series observed at the three ambient BTEX stations during the 2006 sampling campaign in the Sasolburg area

Vaalpark emissions, with the exception of one episode, seem to be within the proposed benzene ambient standard. Toluene levels observed during the 11-month sampling period showed similar trends than those observed in 2002 and 2003 (see Figure 4.27). Zamdela emissions remain the highest relative to the Primary school (A.J. Jacobs) and Vaalpark. The lower toluene levels observed in 2006 compared to 2002 can be associated with the introduction of natural gas, since no other significant change in the source profile took place since 2002.

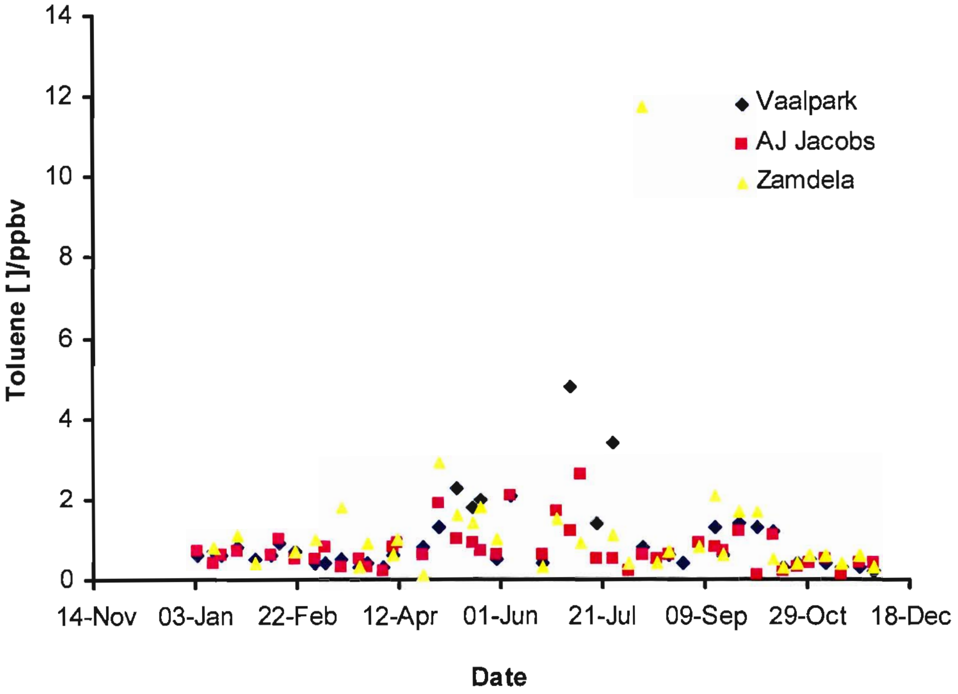


Figure 4.27: Toluene time-series observed at the three ambient BTEX stations during the 2006 sampling campaign in the Sasolburg area

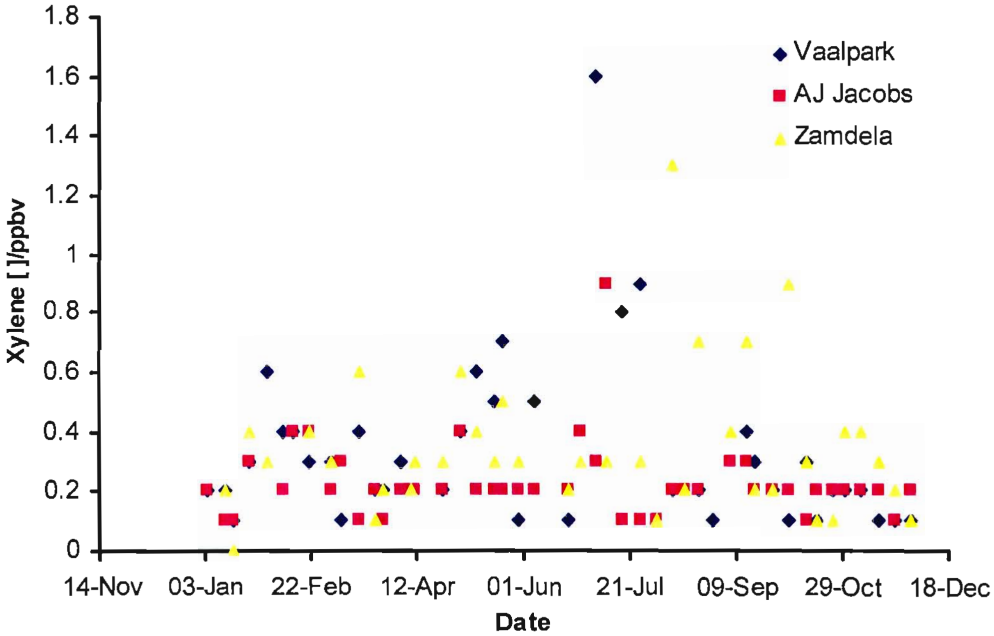


Figure 4.28: Xylene time-series observed at the three ambient BTEX stations during the 2006 sampling campaign in the Sasolburg area

The xylene and ethylbenzene concentration profiles (Figures 4.28 and Figure 4.29, respectively), have indicated similar trends to one another.

Zamdela remained the site with the highest observed concentrations, followed by the Primary school and Vaalpark.

A similar peak in concentration levels observed in the toluene time-series is observed in the ethylbenzene- and xylene time series. The fact that the benzene time-series lacks such a peak indicates that analytical error cannot be assumed the reason. A plausible explanation is that an incident involving these species occurred, and that these chemicals were released in substantial amounts during a short time period. This could, however, not be confirmed.

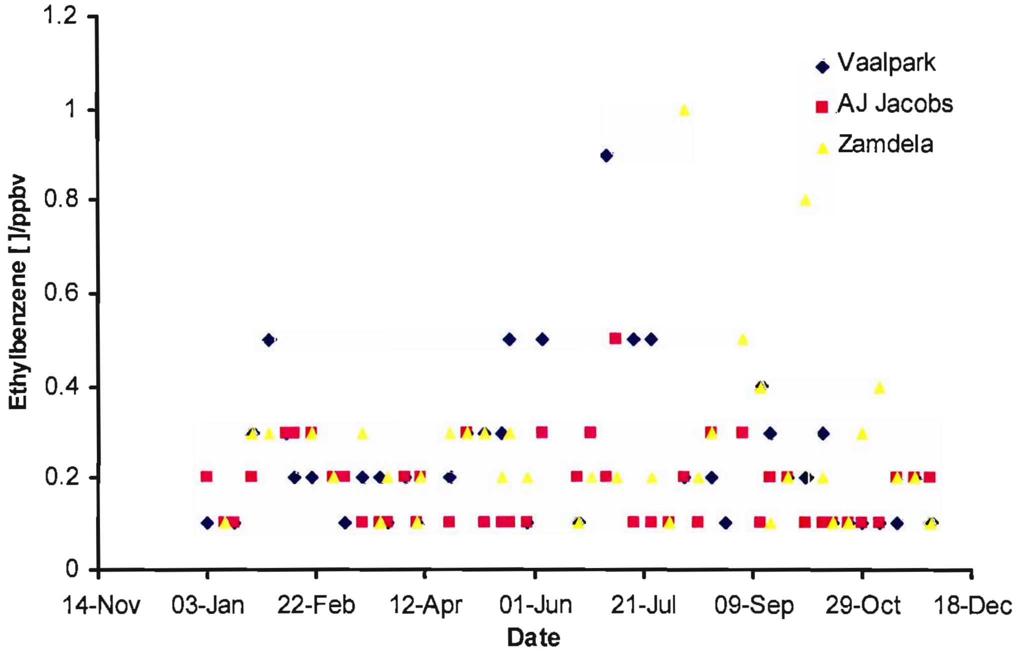


Figure 4.29: Ethylbenzene time-series observed at the three ambient BTEX stations during the 2006 sampling campaign in the Sasolburg area

Table 4.8 is a summary of the average BTEX concentrations observed over the 11-month sampling period. As indicated previously in the time series discussions, it is clear that the concentration levels are much lower than in 2002 and 2003.

Table 4.8: Monthly BTEX averages (ppbv) obtained at the three stations situated in the Sasolburg area during the 2006 study period (number of observations = 135)

Species	J	F	M	A	M	J	J	A	S	O	N	Ave
Primary School												
Benzene	0.3	0.4	0.5	0.7	0.4	0.8	0.9	0.5	0.4	0.4	0.3	0.5 ± 0.2
Toluene	0.6	0.7	0.5	0.6	1.0	1.5	1.2	0.5	0.9	0.4	0.4	1.0 ± 0.4
Xylene	0.2	0.3	0.2	0.2	0.2	0.3	0.4	0.2	0.3	0.2	0.2	0.3 ± 0.1
Ethylbenzene	0.2	0.3	0.1	0.2	0.1	0.3	0.2	0.2	0.2	0.1	0.2	0.2 ± 0.1
Vaalpark												
Benzene	0.4	0.5	0.4	0.5	0.7	0.9	0.4	0.5	0.5	0.5	0.3	0.5 ± 0.2
Toluene	0.7	0.7	0.4	0.6	1.6	1.3	3.1	0.6	1.1	0.7	0.3	0.7 ± 0.8
Xylene	0.2	0.4	0.2	0.2	0.5	0.3	1.2	0.2	0.3	0.2	0.1	0.2 ± 0.3
Ethylbenzene	0.2	0.3	0.2	0.2	0.3	0.3	0.7	0.2	0.3	0.2	0.1	0.2 ± 0.2
Zamdela												
Benzene	0.5	0.5	0.5	0.9	0.6	0.9	0.7	0.6	0.5	0.5	0.4	0.6 ± 0.2
Toluene	1.0	0.6	1.0	0.6	1.7	0.9	1.0	3.3	1.3	0.7	0.5	1.0 ± 0.8
Xylene	0.2	0.4	0.3	0.3	0.4	0.3	0.3	0.6	0.4	0.4	0.3	0.3 ± 0.1
Ethylbenzene	0.2	0.3	0.2	0.2	0.3	0.2	0.2	0.4	0.3	0.3	0.2	0.3 ± 0.1

The 2006 BTEX dataset has confirmed that winter levels exceed those of the summer periods. This finding is consistent with the 2002 and 2003 findings. It is also clear that the 2006 benzene concentration levels do not exceed the proposed ambient benzene standard of 1.6 ppbv (5 μg. m^{-3}). As previously discussed, the only feasible explanation for this change in the concentration profile is the introduction of natural gas.

Furthermore, comparing the two sampling periods (Table 4.9) it becomes clear that the most significant BTEX ambient concentration improvement took place at Zamdela. This was expected, since the monitoring site is situated next to the fence line of the facility that changed its feedstock to natural gas. The effect that sampling time (24 hours compared to 8-hour sampling in 2002) may have on the data set has already been discussed.

Table 4.9: Comparison between the mean average BTEX concentrations (ppbv) at the three Sasolburg sampling sites for the 2002 and 2006 study periods

Site	Primary school		Vaalpark		Zamdela	
Year	**2002**	**2006**	**2002**	**2006**	**2002**	**2006**
Benzene	1.0	0.5	0.8	0.5	3.7	0.6
Toluene	1.1	1.0	1.2	0.7	3.6	1.2
Xylene	1.3	0.3	2.5	0.2	1.8	0.3
Ethylbenzene	0.7	0.2	1.0	0.2	0.7	0.3

It seems therefore that the conclusion made after the 2002 study, whereby industrial emissions were postulated to play an overwhelming role in determining BTEX levels in the study area, was valid

4.3 CONCLUSION

The 2002 study clearly indicated that benzene, toluene, xylene and ethylbenzene are ubiquitous throughout the study area. The results have indicated the influence of industrial emissions on observed ambient BTEX levels. The influence of meteorological conditions, notably temperature, wind speed and direction and low-level surface inversion on the BTEX profile has been shown. Although meteorological coupling, based on Hysplit back trajectory modelling between Johannesburg and the study area has been proven; the impact thereof on observed BTEX levels at the sites was shown to be limited. Seasonal differences in the oxidation potential and oxidation rate of BTEX in the region brought about by a decrease in the photolysis rate coefficient (jO^1D) during the winter months were calculated. The impact of this change on the BTEX abundance was, however, shown to be small compared to entrainment brought about by low-level surface inversion and stable atmospheric conditions during the winter.

The comparative study undertaken in 2003 has shown that the findings based on the 2002 data set are valid and a true reflection of the BTEX concentration levels in the study area at that time.

The 2006 campaign has shown marked improvements in BTEX concentrations. The introduction of natural gas to the area has brought with it significant improvement in specifically benzene emissions.

Furthermore, the study has indicated that levels observed within the study area compare favourably with global benzene trends of between 1 and 50 ppbv. Xylene, ethylbenzene and toluene levels have shown a similar trend, although the levels observed in the Sasolburg area seem to be at the lower end of globally observed values (see Paragraph 2.2.6). Benzene concentration levels in Sasolburg were observed to be much lower than levels reported in high density freeway conditions in Johannesburg (9.8 ppbv) (see Table 2.8). Standard deviations on mean BTEX values have been shown to be high, compared to the results obtained in the United Kingdom (see Table 2.7). These higher deviations may be attributed to complex source dynamics in the Sasolburg area, compared to the United Kingdom, where BTEX concentration profiles are dominated by vehicle emissions that seem to be more constant by nature.

CHAPTER 5

ASSESSMENT OF THE IMPACT ASSOCIATED WITH AMBIENT BTEX SPECIES IN THE SASOLBURG AREA

In this Chapter...

This chapter will describe the methodology used to assess the direct and indirect impacts associated with BTEX pollution (Par. 5.1). The benzene results obtained during a BTX passive sampling study undertaken in 2004 are discussed (Par. 5.2.1.1). A comparative benzene study undertaken at a control site (Potchefstroom) is also discussed (Par. 5.2.1.2). The results from both the Sasolburg and Potchefstroom sites are examined utilising the Margin of Exposure approach (MOE) (Par. 5.2.1.3). Results from the 2006, 24-hour canister sampling campaign are compared with the 2004 findings, once more using the MOE approach (Par. 5.2.1.3). The relative contribution of BTEX to ozone and SOA formation is discussed (Par. 5.2.2). Conclusions based on these findings are given in Paragraph 5.3.

5.1 EXPERIMENTAL PROCEDURE

5.1.1 Direct Benzene Health Impact Assessment

5.1.1.1 Methodology

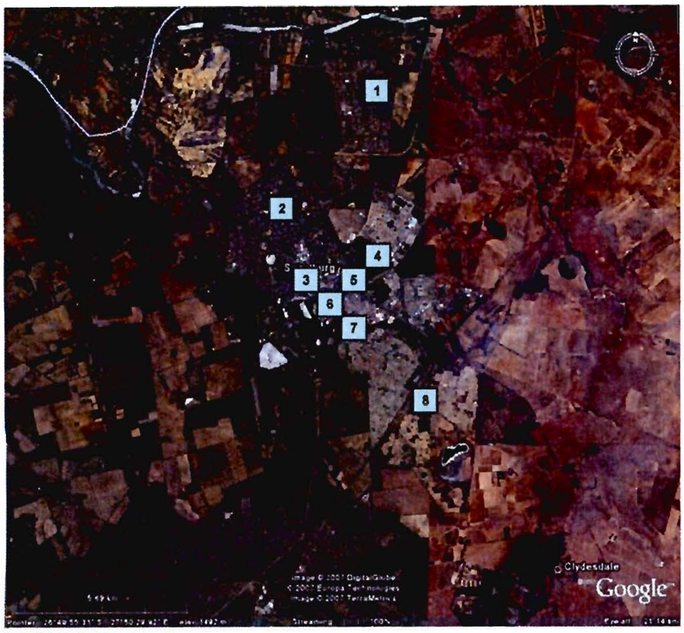
Passive samplers (see Figure 5.1) are cost effective alternatives to active sampling for BTX in ambient air. Due to the potentially high variability of BTX concentration levels in the Sasolburg area, investigations into the chronic health effect of benzene may also require a sampler with longer exposure duration than the typical < 12 hours used for active sampling (Cohen *et al.*, 1990).

Passive samplers were chosen because they are relatively inexpensive to use, as well as reliable. Typical correlations between diffusive and active samplers for benzene, toluene, ethylbenzene and xylene are $r^2 = 0.943$ (see Paragraph 2.2.4, Figure 2.6) (IVL, 1998).

Figure 5.1 is a photograph of a commercial BTX sampler used in this study. The BTEX samplers were supplied by the IVL: Swedish Environmental Research Institute. This study was conducted in 2004 over nine months at eight sites in the greater Sasolburg area (see Figure 5.2). Average exposure times for the passive samplers at the sites were 30 days.

Meteorological information was obtained from the Vereeniging Weather Station. Three electrified residential sites, three industrial sites, one semi-electrified site and one non-electrified site were chosen. Sites 1, 3, 4 and 7 are the Vaalpark, Primary school, Industrial and Zamdela sites described in Chapter 4 (see Paragraph 4.1.1 for further detail regarding site characteristics). Site 2 is situated in close proximity to the Sasolburg Hospital and represents the north-west boundary of Sasolburg. This site is considered to be mainly influenced by sources situated to the north of the study area. Site 8 is situated in an area dominated by domestic coal burning and represents the southern boundary of the study area. Sites 4, 5 and 6 are situated within the fence line of a petrochemical facility and therefore represent industrial air.

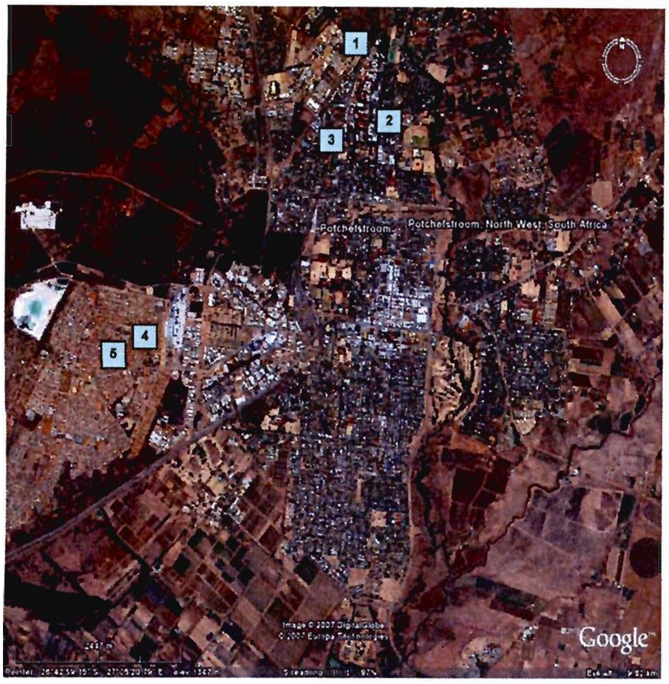
Figure 5.1: Illustration of BTX Passive sampler used during the 9-month study period



1. Electrified Residential
2. Electrified Residential
3. Electrified Residential
4. Industrial
5. Industrial
6. Industrial
7. Semi-Electrified Residential
8. Non-electrified Residential

Figure 5.2: Position of the sampling sites in the greater Sasolburg area during the health risk assessment (Google.earth.com)

In order to asses the findings, a similar sampling campaign was conducted at a control site (Potchefstroom) over a similar period of nine months. (see Figure 5.3 for control site sampling positions). These results will be compared to the results in the Sasolburg area. Five sites were chosen within the Potchefstroom area. Site 1 is situated in close proximity to the University entrance and may be influenced by vehicle emissions, while Site 2 is situated in a residential area. Site 3 is situated in a residential area in close proximity to a filling station. Sites 4 and 5 are situated in close proximity to coal burning activities, with Site 5 being an area where coal is used predominantly as energy source.



1. Electrified Residential
2. Electrified Residential
3. Electrified Residential (filling Station)
4. Semi-electrified Residential
5. Non-electrified Residential

Figure 5.3: Potchefstroom passive sampling network layout during health risk assessment (Google.earth.com)

The margin of exposure (MOE) approach was used to evaluate the Sasolburg and Potchefstroom residents' exposure to benzene at the different sites. Given the fact that the mode of action of benzene exposure-induced leukaemia is not conclusive to support a non-linear dose-response analysis approach, the MOE serves as a default approach (US-EPA, 1998).

The MOE is defined as "the lethal exposure dose resulting in 10 percent of population mortality (LED_{10}) or other point of departure (POD) divided by the real or postulated exposure". The point of departure is the dose-response point that indicates the start of a low-dose extrapolation (IRIS, 2001).

Benzene exposure, based on observations by Rinsky *et al.* (1981, 1987) may increase the risk of contracting leukaemia at the level of 40 ppm-years of cumulative exposure. Therefore, benzene exposure at the 40 ppm-years level would be equivalent to a lifetime (76 years) exposure of 120 ppbv. Consequently, 120 ppbv would be a reasonable point of departure (POD) where the area under the dose-response curve is uncertain (US-EPA, 1998). Rinsky's exposure estimates are considered the lowest currently available (Duarte-Davidson *et al.*, 2001) and therefore the 120 ppbv POD seems the most conservative and appropriate to use in this study. *If the observed* ambient benzene concentration levels are compared with the POD (120 ppbv), the associated cancer risk can be determined for the population residing in the area. For example: Assuming the general lifetime exposure to benzene is 4.7 ppbv, a MOE of 26 will be derived. It is clear from this approach that as the MOE value increases, the risk decreases and vice versa.

Significant changes in the source characteristics of the region associated with industrial fuel switching from coal to natural gas in 2005, have necessitated the need to screen the 2006, 24-hour canister sampling campaign results utilising the MOE approach. The experimental approach is discussed in Paragraph 4.1. The three sampling sites chosen for the 2006 canister sampling programme (Par. 4.1.2) correspond with Sites 1, 3 and 7 chosen during the passive sampling campaign in Sasolburg.

5.1.2 Indirect BTEX Impact Assessment

5.1.2.1 Methodology

Ozone and Secondary Organic Aerosol (SOA) formation associated with Volatile Organic Compounds (VOCs) have been described in Chapter 2 as important secondary air pollutants, which may have a detrimental impact on human health and the environment. In order to determine the indirect impacts of BTEX species in the Sasolburg area, the 2002 BTEX data set discussed in Chapter 4 has been used to assess the relative contribution of BTEX to ozone and SOA formation. Published Photochemical Ozone Creation Potential (POCP) data for the selected VOCs have been used to determine the relative contribution of BTEX to ozone formation. A similar approach was followed in assessing the contribution of BTEX species to SOA levels in the study area.

5.2 RESULTS

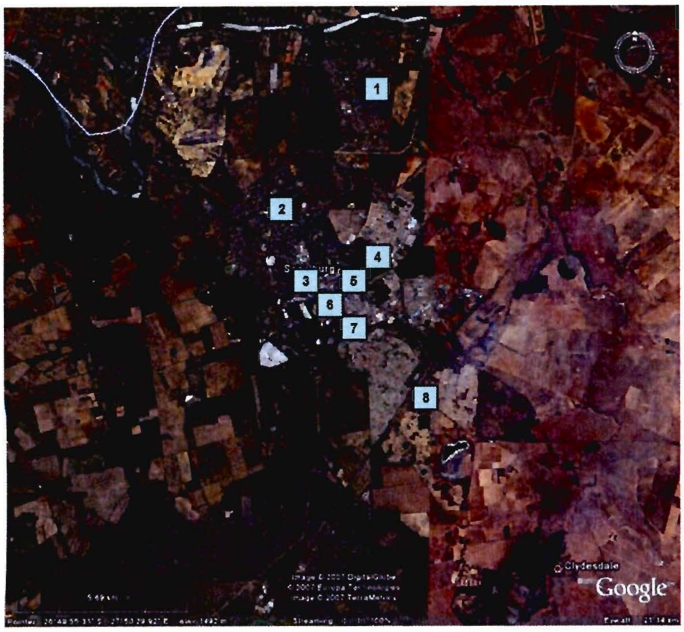
5.2.1 Direct Benzene Health Impact Assessment

Chapter 4 highlighted the need to assess the health impact of benzene on the community residing in the study area, due to elevated annual benzene results. The passive sampling campaign enabled the determination of benzene averages based on a monthly time-integrated exposure of samples. This was essential, since benzene health effects are based on long-term exposure as explained in Paragraph 5.1.1. The results obtained for the Sasolburg area are discussed in Section 5.2.1.1.

5.2.1.1 Sasolburg Benzene Concentration Profile

The nine-month mean benzene concentration determined during the health assessment (3.5 ppbv) was substantially higher than the averages obtained during the 2002 and 2003 sampling campaigns (1.8 and 1.5 ppbv, respectively), if the observed benzene concentration at the same four sites is taken into consideration. The canister sampling was conducted only during the day-time in 2002 and 2003 (Par 4.1). Considering the observations of Barletta *et al.* (2002), which indicated that night-time concentrations of hydrocarbons are higher than levels observed during the day-time (see Paragraph 2.2.6), the reason for the higher values observed during the passive sampling campaign becomes clear. Barletta postulated low-level inversion during the night-time as the reason for these higher levels.

The concentration levels observed at the eight stations are shown in Figure 5.4. The mean benzene levels increased towards the Central Business District (CBD) and industrial areas, located in the centre of the map. The remote sites (Site 1 and Site 8) indicated much lower levels. Similar findings were made during the 2000, 2002 and 2003 campaigns (Chapter 3 and Chapter 4).



Mean Benzene Concentration (ppbv)

1. Electrified Residential	1.9
2. Electrified Residential	1.5
3. Electrified Residential	2.4
4. Industrial	3.9
5. Industrial	11.3
6. Industrial	4.7
7. Non-electrified Residential	5.6
8. Non-electrified Residential	1.9

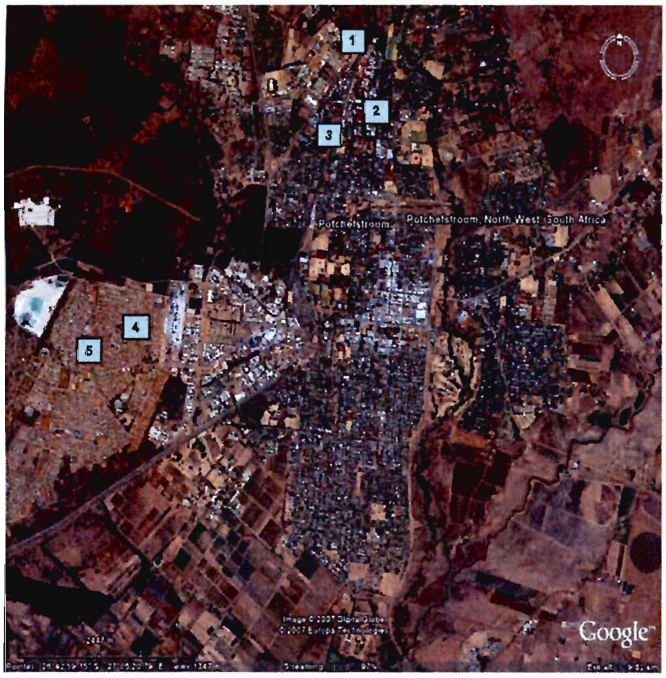
Figure 5.4: A map indicating the position of the monitoring sites and the observed annual average benzene concentration at each of the sites (Google.earth.com).

The very high levels of benzene experienced at industrial sites 5 and 6 will influence the benzene levels observed at the semi-electrified residential area; providing the prevailing wind direction is from the north-west. This highlights the importance of fugitive emissions released at low level on the health of the community residing in close proximity to possible sources. The impact of low-level emissions on ambient air quality in the study area has been highlighted in Chapter 3 and 4. The study area is particularly plagued by the phenomena of residential and industrial region integration. Residential areas are adjacent to chemical industries, making air quality management a challenging task in the area. The situation becomes even more complex if one considers that residential coal burning, taking place in close proximity to industrial areas, is the norm rather than the exception. This highlights the need for fence-line monitoring, linked to wind direction and speed observations as a means to determine source contributions.

Paragraph 5.2.1.3 will compare the results obtained in the study area with those of the control site (Paragraph 5.2.1.2) utilising the Margin of Exposure approach to assess the health impact of the observed levels (see Paragraph 5.1.1).

5.2.1.2 Potchefstroom Benzene Concentration Profile

The control site included the city of Potchefstroom, which is situated 90 kilometres north-west of Sasolburg. The results obtained are shown in Figure 5.5. It is clear from the data obtained at these sampling sites that the ambient benzene levels at Potchefstroom are much lower than levels observed in the Sasolburg area. The only exception was the sampling site situated near a filling station (Site 3), which compared favourably with results obtained near the industrial centre of Sasolburg.



Benzene Concentration (ppbv)

1. Electrified Residential	0.3
2. Electrified Residential	0.3
3. Electrified Residential (filling Station)	4.8
4. Semi-electrified Residential	0.4
5. Non-electrified Residential	0.4

Figure 5.5: Map showing the position of the sampling sites and benzene annual average concentrations in parts per billion at Potchefstroom (Google.earth.com)

The annual average for the Potchefstroom sampling sites was 0.35 ppbv (excluding the filling station), which is considerably lower compared to the Sasolburg mean concentration value of 4.15 ppbv (industrial sites included). The concentration levels observed in the Potchefstroom area also comply with the proposed ambient annual standard for benzene of 1.6 ppbv.

Surprisingly, domestic coal burning in Potchefstroom (Sites 3 and 4) only marginally influenced benzene levels, while the influence of vehicle emission in Sites 1 and 4 was less than expected, since Site 1 was situated next to a busy road entrance to the University. Adequate ventilation in the sampling area is proposed as the reason for these lower BTEX levels.

Comparing the residential sites in Sasolburg with those in Potchefstroom, it becomes evident that the residential areas in Sasolburg are experiencing much higher levels of benzene than Potchefstroom, based on the 2004 data. Vehicle emissions are not playing a significant role in Potchefstroom, as shown by the low levels observed at the University entrance.

5.2.1.3 Margin of Exposure Assessment

- *Passive Sampling Results*

In Paragraph 5.1.1.1, the principals behind the MOE approach were discussed. Moreover, the approach indicates that the larger the margin, the smaller the likelihood of contracting cancer due to benzene exposure becomes. Table 5.1 summarises the findings of both the Sasolburg and Potchefstroom studies.

Table 5.1: Summary of Benzene results with related Margin of Exposures (MOEs) in the Sasolburg and Potchefstroom areas during 2004 (n = 9/site)

Sampling Site	Town	Nine Month Average (ppbv)	MOE
Electrified Residential	Sasolburg	1.9 ± 0.3	63
Electrified Residential	Sasolburg	1.5 ± 0.3	80
Electrified Residential	Sasolburg	2.4 ± 0.5	50
Industrial Residential	Sasolburg	3.9 ± 0.9	31
Industrial	Sasolburg	11.3 ± 2.5	11
Industrial	Sasolburg	4.7 ± 1.0	26
Semi Electrified Residential	Sasolburg	5.6 ± 1.3	21
Non-electrified Residential	Sasolburg	1.9 ± 0.7	63
Electrified Residential	Potchefstroom (Control)	0.3 ± 0.1	400
Electrified Residential	Potchefstroom(Control)	0.3 ± 0.1	400
Electrified Residential (Filling Station)	Potchefstroom (Control)	4.8 ± 0.8	25
Semi-Electrified Residential	Potchefstroom(Control)	0.4 ± 0.2	300
Non-electrified	Potchefstroom(Control)	0.4 ± 0.1	300

It follows from Table 5.1, that the MOE approach confirmed previous findings that the Sasolburg CBD and industrial areas do pose an unacceptable high risk, if compared to the proposed benzene ambient standard of 1.6 ppbv, which aims to minimise the potential health risk associated with *benzene in a* healthy population of people (Chapters 3 and 4). The high MOEs experienced at the more remote sites are, however, encouraging, illustrating that the benzene problem is more localised in the Sasolburg CBD area. Nevertheless, the close proximity of residential areas to industrial activity in the Sasolburg area, does pose a potential health problem. This is clear from the low MOEs experienced at the semi-electrified area in the Sasolburg area. The effect of domestic coal burning in the Vaal Triangle is, however, expected to be significant, compared to the control site. This can be attributed to a much higher population density in the Sasolburg area compared to that of Potchefstroom.

24-hour canister results

Table 5.2 summarises the mean benzene concentrations and associated MOEs at three sites in Sasolburg during 2004 and 2006, respectively.

Table 5.2: Summary of benzene results with related Margin of Exposures (MOEs) in the Sasolburg area during the 2004 passive sampling campaign (n = 9/site) and the 2006, 24-hour canister campaign (n = 48/ site)

Sampling Site	2004 passive sampling campaign		2006, 24-hour canister campaign	
	Average (ppbv)	MOE	Average (ppbv)	MOE
Electrified Residential (Vaalpark)	1.9 ± 0.4	63	0.5 ± 0.4	240
Electrified Residential (Primary School)	2.4 ± 0.5	50	0.5 ± 0.5	240
Semi-electrified Residential (Zamdela)	5.6 ± 1.3	21	0.6 ± 1.3	200

It is clear from Table 5.2 that benzene concentration levels in the Sasolburg area have drastically been reduced since 2004. The high MOE values of between 200 and 240 in 2006 compared to levels ranging from 21 to 63 in 2004 are indicative of this. In Chapter 4, the industrial switching of feedstock from coal to natural gas has been postulated as a major reason for these marked improvements in the region. Furthermore, the *introduction* and successful uptake of catalytic cars in South Africa may have contributed to lower benzene emissions from vehicles.

5.2.2 Indirect BTEX Impact Assessment

Table 5.3 summarises the most prominent VOC species detected utilising the US-EPA compendium method TO-14a, during the 2002 Sasolburg BTEX study, while Table 5.4 summarises the POCP values for each of the species in relation to ethylene.

Table 5.3: Summary of the most prevalent VOC species identified over a 10-month canister sampling programme in the Sasolburg area (Jan 2002 - Nov 2002) (Number of samples = 140)

VOC Species	Max 8 hr [ppbv]	Annual 8hr Mean [ppbv]
Methylene Chloride	11.8	0.4
Chloroform	10.0	0.2
Benzene	16.9	1.8
Trichloroethylene	2.4	<0.1
Toluene	19.9	1.9
Tetrachloroethylene	0.9	<0.1
Ethylbenzene	2.9	0.8
Xylene	8.9	1.7
Styrene	25.9	0.9
1,3,5-Trimethylbenzene	8.8	0.1
1,2,4-Trimethylbenzene	7.1	0.6

Assessing the ozone forming potential of species detected, it becomes clear that substituted benzene derivates such as 1,3,5- trimethylbenzene have the greatest potential to form ozone, followed by o-xylene and toluene (see Table 5.4). The potential for benzene to form ozone is indicated as being relatively low.

Table 5.4: POCP values for selected organic compounds relative to ethylene (Derwent *et al.*, 1998)

VOC Species	POCP
Ethylene	100.0
Chloroform	2.3
Benzene	21.8
Toluene	63.7
Tetrachloroethylene	2.9
Trichloroethylene	32.5
Ethylbenzene	7.3
o-Xylene	105.0
Styrene	14.2
1,3,5-Trimethylbenzene	138.1
1,2,4-Trimethylbenzene	127.8

Figure 5.6 illustrates the potential of the different species to form ozone relative to the ozone forming potential of benzene.

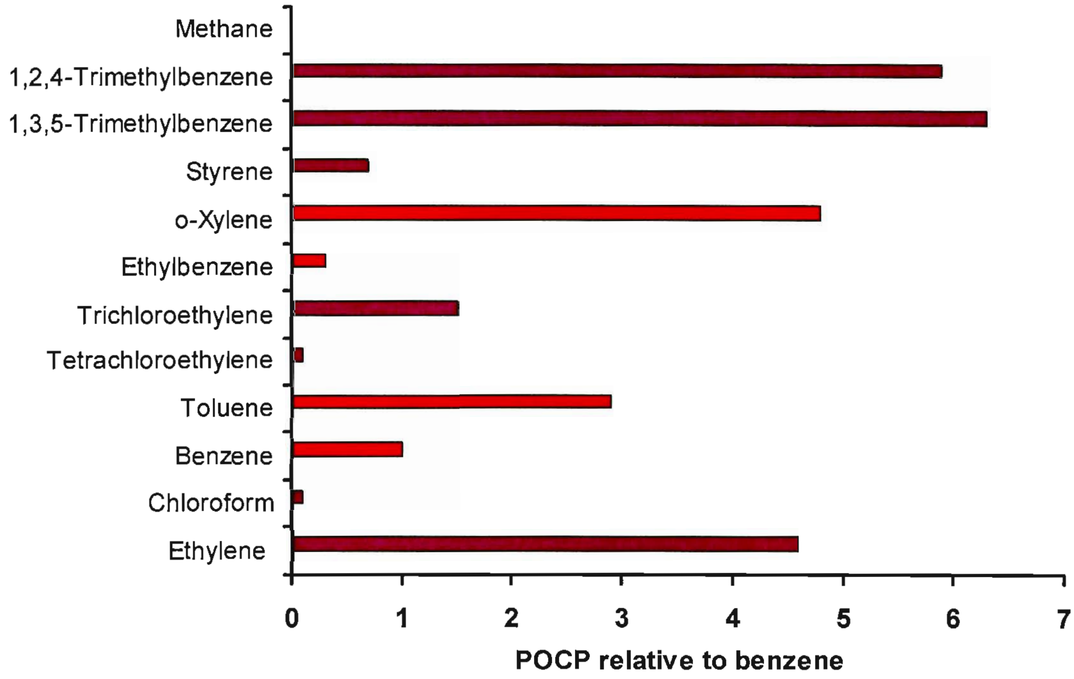


Figure 5.6: POCP for selected VOCs in relation to the ozone forming potential of benzene

In assessing the relative contributions associated with BTEX, o-xylene has been found to have the greatest potential to form ozone, followed by toluene, benzene and ethylbenzene (see Figure 5.5).

If consideration is given to the abundance of these BTEXs, especially benzene (mean < 2 ppbv) in the study area, the impact of BTEX on observed ground-level ozone concentration levels at any time must be considered small compared to the ozone formed due to the presence of methane (> 1.5 ppm), carbon monoxide (>0.4 ppm) and other NMHC compounds (>2 ppm) associated with industrial and biogenic sources in the area. Therefore, it can be assumed that the indirect impact of BTEX due to the formation of ozone in the study area on human health and the environment at large is small.

Due to the fact that only selected hazardous VOCs have been analysed, the qualitative contribution of the BTEX species to ground-level ozone concentration levels in the area could not be established. A detailed VOC emission inventory, including biogenic VOCs, would be needed to conduct such a study.

In Chapter 2 the SOA yield associated with BTEX was discussed. It has been shown that the contribution of benzene to SOA formation in rural areas is much higher than previously estimated. The importance of knowing the ambient NO_X concentration when assessing percentage yield associated with aromatics and specifically benzene was highlighted. Assuming a low NO_X environment (<100 ppb) exists over Sasolburg, theoretical yields for xylene of between 35% and 37% can be obtained, compared to between 29% and 31% for toluene and 37% for benzene. In view of the relatively low BTEX concentration levels (< 2 ppbv) during the study period in relation to other NMHC species (>2 ppm), a small contribution to SOA levels due to the presence of BTEX is expected (Seinfeld, 2008).

Unfortunately, the contribution of BTEX to SOA abundance in the study area, in relation to other species, could not be assessed due to a lack of a comprehensive VOC emission inventory for the area.

5.3 CONCLUSION

The 2004 health risk assessment (margin of exposure assessment) clearly indicated that benzene levels in the study area pose a risk to community health. The much lower benzene levels observed at the control site (Potchefstroom) were indicative of the problem facing the study area. The close proximity of residential areas to industrial activity has been highlighted as a serious concern and a hurdle in solving the problem. The Sasolburg area exceeded the proposed ambient benzene standard (1.6 ppbv) in certain areas in 2004, confirming the observation made in Chapters 3 and 4, that the ambient levels of benzene are a cause of concern based on the 2002 and 2003 study observations.

Comparing the 2004 results with observations made in 2006, it became clear that the situation has improved significantly since the introduction of natural gas into the region in 2005. MOE values of 200 to 240 in 2006 compared to MOE values of 21 in 2004 in Sasolburg clearly indicated a substantial improvement with regard to the exposure of the Sasolburg community to unacceptable levels of benzene.

Comparing these results with levels of 0.2 ppbv – 1.3 ppbv (MOE values of 600 – 92) experienced in the United Kingdom (Ryedale DC, 2006), it becomes clear that benzene exposure in the Sasolburg community, based on the 2006 data compares favourably with findings made in the United Kingdom.

Indirect impacts associated with BTEX, including ozone and SOA formation, were discussed. The formation of these secondary pollutants is, however, expected to be limited due to the low abundance of the precursor species (BTEX) in the ambient air over the study area compared to other NMHC species. Therefore, the direct health impacts associated with BTEX are considered the dominant risk factor associated with these compounds in the study area.

CHAPTER 6

CRITICAL EVALUATION AND RECOMMENDATIONS

In this Chapter…

The study as a whole is critically evaluated against the goals stated for the project (Par. 6.1). Future challenges and research opportunities are also entertained (Par. 6.2).

6.1 PROJECT EVALUATION

The objectives and goals for the study were indicated in Chapter 1. A critical evaluation of the outcome of this study in relation to the objectives will not only highlight the success of the study and its contribution it has made to our understanding of volatile organic pollutants, but will also indicate possible future research based on the experience gained during the execution of this study.

i) The determination of the lower tropospheric BTEX concentration profile for the Sasolburg and South African Highveld areas was successfully completed. Average benzene levels, observed across the Mpumalanga area (1.4 ppbv), were found to be substantially lower than levels observed in Sasolburg (7.4 ppbv). Moreover, the study has shown, for the first time, the predominant impact of industrial emissions on observed ambient BTEX concentration levels in Sasolburg and the Mpumalanga Highveld area. The comparison between the Mpumalanga and Sasolburg ambient BTEX concentration levels was the key in assessing the severity of BTEX pollutants in the study area. The findings of the study not only gave valuable information on lower tropospheric and ground level BTEX concentration levels, but also served as a justification for further research on BTEX species in the Sasolburg area. The fact that pending ambient benzene standards were exceeded in the Sasolburg area (1.6 ppbv) also confirmed the need for further research.

ii) The compilation of a ground-level BTEX concentration profile for the Sasolburg area was also successfully completed. The development of the BTEX profile is seen as a breakthrough, since no such profile of this nature has ever been compiled for an area in South Africa. Results obtained indicated that BTEX species are ubiquitous in the ambient air over the Sasolburg area. Ambient benzene concentration levels (1.8 ppbv) were shown to exceed pending ambient standards of 1.6 ppbv. These findings confirmed the observations made during the 2000 study that the levels of benzene in the Sasolburg area were unacceptable. In contrast, the United Kingdom National Non-automatic Monitoring Network has indicated annual average benzene levels of between 0.16 ppbv and 1.28 ppbv for the period 2002-2003 (Ryedale DC, 2006). The impact of Johannesburg on observed BTEX concentration levels in the Sasolburg area was also postulated. However, the impact of these external sources on the BTEX abundance was shown to be small compared to entrainment brought about by low-level surface inversion and stable atmospheric conditions during the winter. A follow-up study undertaken in 2003 confirmed the findings of 2002, and thereby stressed the validity of the data set.

Furthermore, the incorporation of a sampling campaign in 2006, utilising a 24-hour canister-sampling regime, has shown the drastic reduction in ambient benzene concentration levels that can be achieved if emissions are mitigated at source (see Table 6.1). The fuel switching from coal to natural gas in the area, commissioned in 2005, brought with it significant reductions in air emissions, notably benzene. The 2006 study did not form part of the initial scope of this work, but given the significance of these steps taken by industry, a decision was made to incorporate these findings.

Table 6.1: Comparison between the mean average BTEX concentrations (ppbv) at the three Sasolburg sampling sites for the 2002 and 2006 study periods

Site	**Primary School**		**Vaalpark**		**Zamdela**	
Year	**2002**	**2006**	**2002**	**2006**	**2002**	**2006**
Benzene	1.0	0.5	0.8	0.5	3.7	0.6
Toluene	1.1	1.0	1.2	0.7	3.6	1.2
Xylene	1.3	0.3	2.5	0.2	1.8	0.3
Ethylbenzene	0.7	0.2	1.0	0.2	0.7	0.3

In order to assess the effectiveness of the reduction strategies by industry, a comparison between the study area and similar industrial areas, locally and internationally, needs to be made. Table 6.2 indicates benzene levels experienced at several densely populated areas with similar industrial activity levels.

Table 6.2: Comparison between the average benzene concentration (ppbv) levels at several densely populated areas with similar industrial activities

City	**Concentration ppbv**	**References**
Sasolburg (2002)	1.8	Current study
Sasolburg (2006)	0.5	Current study
Table View, Cape Town	1.4 – 1.9	Burger, 2006
Durban South Basin	3.5	Weekes, 2002
São Paulo (Brazil)	5.2	Gee & Sollars, 1998
Mexico City	1.7	Bravo et al., 2002
Santiago (Chile)	4.6	Gee &Sollars
Baltimore(USA)	2.3	Vukovich, 2000
Alabama (USA)	(0.2 – 2.0) ppb	USEPA, 2006
Austen, Texas	0.5 ppb	USEPA, 2006
Pascagoula, Mississippi	0.4 ppb	USEPA, 2006

Considering the benzene levels experienced at locations with similar industrial activity and temperature regimes compared to the study area, notably the southern regions of the United States of America and the Durban South Basin, it becomes clear that in the study area benzene levels compare favourably with levels experienced in South Africa and internationally, after the implementation of natural gas. This finding highlights the effectiveness of cleaner feedstock in industrial processes as part of the strategy to reduce an industry's environmental footprint.

iii) The assessment of the direct health impacts associated with ambient benzene levels in Sasolburg and Potchefstroom (control site) was deemed to be successful.

The health risk assessment, conducted in 2004, made use of passive samplers to gather information on benzene ambient levels at eight sites in the Sasolburg area. In order to assess the Sasolburg benzene findings, a similar study was embarked on in Potchefstroom (largely non-industrial site). Passive samplers have been used in South Africa to assess inorganic ambient levels at remote sites for some time. This study, however, allowed the determination of BTX concentration levels over extended periods. A study of this magnitude and duration, involving BTX passive samplers, has not previously been undertaken in South Africa. This study confirmed the value of this methodology in obtaining sound data in a cost-effective manner. The study brought with it a realisation that benzene levels in the Sasolburg area were unacceptable. Average benzene concentration levels of 4.2 ppbv, compared to observed levels of 1.2 ppbv in Potchefstroom, highlighted the problem. Moreover, this study confirmed the exceeding of the pending benzene ambient standard of 1.6 ppbv in the Sasolburg area for the third time. The study therefore underlined the fact that the establishment of a priority area, including the Sasolburg area (based on the 2000 to 2004 results discussed in Chapters 3 and 4), was the correct step taken by the South African Government.

iv) An assessment of the indirect impacts associated with BTEX induced ozone and secondary organic aerosol formation was also embarked upon and successfully completed. Qualitative analysis of the information, however, indicated a possible small impact compared to the direct impact of BTEX exposure.

In light of these findings, the overall study is deemed successful, considering the fulfilment of the stated goals, accompanied by the realisation that each study undertaken has contributed to the understanding of ambient BTEX pollutants and its impact over the study area and in South Africa. Moreover, the study has shown that similarities do exist between locally and internationally observed BTEX trends. This realisation is fundamental in managing VOC pollution in South Africa. International mitigation strategies for hydrocarbons may therefore succeed in South Africa, especially given the fact that the study proved that the South African situation is not as unique as previously envisaged. Table 6.3 aims to summarise the findings obtained during the study.

Table 6.3: Summary of findings obtained during the BTEX study

Aspect	Key Findings
Lower tropospheric BTEX assessment (Chapter 3)	The study highlighted that ambient BTEX levels were at dangerous levels, with benzene exceeding the proposed ambient standard of 1.6 ppbv at all the monitoring sites. Comparison of the ratio between benzene and toluene in background air strongly suggests strong sources of benzene exist in the region and the relative abundance of benzene compared to toluene only falls to typical industrial/urban levels when such air is mixed into the air masses. In-flight studies undertaken over the Mpumalanga Highveld and the Sasolburg area highlighted the impact of industrial emissions on ambient BTEX levels in the region.
2002 Canister Sampling Campaign (Chapter 4)	Taking into account the oxidation potential of the region, the meteorological conditions and the position of sources in relation to the sampling sites, it becomes clear that industrial pollution sources residing in the study area have a profound impact on local ambient BTEX concentration levels. The impact of these sources is amplified by the entrainment of industrial pollution during the winter months, and recirculation of pollution over the study area.
2003 Canister Sampling Campaign (Chapter 4)	The comparative study undertaken in 2003 has shown that the findings based on the 2002 data set are valid and a true reflection of the BTEX concentration levels in the study area at that time.
2006 Canister Sampling Campaign (Chapter 4)	The study has indicated that levels observed within the study area compare favourably with global BTEX trends. The introduction of natural gas to the area has brought with it significant improvements in BTEX emissions.
2004 and 2006 Health impact assessment (Chapter 5)	The 2004 health risk assessment clearly indicated that benzene levels in the study area pose a risk to community health The close proximity of residential areas to industrial activity has been highlighted as a serious concern and hurdle in solving the problem. Lower benzene levels observed at the control site (Potchefstroom) are indicative of the problem facing the study area. Comparing the 2004 results with observations made in 2006, it became clear that the situation has improved significantly since the introduction of natural gas into the region in 2005.

6.2 FUTURE CHALLENGES

Recommendations based on this research work are indicated below:

i) South Africa generally lacks information on hydrocarbon pollution in ambient air. The atmospheric transport and fate of VOC species under South African conditions are not well understood. The importance of these factors in determining the actual impact of hydrocarbon species on local, national and regional air quality can only be assessed once this information becomes available.

ii) Source-receptor relationships are unknown, mainly due to the absence of source data. Receptor modelling is still in its infancy, with models not calibrated to suit South African conditions. The incorporation of relevant meteorological information unique to the southern African continent into these models needs to take place. The understanding of source-receptor relationships under South African conditions is of the utmost importance if realistic management plans aimed at reducing pollution at source are to succeed.

iii) Information on the impact of hazardous VOC species on the receiving environment is still lacking in South Africa. These include both the natural and man-made environments. This needs to receive urgent attention if effective legislation incorporating measures to reduce significant impact from hydrocarbon pollutant species are to be implemented.

iv) The influence of hydrocarbon-induced particulate formation in South Africa, and the role it plays in the chemistry and transport of pollutants is not well understood. Furthermore, the role these particulate matter plays in hydrology and ecosystem dynamics needs to be investigated.

v) The study needs to be expanded to include other hazardous volatile organic pollutant species. The cumulative impact associated with hydrocarbons has not been addressed in this study and should form part of the scope of future research on volatile organic pollutants.

vi) The study needs to be expanded to other metropolitan areas where industrial activity dominates. The information obtained from such an initiative will greatly assist policy makers in identifying areas of concern.

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