

Spatial and Temporal assessment of pollutants in the Highveld Priority Area, South Africa

A. S. M. Lourens

B.Ing

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Supervisor: Prof. J. J. Pienaar

Co-supervisors: Dr. J. P. Beukes and Dr. P. G. van Zyl

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Abstract

One of the major concerns that has been facing South Africa in recent years is the amount of gaseous pollutants emitted into the atmosphere. The Mpumalanga province is largely an industrialised area, which contributes approximately 83% to the country's total coal production. Eastern Gauteng and western Mpumalanga were identified as an air pollution hotspot and therefore declared the Mpumalanga *Highveld Priority Area* (HPA) on 4 May 2007. Diverse anthropogenic activities in this region result in high levels of organic aromates, such as benzene, toluene, ethylbenzene, and xylene (BTEX), as well as nitrogen dioxide (NO₂), sulphur dioxide (SO₂) and ozone (O₃).

The monitoring of inorganic gases with active and passive samplers is well established in South Africa. In contrast, very little data exists for volatile organic compounds (VOCs), which necessitates the measurement of these gases. Therefore, the primary aim of this research project is to determine the spatial and temporal distribution of BTEX, NO₂, SO₂, and O₃ in the HPA. A vertical assessment of BTEX was also conducted, in order to compare the upper atmospheric concentrations with the ground-level measurements. Lastly, all data were compared to the current legislation, in order to establish compliance.

Eight sites, within a grid of 600 km², were selected for the sampling. Passive sampling for the selected criteria pollutants was conducted on a monthly basis for a period of one year. The ground-level concentrations of BTEX were measured with Tenax TA adsorbent tubes, while NO₂, SO₂ and O₃ were measured with passive samplers developed and used by the Atmospheric Chemistry Research Group of the North-West University. Vertical BTEX profiles were obtained with a Cessna 182 during a two-day winter and a two-day summer field campaign utilising 6L TO-14 canisters and absorbent tubes. Flights were undertaken at two altitudes, 500 ft and 1 500 ft above ground level (AGL), and on three flight paths.

VOC samples were analysed, by using a gas chromatograph attached to a mass spectrometer for detection. Adsorbent tube samples were introduced into the system by a thermo desorber, while the canister had a slight modified inlet. Sulphurdioxide and O₃ analyses were done on an Ion Chromatograph, while a UV-visible Spectrophotometer was used for NO₂ analysis.

The spatial distribution of NO₂, SO₂, and BTEX indicated an increase towards the western parts of the HPA. This can be attributed to the prevailing north-easterly winds, as well as the

increased industrial activity in the western parts. The rural areas such as Balfour and Delmas were influenced by the industrial activities in the surrounding areas.

The temporal distribution of the inorganic gaseous species NO_2 , SO_2 , and O_3 indicated seasonal trends. The NO_2 and SO_2 peaked during winter because of meteorological conditions that trap and recirculate the air mass, as well as increased household and biomass combustion. The O_3 peak during spring could be explain by the CO peak, which is probably the most important O_3 precursor species in South African conditions. The CO peak occurred due to increased veld fires during the dry season. No seasonal trend was observed for BTEX.

From the vertical BTEX assessment, it was clear that no significant difference exists between the upper atmospheric concentrations and the ground-level measurement. A good comparison between the canisters and adsorbent tubes was found.

All the measured species were below their national- and proposed standards. However, the higher levels of SO_2 , NO_2 , and BTEX, measured in the western parts of the HPA, require attention. Witbank was the most polluted municipal area that was monitored.

Opsomming

Die vrystelling van atmosferiese besoedelstowwe in Suid Afrika is tans kommerwekkend. Die Mpumalanga provinsie is hoogs geïndustrialiseerd en dra by tot ongeveer 83 % van die steenkool produksie in Suid-Afrika. Gedeeltes van Oos-Gauteng en Wes-Mpumalanga is op 4 Mei 2007 as die Mpumalanga *Hoëveld Prioriteitsgebied* verklaar. Diverse antropogeniese aktiwiteite in hierdie area veroorsaak hoër konsentrasies organiese en anorganiese gaskontaminante in die atmosfeer. Organiese gaskontaminante sluit in benseen, tolueen, etielbenseen en xileen (BTEX), waar anorganiese gaskontaminante stikstofdoksied (NO_2), swaweldoksied (SO_2), en osoon (O_3) insluit.

Die monitering van anorganiese gasse met aktiewe en passiewe meetinstrumente is reeds goed gevestig in Suid-Afrika, terwyl daar beperkte data vir Vluchtige Organiese Verbindings (VOVs) beskikbaar is. Met laasgenoemde in ag genome het die studie gepoog om grondvlakmetings van BTEX, NO_2 , SO_2 en O_3 , asook hoër atmosferiese (< 1500 voet bo grond vlak) BTEX-vlakke te bepaal. Die gemete resultate is met die huidige nasionale regulasies vergelyk.

Agt meetstasies oor 'n area van 600 km^2 was geselekteer vir die meetinge. Passiewe meetings vir die besoedelstowwe is op 'n maandeliks basis uitgevoer vir 'n periode van een jaar. BTEX-vlakke is met Tenax TA adsorpsiebuis gemeet en NO_2 , SO_2 en O_3 is met passiewe monsternemers, ontwikkel deur die Atmosferiese Chemie Navorsingsgroep van die Noord-Wes Universiteit, bepaal. Vertikale BTEX-profiel is met 'n Cessna 182 vliegtuig, toegerus met die nodige instrumentasie, tydens 'n twee-dag somer en –winter veldtog bepaal. Adsorpsiebuis, sowel as 6L TO-14-vakuumhouers, is tydens hierdie metinge gebruik. Vlughte is op twee verskillende hoogtes gemeet, 500 voet en 1 500 voet bo grond vlak (BGV), met drie vlieg roetes.

Die VOV monsters is geanaliseer deur gebruik te maak van 'n gas chromatograaf gekoppel aan 'n massaspektrometer vir deteksie. Die adsorpsiebuis monsters is gekonsentreer op 'n termiese desorbeerder, terwyl die vakuumhouers op dieselfde instrument met 'n klein inlaatmodifikasie gehanteer is. Swaeldoksied en O_3 analyses is op 'n ionchromatograaf uitgevoer en NO_2 monsters op 'n uv-sigbare spektrofotometer.

Die hoë digtheid industriële ontwikkelings in die weste van Mpumalanga, asook 'n heersende noord-oostelike wind gedurende die meettydperk het daartoe gelei dat hoër NO_2 -, SO_2 - en BTEX-konsentrasies in die weste gemeet is. Uit die resultate is dit duidelik dat landelike

gebiede soos Balfour en Delmas deur die industriële aktiwiteite van die omliggende areas beïnvloed word.

Duidelike seisoenale tendense is waargeneem vir die anorganiese gasverbindings NO_2 , SO_2 en O_3 . NO_2 en SO_2 konsentrasies was die hoogste gedurende wintermaande as gevolg van meteorologiese kondisies. Stabiele inversielae wat voorkom in die winter keer die vertikale beweging en dispersie van gasse in die atmosfeer wat lei tot hoër konsentrasies van die kontaminante. Tydens wintermaande is daar ook verhoogde huishoudelike en biomassa verbrandingsprosesse wat bydra tot hoër konsentrasies van die gaskontaminante. Die gemete O_3 piek gedurende die lentemaande kan toegeskryf kan word aan die fotochemiese reaksies wat plaasvind in die atmosfeer asook die verhoogde CO vlakke gedurende dié tyd van die jaar. Die droë warm klimaat veroorsaak 'n toename in veldbrande wat lei tot die toename in CO vlakke. Grondvlakmetings van BTEX het geen seisoenale afhanklikheid getoon nie.

Vertikale benseenprofile (500 en 1500 voet bo grondvlakke) het nie noemenswaardige verskil van grondvlakmetinge getoon nie. Die resultate verkry van vakuumhouers en adsorpsiebuise het goed ooreengekom.

Al die konsentrasies van die gaskontaminante was laer as die nasionale- en voorgestelde standaarde. Alhoewel, die hoë vlakke van SO_2 , NO_2 en BTEX wat in die westelike gedeelte van die HPA gemeet is, aandag benodig. Witbank is geïdentifiseer as die mees besoedelende munisipale area wat gemonitor is.

Table of Contents

ACKNOWLEDGEMENTS	i
ABSTRACT	ii
OPSOMMING	iv
TABLE OF CONTENTS	vi
LIST OF FIGURES	x
LIST OF TABLES	xii
GRAPHICALY LAYOUT OF STUDY	xi

Chapter 1 Introduction

1.1. INTRODUCTION	1
1.2. PROBLEM STATEMENT	2
1.3. RESEARCH OBJECTIVES	3

Chapter 2 Literature Survey

Graphical layout of Chapter 2	4
2.1. INTRODUCTION TO AIR POLLUTION	5
2.1.1. TYPES OF AIR POLLUTANTS	6
2.1.1.1. Gaseous pollutants	7
2.1.1.2. Particular matter	8
2.1.2. POLLUTANT SOURCES	8

2.1.2.1.	Natural sources	8
2.1.2.2.	Anthropogenic sources	8
2.2.	SELECTION OF SPECIES STUDIED	9
2.2.1.	VOLATILE ORGANIC COMPOUNDS - BENZENE, TOLUENE, ETHYLBENZENE, XYLENE	9
2.2.2.	INORGANIC GASEOUS SPECIES - NITROGEN DIOXIDE, SULPHUR DIOXIDE AND OZONE	13
2.2.2.1.	Nitrogen dioxide	13
2.2.2.2.	Sulphur dioxide	14
2.2.2.3.	Ozone	14
2.3.	BTEX, NITROGEN DIOXIDE, SULPHUR DIOXIDE, AND OZONE	15
2.3.1.	GAS-PHASE TROPOSPHERIC CHEMISTRY	15
2.3.1.1.	Formation of hydroxyl radical	15
2.3.1.2.	Nitrogen oxides	16
2.3.1.3.	Volatile organic compounds	17
2.3.1.4.	Ozone	19
2.3.1.5.	Sulphur dioxide	20
2.3.2.	HEALTH EFFECTS AND ECOLOGIC IMPACTS CAUSED BY POLLUTANTS	21
2.3.2.1.	Human health	21
2.3.2.2.	Impacts on ecology	23
2.3.3.	AIR QUALITY STANDARDS AND GUIDELINES	23
2.3.3.1.	Volatile organic compounds	23
2.3.3.2.	Inorganic gaseous species	24
2.4.	CLIMATOLOGY OF SOUTH AFRICA	25
2.5.	MPUMALANGA	28
2.5.1.	GEOGRAPHY	28
2.5.2.	AIR POLLUTION	29
2.5.2.1.	Industries	30
2.5.2.2.	Power stations	30

2.5.2.3. Road traffic	31
2.5.3. METEOROLOGICAL FACTORS INFLUENCING AIR QUALITY IN THE MPUMALANGA HIGHVELD REGION	31
2.6. CONCLUSION	32

Chapter 3

Experimental Procedures

Graphical layout of Chapter 3	33
3.1. GROUND BASE MEASUREMENTS	34
3.1.1. SITE SELECTION	34
3.1.2. SAMPLING METHODS	35
3.1.2.1. Volatile organic compounds sampling with adsorbent tubes	36
3.1.2.2. Inorganic gaseous sampling with diffusive samplers	45
3.2. FLIGHT CAMPAIGN	50
3.2.1. SITE SELECTION	50
3.2.2. SAMPLING METHOD	51
3.2.2.1. Adsorbent tubes	52
3.2.2.2. Canisters	53

Chapter 4

Results and Discussion

Graphical layout of Chapter 4	57
4.1. DATA SET	58
4.2. SPATIAL DISTRIBUTION OVER THE HIGHVELD	63
4.2.1. INORGANIC GASEOUS CONCENTRATIONS	63

4.2.2. BTEX CONCENTRATIONS	66
4.3. TEMPORAL DISTRIBUTION OVER THE HIGHVELD	67
4.3.1. INORGANIC CONCENTRATIONS	67
4.3.2. BTEX CONCENTRATIONS	72
4.4. VERTICAL BTEX PROFILES	75
4.5. COMPARISON WITH AMBIENT AIR STANDARDS AND GUIDELINES	81
4.6. CONCLUSION	82

Chapter 5

Project Evaluation and Future Perspectives

5.1 INTRODUCTION	83
5.2 PROJECT EVALUATION	83
5.3 GENERAL CONCLUSION	84
5.4 FUTURE PERSPECTIVES	85

REFERENCES	86
APPENDIX A: WIND ROSES	97

List of Figures

Chapter 2:

Figure 2.1: The world sulphur emissions trend (IPCC, 2001)	14
Figure 2.2: Tropospheric NO cycle (Atkinson, 1998)	16
Figure 2.3: Tropospheric degradation and transformation reactions of volatile organic compounds (Atkinson, 1998)	18
Figure 2.4: General seasonal circulation in southern Africa (Sandham, 2008; Thyson, 1986)	26
Figure 2.5: Wet and dry effects on climatology in southern Africa	27
Figure 2.6: Map of Mpumalanga Province, South Africa (TGC, 2007)	29

Chapter 3:

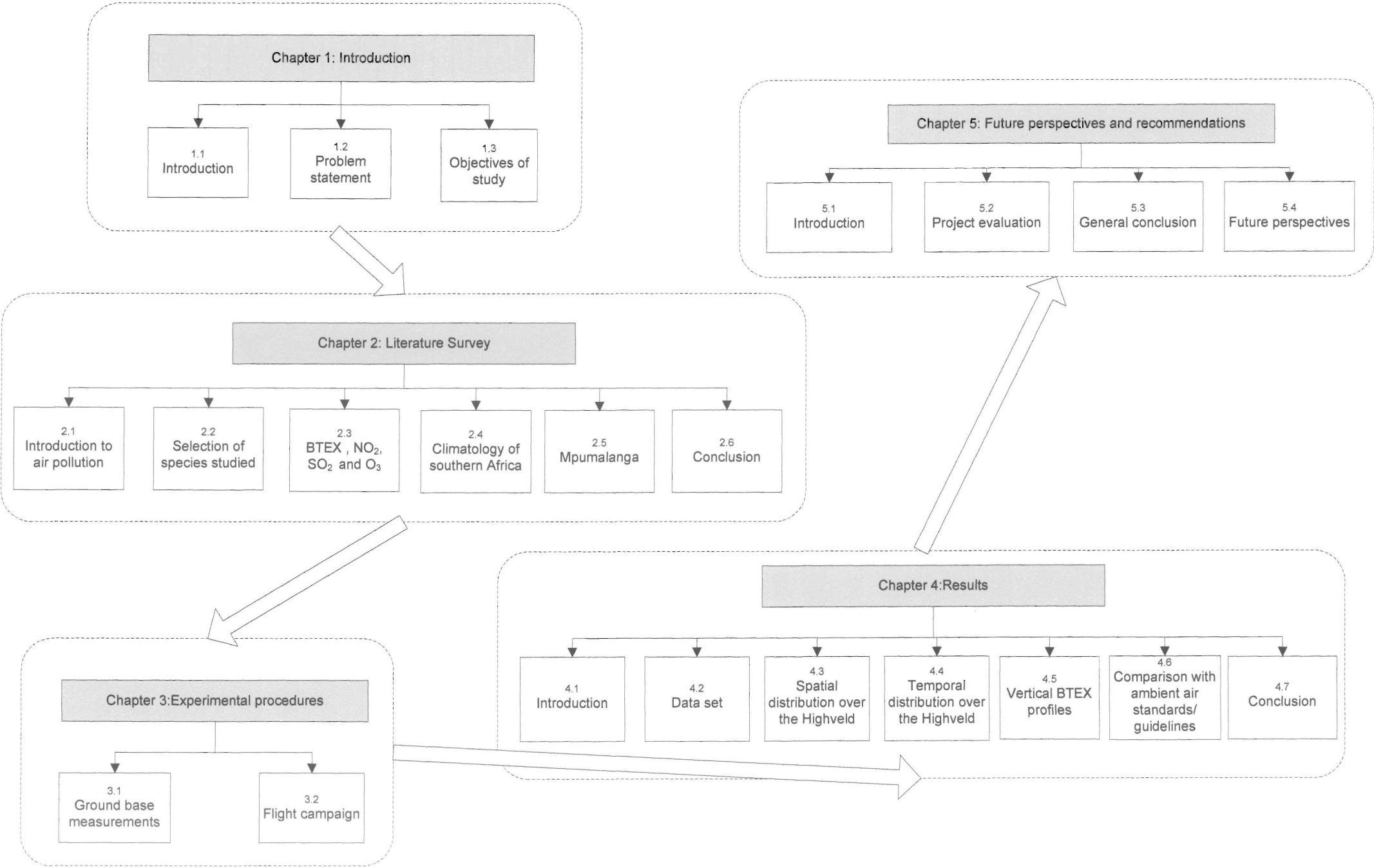
Figure 3.1: Geographical layout of sample stations	35
Figure 3.2: Adsorbent tubes fitted with diffusive caps used for ground-level sampling	36
Figure 3.3: Stainless steel tube (EPA, 1997)	38
Figure 3.4: Illustration of axial diffusion in passive samplers	39
Figure 3.5: (a) Aluminium Sampler stand, (b) Sampler hood with aluminium rail, (c) Mounted Sampler stand at Carolina	42
Figure 3.6: Analysis equipment: (a) Perkin-Elmer Turbo matrix desorber, Hewlett Packard Agilent 6890 gas chromatograph, (b) coupled to Micromass AutoSpec TOF mass spectrometer	43
Figure 3.7: Gas chromatographs of a typical sample	44
Figure 3.8: Schematic representation of a diffusive sampler (Dhammapala, 1996)	45
Figure 3.9: Passive samplers used during the research project	46
Figure 3.10: Ion Dionex Chromatography module/SP system	48
Figure 3.11: Sulphate chromatogram for ground samples collected during the field campaign	49
Figure 3.12: Nitrate chromatogram for ground samples collected during the field campaign	49
Figure 3.13: Varian Cary 50 UV-visible spectrophotometer	50
Figure 3.14: Flight paths	51
Figure 3.15: a) Cessna 182 used during flight surveys, b) Reverse inlet nozzle connected to the aircraft wing	51
Figure 3.16: Flight path logged by the GPS for the (a) winter (24 and 25 July 2007) and (b) summer (4 and 5 March 2008) surveys	52
Figure 3.17: Sequence sampler	53
Figure 3.18: 6-L TO canister with flow controller	54

Figure 3.19: Automated cleaning system	55
Figure 3.20: 2B Technologies Ozone Monitor	56

Chapter 4:

Figure 4.1: Spatial distribution of inorganic pollutants in the Highveld Priority Area	63
Figure 4.2: Wind roses measured in 2006 (left) and 2007 (right) near Secunda (data obtained from Sasol)	64
Figure 4.3: Annual wind roses measured at Carolina for 2007 to 2008 (data obtained from SA Weather Service)	64
Figure 4.4: Spatial distribution of BTEX gases in the HPA	66
Figure 4.5: Monthly mean concentrations of inorganic gases over the HPA	67
Figure 4.6: Annual rainfall over the Highveld region during the study period (data from SA Weather Service)	68
Figure 4.7: Temporal distribution at each site: (a) Balfour, (b) Delmas, (c) Witbank, (d) Carolina, (e) Ermelo, (f) Amersfoort, (g) Standerton, (h) Vanderbijlpark (values in ppb)	71
Figure 4.8: Monthly mean concentrations of BTEX over the HPA	72
Figure 4.9: The temporal distribution of BTEX for all the stations: (a) Balfour, (b) Delmas, (c) Witbank, (d) Carolina, (e) Ermelo, (f) Amersfoort, (g) Standerton, and (h) Vanderbijlpark (values in ppb)	
Figure 4.10: Flight paths during the measurement of the BTEX vertical profiles	74
Figure 4.11: Benzene concentrations for the three flight paths and two flight levels for the canister and Carbotrap™ 300 tubes samplers on 24 July 2007	76
Figure 4.12: Benzene concentrations for the three flight paths and two flight levels for the canister and Carbotrap™ 300 tubes samplers on 25 July 2007 (Tube data on the Balfour flight was lost due to power failures)	77
Figure 4.13: Benzene concentrations for the three flight paths and two flight levels for the canisters on 4 and 5 March 2008	78
Figure 4.14: Average benzene concentrations measured during the vertical profile campaigns	79

Graphical layout of Study



List of Tables

Chapter 2:

Table 2.1: Emission rates of natural and human origin	7
Table 2.2: Chemical properties of BTEX (Encarta, 2008)	11
Table 2.3: Concentrations (ppb) of BTEX in various cities	12
Table 2.4: Lifetimes of BTEX in troposphere (Atkinson, 1991)	19
Table 2.5: Toxicological and carcinogenic health effects of pollutants	21
Table 2.6: Ambient Air Quality standards based on the South African National Environment Management Air Quality Act (SA, 39/2004)	24
Table 2.7: Ambient Air Quality guidelines and standards of inorganic gases for various countries and organisations	24

Chapter 3:

Table 3.1: Sorbent characteristics for volatile organic compounds (EPA, 1997)	38
Table 3.2: Theoretical and experimental uptake rates	42

Chapter 4:

Table 4.1: One year data set for the inorganic gaseous species at selected sites in the Highveld Priority Area (ppb)	60
Table 4.2: One year data set for the BTEX species at selected sites in the Highveld Priority Area (ppb)	62
Table 4.3: Annual average concentrations of pollutants	82

Chapter 1:

Introduction

"I'm not an environmentalist. I'm an Earth warrior."

Darryl Cherney

1.1 INTRODUCTION

Air quality in urban and industrialised areas is becoming a major concern for governments, industries, and citizens worldwide. Air pollution is caused either through natural or anthropogenic (human) activities. Natural emissions include volcanic eruptions, fires, and dust storms, while emissions from human activities primarily involve various combustion processes and traffic emissions (Fellenberg, 1997).

Some of the gaseous species emitted in large amounts into the atmosphere absorb infrared radiation, causing the earth's atmospheric temperature to increase. This effect is termed the *greenhouse effect* (IPCC, 2007). In the nineteenth century, the industrial revolution spread across the world. This led to an increase in anthropogenic emissions due to the sudden increase in the consumption of non-renewable resources for energy generation and transportation.

Scientific and public awareness of climate change and air quality (more related to health and environmental impacts) has increased dramatically in the past decade. The Intergovernmental Panel for Climate Change (IPCC) conducts a report every six years, compiling the most recent findings over the period. In the latest report, *IPCC fourth assessment report: Climate change 2007*, it concluded that the increase in globally average atmospheric temperatures since the mid-twenties are very likely to be due to the observed increase in anthropogenic greenhouse gases (IPCC, 2007). Carbon dioxide (CO₂), tropospheric ozone (O₃), carbon monoxide (CO), are examples of typical greenhouse gases of which the concentrations have increased due to anthropogenic activities.

Some pollutants become harmful when they reach critical concentration levels or when secondary, more harmful and toxic, compounds are formed due to reactions between different species (Gammage and Kay, 1987). These pollutants include both organic and inorganic gaseous species, such as sulphur dioxide (SO_2), methane (CH_4), nitrogen dioxide (NO_2), and volatile organic compounds (VOCs). Adverse human health effects are associated with the above-mentioned atmospheric pollutants; they are also harmful to ecosystems. Benzene is extremely carcinogenic and is associated with leukaemia, whereas toluene can cause problems, such as fetal malformation (Ma *et al.*, 2002). Ozone, which is highly phytotoxic, causes damage to crops and native vegetation (Parra *et al.*, 2006). Nitrogen oxides (NO_x) and SO_2 have long-term effects of pulmonary asthma and chronic bronchitis, respectively (Kampa and Castanas, 2007).

Nitrogen dioxide is the most prominent air pollutant in the atmosphere and a key species in photochemical O_3 production. Sulphur dioxide is mainly produced by the combustion of fossil fuels (coal and oils) and by domestic heating. It can also react photochemically or catalytically with other pollutants to form sulphur trioxide, sulphuric acid, and sulphates (Elsom, 1987). The oxidation products of both SO_2 and NO_2 are also present in acid rain.

Volatile organic compounds are organic gaseous species with vapour pressures high enough ($> 0.13 \text{ kPa}$) to be easily vapourised—under normal conditions—into the atmosphere, and are emitted from urban (vehicles, aeroplanes, and ships), industrial (factories, refineries, and power plants) and natural sources (groundWork, 2003). Volatile organic compounds are primarily produced from the combustion of fossil fuels, a key product in the petrochemical, transportation, and energy generation industries. The environmental impact of VOC emissions range from changes in the population of terrestrial and aquatic ecosystems to the extinction of vulnerable species (UNEP, 1997). Volatile organic compounds also play a significant role in particle (Reisell *et al.*, 2003) and ozone formation (Atkinson, 2000), thus modifying the oxidising capacity of the atmosphere (Parra *et al.*, 2006).

1.2 PROBLEM STATEMENT

The Mpumalanga Highveld is known (Held *et al.*, 1996) for its diverse anthropogenic activities, which include agriculture, metallurgical and mining operations, petrochemical plants, power generation, coal dumps, and transportation (Freiman and Piketh, 2002). These activities contribute to elevated levels of organic and inorganic gaseous species,

which include benzene, toluene, ethylbenzene, and xylene (BTEX), as well as NO₂, SO₂, and O₃.

The dry and cold winters experienced in the Highveld also result in increased occurrences of biomass burning (fires) and combustion for domestic heating, which contribute to higher levels of organic and inorganic gaseous species. Primary pollutants emitted into the atmosphere also react with other species, leading to the formation of secondary pollutants.

Regulatory bodies have responded to this, in order to improve the air quality in highly industrialised areas in South Africa. In the last quarter of 2007, the Minister of Environmental Affairs and Tourism proclaimed Eastern Gauteng and Western Mpumalanga as a national priority area termed the *Highveld Priority Area* (HPA; SA, 2007).

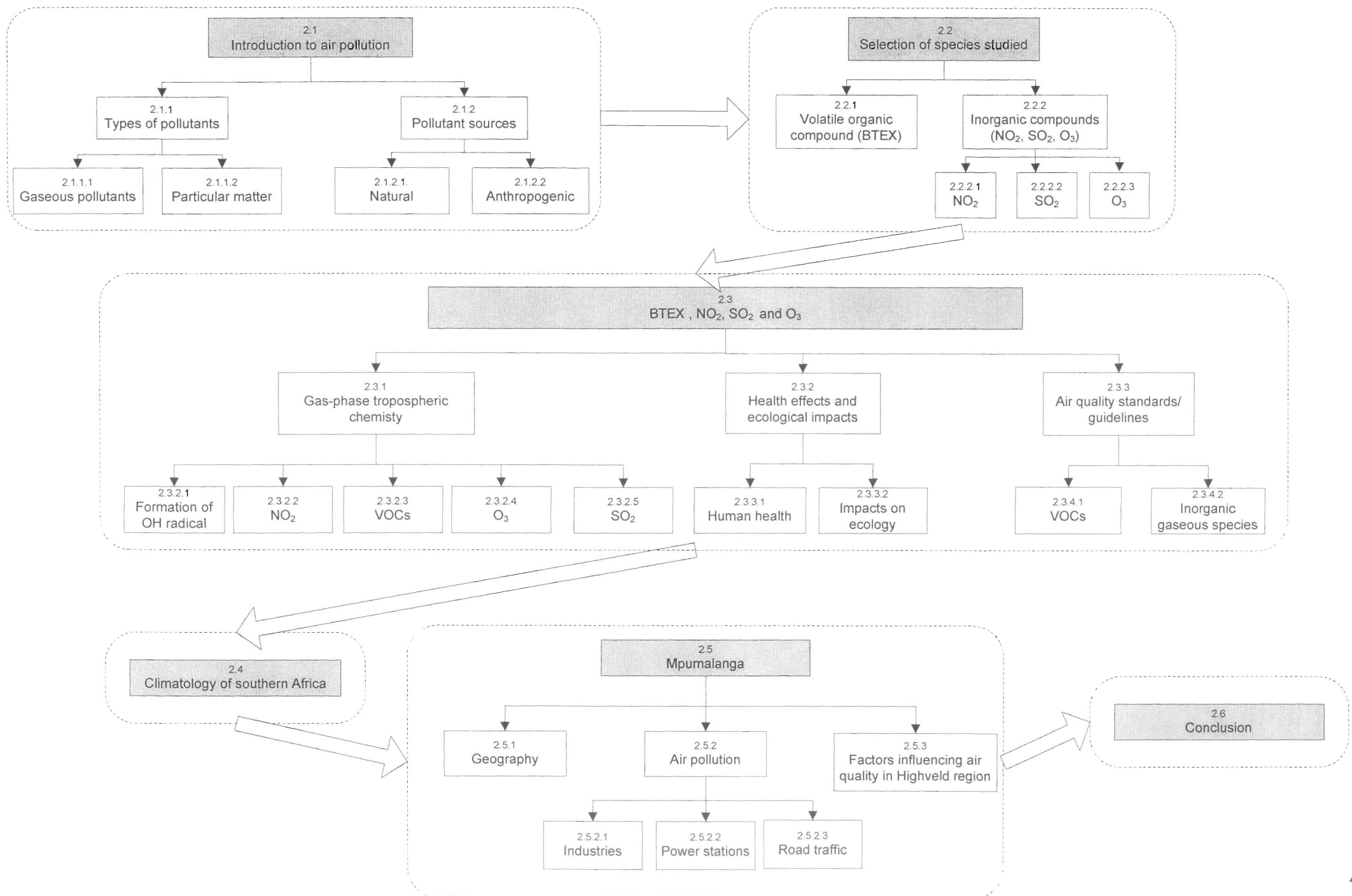
The monitoring of inorganic gases with active and passive samplers is well established in South Africa (Martins, *et al.*, 2007). In contrast, very little data exists for VOCs, which necessitates the measurement of these gases. The primary aims of this investigation were to determine the spatial and temporal distribution of the organic pollutants BTEX and the inorganic gaseous species NO₂, SO₂, and O₃ in the HPA. The species were chosen for their relevance to national regulations, possible sources within the HPA, and their possible health and environmental impacts.

1.3 RESEARCH OBJECTIVES

The objectives of the study are:

- i) to establish an ambient BTEX, SO₂, NO₂, and O₃ passive sampling network in the HPA, operating for at least one full year;
- ii) to determine a temporal assessment for all the above-mentioned species;
- iii) to determine a spatial assessment for all the above-mentioned species;
- iv) to conduct a vertical assessment of BTEX concentrations, in order compare the upper atmospheric concentrations with ground-level data; and
- v) to compare measured results to current national standards and guidelines.

Graphical layout of Chapter 2



Chapter 2:

Literature Survey

"We do not inherit the earth from our ancestors; we borrow it from our children."

(Ancient Indian proverb)

2.1 INTRODUCTION TO AIR POLLUTION

The earth's atmosphere is divided into different layers based on rapid temperature and pressure fluctuations with increasing altitude. The five most important layers are termed the troposphere, stratosphere, mesosphere, thermosphere, and exosphere. The troposphere is the nearest to the earth's surface and the densest layer. This layer covers in its widest extent approximately the first ~16 km from the earth's surface and consists of 78.08 % nitrogen, 20.95 % oxygen, 0.93 % argon, 0.036 % carbon dioxide, varying amounts of water vapour (depending on the altitude and temperature), and trace amounts of other gases (Atkinson, 2000). The troposphere is the primary layer where chemical species are involved in various complex chemical reactions. It is also the region where weather occurrences are predominant. Both the tropospheric and stratospheric regions are affected by air pollution.

Air pollution can be defined as any gaseous, liquid, or solid substance present in the atmosphere, which interferes with the comfort, health, and welfare of humans and/or animals (EPA, 2000). Atmospheric concentrations higher than their natural ambient air levels have a measurable effect on vegetation and cause damage to ecosystems.

Although gaseous species released into the atmosphere because of human activities, contribute only in small concentrations (parts per million (ppm) or parts per billion (ppb)), it leads to changes in the environment to occur quicker than it would naturally take place (Fellenberg, 1997). The IPCC compiles a report approximately every six years that builds on previous assessments and incorporates new research findings in every review. The latest report gives the most recent information concerning climate change and describes the progress in understanding human and natural drives towards climate change, observed

climate change, climatic processes, the complexity of the climate system, and attribution. It also estimates future climate change and its impacts (IPCC, 2007). A few key findings reported on in the Fourth Assessment Report (IPCC, 2007) are:

- The earth's surface temperatures has increased since 1950.
- Changes in extremes of temperature are consistent with warming.
- The world's oceans have warmed since 1955, accounting over this period for more than 80 % of the changes in the energy content of the Earth's climate system.
- Tropospheric water vapour is increasing.

These findings show that there is a definite increase in the rate of global climate change and its impact on the environment. Greenhouse gases contribute significantly to global climate change, since they effectively absorb infrared radiation, causing the earth's atmospheric temperature to increase. Should greenhouse gas emissions continue at or above current rates, by 2100, ecosystems will be exposed to atmospheric CO₂ levels substantially higher than in the past 650,000 years. Global temperatures will be at least among the highest experienced in the past 740,000 years. This will alter structure, reduce biodiversity, and disturb the functioning of most ecosystems (IPCC, 2007).

Health and welfare of humans are also affected by air pollution. Statistics for the health effects based on particular matter (PM) estimate that ambient air pollution causes about 5 % of trachea, bronchus, and lung cancer; 2 % of cardiorespiratory diseases; and 1 % of respiratory infections globally (WHO, 2002). In 2008, the World Health Organization estimated that there are approximately two million premature deaths per year in the world that can be linked to air pollution directly or indirectly (WHO, 2008). Various studies have also revealed that an increase in air pollution is associated with an increase in mortality and hospital admissions (Brunekreef and Holgate, 2002; Suwa, *et al.*, 2002).

Although scientific and public awareness of global change in the climate and its impact on the environment has increased, the above findings emphasise the necessity for effectively *controlling and monitoring air quality in polluted areas worldwide.*

2.1.1 TYPES OF AIR POLLUTANTS

Although pollutants have different sources, chemical composition, transmissions, and impacts on the environment and its inhabitants, they share some similarities and can therefore be categorised. Two main types of air pollutants are gaseous species and

particular matter (for example PM₁₀ and PM_{2.5}).

2.1.1.1. Gaseous pollutants

Gaseous pollutants consist of organic and inorganic compounds. Examples of organic compounds are VOCs, CH₄, hydrocarbons, and halogenated gases, while inorganic compounds include NO₂, N₂O, SO₂, O₃, CO, and CO₂. These species contribute significantly to air pollution and climate change with CO₂, CO, O₃, CH₄, N₂O, and halogenated carbons known as greenhouse gases. In the nineteenth century, the industrial revolution spread across the world. This led to an increase in the emissions of these species from anthropogenic activities due to the sudden increase in consumption of non-renewable resources for energy generation and transportation. A major source of gaseous pollutants is the combustion of fossil fuels, which emits NO_x, SO₂, CO, CO₂, VOCs, and heavy metals into the atmosphere. These species induce further chemical reactions in the troposphere, and could lead to the formation of harmful and more toxic compounds (Graedel and Crutzen, 1997). Table 2.1 summarises the annual average global gaseous emissions from natural and anthropogenic sources (Fellenberg, 2002)

Table 2.1: Emission rates of natural and human origin

Emission	Natural (Tg (10 ¹²)/yr)	Anthropogenic (Tg (10 ¹²)/yr)
Carbon dioxide (CO ₂)	To large	7100
Hydro-carbons (H-C)	855	105
Ammonia (NH ₃)	10.6*	10.6*
Nitrogen oxide (N ₂ O)	8.1/4.1*	9.6/10.8*
Nitrogen dioxide (NO _x)	8.8*	43.1*
Sulphur dioxide (SO ₂)	34	78

* Values obtained from IPCC, 2007

Carbon monoxide is produced from the incomplete combustion of carbon-based materials, whereas CO₂ is formed by the complete oxidation of these materials (Fellenberg, 2002). Carbon dioxide concentrations increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005, with a higher annual concentration growth rate of 1.9 ppm in the past ten years (IPCC, 2007).

2.1.1.2. Particular matter

Aerosols are the suspension of solid or liquid particles in gas (Kampa and Castanas, 2007). These particles are categorised according to their aerodynamic particle diameter: *ultra fine* particles are smaller than 0.1 µm, *fine* particles are smaller than 1 µm, whereas *coarse* particles are larger than 1 µm. Natural emissions of particular matter originate from volcanic eruptions, forest fires, dust storms, or spray from seawater, whereas anthropogenic sources include traffic, agriculture, chemical, and mining industries.

2.1.2 POLLUTANT SOURCES

Gaseous species and particulate matter can be released into the atmosphere by means of processes that occur naturally or by anthropogenic (human) sources.

2.1.2.1 Natural sources

Gaseous species, such as NO_x, SO₂, CO, CO₂, CH₄, and NH₃ are released into the atmosphere through natural occurring phenomena. Natural emissions include volcanic eruptions, fires, dust storms, and decomposition of animal and plant materials (Fellenberg, 1997).

Organic compounds can be emitted naturally from wetlands, biomass burning, and plant surfaces. It is estimated that 150 million tons of non-methane organic compounds (NMOC) are naturally emitted from vegetations annually (IPCC, 2007; Hein *et al.*, 1997). Non-methane organic compounds include isoprene (2-methyl-1,3-butadiene) a series of CH₁₀₋₁₆ monoterpenes, C₁₅H₂₄ sesquiterpenes, methanol, cis-3-hexen-1-ol and cis-3-hexenyl acetate, and other Biogenic Volatile Organic Compounds (BVOCs).

2.1.2.2 Anthropogenic sources

Pollution from anthropogenic activities includes the release of pollutants from various combustion processes, such as chemical, petrochemical, mining, and automobile industries. These emitted species are known as primary pollutants, which could react with other

compounds already present in the atmosphere to form secondary pollutants, which can be even more toxic than the species originally emitted (Camela and Caude, 1995).

Traffic is a major source of VOC emissions, especially in urban areas (Reisell *et al.*, 2000; Esteve-Turrillas *et al.*, 2007). According to Pfeffer (1994), 90 % of the benzene in ambient air is produced by traffic emissions. Other gases, such as NO₂, CO, and CO₂ are also emitted from vehicle emissions.

In his book, *Beyond Global Warming: Ecology and global change*, Vitousek wrote: "There is a number of global environmental changes of which we are certain that they are going on and certain that they are human-caused". Anthropogenic pollution is a major contributor to environmental change, and it is primarily driven by the rapidly growing human population and high rates of resource consumption.

2.2 SELECTION OF SPECIES STUDIED

2.2.1 VOLATILE ORGANIC COMPOUNDS-BENZENE, TOLUENE, ETHYLBENZENE, XYLENE

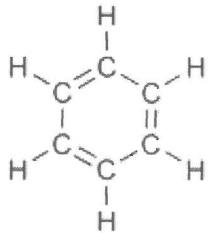
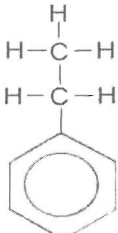
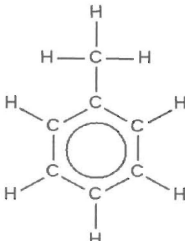
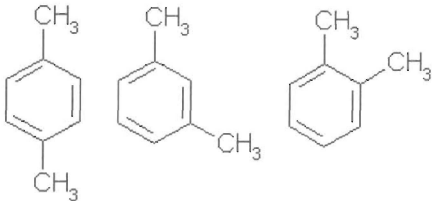
Organic compounds can be categorised into volatile (VOC), non-volatile (n-VOC) and semi-volatile compounds (s-VOC) based on their vapour pressures (Fellenberg, 1997). They are ever-present in the environment, both on micro- and macro-scale. A vapour pressure greater than 0.13 kPa is conventionally used to distinguish them from less volatile organics. Volatile organic compounds participate in numerous reactions in the atmosphere (see Section 2.3.2) to form secondary pollutants (Fellenberg, 1997).

According to the United States Environmental Protection Agency (EPA), VOCs are broadly defined as "those compounds of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammoniumcarbonate) which form ozone through atmospheric photochemical reactions in the presence of sunlight" (EPA, 2008).

Volatile organic compounds and their reaction products are increasingly regarded as posing adverse risks to public and occupational health, as well as to biological and physical environments (EC, 1998).

BTEX is an acronym for benzene, toluene, ethylbenzene, and xylene (that is m-, p-xylene and o-xylene). These aromatic compounds are an important fraction of non-methane hydrocarbons, which are the most commonly monitored VOCs worldwide. Owing to the ubiquity of their emissions, BTEX can be detected everywhere, even in rural areas (Dewulf, 1992). These aromatic hydrocarbons have similar properties as well as chemical and industrial uses, which are summarised in Table 2.2 on the following page.

Table 2.2 Chemical properties of BTEX (Encarta, 2008)

Properties	Benzene	Ethylbenzene	Toluene	Xylene
IUPAC name	1,3,5- cycloexatriene	Ethylbenzene	Methylbenzene or phenylmethane	para-xylene, meta-xylene, ortho-xylene
Chemical Structure				
Density	0.87 g/mL, liquid	0.867 g/mL, liquid	0.8669 g/mL, liquid	0.864 g/mL, liquid
Molecular weight	78.1121 g/mol	106.167 g/mol	92.14 g/mol	106.16 g/mol
Uses	Benzene is used as a constituent in motor fuels; as a solvent for fats, waxes, resins, oils, inks, paints, plastics, and rubber; in the extraction of oils from seeds and nuts; and in photogravure printing	Petrochemical industries, primary compound in production of styrene	Common solvent, paint thinners, silicone sealants, printing ink, adhesives	Mixed xylenes are used in the production of ethylbenzene; as solvents in products, such as paints and coatings; and are blended in gasoline
Emission sources	Oil and natural gases, traffic emissions	Consumer products, gasoline, pesticides, solvents, carpet glues, varnishes, paints, and tobacco smoke	Automobile emissions, disposal of industrial and consumer products that contains toluene	Fugitive emissions from industrial sources, from auto exhaust, and through volatilisation from their use as solvents
Vapour pressure	95.2 mm Hg at 25°C	9.53 mm Hg at 25°C	28.4 mm Hg at 25°C	6.72 mm Hg at 21°C

BTEX concentrations differ from place to place depending on a variety of factors, such as population density, fuel consumption, and industrial areas. Table 2.3 gives a comparison of BTEX concentrations measured at different places in the world. From this data, it can be seen that toluene levels are predominantly higher than benzene. Toluene concentrations have been found to be the highest in major metropolitan areas of southern Africa (Burger, 2006; Oosthuizen *et al.*, 1998).

Table 2.3: Concentrations (ppb) of BTEX in various cities

Cities	Benzene	Toluene	Ethyl-benzene	(<i>m, p</i>)-Xylene	<i>o</i> -Xylene	References
Liverpool	0.89	2.08	0.87	2.68	1.30	Derwent <i>et al.</i> , 2000
Yokohama	0.38-1.13	1.23 - 8.95	0.12-0.88	0.23-0.46	0.03-0.18	Yamamoto <i>et al.</i> , 2000
UC London	1.87	3.62	0.73	2.14	0.8	Derwent <i>et al.</i> , 2000
Birmingham	1.02	2.04	0.48	1.45	0.48	Derwent <i>et al.</i> , 2000
Cardi	1.21	2.17	0.4	1.21	0.44	Derwent <i>et al.</i> , 2000
Leeds	1.04	2	0.38	1.13	0.42	Derwent <i>et al.</i> , 2000
Edinburgh	0.7	1.28	0.31	0.82	0.39	Derwent <i>et al.</i> , 2000
Harwell	0.38	0.6	0.16	0.38	0.2	Derwent <i>et al.</i> , 2000
Bristol	1.22	2.66	0.5	1.47	0.67	Derwent <i>et al.</i> , 2000
London	2.7	7.2	1.4	3.7	1.5	Monod <i>et al.</i> , 2001
São Paulo	5.2	7.4	1.4	4.2	1.4	Colón <i>et al.</i> , 2001
Berlin	6.9	13.8	2.8	7.5	2.9	Monod <i>et al.</i> , 2001
Seoul	1	6.4	0.7	2.3	0.8	Na and Kim., 2000
Santiago	6.11	22.17	—	10.81	3.8	Chan, Ozkaynak and Spengler, 2001
Bombay	4.29	2.95	0.09	0.3	0.51	Mhoan Rao <i>et al.</i> , 1997
Quito	1.57	4.04	0.51	1.47	0.46	Gee and Sollars, 1998

Benzene, toluene, ethylbenzene, xylene, naphta, ethylene oxide, methyl ethyl ketone, acetone, and other light hydrocarbon compounds are examples of VOCs. Volatile organic

compounds are an important sub-group of air pollutants and are present in any urban and industrial region. They play a significant role in ozone formation (Atkinson, 2000) and modifying the oxidising capacity of the atmosphere (Parra *et al.*, 2006). When monitoring VOCs in industrialised and urban areas, the BTEX group is generally the most common measured species. The Mpumalanga HPA has several industrial processes that could emit VOCs. The scope of this research project is to determine the spatial and temporal distribution of VOCs. However, it is impossible to monitor all the hazardous volatile organic compounds. For the purpose of this project, only BTEX is focused upon. Benzene is currently the only VOC for which standards and guidelines were established in the new Air Quality Act (SA, 39/2004).

2.2.2 INORGANIC GASEOUS SPECIES - NITROGEN DIOXIDE, SULPHUR DIOXIDE AND OZONE

Nitrogen dioxide and SO₂ are some of the key species in the atmosphere that influence productivity in the biosphere (Ferm and Svanberg, 1998). Sulphur dioxide can also react photochemically or catalytically with other pollutants to form sulphur trioxide, sulphuric acid and sulphates (Elsom, 1987). Nitrogen dioxide is the most prominent air pollutant and a key species in photochemical ozone production. High-level atmospheric ozone measurements indicate potential intrusions of VOC plumes in an area with high NO₂ emission sources.

2.2.2.1 Nitrogen dioxide

Nitrogen oxides NO_x, (total concentration of NO and NO₂) are produced either by means of human activities, such as traffic, power plants, biomass combustion, and agricultural processes (EPA, 2000), or naturally by the oxidation of NH₄⁺ and the reduction of NO₃⁻ in the biosphere. Nitrogen dioxide is the most prominent air pollutant and is converted to NO in the presence of sunlight, which oxidises to NO₂ during reactions with ozone (for more detail see Section 2.3). Therefore, during the day, the NO/NO₂ ratio is in equilibrium. Nitrogen dioxide is also toxic and cause severe health problems (see Section 2.3.2).

2.2.2.2 Sulphur dioxide

Elsom (1987) describes sulphur dioxide as a colourless gas that is emitted mainly from stationary sources that burn fossil fuels, such as power plants, ore smelters, and refineries. Elevated levels of sulphur dioxide are associated with high levels of particulates and other pollutants (such as sulphates and sulphuric acid mists), which may cause respiratory problems and are precursors to acid deposition (DES, 2008). The majority of sulphur-

containing compounds in the atmosphere are carbonyl sulphide, carbon disulfide, dimethyl sulphide, H_2S , SO_2 , and SO_3 . Figure 2.1 indicates the world sulphur emission trends from 1850 to 2000, obtained from various studies conducted over decades.

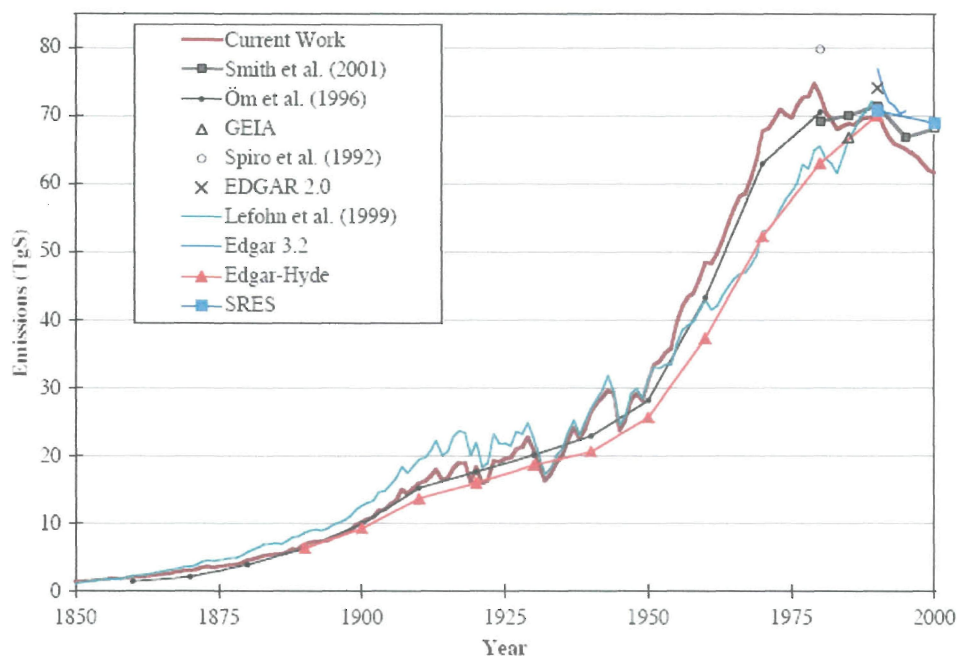


Figure 2.1: The world sulphur emissions trend (IPCC, 2001)

A rapid increase in SO_2 emission since the late eighteenth century is noticeable, which indicates the beginning of the industrial revolution and increased power generation. In the late twentieth century, global awareness of air quality increased, which forced industries and governments to take drastic measures. More recently, the ambient concentrations in especially First World countries have started to decrease, which is mainly attributed to the fact that lower sulphur-containing fuel has been increasingly used in recent times (ICPP, 2007).

2.2.2.3 Ozone

Tropospheric ozone is formed as result of chemical reactions between O_2 , NO_x , and VOCs in the presence of sunlight, which are also the key components of smog. Tropospheric O_3 is perhaps one of the most widespread gaseous pollutant species. A study has shown that during summer, daytime ozone levels correlate strongly with temperature, higher temperatures yield higher O_3 (IPCC, 2007).

Nitrogen dioxide and SO_2 were included in the scope of this study and since the atmospheric chemistry of tropospheric O_3 is closely linked to several sulphur-, nitrogen-, and VOC-

containing species, O₃ measurements were included. Nitrogen dioxide, SO₂, and tropospheric O₃ are considered criteria pollutants in the new Air Quality Act (SA, 39/2004), for which standards and guidelines have been set (NEMA, 2004).

BTEX, nitrogen dioxide, sulphur dioxide, and ozone are examined in the following section.

2.3 BTEX, NITROGEN DIOXIDE, SULPHUR DIOXIDE, AND OZONE

2.3.1 GAS-PHASE TROPOSPHERIC CHEMISTRY

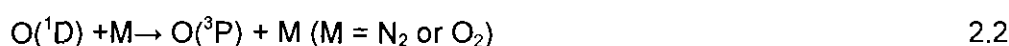
As already mentioned, the tropospheric layer is where most of the species are present as a result of surface emissions. The troposphere, especially in pollutant urban atmospheres, contains different organic and inorganic species, which leads to a series of chemical and physical transformations. These transformation processes could, for instance, result in the formation of ozone and smog.

Tropospheric chemistry involves the partial or complete degradation of almost all the organic and inorganic species emitted into the atmosphere. The formation and removal processes of ozone are essential to tropospheric chemistry (Seinfeld and Pandis, 1998).

2.3.1.1 Formation of hydroxyl radical

The key to understanding tropospheric chemistry begins with understanding the role of the hydroxyl (HO[•]) radical. This short-lived radical is the most important species in tropospheric chemistry. Although O₂ and O₃ are the most abundant oxidants in the atmosphere, they have large bond energies and are generally unreactive, which means the HO[•]-radical is the primary oxidising species in the atmosphere. The oxidation of atmospheric species can be very complex.

Photolysis of low ozone levels (at wavelengths < 319nm), present in the troposphere, are considered to be the start of all the atmospheric oxidation reactions. Both ground state (O) and excited singlet (O(¹D)) atoms are produced (Atkinson, 1998):



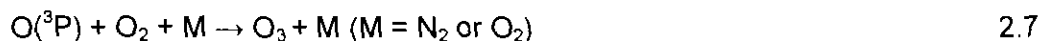
The singlet O(¹D) oxygen atom reacts with water vapour and generates two HO[•]-radicals:



Once the HO[•]-radical is formed it reacts virtually with all the atmospheric trace species present in the troposphere. The gaseous species that do not react with the HO[•]-radical have longer lifetimes and are transported into the stratosphere, where they are photochemically destroyed (Seinfeld and Pandis, 1998; Atkinson, 1998).

2.3.1.2 Nitrogen oxides

Should the photolysis of O₃ be considered the start of tropospheric chemistry, then NO₂ must then be considered the precursor to all chemistry in the troposphere (Pienaar and Helas, 1996). Once released into the atmosphere, this abundant species undergoes a series of chemical reactions (Fellenberg, 2000; Atkinson, 1999; Colbeck, 1994):



These reactions interconvert NO, NO₂, and O₃, shown in Figure 2.2, below.

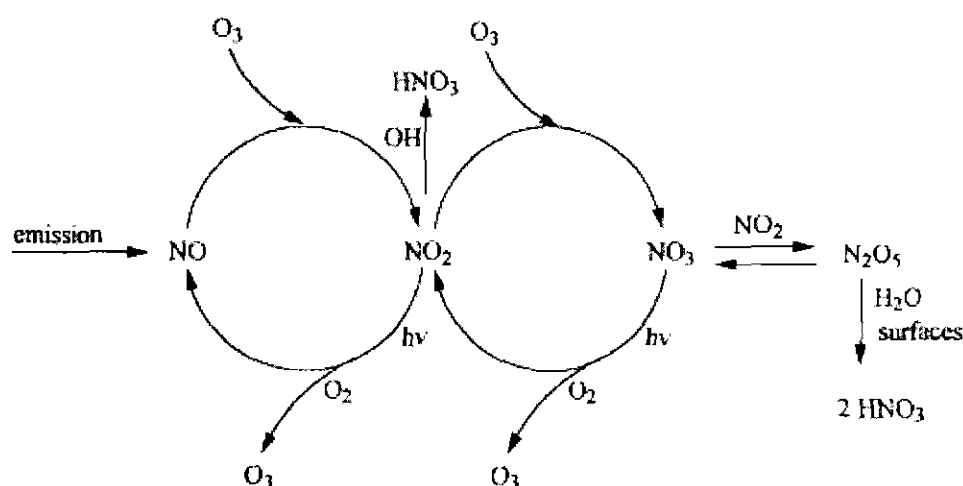


Figure 2.2: Tropospheric NO cycle (Atkinson, 1998)

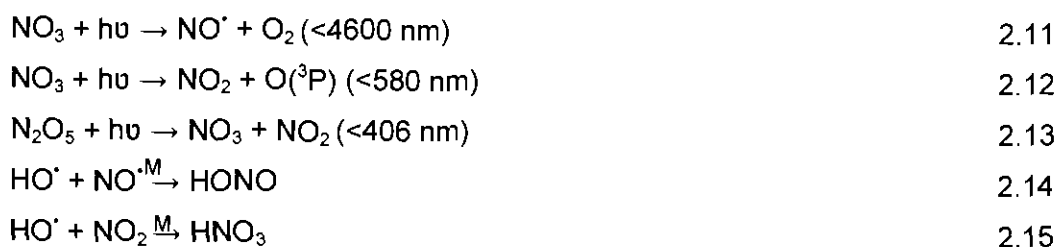
Furthermore the reaction of NO₂ and O₃ leads to the formation of the nitrate radical (NO₃[•])



which reacts rapidly (lifetime of 5s) with NO in the presence of sunlight to form NO again, as well as NO₂:



Photolysis of other nitrogen oxides in the troposphere is:



The HO^* -radical reaction with NO_2 is a major depleting process for NO_x during daytime hours (Atkinson, 2000). High NO_2 levels have been found in urban areas in the morning, due to increased motor vehicle activities.

2.3.1.3 Volatile organic compounds

Although the hydroxyl radical is the key reactive species in the chemistry of ozone formation, the VOC-HO^* reaction initiates the oxidation sequence. Nitrogen oxides and VOCs are in constant competition for the HO^* radical. With a high ratio of VOC to NO_x , the HO^* will predominantly react with VOCs; in contrast with low VOCs to NO_x ratios, NO_x will dominate. The hydroxyl radical only reacts with VOCs and NO_2 at a equal rate when the $\text{VOC}:\text{NO}_2$ concentration ratio is a certain value. This value depends on the particular VOC or mix of VOCs present (Seinfeld and Pandis, 1998).

The transformation and degradation reactions of VOCs that occur in the troposphere can be represented by Figure 2.3 below. The most important radicals are the alkyl or substituted alkyl radicals (R^*), alkyl peroxy or substitute alkyl peroxy radicals (RO_2^*), and alkoxy or substitute alkoxy radicals (RO^*).

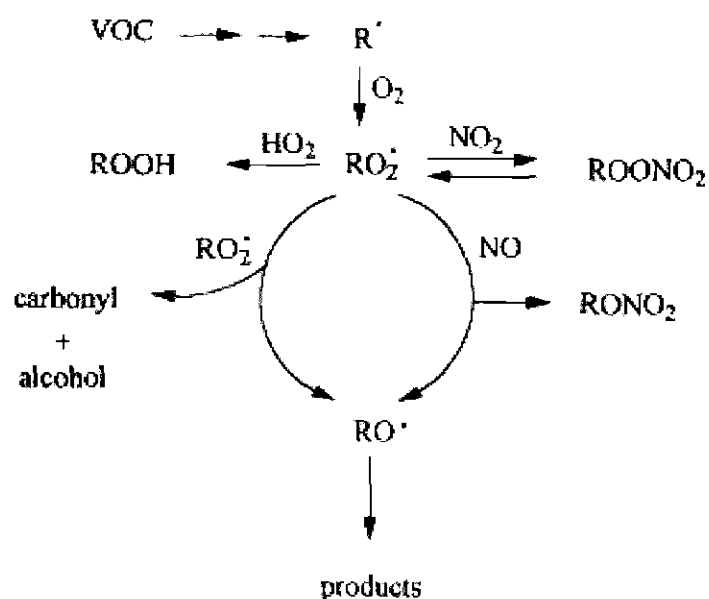
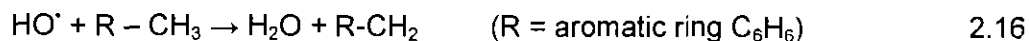


Figure 2.3: Tropospheric degradation and transformation reactions of volatile organic compounds (Atkinson, 1998)

The reaction of hydrocarbon with HO• radicals can be described by the following reactions:



Aromatic compounds can react with the HO•-radical by means of two different pathways, termed major or minor pathways. The minor pathway involves H-atoms abstraction from C-H bonds for benzene, or alkyl-substituted aromatic hydrocarbon for the alkyl-substituent groups. The major pathway involves an addition reaction with the HO•-radical to the aromatic ring (Seinfeld and Pandis, 1998).

An alkyl-substituted hydroxycyclohexadienyl radical is formed when H-atoms are abstracted from the C-H bond after the addition of HO•-radical. The HO•-radical addition reaction is reversible due to the lifetimes of benzene and toluene (see Table 2.4) in the atmosphere and thermal decomposition of HO•-aromatic adduct:



The degradation reactions include:



or for radical with ≥ 3 carbon atoms



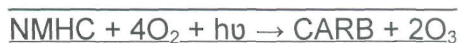
The removal and transformation processes for VOCs in the troposphere include wet and dry deposition, photolysis, reactions with $(-\text{HO}^\bullet)$ radicals, $(-\text{NO}_3^\bullet)$ radicals, and reactions with O_3 (Seinfeld and Pandis, 1998). The overall lifetime of these compounds are the sum of the above-mentioned processes. Lifetimes for BTEX compounds are listed in Table 2.4. Benzene and toluene have longer lifetimes than m-xylene due to lower reactivity with $(-\text{HO}^\bullet)$ and $(\text{NO}_3^\bullet)$ radicals (Colbeck *et al.*, 1994; WHO, 2008).

Table 2.4: Lifetimes of BTEX in troposphere (Atkinson, 1991)

Compound	$\text{HO}^\bullet$	$\text{NO}_2^\bullet$	O_3
Benzene	12 days	>4 yr	>4.5 yr
Toluene	2.4 days	1.9 yr	>4.5 yr
m-Xylene	7 hr	200 days	>4.5 yr
Benzaldehyde	1.1 days	18 days	

2.3.1.4 Ozone

The only way by which ozone is known to be formed in the troposphere starts with the photolysis of NO_2 (Wayne, 1985). The chemistry of ozone formation is also very complex and sometimes non-linear concerning NO_x/VOC ratios (Burger, 2006). This causes O_3 levels to increase when NO_x/VOC ratios are low. Ozone plays an important role in the composition of the troposphere due to its role in the formation of excited oxygen atoms and its interaction with the $\text{HO}^\bullet$ -radical (reaction 2.2 to 2.4). The photochemical formation of ozone can be described in a simplified form by the following reactions (Liu *et al.*, 1987):



In the above reactions, NMHC indicates the mixture of non-methane hydrocarbons and CARB represents the carbonyl compounds. Ozone concentration generally fluctuates over a 24-hour period, since sunlight is essential for ozone formation. Nitrogen oxide emissions are also a determining factor. At night, O₃ levels are low, since no photochemical formation takes place, and these levels are further reduced due to the oxidation of NO to NO₂. The seasonal trends show higher levels of tropospheric O₃ across a large region in the north of South Africa during spring (Olab *et al.*, 2006). This can be attributed to the increased NO_x and CO emissions from biomass burning, which occurs with a high frequency during this period.

2.3.1.5 Sulphur dioxide

Sulphur dioxide participates in various transformations reactions in the atmosphere, with the most important reactions involving oxidation and acid formation (Fellenberg, 2000). During oxidation reactions, excited oxygen atoms react with water vapour to form the hydroxyl radical (as mentioned in Section 2.2.3)



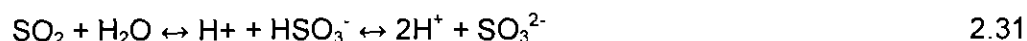
The residence time of SO₂ in the atmosphere ranges between twelve hours and six days (Kellogg *et al.*, 1972). The reactive HO[•]-radicals react with SO₂ and form sulphuric acid:



While reactions with ozone produce sulphur trioxide:



Sulphurous acid is formed through the reaction of water and sulphur dioxide, which is captured by water droplets and removed from the atmosphere as acid rain:



2.3.2 HEALTH EFFECTS AND ECOLOGIC IMPACTS CAUSED BY POLLUTANTS

2.3.2.1 Human health

Air pollutants from anthropogenic sources, depending on the concentration, duration, and exposure method, can cause serious health problems. Pollutants can enter the bloodstream on various ways, which include inhaling, which can affect the lungs and respiratory tract directly; physical contact, such as eating products where pollutants accumulated on plants and vegetation; and through the skin and eyes, by coming in direct contact with pollutants (Kampa and Castanas, 2007).

Toxicological research has revealed that many VOCs have various reversible and irreversible effects on the human body, ranging from acute anaesthesia to long-term effects, such as induction of carcinomas (WHO, 1987; Lippman, 1992). Benzene is classified as a human carcinogen (EPA, 1997). Studies have also indicated that benzene contributes to a variety of blood-related disorders, is known to produce acute leukaemia, and attacks the central nervous system. Instant exposure to concentrations as high as 250 ppm to 500 ppm can cause drowsiness, headache, and nausea (Sheretz, 1998).

Ozone is highly phytotoxic, causing damage to crops and native vegetation (Parra *et al.*, 2006), whereas NO_x and SO₂ have respectively long-term effects of pulmonary asthma and chronic bronchitis (NAQMP, 2006). Table 2.5 summarises the toxicological and carcinogenic health effects of pollutants considered in this research project:

Table 2.5: Toxicological and carcinogenic health effects of pollutants

Compounds	Toxicological effects	Carcinogenic effects
Ozone	• Irritation of respiratory system • Repeated exposure damages lungs (Animal studies) • Aggravation of asthma • Aggravation of chronic lung diseases	• None
Nitrogen dioxide	• Eye, nose, and throat irritation • Repeated exposure results in pulmonary	• None

	asthma • Prolonged exposure causes chronic bronchitis	
Sulphur dioxide	• Breathing problems, respiratory illness • Changes in the lungs' defences • Worsening respiratory and cardiovascular disease • Most sensitive for people with asthma or chronic lung or heart disease	• Respiratory effects
Benzene	• High concentrations cause neurotoxic symptoms • Persistent exposure results in bone marrow injury • Produces acute nonlymphocytic leukaemia and attacks the central nervous system	• A known human carcinogen (EPA, 1997) • Leukaemia
Toluene	• Causes headache, confusion, and memory loss • Attacks the central nervous system (≥ 100 ppm; Sheretz, 1998)	• Not carcinogenic (EPA, 1997)
Ethylbenzene	• Skin and mucous membrane irritation • Extreme eye and nose irritation ($\geq 5\,000$ ppm; Sheretz, 1998)	• Possibility of being carcinogenic (WHO IARC, 2000)
Xylene	• Causes anorexia • Causes vomiting and dizziness (≥ 350 ppm)	• Teratogenic to the foetus of pregnant women (Sheretz, 1998)

2.3.2.2 Impacts on Ecology

Ecotoxicological research indicates that the impact of air pollution on the eco-systems ranges from changes in the population of terrestrial and aquatic ecosystems to the extinction of vulnerable species (Scholes *et al.*, 1996). Agricultural crops have also been proven to be damaged after exposure to VOCs (Bates, 1994). Tropospheric ozone is the main contributor in the decline of forest growth and crop yields. Studies show that exposure to ozone levels as low as 0.08 ppmv can cause up to 10 % yield decline of certain species during their growing season (Bates, 1994). Tree leaves are damaged, which has a negative impact on vegetation appearances. Plants are restricted to producing and storing food, making them more susceptible to diseases, insects, other pollutants, competition, and harsh weather (EPA, 2008).

Mansfield *et al.* (1991) find that a strong correlation exists between SO₂ ambient levels and the development of fungal diseases on several species of Winter Barley, which reduces growth and yield. Nitrogen oxides and sulphur dioxide participate in tropospheric ozone production, as well as acid rain formation, which is associated with the acidification of lakes and streams, accelerated corrosion of buildings and monuments, and reduced visibility.

2.3.3 AIR QUALITY STANDARDS AND GUIDELINES

In order to improve the air quality worldwide, federal and state agencies (such as EPA, WHO) have developed standards and guidelines and to reduce pollutant emissions. These standards and guidelines are intended to protect the public against severe health effects.

2.3.3.1 Volatile organic compounds

Scientific and public awareness to the threat that VOCs, especially benzene, may pose to humans and the environment has prompted their regulation. Many initiatives have been launched to reduce the emissions of VOCs, particularly in the most industrialised countries where local and regional levels, as well as the effects, are most pronounced.

Benzene is the only hydrocarbon species included in the new South African legislation with a current standard value of 1.6 ppb (SA, 2004). The air quality standard for benzene in United Kingdom is set at a value of 3.76 ppb by the Department of Environmental Quality. In Scotland and Ireland, an Air Quality Standard of 1 ppb was established (AEA, 2004).

2.3.3.2 Inorganic gaseous species

Table 2.6 summarises the existing ambient air standards for inorganic gaseous species in the South African National Environment Management: Air Quality Act (SA, 39/2004).

Table 2.6: Ambient Air Quality standards based on the South African National Environment Management: Air Quality Act (SA, 39/2004)

	NO/ ppb	NO ₂ / ppb	SO ₂ / ppb	O ₃ / ppb
Instantaneous peak	1400	500	185	250
Max 1-hour average	800	200		120
Max 24-hour average	400	100	48	
1-month average	300	80		
Annual average	200	50	19	

In Table 2.7, the South African ambient air quality standards are compared with international ambient air quality standards.

Table 2.7: Ambient Air Quality guidelines and standards of inorganic gases for various countries and organisations

Authority	NO ₂ / ppb		SO ₂ / ppb		O ₃ / ppb	
	Standard	Guideline	Standard	Guideline	Standard	Guideline
SA Standards (Air Quality Act 39 of 2004)	50		19			
WHO		21		30		61
World Bank (General Environmental Guidelines)				19		
United Kingdom	21 ^a		11		50	
EPA	53		30		120 ^b 75 ^c	
Australian Standards	30		20		100 ^b	
Canada	52		11		10 51 ^b	

Korea	50		20		100 ^b 60 ^c	
European Community	21		46 ^a		120 ^c	

^a 24-hour average

^b 1-hour average

^c 8-hour average

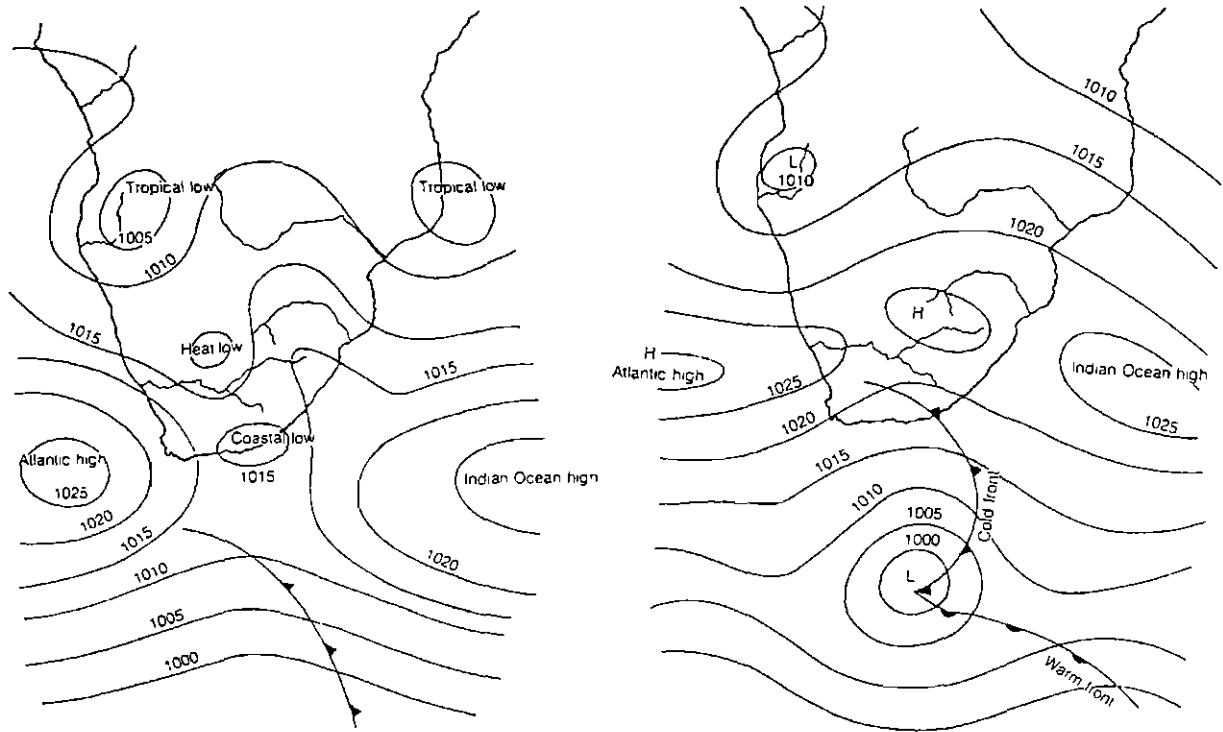
^d 1-month average

Globally, the standards are relatively in the same range. Nitrogen dioxide, SO₂, and O₃ concentrations in southern Africa decreased from 1995 to 2001, with a slight increase from 2001 to 2005 (Martins, *et al.*, 2007). Data from various monitoring stations nationwide indicate that the annual and daily SO₂ concentrations seem to be well below the given standards (Eskom, 2002; SA, 2001; Sasol, 2002) with monthly NO₂ and SO₂ concentrations ranging from 0.2 to 6 ppb and 0.2 to 7 ppb respectively. Ozone concentrations range from 10 to 57 ppb.

The climatology of South Africa is explained in the next section.

2.4 CLIMATOLOGY OF SOUTHERN AFRICA

As mentioned in the preceding sections, temperature and water vapour have an important impact on pollutants, especially ozone, concentrations. The climatology of the region is therefore important. Figure 2.4 shows the seasonal circulation with high and low pressure cells, while Figure 2.5 shows the result of pressure cells on wet and dry effects.



(a) (b)
Figure 2.4: General seasonal circulation in southern Africa (Sandham, 2008; Thyson, 1986)

(a) the basic element in the pattern of pressure distribution for mid-summer; and
 (b) the basic elements in the pattern of pressure distribution for winter

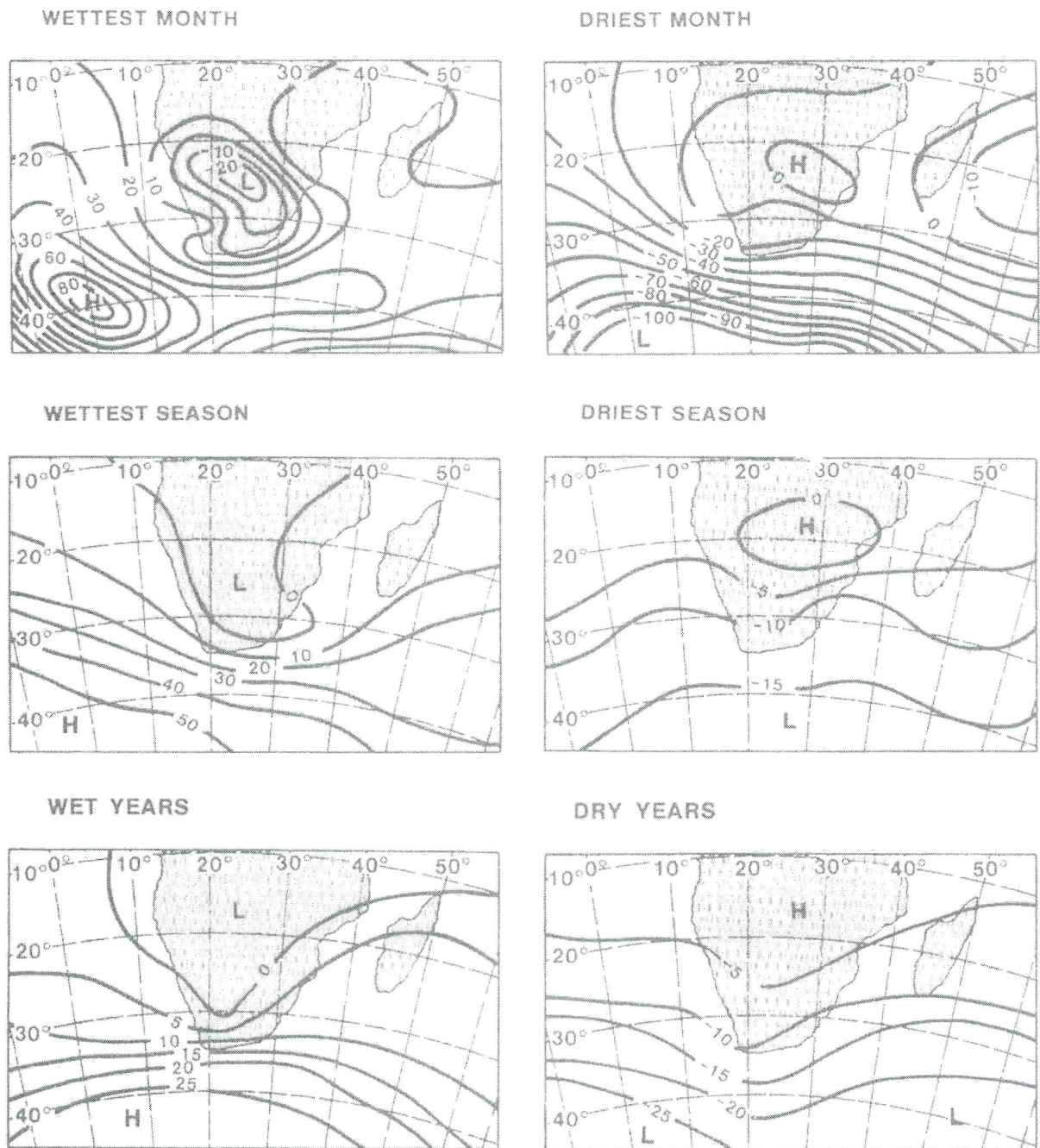


Figure 2.5: Wet and dry effects on climatology in southern Africa.

The mean 500 hPa deviations (gpm) for the wettest January (1978) and driest January (1969); the wettest summer (1975/1976) and the driest summer (1965/1966); all the wet months in the extended wet spell of 1972/1973 to 1978/1979; and all the dry months in the extended dry spell of 1963/1964 to 1970/1971. The symbols H and L indicate relative states only (Sandham, 2008; Thyson, 1986)

Southern Africa is situated in the subtropical high-pressure belt (which circles the globe between 25°S and 30°S), where it is influenced by several high-pressure cells. Anti-cyclonic conditions prevailed over southern Africa throughout the year. This can be due to the dominance of three high pressure cells (the South Atlantic high-pressure cell off the west

coast, the South Indian high-pressure cell off the east coast, and the continental high-pressure cell over the interior (DEAT, 2007).

In the summer months, the anti-cyclonic belt weakens and shifts southwards, allowing the tropical easterly flow to resume its influence over South Africa. Low air pressure conditions prevail over the interior of South Africa with generally unstable meteorological conditions, which increase the vertical motion and dispersion of pollutants in the atmosphere (Thyson *et al.*, 1996).

During the winter, however, stable conditions with low wind speeds prevail over most parts of the country. Winters are characterised by the formation of inversion layers inhibiting vertical atmospheric mixing, and in general, weaker removal processes, effectively trapping pollutants between these layers. The first elevated inversion layer is located at an altitude of three kilometres over the plateau. Upper air winds blow predominantly from a westerly direction, which causes large quantities of pollutants to be transported to the Indian Ocean (Freiman and Piketh, 2002). During summer, this first elevated layer increases to between four and five kilometres over the plateau. Cloudlessness (experienced for most winter months over the region) ensures full intensity of incoming solar radiation, which enhances photochemistry and results in the accumulation of photochemical smog in some areas (DEAT, 2007).

2.5 MPUMALANGA

The Mpumalanga Province is not only known for its extraordinary natural beauty of forests, mountains, rivers, waterfalls, and wildlife parks, but also for its economical contribution through industrial, mining, and agricultural productions. Mpumalanga accounts for more than 80 per cent of the coal production in South Africa, and contributes 6.8 per cent to this country's economy (SA, 2006).

2.5.1 GEOGRAPHY

The Mpumalanga Province is situated (latitude 25.2° to 27.2°S and longitude 27.2° to 29.2°E) on the eastern side of Gauteng, north of KwaZulu-Natal, with Swaziland and Mozambique as borders. The province have an area of 79 490 km² with a total population of 3.5 million (almost 7 % of country's people; Encarta, 2007).

Mpumalanga is geographically divided by the Drakensberg Escarpment into an eastern (low

altitude) and western (high altitude) part. The eastern part, called the Lowveld consists mainly of subtropical savannah plains (this is the result of the warm Indian Ocean and latitude), while the western part, the Highveld, consists mostly of grassland.

The Highveld extends from the eastern parts of Gauteng to Middelberg in the north and the edge of the escarpment in the east. Main towns in the Highveld include Balfour, Belfast, Bethal, Carolina, Ermelo, Middleburg, Secunda, Standerton, Volksrust, Witbank, and Benoni. Nelspruit is the capital of the Mpumalanga Province situated in the Lowveld as indicated in Figure 2.6, below.

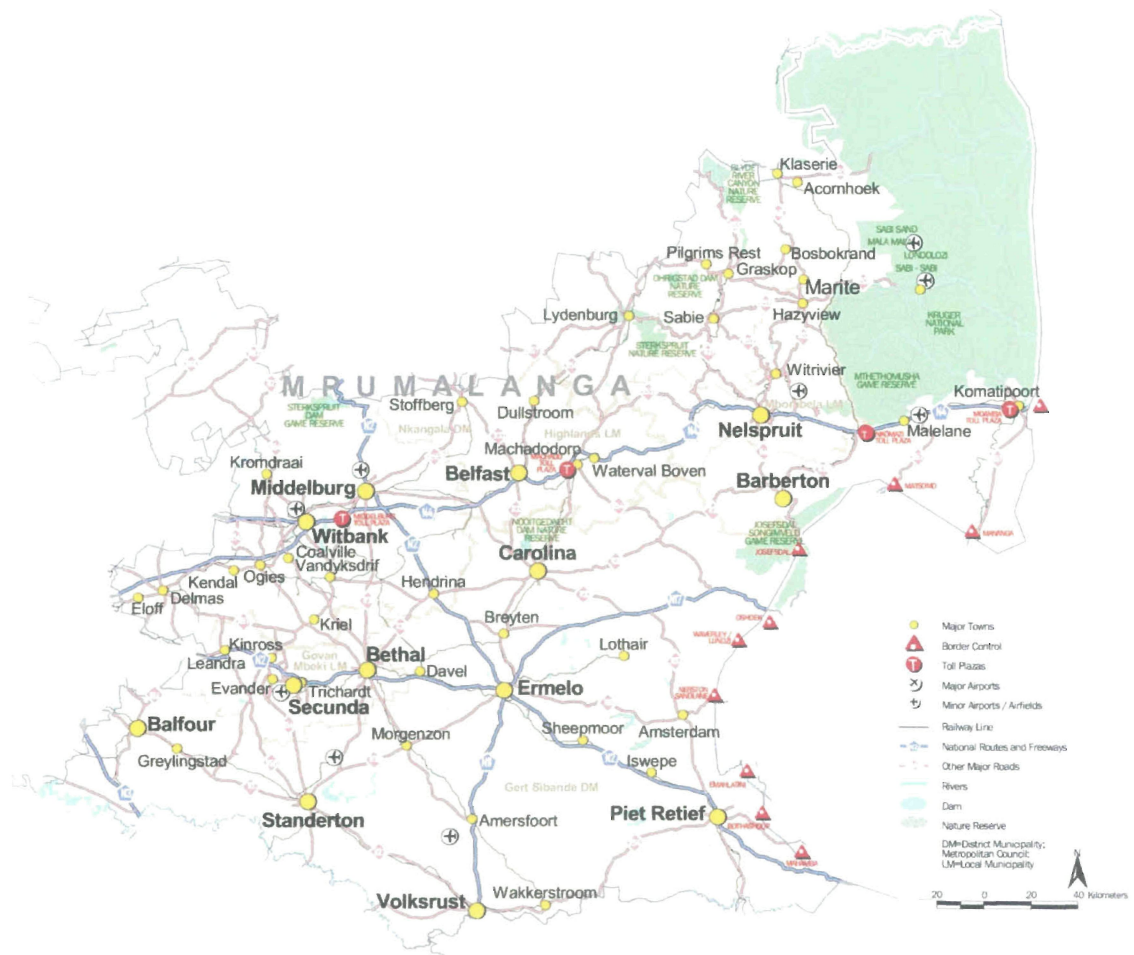


Figure 2.6: Map of Mpumalanga Province, South Africa (TGC, 2007)

2.5.2 AIR POLLUTION

The air quality in the Mpumalanga Highveld region is one of the major concerns for both the government and industry. The Minister of Environmental Affairs and Tourism proclaimed the eastern Gauteng and western Mpumalanga as a priority area termed the HPA (SA, 2007). A wide variety of air pollution is produced from sources ranging from veld fires to industrial processes, agriculture, mining activities, and domestic use of fossil fuels (State of

Environment, 2003). These activities are responsible for producing different pollutants ranging from VOCs, inorganic gases, heavy metals, particular matter, and odours.

2.5.2.1 Industries

Mpumalanga is rich in coal reserves with SASOL, a large coal-to-Liquid (CTL) facility, situated in Secunda. SASOL not only mines coal, but also produces a variety of chemicals, solvents, polymers, fertilisers, and commercial explosives (Sasol, 2007). Industrial solvents include ketones, mixed alcohols, propanol, ethyl acetate, and acetic acid. Inorganic and organic gases are emitted into the atmosphere during synthetic fuels, polymers, chemical, and fertilisers processes, which contribute to the air quality.

Besides the big coal deposit in the central region, there are gold deposits in the western side with chromite, magnetite, silicon, and iron deposits in the north and western side of Mpumalanga. In the eastern side, nickel, gold, asbestos, copper, cobalt, and antimony are mined (Freight transport data bank, 2004).

Highveld Steel (situated near Witbank) is the country's second largest steel maker and the world's biggest producer of vanadium. Columbus Steel, the country's only large stainless steel manufacturer is also situated in the Middelburg region.

2.5.2.2 Power stations

Around 80 % of the power production in South Africa is generated in Mpumalanga. This is due to the large coal deposits, which reduces transportation costs (Eskom, 2002). Of the 24 power generation facilities owned by Eskom, 13 are coal driven and 11 are situated in Mpumalanga. Three coal-fired power stations have been recommissioned since early 1990, to meet the growing demand of electricity. The power stations are:

- Arnot (approximately 50 km east of Middelburg);
- Duvha (approximately 15 km east of Witbank);
- Hendrina (approximately 40 km south of Middelburg)
- Kendal (Witbank);
- Kriel (between Ogies and Kriel);
- Majuba (between Volsrust and Amersfoort);
- Matla (approximately 30 km from Secunda);
- Tutuka (between Standerton and Bethal, approximately 25 km from Standerton) ;

- Camden (situated close to Ermelo);
- Grootvlei (close to Balfour); and
- Komati (situated between Middelburg and Bethal).

As previously mentioned, the combustion of coal is a major source of pollutants, such as sulphur dioxide, nitrogen dioxide, and particulates. Sulphur- and nitrogen dioxide emissions ranged between 1728 to 1876 kt/yr and 760 to 930 kt/yr respectively from 2003 to 2007 (Eskom, 2007). Although emissions have increased since 1994, measured SO₂ and NO₂ monthly concentrations are still well below DEAT guidelines of 50 ppb and 200 ppb respectively. Annegarn *et al.* (1996) and Rorich *et al.* (1995) reported high SO₂ levels in the surrounding areas of power plants in the Mpumalanga Highveld.

2.5.2.3 Road traffic

Mpumalanga is predominantly rural with approximately 61 % of the population living in rural areas. Vehicle emission sources contribute to nitrogen oxide and sulphur dioxide emissions. Although sulphur content in petrol has been reduced from 5000 ppm to 3000 ppm since 1996, VOC emissions (particularly benzene, 1,3 butadiene, formaldehyde, acetaldehyde) have increased significantly. The traffic emissions in Mpumalanga, in comparison to industries and power stations, contribute less to air pollution.

2.5.3 METEOROLOGICAL FACTORS INFLUENCING AIR QUALITY IN THE MPUMALANGA HIGHVELD REGION

Climatic conditions affect the air quality in the Highveld region. Factors, such as regional air movements, local climate, and rainfall influence the distribution of pollutants inside the province, as well as to neighbouring provinces and countries.

Dispersion of atmospheric pollutants is affected by the distinct summer and winter weather patterns of the Mpumalanga Highveld. During the summer months, unstable conditions result in mixing of air and rapid dispersion of pollutants in the atmosphere, especially in the Highveld region. In winter months, a persistent high-pressure system exists, causing clear skies and pronounced temperature inversions at night. The temperature inversion layer traps the air pollutants in the lower atmosphere, increasing pollutant concentrations and contributing to poor air quality (Preston-Whyte and Thyson, 1988).

Air is mostly transported to the Highveld from the Atlantic Ocean with other flows from the Indian Ocean, subtropical Africa, and over southern Africa. During winter, air flow from the Indian Ocean predominates; while in summer, flows from the Atlantic ocean dominate (Freiman and Piketh, 2002).

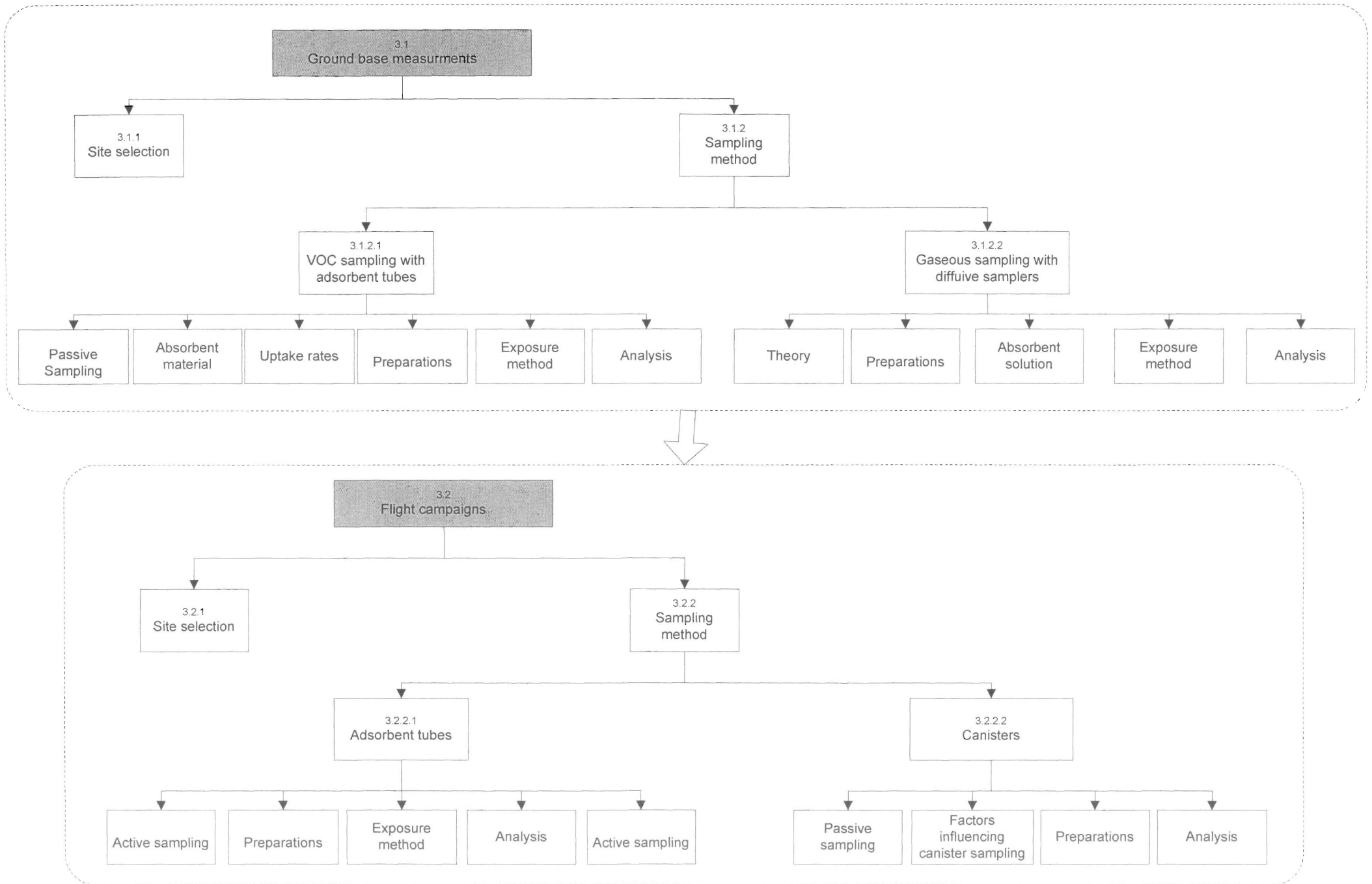
The annual rainfall in the eastern Highveld is between 500 and 900 mm, with higher deposition particularly in the Lowveld of Mpumalanga. The annual precipitation in the Highveld region increases from west to east, averaging from 510 to 760 mm (Britannica, 2008). Typical rainfall period for the Highveld is from October to February. Pollutants are removed from the atmosphere through wet deposition. Sulphur dioxide emissions produce acid rain, which have a negative effect on agricultural productivity. Half of South Africa's agricultural productive land is situated in Mpumalanga.

2.6 CONCLUSION

From the preceding discussion, it is clear that VOCs (i.e. BTEX) and inorganic gases (i.e. NO_2 , SO_2 , O_3) play important roles in tropospheric chemical reactions and contribute to air pollution. *These pollutants also negatively influence human well-being and ecological systems.*

Monitoring of inorganic gases with active and passive samplers is well established in South Africa. In contrast, very little data exists for VOCs, which necessitates the measurement of these gases. In order to assess the potential impact of BTEX, NO_2 , SO_2 , and O_3 in the HPA, a one-year study of the spatial and temporal distribution of these species was conducted.

Graphical layout of Chapter 3



Chapter 3:

Experimental Procedures

*"There's so much **pollution** in the **air** now that if it weren't for our lungs there'd be no place to put it all."*

Robert Orben

3.1 GROUND BASE MEASUREMENTS

Field measurements for SO₂, NO₂, O₃, and BTEX were conducted in the Mpumalanga HPA.

3.1.1 SITE SELECTION

Ground-level sampling commenced in August 2007 and was conducted for a year on a monthly basis up until July 2008. Eight sites were chosen to represent a sampling grid that covered 600 km². The sites were located in the following cities and towns: Balfour, Delmas, Witbank, Carolina, Ermelo, Amersfoort, Standerton, and Vanderbijlpark, which gave a good representation of the HPA. The site locations ranged from highly industrialised areas, such as Witbank and Vanderbijlpark to more rural areas, such as Carolina and Amersfoort. The geographical layout of the sampling points is shown in Figure 3.1, below.

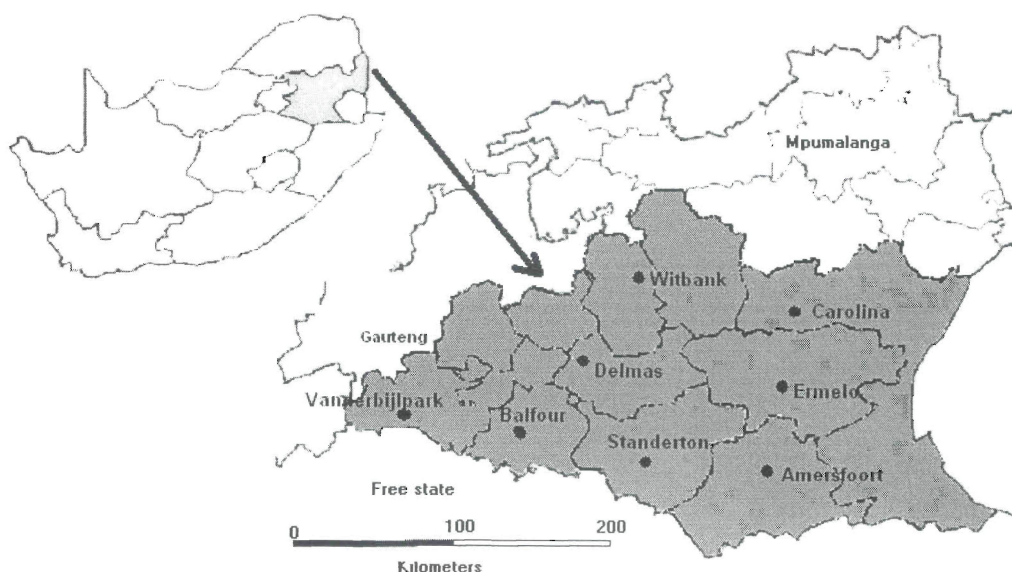


Figure 3.1: Geographical layout of sample stations

3.1.2 SAMPLING METHODS

The atmosphere contains a heterogeneous mixture of gases, liquids, and solid particles (see Section 1 to 2.2.4), which complicates the monitoring and control of air quality (Camela and Caude, 1995). When selecting the most suitable sampling method, certain factors had to be taken into consideration. The samplers had to be cost effective, easy to use, environmentally friendly, efficient, maintenance free, and not requiring field calibration. Samplers that do not require electricity for operation were preferred, since it negated the need for electrical power, which was not always accessible. Smaller and lighter samplers were also more ideal, since they were easier to transport.

3.1.2.1 Volatile organic compounds sampling with adsorbent tubes

During this study the concentration of VOCs in ambient air were determined with adsorbent tubes. Perkin-Elmer 6.25 o.d. mm adsorbent tubes were used with a cross section area of 0.18 cm^2 and diffusion length of 1.7 cm. Figure 3.2 shows such tubes.



Figure 3.2: Adsorbent tubes fitted with diffusive caps used for ground-level sampling

This method is very popular amongst environmentalists and scientists due to accurate and reliable results obtained (Zabiegała *et al.*, 2002). It has an advantage over canisters in that larger volumes can be sampled (Camela *et al.*, 1995).

Adsorbent material

Characteristics of different sorbents are given in Table 3.1 on the next page (EPA, 1997). The efficiency of the sorbent is determined by the adsorbent capacity of the sorbent material, with larger loadability of the sorbent leading to larger possible sampling volumes. Concentrations of some compounds can be determined at levels as low as 100 ppt (Camela and Caude, 1995).

Tenax TA and Carbotrap 106 porous polymeric material are the most frequently used sorbent materials, particularly for VOC sampling (Parra *et al.*, 2006; McClenny, Olivier, Jacumin & Daughtrey, 2002). Although Tenax TA is a weaker adsorbent than Chromosorb 102/106, it contains a hydrophobic co-polymer, which enables sampling without the retention of water vapour (ThermoMatrix, 2007). During this research project, Tenax TA adsorbent tubes were used for ground-level sampling of VOCs.

Table 3.1 Sorbent characteristics for volatile organic compounds (EPA, 1997)

Sample Tube Sorbent	Approx. Analyte Volatility range	Max. Temp (°C)	Specific Surface Area (m²/g)	Example of Analytes
CarbotrapC ®/ CarbopackC ®	n-C ₈ to n-C ₂₀ , Alkyl benzene and aliphatic compounds	400	12	Alkyl benzenes, PATD, PCBs
Tenax® TA	n-C ₇ to n-C ₃₀ ,	350	35	Aromatics except benzene, non- polar compounds(pb>100°C), such as aliphatic hydrocarbons from n-C7 and less volatile polar compound (pb>150°C)
Tenax GR	Bp 100°C to 450°C n-C ₇ to n-C ₃₀ ,	350	35	Alkyl benzenes, PATD, PCBs, and the same as for Tenax TA
Carbotrap ®/ CarbopackB®	n-C ₅ to n-C ₁₄ ,	400	100	A wide range of VOCs, including ketones, aldehydes, and all polar compounds within the volatility range specified
Chromosorb® 102	bp 50°C to 200°C	250	350	Suits a wide range of VOCs including, oxygenated compounds and haloforms less volatile than methylenechloride
Chromosorb® 106	bp 50°C to 200°C	250	750	Suits a wide range of VOCs including, hydrocarbons from n-C ₅ to n-C ₁₂ . Also good for volatile oxygenated compounds

Passive sampling

The central portions of the tubes used are packed with 0.1 to 2 g solid adsorbent material that, is either a porous polymer or charcoal (EPA, 1997). In Figure 3.3, an example of a stainless steel adsorbent tube is shown.

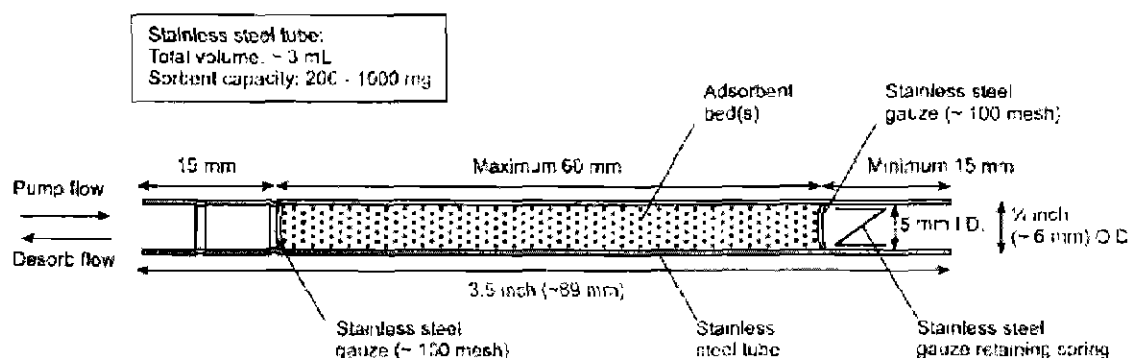


Figure 3.3: Stainless steel tube (EPA, 1997)

Passive sampling (diffusive sampling) involves the flow of ambient air through adsorbent tubes by means of diffusion. The rate of diffusion is governed by Fick's Law of Diffusion, and it is influenced by physical parameters, such as gaseous diffusion through a static layer or porous material (Brown, 1999). Air is not forced through the tube by a pump.

Uptake rates

The uptake rates for compounds can either be theoretically derived from Fick's Law or experimentally determined. The axial diffusion of adsorbent tubes placed in the vertical position is shown Figure 3.4 on the following page.

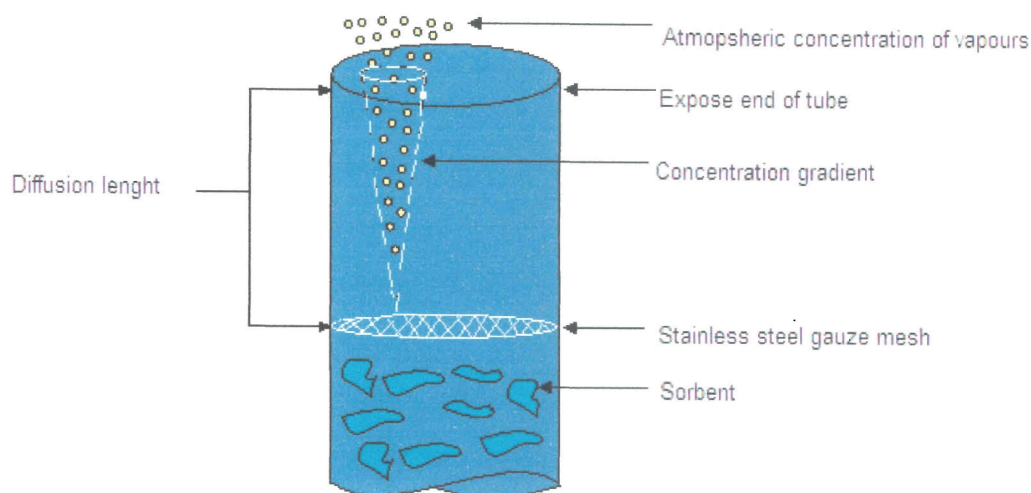


Figure 3.4: Illustration of axial diffusion in passive samplers

The theoretical uptake rates can be derived from Fick's First Law of Diffusion from the following equations:

$$J = \frac{D}{l(C_1 - C_2)} \quad 3.1$$

where

J = diffusive flux ($\mu\text{g m}^{-2} \text{s}^{-1}$);

D = diffusion coefficient of analyte ($\text{m}^2 \text{s}^{-1}$);

C_1 = Concentration of analyte at beginning of diffusion layer ($\mu\text{g.m}^{-3}$);

C_2 = Concentration of analyte at the end of diffusion layer ($\mu\text{g.m}^{-3}$); and

l = diffusion path length (m).

The ideal theoretical uptake rate (U) is determined by:

$$U = \frac{D \times A}{l} \quad 3.2$$

where

A = cross-sectional area of the diffusive path, or the equivalent sorption surface (cm^2);

l = length of static layer of sample (cm);

D = diffusion coefficient ($\text{cm}^2 \cdot \text{min}^{-1}$); and

U = ideal uptake rate (mL/min).

With the known ideal uptake rate, the atmospheric concentrations of the compound can then be determined:

$$C = \frac{X}{U_p \times t} \quad 3.3$$

C = atmospheric concentration (cm³/min);

U_p = Ideal uptake rate (cm³ min⁻¹);

X = amount of the analyte which is adsorbed on the tube (ng); and

t = time of exposure (min).

Uptake rates are usually given in units of ng.ppm⁻¹.min⁻¹ or pg.ppb⁻¹.min⁻¹, to give atmospheric concentrations in ppm or ppb. U_p is the uptake rate at ambient conditions. The conversion of U (cm³.min⁻¹) to U_p (ng.ppm⁻¹.min⁻¹) is:

$$U_p = \frac{U \times M \times 293 \times P}{24.5 \times T \times 101.1} \quad 3.4$$

U' = Ideal diffusive uptake rate (ng.ppm⁻¹.min⁻¹);

M = Molecular mass of analyte (g/mol);

P = pressure of sampled atmosphere during sampling (kPa);

T = temperature of ambient air sampled (K); and

24.5 l/mol = Molar gas volume at 760 mm Hg and 25 °C at 298K.

Table 3.2 presents the theoretical and experimental uptake rates determined for each one of the compounds measured.

Table 3.2: Theoretical and experimental uptake rates

Component	Diffusion Coefficient (cm ² /s)	Molecular Weight (g/mol)	Uptake Rate (cm ³ /min)	Theoretical Uptake Rate (ng/ppm.min)	Experimental Uptake Rate (ng/ppm.min)
Benzene	9.32E-02	78.10	0.59	1.90	0.70±0.09 ^a
Toluene	8.49E-02	92.10	0.54	2.04	1.03±0.26 ^a
Ethylbenzene	7.55E-02	106.20	0.48	2.09	1.50±0.40 ^c
o Xylene	6.88E-02	106.20	0.44	1.90	1.46±0.67 ^a
m,p Xylene	7.27E-02	106.20	0.46	2.01	1.46±0.67 ^a

^a Uptake rates obtained from Markes International Limited (2006).

^b Uptake rates obtained from the Diffusive Monitor Issue 12 (2001).

^c Uptake rate obtained from Potter (2008).

The theoretical uptake rate is only an indication of the ideal uptake rate for each component, for the specific tube and packing material, but does not include other changing variables, such as exposure time and wind speed. Ethylbenzene is the only compound studied for which the experimentally determined uptake rate, for an exposure time of four weeks on Tenax TA, that could not be found in literature. The reason is that Tenax is a non-ideal sorbent for ethylbenzene (Potter, 2008), thus an extrapolated value relative to the other compounds were used. Since the value was extrapolated, a relative large error of 0.4 ng/ppm.min was assumed.

Preconditioning of adsorbent tubes prior sampling

The adsorbent tubes were tested for leaks and preconditioned with helium for 30 minutes at 350°C at a flow of 50 cm³.min⁻¹ before they were used. After treatment, the tubes were sealed with Swagelok® brass ¼" caps (P/N 0990-8851) and stored in a fridge at temperatures below 18 °C prior to sampling. Tubes have a maximum lifetime of two years when used frequently.

Exposure method

The samplers were exposed in an aluminium stand specially manufactured by the Instrument Technicians at the Potchefstroom campus of the North-West University. The aluminium stands (Figure 3.5a) consisted of a 1.5 m shaft and a hood for protecting the samplers.

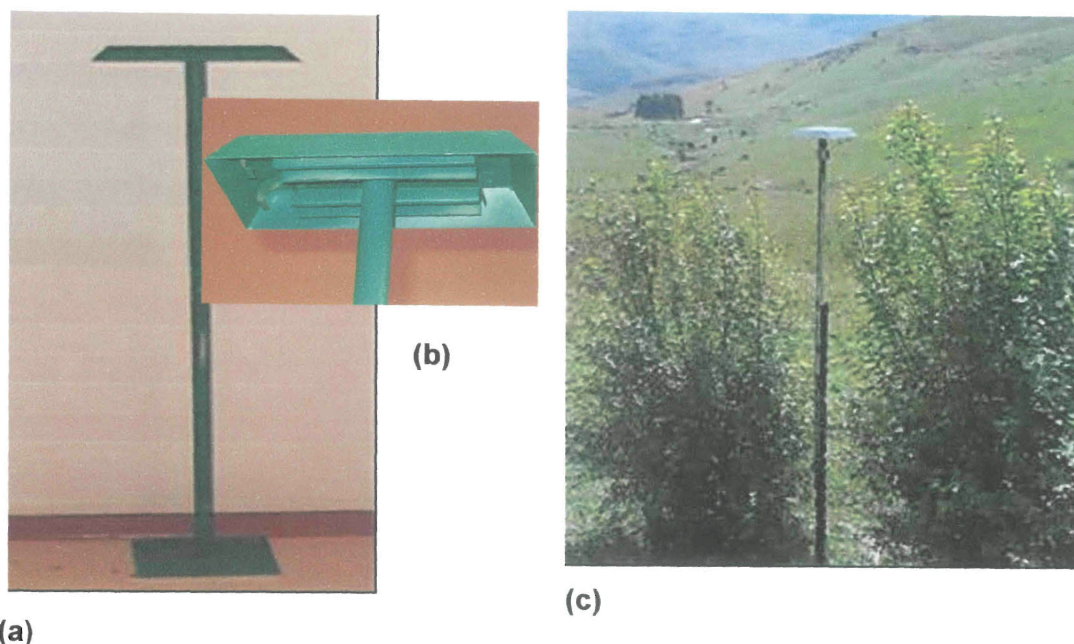


Figure 3.5: (a) Aluminium Sampler stand, (b) Sampler hood with aluminium rail, (c) mounted Sampler stand at Carolina

The Swagelok caps were removed from the tubes before exposure in the field and replaced with diffusive caps for effective air movement through the tubes. The tubes were placed upside down onto the shaft of the stand into a special fitting (Figure 3.5b). After the sampling period, the diffusive caps were removed and sealed-off with the Swagelok caps. The exposed tubes were wrapped individually in aluminium foil and stored at conditions below 18°C before they were analysed.

Analysis of tubes

The Tenax TA absorbent tubes were analysed using an Marks International Unity Thermal Desorber, Agilent Technologies 7890A gas chromatograph (GC) connected to an Agilent Technologies 5975C VL Micromass Autospec mass spectrometer (MS), and on a Perkin-Elmer Turbo matrix desorber, Hewlett Packard Agilent 6890 gas chromatograph coupled to Micromass AutoSpec TOF Mass Spectrometer, in compliance with the EPA TO-17 compendium and NIOSH 2549 method. Figure 3.6 shows the GC-MS system.

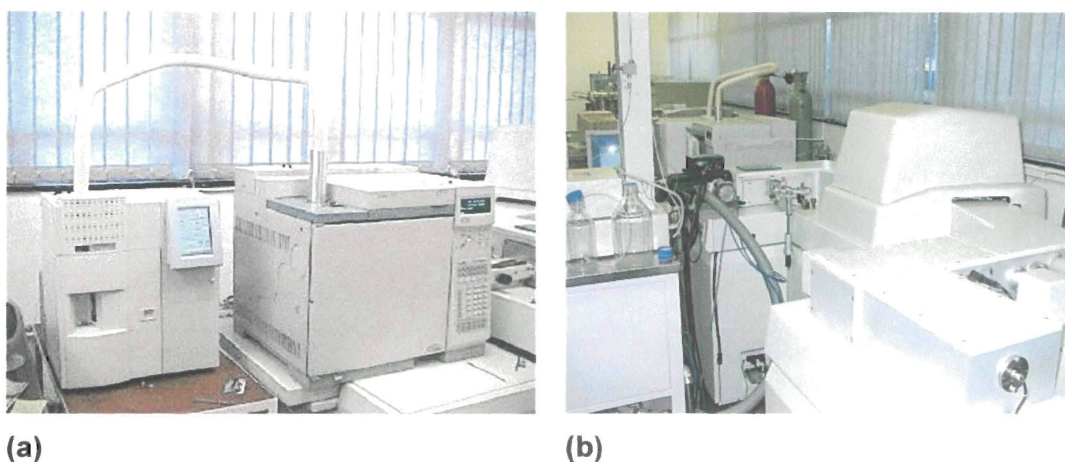


Figure 3.6: Analysis equipment: (a) Perkin-Elmer Turbo matrix desorber, Hewlett Packard Agilent 6890 gas chromatograph, (b) coupled to Micromass AutoSpec TOF mass spectrometer

The tubes were analysed by using a two-stage thermal desorption method. The samples were first tested for leaks and then purged with zero air to reduce the risk of adsorbent oxidation during desorption. Thereafter, the samples were heated for five minutes. The volatiles in the sample were swept by nitrogen gas to a cold trap (-30°C) where they were re-concentrated for four minutes. At the end of this period, the cold trap was heated rapidly for five minutes. Thermal desorption was then used to transfer the concentrated VOCs from the cold trap to the gas chromatograph for separation and detection with the MS.

Typical GC chromatographs are shown in Figure 3.7.

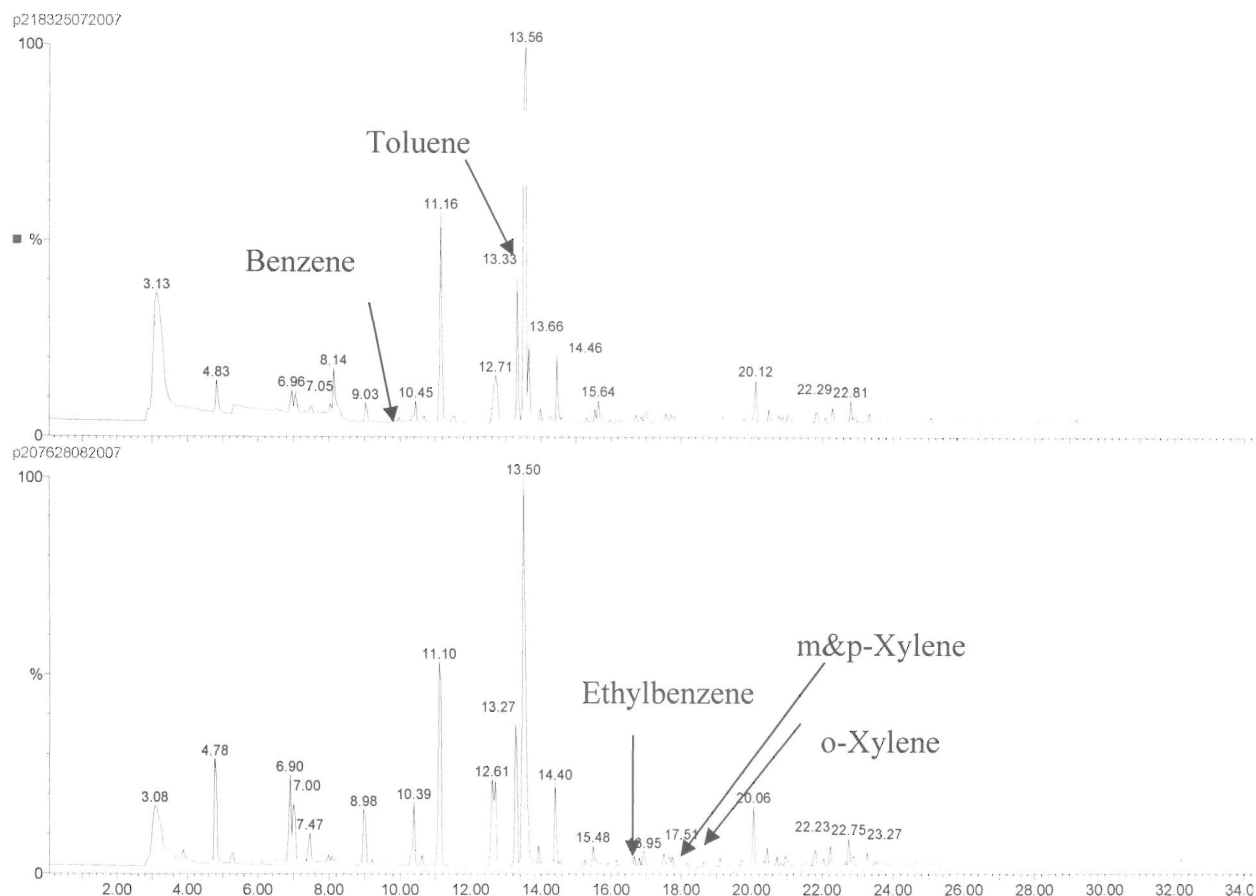


Figure 3.7: Gas chromatographs of a typical sample

Benzene is the small peak at 9:45, which is not always detected at this resolution with toluene peak at 13:22 to 13:27, 16:40 to 16:41 that of ethyl benzene, while the m,p-Xylene peak was at 16:58 to 17:00 and o-Xylene at 17:40. The peaks were so closely packed that a compound, such as benzene, could easily be mistaken for the compound peaking at 10:45 and 10:39, should high resolution GC-MS analysis not have been used. A MS spectrum is not included.

3.1.2.2 Inorganic gaseous sampling with diffusive samplers

Theory

The Atmospheric Chemistry Research Group at the North-West University has demonstrated the effectiveness of monitoring tropospheric inorganic gas pollutants with passive sampling since 1995 (Martins *et al.*, 2007; Dhammapala, 1996). The same principle of diffusion applies for these diffusive samplers as discussed previously (see Section 3.1.2). Figure 3.8 gives a graphical representation of the inorganic gaseous passive samplers used in this research project.

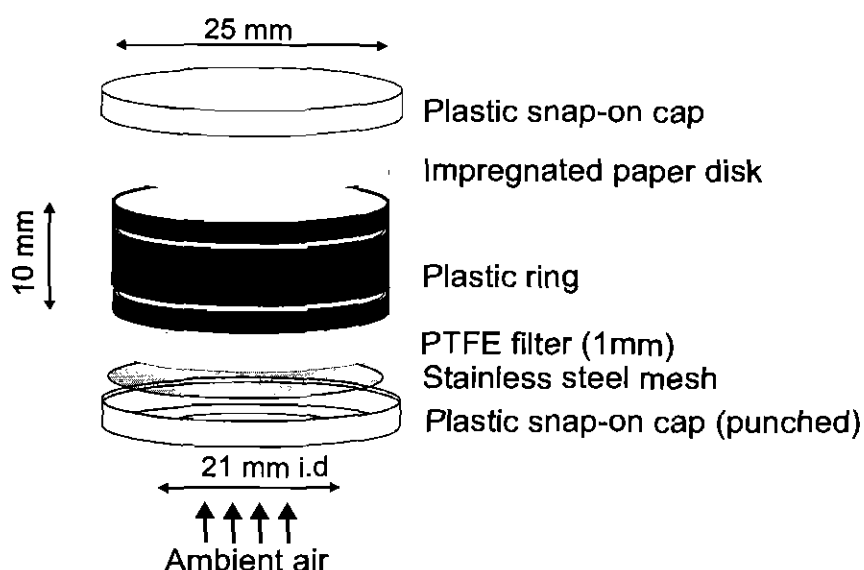


Figure 3.8: Schematic representation of a diffusive sampler (Dhammapala, 1996)

The sampler consists of two plastic snap-on caps with a stainless steel mesh (25 mm o.d., thickness of 160 μm and porosity of 40 %) and PTFE filter (25 mm o.d., 175 μm and porosity of 85 %) to prevent aerosols entering. A Whatman paper filter, which is treated with a chemical to specifically react and trap the pollutant of interest, was placed at the rear end of the sampler. The plastic snap-on caps were held together by a plastic ring. Figure 3.9 shows the passive samplers used during the study.



Figure 3.9: Passive samplers used during the study

Preparation method

The preparation method that was used in this study is described by Dhammapala (1996). All the parts of the passive samplers were washed with EXTRAN sonicated in de-ionised water and air dried before they were used. The Whatman filters were sonicated at least four times with water and methanol consequently, after which they were air-dried in a vacuum desiccator.

The absorbing solution was carefully spread over the surface of the Whatman filter with a micro-pipette, and then loaded against the snap-on cap casing, which was then attached to the ring casing. On the other end, the Teflon filter was loaded against the steel mesh inside the snap-on punched cap, and then onto the ring casing as seen in Figure 3.8.

All the samples were marked with a date, sites, and gaseous species, before being sealed in a plastic vial for transportation. Laboratory blank samples were also prepared the same day, to compensate for any systematic errors and contamination present in the reagents, vials, or Whatman filters. Cellulose filters were impregnated with different absorbent solutions, to determine NO_2 , SO_2 , and O_3 concentrations in the atmosphere.

Absorbent solution

Nitrogen dioxide samplers

A solution containing NaOH and NaI dissolved in methanol and water was used as absorbent to collect NO_2 . During the absorption process, NO_2 is converted into nitrite (NO_2^-) and is chemically trapped on the filter as shown by Equation 3.5.



NaOH was added, to keep the pH at 13 or higher, in order to stabilise the NO_2^- species, which can otherwise be oxidised to NO_3^- by O_3 , should the pH drop to 12 or lower. I^- was added in excess, to prevent atmospheric oxidants, which can oxidise this species to I_2 , from diffusing into the sampler (Martins *et al.*, 2007).

Ozone samplers

Cellulose filters were impregnated with nitrite. Ozone was measured indirectly by determining the amount of nitrate that is formed during the reaction:



The absorbing solution consisted of 1 % (w/v) NaNO_2 , 1% (w/v) K_2CO_3 , and 2 cm^3 glycerol dissolved in a 100 cm^3 70 % water/ 30 % methanol mixture. K_2CO_3 kept the solution at a pH of 12. Oxidation of NO_2^- does not take place above pH 12. Collection efficiency tests have shown that ozone reacts optimally with nitrite when the nitrite and carbonate species come from salts of different metals. This can be due to the higher hygroscopicity of crystals that are formed when the mixed sodium and potassium crystals are formed (Martins *et al.*, 2007; Dhammapala, 1996).

Sulphur dioxide samplers

NaOH was used as the impregnating solution in the sorption process of SO_2 , which is given in Equation 3.7. This is the same sampling and analysing method used and developed by the IVL in Sweden and internationally accepted (Martins *et al.*, 2007).



The absorbing solution was prepared by dissolving 1 g NaOH in less than 15 cm^3 de-ionised water, and diluting it to 100 cm^3 with methanol. The reaction product of the above equation is the unstable SO_3^{2-} species that undergoes oxidation with oxygen and a variety of other catalysts present in trace quantities in the atmosphere, to form stable SO_4^{2-} species (Martins *et al.*, 2007; Dhammapala, 1996).

Exposure method

The passive samplers were removed from their vials on arrival at the site, and slid into a bracket on the aluminium rail with the front of the sampler facing down (see Figure 3.5).

After the exposure period, the samples were replaced in their vials and stored below 18°C before analysis.

Analysis of samples

Inorganic gaseous species were analysed with an ion chromatograph and a UV-visible spectrophotometer as described by Martins *et al.* (2007). Sulphur dioxide and O₃ samples were analysed on a suppressed Ion Dionex Chromatography system (ICS-300) fitted with an Ionpac AS18 (2x50mm) analytical column, Ionpac AG18 (2x50mm) guard column, and ASRS Ultra 11 2mm self-regulating Suppressor.



Figure 3.10: Ion Dionex Chromatography module/SP system

Samples were prepared for Ion Chromatograph (IC) analysis by removing the Whatman filter from the sampler and placing it in a clean vial. Since O₃ concentrations were higher in ambient air than SO₂ and NO₂, O₃ samples were dissolved in 25 cm³ de-ionised water, while 5 cm³ de-ionised water was added to SO₂ and NO₂ samples. The samples were then de-ionised for 15 minutes before they were analysed in the IC. A five-point calibration curve was determined for SO₂ analysis, by preparing standards at 1, 2.5, 5, 10, and 50 ppm; while O₃ was calibrated at 0.1, 1, 2, 5, and 10 ppm.

Typical chromatographs of SO₂ samples collected during the field campaign are given in Figure 3.11 and 3.12.

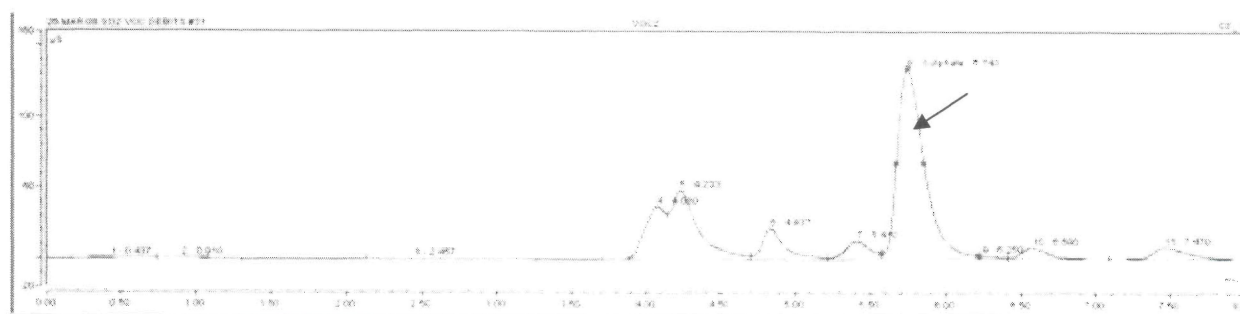


Figure 3.11: Sulphate chromatogram for ground samples collected during the field campaign

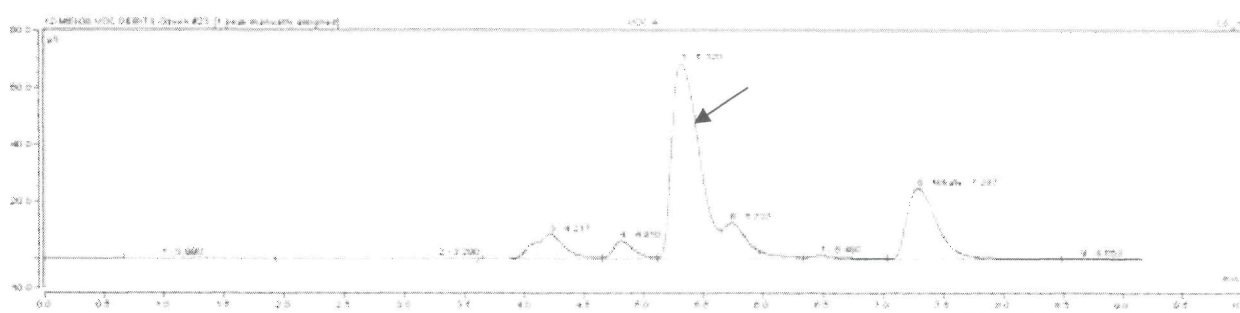


Figure 3.12: Nitrate chromatogram for ground samples collected during the field campaign

Nitrogen dioxide samples were analysed on a Varian Cary 50 UV-visible spectrophotometer (Figure 3.13), since interference exists on the IC. The samples were leached in 5 cm³ of de-ionised water, and then treated with 5 cm³ of the diazotising agent before their absorbance was scanned at 540 nm. The diazotising agent consists of sulphanilamide, naphthylethylenediamine dihydrochloride (NEDA) and H₂PO₄. A five-point calibration curve was determined for NO₂ analyses, by preparing standards at 0.1, 1, 2.5, 5, and 12.5 ppm.

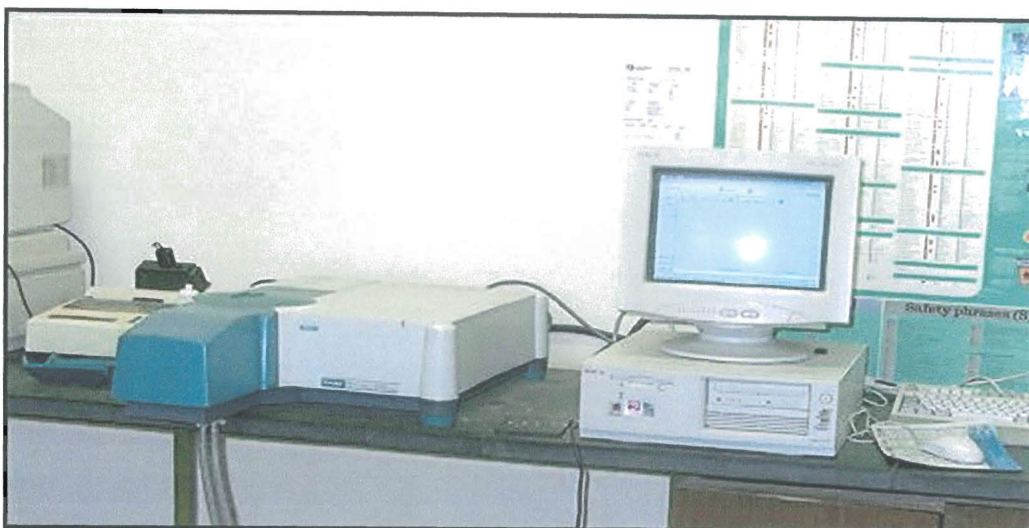


Figure 3.13: Varian Cary 50 UV-visible spectrophotometer

3.2 FLIGHT CAMPAIGN

Vertical profiles for BTEX compounds were determined during a summer and winter campaign.

3.2.1 SITE SELECTION

The flight paths that were chosen for the two vertical profiling campaigns (summer and winter) covered an area within a 100 km radius of Secunda. Flights were undertaken at 500 and 1500 ft above ground level (AGL). These heights were chosen to determine the BTEX levels below the inversion layer and just below the mixing layer, in order to distinguish between ground-level and high-stack emissions. The flight paths are presented in Figure 3.14.

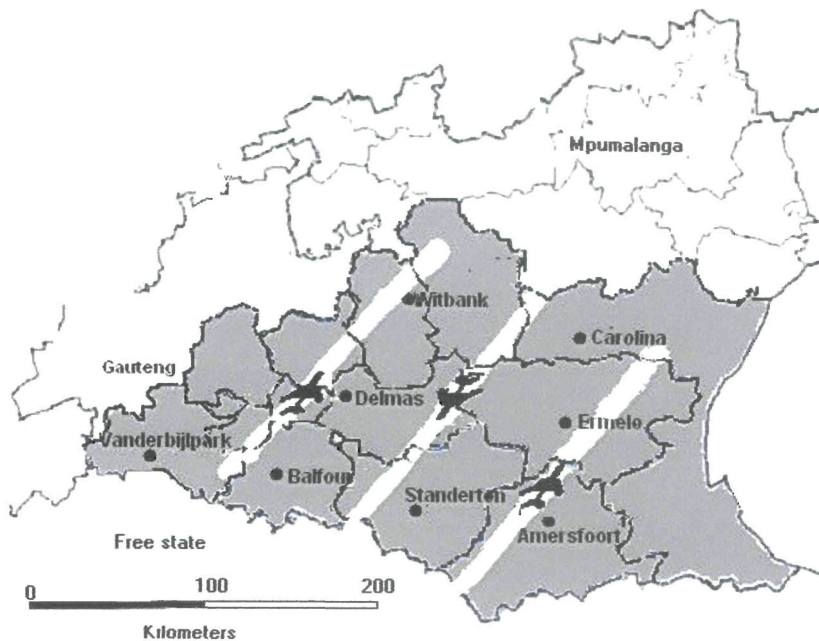


Figure 3.14: Flight paths

3.2.2 SAMPLING METHODS

A Cessna 182 light aircraft equipped with specially designed VOC- and ozone-monitoring equipment was used. The winter flights were undertaken in the end of July 2007 and the summer flights in the first week of March 2008. Figure 3.15 shows the Cessna 182 and the reverse inlet nozzle.

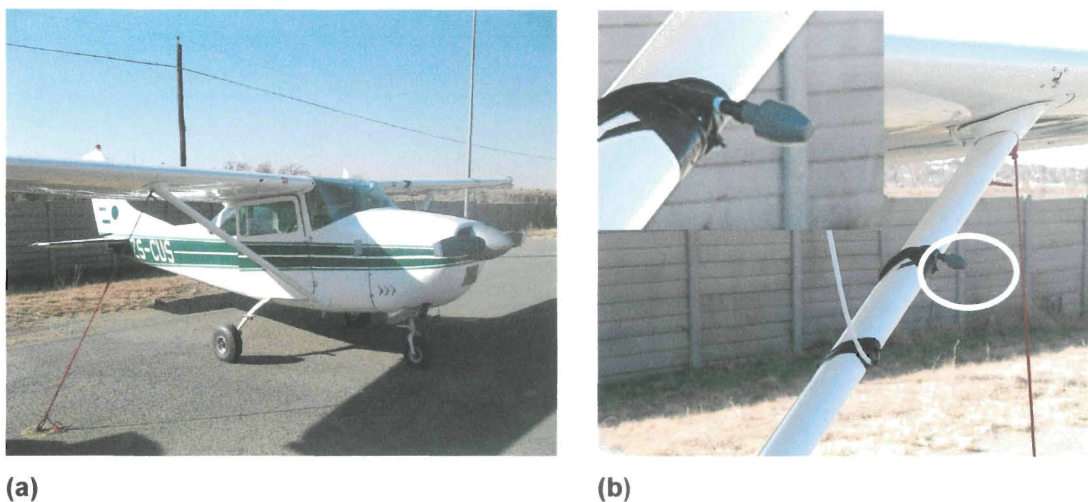


Figure 3.15: a) Cessna 182 used during flight surveys, b) Reverse inlet nozzle connected to the aircraft wing

All flight paths were logged by a GPS (see Figure 3.16) and were on the same route. The flight paths were from Balfour to Ogies, Kriel to VAL Secunda, and Standerton to Davel,

which will be called Balfour (Balfour to Ogies), Kriel (Kriel to VAL Secunda), and Standerton (Standerton to Davel) in this dissertation.

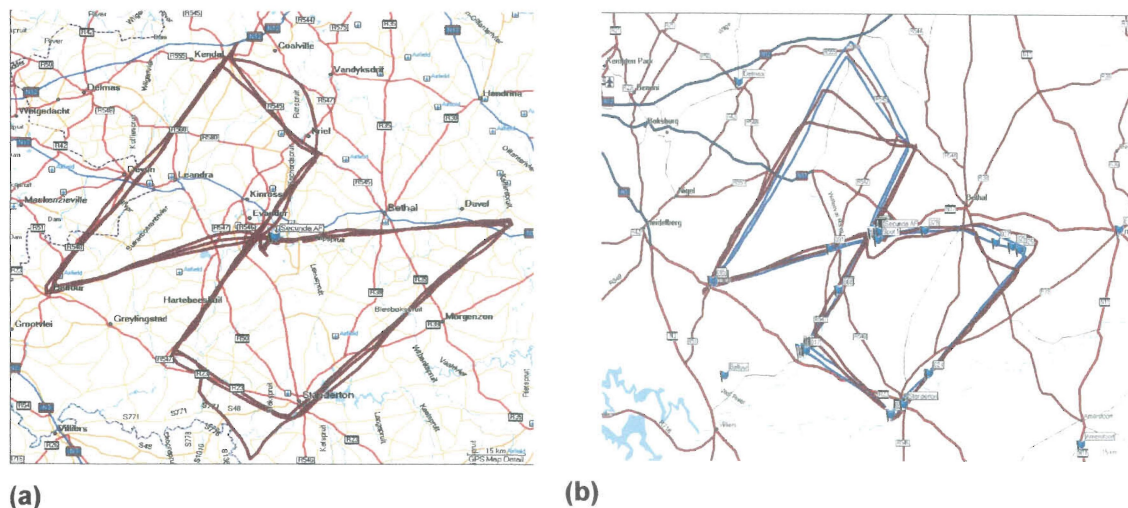


Figure 3.16: Flight path logged by the GPS for the (a) winter (24 and 25 July 2007) and (b) summer (4 and 5 March 2008) surveys

3.2.2.1. Adsorbent tubes

Active sampling

The same adsorbent tubes as described earlier (see Section 3.2.2.1) were used for the vertical profiles. During active sampling, air is forced through the sorbent bed with a pump. A disadvantage of this method is the possible occurrence of breakthrough volumes. This happens when the airflow through the tube is too high causing the VOC concentration on the adsorbent material to increase, with the consequence that adsorption on packing is exceeded. Air samples were therefore collected over a specific time to ensure that breakthrough did not occur, and the pump flow-rate was adjusted to prevent breakthrough.

Flow rates of 185~200 mL/min were used and samples were collected over a period of 20 minutes. These collection volumes and times are within the specification indicated by the EPA TO 17a method (EPA, 1997).

Absorbent material

Adsorbent tubes packed with Carbotrap 300 were used for the winter campaign and Tenax TA for the summer measurements.

Exposure method

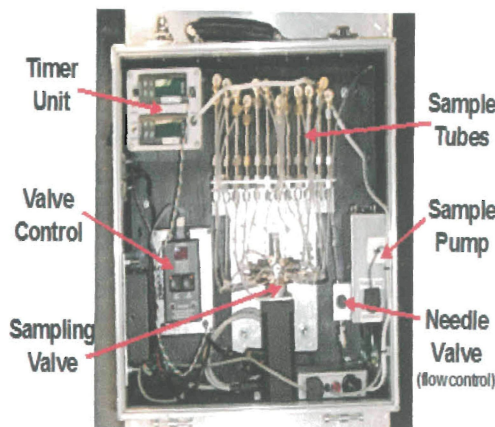


Figure 3.17: Sequence sampler

A sequence sampler developed by Leeds University (in the UK) was used to measure tropospheric BTEX concentrations. A needle valve controls the air that enters through the sample pumped. After the sampling period, the valve control seals the utilised tube and prepares the next tube for sampling.

Analysis

The tubes were analysed on the same system as described in Section 3.2.1.2.

3.2.2.2. Canisters

Stainless steel canisters can also be used for BTEX sampling, and have been used extensively in various parts of the world in several studies where hydrocarbons, especially VOCs, were sampled in ambient air (Camela and Caude, 1995). Polished 6 L TO stainless steel SUMMA canisters were used during this investigation.

Active sampling

During this study an orifice flow controlled air inlet was used. The volume of air sampled was calculated from the flow rate and sampling time. After the canisters were filled they were closed and sent to the laboratory for GC-MS analysis. Figure 3.18 shows the canisters with flow controllers used during the flight campaigns.



Figure 3.18: 6 L TO canister with flow controller

Factors influencing canister sampling

Previous studies conducted by Zielinska *et al.* (1996) show the effect of canister history (age, cleaning method, and quality) on the more polar hydrocarbons, as well as the higher molecular mass hydrocarbons. The loss of air during storage is also not constant over a period, but is dependent on canister design. Losses for C5-C9 were reported to be as high as 20 % (Zielinska *et al.*, 1996). Studies show most of the non-polar VOCs were stable in humidified passivated canisters for at least seven days, and for some of the compounds up to thirty days (Lewis and Gordon, 1996).

The presence of water in air samples can cause serious problems, such as ice formation and blocking of the cryogenic trap (Lewis and Gordon, 1996). Large amounts of water present in an air sample could cause that the water vapour pressure to exceed the saturation vapour pressure, and the water vapour could then condense on the inside of the canister wall during sampling (Burger, 2006).

Preparation of canisters before sampling

Before sampling, all the canisters were tested for leaks. The canisters were filled with zero air and the pressure measured before and after a period of 24 hours. Possible leaks were identified should the pressure have varied by more than 13.8 kPa. All the canisters were

cleaned according to the standard EPA TO-14A method. The automated cleaning system is shown in Figure 3.19 below.

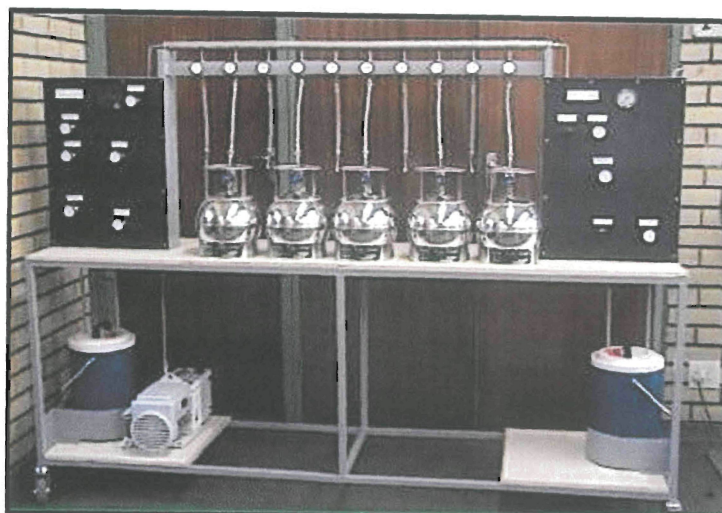


Figure 3.19: Automated cleaning system

The cleaning system has the capability to clean ten canisters at the same time. Liquid nitrogen (used as the cryogen) was added to both the zero air trap and the vacuum pump. During the evacuation process, the pressure was dropped to below 0.05 mm Hg for an hour. Zero air was used to pressurise the canisters. Flushing and evacuation for three cycles were carried out at room temperature with humidified air. The final pressure of the canisters ranged between -25 and -30 mm Hg.

Analysis of canisters

The canisters were analysed using the same GC-MS system as described in Section 3.1.2.1, with a slight modification.

The canisters were pressurised with zero air before being introduced in the TD to be analysed. A suitable calibration standard was obtained from Supelco (Cat no: 41900-U) containing 39 VOCs (100ppb), which was also used as external standard. Before analysis, the system was cleaned with zero air for 40 minutes at a desorption rate of 100 Pnu, to ensure that all the possible impurities were removed. An air sample was withdrawn from the canister and introduced into the Perkin-Elmer Turbo matrix thermal desorber, where it was primary desorbed for four minutes at 50°C. Air was then cold trapped (-30°C) for four minutes by using liquid carbon dioxide. The temperature was increased at a rate of 7°C.min⁻¹ up to 250°C and held for 10 minutes at this value. The column used was a Perkin-Elmer PE-1.60 m, 320 µm id, 1 µm film thickness. A Micromass Autospect TOF mass spectrometer was used as a detector to identify the different compounds. The spectra obtained were similar to those shown in Figure 3.7.

The VOCs present in the samples were quantified by using a response factor obtained from the Supelco standard. The external calibration standard provided retention times that were converted to the scan numbers, which were used to identify the VOCs in the samples. The identification was confirmed using the MS-spectra of the compound. A response factor (R_f) for the VOCs in the standard was calculated by using the following equation:

$$R_f = \frac{\text{Area of VOC in standard}}{\text{Concentrations of VOC}_{\text{standard}} (\text{ppm}) \times \text{time (min)} \times \text{flow rate (cm}^3 \cdot \text{min}^{-1})} \quad 3.8$$

The concentration of the VOCs in the sample was then calculated using the following formula:

$$C_{\text{unknown (ppm)}} = \frac{\text{Dilution factor (only for canisters)} \times \text{area of the VOC in sample}}{\text{time (min)} \times \text{flow rate (cm}^3 \cdot \text{min}^{-1}) \times R_f} \quad 3.9$$

Ozone monitor

Tropospheric O_3 concentrations were measured during the flight campaigns, by using a 2B Technology Ozone Monitor model 202. This instrument logs the average O_3 concentration (ppbv), internal cell temperature, and pressure every minute into the internal memory. The data was subsequently downloaded using the software Tera Term Pro version 2.3.

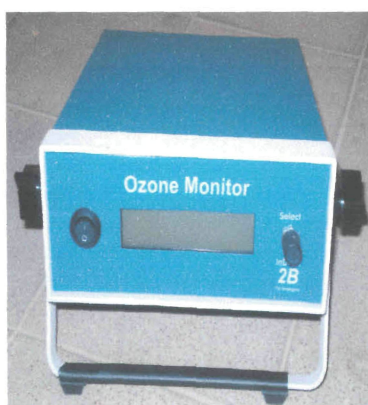
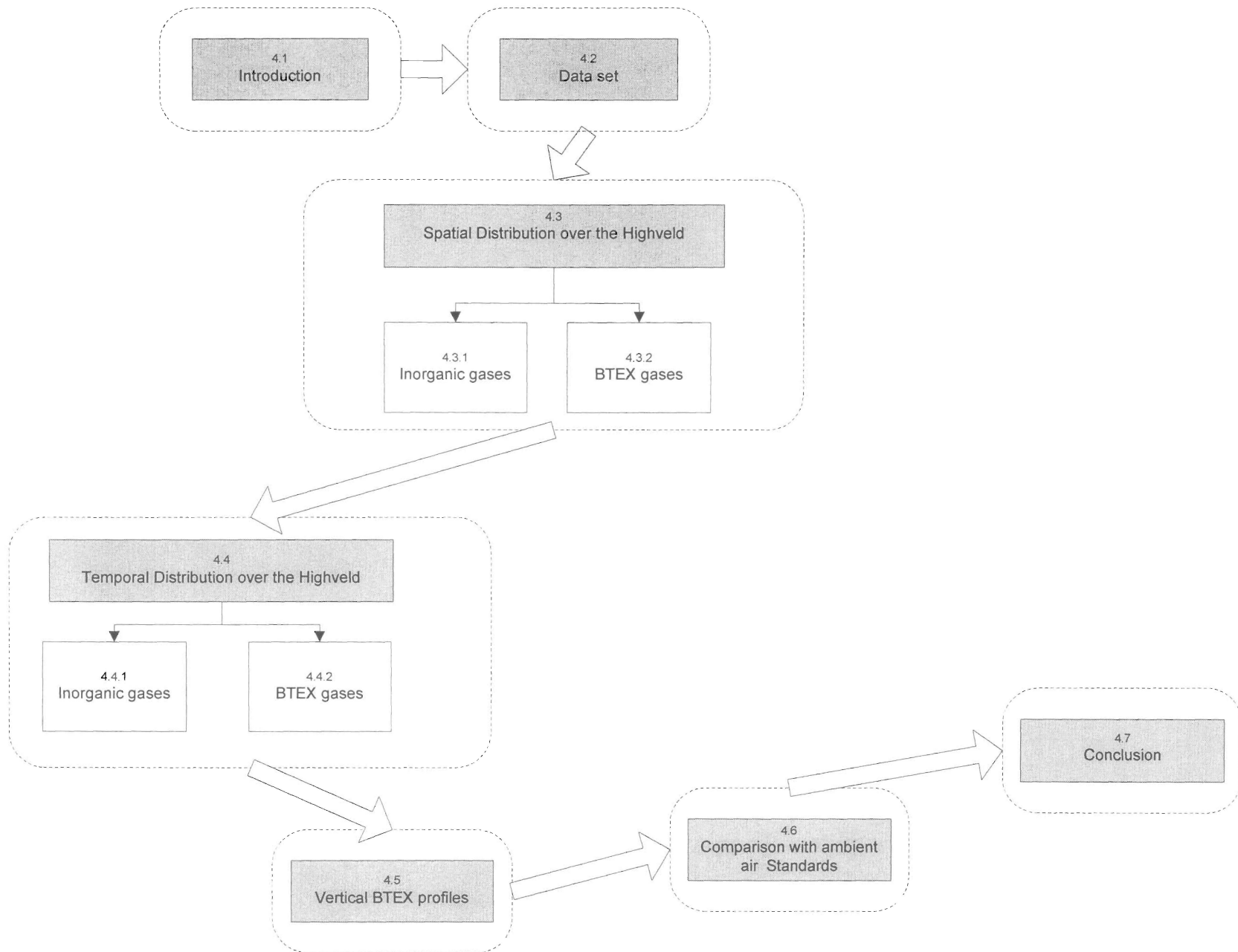


Figure 3.20: 2B Technologies Ozone Monitor

Graphical layout of Chapter 4



Chapter 4:

Results and Discussion

"It isn't pollution that's harming the environment. It's the impurities in our air and water that are doing it."

Dan Quayle

4.1 DATA SET

In Table 4.1, the concentrations of the inorganic gaseous species measured during this investigation are listed.

All the concentrations were measured with passive samplers on a monthly basis for a period of one year. Measured NO₂ concentrations ranged from a minimum of 0.8 ppb to a maximum of 14.03 ppb. Sulphur dioxide levels were between 1.8 ppb up to as high as 24 ppb, while O₃ ranged from a low of 8 ppb to a maximum of 46 ppb. The highest NO₂ and SO₂ concentrations were measured throughout the year at the sites stationed in Witbank and Vanderbijlpark. These sites are situated in highly industrialised areas which lead to the higher concentrations of these pollutants. The lowest NO₂ and SO₂ concentrations were measured at the rural sites Carolina, Balfour, and Amersfoort. Ozone concentrations, in contrast, were the highest in the rural areas and the lowest in the more industrialised areas.

Table 4.1: One year data set of for the inorganic gaseous species at selected sites (ppb)

Stations	Species	2007					2008						
		Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.
Balfour	NO ₂	2.8	3.0	3.7	5.1	2.1	3.0	1.9	3.1	3.8	2.6	1.7	3.2
	SO ₂	4.3	6.2	3.5	3.0	5.6	6.2	4.8	5.3	4.5	4.5	5.8	6.4
	O ₃	19.3	37.04	44.1	42.7	25.2	24.6	30.0	26.4	26.9	8.9	14.4	21.5
Delmas	NO ₂	9.6	8.9	8.5	10.6	7.6	5.1	6.1	8.5	13.2	9.0	8.4	14.0
	SO ₂	8.8	5.3	7.2	3.1	13.2	7.7	11.0	10.8	8.0	8.4	8.2	12.8
	O ₃	8.4	26.8	35.5	20.0	23.3	10.0	19.3	16.5	18.3	5.0	4.0	8.30
Witbank	NO ₂	6.8	7.7	8.7	10.3	5.6	5.6	5.7	8.8	14.3	9.7	8.1	11.2
	SO ₂	12.7	9.4	5.4	4.0	10.4	12.7	7.3	13.8	18.8	18.0	21.3	24.0
	O ₃	10.3	29.0	34.8	25.7	17.0	14.5	15.4	22.0	21.	5.5	4.2	8.2
Carolina	NO ₂	2.6	2.5	2.7	2.9	0.8	-	1.1	1.6	2.8	1.8	2.1	3.1
	SO ₂	6.6	3.3	2.2	2.0	1.8	1.9	2.5	3.1	4.6	5.6	7.8	7.9
	O ₃	22.3	42.3	45.6	25.2	31.0	18.0	24.6	23.1	33.7	12.0	19.9	22.5
Ermelo	NO ₂	7.2	8.8	6.3	10.4	1.9	4.0	5.2	7.0	11.6	9.2	7.3	9.8
	SO ₂	8.6	5.3	5.1	5.2	4.1	3.9	3.9	4.9	7.2	7.2	7.8	10.2
	O ₃	-	24.9	44.6	27.6	22.8	18.0	17.6	18.8	23.4	6.8	9.0	14.1
Amersfoort	NO ₂	2.8	4.8	2.5	4.5	1.8	1.7	1.0	2.7	3.2	2.8	2.3	4.5
	SO ₂	4.6	3.7	6.4	5.3	4.5	4.2	2.2	4.5	5.1	5.5	6.9	9.7
	O ₃	15.0	33.9	39.3	31.2	23.5	25.4	24.7	22.2	28.1	7.0	13.5	16.4
Standerton	NO ₂	6.0	7.7	7.6	8.0	3.9	3.7	3.3	5.0	8.4	6.2	5.9	8.4
	SO ₂	5.5	17.0	5.3	4.3	6.8	5.7	3.7	3.6	4.2	4.8	6.7	6.4
	O ₃	14.1	23.4	40.5	22.4	18.8	18.7	20.5	18.5	19.1	5.7	5.0	13.0
Vanderbijlpark	NO ₂	-	-	-	3.6	4.8	3.8	3.2	13.7	7.8	11.5	9.6	12.4
	SO ₂	-	-	-	2.2	9.8	6.2	6.6	7.4	8.0	8.0	6.1	8.4
	O ₃	-	-	-	-	29.9	9.6	19.1	18.1	12.2	9.4	4.3	9.6

In Table 4.2, the complete set of data for the BTEX species determined are listed. Benzene concentrations ranged between 0.04 ppb and 6.2 ppb, while toluene concentrations were between 0.01 ppb and 5.3 ppb. Low concentrations of ethylbenzene, m- and p-xylene, and o-xylene were measured at all the sites during the sampling period. The concentrations of ethylbenzene ranged from 0.01 ppb to 0.7 ppb, m- and p-xylene levels were between 0.01 ppb and 1.3 ppb, and o-xylene levels ranged between 0.01 ppb to 0.7 ppb. At some stations, ethylbenzene and m- and p-xylene were not detected at all during the last months of sampling. Higher BTEX concentrations coincided with the higher NO₂ and SO₂ levels measured at the sites situated in industrialised areas. As shown in Table 4.2, no results were obtained for the month of October. This was due to problems encountered with the analyses of the sampling tubes. The analytical instrumentation was damaged due to power outages occurring at the time of analysis, which resulted in the loss of data.

Monthly BTEX concentrations have not been measured before in the greater Highveld region. Therefore, data could not be compared to other results in this area. The BTEX concentrations obtained during this investigation were compared to levels reported in other parts of the world (Derwent *et al.*, 2000). Although BTEX levels were lower than the concentrations measured in London, Chile, and São Paulo these cities are far more industrialised than the South African Highveld.

From this comprehensive data set, a spatial and temporal distribution of the gaseous pollutants present in the atmosphere in the Mpumalanga Highveld was compiled.

Table 4.2: One year data set for the BTEX species at selected sites in the Highveld Priority Area (ppb)

Stations	Gaseous species	2007						2008					
		Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.
Balfour	B	0.2	0.7	-	0.9	0.3	1.1	0.1	0.2	0.5	0.4	0.1	0.3
	T	0.2	0.4	-	0.7	0.3	0.2	0.1	0.2	0.4	0.4	0.2	0.7
	E	0.04	0.1	-	0.1	0.04	0.1	0.01	0.02	0.1	0.1	0.04	0.1
	m&p-X	0.06	0.06	-	0.3	0.07	0.05	0.03	0.03	0.1	0.1	0.04	0.1
	o-X	0.01	0.13=	-	0.1	0.1	0.02	0.01	0.02	0.1	0.1	BDL	0.1
Delmas	B	1.7	1.6	-	1.2	0.5	1.0	0.44	0.8	1.1	1.1	1.95	1.2
	T	3.7	1.7	-	2.9	1.1	1.0	0.39	1.2	1.7	3.1	1.85	2.6
	E	0.3	0.4	-	0.5	0.2	0.1	0.11	0.2	0.3	0.5	0.29	0.5
	m&p-X	0.1	0.06	-	0.3	0.07	0.05	0.03	0.03	0.1	0.1	0.04	0.01
	o-X	0.01	0.1	-	0.1	0.02	0.02	0.01	0.02	0.1	0.1	BDL	0.05
Witbank	B	0.8	1.3	-	1.1	0.5	7.0	0.5	1.3	1.8	2.0	1.4	1.4
	T	1.0	0.9	-	1.2	1.00	5.3	0.4	1.4	1.7	2.3	1.4	1.4
	E	0.1	0.2	-	0.2	0.1	0.2	0.1	0.2	0.3	0.7	0.2	0.2
	m&p-X	0.3	0.03	-	0.5	0.4	0.3	0.3	0.3	0.2	0.7	0.4	0.5
	o-X	0.4	0.03	-	0.2	0.1	0.09	0.1	0.2	0.2	0.3	0.2	0.3
Carolina	B	0.2	0.3	-	0.5	0.6	0.1	0.08	0.2	0.4	0.4	0.16	0.11
	T	0.1	0.03	-	0.2	1.4	0.8	0.01	2.2	0.3	0.2	0.22	0.1
	E	0.07	0.08	0.04	0.01	0.01	BL	0.04	0.02	0.2	BDL	BDL	0.1
	m&p-X	0.02	0.04	-	BDL	0.02	0.01	0.01	0.01	0.1	0.2	BDL	BDL
	o-X	0.01	0.1	-	BDL	0.01	BDL	BDL	0.03	0.2	0.02	BDL	BDL
Ermelo	B	0.5	0.8	-	0.6	0.5	0.2	0.2	0.3	0.8	0.9	0.4	0.6
	T	0.4	0.5	-	0.5	1.7	0.3	0.1	0.5	1.6	1.0	1.0	0.6
	E	0.08	0.3	0.2	0.07	0.3	0.04	0.04	0.1	0.2	0.3	0.1	BL
	m&p-X	0.1	0.01	0.01	0.1	0.3	0.1	0.1	0.1	0.1	0.3	0.2	0.2
	o-X	0.04	0.03	-	0.06	0.1	0.03	0.04	0.06	0.2	0.2	0.1	0.1
Amersfoort	B	2.4	2.0	0.04	0.4	0.3	0.2	0.06	0.2	0.3	0.3	0.1	0.2
	T	0.1	2.2	0.03	0.3	0.1	0.05	0.01	0.1	0.2	0.2	0.2	0.2

	E	0.07	0.1	0.04	0.03	0.05	BDL	0.01	BDL	0.01	BDL	0.01	0.1	BDL	BDL
	m&p-X	0.05	0.01	0.02	BDL	0.02	0.01	0.01	0.01	0.01	0.01	0.05	BDL	BDL	BDL
	o-X	0.03	0.03	-	BDL	0.01	BDL	BDL	0.01	0.01	0.01	0.03	BDL	BDL	BDL
Standerton	B	6.2	0.7	0.4	0.1	0.3	0.3	0.2	0.8	0.8	0.6	1.0	0.6	0.6	0.6
	T	0.7	0.5	0.2	1.8	0.7	0.4	0.2	0.7	1.5	0.7	1.4	0.7	1.0	1.0
	E	0.1	0.4	0.2	0.2	0.1	0.07	0.1	0.1	0.2	0.1	0.5	0.1	0.2	0.2
	m&p-X	0.2	0.03	-	0.5	0.2	0.2	0.2	0.2	0.1	0.3	0.5	0.3	0.6	0.6
	o-X	0.01	0.1	-	0.15	0.1	0.06	0.05	0.12	0.2	0.2	0.3	0.2	0.2	0.2
Vanderbilpark	B	-	-	-	1.1	1.1	1.4	0.6	1.3	1.7	1.2	2.4	1.2	1.3	1.3
	T	0.7	0.5	0.2	1.8	0.7	0.4	0.2	0.7	1.5	0.7	1.4	0.7	1.0	1.0
	E	-	-	0.5	0.3	0.2	0.2	0.1	0.2	0.3	0.3	1.3	0.3	0.3	0.3
	m&p-X	-	-	-	0.8	0.4	0.4	0.2	0.2	0.3	0.7	1.3	0.7	0.9	0.9
	o-X	-	-	-	0.2	0.2	0.1	0.1	0.2	0.5	0.3	0.4	0.3	0.4	0.4

4.2 SPATIAL DISTRIBUTION OVER THE HIGHVELD

4.2.1 INORGANIC GASEOUS CONCENTRATIONS

The spatial distribution of the annual average concentrations of the inorganic gases is presented in Figure 4.1. There is an increase in NO₂ and SO₂ levels towards the western parts of Mpumalanga. As previously mentioned, higher SO₂ and NO₂ concentrations coincided with sites near increased industrial activity, such as Witbank and Vanderbijlpark, whereas lower concentrations were observed at the more rural sites, such as Balfour, Carolina, and Amersfoort. Witbank is a highly industrialised city that is surrounded by power stations and mining industries, as well as a nearby petrochemical plant (see Section 2.5.2). This gives an explanation for the high SO₂ and NO₂ concentrations measured consistently at Witbank, which can be attributed to burning of fossil fuels and other combustion processes that process sulphur containing materials.

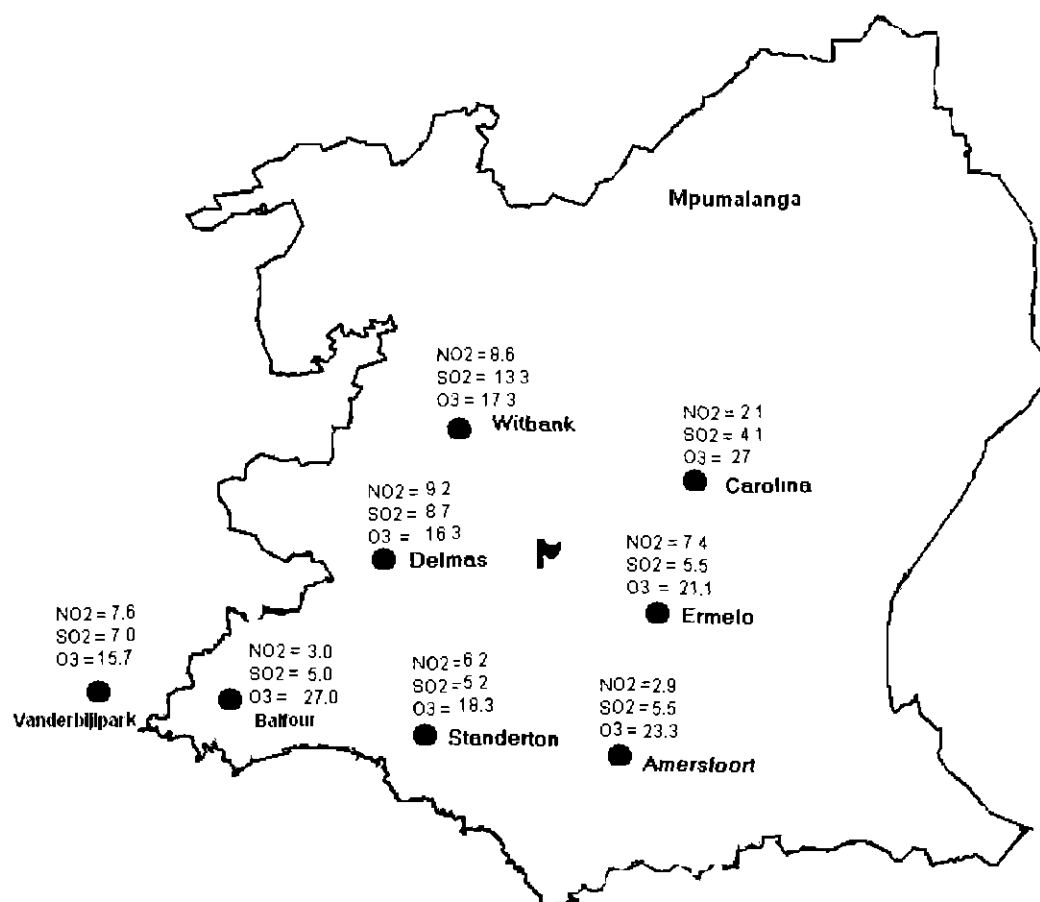


Figure 4.1: Spatial distribution of inorganic pollutants in the Highveld Priority Area

The wind roses shown in Figure 4.2 were measured near Secunda (indicated by the flag in Figure 4.1) for two consecutive years (2006 and 2007). These wind roses represent the annual prevailing wind speeds and wind direction and could be used as representative of the prevailing wind in the area where monitoring was conducted. From Figure 4.2, it can be seen that a north-easterly wind was predominant.

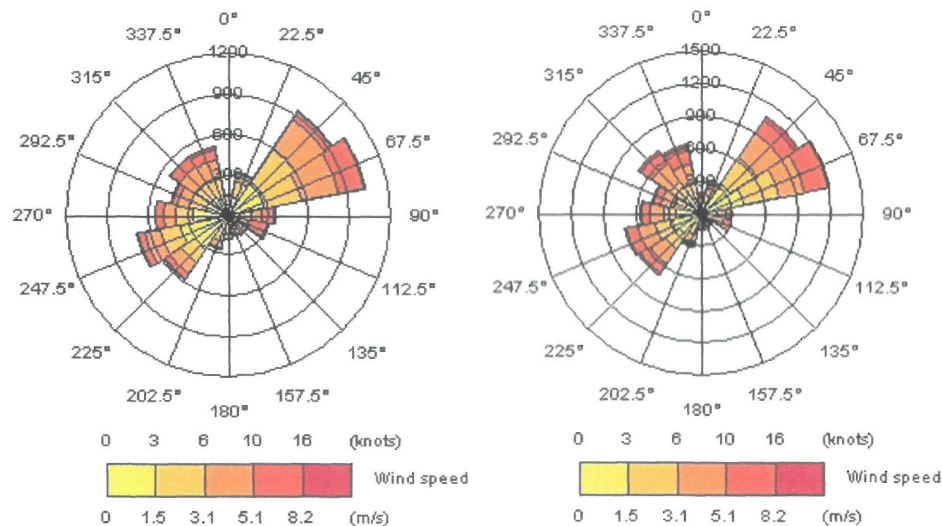


Figure 4.2: Wind roses measured in 2006 (left) and 2007 (right) near Secunda (data obtained from Sasol)

Annual wind roses were also obtained from the South African Weather Service for Carolina, Vereeniging, Witbank, Standerton, and Ermelo. The wind rose obtained for Carolina (Figure 4.3), which is situated north-west from Secunda, indicates an annual wind direction predominately from the north-east. The wind roses of the other site showed a similar pattern (see Appendix A).

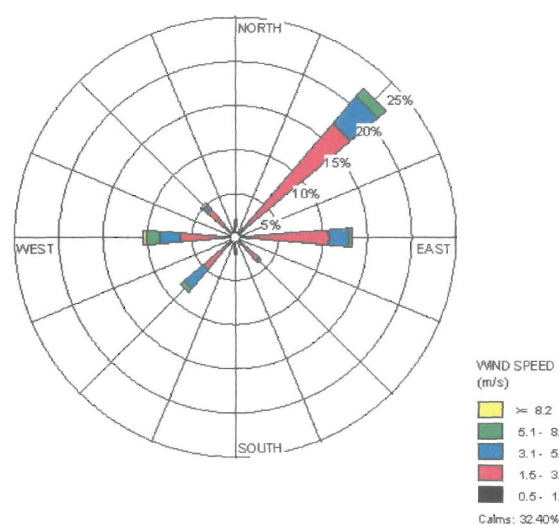


Figure 4.3: Annual wind roses measured at Carolina for 2007 to 2008 (data obtained from SA Weather Service)

The rural sites Balfour and Delmas in the western parts of Mpumalanga are located downwind from industrialised regions, such as Witbank and Secunda, and are clearly influenced by the pollution of these industrial areas. Higher SO₂ and NO₂ concentrations than what were initially expected were measured at these sites. Carolina and Amersfoort, which is situated up-wind in the eastern part, had very low SO₂ and NO₂ concentrations, and were not influenced by pollution of Witbank and Secunda.

4.2.2 BTEX CONCENTRATIONS

The spatial distribution of annual average concentrations of BTEX in the HPA is shown in Figure 4.4.

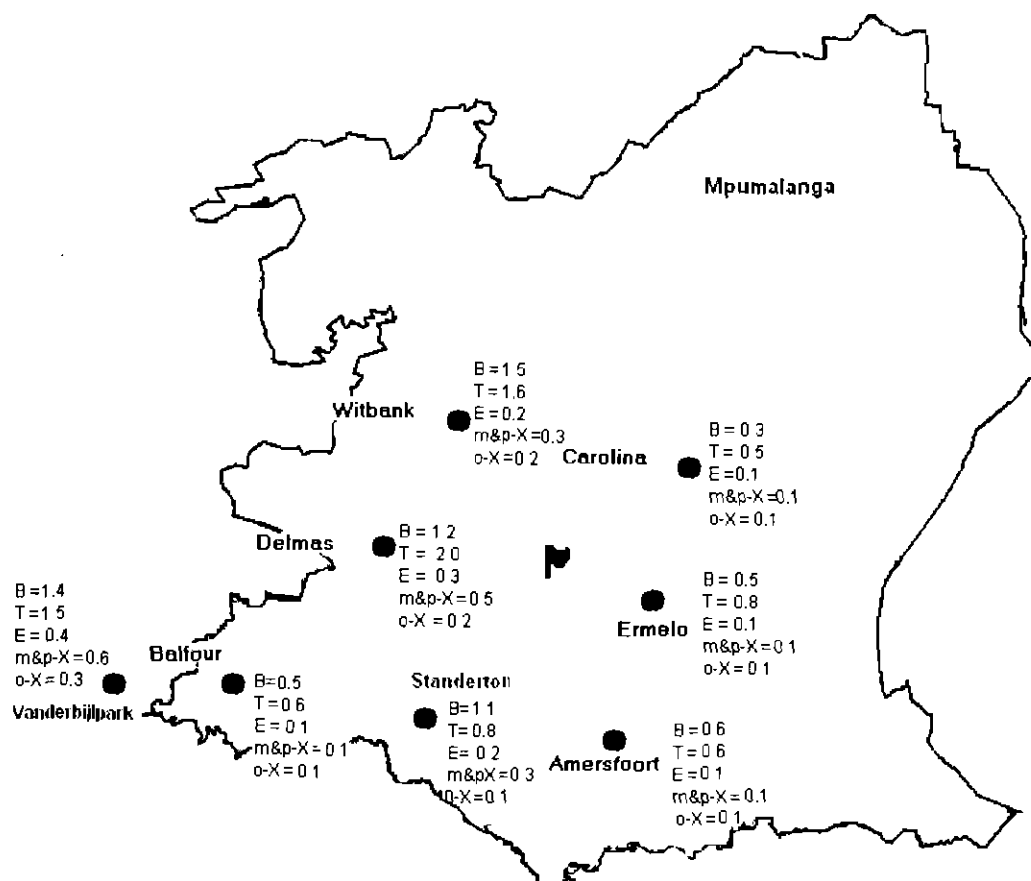


Figure 4.4: Spatial distribution of BTEX gases in the HPA

A similar spatial trend that was observed for NO_2 and SO_2 was obtained for BTEX, where higher BTEX concentrations were measured in the western parts and the lower values recorded in the east. The highest benzene and toluene concentrations were measured at Witbank and Vanderbijlpark. These higher measurements can partially be explained by the occurrence of larger urban centres and extensive industrial activities in these areas. The prevailing north-easterly winds (Figure 4.2 and 4.3) also contributed to the high BTEX levels on the western side. As discussed previously, Delmas and Balfour are noticeably influenced by industrial emissions, since these areas are in the path of the prevailing wind.

4.3 TEMPORAL DISTRIBUTION OVER THE HIGHVELD

4.3.1 INORGANIC CONCENTRATIONS

The monthly mean concentrations for inorganic gaseous species over the HPA are presented in Figure 4.5. The error bars on the graph indicate the maximum and minimum concentrations measured at the different sites.

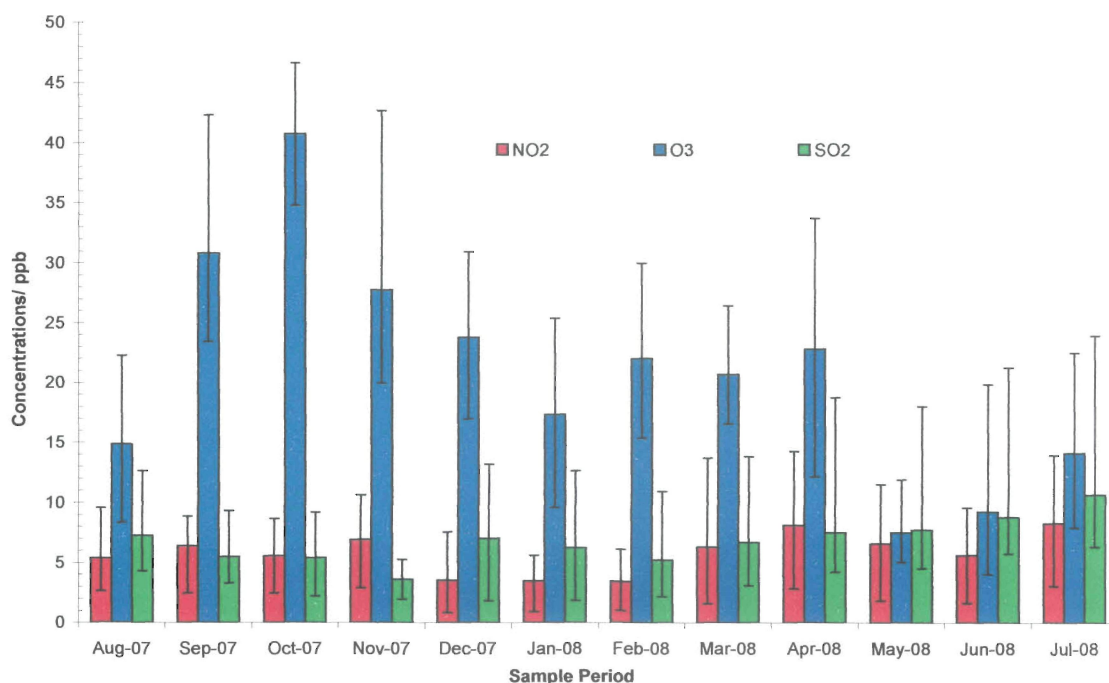


Figure 4.5: Monthly mean concentrations of inorganic gases over the HPA

Seasonal trends were observed, with NO₂ and SO₂ peaking during winter, while O₃ peaked in spring. Nitrogen dioxide and SO₂ peaks can be explained by the difference in meteorological conditions experienced in the Highveld during winter and summer. The warmer and wetter summers are associated with relatively unstable meteorological conditions, which increase the vertical motion and dispersion in the atmosphere. In contrast, winters are characterised by the formation of inversion layers, inhibiting vertical atmospheric mixing, and in general, weaker removal processes, effectively trapping the primary pollutants Sulphur dioxide and NO₂ (Freiman and Piketh, 2002; Thyson *et al.*, 1996). Increased occurrences of biomass burning (veld fires) and combustion for domestic heating during winter also contribute to elevated levels of SO₂ and NO₂.

The seasonal trend observed for O_3 can be explained by formation and degradation reactions that takes place in the atmosphere. Several compounds are regarded as O_3 precursors (EPA, 2006). One such a precursor species is CO. The photochemical reactions involving NO_2 and CO, leading to the formation of O_3 , are given by the equations below (see also Section 2.3.2.) (Pienaar and Helas, 1996).



The higher O_3 concentrations obtained in spring can be ascribed to the increased concentrations of CO during that time of the year. The higher CO concentrations during spring are due to increasing veld fire activities that occur before the rain season starts (Laakso *et al.*, 2008). Figure 4.6 gives the annual rainfall over the Highveld during the sampling period. The stable pre-rain season conditions during spring are verified by the lack of rain during that time period (that is August to October).

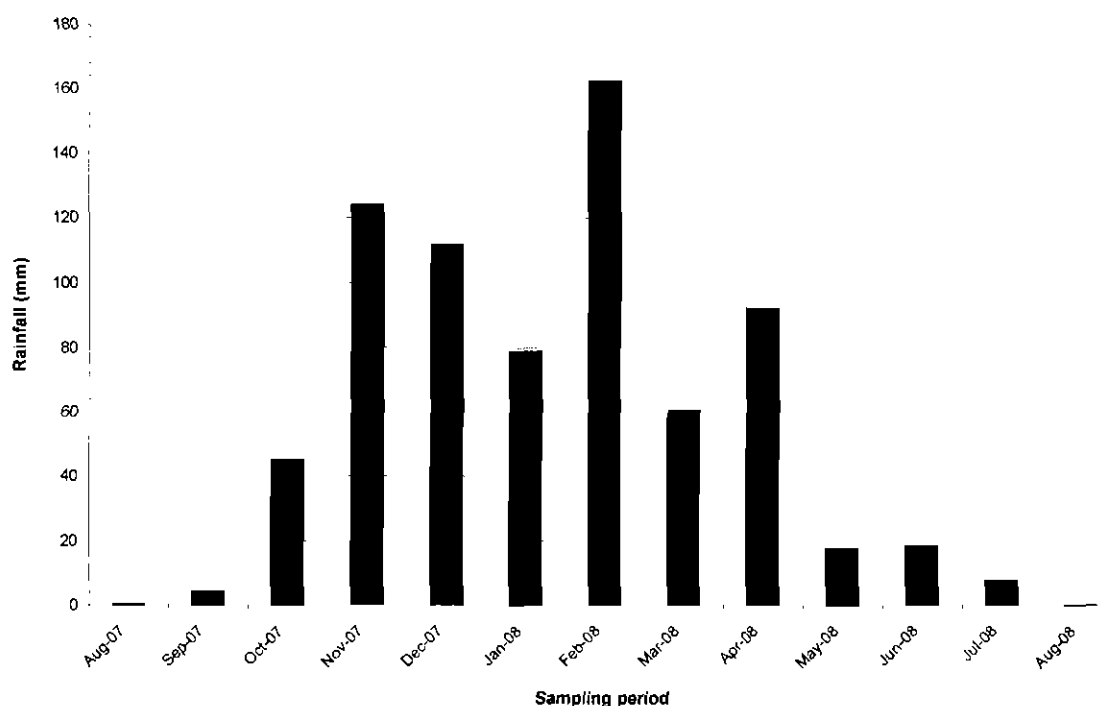
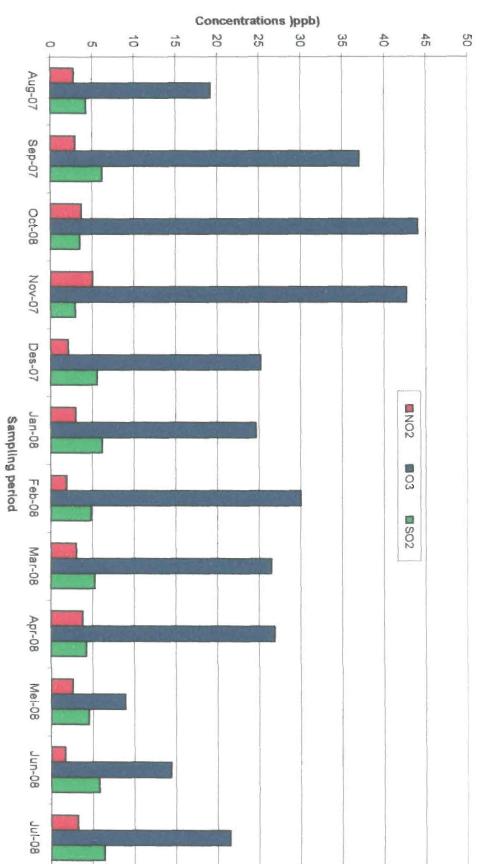


Figure 4.6: Annual rainfall over the Highveld region during the study period (data from SA Weather Service)

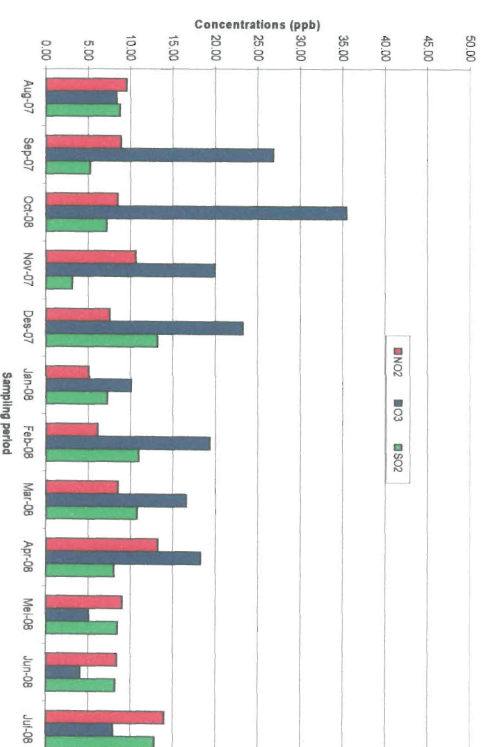
The O₃ concentrations measured in May and June 2008 were below 10 ppb, which raised a concern. Although previous measurements of O₃, such as in the DEBITS programme (Martins *et al.*, 2007), also obtained the lowest O₃ concentrations in the winter, the levels usually ranged between 10 and 15 ppb. However, the experimental data could be verified by comparing to data acquired with active samplers in the same region during the same period.

The seasonal trends observed for the inorganic gaseous species at all of the stations are presented in Figure 4.7 (a) to (h).

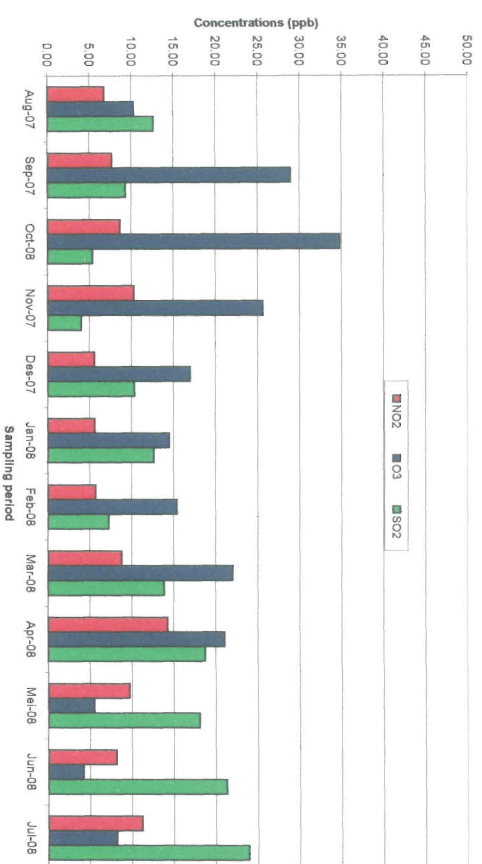
Balfour



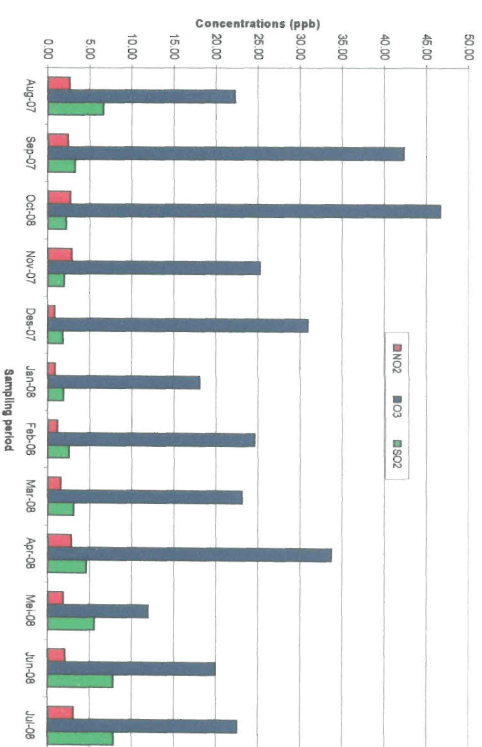
Delmas

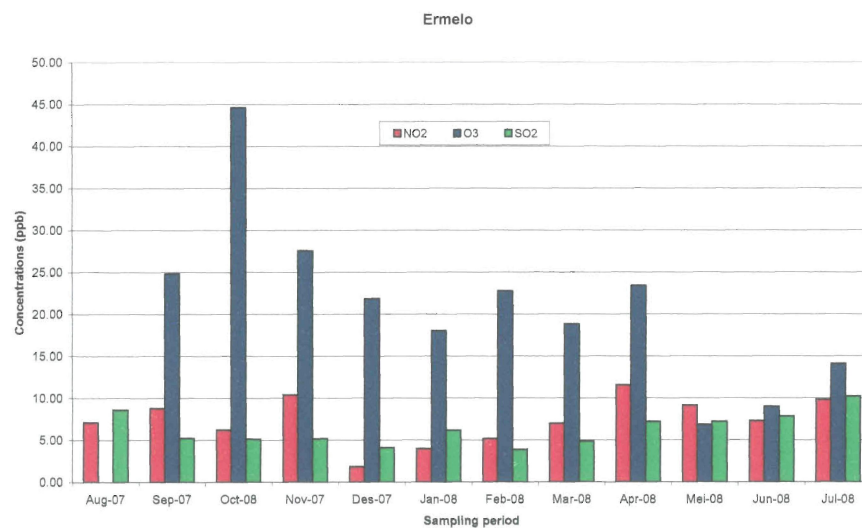


Witbank

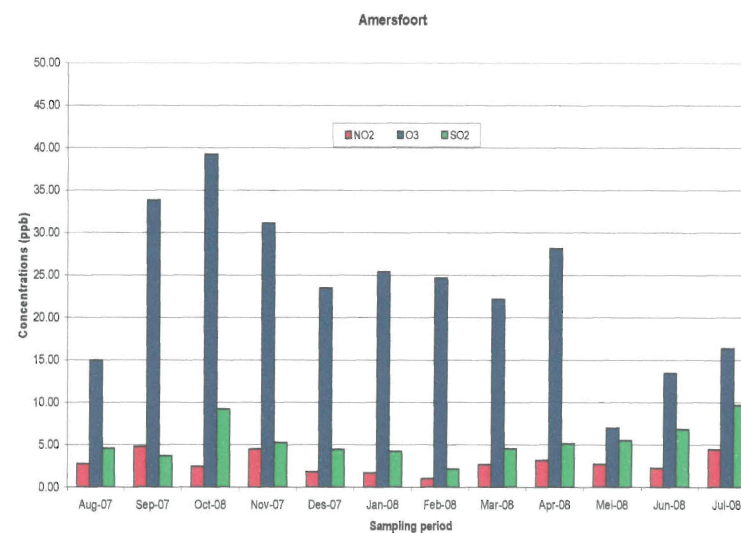


Carolina

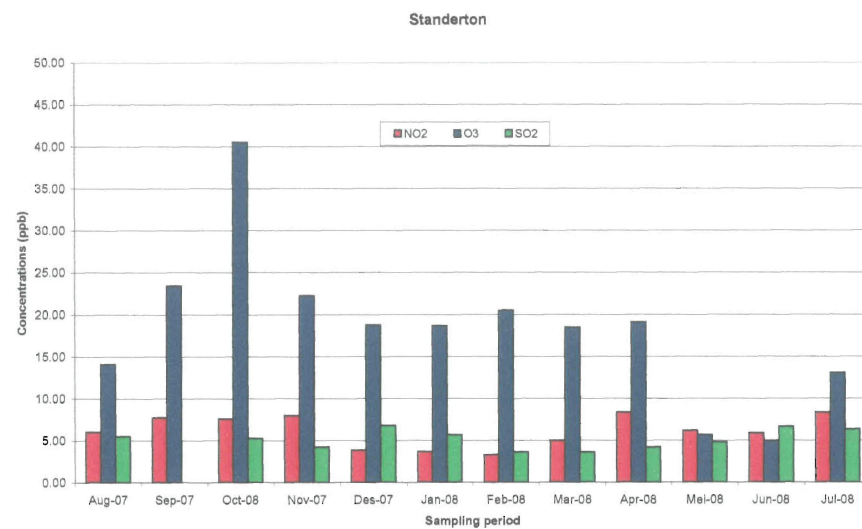




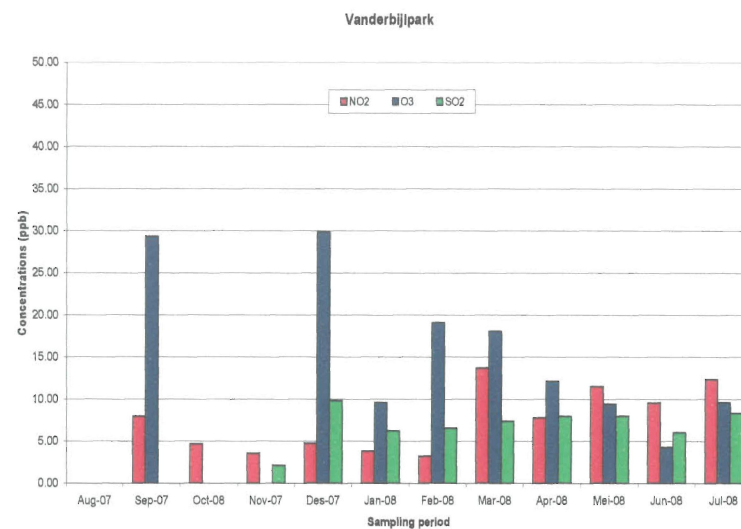
(e)



(f)



(g)



(h)

Figure 4.7: Temporal distribution at each site: (a) Balfour, (b) Delmas, (c) Witbank, (d) Carolina, (e) Ermelo, (f) Amersfoort, (g) Standerton, and (h) Vanderbijlpark (values in ppb)

These figures show that the same seasonal trend was observed at all the stations. Although the concentrations measured at the Vanderbijlpark station from September to November were discarded due to logistical problems, a partial seasonal trend could still be observed.

4.3.2 BTEX CONCENTRATIONS

The monthly mean concentrations for BTEX measured in the HPA are presented in Figure 4.8. The error bars indicate the maximum and minimum concentrations for the eight stations.

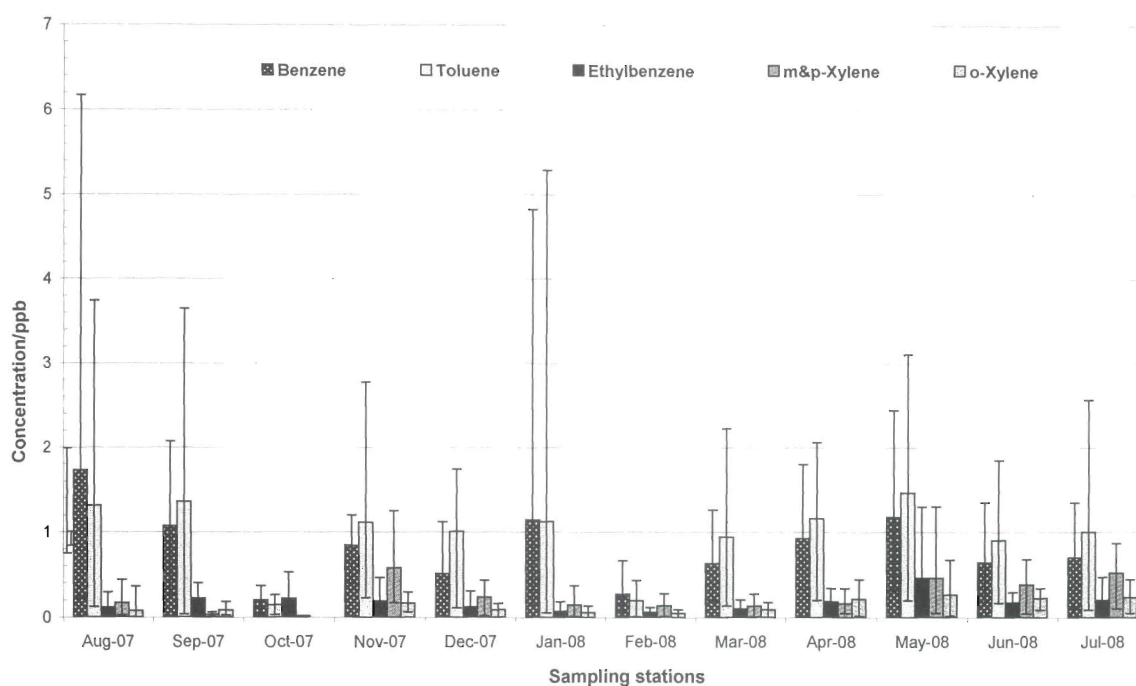
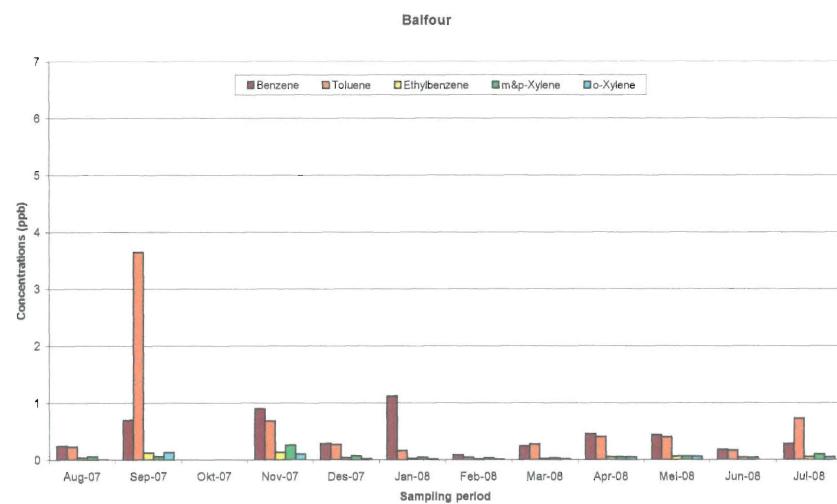
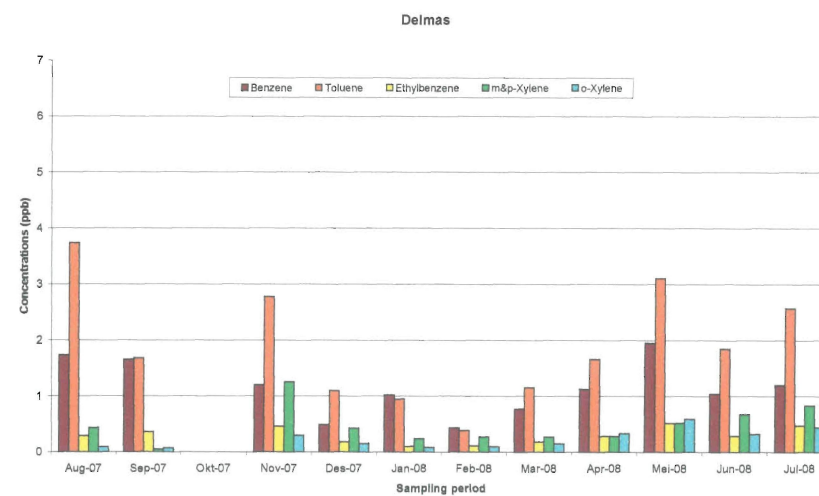


Figure 4.8: Monthly mean concentrations of BTEX over the HPA

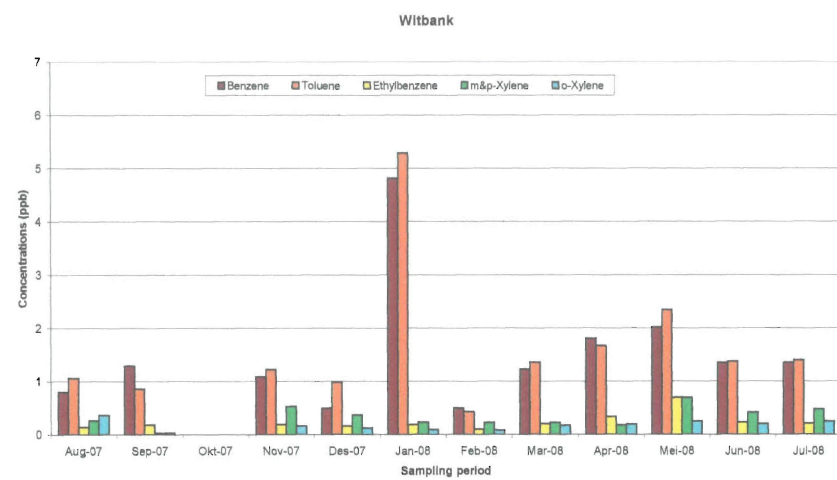
Although seasonal trends were expected, no distinct seasonal trend was observed for any of the BTEX compounds. The lack of a distinct trend was obtained at all the stations as can be seen in Figure 4.9 (a) to (h).



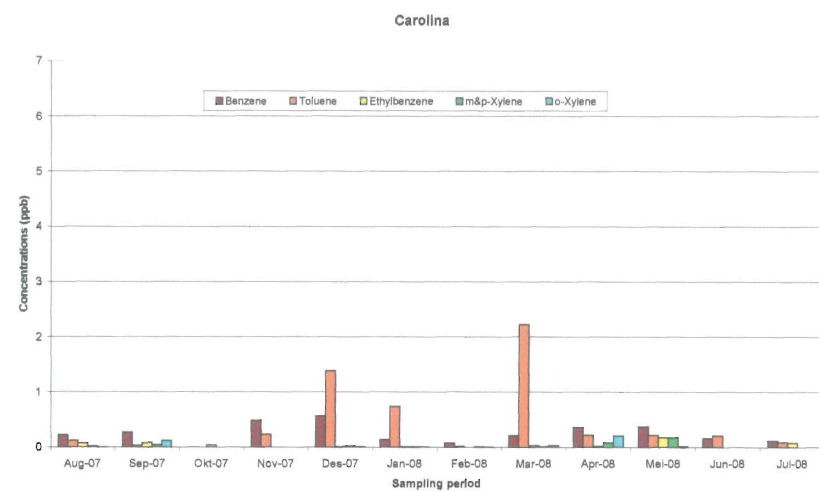
(a)



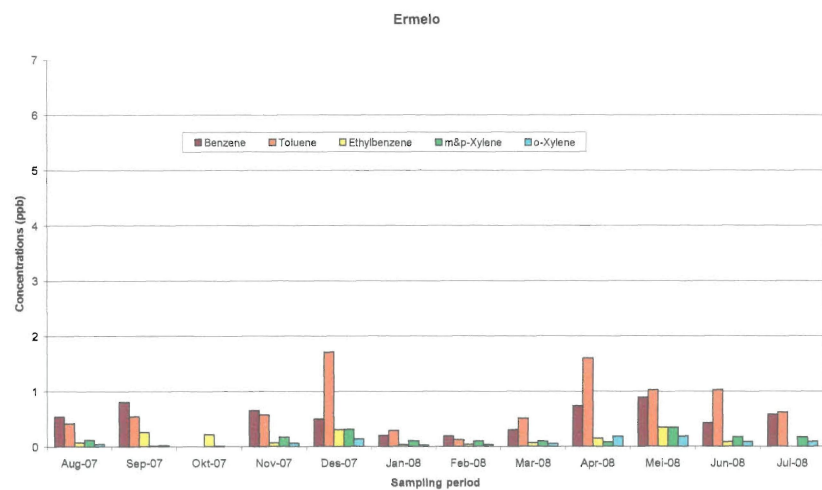
(b)



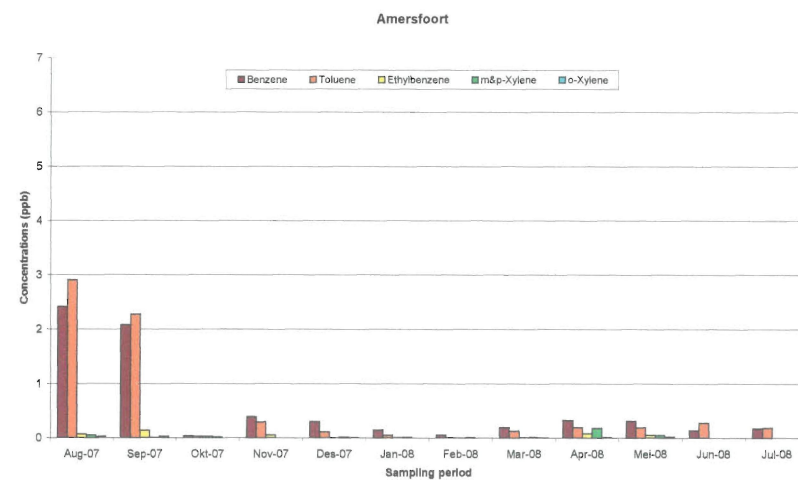
(c)



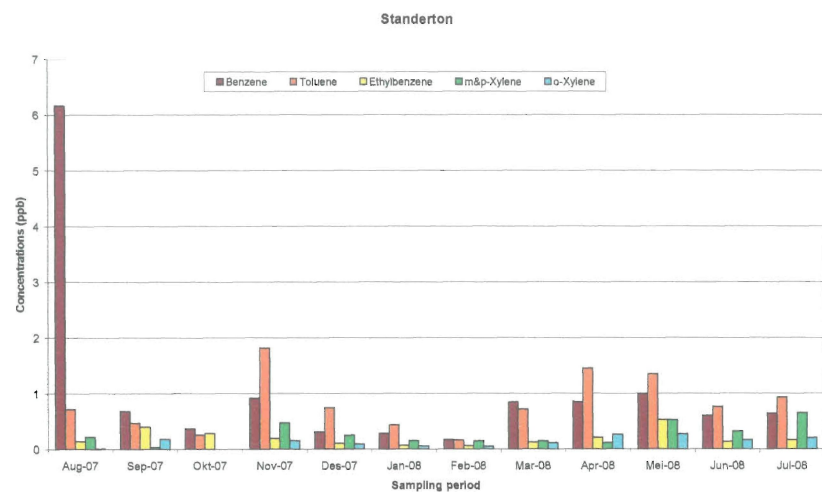
(d)



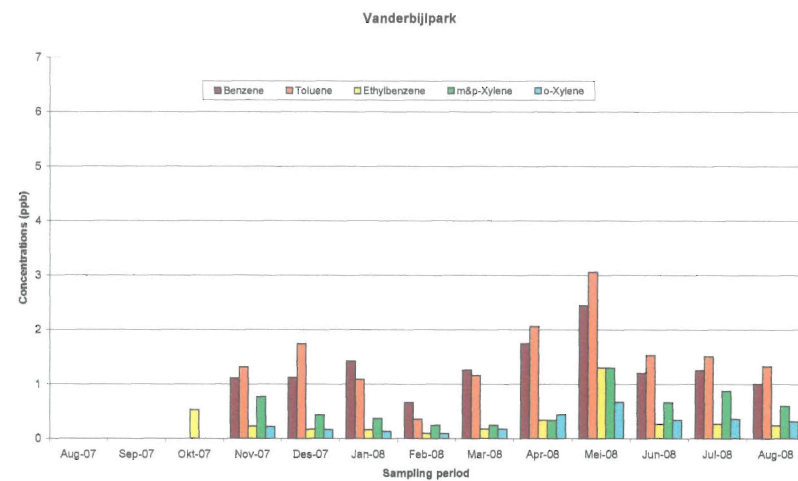
(e)



(f)



(g)



(h)

Figure 4.9: The temporal distribution of BTEX for all the stations: (a) Balfour, (b) Delmas, (c) Witbank, (d) Carolina, (e) Ermelo, (f) Amersfoort, (g) Standerton, and (h) Vanderbijlpark (values in ppb)

The lower levels of ethylbenzene and xylene can possibly be attributed to their photochemical reactivity, leading to faster degradation (Parra *et al.*, 2006). Although toluene has an atmospheric lifetime of around two to four days and benzene has a lifetime of twelve days, higher toluene than benzene values were consistently obtained at all the sites. This indicates possible higher toluene emission rates.

4.4 VERTICAL BTEX PROFILES

Vertical BTEX profiles were determined during a two-day winter and a two-day summer campaign, in order to assess the potential differences between the ground-level and lower tropospheric atmosphere (≤ 1500 ft above ground level) BTEX levels. The flight paths are presented in Figure 4.10. Since benzene has been identified by the government as the only organic criteria pollutant the discussion of the results obtained is given in view of the benzene concentrations measured. Toluene, ethylbenzene, and xylene showed similar profiles.

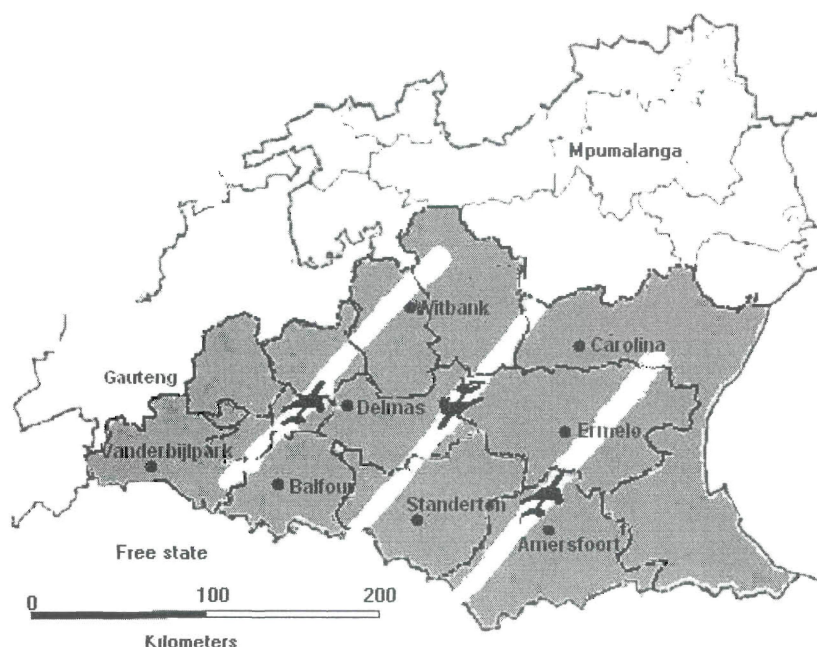


Figure 4.10: Flight paths during the measurement of the BTEX vertical profiles

In Figure 4.11, the benzene results acquired on the first day of the winter campaign for the three flight paths and two altitudes are shown. The concentrations measured with the canisters and Carbotrap™ 300 adsorbent tubes are also compared. A good comparison was found between the canister and tube results for the Standerton flight path. Although the correlations were reasonable, the tube value at 500 ft on the Balfour flight were much higher than any other value. No explanation can be given for this discrepancy at this stage.

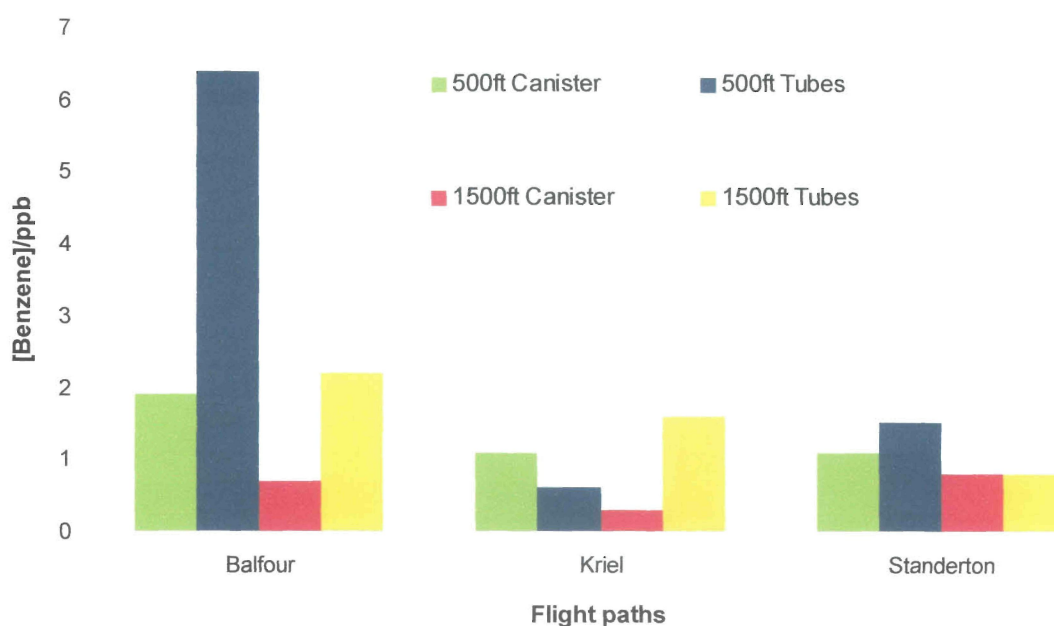


Figure 4.11: Benzene concentrations for the three flight paths and two flight levels for the canister and Carbotrap™ 300 tubes samplers on 24 July 2007

As slight north-westerly winds were experienced on the 23 and 24 July, pollution from the Johannesburg region may therefore explain the slight BTEX concentration gradient away from Johannesburg. The increase towards the western parts is also in agreement with the ground-level measurements obtained.

In Figure 4.12 on the next page, the benzene results during the winter campaign on the 25 July 2007 are given.

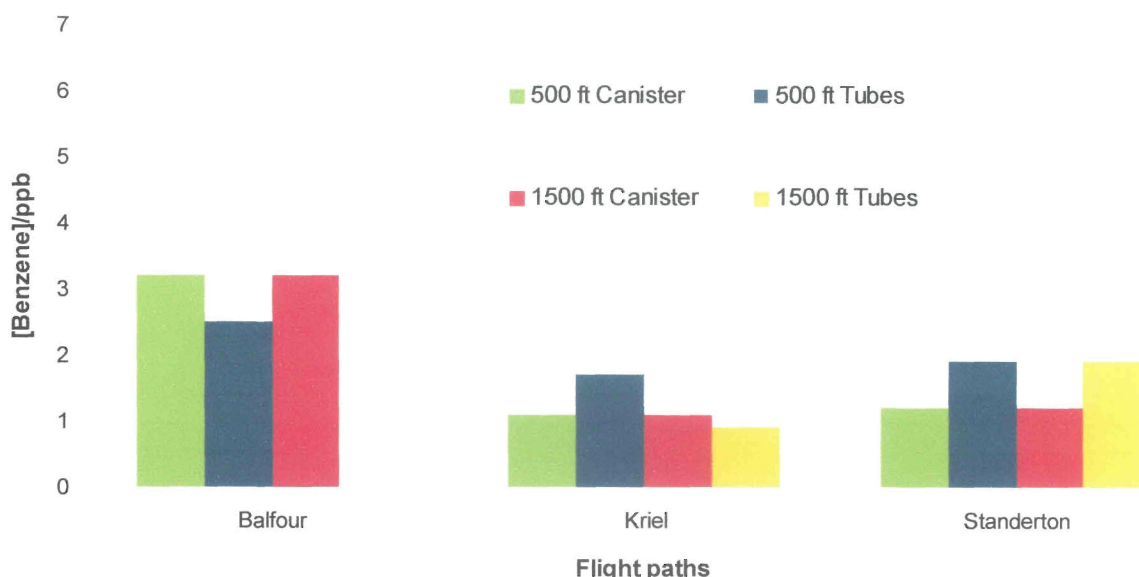


Figure 4.12: Benzene concentrations for the three flight paths and two flight levels for the canister and Carbotrap™ 300 tubes samplers on 25 July 2007¹

A very good correlation was found between the canister and tube results for all the flight on the 25 July 2007 (the tube sample that was taken at 1500 ft for the Balfour flight path could not be analysed due to a power outage on the instrumentation during the analysis of the sample). The concentrations on Balfour flight path again seem to be slightly higher than on the other flight paths. This can be explained by the westerly winds experienced the day before and on the first day of sampling. Again, pollution from the Johannesburg region may have contributed to these slightly higher levels.

During the summer field campaign in the beginning of March 2008, canisters and Tenax TA adsorbent tubes were used. Tenax TA tubes proved to be inefficient for active sampling, and almost none of the BTEX compounds could be detected during the analyses. Although Tenax TA is a good adsorbent for BTEX at lower flow rates or at diffusive uptakes rates, it seems to be ineffective for active sampling at high flow rates. The reason for this can possibly be related to the smaller surface areas of Tenax TA. Tenax TA has a surface area of 35 m²/g, whereas Carbotrap™ 300 has an area of 100 m²/g.

In Figure 4.13 on the following page, the benzene results acquired with the canisters during the summer campaign are shown.

¹ Tube data on the Balfour flight was lost due to power failures

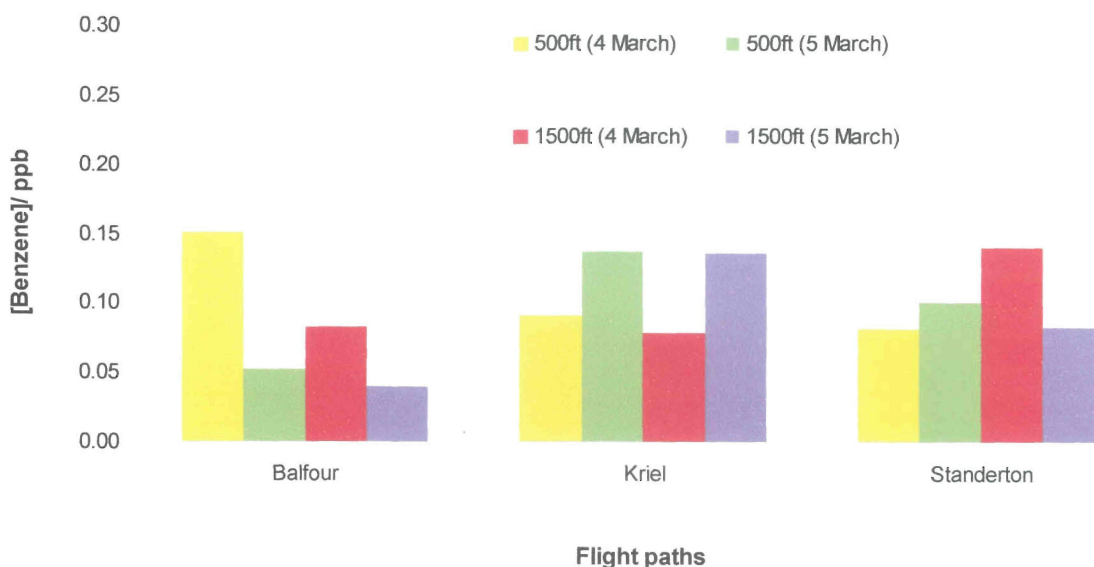


Figure 4.13: Benzene concentrations for the three flight paths and two flight levels for the canisters on 4 and 5 March 2008

Similar benzene levels were found for all of the different flight paths during the two days of sampling with the exception of the measurement obtained during the Balfour flight path on the first day. This could be a consequence of the fact that the flight that was supposed to be taken at 500 ft was actually taken at 800 ft due to a thick cloud mass preventing the flight at a lower altitude. In general, the benzene concentrations measured during the summer campaign were significantly lower than the levels reported during winter campaign. Although Standerton shows a slightly higher concentration at 1 500 ft on 4 March, the difference between the levels measured at the two altitudes is too small to draw any conclusions with certainty. The presence of clouds could have resulted in this much lower values than observed during the winter campaign.

In Figure 4.14, a comparison of the average concentrations measured with the canisters during the winter and summer campaign is presented.

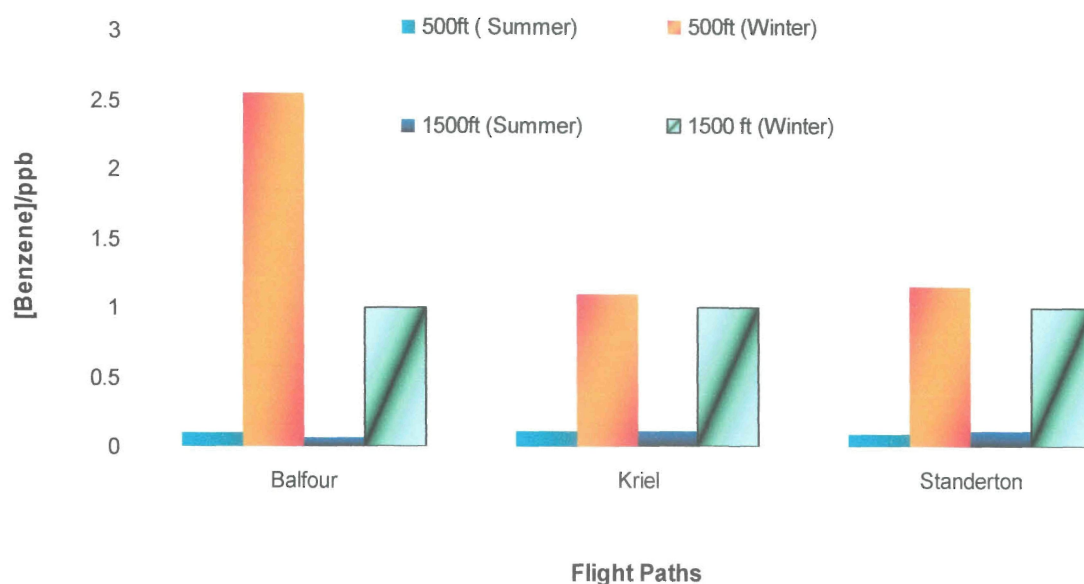


Figure 4.14: Average benzene concentrations measured during the vertical profile campaigns

Due to logistical and cost implications, limited vertical BTEX data was acquired. This makes the identification of trends difficult. There is, however, a noticeable difference between the July and March campaigns. This observation could purely be coincidental and an artefact of the limited data, since no clear seasonal trend was observed for the ground-level monitoring, which was conducted over a entire year (Figure 4.8 and 4.9). In general, the benzene levels were below the 1.6 ppb annual proposed standard, which was only exceeded once—considering that no daily guideline exists.

Ozone gives an indication of the oxidation potential of the atmosphere and was therefore also measured during the vertical profile campaign. The average O_3 concentrations recorded during the winter campaign were 28 ppb and 34 ppb, on the first and the second days respectively, while O_3 levels during the summer campaign were 21 ppb and 23 ppb. The higher O_3 levels recorded during the winter measurements can be related to the increase in biomass burning. The more stable meteorological conditions experienced in winter also contribute to higher O_3 levels.

The benzene values obtained from the vertical profile campaigns were compared to the values determined in the SAFARI 2000 program. Measurements were obtained with a prototype airborne gas chromatograph system constructed at the University of Leeds, which was fitted on a Aero commander aircraft for in flight analysis of non-methane hydrocarbons (Whalley *et al.*, 2004). This ORAC (Organics by Real-time Airborne Chromatograph) is a unique instrument that collects and analyses samples every five minutes and has a detection

limit of less than 50 ppt. Averaged benzene levels reported for flights over the Mpumalanga Highveld in this campaign were in the order of 1.0 ppb (Van der Walt, 2007).

Finally, the results are compared with ambient air standards and guidelines in the next section.

4.5 COMPARISON WITH AMBIENT AIR STANDARDS AND GUIDELINES

National air quality standards guidelines have been established for criteria pollutants, which include SO₂, NO₂, O₃ and benzene (Section 2.3.5). The measured concentrations of these pollutants were compared to the standards and guidelines. Table 4.3 lists the measured annual average concentrations of the pollutants together with their corresponding national ambient air quality standards and guidelines (SA, 2004).

Table 4.3: Annual average concentrations of pollutants

	Annual average / ppb			
	NO ₂	SO ₂	O ₃	Benzene
Standard	50	19	-	-
Guideline	50		-	1.6
Balfour	3.0	5.0	26.7	0.5
Delmas	9.2	8.6	16.3	1.2
Witbank	8.6	13.2	17.3	1.5
Carolina	2.1	4.1	26.8	0.3
Ermelo	7.4	6.3	21.1	0.5
Amersfoort	2.9	5.2	23.3	0.6
Standerton	6.2	5.2	18.3	1.1
Vanderbijlpark	7.6	7.0	15.7	1.4

The data above indicates that the annual average concentrations for all the gaseous species measured at the sites were below the annual standards and guidelines. The results obtained are particularly significant for benzene, which is the only hydrocarbon species included in the new legislation. Concerns that were based mainly on previous aircraft results, have been raised that ambient benzene concentrations in the HPA are significantly higher than the guidelines. However, a comprehensive investigation of benzene levels in the HPA has not been conducted up to now. Monthly benzene concentrations measured at the eight stations were near and/or below (in some instances far below) the annual average guideline of 1.6 ppb. This value is, however, difficult to interpret since no monthly standard or guideline exists.

Of the species monitored considered during this investigation, only NO₂ has a national monthly average standard, that is 80 ppb (Section 2.3.5). None of the monthly concentrations measured for NO₂ exceeded this standard and guideline. The SO₂

concentration measured at Witbank is of concern, since it is much higher than the background concentrations measured in southern Africa (Martins *et al.*, 2007), with concentrations ranging from 0.2 ppb at Louis Trichardt to 1.2 ppb at Cape Point.

The current South African legislation does not provide monthly standards or guidelines for O₃. A one-hour average standard of 120 ppb is given. No conclusion can therefore be made concerning the measured values in terms of the standards and guidelines.

4.6 CONCLUSION

From the results presented in this chapter, it can be concluded that although the concentrations of all the gaseous pollutants measured are below the standards and guidelines, the continuous monitoring of these gaseous species is required. Inorganic species measured (i.e. NO₂, SO₂ and O₃) showed a clear seasonal trend, while the BTEX species did not. Sulphur dioxide, NO₂, and BTEX concentrations were the highest in the western part of Mpumalanga and the Witbank area seems to be the most polluted municipal area.

Chapter 5 will conclude this dissertation and present recommendations for future research.

Chapter 5:

Project Evaluation and Future Perspectives

"Man must feel the earth to know himself and recognize his values ... God made life simple.

It is man who complicates it."

Charles A. Lindbergh

5.1 INTRODUCTION

Chapter 4 presented and discussed the results of the research project. This chapter will evaluate the research project based on this results and make recommendations for future studies. In this chapter, the project is evaluated by considering and weighing up the successes and shortcomings encountered for each objective of this investigation in Section 5.1. Thereafter, general conclusions are drawn in Section 5.2. Finally, in Section 5.3, several future recommendations, drawn from the results, are suggested.

5.2 PROJECT EVALUATION

This section reviews the results of the research project in relation to each objective given in Chapter 1.

Objective 1: To establish an ambient BTEX, SO₂, NO₂, and O₃ passive sampling network in the Highveld Priority Area, operating for at least one full year

This objective was accomplished successfully. A passive sampling network for BTEX, SO₂, NO₂, and O₃ was started in August 2007. Eight sites, within a sampling grid of 600 km², were operated for a period of one year (August 2007 to July 2008). No major logistical problems were experienced during the sampling period and a network was successfully established and operated for one year.

Objective 2: To determine a temporal assessment for all the species studied

From the results of the inorganic gaseous species, seasonal trends were successfully obtained for NO₂, SO₂, and O₃. Nitrogen dioxide and SO₂ peaked during winter, as a result of meteorological conditions that trapped and recirculated the air mass. Increased household combustion also contributed to higher concentrations in winter. Ozone peaked in spring. This coincided with the peak of CO concentrations, which is probably the most important O₃ precursor species within the South African context. No seasonal trend was observed for BTEX, which was surprising, as it was expected that these species would also peak in winter due to trapping and recirculating meteorological conditions.

Objective 3: To determine a spatial assessment for all the species studied

This aim was successfully completed by calculating the annual average concentrations for all the sites. It was found that there is an increase in NO₂, SO₂, and BTEX concentrations towards the western parts of Mpumalanga, which was attributed to the prevailing north-easterly winds and increased industrial activity in the western parts. The rural areas, such as Delmas and Balfour were influenced by the industrial activities in the surrounding areas.

Objective 4: To conduct a vertical assessment of BTEX concentrations, in order to compare the upper atmospheric concentrations with ground-level data

A two-day winter and two-day summer flight campaign were undertaken. No significant difference between the upper atmospheric concentrations and the ground-level measurements were found. During these experiments, a 6 L TO canister and tube samplers' results were compared. Good agreement between results was obtained. It was, however, found that CarbotrapTM 300 rather than Tenax TA should be used during the active sampling of upper air VOC concentrations and at high flow rates. Although all the concentrations throughout the campaign were in the same order of magnitude, it has to be stated that a two-day winter and summer vertical profile campaign is insufficient to determine any seasonal variations. The limited vertical assessment data is a weakness of this study. Cost constraints were the major limiting factor, since the project budget did not make provision for more flights.

Objective 5: To compare measured results to current national standards and guidelines

The comparison between the measured concentrations and national standards and guidelines showed that all the measured gaseous species levels are within governmental regulations. Ozone could not properly be compared, since O₃ only has instantaneous, one-hour and eight-hour averaged standards.

5.3 GENERAL CONCLUSIONS

In general, it can be concluded that this research project was successfully completed, based on the review of the objectives above. Comparison of results to legislation demonstrates that care needs to be taken in order to rectify air quality problem, especially in the Witbank, Delmas, and Vanderbijlpark areas. From the spatial and temporal distribution, a clear increase towards the western part of Mpumalanga was observed. A few shortcomings were identified that could have improved the quality of this research project; these are discussed in the next section in terms of future recommendations.

5.4 FUTURE PERSPECTIVES AND RECOMMENDATIONS

Gaseous pollutants can have several negative impacts on both humans and the environment, which necessitates the monitoring of pollutants. From the results, the following future perspectives and recommendations are suggested:

- Although the concentrations measured in the Highveld are below national standards and guidelines, the continuous measurements of these pollutants are required. This is because an increase in the concentrations of gaseous species over the past couple of years was observed when experimental data from this investigation was compared to previous investigations.
- Long-term measurements might give insight into possible seasonal BTEX variations, should any exist.
- In order to verify the influence of CO on O₃ formation, other parameters also need to be measured in future studies. These include CO concentrations, humidity, and solar radiation.

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Appendix A:

Wind Roses

This section shows the wind roses compiled during the sampling period. Annual wind roses are displayed in Figures A1 to A4.

Annual wind roses over the Highveld region during the sampling period

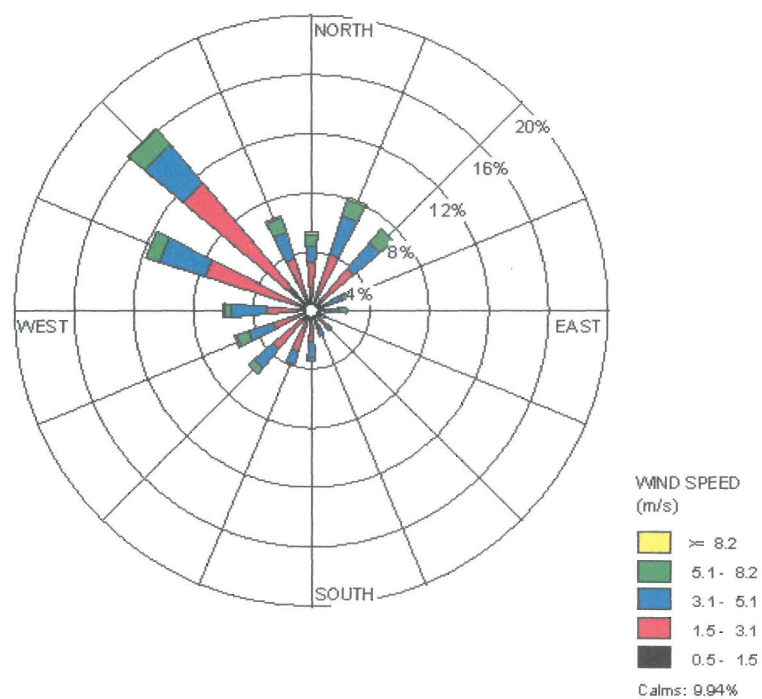


Figure A.1: Annual wind rose for Vereeniging

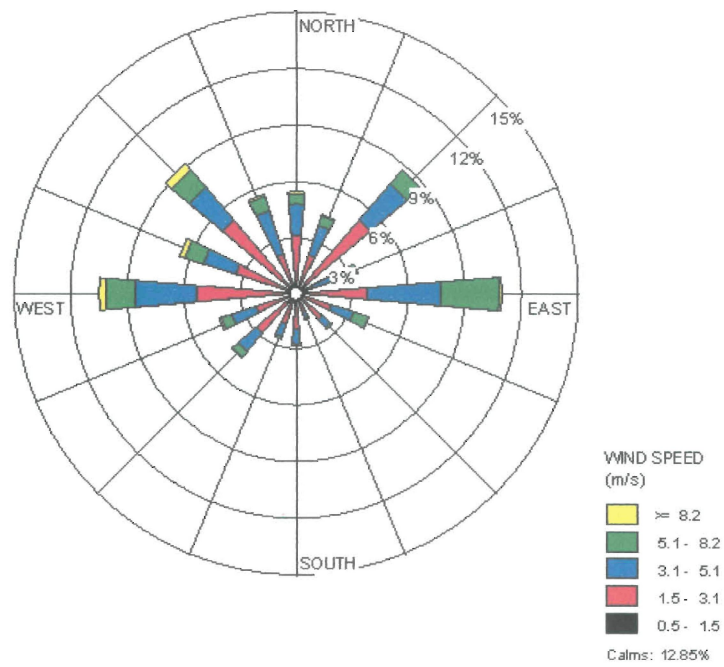


Figure A.2: Annual wind rose for Witbank

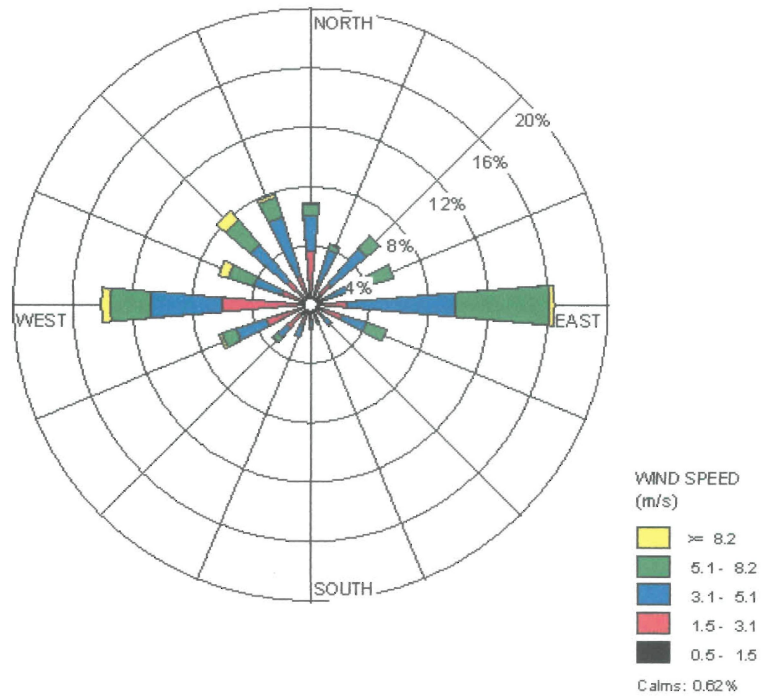


Figure A.3: Annual wind rose for Ermelo

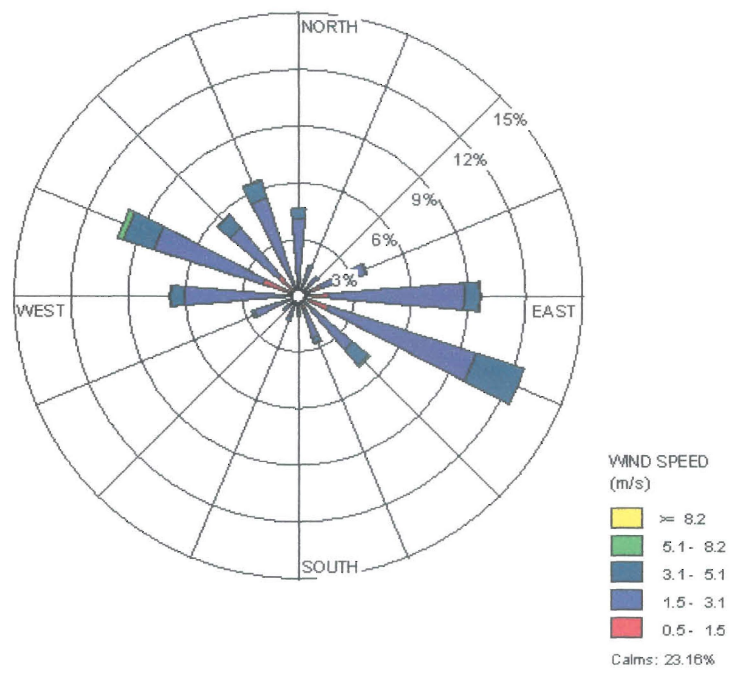


Figure A.4: Annual wind rose for Standerton