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An Assessment of BTEX Concentrations from Various Fuel Depots in Parts of South Africa.

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DECLARATION

I declare that this research report is my own unaided work. It is submitted in partial fulfilment of the requirements for the degree of Master of Science in the School of Geography, Archaeology and Environmental Studies at the University of Witwatersrand, Johannesburg. It has not been submitted previously for any degree or examination at any other University.

(Signature of candidate)

__28__ day of _January_ 2019 __ in _Braamfontein__

ABSTRACT

Volatile organic compounds (VOCs) are regarded major air pollutants as they have properties hazardous to the environment. They also play a vital role on the regional scale in the production of acid rain and photochemical ozone formation. The expansion of industries, growth in cities and wide use of vehicles has led to an increase in concerns about VOC being emitted into the atmosphere, particularly the BTEX (Benzene, toluene, ethyl-benzene and xylene) group as they are known to be potentially hazardous to both human and environmental health. The major sources of BTEX into the atmosphere are petroleum refineries, petrochemical facilities, automobiles, the use of solvents, combustion of fossil fuel and distribution of petroleum products.

The focus of this study was on assessing the BTEX concentrations from specific fuel depots in parts of South Africa. The seasonal variations and relationship between concentrations and the climatic conditions of the areas are also determined. Passive samplers were used to monitor the BTEX concentrations at depots that were located in industrial and mixed-use urban areas. The weather conditions for the areas were also acquired in order to understand the relationship between the BTEX concentrations and weather conditions. The monitoring was conducted quarterly from October 2015 up until January 2018.

The concentrations of BTEX compounds were determined and results obtained indicate that toluene was the most abundant compound at the monitored sites except at one site in the northern part of the country. A trend observed was that concentrations of benzene were lower in comparison to those of toluene while xylene concentrations were higher than those of ethylbenzene at all site during the various sampling periods. The T/B ratios calculated showed that majority of the sampling points were influenced by emission from traffic and mobile sources, industrial facilities or point sources and evaporative sources. Although the fuel depots monitored were the main sources of BTEX, the surrounding facilities and industries

were also noted as potential sources in various sampling points particularly in sites located within industrial areas. The depots within the industrial areas had higher T/B ratios as compared to those in urban mixed-use areas, which could be caused by the use of gasoline and other solvents in industrial processes.

There were noted variations with regards to the weather conditions around the different sites, the influence of temperature on the recorded BTEX concentrations was significant throughout the sampling periods except in October 2017. The influence of other climatic conditions such as wind speed on BTEX concentration was less clear at most of the monitored sites. There were no distinct seasonal patterns established in the recorded BTEX concentrations throughout the different seasons.

PREFACE

The dissertation comprises six chapters. **Chapter 1** provides an outline of the background of the study, justification for the study together with the aims and objectives. **Chapter 2** presents a review of current literature. **Chapter 3** highlights the methodology used for data collection and approach used to analyse the data. **Chapter 4** presents the results of the BTEX concentrations, ratios, synoptic circulation and climatic conditions over the study area. **Chapter 5** provides a discussion of the significance of the results. **Chapter 6** outlines the conclusions and recommendations for future studies.

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1. Introduction

Recently the growth of cities, rapid industrialization and increased use of vehicles has led to increasing levels of air pollution together with their related impacts globally (Schwela, 2010). The atmosphere is earth's largest shared resource which plays a role in protection and supporting life through the absorption of dangerous ultraviolet solar radiation, warming the surface and temperature reduction (Sengupta *et al.*, 2003). The important roles the atmosphere plays are threatened by introduction of pollutants into the atmosphere through anthropogenic activities. Environmental legislations and guidelines are therefore formulated to reduce and regulate the pollutants released into the atmosphere from different activities.

Volatile Organic Compounds (VOCs) form part of hazardous air pollutants (HAPs) which are gaseous pollutants present in air in trace amounts which are toxic and may become hazardous to human, plant or animal life (Gunatilaka, 2003). Benzene, toluene, ethylbenzene and xylene (BTEX) compounds are categorised as VOCs that are involved in formation of ground-level ozone and photochemical smog, which causes concern around human health and also affect the environment (Rad *et al.*, 2014). BTEX enters the atmosphere during the manufacture or use of substances or products containing the compounds such as diesel fuel, home heating oil and gasoline (Rad *et al.*, 2014). The major sources of VOCs are petroleum refineries, petrochemical industries, automobiles, combustion of fossil fuels and biomass, use of solvents and distribution of petroleum products (Mohan and Ethirajan, 2012). Globally, air quality guidelines are adopted for (BTEX) with the aim to reduce concentration of compounds to lower levels at certain periods (Gunatilaka, 2003).

The expansion of industries has influenced the air quality monitoring studies in South Africa and globally (Lourens *et al.*, 2011). Despite various studies on BTEX concentrations such as Gunatilaka, 2003; Cetin *et al.*, 2003; Gallego *et al.*, 2008; Hoque *et al.*, 2008; Correa *et al.*, 2012 and others, investigating different sources of pollutants, health risk assessment together with spatial and temporal distribution of the pollutants, there are few local studies focusing on concentrations of BTEX,

seasonal variations and relationships between emissions and the climatic conditions of the area together with modelling BTEX pollutants. Gunatilaka (2003) conducted a study in Christchurch, New Zealand assessing annual average concentrations of BTEX, trends and seasonal variations however the study was done in residential areas and also in the city as opposed to industrial areas. The results of the study indicated that the BTEX concentrations were higher in winter months than the other periods of the year on all sites (Gunatilaka, 2003). The higher concentration recorded in the winter months were influenced by domestic fuel heating and the cold calm conditions. Concentrations of BTEX measured at sites in the inner residential area showed a similar pattern however a site 30 km away from a fuel station had high concentrations (Gunatilaka, 2003). Correa *et al* (2012) investigated the impacts of BTEX emissions from a gas station in Brazil using dispersion modelling and identifying sources of emissions. The results from the dispersion model indicated that the concentrations of BTEX were greater even 150m away from the gas stations than those found in downtown area of Rio de Janeiro (Correa *et al.*, 2012). Lourens *et al* (2011) indicated that the BTEX were high in industrial areas in Witbank, Delmas and Vanderbijlpark in a study conducted in the Highveld of South Africa. According to Singh *et al* (2013), BTEX concentrations were usually high around a petroleum refinery as compared to nearby villages. The studies indicated that air quality monitoring around gas stations is important and should be given more attention.

Government Notice 248, Gazette number 33064 (South Africa) publishes and defines the Listed Activities and Associated Minimum Emission Standards Identified in Terms of Section 21 of the National Environmental Management: Air Quality Act, 2004 (Act No. 39 of 2004). The listed activities result in atmospheric emissions which have or may have a significant detrimental effect on the environment, including health, social conditions, economic conditions, ecological conditions or cultural heritage (Department of Environmental Affairs, 2012). Petroleum products are believed to contribute to atmospheric emissions that have negative impacts on the environment and people therefore their storage and handling is important. Fuel depots are classified under Subcategory 2.4 which involves the storage of petroleum

products (Department of Environmental Affairs, 2012). The operation within fuel depots is contributes to the release of pollutants into the atmosphere through the evaporation of fuel, spillage, storage tanks, pump bay and waste areas (Cetin et al., 2003). Therefore, fuel depots form part of the sources of BTEX pollutants in both urban and industrial atmosphere as the fuels handled contain substantial amounts of the pollutants.

Ambient air quality monitoring programmes and modelling are established to evaluate, control and regulate the air pollutants from industry. Air quality monitoring consists of the collection of data to measure the concentrations of air pollutants in the ambient atmosphere. Monitoring is important in identifying the extent and source of any pollutants and it also provides the basis for developing appropriate control strategies as well as assessing their effectiveness (Schwela, 2010). Mostly air quality assessment is influenced by the need to determine whether or not certain standards and guidelines have been exceeded (World Health Organisation, 2005). Another objective of the assessment could be to provide information required to estimate population exposure together with the effects on the health of the population. Compliance with regards to air quality standards and guidelines is then determined by comparing measured concentrations of certain pollutants to corresponding health-based air quality standards as well as guidelines (World Health Organisation, 2005).

South Africa is considered to have diverse anthropogenic pollutant sources which include petrochemical industries due to its highly industrialised economy (Lourens *et al.*, 2011). The quantity of pollutants emitted into the atmosphere by different sources and the dispersion of the pollutants contribute to the ambient air quality (Sengupta, 2003). The dispersion potential of pollutants in the atmosphere are influenced by complex meteorological parameters such as circulation, temperature, wind direction and speed, which demonstrated well through dispersion models. As highlighted, the few local studies do not supply information with enough spatial variability of BTEX pollutants particularly around fuel depots and therefore, it was essential that this

study was conducted to determine the average concentrations, seasonal variations of concentrations of pollutants, relationships between BTEX concentrations to climatic conditions.

1.1. Justification of the Study

The growth in the industries in South Africa implies more emissions released from the industries therefore it is vital to understand the emissions from specific sources. It was noted that monitoring of inorganic species with active and passive samplers is well established in South Africa (Lourens *et al.*, 2011). However little data exist for VOCs monitoring (Lourens *et al.*, 2011). Recently, studies about VOCs have become popular specifically the BTEX compounds due to them causing adverse health effects, influencing photochemical smog and tropospheric ozone formation (Lourens *et al.*, 2011; Jaars *et al.*, 2014; Moolla *et al.*, 2015). One of the sources of BTEX noted in various international and local studies are fuel depots as they involve the storage and distribution of refined products which involve operations that may lead to a potential source of evaporation, loss and occupational exposure problem to employees (Singh *et al.*, 2016). The analysis of BTEX concentrations from fuel depots is important within developing countries as the transport systems depend on the fuel mostly stored in these depots. The studies relating to BTEX concentrations at fuel depots are limited as most studies focus on refuelling stations (Lovino *et al.*, 2009; Moolla *et al.*, 2015). This study aims to contribute towards the limited knowledge base regarding BTEX concentrations at fuel depots within the South African context.

The dispersion of pollutants from their sources to surrounding areas is dependent on the climatic conditions of the area such as temperature, precipitation, wind speed and direction (Jaars, 2012). The seasonal variations of BTEX concentrations have been investigated in South Africa and a majority of international studies have investigated the variations in different areas such as industrial, urban and residential. The influence of climatic conditions on BTEX concentration forms part of many studies as it provides an understanding of the variations in concentrations in relation to the prevailing climate. In South Africa studies that have focused on seasonal

variations of BTEX concentrations were conducted in a priority area, measurement station and mixed-used areas while very few studies were done on fuel depots (Lourens et al., 2011; Jaars et al., 2012; Jaars et al., 2014; Moolla et al., 2015). The analysis of seasonal variations of BTEX concentration in fuel depots is also limited and the study seeks to contribute to the understanding by evaluating relationship between climatic conditions and pollutant concentrations. Furthermore, the study will evaluate the concentration hotspots and the interspecies ratios among BTEX pollutants.

1.2. Aims of the Study

The aim of this study is determine the BTEX concentrations from specific fuel depots in parts of South Africa, to assess the seasonal variations and relationship between BTEX concentrations and the climatic conditions of the areas.

1.3. Objectives

The objectives of the study are to:

- Determine the average concentrations of BTEX from specific fuel depots
- Evaluate the influence of wind speed and direction on BTEX concentrations from specific fuel depots
- Determine the seasonal variations of BTEX concentrations from specific fuel depots
- Establish the relationship between BTEX concentrations and climatic conditions of the area i.e. temperature.

1.4. Location of Study Area

The study was conducted in fuel depots located in Alberton, Witbank, Kroonstad, Rocky's Drift, Island View, Port Elizabeth, Ladysmith and Kimberley. The depots were situated within industrial and mixed-use urban areas across the various provinces of South Africa.

2. Literature Review

2.1. Introduction

The research interest around BTEX compounds has grown as there is an increase in activities such as industrialization and urban growth that contribute to the introduction of pollutants into the atmosphere. BTEX compounds are of importance to this study as this class of air pollutants is mainly generated from fuel related activities and fuel depots are major contributors to that. The attention to BTEX compounds is also influenced by the fact that the compounds are potentially hazardous to the environment and humans. The literature review will look at various areas of research undertaken around the nature of BTEX pollutants, their dispersion in the atmosphere, seasonal variations of BTEX concentrations, BTEX ratios and atmospheric chemistry related to BTEX pollutants. The literature will also provide a background of the climatic conditions of South Africa together with findings from other studies around the effects of climatic conditions on BTEX concentrations.

2.2. Ambient Air Quality

The atmosphere acts as a repository for pollutants originating from industrialisation, urban growth, transport, power generation, waste generation, biomass burning and changing consumption patterns (South Africa Environment Outlook, 2012). Ambient air quality describes the airborne pollutants concentrations (both physical and chemical) in the atmosphere which a population can be exposed to (South Africa Environment Outlook, 2012). According to South African Environment Outlook (2012), ambient air quality has deteriorated in most developing countries therefore people are exposed to pollutants levels above recommended limits. Some pollutants emitted undergo chemical transformation with other compounds and may pose health risks to the populations exposed (Queensland Government, 2012). The elements linking air quality and the concentration of certain pollutants to apparent health effects or condition are: the level of exposure and the duration of exposure to the pollutant (Rad *et al.*, 2014). The deterioration of ambient air quality levels together with the realisation of associated health effects has led to international and national efforts such as air quality standards and limits. The air quality limits and

thresholds are vital to ensure the success of air quality management programmes (USEPA, 2014). Air quality limits illustrate the levels of exposure to pollution that are safe for people over specified periods. Although the air quality limits are not part of the study it is important to note that a limit for benzene was set as pollutants are associated with health risks.

2.3. Nature of BTEX Pollutants

The BTEX group are aromatic hydrocarbons that are constituents of gasoline and diesel that also occur naturally, the compounds are also present in kerosene and fuel oils (Scottish Environmental Protection Agency, 2012). The compounds are used in the processing of petroleum products and production of consumer goods. Queensland Department of environment and heritage protection (2012) indicated that petrochemical stations contribute largely to BTEX emissions as the percentage of the compounds in unleaded petrol is approximately 1 to 2 percent. According to Hoque *et al* (2008), gasoline vehicular exhausts were established as the major sources of BTEX in Delhi through an investigation of their spatial and temporal distributions. There are trace amounts of BTEX contained in cigarettes, therefore smoking is also a minor source (Scottish Environmental Protection Agency, 2012). Similar to other VOCs, BTEX compounds are constituents in the formation of ground level ozone and other photochemical oxidants in the troposphere that may affect crops and materials (Hoque *et al.*, 2008). In a study conducted in the Highveld of South Africa, which aimed to determine the spatial and temporal distributions of NO₂, SO₂, O₃ and BTEX in both industrial and remote area, highest BTEX concentrations were determined at Witbank, Delmas and Vanderbijlpark which are industrialised areas (Lourens *et al*, 2011).

Although BTEX compounds are usually assessed as a group, the individual compounds have various effects and standards both internationally and locally. The United States – Environmental Protection Agency classified benzene as a Group A, known human carcinogen of medium carcinogenic hazard whereas toluene, ethylbenzene and xylene are classified as Group D, not classifiable as to human

carcinogenicity (Beim *et al.*, 2001). Inhalation is the dominant route of exposure to BTEX where effects may be caused in different parts of the body (Agency for Toxic Substances and Disease Registry, 2007). Although this study focused on determining the average BTEX concentrations, seasonal variations together with dispersion modelling of the pollutants from fuel depots, it is essential to note the various sources of BTEX and related effects. The influence of climatic conditions on the pollutants will be discussed in the following sections.

2.4. Dispersion of Pollutants in the Atmosphere

Air pollutants are dispersed by winds from their sources to other areas posing the problem of environmental trans-boundary pollution. Air quality is therefore dependent on the quantity of pollutants emitted into the atmosphere through different sources and the dispersion of the pollutants (South African Environmental Outlook, 2012). The transportation, dispersion and deposition of pollutants is therefore largely determined by the meteorological and topographical conditions of the area (Sharan *et al.*, 1996). The transportation of pollutants in the atmosphere happens through two processes namely: vertical and horizontal transportation. Atmospheric stability structure controls the vertical transportation while the local winds near the surface and the large-scale circulation in synoptic fields both influence horizontal transportation (Tyson and Preston-Whyte, 2000).

Dispersion potential is the ability of the atmosphere to dilute and remove pollution therefore the level of pollution in the area is dependent on the dispersion potential of the atmosphere (Jagathlal, 2012). According to Sharan *et al.* (1996), the dispersion of pollutants in the atmosphere is governed by two mechanisms, which are the mean air flow that transports the pollutants downwind and turbulent velocity fluctuations which disperses the pollutants in all directions (Sharan *et al.*, 1996). Research indicates that meteorology and topography have an impact on the dispersion of pollutants in the atmosphere (Sharan *et al.*, 1996; Tyson and Preston-Whyte, 2000; Ahrens, 2009). The dispersion of pollutants in the atmosphere depends on prevailing meteorological conditions in terms of wind speed, solar insolation, mixing height and

atmospheric stability with respect to space and time (Liebenberg-Enslin and Venter, 2005). As highlighted earlier, the dispersion potential is determined by the prevailing climatic conditions therefore it is essential that South Africa's conditions are considered.

The southern African subcontinent consists of a different set of meteorology and physical characteristics that largely affect the transportation, recirculation, emission and atmospheric chemistry of pollutants in the atmosphere (Garstang *et al.*, 1996). The anticyclones have a dominating effect on all the circulation patterns that occurs over South Africa. Large-scale recirculation of air takes place south of 10° S and regionally within parts of the country in South Africa (Garsteng, *et al.*, 1996). The descending portion of the Hadley cell which influences the anticlockwise movement of VOCs over the country causes the recirculation of pollutants (Tyson *et al.*, 1996; Frieman and Piketh, 2003). The recirculation increases concentration of aged BTEX pollutants as they may reside over the interior of South Africa for a longer period (Frieman and Piketh, 2003). The atmospheric lifetime of the BTEX pollutants, determine the amount that can be recirculated. The effects of climatic conditions on BTEX pollutants in the atmosphere will be discussed in detail.

2.5. Effects of Climatic Conditions on BTEX Pollutants

The atmosphere is a complex analytical system with sharp variations in pollutants levels over time, location and differences in climatic conditions (Kinney, 2008). Due to the fact that emissions, transport, dilution, chemical transformation and deposition of air pollutants are influenced by meteorological conditions this implies that weather and climate play an important role in determining the patterns of air quality over various scales in time and space (Kinney, 2008). The influence of ambient climatic conditions to VOCs in general have resulted in their variations spatially and temporally (Roukos *et al.*, 2009). An understanding of the regional together with local climatic conditions that affect the BTEX pollutants is essential to determine the pollutants concentrations in the atmosphere and broaden the knowledge on the influence of the climatic conditions on the pollutants. The atmospheric stability,

changes in mixing heights, effect of wind systems, variations in temperature and circulation patterns influence the daily and seasonal fluctuations in pollutants concentrations in the atmosphere.

2.5.1. Regional Climatic Conditions

South Africa is located between the latitudes 22° and 33° South, which implies that its climate is dominated by the belt of subtropical highs which are the South Atlantic High, Kalahari High and the South Indian High as illustrated in Figure 2.1 (Tyson and Preston-Whyte, 2000). In addition to the subtropical highs, the weather in South Africa is also determined by the oceans, altitude of the sub-continent and the interior plateau (Jury, 2012). The lower tropospheric circulation at an average of 800hpa geospatial height is dominated by the semi-permanent subtropical anticyclones while the regional circulation over the continent is dominated by the sinking Hadley high pressure cell (Tyson *et al.*, 1996b; Piketh *et al.*, 1999). The anti-cyclonic circulation of air influences formation of stable atmospheric conditions which lead to resistance of the vertical movement of air parcel (Ahrens, 2009; Krol *et al.*, 2011). The characteristics of the semi-permanent anticyclone circulations such as stability and depth result in the formation of the South African layer which covers most parts of the country during the dry seasons (Piketh *et al.*, 1999).

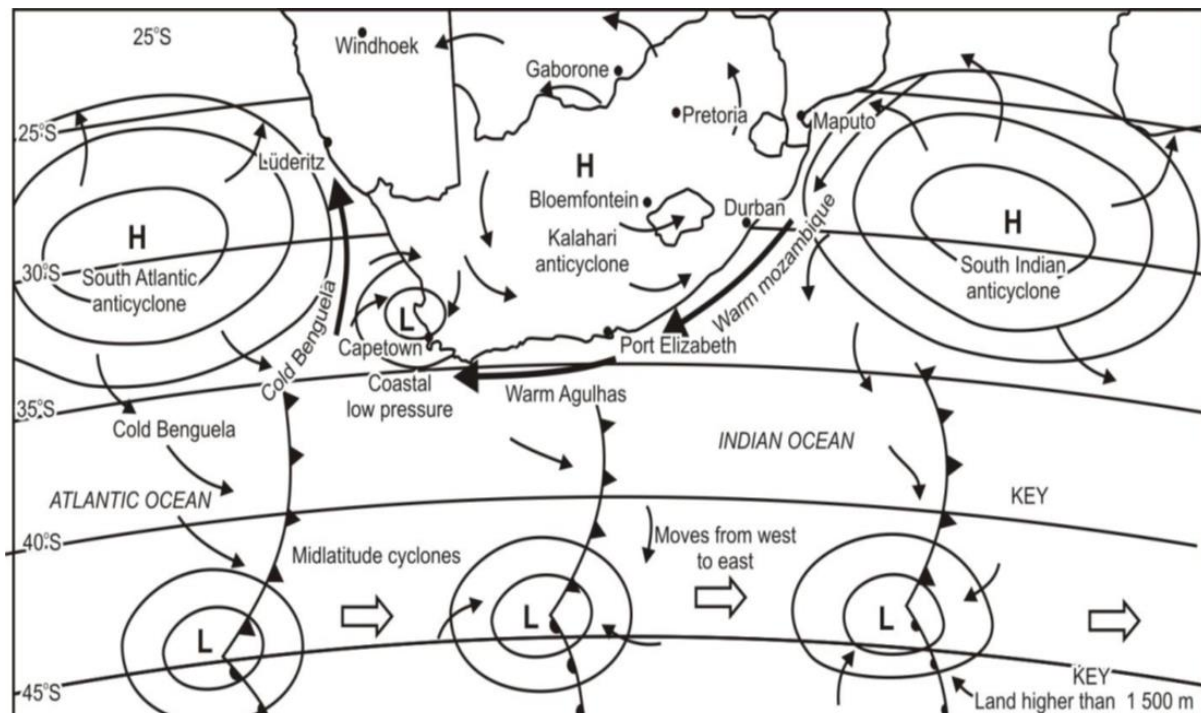


Figure 2.1: The dominant circulation types over Southern Africa (After Preston-Whyte and Tyson, 2000)

A large part of South Africa is situated on a plateau, with regions that are cooler and dry in winter. The Mozambique current on the east influences weather in areas adjacent to it, causing the air to be warmer, humid and unstable also increasing rainfall (Jury, 2012).

The occurrence of the large-scale anticyclonic activities over the subcontinent result into subsidence inversion over South Africa with pervasive consequences during the winter season. The subsidence inversion lasts for longer periods in winter and reduces the dispersion of pollutants in the atmosphere over the plateau as it causes little diurnal variation and constant afternoon mixing depth (Tyson and Preston-Whyte, 2000). There is a sinking movement of air which sustains the inversion and trap the aerosols and trace gases originating from surface and boundary layers over the continent (Garsteng, *et al*, 1996).

Pollutants from low-level sources are controlled by surface inversion and they are trapped below the inversion layer at night (Annergan *et al*, 1996). The inversion layer

inhibits the vertical movement of air as it caps the pollutants and the impact of the mixing depth also has an effect. The mixing layer is the region between the ground and the base of the inversion (Ahrens, 2009). The concentrations of air pollutants at ground level are significantly impacted by the depth of the mixing layer thus a decrease in mixing depth cause less air where pollutants could be diluted (Ahrens, 2009). During winter the interior of South Africa experiences reduced mixing depth which is influenced by the occurrence of anticyclonic circulation thereby increasing the concentrations of air pollutants in the season (Tyson and Preston-Whyte, 2000; Ahrens, 2009). The regional climatic conditions will have impact on the concentrations of BTEX pollutants as the anticyclonic circulations, subsidence inversion and reduced mixing depth both impact the dispersion and dilution of pollutants in the atmosphere.

2.5.1.1. Atmospheric Characteristic

Atmospheric stability plays a fundamental role in the dispersion of pollutants therefore it can also influence fluctuations in the pollution levels. Atmospheric stability is the extent to which vertical motion occurs or the degree of turbulence in the atmosphere (Sharan *et al.*, 1996). Atmospheric stability directly affects the vertical dispersion of pollutants and indirectly affects the horizontal movement of air. Anticyclonic circulation pattern is related to atmospheric stability which restricts vertical movement of air thereby increasing the air pollutant concentrations in the atmosphere (Tyson and Preston-Whyte, 2000; Ahrens, 2009). The air pollutant concentrations increase as their residence times increase over a specific area (Tyson and Preston-Whyte, 2000).

Due to the descending nature of air masses in the region there are frequently occurring discontinuities that impact the pollutants transportation in the atmosphere (Frieman and Tyson, 200). Multiple persistent stable layers occur over the subcontinent and they control the transport of pollutant as air masses may be trapped within the stable layers after convection from the lower troposphere took place (Garsteng, *et al*, 1996). Four stable layers' form over South Africa, the first occurs at the top of the mixing layer and is centred around 700 hPa. The second

layer is produced and sustained by surface inversion and it occurs at approximately 500 hPa. The third layer exists at 350 hPa between the main subsidence feature and the tropopause, the layer is vital for the transport of ozone. The fourth layer may be associated with the tropopause and it occurs at 850 hPa between the plateau and ocean (Garsteng, *et al*, 1996; Tyson *et al.*, 1996b). The breaking of the stable layers is controlled by the passage of westerly wave disturbances. The persistent stable layers restrict vertical transportation of surface generated species and also inhibit the horizontal transport between layers thereby causing an increase in pollution concentrations (Garsteng, *et al*, 1996; Tyson *et al.*, 1996b). The two lowest layers are the most significant in restricting the vertical and horizontal transportation of pollutants. The structure of the absolute stable layers is influenced by the common synoptic circulations over South Africa which are semi-permanent continental anticyclones, transient mid-latitude ridging anticyclones quasi-stationary easterly waves, and westerly baroclinic disturbances as they control convergence and divergence (Tyson *et al.*, 1996; Preston-Whyte and Tyson, 2000).

There are decreased pollutant concentrations in summer over South Africa due to the increased vertical instability in the boundary layer of the atmosphere (Tyson and Preston-Whyte, 2000). When a parcel of air is warmer than its surroundings causing convective uplift then instability occurs (Ahrens, 2009). The atmospheric instability is favoured by convective uplift which usually occurs in the Highveld of South Africa in summer as the ground heats up (Tyson and Preston-Whyte, 2000). Atmospheric instability influences occurrence of convectional thunderstorms which remove air pollutants through wet deposition (Tyson and Preston-Whyte, 2000; Ahrens, 2009). The regional climatic features such as stable layers, inversion and anticyclonic circulation restrict vertical mixing causing an increase in the pollution levels over southern Africa.

2.5.2. Local Climatic Conditions

The formation of local topographically induced winds depends largely on the geography and the time of the day (Turner *et al.*, 1995). The circulation patterns have a significant impact on the regional winds and also control the transportation of low-level emission pollutants. The thermo-topographic interactions can disperse pollutants for example valley breeze and gravity winds (Ahrens, 2009). The wind patterns determine where air pollution originating from various sources will end up (Ahrens *et al.*, 2009). The dilution rate of pollutants depends on the function of wind velocity and atmospheric stability. Wind speed has an influence on how far downwind pollutants may be transported, rate of dilution in the atmosphere and level of mechanical turbulence. A decrease in wind speed causes an increase in the pollution concentrations as it restricts horizontal dispersion and dilution (Tyson and Preston-Whyte, 2000; Ahrens, 2009). The dispersion of pollutants and the rate of dilution of air increases with an increase in wind speed (Tyson and Preston-Whyte, 2000; Ahrens, 2009). Therefore, on calm days the pollutants concentrations will be high compared to days with strong flow which influences the dispersion of pollutants. The wind velocity, direction, humidity together with temperature govern the dispersion potential of pollutants in a certain area. Wind direction determines the horizontal path that the pollutants will follow in the atmosphere (Tyson and Preston-Whyte, 2000; Ahrens, 2009). The direction that pollutants follow together with the extent of cross wind spreading is dependent on the wind direction and its variability (Tyson and Preston-Whyte, 2000)

In a study conducted in India around a petroleum refinery the wind speed and direction had a great impact on distribution of concentrations of BTEX in the atmosphere (Singh *et al.*, 2013). Cetin *et al* (2003), established that wind speed and temperature influenced the variability of BTEX concentrations around a petroleum complex and petroleum refinery. An increase in wind speed and temperature resulted in increased BTEX concentrations (Cetin *et al.*, 2003). Various studies also provided similar results with regard to the influence of wind speed, direction and

temperature on BTEX concentrations (Galindo *et al.*, 2016; Ceron-Breton *et al.*, 2015; Marc *et al.*, 2015; Yurdakul *et al.*, 2013; Kinney, 2008).

Lower average ambient temperature has been linked to the accumulation of pollutants in the atmosphere as it influences slow movement of air masses in the upper atmosphere over South Africa (Moolla *et al.*, 2015). South Africa experiences dry and wet seasons which influence the precipitation patterns (Jaars, 2012). In the dry season, almost no precipitation occurs over the interior while precipitation is received throughout the wet seasons. The precipitation cycle affects the pollutant concentrations as scavenging of pollutants increases in the wet seasons while pollutants concentrations are higher during dry months (Jaars, 2012). The dispersion of pollutants is influenced by various climatic conditions such as wind speed, direction and temperature. Climatic conditions are fundamental for the dispersion of pollutants through determining the diluting effect of the atmosphere therefore forming a great part of dispersion modelling (Mkhonto, 2013). According to Lourens *et al* (2011), accurate climatic data from a weather station within the study area is essential for best modelling results. Due to the different factors that influence the weather over South Africa, the country has different seasons with varying weather conditions that influence the concentrations of pollutants in the atmosphere.

2.6. Seasonal Variations of BTEX Concentrations

South Africa experiences four seasons which are summer, autumn, winter and spring. The different seasons are associated with various climatic conditions which may affect the BTEX concentrations in the atmosphere. Seasons are noted to be influential on the levels of pollutants concentrations. The anti-cyclonic circulation traps pollutants and causes increase in pollutant concentration during the winter season contributing to poor air quality (Preston-Whyte and Tyson, 1988). During the summer season, the anti-cyclonic belt weakens and shifts southwards then the tropical easterly flow resumes its influence over the interior (Jaars, 2012).

The seasonal variations of BTEX concentrations have been observed in various international and local studies. According to Cetin *et al* (2003), BTEX concentrations generally increase with a decrease in temperature and wind speed. In a study for the assessment of VOCs around a petrochemical complex and a petroleum refinery in Turkey, concentrations were highest in summer followed by autumn (Cetin *et al.*, 2003). Increased dispersion conditions result from high wind speed, therefore lower concentrations may be expected during seasons with high wind speed (Cetin *et al.*, 2003). In a study conducted around Delhi in India, the lowest concentrations were observed during summer and highest during winter (Singh *et al.*, 2016). The high levels of BTEX in winter as compared to spring and summer seasons were influenced by the low dispersion due to the stable atmosphere during winter season, reduction in VOCs removal in winter because of slow down in photochemical reactions as a result of short day length and lower solar intensity (Singh *et al.*, 2016). Gunatilaka (2003) indicated that concentrations of BTEX were high in the winter months as compared to results from the rest of the year in a study conducted in Christchurch; the cold calm conditions experienced in winter were conducive to high concentrations of BTEX compounds. During the seasons with conditions that are calm together with prevailing atmospheric stability, pollutants are hindered from dissipating faster (Hoque *et al.*, 2008). Temperature inversion develops below the level of escarpment and prevents moist air from entering the interior in winter which limits the dilution process of pollutants therefore pollutants may have higher concentrations in this season (Hoque *et al.*, 2008). In most international studies the BTEX seasonal trends observed can be addressed by the seasonal characteristics of prevailing meteorology, variations in the source strength and availability of hydroxyl radical and insolation for the removal of VOC species from the atmosphere (Hoque *et al.*, 2008). The variations of BTEX concentrations may be well represented through iso-concentration mapping which indicates the different concentrations of the different pollutants.

Lourens *et al* (2011) indicated that there were no distinct seasonal trends observed in a study for assessment of gaseous pollutants in the Highveld of South Africa.

Similarly, in a study conducted in Welgegund, South Africa where measurements of the aromatic hydrocarbons in ambient air were conducted, there were no distinct seasonal patterns observed (Jaars *et al.*, 2014). In another assessment of VOCs at a site with high atmospheric variability in North-West province, no distinct seasonal cycles were observed for aromatic hydrocarbons as concentration levels were high in February and March 2011 however in the following year (2012) in the same months the concentration levels were low (Jaars, 2012). In most local studies investigating BTEX or aromatic hydrocarbons in general, no distinct seasonal variations have been observed.

2.7. BTEX Ratios

The interspecies ratios have been taken as indicators of the age of the air mass and emission source tracers (Hoque *et al.*, 2008; Jaars, 2012; Singh *et al.*, 2016). The BTEX interspecies ratio values also depend on the climatic conditions of the region together with the types of emission sources into the air (Gaur *et al.*, 2016). The ratios may also be used to estimate the air photochemical reactivity based on the assumption that BTEX pollutants have different degradation rates in the air (Lovino *et al.*, 2009; Jaars *et al.*, 2012). In comparison to benzene most of the aromatic hydrocarbons are more reactive, toluene/benzene (T/B), (m,p)-xylene/benzene ((m,p)-X/B), o - xylene/benzene (o-X/B) and (m,p)-xylene/ethylbenzene ((m,p)-X/E) ratios can provide additional information such as the distance of emission source and estimated photochemical age of the air mass (Jaars, 2012). The toluene to benzene (T/B) ratio is commonly used as an indicator of traffic emissions as the two hydrocarbons are constituents of gasoline and are emitted by car exhausts into the atmosphere (Hoque *et al.*, 2008). The T/B ratio decreases with an increase in the distance from the sources and increases with increasing anthropogenic emissions (Jaars, 2012). The (T/B) ratio also provides an indication of whether the source is a point source or a mobile source (Monod *et al.*, 2001; Singh *et al.*, 2016). The lifetime of toluene in the atmosphere is 5 times shorter than the lifetime of benzene which is due to the rate of photochemical degradation of toluene. The T/B ratios will be outlined further under the methodology in Section 3.3.2.

Toluene and benzene are both sensitive to photochemical reactions, therefore an increase in temperature causes their concentrations to decrease (Gallego *et al.*, 2008; Król *et al.*, 2012). The ratio values can be classified for fresh emission originating from traffic, mobile sources and point sources (Monod *et al.*, 2001; Jaars *et al.*, 2012). The different T/B ratio values indicate the various sources as follows: value of one indicates fresh emission from traffic, values between 2 and 3 indicate mobile sources while higher values are related to industrial facilities and area/ point sources (Monod *et al.*, 2001; Jaars *et al.*, 2012). Monod *et al.* (2001), established that the xylene and ethylbenzene (X/E) ratio may be constant throughout different sources therefore it is useful in investigating the source and age of photochemical plume as the pollutants decay at differing rates from OH oxidation. Observed similar and persistent ratio values from different locations may indicate single source of emission. The ratios may also be used to understand the dependence of concentrations on intensity of solar actinic flow which may indicate the role of photochemical processes in the atmosphere (Lovino *et al.*, 2008). The interspecies ratios also illustrate some seasonal variations in relation to different climatic conditions (Pilidis *et al.*, 2005).

An investigating conducted in Delhi, India revealed that there were differences of T/B ratios in Delhi as compared to other cities such as Hong Kong, Bangkok and Sydney (Hoque *et al.*, 2008). According to Hoque *et al.* (2008), the differences of T/B ratios among different cities may indicate a difference between their vehicular types, fuel consumption and industrial activities. In a study carried out in North West Province in South Africa, the ratios observed demonstrated a seasonal pattern with the maximum in summer and minimum in winter (Jaars, 2012). The T/B ratios were found to be between 2.5 and 3.5 in urban areas where vehicle exhaust is primary source while in industrialised cities ratios were higher than 4.5 (Galindo *et al.*, 2016). The reactivity of the BTEX species in the atmosphere may involve some chemical reactions influenced by the species characteristics, atmospheric conditions and the climate of the area.

2.8. Atmospheric Chemistry

In the atmosphere pollutants can be chemically altered through photochemical reactions and atmospheric chemical transformation (Seinfeld and Pandis, 2006). In a photochemical reaction, the sunlight may have enough energy to break the molecules apart and in the atmospheric chemical transformation, two molecules interact and undergo a chemical reaction in order to produce a new species (Seinfeld and Pandis, 2006). Atmospheric chemical transformations may occur homogeneously or heterogeneously. During transportation in the atmosphere, most pollutants are likely to participate in chemical reactions that transform their chemical and physical forms.

The average lifetimes or residence time for substances are determined by averaging the histories of all molecules found in the substance together with reactivities against HO radicals. The removal processes of atmospheric species may be through deposition (dry and wet) together with photochemical reactions (Yurdakul *et al.*, 2013). The lifetimes of pollutants can range from seconds to millions of year depending on the effectiveness of the removal process (Seinfeld and Pandis, 2006). Generally, VOCs react with hydroxyl radicals to form tropospheric ozone in the presence of NO_x and sunlight (Dutta *et al.*, 2009). Implications related to visibility and climate change may also be linked to VOCs as they are involved in aerosol generation. Xylenes take part in the photo-oxidation reactions which include the conversion of nitric oxide to nitrogen dioxide, with m-xylene being the most reactive isomer (Dutta *et al.*, 2009).

The reactive routes for VOCs include OH-initiated photochemical oxidation, photolysis in the troposphere and stratosphere together with reactions with species such chlorine atoms and nitrate radical (Yurdakul *et al.*, 2013). The reaction between NO_x and VOCs in the troposphere is the main process for production of photochemical ozone (Atkinson, 2000). In the presence of sunlight VOCs are oxidised into simpler molecules such as CO or intermediate VOCs due to the chain reactions mainly driven by hydroxyl radicals. As a result of the hydroxyl driven reactions, the chemical removal of VOCs in the atmosphere is more significant in

summer than in winter as there is greater photochemical activity influenced by enhanced solar flux, temperature and higher hydroxyl radical concentration in summer. The changes in the chemical reactions in different seasons may also contribute to the seasonal variation of the BTEX pollutants in the atmosphere.

The hydroxyl radicals are species with a short lifetime however they play a vital role as chemical scavengers of the atmosphere to clean the harmful organic pollutants. The atmospheric lifetime of BTEX compounds also play a role in their reactivity, benzene has a lifetime of 9.4 days while toluene and xylenes have lifetime of 1.9 days and ≤ 20.3 hours respectively (Galindo *et al.*, 2016; Monod *et al.*, 2001). The meteorological conditions such as high average ambient temperatures, high levels of insolation and low relative humidity both accelerate the degradation of VOCs in the atmosphere with the hydroxyl radicals' reactions (Krol *et al.*, 2011). An increase in ambient air temperature causes a decrease in the benzene concentration therefore the lifetime of benzene is shorter in summer months. The photochemical degradation of BTEX compounds is enhanced in the summer season by the prevailing climatic conditions. The concentrations of BTEX compounds are affected by the climatic conditions and atmospheric chemistry as these influence different reactions involving BTEX compounds.

2.9. Motivation

Studies about BTEX compounds have grasped attention recently as they are part of VOCs and also due to their contribution to troposphere ozone, photochemical smog formation and possibilities of causing adverse health effects (Hoque *et al.*, 2008). However, in South Africa very little data exist for VOCs monitoring whereas monitoring of inorganic species with active and passive samplers is well established (Lourens *et al.*, 2011). According to Lourens *et al* (2011), the measurement of air pollutants conducted by industries and various municipalities do not necessarily provide a good representation of the larger areas. Although it is acknowledged that data exist, most of the data are not published and evaluated therefore there may also be questions about its quality. There were some major studies conducted

around BTEX investigations with focus on measurement of pollutant concentrations, exposure of petrol attendants to pollutants and spatial and temporal assessment of the pollutant across South Africa (Lourens *et al.*, 2011; Jaars *et al.*, 2014; Moolla *et al.*, 2015). There are various sources of BTEX and studies conducted usually focus on broader sources of pollutants (Rad *et al.*, 2014). International and local studies have established that the climatic conditions of an area have an influence on the behaviour of pollutants in the area (Preston-Whyte and Tyson, 1988; Garsteng, *et al.*, 1996; Cetin *et al.*, 2003; Hoque *et al.*, 2008; Jaars, 2012; Jagathlal, 2012). In the South African context studies conducted around the assessment of BTEX or aromatic hydrocarbons have indicated that there were no distinct seasonal variations in BTEX concentrations while international studies report that seasonal variations were observed in BTEX concentrations (Gunatilaka, 2003; Hoque *et al.*, 2008; Lourens *et al.*, 2011; Jaars, 2012; Jaars *et al.*, 2014; Singh *et al.*, 2016). This study aims to assess the average BTEX pollutants from fuel depots and also determine the seasonal variations of the pollutants.

3. Methodology

The chapter outlines the different methodological consideration used throughout the research project. The various sections within the methodology include: the site description, research approach and the design which elaborates the sampling methods together with the data analysis. The site description gives an outline of the environmental, operational and need to include the sites in the research. The research approach defines the technique which was adopted for the collection of data for the study.

3.1. Site Description

The air quality monitoring was conducted in eight fuel depots that store petroleum products across South Africa (Figure 3.1). The criteria used for selection of sites were: comparability with a previous project and representation of different land-use areas. The facilities are mostly located within industrial use areas and also mixed-use urban areas. Three facilities are situated in industrial areas in Rocky's Drift, Port Elizabeth and Island View. The other facilities are located within mixed-use urban

areas in Witbank, Kroonstad, Kimberley, Ladysmith and Alberton. The Kroonstad site is divided into two smaller sites neighbouring each other. The depots consist of tanks for storage of petroleum products, small tanks which are not legislated to carry active products, rail areas and loading gantries. The tanks operating within the depots may differ at times as tanks may be undergoing maintenance processes (Table 3.1).

Table 3.1: The details of the fuel depots including names, coordinates, extent, number of tanks, fuel stored and province in which depot is located.

Province	Name of depot	Coordinates	Extent (m ²)	Number of tanks	Fuel stored
Gauteng	Alberton	26°17'38.98"S	54400	8	Paraffin, petrol, diesel 50 ppm and 500 ppm.
Mpumalanga	Rocky's Drift	25°22'43.46"S 30°58'36.86"E	44375	5	Petrol, diesel 50 ppm and 500 ppm.
Mpumalanga	Witbank	25°51'34.20"S 29°10'1.01"E	47100	8	Paraffin, petrol, diesel 50 ppm and 500 ppm.
Free State	Kroonstad site 1 & site 2	27°40'38.97"S 27°13'38.38"E	38256	10	Petrol, diesel 50 ppm and 500 ppm.
Free State	Kroonstad Site 2	27°40'34.55"S 27°13'34.46"E	20500	5	Petrol, diesel 50 ppm and 500 ppm
Kwazulu-Natal	Ladysmith	28°32'38.22"S 29°47'22.29"E	24000	6	Petrol, Paraffin, Diesel 50 and 500.
Kwazulu-Natal	Island View	29°53'25.96"S 31° 2'19.65"E	53300	8	Petrol, diesel 50 ppm and 500 ppm
Eastern Cape	Port Elizabeth	33°58'7.18"S 25°38'20.28"E	11600	8	Paraffin, petrol, jet fuel, diesel 50 ppm and 500 ppm.

Northern Cape	Kimberley	28°45'59.30"S 24°46'2.45"E	3825.6	5	Paraffin, petrol, diesel 50 ppm and 500 ppm.
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The tanks are horizontal and vertical fixed roof tanks; the tank specifications are essential due to different emission rates for each tank. The location of the facilities in different provinces will be advantageous as it will allow the study to cover a gradient of climatic conditions. The location and names of the facilities are illustrated in Figure 3.1.

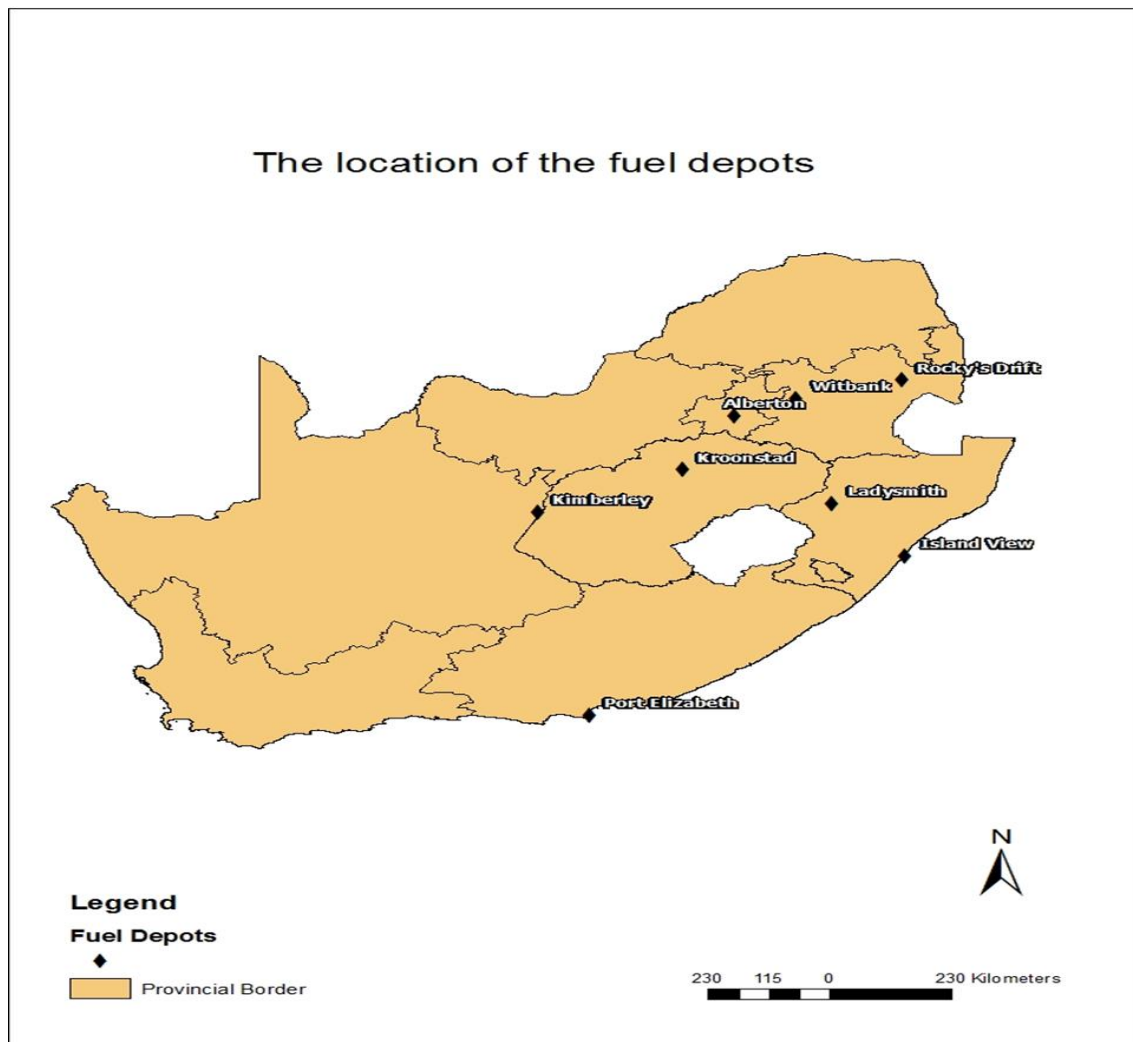


Figure 3.1: Map showing the location and names of the depots in different provinces across South Africa.

3.2. Research Approach

The research adopted a quantitative research approach. The air quality monitoring methods used were aimed to measure the concentrations of air pollutants in the atmosphere through passive samplers. The pollutants focused on were BTEX compounds. This study used random sampling procedure and collection of existing measurements to gather information in the form of a quantitative approach. In comparison to qualitative research, this research approach produces findings that can be applied to other populations whereas in qualitative research findings are specific to the case being studied. The collected data was then analysed through statistical analysis, mapping and comparisons within the different sets of data. Quantitative research is specific in its surveying and experimentation as it develops upon theories that are already established. The data was then interpreted in relation to existing relationships together with newly found ones.

3.3. Research Design

The research design ensures that the obtained data will be able to address the research questions or objectives as unambiguously as possible (Yin, 2003). This particular research adopted an experimental quantitative research to assess the BTEX concentrations from fuel depots in South Africa. The first section involved data collection from fuel depots and weather stations in the area surrounding the depots. The following are the specific data sets that were collected: tank specifications, types of fuel, BTEX concentrations and environmental data including climate data. The collected data was analysed through a flame ionisation detector (FID) gas chromatograph, WRPLOT, SPSS software and ArcGIS then used in the assessment of BTEX concentrations together with determining the seasonal variations and further examining the relationship between emissions and climatic conditions of the area.

3.3.1. Sampling Methods

a) Passive Samplers

There are three distinct forms of air quality monitoring which are active sampling, real-time monitoring and passive sampling (Gunatilaka, 2003). This study used passive sampling for collection of data. Passive sampling involves the measurement of the concentration of any analyte as a weighted average over the sampling period. According to Gunatilaka (2003), for large spatial distributions passive samplers provide a cost-effective method for determining concentrations. Radiello passive monitors by Fondazione Salvatore were used. The Radiello passive monitors consisted of cylindrical adsorbing cartridge housed coaxially inside a cylindrical diffusive body of polycarbonate as well as micro-porous polyethylene (Fondazione Salvatore Maugeri, 2006). The adsorbing cartridges placed inside the diffuse body were inserted into a mounted support plate then placed inside a mountable shelter. The shelter with monitors inside was installed 2-3 meters above ground attached to a structure that is not easily accessible such as pole or fence to avoid disturbance or damage. The radiello samplers had higher capacity, experimentally determined sampling rates and were easy to handle. The other advantages of passive sampling include simplicity, no power requirements, unattended operation and the ability to produce accurate results (Zabiegala *et al.*, 2010). The monitors were installed around the tank farm, loading gantry, workshop and rail area within the depot to measure average values for emissions from the listed areas. The decision for location of installation was taken based on the assessment of activities that may release BTEX concentrations around the depot. The number of monitors installed differed per site as some sites were designed without the workshop and rail area or the areas have been declared to be non-functional. Three or four monitors were installed around the perimeters of the site. Figure 4 illustrates the radiello passive samplers.

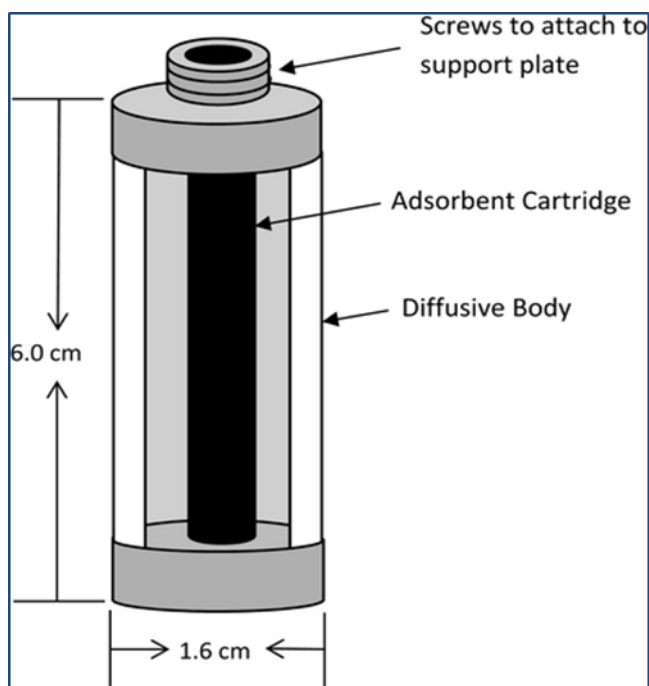


Figure 3.2:Radiello Passive Samplers (Fondazione Salvatore Maugeri, 2006)

The study was part of an air quality monitoring programme initiated in June 2015 by a team of consultants from Mamadi Sustainability together with the researcher. The researcher was involved in conducting the site visits and data compilation from the project inception stage to date. The monitoring was conducted from April 2017 to January 2018 and data collected in the previous years from (2015-2016) was also used in the study as indicated in Table 3.1. The monitors measured BTEX concentrations over a period of seven days on site then removed for analysis. It is important to note that the Ladysmith and Kimberley sites were monitored until July 2017 as operations were stopped at the sites.

Table 3.2: BTEX Monitoring Data Collection schedule indicating data collected in the previous campaign and data collected in the recent campaign.

BTEX DATA (PASSIVE SAMPLERS)										
		Previous Data					Data collected			
Place	Rural/ Urban/ Industrial	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Alberton	Urban (Mixed-use)	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Rocky's Drift	Industrial	6 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Witbank	Urban (Mixed-use)	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Kroonstad Site 1	Urban (Mixed-use)	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Kroonstad Site 2	Urban (Mixed-use)	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Ladysmith	Urban (Mixed-use)	6 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	–	–
Island View	Industrial	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Port Elizabeth	Industrial	5 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days
Kimberley	Urban (Mixed-use)	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	7 Days	–	–

**Days indicate the period sampler stayed on site.*

The radiello samplers for BTEX monitoring stayed on site for a maximum of seven days. In the previous sampling programme, there were instances where samplers were deployed from site before seven days as the radiellos may stay any days between one to seven days. The exposure days were kept constant to ensure that the results compared were obtained within similar periods. Sampling was duplicated at a chosen site for quality assurance purposes. The facilities and the number of samples taken are indicated in Table 3.2. The passive samplers were analysed for

the BTEX average concentrations at a chosen laboratory, section 3.3.2. outlines the analysis.



Figure 3.3: Radiello Passive samplers on the mounted support plate placed inside a mountable shelter on site.

Table 3.3: The number of samples collected per fuel depot

Name of fuel depot	Number of passive samplers per site	Sampling Periods	Total samples collected
Alberton	4	4	16
Rocky's Drift	4	4	16
Port Elizabeth	4	4	16
Witbank	4	4	16
Island View	4	4	16
Ladysmith	4	2	8
Kroonstad Site 1	3	4	12
Kroonstad Site 2	3	4	12
Kimberley	3	2	6

As indicated in Table 3.2, the Kroonstad site is divided into two sites. The two sites have minimum operations as compared to the other depots. The Kimberley site was undergoing a closure process therefore not all tanks and areas were operating. Due to the differences in operations, the Kroonstad site 1 and 2 together with the Kimberley site were monitored with three passive samplers each site.

3.3.2. Data Analysis

a) BTEX Concentration Data

After the radiello monitors had stayed on site for the required period they were collected and placed inside sampling tubes then sent to the laboratory for analysis. Chemtech Laboratory services in Pretoria were used for analysis, the laboratory is SANAS accredited according to ISO guide 17025. At the laboratory the cartridges were removed from the sampling tube as VOCs were trapped by adsorption. The VOCs were recovered by carbon disulphide displacement and the analysis was done through an FID gas chromatograph in the laboratory. BTEX loading was performed by injecting precisely known amounts of vaporized standard solution in carbon disulphide of the five compounds under nitrogen flow. The mixture was then kept at 4°C and cartridges were stabilised for analysis with FID gas chromatograph.

After analysis at the laboratory, the concentrations of the different compounds i.e. benzene, toluene, ethylbenzene, and xylenes were reported in $\mu\text{g}/\text{m}^3$. Data collected through the radiello passive samplers was used to calculate the average BTEX and T/B ratios. The samplers reported BTEX concentration as a time weighted average therefore to establish the averages the sampling period will be considered. Data from different seasons was compared to establish the seasonal variations. As discussed in the literature review the dispersion of BTEX concentrations is dependent on climatic parameters therefore concentrations from different season will be related to the prevailing climatic conditions.

b) Statistical Analysis

The SPSS software was used for statistical analysis. The average and standard deviation for the BTEX emissions were then determined. The BTEX concentration ratios were calculated to compare the BTEX pollutant sources among the different fuel depots. As indicated in the site description, the fuel depots are located in urban mixed use area and also industrial therefore it was important that the concentration ratios were compared. The interspecies ratios were also determined to estimate the pollution sources and the air photochemical reactivity which is based on the assumption that BTEX pollutants have different degradation rates in the air (Lovino *et al.*, 2009; Jaars *et al.*, 2012). The ratio between toluene and benzene (T/B) was calculated as this ratio is a good indicator of the source of pollutant, indicating whether it is a point source or a mobile source as indicated in Table 3.3 (Monod *et al.*, 2001; Singh *et al.*, 2016). The ratio values can be interpreted as follows: ratio value of one indicates fresh emission originating from traffic, values between 2 and 3 indicate mobile sources and higher ratio values indicate point sources (Monod *et al.*, 2001; Jaars *et al.*, 2012).

Table 3.4: T/B ratios and the various sources they indicate (Monod *et al.*, 2001; Jaars *et al.*, 2012).

T/B Ratio	Source
1	Fresh emission originating from traffic
2-3	Mobile sources
3-4	Mobile and evaporative sources
>4	Industrial facilities and / point sources

As discussed in the literature review the T/B ratios can be used to understand the sources of BTEX pollutants and persistency in ratios in different locations usually indicates that the pollutants have similar sources.

c) Weather Data

As noted in the literature review, ambient weather conditions have an influence in the variation of BTEX concentrations in the atmosphere therefore measuring weather

conditions through the monitoring programme was essential. The climatic database from South African Weather Services was used to acquire the following data: cloud cover, upper air temperature, pressure, relative humidity, precipitation, wind speed and direction. Weather stations were identified close to each fuel depot for collection of the climate data on a daily basis. Wind conditions were useful to identify the sources of measured BTEX concentrations, wind rose plots were used to illustrate the wind frequency statistics. The wind data: speed, direction and frequency was compiled in an excel spreadsheet to generate wind roses. WRPLOT freeware was used to create the wind roses (Lakes Environmental). The wind roses were used to account for the influence of wind speed and direction on the dispersion of the BTEX concentrations.

3.4. Limitations

The limitations to the project were related to the cost, time and feasibility of sampling involved in the study. There was limited time to conduct sampling. This implies that the seasonal variations with regards to BTEX were only observed for a year and data from previous monitoring programme was utilised where possible. The location of the fuel depots in different provinces also posed a limitation as the depots could not be visited often i.e. monthly, due to travelling costs and time. The BTEX concentrations were therefore monitored quarterly and no temporal variations in the concentrations were assessed. The study does not provide correlation coefficients between the concentrations and climatic conditions as the sampling period for radiello samplers differed from the times at which climatic conditions were recorded. The seasonal variations were determined as sampling was conducted in different seasons. The design and techniques also posed some limitations to the study as only passive samplers were used to measure BTEX concentrations. The use of passive together with active monitors is more advantageous as the concentrations obtained from the different methods can be compared. In this study the design was limited to passive samplers with the consideration of costs and easy access. The study focuses mainly on fuel depots therefore it may not provide in-depth relationships of BTEX ratio related to other sources.

4. Results

The results of the synoptic circulation, climatic conditions over the study site and BTEX concentrations are presented in this chapter. The regional and local climatic conditions play a vital role in the emission, transportation, dilution, chemical transformation and deposition of air pollutants in the atmosphere. Therefore, it is important to understand the circulation and climatic conditions over the study area (Kinney, 2008). The recorded BTEX concentrations and the BTEX ratios that were determined to ascertain the source of pollution within the depots. The study was conducted in fuel depots in Alberton (ALB), Witbank (WIT), Kroonstad (KST), Rocky's Drift (RCD), Island View (IV), Port Elizabeth (PE), Kimberley (KMB) and Ladysmith (LDS).

4.1. Field Observations

As highlighted in the methodology chapter, the sites were located in industrial and urban mixed-use areas. The sites found within industrial areas were Rocky's Drift, Island View and Port Elizabeth while the Alberton, Witbank, Kroonstad, Ladysmith and Kimberley depots were with urban mixed-use areas. Rocky's drift site was located close to agricultural spanning and manufacturing plants such as brick farm, Timbercity, Nieuwco, Oasis water, granite designs, Breet construction, Secured storage and Bird machines (Figure 4.1).



Figure 4.1: The Rocky's Drift site with surrounding facilities and labels indicating sampling points.

The Island View site was surrounded by petrochemical storage facilities (Petrosa, Sapref and Total), Fynnlads Refineries and the Durban harbour (Figure 4.2.)



Figure 4.2: The Island View depot (highlighted in pink) and labels indicating the sampling points.

The Shell Port Elizabeth depot is located in a mixed-use industrial area in the Eastern Cape Province. The depot is surrounded by unused storage tanks, coal deposits, railway, the harbour and Humewood residential suburb.



Figure 4.3: Port Elizabeth Depot with its surrounding facilities and labels indicating the sampling points.

The Alberton site was next to the suburb of General Alberts Park, to the east of the site was the Foresta Timber and Boards factory. On the southern side was the Duro processing plant and the suburb of Randhart to the west (Figure 4.4).



Figure 4.4: The Alberton depot (highlighted in pink) and labels indicating the sampling points. The Witbank site was surrounded by factories such as Samancor, Scew metals groups, Glencore alloys, suburb of Ferrobank and coal fields around the site (Figure 4.5).



Figure 4.5: Witbank Depot with its surroundings and labels indicating the sampling points.

Kroonstad site was divided into two sites which were separated by a road. The two sites were surrounded by BP and TotalSA Depots, Barend Wessel dam, agricultural holdings, residential areas of Panorama, Suidrand and a train station (Figure 4.6).



Figure 4.6: Kroonstad site 1 and site 2 with label indicating the sampling locations for both sites.

In Kimberley, the site was situated in close proximity of Fabricia industrial area, BJ Vorster airport, Pavillion mall and Monument heights residential area. There was also a main road from the mall leading to airport which passed close to the Kimberley site (Figure 4.7).



Figure 4.7: Kimberley depot with surrounding facilities and labels indicating the sampling points.

The Ladysmith depot (highlighted in pink) was surrounded by an unknown depot, a residential suburb, rail tracks used by freight trains, Malibu palms residential area and the Ladysmith country club (Figure 4.8).



Figure 4.8: Ladysmith depot with its surrounding sites and labels indicating the sampling points.

4.2. BTEX Concentrations

4.2.1. Benzene and Toluene

The concentrations for the Alberton, Witbank, Kroonstad site 1 and 2, Rocky's Drift, Port Elizabeth, Kimberley and Ladysmith sites were recorded and compared for the October 2015, February 2016, June 2016, October 2016, January 2017, April 2017, July 2017, October 2017 and January 2018 sampling periods at all monitoring sites.

4.2.1.1. Alberton

The concentrations of toluene were higher than those of benzene for the majority of the sampling periods over the different sampling points at the Alberton site as presented in Table 4.1. The toluene concentrations ranged between 4.34 $\mu\text{g}/\text{m}^3$ and 285.39 $\mu\text{g}/\text{m}^3$ while those of benzene were between 2.62 $\mu\text{g}/\text{m}^3$ and 144.24 $\mu\text{g}/\text{m}^3$. During the October 2016 sampling period the highest concentrations of both toluene and benzene were measured at sampling point ALB-1, the concentrations were extremely high as compared to the other concentrations for all the sampling periods (Figure 4.9). The lowest concentrations of toluene and benzene were recorded at sampling point ALB-4 in January 2017.

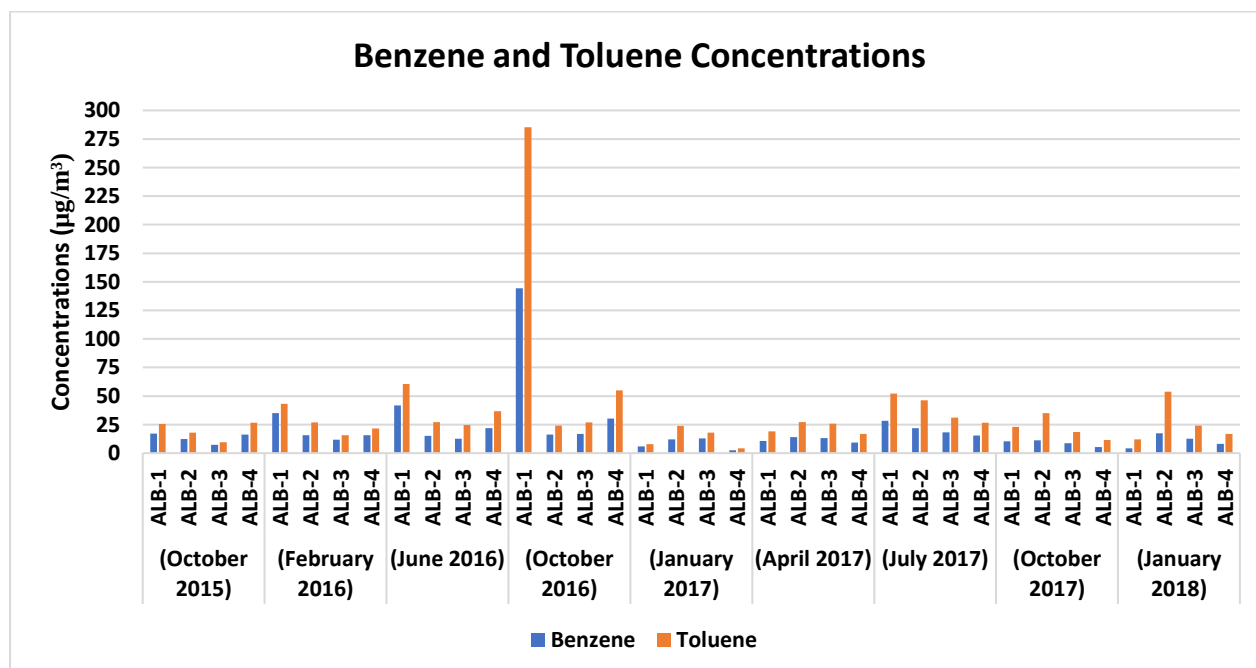


Figure 4.9: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Alberton depot during 9 sampling campaigns.

4.2.1.2. Witbank

The concentrations of toluene were lower than benzene at most of the sampling points during the monitoring periods as indicated in Table 4.2. The benzene concentrations were higher than toluene during the October 2015, June 2016, July 2017, October 2017 and January 2018 sampling periods. In February 2016, toluene was higher than benzene at sampling point WIT-2. The concentrations of benzene ranged between 1.83 $\mu\text{g}/\text{m}^3$ and 55.59 $\mu\text{g}/\text{m}^3$ while those for toluene were between 2.25 $\mu\text{g}/\text{m}^3$ and 46.51 $\mu\text{g}/\text{m}^3$. The sampling point WIT-4 had higher concentrations for both benzene and toluene in October 2015, February 2016, June 2016 and October 2016 as illustrated in Figure 4.10. The highest concentrations of benzene and toluene were recorded in October 2016.

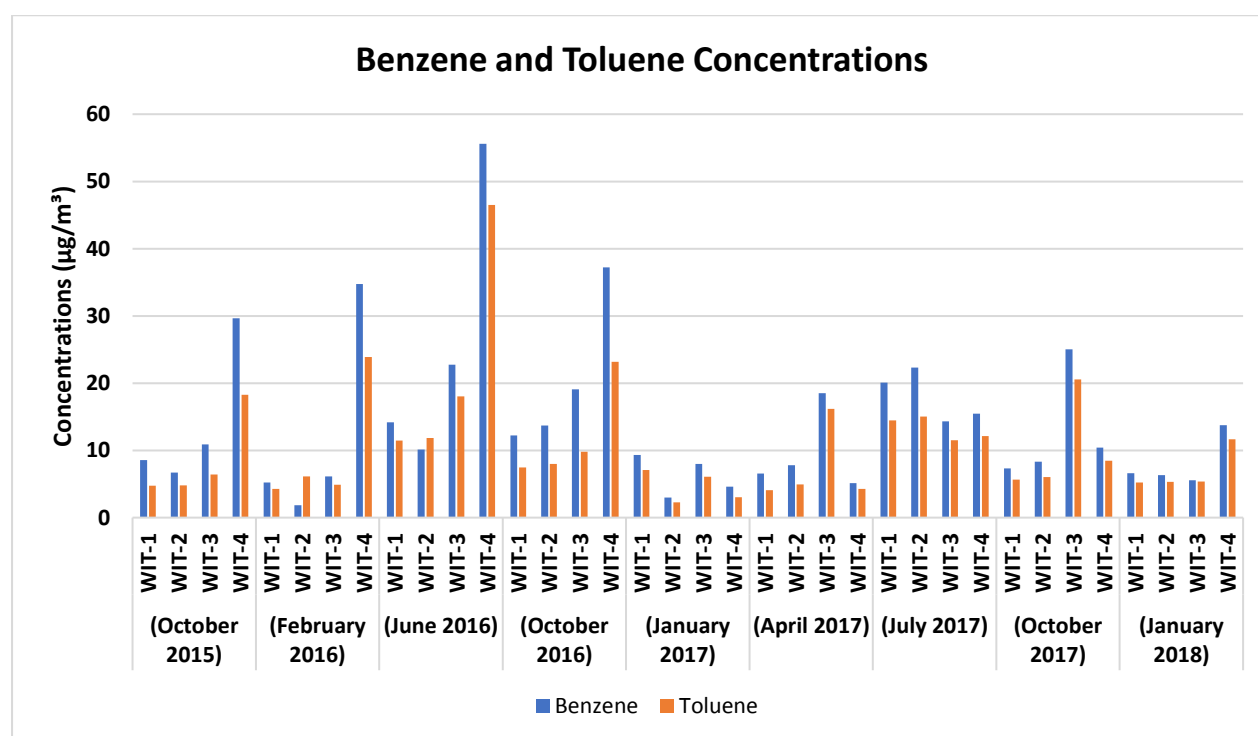


Figure 4.10: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Witbank depot during 9 sampling campaigns.

4.2.1.3. Kroonstad Site 1

The benzene and toluene concentrations measured at Kroonstad Site 1 on the different sampling periods showed a variation as presented in Table 4.3. During the October 2015 and January 2018 sampling period, the toluene concentrations were higher than those recorded throughout the other sampling periods at Kroonstad site 1. The toluene levels were more elevated than the benzene concentrations at majority of sampling points throughout the sampling periods as illustrated in Figure 4.11. The highest concentration of toluene was $19.42 \mu\text{g}/\text{m}^3$ which was measured in October 2015 while the lowest concentration was $4.33 \mu\text{g}/\text{m}^3$ which was also recorded in October 2016. The highest concentration of benzene was $11.88 \mu\text{g}/\text{m}^3$ recorded while the lowest concentration was $3.49 \mu\text{g}/\text{m}^3$ recorded in October 2015 and October 2016 respectively.

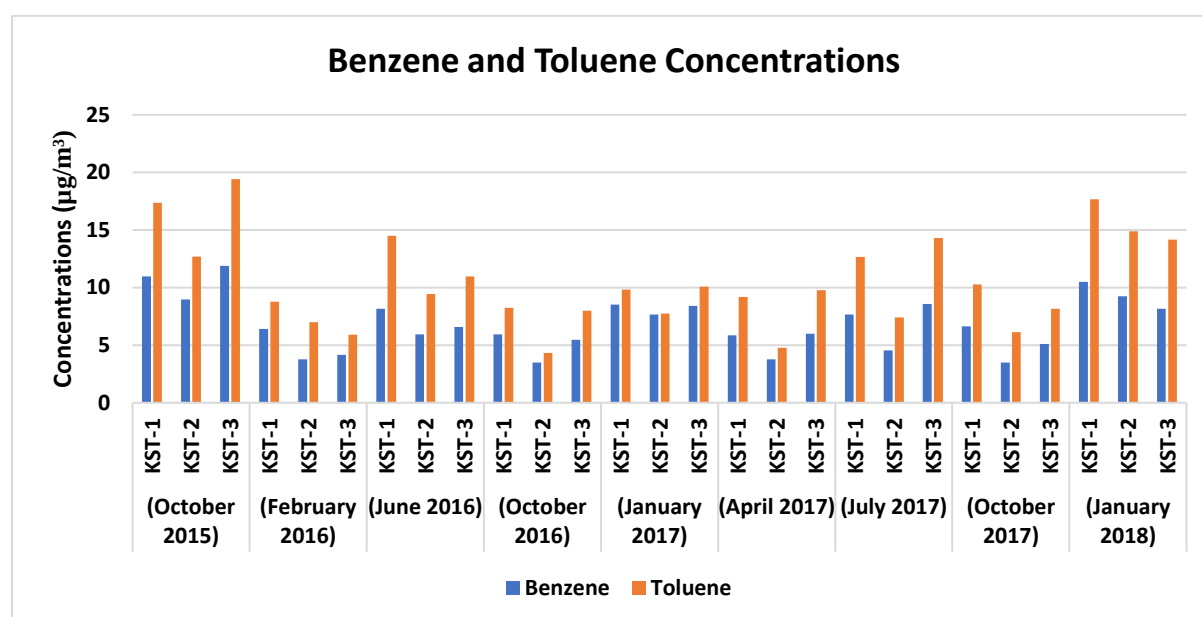


Figure 4.11: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kroonstad Site 1 during 9 sampling campaigns.

4.2.1.4. Kroonstad Site 2

The toluene concentrations ranged between $3.27 \mu\text{g}/\text{m}^3$ and $10.5 \mu\text{g}/\text{m}^3$ while those of benzene were between $1.78 \mu\text{g}/\text{m}^3$ and $6.42 \mu\text{g}/\text{m}^3$ as presented in Table 4.4. The highest concentration of toluene was recorded during the February 2016 sampling period while the lowest concentration of toluene was recorded in April 2017. The highest and lowest concentrations of benzene were measured in January 2017 and

February 2016 respectively. The results for benzene and toluene recorded at the various sampling points at the Kroonstad Site 2 showed that the toluene concentrations were slightly higher than the measured benzene concentrations except in January 2017 at sampling point KST-6 as illustrated in Figure 4.12. In February 2016, June 2016 and July 2017, the toluene concentrations were significantly higher compared to benzene at sampling points KST-5 and KST-6.

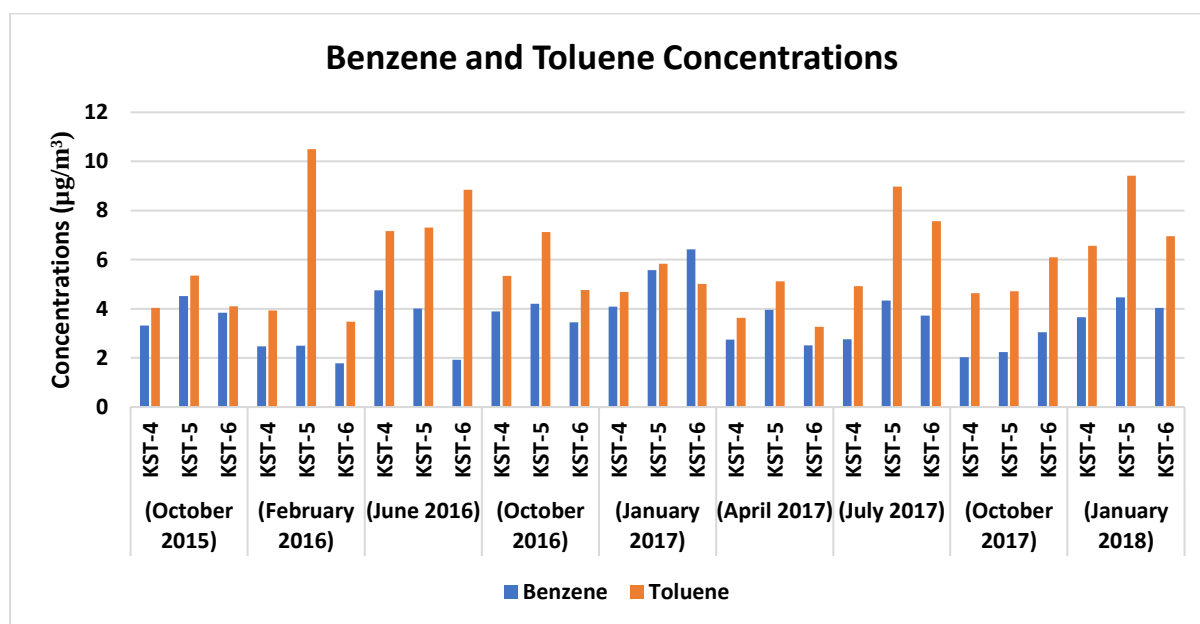


Figure 4.12: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kroonstad Site 2 during 9 sampling campaigns.

4.2.1.5. Rocky's Drift

The recorded concentrations of toluene and benzene showed a variation over the various sampling periods with toluene being the most abundant for the majority of the sampling points as indicated in Table 4.5. The lowest concentration of toluene was $0.54 \mu\text{g}/\text{m}^3$ recorded in April 2017 while the highest concentration was $24.40 \mu\text{g}/\text{m}^3$ which was recorded in July 2017. The benzene concentrations ranged between $0.50 \mu\text{g}/\text{m}^3$ and $9.59 \mu\text{g}/\text{m}^3$, the lowest concentration measured in April 2017 and the highest concentration measured in July 2017. The sampling point RCD-2 recorded toluene concentrations that were higher than other sampling points throughout all the sampling periods as shown in Figure 4.13. In April 2017, the

sampling point RCD-1 recorded low concentrations with a very slight difference between the toluene and benzene concentrations.

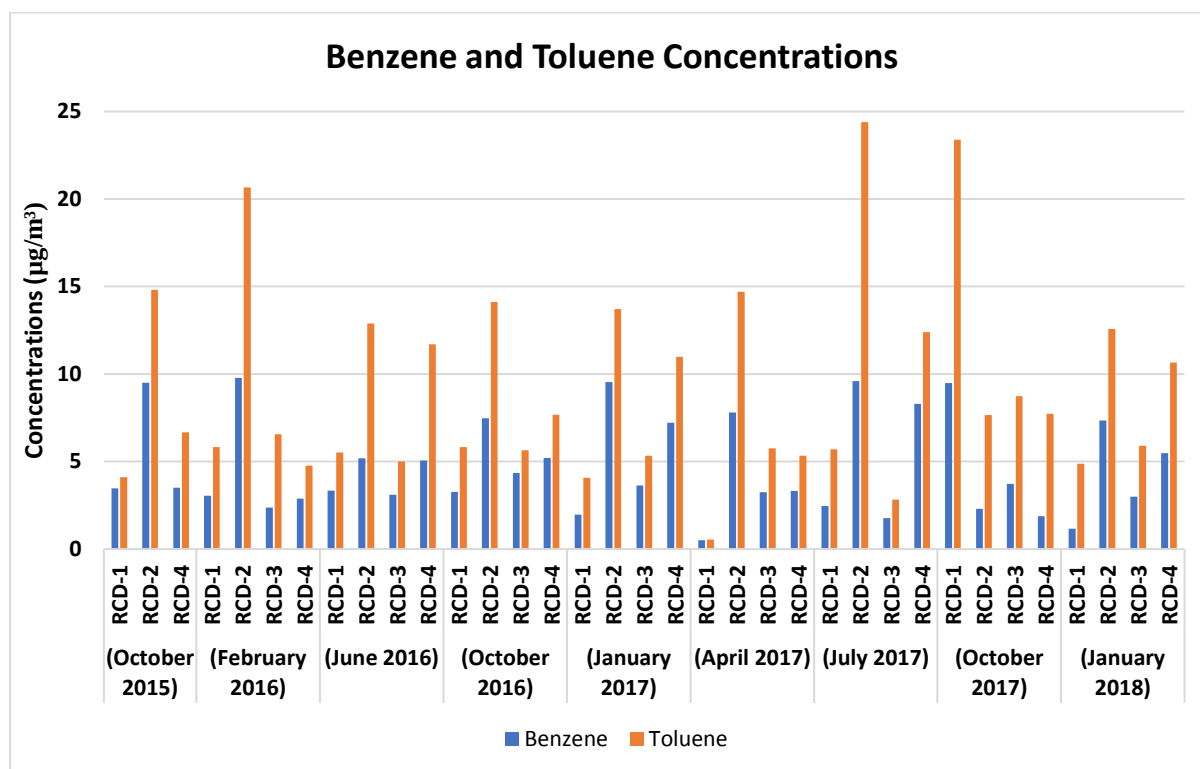


Figure 4.13: Benzene and Toluene Concentrations (One week average in µg/m³) at the Rocky's Drift depot during 9 sampling campaigns.

4.2.1.6. Island View

The recorded toluene concentrations were higher in October 2017, February 2016 and July 2017 while they were lowest in June 2016 as indicated in Table 4.6. The concentration of toluene ranged between 3.16 µg/m³ and 118.29 µg/m³. The highest concentration of benzene was 73.80 µg/m³ recorded in October 2017 while the lowest concentration was 2.6 µg/m³ recorded in June 2016. The toluene concentrations were higher than those of benzene for the majority of the sampling periods across the majority of points except at sampling point IV-4 in February 2016 (Figure 4.14). The sampling point IV-4 had lower concentrations for both benzene and toluene as compared to the other sampling points in October 2015, February 2016, June 2016, January 2017 and April 2017.

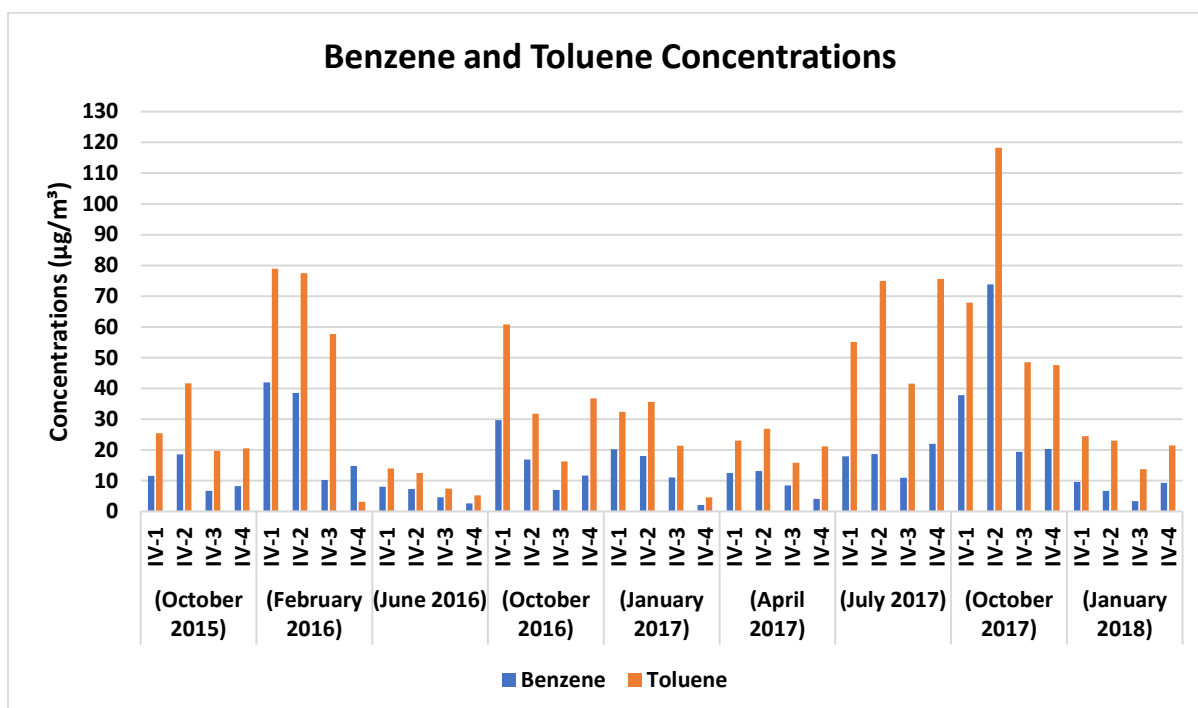


Figure 4.14: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Island View depot during 9 sampling campaigns.

4.2.1.7. Port Elizabeth

Similar to the trend from other sites, the toluene concentrations were high in comparison to those of benzene for all the sampling periods at the Port Elizabeth depot (Table 4.7). The concentrations of toluene were ranging between $3.14 \mu\text{g}/\text{m}^3$ and $110.89 \mu\text{g}/\text{m}^3$, with the lowest concentration measured in April 2017 and the highest concentration measured in June 2016. The highest concentration of benzene was $18.57 \mu\text{g}/\text{m}^3$ measured in July 2017 while the lowest concentration of benzene was $1.3 \mu\text{g}/\text{m}^3$ recorded in April 2017. In June 2016, the toluene concentrations were more elevated at all sampling points particularly PE-2. Figure 4.15 shows that the toluene concentrations were low for most sampling points while PE-2, PE-3 and PE-4 had higher concentrations in June 2016. Generally, the concentrations of benzene and toluene were below 10 for most sampling points with a few points that had elevated concentrations in October 2015, June 2016 and July 2017.

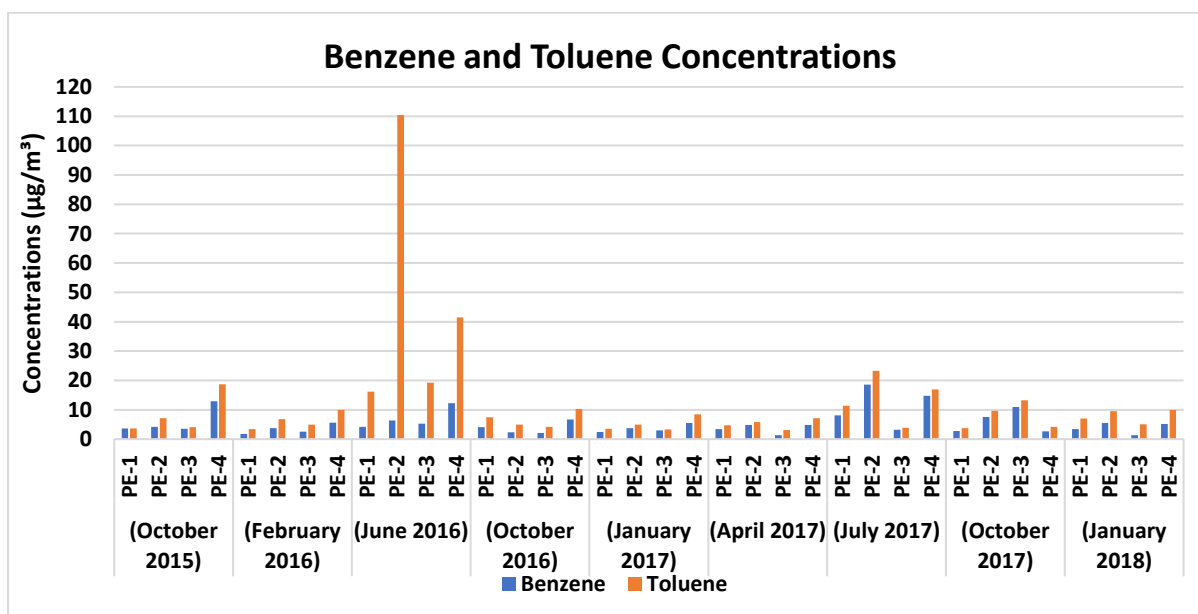


Figure 4.15: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Port Elizabeth depot during 9 sampling campaigns.

4.2.1.8. Kimberley

The toluene concentrations were higher than those of benzene for the most of sampling points during the various sampling periods except in October 2015 and January 2017 (Table 4.8). At the Kimberley site, the toluene concentrations were highest in February 2016 and July 2017 while they were lowest in January 2017. The concentrations of toluene were ranging between $0.78 \mu\text{g}/\text{m}^3$ and $4.50 \mu\text{g}/\text{m}^3$. The highest concentration of benzene was $4.03 \mu\text{g}/\text{m}^3$ recorded in January 2017 while the lowest concentration was $0.58 \mu\text{g}/\text{m}^3$ also recorded in January 2017. The sampling points KMB-1 and KMB-3 recorded benzene concentrations that were higher than those of toluene during the October 2015 and January 2017 sampling period (Figure 4.16). In July 2017, sampling points KMB-1, KMB-2 and KMB-3 had elevated concentrations for both toluene and benzene in comparison to the concentrations measured throughout the other sampling periods.

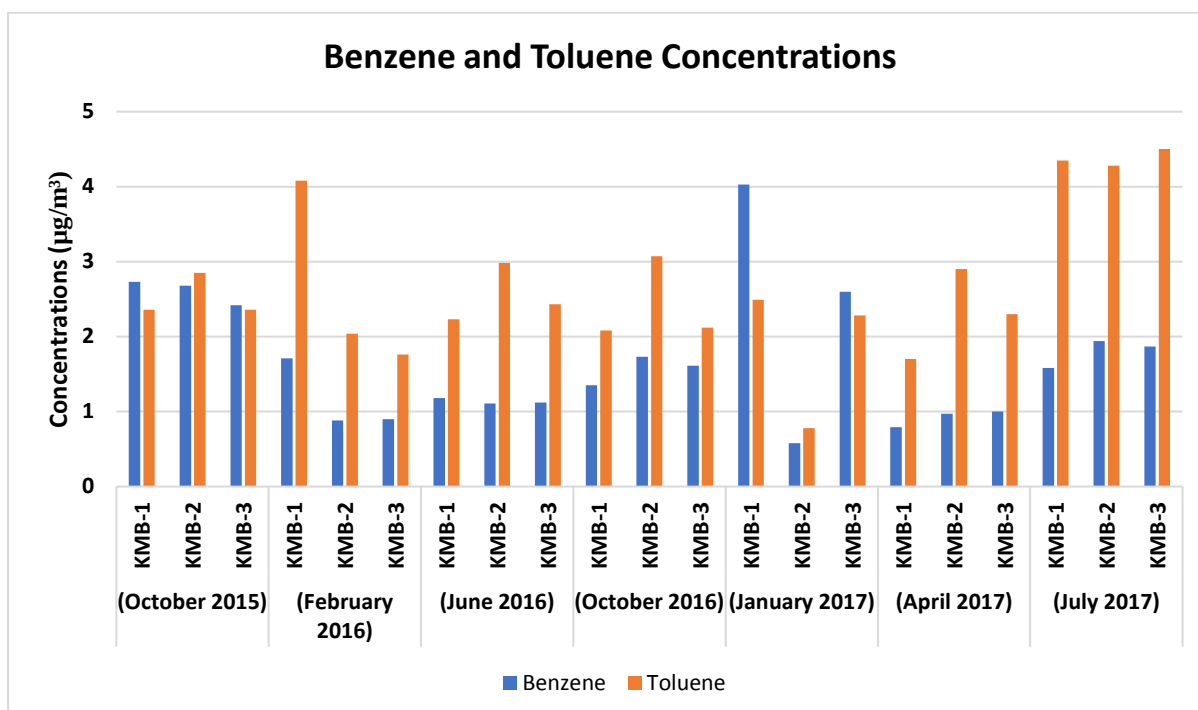


Figure 4.16: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kimberley depot during 7 sampling campaigns.

4.2.1.9. Ladysmith

The concentration of toluene was higher than that of benzene for the majority of the sampling periods over the different sampling points (Table 4.9). The toluene concentrations were ranging between $2.11 \mu\text{g}/\text{m}^3$ and $146.28 \mu\text{g}/\text{m}^3$ while those of benzene were between $1.23 \mu\text{g}/\text{m}^3$ and $85.15 \mu\text{g}/\text{m}^3$. The concentrations of toluene and benzene measured at the Ladysmith site throughout all the sampling periods are presented in Figure 4.17. During the June 2016 sampling period, the toluene and benzene concentrations were anomalously high for all the sampling points. The lowest concentrations of toluene and benzene were recorded at sampling point LDS-1 in April 2017.

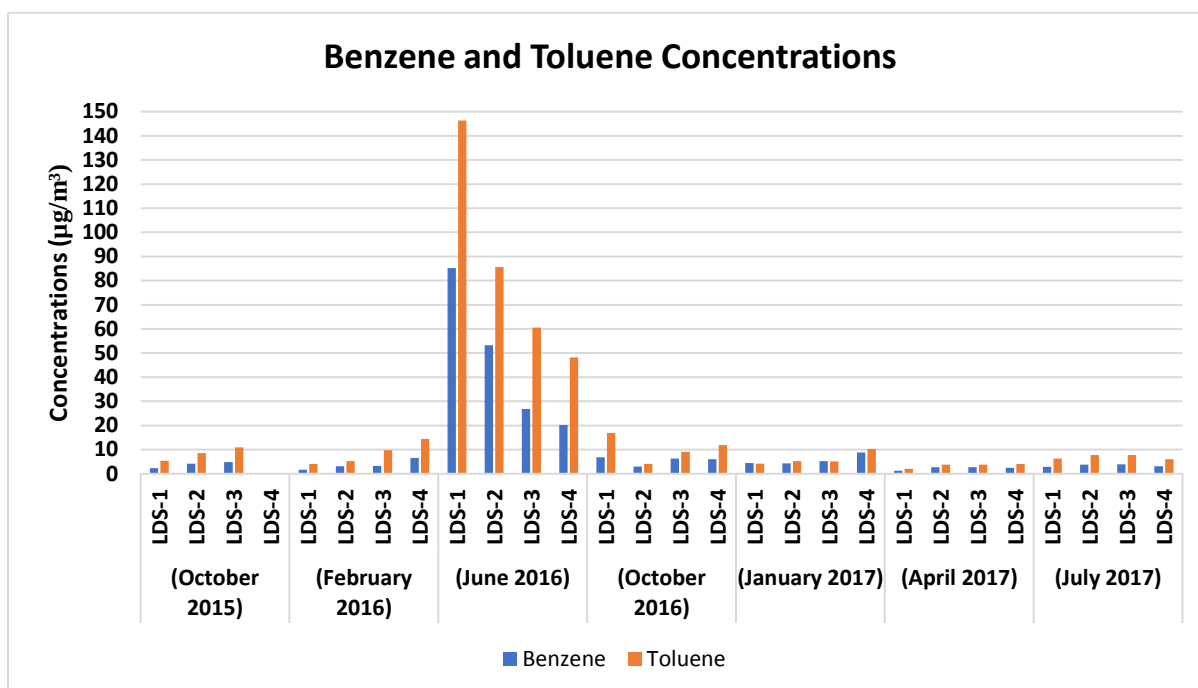


Figure 4.17: Benzene and Toluene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Ladysmith depot during 9 sampling campaigns.

The majority of sites showed a similar trend with regards to the concentrations of toluene and benzene except Witbank which had benzene concentrations which were higher than toluene throughout the different sampling periods. The toluene concentration was highest during the October 2016 sampling period followed by June 2016, February 2016, October 2015, January and April 2017. The climatic conditions and site operations during the sampling period may be responsible for the variations in the recorded concentrations. The benzene levels were highest during the October 2016 sampling period followed by June 2016, February 2016, October 2015, January and April 2017. Literature revealed that high concentrations of toluene have been observed compared to other VOCs in various studies (Lai et al., 2013).

4.2.2. Ethyl-benzene and Xylene

4.2.2.1. Alberton

The concentrations of xylene were higher than those of ethyl-benzene for majority of monitored sampling points throughout most sampling periods except in July 2017 and October 2017 (Table 4.10 and Figure 4.18). The concentrations of xylene were ranging between $2.11 \mu\text{g}/\text{m}^3$ and $179.97 \mu\text{g}/\text{m}^3$ while the ethylbenzene

concentrations ranged between 1 $\mu\text{g}/\text{m}^3$ and 53.87 $\mu\text{g}/\text{m}^3$. The high xylene concentration was measured in October 2016 while the lowest was measured in July 2017. The highest concentration of ethyl-benzene was measured in October 2017 while the lowest was measured in January 2017. In October 2016, sampling point ALB-1 had an exceptionally high xylene concentration in comparison to all the sampling points. In July 2017 and October 2017, the concentrations of ethylbenzene were higher than those of benzene at all sampling points in Alberton, which was different from the trend observed throughout the other sampling periods.

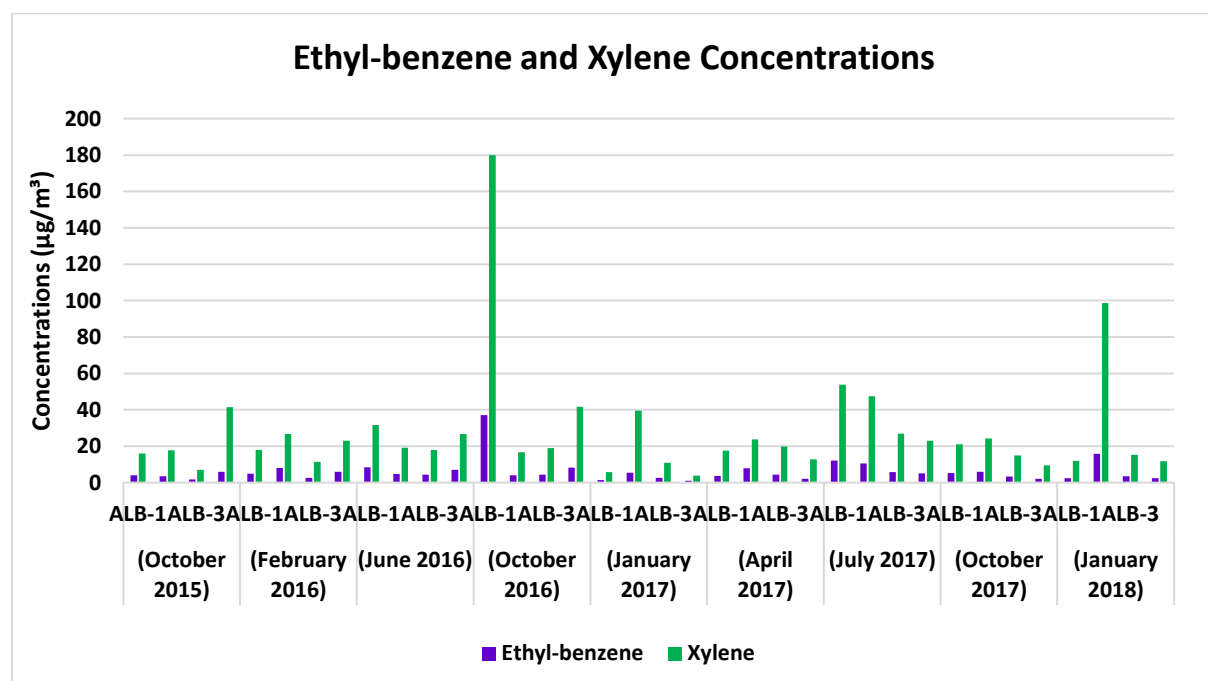


Figure 4.18: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Alberton depot during 9 sampling campaigns.

4.2.2.2. Witbank

The xylene concentrations were higher compared to those of ethyl-benzene at the majority of the sampling periods except in January 2017 (Table 4.11). The concentrations of xylene were ranging between 0.83 $\mu\text{g}/\text{m}^3$ and 24.11 $\mu\text{g}/\text{m}^3$ while the ethylbenzene concentrations ranged between 0.73 $\mu\text{g}/\text{m}^3$ and 7.06 $\mu\text{g}/\text{m}^3$. In January 2017, the concentration of ethylbenzene was higher than that of xylene at the sampling points WIT-2 and WIT-4 which differed from the trend observed at other sampling points during the same period as indicated in Figure 4.19. In June 2016,

the concentrations of xylene were significantly higher in comparison to the concentrations recorded during the other sampling periods.

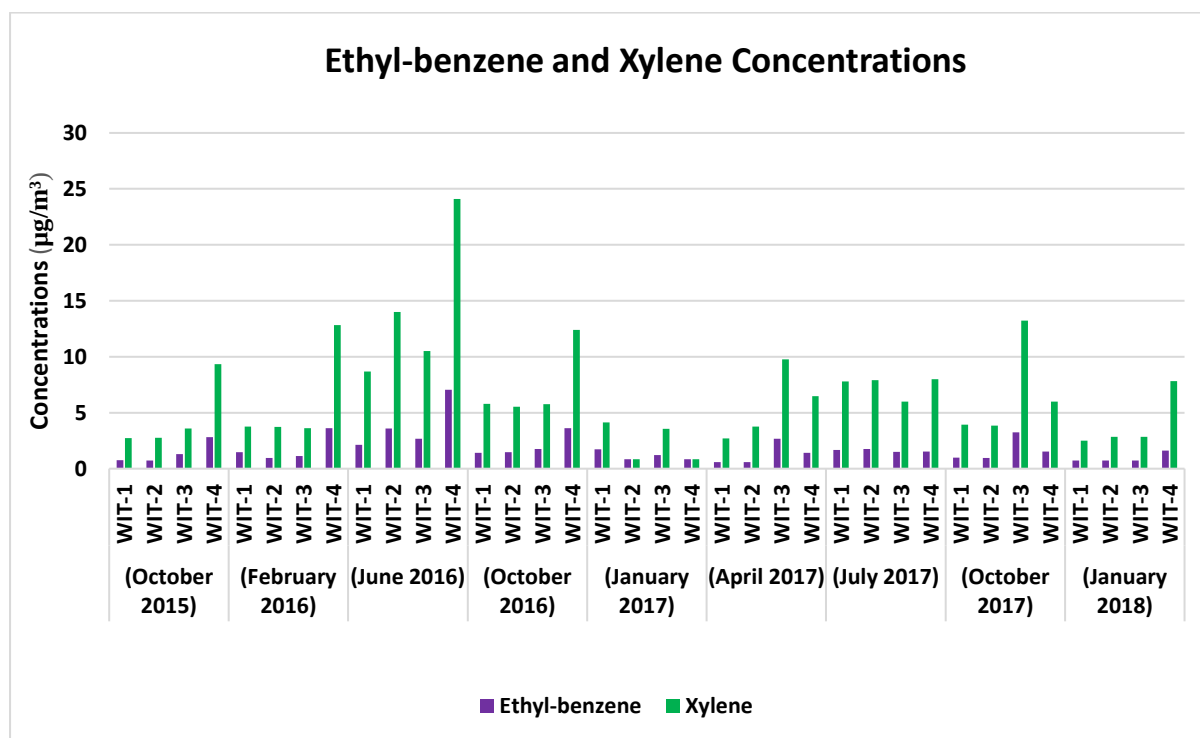


Figure 4.19: Ethyl-benzene and Xylene Concentrations (One week average in µg/m³) at the Witbank depot during 9 sampling campaigns.

4.2.2.3. Kroonstad Site 1

The concentrations for xylene were higher than the concentrations of ethyl-benzene for all the monitored sampling points during all the sampling periods (Table 4.12 and Figure 4.20). The highest concentration of xylene was 15.47 µg/m³ measured in February 2016 while the lowest concentration was 1.97 µg/m³ measured in October 2016. The concentrations of ethyl-benzene were ranging between 0.73 µg/m³ and 2.88 µg/m³, with the lowest concentration measured in February 2016 and the highest concentration in October 2015.

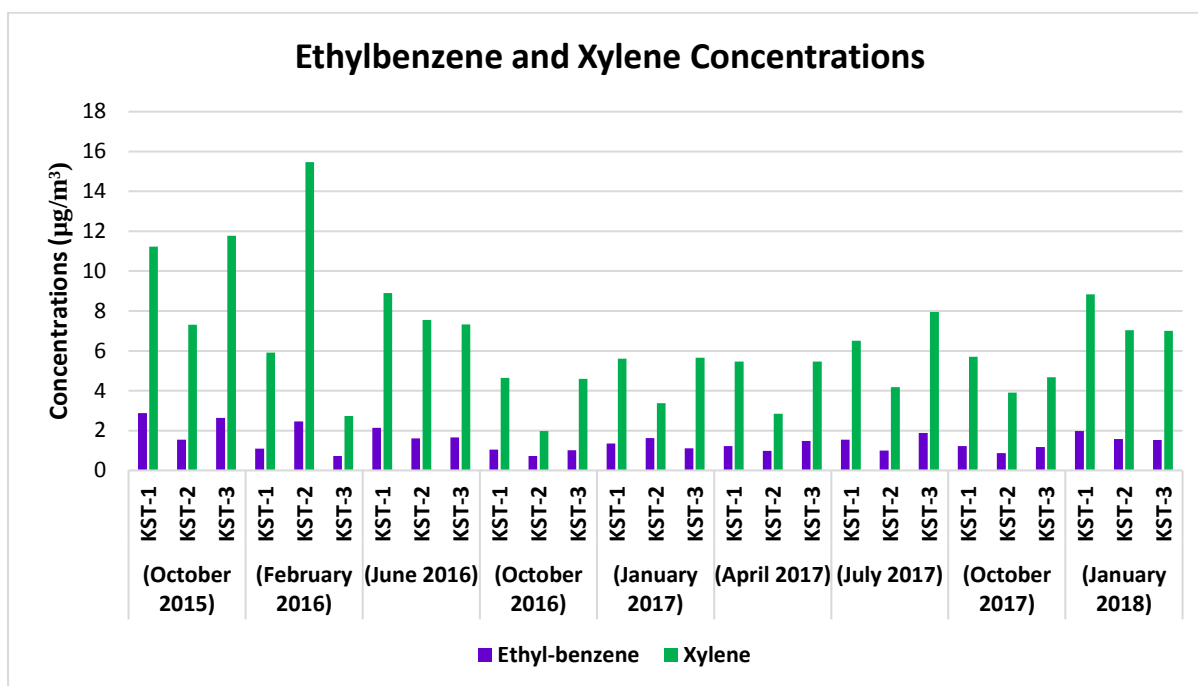


Figure 4.20: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kroonstad Site 1 during 9 sampling campaigns.

4.2.2.4. Kroonstad Site 2

At Kroonstad site 2, the recorded xylene concentrations were slightly higher than those of ethyl-benzene throughout the various sampling periods (Table 4.13). The xylene and ethyl-benzene concentrations recorded at Kroonstad site 2 during all the sampling periods are represented in Figure 4.21. The xylene concentrations were ranging between $0.57 \mu\text{g}/\text{m}^3$ and $14.02 \mu\text{g}/\text{m}^3$ while those of ethyl-benzene were between $0.1 \mu\text{g}/\text{m}^3$ and $3.07 \mu\text{g}/\text{m}^3$. The highest concentration of xylene was recorded during the October 2015 sampling period while the lowest concentration was recorded in April 2017. The highest and lowest concentrations of ethyl-benzene were measured in July 2017 and October 2015 respectively.

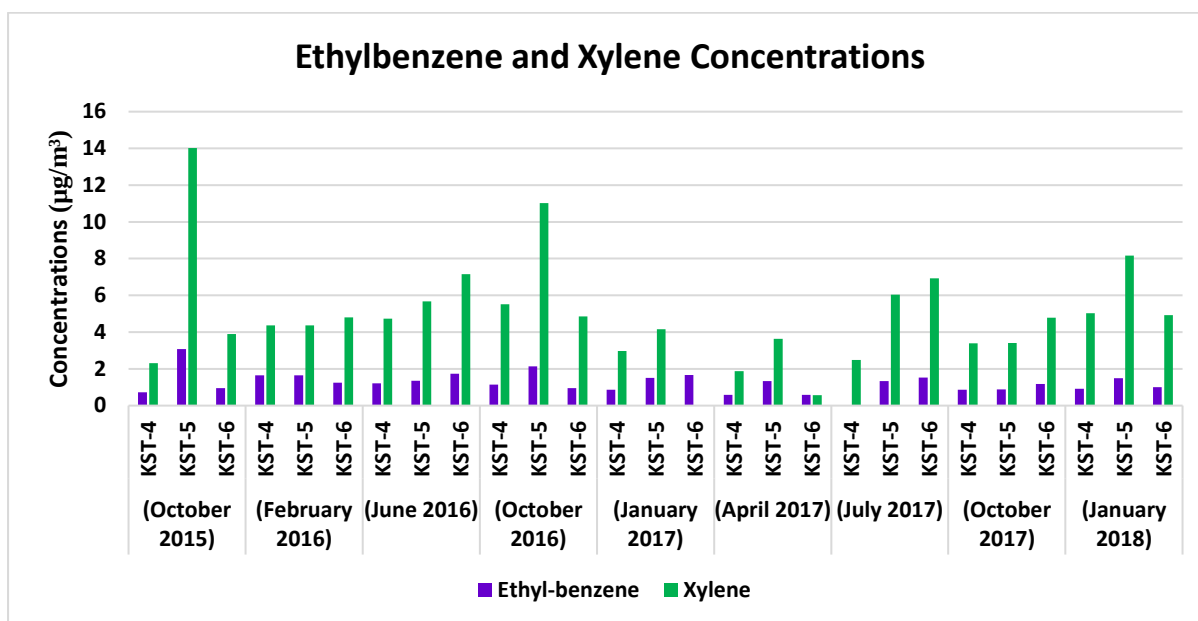


Figure 4.21: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kroonstad Site 2 during 9 sampling campaigns.

4.2.2.5. Rocky's Drift

There was a great variation with regards to the concentrations of ethyl-benzene and xylene throughout all the sampling periods at Rocky's Drift depot as illustrated in Table 4.14 and Figure 4.22. The concentrations of xylene were significantly higher compared to those of ethyl-benzene at all monitored sampling points during all the sampling periods. The highest concentration of xylene was $14.53 \mu\text{g}/\text{m}^3$ measured in October 2017 while the lowest concentration was $0.57 \mu\text{g}/\text{m}^3$ measured in April 2017. The highest concentration of ethyl-benzene was $8.95 \mu\text{g}/\text{m}^3$ measured in October 2017 while the lowest concentration was $0.73 \mu\text{g}/\text{m}^3$ measured in July 2017. In April 2017, the concentrations of ethylbenzene and xylene showed a slight difference at sampling point RCD-1. All the sampling points had elevated concentrations of xylene.

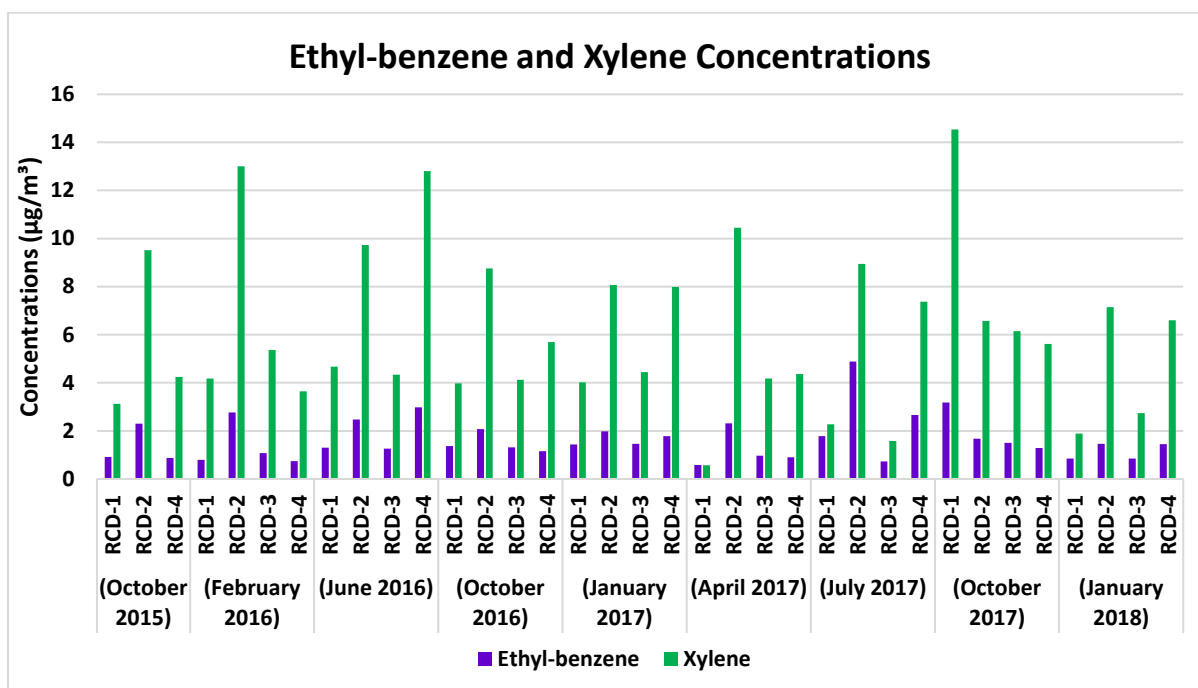


Figure 4.22: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Rocky's Drift depot during 9 sampling campaigns.

4.2.2.6. Island View

Concentrations of ethyl-benzene and xylene measured at Island View depot during the October 2015, February 2016, June 2016, October 2016, January 2017, April 2017, July 2017 and October 2017 sampling periods xylene are presented in Table 4.15 and Figure 4.23. The concentrations of xylene were higher than those of ethyl-benzene for the majority of sampling points throughout the various periods. The highest concentration of xylene recorded was $75.12 \mu\text{g}/\text{m}^3$ measured in October 2017 while the lowest concentration was $2.45 \mu\text{g}/\text{m}^3$ recorded in June 2016. The highest concentration of ethyl-benzene was $14.63 \mu\text{g}/\text{m}^3$ measured in October 2017 while the lowest concentration of ethyl-benzene measured was $0.64 \mu\text{g}/\text{m}^3$ in June 2016.

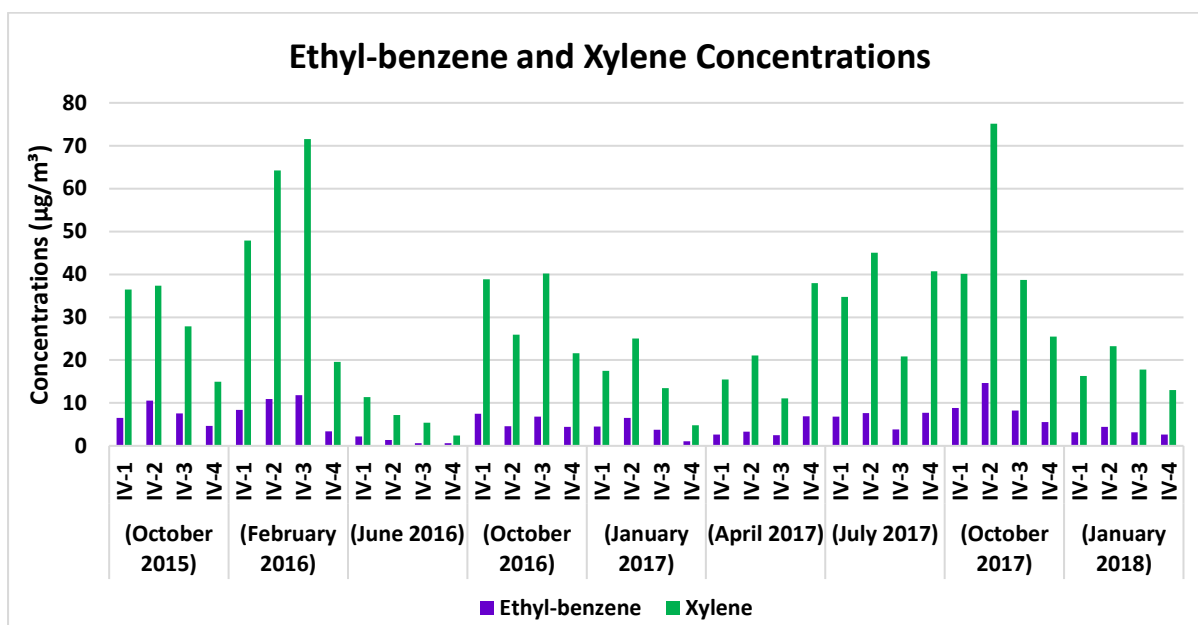


Figure 4.23: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Island View depot during 9 sampling campaigns.

4.2.2.7. Port Elizabeth

The xylene concentrations were high compared to those of ethyl-benzene during most sampling periods except in July 2017 where concentrations of ethyl-benzene were more elevated (Table 4.16). The highest concentration of ethyl-benzene was $23.64 \mu\text{g}/\text{m}^3$ measured in July 2017 while the lowest concentration was $0.57 \mu\text{g}/\text{m}^3$ which was recorded in October 2016. The highest concentration of xylene was $43.77 \mu\text{g}/\text{m}^3$ measured in June 2016 while the lowest concentration was $0.83 \mu\text{g}/\text{m}^3$ recorded in January 2017. In June 2016, the xylene concentrations were significantly higher at sampling points PE-2 and PE-4 as shown in Figure 4.24. In July 2017, the ethyl-benzene concentrations were anomalously high exceeding those of xylene at sampling points PE-2 and PE-4.

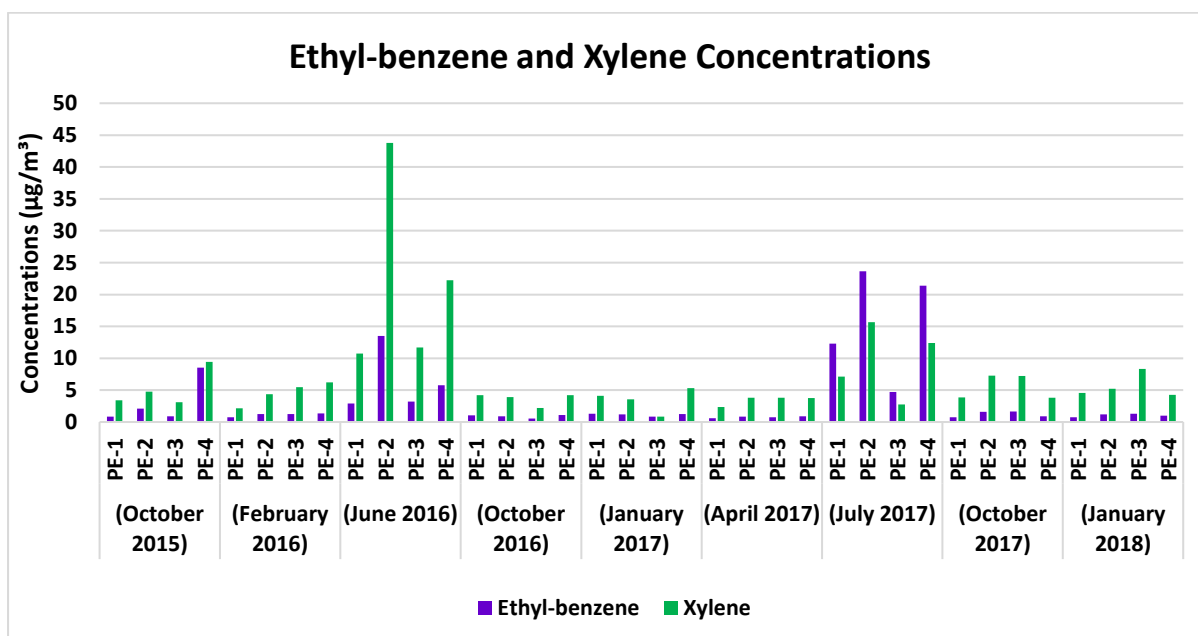


Figure 4.24: Ethyl-benzene and Xylene Concentrations (One week average in µg/m³) at the Port Elizabeth depot during 9 sampling campaigns.

4.2.2.8. Kimberley

The measured concentrations of xylene were higher than those of ethyl-benzene for the majority of the sampling points over the different sampling periods at the Kimberley site. In February 2016, January 2017, April 2017 & July 2017 a few sampling points showed a different trend wherein concentrations of ethyl-benzene were slightly higher than those of xylene (Table 4.17 and Figure 4.25). The xylene concentrations were ranging between 0.66 µg/m³ and 4.48 µg/m³ while those of ethyl-benzene were between 0.46 µg/m³ and 1.04 µg/m³. The highest concentrations of both xylene and ethyl-benzene were measured at sampling point KMB-1 during the February 2016 sampling period.

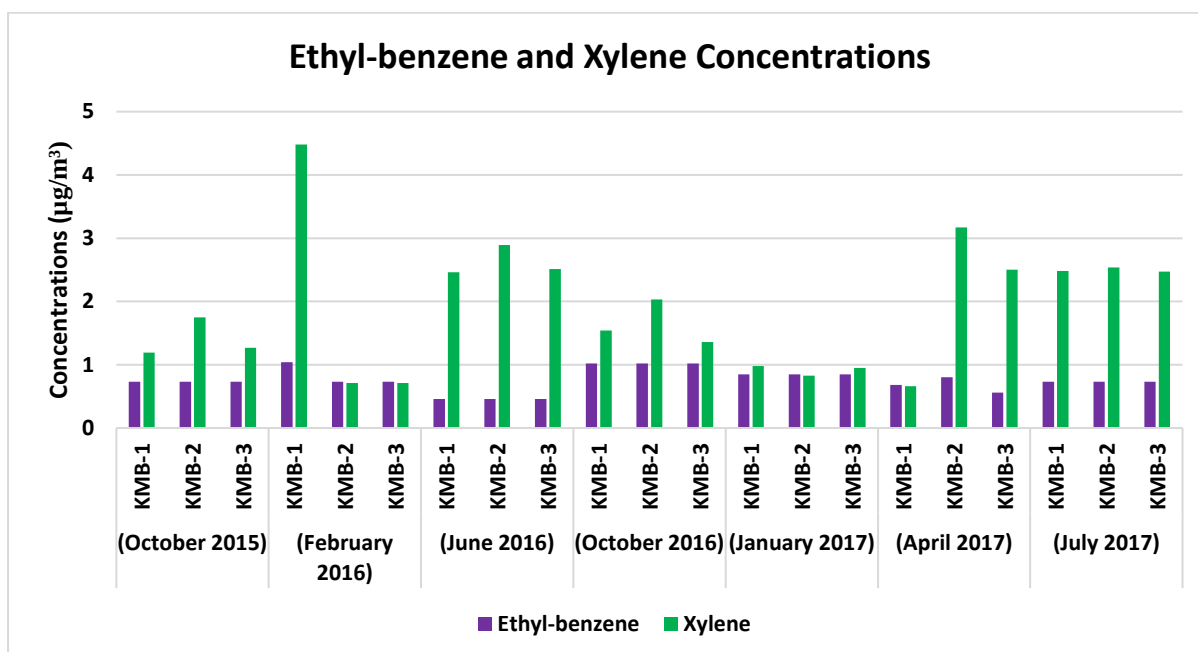


Figure 4.25: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Kimberley depot during 7 sampling campaigns.

4.2.2.9. Ladysmith

Similar to the trend from other sites, the xylene concentrations were high compared to those of ethyl-benzene for all the sampling periods at the Ladysmith depot. The concentrations of xylene were ranging between $2.4 \mu\text{g}/\text{m}^3$ and $77.14 \mu\text{g}/\text{m}^3$, with the lowest concentration measured in April 2017 and the highest concentration measured in June 2016. The highest concentration of ethyl-benzene was $16.59 \mu\text{g}/\text{m}^3$ measured in June 2016 while the lowest concentration of ethyl-benzene was $0.53 \mu\text{g}/\text{m}^3$ recorded in April 2017. In June 2016, the xylene and ethyl-benzene concentrations were more elevated at all sampling points particularly LDS-1 where the highest concentration for both was recorded. Figure 4.26 shows the xylene and ethyl-benzene concentrations measured at Ladysmith.

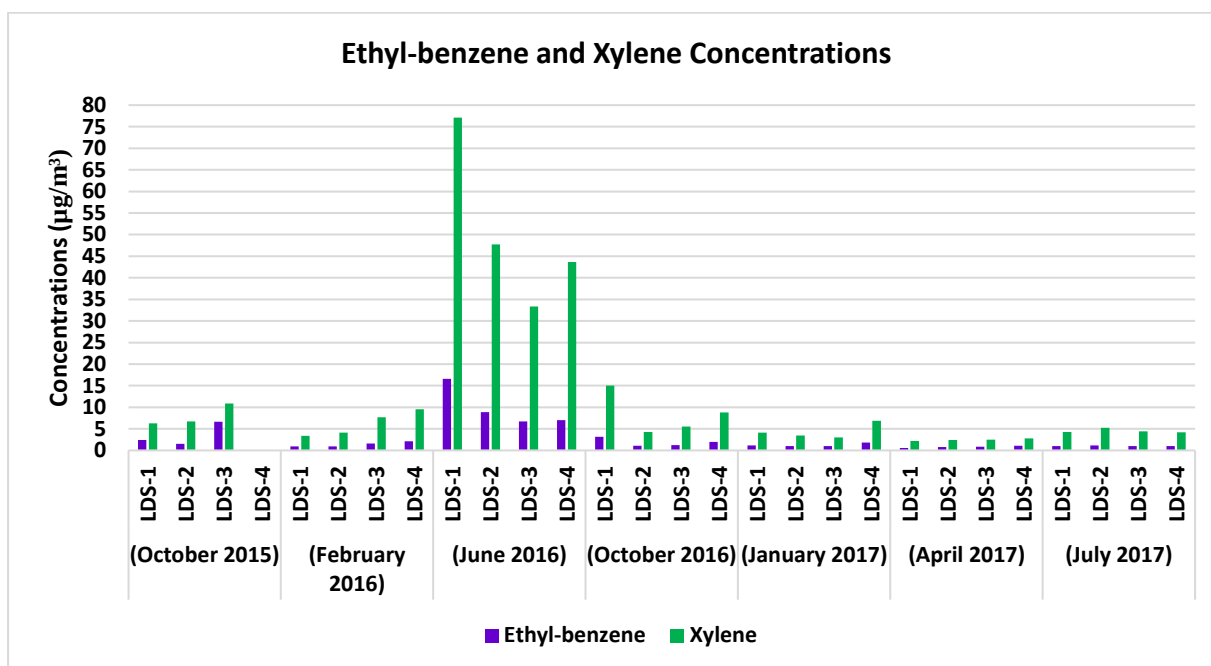


Figure 4.26: Ethyl-benzene and Xylene Concentrations (One week average in $\mu\text{g}/\text{m}^3$) at the Ladysmith depot during 7 sampling campaigns.

The observed trend with regards to the concentrations of ethyl-benzene and xylene showed that the xylene concentrations were higher than those of ethyl-benzene at the majority of sites for the different sampling periods. The ethyl-benzene concentrations were higher in October 2017 and October 2016. The xylene levels were highest in October 2016, followed by June 2016, February 2016, October 2015, January 2018, July 2017 and January 2017.

4.3. BTEX Ratios

According to Monod et al., (2001), the Toluene/Benzene(T/B) ratio may be used to determine whether the sources are fresh emissions from traffic, mobile and evaporative sources or industrial facilities (Table 3.3 in methods). Essentially, the T/B ratios were determined for the various sampling period at all the monitoring sites to understand the sources of BTEX for specific sampling points. The ratios for each sampling period will be presented in the following sections.

4.3.1. October 2015

The measured concentrations of BTEX compounds for the October 2015 sampling period are represented in Table 4.19 with the total BTEX and the T/B ratio. The total BTEX ranged between 6.78 µg/m³ and 108.06 µg/m³.

Table 4.1: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the October 2015 sampling period

Sites	Benzene (µg/m ³)	Toluene (µg/m ³)	Ethyl-benzene (µg/m ³)	Xylene (µg/m ³)	Total BTEX	Toluene/Benzene Ratio
KST-1	10.96	17.36	2.88	11.23	42.43	1.58
KST-2	8.98	12.68	1.55	7.31	30.52	1.41
KST-3	11.88	19.42	2.64	11.78	45.72	1.63
KST-4	3.32	4.04	0.73	2.31	10.40	1.22
KST-5	4.52	5.35	3.07	14.02	26.96	1.18
KST-6	3.84	4.1	0.96	3.9	12.80	1.07
KMB-1	2.73	2.36	0.73	1.19	7.01	0.86
KMB-2	2.68	2.85	0.73	1.75	8.01	1.06
KMB-3	2.42	2.36	0.73	1.27	6.78	0.98
RCD-1	3.47	4.11	0.91	3.12	11.61	1.18
RCD-2	9.51	14.81	2.3	9.52	36.14	1.56
RCD-4	3.51	6.66	0.88	4.24	15.29	1.90
ALB-1	17.17	25.57	4	16.04	62.78	1.49
ALB-2	12.35	18	3.51	17.7	51.56	1.46
ALB-3	7.35	9.54	1.77	7.09	25.75	1.30
ALB-4	16.3	26.59	5.88	41.48	90.25	1.63
WIT-1	8.55	4.76	0.75	2.72	16.78	0.56
WIT-2	6.68	4.78	0.73	2.76	14.95	0.72
WIT-3	10.87	6.4	1.3	3.6	22.17	0.59
WIT-4	29.63	18.29	2.83	9.35	60.10	0.62
PE-1	3.68	3.68	0.85	3.41	11.62	1.00
PE-2	4.13	7.1	2.09	4.78	18.10	1.72
PE-3	3.47	4.11	0.91	3.12	11.61	1.18
PE-4	12.87	18.7	8.52	9.44	49.53	1.45
IV-1	11.53	25.38	6.5	36.46	79.87	2.20
IV-2	18.53	41.65	10.52	37.36	108.06	2.25
IV-3	6.71	19.67	7.55	27.9	61.83	2.93
IV-4	8.22	20.57	4.68	14.94	48.41	2.50
LDS-1	2.36	5.32	2.42	6.26	16.36	2.25
LDS-2	4.2	8.59	1.54	6.75	21.08	2.05
LDS-3	4.82	10.88	6.63	10.88	33.21	2.26
LDS-4	-	-	-	-	-	-

***RCD-3 & LDS-4 samplers were damaged**

The T/B ratio values ranged between 0.56 and 2.93. The Island View site had the highest T/B ratio at sampling point IV-3 with a ratio of 2.93 indicating that the

sampler was influenced by a mobile source. The sampling points IV-1, IV-2, IV-4, LDS-1, LDS-2 and LDS-3 also had T/B ratios between 2 and 3 which indicated that they were also influenced by a mobile source. The majority of the sampling points had T/B ratios that were below 2 and mostly above 1. Research showed that the T/B approaching a value of 1 indicates traffic-originating emission sources (Gaur et al., 2016). Although there is no specific value set for the T/B ratios below 2, the ratios could be related to emission from traffic. The T/B ratios indicate that mobile sources influenced the concentrations of BTEX at the site which could be the tankers moving to the loading gantries and also other mobile sources around the site.

4.3.2. February 2016

The recorded concentrations of BTEX compounds for the February 2016 sampling period are represented in Table 4.20 together with total BTEX and T/B ratios. The total BTEX ranged between 8.06 $\mu\text{g}/\text{m}^3$ and 191.10 $\mu\text{g}/\text{m}^3$.

Table 4.2: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the February 2016 sampling period.

Sites	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl- benzene ($\mu\text{g}/\text{m}^3$)	Xylene ($\mu\text{g}/\text{m}^3$)	Total BTEX	Toluene/ Benzene Ratio
KST-1	6.4	8.78	1.09	5.92	22.19	1.37
KST-2	3.76	6.99	2.46	15.47	28.68	1.86
KST-3	4.15	5.9	0.73	2.74	13.52	1.42
KST-4	2.47	3.93	1.64	4.36	12.40	1.59
KST-5	2.5	10.5	1.65	4.36	19.01	4.20
KST-6	1.78	3.48	1.25	4.8	11.31	1.96
KMB-1	1.71	4.08	1.04	4.48	11.31	2.39
KMB-2	0.88	2.04	0.73	0.71	4.36	2.32
KMB-3	0.9	1.76	0.73	0.71	4.10	1.96
RCD-1	3.05	5.83	0.8	4.18	13.86	1.91
RCD-2	9.78	20.66	2.76	13	46.20	2.11
RCD-3	2.37	6.55	1.07	5.36	15.35	2.76
RCD-4	2.89	4.76	0.74	3.65	12.04	1.65
ALB-1	35.11	43.03	4.92	17.94	101.00	1.23
ALB-2	15.61	27.02	8.01	26.77	77.41	1.73
ALB-3	11.71	15.58	2.62	11.36	41.27	1.33
ALB-4	15.83	21.54	5.97	23.06	66.40	1.36
WIT-1	5.24	4.28	1.48	3.75	14.75	0.82
WIT-2	1.83	6.13	0.97	3.72	12.65	3.35
WIT-3	6.12	4.9	1.14	3.63	15.79	0.80

WIT-4	34.74	23.88	3.61	12.84	75.07	0.69
PE-1	1.78	3.38	0.73	2.17	8.06	1.90
PE-2	3.69	6.78	1.26	4.38	16.11	1.84
PE-3	2.58	4.93	1.24	5.46	14.21	1.91
PE-4	5.55	9.93	1.33	6.22	23.03	1.79
IV-1	41.98	78.88	8.39	47.89	177.14	1.88
IV-2	38.53	77.46	10.91	64.2	191.10	2.01
IV-3	10.18	57.7	11.84	71.58	151.30	5.67
IV-4	14.78	3.16	3.4	19.59	40.93	0.21
LDS-1	1.69	4.08	0.9	3.38	10.05	2.41
LDS-2	3.18	5.26	0.93	4.11	13.48	1.65
LDS-3	3.26	9.68	1.6	7.66	22.20	2.97
LDS-4	6.6	14.37	2.09	9.55	32.61	2.18

Literature revealed that the different T/B ratios show the various sources of BTEX depending on the value indicators. The T/B ratios values were between 0.21 and 5.67. The Island View sampling point IV-3 had a T/B ratio of 5.67 which indicated that sampler was influenced by a point source. Sampling point KST-5 had a T/B ratio of 4.20 which showed that the sampler was also under the influence of a point source. In Witbank site, the sampling point WIT-2 had a T/B ratio of 3.35 which indicated that the sampler was impacted by a mobile and evaporative source. The sampling points KMB-1, KMB-2, RCD-2, RCD-3, IV-2, LDS-1, LDS-3 and LDS-4 had T/B ratios between 2 and 3 which indicated that they were under the influence of a mobile source. All the other sampling points had T/B ratios lower than 2.

4.3.3. June 2016

The concentration of BTEX compounds recorded during the June 2016 sampling period are shown in Table 4.21 with the total BTEX and T/B ratio.

Table 4.3: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the June 2016 sampling period.

Sites	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl- benzene ($\mu\text{g}/\text{m}^3$)	Xylene ($\mu\text{g}/\text{m}^3$)	Total BTEX	Toluene/ Benzene Ratio
KST-1	8.17	14.49	2.13	8.9	33.69	1.77
KST-2	5.93	9.44	1.6	7.55	24.52	1.59
KST-3	6.58	10.96	1.65	7.32	26.51	1.67
KST-4	4.75	7.17	1.22	4.73	17.87	1.51
KST-5	4.01	7.31	1.36	5.68	18.36	1.82
KST-6	1.92	8.84	1.74	7.16	19.66	4.60

KMB-1	1.18	2.23	0.46	2.46	6.33	1.89
KMB-2	1.11	2.98	0.46	2.89	7.44	2.68
KMB-3	1.12	2.43	0.46	2.51	6.52	2.17
RCD-1	3.34	5.52	1.3	4.67	14.83	1.65
RCD-2	5.18	12.89	2.47	9.73	30.27	2.49
RCD-3	3.1	5.01	1.26	4.34	13.71	1.62
RCD-4	5.05	11.69	2.98	12.8	32.52	2.31
ALB-1	41.72	60.54	8.33	31.72	142.31	1.45
ALB-2	15.03	27.12	4.67	19.06	65.88	1.80
ALB-3	12.54	24.78	4.32	17.92	59.56	1.98
ALB-4	21.9	36.73	6.96	26.68	92.27	1.68
WIT-1	14.17	11.47	2.14	8.68	36.46	0.81
WIT-2	10.11	11.86	3.58	13.99	39.54	1.17
WIT-3	22.75	18.04	2.68	10.51	53.98	0.79
WIT-4	55.59	46.51	7.06	24.11	133.27	0.84
PE-1	4.16	16.21	2.89	10.74	34.00	3.90
PE-2	6.39	110.39	13.5	43.77	174.05	17.28
PE-3	5.29	19.23	3.21	11.7	39.43	3.64
PE-4	12.28	41.44	5.75	22.24	81.71	3.37
IV-1	8.06	13.95	2.2	11.34	35.55	1.73
IV-2	7.34	12.51	1.38	7.22	28.45	1.70
IV-3	4.55	7.42	0.64	5.39	18.00	1.63
IV-4	2.6	5.21	0.64	2.45	10.90	2.00
LDS-1	85.15	146.28	16.59	77.14	325.16	1.72
LDS-2	53.29	85.62	8.89	47.74	195.54	1.61
LDS-3	26.89	60.59	6.74	33.38	127.60	2.25
LDS-4	20.19	48.14	6.98	43.63	118.94	2.38

The total BTEX ranged between 6.33 µg/m³ and 325.16 µg/m³ while the T/B ratios ranged between 0.79 and 17.28. The sampling point PE-2 and KST-6 had T/B ratios of 17.28 and 4.60 respectively and the ratios indicated that the samplers were influenced by a point source. The sampling points KMB-2, KMB-3, RCD-2, RCD-4, IV-4, LDS-3 and LDS-4 had ratios between 2 and 3 which indicated that they were under the influence of a mobile source. All the other sampling points had T/B ratios lower than 2.

4.3.4. October 2016

The BTEX concentrations for the October 2016 sampling period together with the total BTEX and T/B ratios are presented in Table .22, together with the total BTEX

which was ranging between 5.99 µg/m³ and 646.69 µg/m³ while the T/B ratios ranged between 0.51 and 3.14.

Table 4.4: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the October 2016 sampling period.

Sites	Benzene (µg/m ³)	Toluene (µg/m ³)	Ethyl-benzene (µg/m ³)	Xylene (µg/m ³)	Total BTEX	Toluene/Benzene Ratio
KST-1	5.94	8.25	1.04	4.65	19.88	1.39
KST-2	3.49	4.33	0.73	1.97	10.52	1.24
KST-3	5.47	7.98	1.01	4.59	19.05	1.46
KST-4	3.89	5.34	1.14	5.52	15.89	1.37
KST-5	4.2	7.12	2.14	11.02	24.48	1.70
KST-6	3.45	4.77	0.96	4.86	14.04	1.38
KMB-1	1.35	2.08	1.02	1.54	5.99	1.54
KMB-2	1.73	3.07	1.02	2.03	7.85	1.77
KMB-3	1.61	2.12	1.02	1.36	6.11	1.32
RCD-1	3.26	5.82	1.37	3.98	14.43	1.79
RCD-2	7.48	14.11	2.07	8.76	32.42	1.89
RCD-3	4.35	5.64	1.31	4.13	15.43	1.30
RCD-4	5.2	7.68	1.15	5.69	19.72	1.48
ALB-1	144.24	285.39	37.09	179.97	646.69	1.98
ALB-2	16.29	24	4.07	16.67	61.03	1.47
ALB-3	16.72	26.83	4.34	19.02	66.91	1.60
ALB-4	30.16	54.91	8.16	41.73	134.96	1.82
WIT-1	12.23	7.46	1.41	5.79	26.89	0.61
WIT-2	13.68	7.96	1.46	5.53	28.63	0.58
WIT-3	19.06	9.81	1.77	5.77	36.41	0.51
WIT-4	37.2	23.15	3.63	12.39	76.37	0.62
PE-1	4.08	7.44	1.03	4.19	16.74	1.82
PE-2	2.37	4.92	0.88	3.93	12.10	2.08
PE-3	2.13	4.13	0.57	2.19	9.02	1.94
PE-4	6.7	10.24	1.09	4.23	22.26	1.53
IV-1	29.7	60.79	7.46	38.82	136.77	2.05
IV-2	16.86	31.81	4.57	25.93	79.17	1.89
IV-3	6.99	16.28	6.79	40.19	70.25	2.33
IV-4	11.69	36.76	4.4	21.62	74.47	3.14
LDS-1	6.88	16.94	3.15	15.03	42.00	2.46
LDS-2	3	4	1.11	4.29	12.40	1.33
LDS-3	6.28	9.06	1.23	5.55	22.12	1.44
LDS-4	5.98	11.89	1.99	8.82	28.68	1.99

The sampling point IV-4 had a T/B ratio of 3.14 indicating that the emission was influenced by a mobile and evaporative source. The sampling points PE-2, IV-1, IV-3 and LDS-1 had T/B ratios of 2.08, 2.05, 2.33 and 2.46 respectively. The ratios indicated that the samplers were influenced by a mobile source

4.3.5. January 2017

The measured concentrations of BTEX compounds for the January 2017 sampling period are presented in Table 4.23 together with the total BTEX and T/B ratios.

Table 4.5: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the January 2017 sampling period.

Sites	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl- benzene ($\mu\text{g}/\text{m}^3$)	Xylene ($\mu\text{g}/\text{m}^3$)	Total BTEX	Toluene/ Benzene Ratio
KST-1	8.53	9.84	1.35	5.60	25.32	1.15
KST-2	7.67	7.75	1.63	3.37	20.42	1.01
KST-3	8.42	10.08	1.11	5.65	25.26	1.20
KST-4	4.09	4.69	0.87	2.97	12.62	1.15
KST-5	5.57	5.84	1.51	4.16	17.08	1.05
KST-6	6.42	5.01	1.67	0.01	13.10	0.78
KMB-1	4.03	2.49	0.85	0.98	8.35	0.62
KMB-2	0.58	0.78	0.85	0.83	3.04	1.34
KMB-3	2.60	2.28	0.85	0.95	6.68	0.88
RCD-1	1.96	4.07	1.44	4.02	11.49	2.08
RCD-2	9.54	13.71	1.98	8.06	33.29	1.44
RCD-3	3.64	5.34	1.46	4.44	14.88	1.47
RCD-4	7.21	10.99	1.78	7.98	27.96	1.52
ALB-1	5.77	7.85	1.39	5.75	20.76	1.36
ALB-2	12.10	23.85	5.48	39.49	80.92	1.97
ALB-3	12.92	17.84	2.54	10.92	44.22	1.38
ALB-4	2.62	4.34	1.00	3.79	11.75	1.66
WIT-1	9.31	7.06	1.73	4.14	22.24	0.76
WIT-2	2.98	2.25	0.85	0.83	6.91	0.76
WIT-3	8.00	6.07	1.21	3.57	18.85	0.76
WIT-4	4.59	3.03	0.85	0.83	9.30	0.66
PE-1	2.46	3.47	1.29	4.10	11.32	1.41
PE-2	3.76	4.94	1.19	3.57	13.46	1.31
PE-3	3.01	3.32	0.85	0.83	8.01	1.10
PE-4	5.53	8.38	1.23	5.32	20.46	1.52
IV-1	20.25	32.41	4.49	17.53	74.68	1.60
IV-2	17.97	35.63	6.54	25.03	85.17	1.98
IV-3	11.00	21.40	3.78	13.43	49.61	1.95
IV-4	2.11	4.63	1.09	4.79	12.62	2.19
LDS-1	4.47	4.19	1.15	4.15	13.96	0.94

LDS-2	4.35	5.29	1.02	3.49	14.15	1.22
LDS-3	5.24	5.13	0.99	3.02	14.38	0.98
LDS-4	8.76	10.31	1.8	6.9	27.77	1.18

The total BTEX ranged between 3.04 $\mu\text{g}/\text{m}^3$ and 85.17 $\mu\text{g}/\text{m}^3$ while the T/B ratios ranged between 0.62 and 2.19. The sampling points RCD-1 and IV-4 had T/B ratios of 2.08 and 2.19 respectively which indicated that the samplers were influenced by a mobile source.

4.3.6. April 2017

The BTEX concentrations for the April 2016 sampling period together with the total BTEX and T/B ratios are presented in Table 4.24.

Table 4.6: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the April 2017 sampling period.

Sites	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl- benzene ($\mu\text{g}/\text{m}^3$)	Xylene ($\mu\text{g}/\text{m}^3$)	Total BTEX	Toluene/ Benzene Ratio
KST-1	5.84	9.19	1.23	5.47	21.73	1.57
KST-2	3.77	4.77	0.98	2.84	12.36	1.27
KST-3	5.98	9.77	1.48	5.47	22.70	1.63
KST-4	2.75	3.63	0.58	1.87	8.83	1.32
KST-5	3.96	5.12	1.33	3.64	14.05	1.29
KST-6	2.51	3.27	0.58	0.57	6.93	1.30
KMB-1	0.79	1.70	0.68	0.66	3.83	2.15
KMB-2	0.97	2.90	0.80	3.17	7.84	2.99
KMB-3	1.00	2.30	0.56	2.50	6.36	2.30
RCD-1	0.50	0.54	0.58	0.57	2.19	1.08
RCD-2	7.81	14.70	2.32	10.45	35.28	1.88
RCD-3	3.25	5.75	0.97	4.18	14.15	1.77
RCD-4	3.32	5.33	0.90	4.36	13.91	1.61
ALB-1	10.70	19.10	3.73	17.64	51.17	1.79
ALB-2	13.96	27.06	7.96	23.72	72.70	1.94
ALB-3	13.04	25.75	4.30	19.79	62.88	1.97
ALB-4	9.20	16.85	2.15	12.84	41.04	1.83
WIT-1	6.55	4.09	0.58	2.69	13.91	0.62
WIT-2	7.81	4.94	0.58	3.77	17.10	0.63
WIT-3	18.49	16.15	2.66	9.77	47.07	0.87
WIT-4	5.12	4.25	1.41	6.47	17.25	0.83
PE-1	3.43	4.70	0.58	2.35	11.06	1.37
PE-2	4.79	5.76	0.87	3.80	15.22	1.20
PE-3	1.30	3.14	0.77	3.79	9.00	2.42
PE-4	4.78	7.14	0.88	3.76	16.56	1.49

IV-1	12.55	22.99	2.67	15.50	53.71	1.83
IV-2	13.18	26.89	3.34	21.10	64.51	2.04
IV-3	8.43	15.84	2.51	11.10	37.88	1.88
IV-4	4.09	21.16	6.93	37.96	70.14	5.17
LDS-1	1.23	2.11	0.53	2.22	6.09	1.72
LDS-2	2.74	3.73	0.78	2.4	9.65	1.36
LDS-3	2.70	3.74	0.84	2.50	9.78	1.39
LDS-4	2.42	4.00	1.08	2.81	10.31	1.65

The total BTEX was ranging between 3.83 µg/m³ and 72.70 µg/m³ while the T/B ratios ranged between 0.62 and 5.17. The sampling points KMB-1, KMB-2, KMB-3, PE-3 and IV-2 had T/B ratios which were between 2 and 3, indicating that the concentrations were influenced by a mobile source. The sampling point IV-4 had a T/B ratio of 5.17 indicating that the sampler was under the influence of a point source.

4.3.7. July 2017

The recorded concentrations of BTEX compounds for the July 2016 sampling period are represented in Table 4.25 together with total BTEX and T/B ratios. The total BTEX ranged between

Table 4.7: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the July 2017 sampling period.

Sites	Benzene (µg/m ³)	Toluene (µg/m ³)	Ethyl-benzene (µg/m ³)	Xylene (µg/m ³)	Total BTEX	Toluene/Benzene Ratio
KST-1	7,66	12,66	1,55	6,51	28,38	1,65
KST-2	4,54	7,41	0,99	4,18	17,12	1,63
KST-3	8,59	14,29	1,88	7,95	32,71	1,66
KST-4	2,76	4,92	0	2,48	10,16	1,78
KST-5	4,33	8,98	1,33	6,04	20,68	2,07
KST-6	3,72	7,57	1,53	6,93	19,75	2,03
KMB-1	1,58	4,35	0,73	2,48	9,14	2,75
KMB-2	1,94	4,28	0,73	2,54	9,49	2,21
KMB-3	1,87	4,50	0,73	2,47	9,57	2,41
RCD-1	2,46	5,70	1,78	2,28	12,22	2,32
RCD-2	9,59	24,40	4,88	8,95	47,82	2,54
RCD-3	1,76	2,83	0,73	1,58	6,90	1,61
RCD-4	8,30	12,40	2,66	7,37	30,73	1,49
ALB-1	28,24	52,16	12,03	53,87	146,30	1,85
ALB-2	21,97	46,17	10,58	47,41	126,13	2,10
ALB-3	18,26	31,2	5,82	26,87	82,15	1,71

ALB-4	15,51	26,68	5,11	22,97	70,27	1,72
WIT-1	20,09	14,47	1,67	7,78	44,01	0,72
WIT-2	22,32	15,05	1,77	7,90	47,04	0,67
WIT-3	14,30	11,50	1,50	5,99	33,29	0,80
WIT-4	15,45	12,12	1,52	7,99	37,08	0,78
PE-1	8,1	11,35	12,32	7,13	38,90	1,40
PE-2	18,57	23,29	23,64	15,67	81,17	1,25
PE-3	3,18	3,89	4,72	2,77	14,56	1,22
PE-4	14,77	16,93	21,37	12,42	65,49	1,15
IV-1	17,93	55,10	6,83	34,72	114,58	3,07
IV-2	18,67	74,99	7,62	45,01	146,29	4,02
IV-3	10,93	41,56	3,87	20,86	77,22	3,80
IV-4	21,95	75,61	7,71	40,75	146,02	3,44
LDS-1	2,91	6,3	1,01	4,30	14,52	2,16
LDS-2	3,73	7,74	1,17	5,27	17,91	2,08
LDS-3	3,86	7,82	0,98	4,44	17,10	2,03
LDS-4	3,05	6,02	0,97	4,16	14,20	1,97

The total BTEX ranged between 6,90 µg/m³ and 146,30 µg/m³ while the T/B ratios ranged between 0.67 and 4,02. The T/B ratios were mostly lower than 2 while a few were between 2 and 3. The sampling point IV-2 was the only one with a T/B ratio above 4 which indicated that the sampler was influenced by an industrial or point source. The sampling points IV-1, IV-3 and IV-4 had T/B ratios between 3 and 4 indicating that there was an influence of mobile and evaporative sources. The sampling points KST-5, KST-6, KMB-1, KMB-2, KMB-3, RCD-1, RCD-2, ALB-2, LDS-1, LDS-2 and LDS-3 had T/B ratios between 2 and 3 which indicated that they were influenced by mobile sources.

4.3.8. October 2017

The BTEX concentrations for the October 2017 sampling period together with the total BTEX and T/B ratios are presented in Table 4.26.

Table 4.8: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the October 2017 sampling period.

Sites	Benzene (µg/m ³)	Toluene (µg/m ³)	Ethyl-benzene (µg/m ³)	Xylene (µg/m ³)	Total BTEX	Toluene/Benzene Ratio
KST-1	6,62	10,28	1,22	5,71	23,83	1,55

KST-2	3,48	6,12	0,87	3,9	14,37	1,76
KST-3	5,1	8,16	1,18	4,67	19,11	1,60
KST-4	2,03	4,64	0,86	3,39	10,92	2,29
KST-5	2,24	4,72	0,88	3,41	11,25	2,11
KST-6	3,04	6,09	1,18	4,78	15,09	2,00
RCD-1	9,49	23,39	3,18	14,53	50,59	2,46
RCD-2	2,29	7,66	1,67	6,58	18,20	3,34
RCD-3	3,72	8,73	1,5	6,15	20,10	2,35
RCD-4	1,88	7,72	1,29	5,62	16,51	4,11
ALB-1	10,39	23,11	5,22	21,08	59,80	2,22
ALB-2	11,30	34,95	5,89	24,2	76,34	3,09
ALB-3	8,59	18,39	3,31	14,91	45,20	2,14
ALB-4	5,24	11,40	2,11	9,45	28,20	2,18
WIT-1	7,32	5,66	1	3,94	17,92	0,77
WIT-2	8,31	6,01	0,97	3,85	19,14	0,72
WIT-3	25,03	20,54	3,25	13,23	62,05	0,82
WIT-4	10,40	8,46	1,52	5,98	26,36	0,81
PE-1	2,77	3,75	0,76	3,85	11,13	1,35
PE-2	7,59	9,61	1,58	7,26	26,04	1,27
PE-3	10,98	13,25	1,66	7,21	33,10	1,21
PE-4	2,68	4,15	0,89	3,8	11,52	1,55
IV-1	37,79	67,87	8,81	40,09	154,56	1,80
IV-2	73,80	118,29	14,63	75,12	281,84	1,60
IV-3	19,41	48,53	8,25	38,7	114,89	2,50
IV-4	20,30	47,56	5,55	25,52	98,93	2,34

The total T/B ranged 0,72 and 4,11 while the total BTEX was between 10,92 $\mu\text{g}/\text{m}^3$ and 154,56 $\mu\text{g}/\text{m}^3$. The majority of the sampling points had T/B ratios that were below 2 indicating that the samplers were influenced by emission from traffic. The T/B ratio at sampling point RCD-4 was 4,11 and at sampling ALB-2 it was 3,09 which showed that the samplers were influence by industrial and evaporative sources respectively. The few remaining sampling points were influenced by mobile sources with T/B ratios between 2 and 3.

4.3.9. January 2018

The total BTEX established for all monitored sites ranged between 8,77 $\mu\text{g}/\text{m}^3$ and 185,79 $\mu\text{g}/\text{m}^3$ while the T/B ratios ranged between 0,79 and 4, 20 (Table 4.27).

Table 4.9: BTEX concentrations for all sites, total BTEX and Toluene/Benzene Ratio for the January 2018 sampling period.

Sites	Benzene (µg/m ³)	Toluene (µg/m ³)	Ethyl- benzene (µg/m ³)	Xylene (µg/m ³)	Total BTEX	Toluene/ Benzene Ratio
KST-1	10,5	17,66	1,97	8,83	38,96	1,68
KST-2	9,25	14,89	1,58	7,04	32,76	1,61
KST-3	8,16	14,15	1,52	7	30,83	1,73
KST-4	3,66	6,57	0,91	5,03	16,17	1,80
KST-5	4,47	9,42	1,5	8,17	23,56	2,11
KST-6	4,03	6,95	1,01	4,92	16,91	1,72
RCD-1	1,16	4,87	0,85	1,89	8,77	4,20
RCD-2	7,34	12,58	1,46	7,15	28,53	1,71
RCD-3	2,99	5,9	0,85	2,74	12,48	1,97
RCD-4	5,47	10,66	1,45	6,6	24,18	1,95
ALB-1	4,14	11,94	2,48	12	30,56	2,88
ALB-2	17,33	53,93	15,79	98,74	185,79	3,11
ALB-3	12,74	24,15	3,47	15,26	55,62	1,90
ALB-4	8,17	16,85	2,51	11,81	39,34	2,06
WIT-1	6,58	5,2	0,73	2,49	15,00	0,79
WIT-2	6,3	5,3	0,73	2,86	15,19	0,84
WIT-3	5,53	5,37	0,73	2,85	14,48	0,97
WIT-4	13,74	11,66	1,63	7,83	34,86	0,85
PE-1	3,36	6,99	0,73	4,57	15,65	2,08
PE-2	5,46	9,47	1,22	5,22	21,37	1,73
PE-3	1,38	5,09	1,28	8,35	16,10	3,69
PE-4	5,12	9,97	0,98	4,24	20,31	1,95
IV-1	9,6	24,43	3,18	16,28	53,49	2,54
IV-2	6,65	23,03	4,4	23,26	57,34	3,46
IV-3	3,32	13,72	3,14	17,82	38,00	4,13
IV-4	9,31	21,5	2,63	12,99	46,43	2,31

The majority of T/B ratios were lower than 2 and could be attributed to fresh emissions from traffic. The sampling point RCD-1 and IV-3 were the only two T/B ratios above 4 which indicated that the samplers were influenced by an industrial or point source. The sampling points ALB-2, PE-3 and IV-2 had T/B ratios between 3 and 4 indicating that there was an influence of mobile and evaporative sources. The

sampling points KST-5, ALB-1, ALB-4, PE-1, IV-1 and IV-4 had T/B ratios between 2 and 3 which indicated that they were influenced by mobile sources.

The majority of sampling points showed that the emission around the fuel depots were influenced by mobile and evaporative sources while a few were influenced by point sources. There were no specific mobile sources identified around the depots. Although there was no specific value set for the T/B ratios lower than 2, research reveals that the values approaching 1 could be related to emission from traffic-related sources (Monod et al., 2001). A few sampling points throughout the various sampling periods were influenced by industrial facilities or point sources and for the depots that were located in industrial areas there were industrial facilities in the surrounding area that could be related to the emissions.

4.4. Synoptic Circulation

The synoptic scale circulation patterns will be highlighted for the for the October 2015, February 2016, June 2016, October 2016, January 2017, April 2017, July 2017, October 2017 and January 2018 sampling periods. The detailed synoptic charts for all sampling days are highlighted in appendix 1.

4.4.1. October 2015

The synoptic circulation over South Africa in October 2015 showed the presence of anticyclones over the eastern and western parts of the country (Weathersa.co.za, 2017). At the beginning of the sampling period around the 12th until 15th of October 2015, anticyclones were dominant on the western and the eastern side of the continent. The sampling period was also dominated by surface troughs which persisted over the central interior, north of the country and moved north-east of the country at the beginning and also towards the end of the sampling period (Weathersa.co.za, 2017). There were also upper air cut-off lows and upper air troughs associated with the prevailing circulation during the period. There was a cold front along the south coast on the 13th of October 2015 and also on the last day of the sampling period. The anticyclones persisted for the duration of the sampling

period with some movements towards the south coast of South Africa. The conditions were cool to warm with light rain and some isolated showers over the country. There were hot conditions in Mpumalanga, Kwazulu-Natal, Limpopo, North West and Western Cape. Figure 4.27 indicates the synoptic chart representing the October 2015 sampling period.

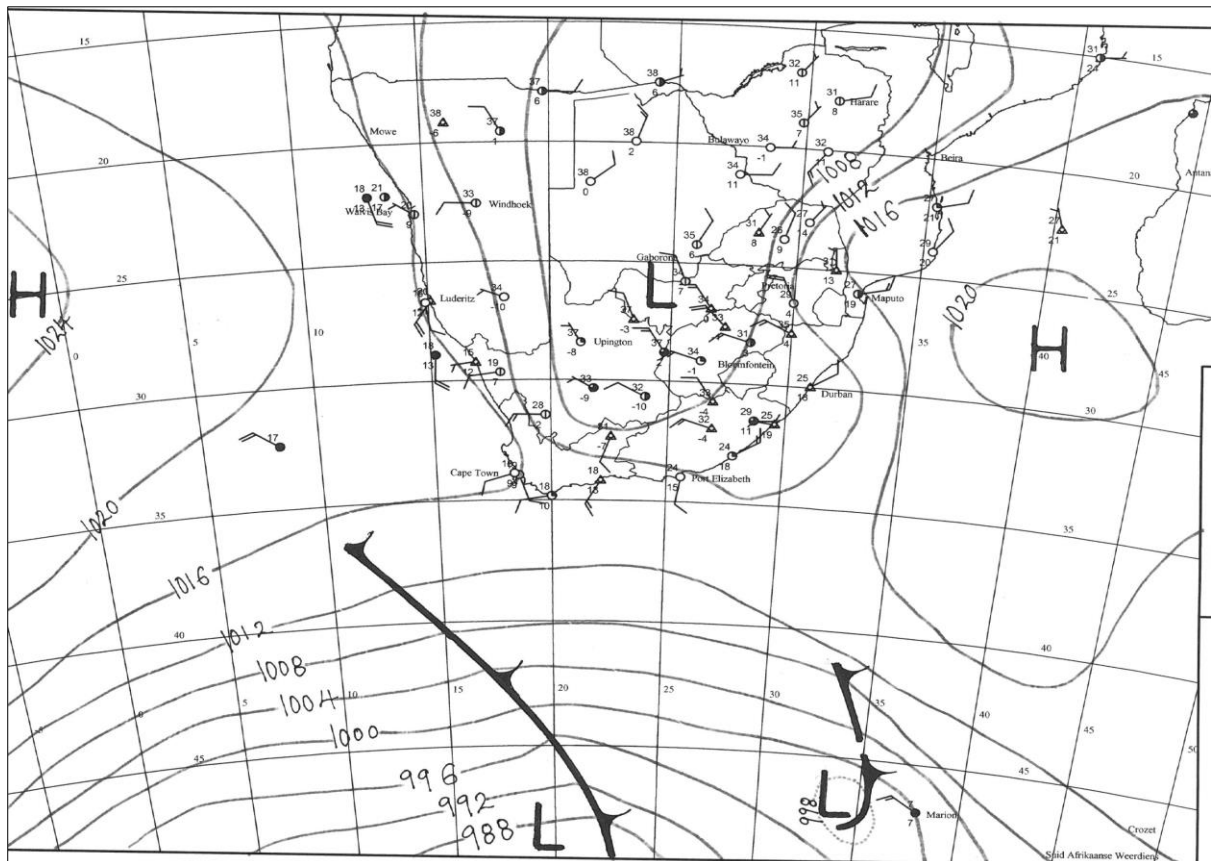


Figure 4.27: Synoptic Chart indicating the dominant circulation patterns on the 12th of October 2015 (Weathersa, 2017)

4.4.2. February 2016

In the February 2016 sampling period, there was a cold front that passed through the country on the second day of sampling accompanied by an anticyclone. The surface trough extended over the central interior on the 03rd of February 2016 (Weathersa.co.za, 2017). The surface trough persisted over the central, western and northern interior throughout the sampling period, associated with anticyclones south and south east of the country (Weathersa.co.za, 2017). The whole sampling period

was dominated by the surface trough which moved over different areas over time (Figure 4.28). Anticyclonic circulations were also dominant during the February 2016. The circulations influenced partly cloudy to cloudy together with cool to warm and hot conditions over the country. There were thundershowers and isolated showers over the eastern interior of the country. There were hot conditions in the Western Cape, North-West, Northern Cape and Kwazulu-Natal provinces.

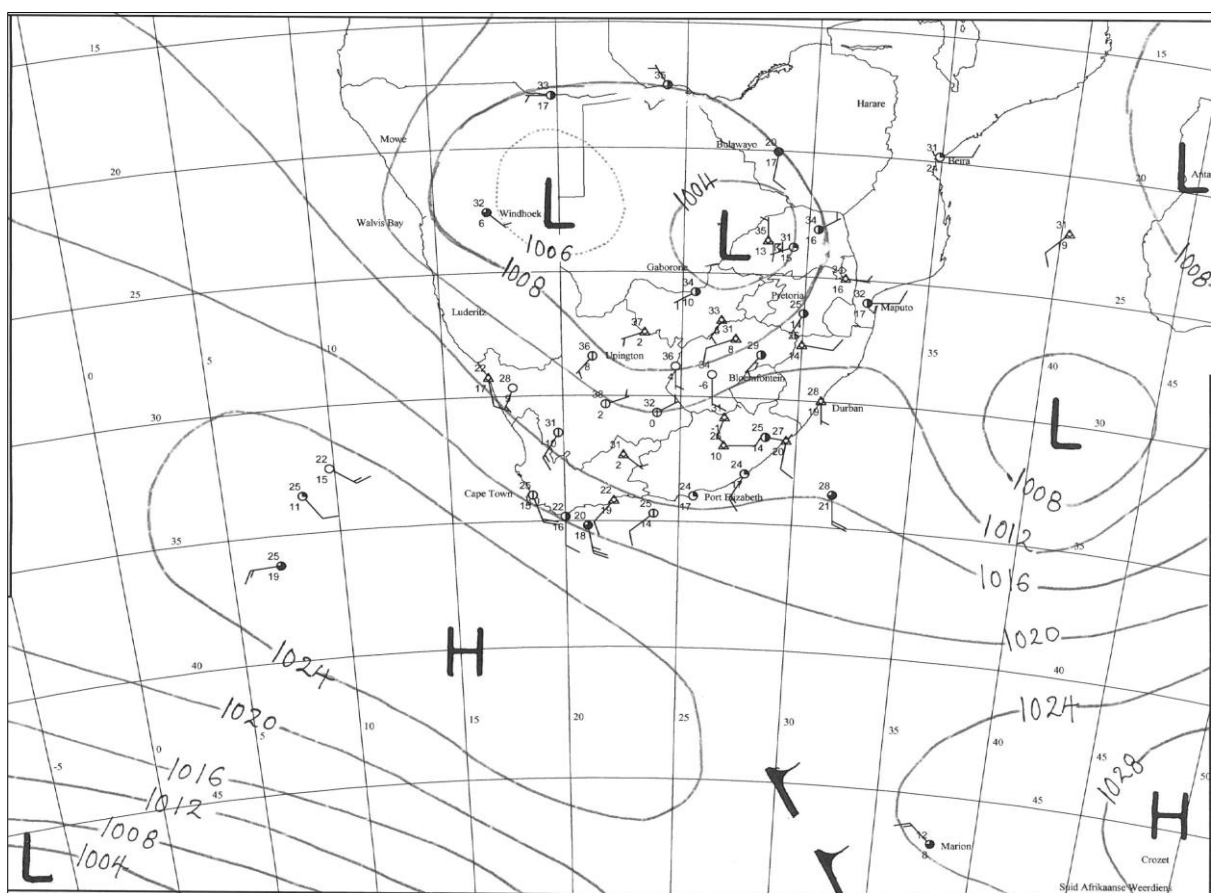


Figure 4.28: Synoptic chart showing the dominant circulation patterns on the 07th of February 2016 (Weathersa, 2017).

4.4.3. June 2016

During the June 2016 sampling period, surface troughs were dominant accompanied by anticyclones over the west and east of the country. At the beginning of the sampling period, there was a surface trough over the western interior and on the 17th

of June the surface trough moved closer to the south coast. The low-pressure trough entered the interior from the south west coast and persisted for two days as indicated in Figure 4.29 (Weathersa.co.za, 2017). The June 2016 sampling period was also dominated by cold fronts on various days: along the east coast with anticyclones on the east and west of the country on the 14th of June, across the Northern and Western cape with an anticyclone behind it on the 15th of June, along the western part of the country on the 19th of June and on the eastern part of the country with an anticyclone behind it on the 20th and 21st of June. Anticyclones were dominant from the west, east and over the country on the 18th, 22nd and the 23rd of June respectively. The dominant anticyclonic circulation towards the end of the sampling period blocked the mid-latitude cyclones from entering into the interior (Weathersa.co.za, 2017). The circulations influenced partly cloudy to cloudy, cold and cool conditions over the country. There were scattered showers and light rain on various days in most parts of the country. Limpopo, Mpumalanga, and Kwazulu-Natal also experienced hot conditions on the 15th, 19th, 20th and 21st of June 2016.

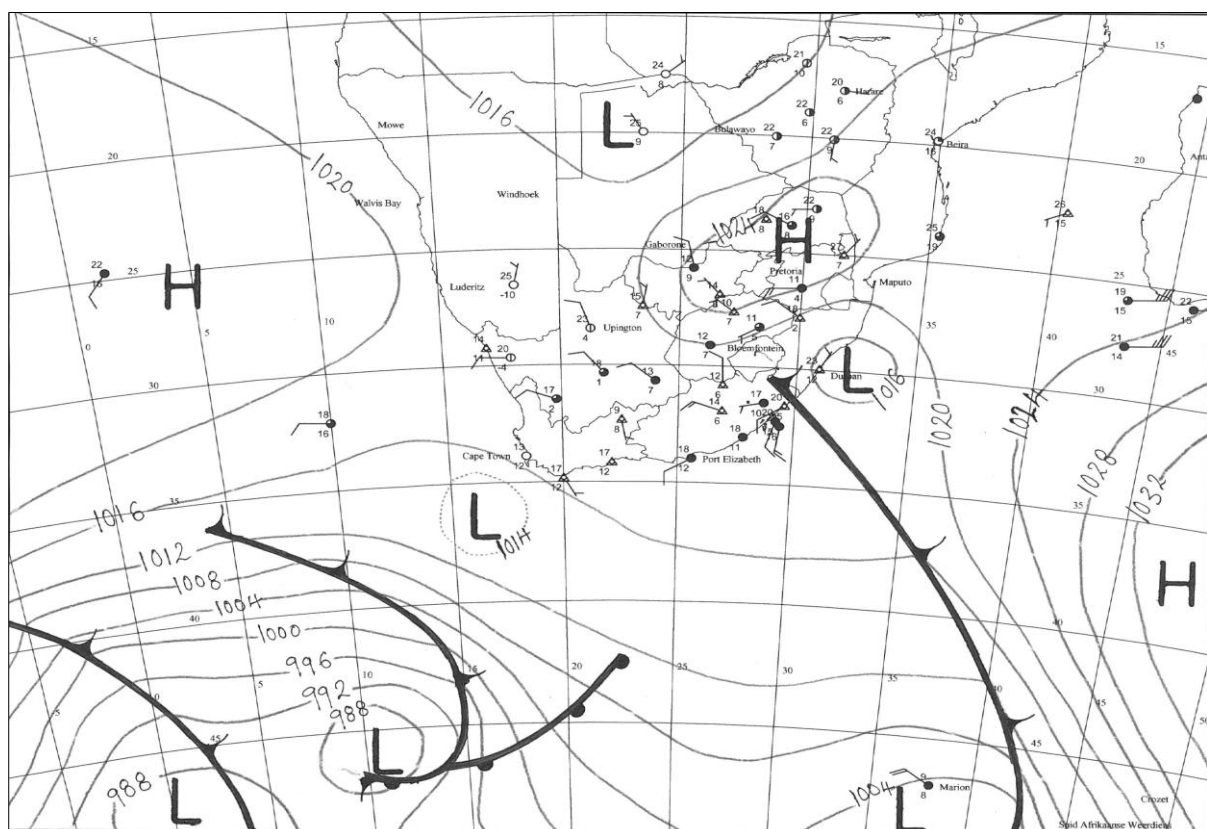


Figure 4.29: Synoptic chart showing the dominant circulation patterns for the June 2016 sampling period (14/06/2016) (Weathersa,2017).

4.4.4. October 2016

The October 2016 sampling period began with an anticyclone over the south-east of the country. The sampling period was dominated by surface troughs over the western interior, central interior and north-eastern interior on the 05th, 08th, 09th, 13th of October then persisted for 7 days until the end of the sampling period (Weathersa.co.za, 2017). The surface troughs also had mid-latitude cyclones and anticyclones. There were cold fronts along the south of the country accompanied by anticyclones behind them on 06th and 11th of October (Figure 4.30). In Port Elizabeth there were high temperatures on the 5th and 10th of October ahead of the cold fronts. Anticyclonic circulations were also dominant on the south and east of the country on the 07th and along the south west coast on the 10th of October 2016 (Weathersa.co.za, 2017). The South Atlantic anticyclone was ridging over the south-eastern and eastern parts of the country on the 12th of October. On the 04th until the 08th of October 2016, there were cloudy, cold and cool conditions with isolated showers and light rain over the country except in Limpopo province where there were hot conditions.

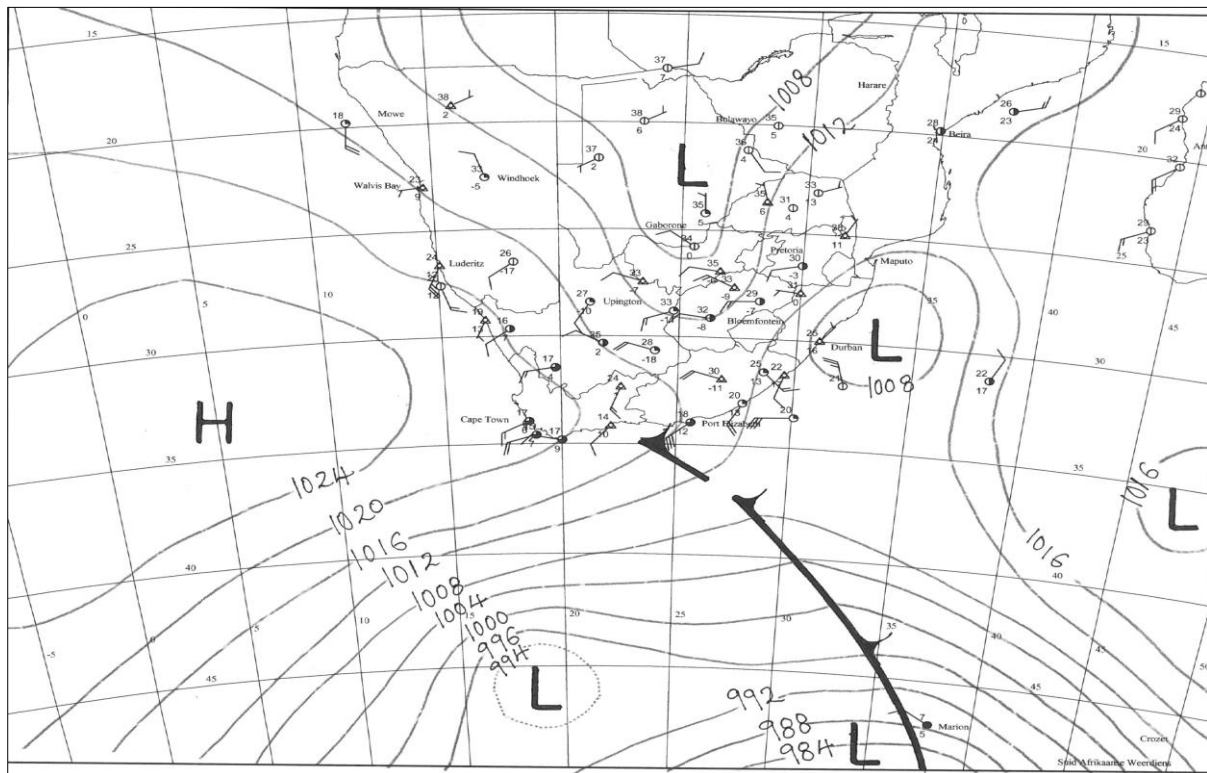


Figure 4.30: Synoptic chart showing the dominant circulation patterns for the October 2016 sampling period (11/10/2016) (Weathersa.co.za, 2017)

4.4.5. January 2017

At the beginning of the January 2017 sampling period, a surface trough was over the western interior with a low and it persisted for two days with anticyclones on the west and east of the country. On the 6th of January 2017, a cold front was located on the eastern part of the country with an anticyclone behind it and a surface trough over the central interior. The surface trough persisted over the central interior and extended over the western interior throughout the sampling period. There were anticyclones ridging over the eastern half of the country, south-west and south-eastern parts of the country towards the end of the sampling period. The surface troughs were dominant along the south-east coast around the 5th and the 9th of January 2017, along with the associated anticyclones as indicated in Figure 4.31 (Weathersa.co.za, 2017). Towards the end of the sampling period, the surface troughs were dominant over the interior blocking anticyclones from entering the country from the western and eastern side of the continent (Weathersa.co.za, 2017). The prevailing synoptic circulations influenced partly cloudy to cloudy and cool to warm conditions with showers and light rain mostly over the eastern half the country

together with isolated showers over the country. Heavy rainfalls occurred over the country at various days from the 04th until the 8th of January 2017 accompanied by hot conditions (Weathersa.co.za, 2017).

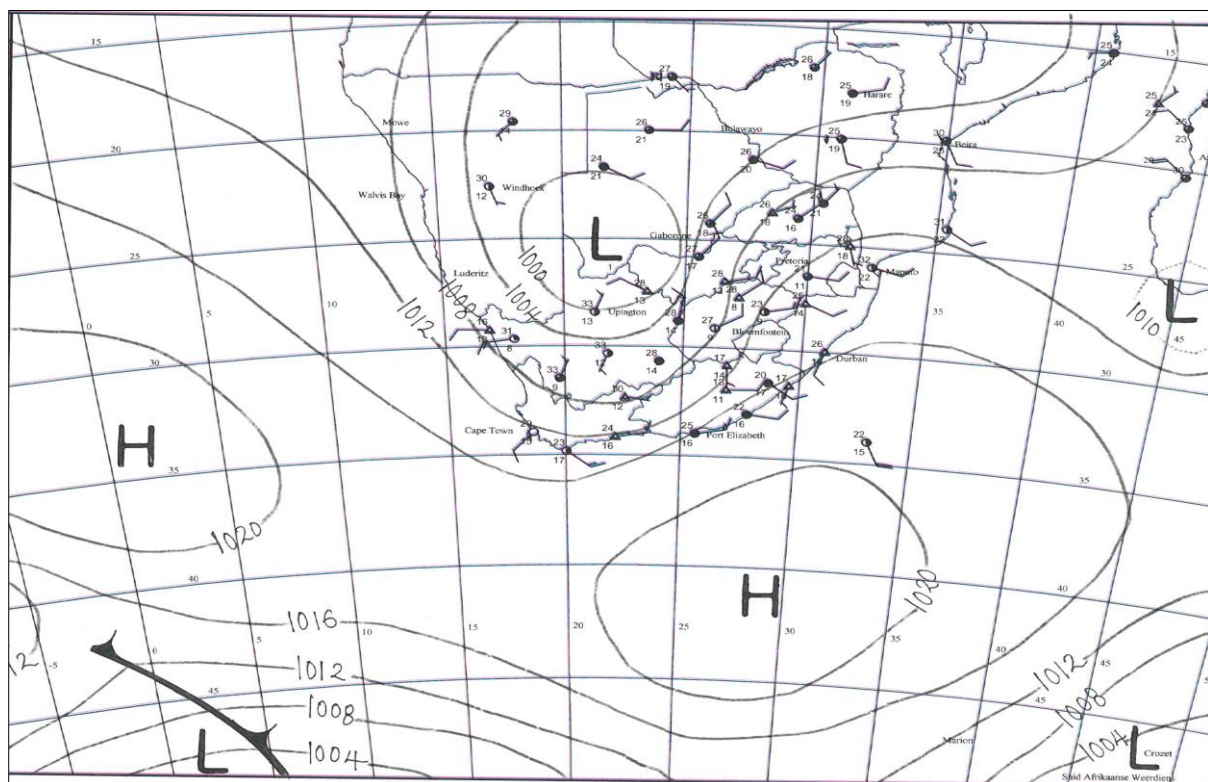


Figure 4.31: Synoptic chart showing the dominant circulation patterns for the January 2017 sampling period (10/01/2017) (Weathersa.co.za, 2017)

4.4.6. April 2017

The April 2017 sampling period began with a surface trough over the central interior with anticyclones on the west and east of the country (Weathersa.co.za, 2017). On the 04th of April 2017, a cold front was located on the southern part of the country with an anticyclone behind it. The following day a cold front moved towards the south-west coast together with the anticyclone. A surface trough extended over the western interior with an anticyclone south of the country on the 6th of April 2017. The surface trough persisted on the 07th, 8th, 9th and 11th of April with an upper air trough

over the western part of the country and an anticyclone over the south-eastern part as shown in Figure 4.24 (Weathersa.co.za, 2017). On the 10th of April, the surface trough moved to the central interior, with a low around the south-east coast and an anticyclone ridging from west of the country. The same conditions as the 10th of April continued on the last day of sampling with an associated cold front. The circulation influenced partly cloudy, cool to warm and hot conditions associated with light rain along the south-west coast from the 03rd until the 05th of April 2017 (Weathersa.co.za, 2017). There were cloudy, warm to hot conditions with rain over most parts of the country from the 06th of April until the end of the sampling period, with heavy rain in Mpumalanga on the 10th and no rain in Western Cape on 11th of April. The rain was mostly influenced by the presence of the surface troughs. There were very hot conditions in Northern Cape, North West, Eastern Cape and Kwazulu-Natal during the sampling period (Weathersa.co.za, 2017).

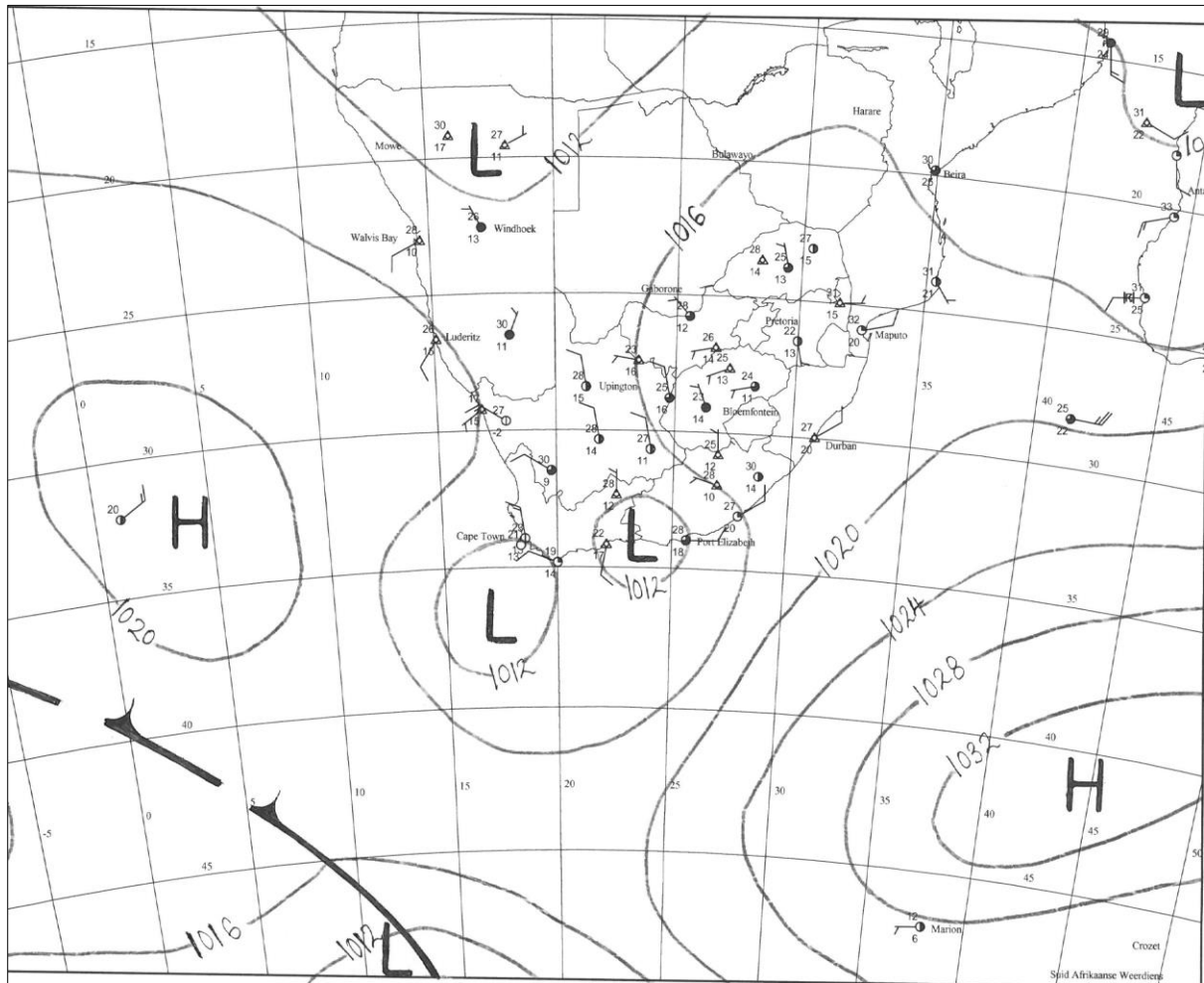


Figure 4.32: Synoptic chart showing the dominant circulation patterns for the April 2017 sampling period (09/04/2017) (Weathersa.co.za, 2017)

4.4.7. July 2017

The July 2017 sampling period began with the presence of a cold front east of the country and a high ridging behind it together with a trough over the interior (Weathersa.co.za, 2017). The weather conditions were therefore cloudy, cool and warm over the country with light rain in Gauteng, Limpopo, North West and Eastern Cape provinces. Throughout the sampling period, anticyclones dominated the weather over the country on the 05th until the 07th of July and also towards the end of the sampling period from the 10th until the 13th of July where they were ridging from west and south-west over the country (Figure 4.25) (Weathersa.co.za, 2017). The weather conditions influenced by the anticyclones were partly cloudy to sunny, cool to warm conditions over the country with hot conditions in Northern Cape and light rain in Limpopo, Mpumalanga, Western Cape, Eastern Cape and Kwazulu-Natal province. On the 04th and the 12th of July, surface troughs were on the western interior and extended over central interior respectively. The surface trough caused partly cloudy to cloudy, cold to cool conditions over the country with light rain in Mpumalanga and Gauteng on the 04th and isolated showers over western Cape and Eastern Cape on the 12th of July. The southern parts of the country were affected by approaching cold front on the 08th and 09th of July, which influenced cold to cool conditions over western Cape as shown in Figure 4.25.

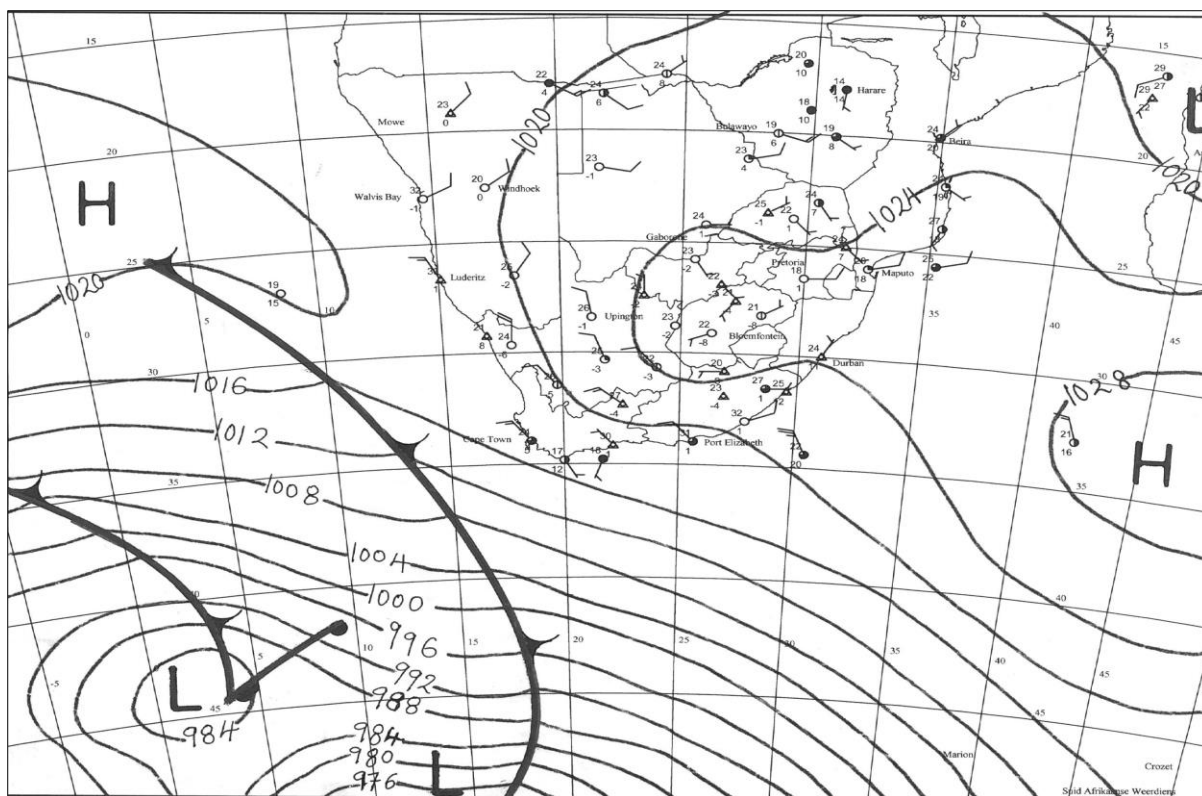


Figure 4.33: Synoptic chart showing the dominant circulation patterns for the July 2017 sampling period (06/07/2017) (Weathersa.co.za, 2017)

4.4.8. October 2017

At the beginning of the October 2017 sampling period, a cold front was located south-west of the country and on the second day of sampling another cold front was over the Eastern cape province with a high pressure ridging behind it (Figure 4.26). The conditions were partly cloudy to cloudy, cool to warm and hot over the country with isolated showers and thundershowers over most parts of the country except Limpopo and Mpumalanga. There were also heavy rains in the eastern cape on the 04th of October which were associated with the cold front. There was a surface trough and associated deep upper-air trough over the central interior of the country on the 05th of October. The surface trough persisted on the 06th and the 07th with anticyclones west and east of the country. The surface trough influenced partly cloudy to cloudy and cool to warm conditions with thundershowers and light rain over the eastern half of the country together with heavy rain in Limpopo. The remainder of the sampling period was dominated by cold fronts east and south-east of the country with associated anticyclones ridging behind. The conditions were partly cloudy to cloudy and cool over the country, while it was very cold in Northern Cape, Eastern

Cape and North West. There were isolated showers and light rain over most part of the country except Western cape and North West while there were heavy rains in Kwazulu-Natal.

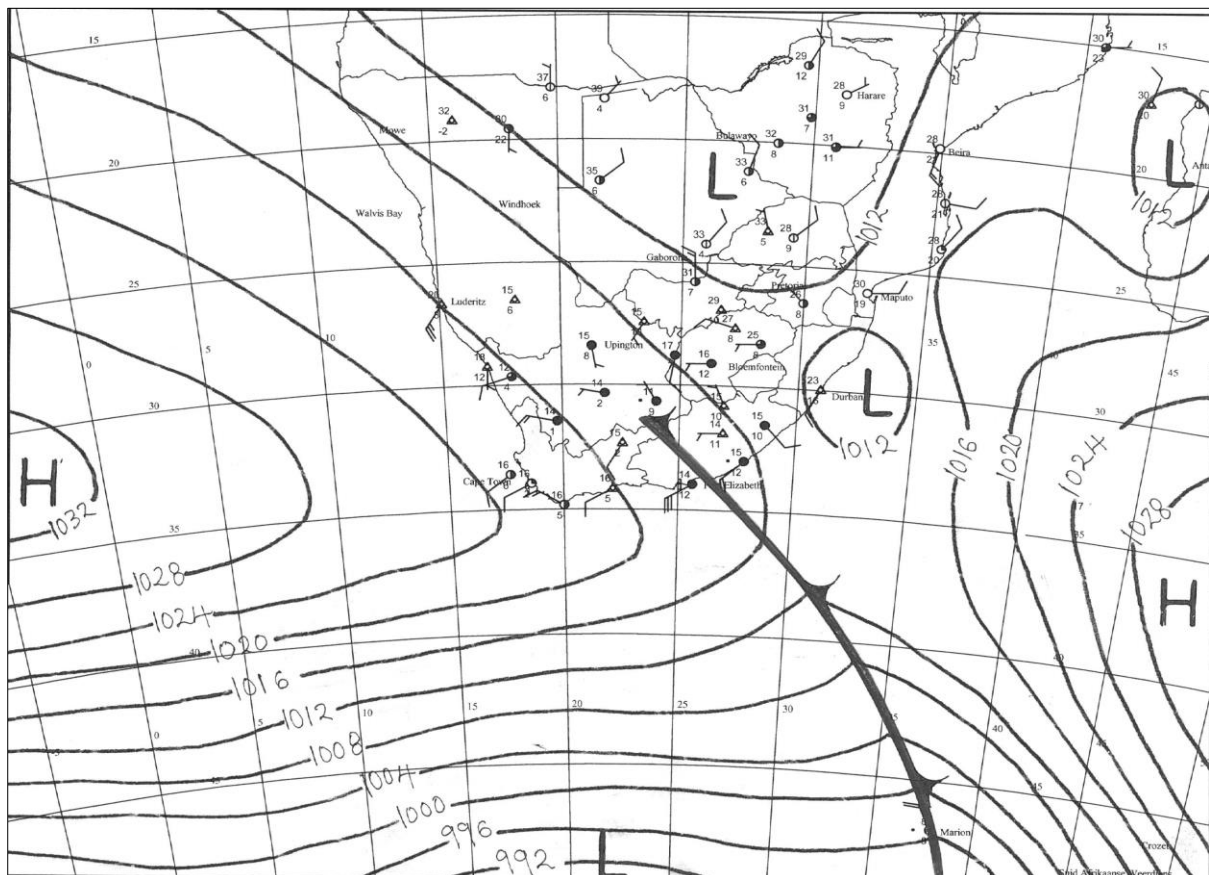


Figure 4.34: Synoptic chart showing the dominant circulation patterns for the October 2017 sampling period (04/10/2017) (Weathersa.co.za, 2017)

4.4.9. January 2018

During the January 2018 sampling period, surface troughs were most dominant over the country. At the beginning of the sampling period the surface trough was extended over the western interior with associated anticyclone on the eastern part of the country. The surface trough persisted from the 11th to the 12th then moved to the central interior on the 13th and persisted until the 14th of January 2018 (Figure 4.27). The surface trough influenced partly cloudy to cloudy and cool to warm or hot conditions with isolated showers in places over the entire country except Gauteng

and Western Cape. On the 13th and 14th of January, there were warm to hot conditions with light rain over North West, Free State, Eastern Cape and Kwazulu-Natal. On the 15th of January 2018, there was a cold front over Kwazulu-Natal, with an anticyclone ridging behind it and a surface trough over the eastern interior. A surface trough extended over the western interior with an anticyclone east of the country and persisted for the next 5 days until the end of the sampling period. The conditions were partly cloudy to cloudy and warm to hot conditions with light rain over North West, Free State, Eastern Cape and Kwazulu-Natal province. There were very hot to extremely hot conditions in Northern Cape, Limpopo, Mpumalanga and Kwazulu-Natal.

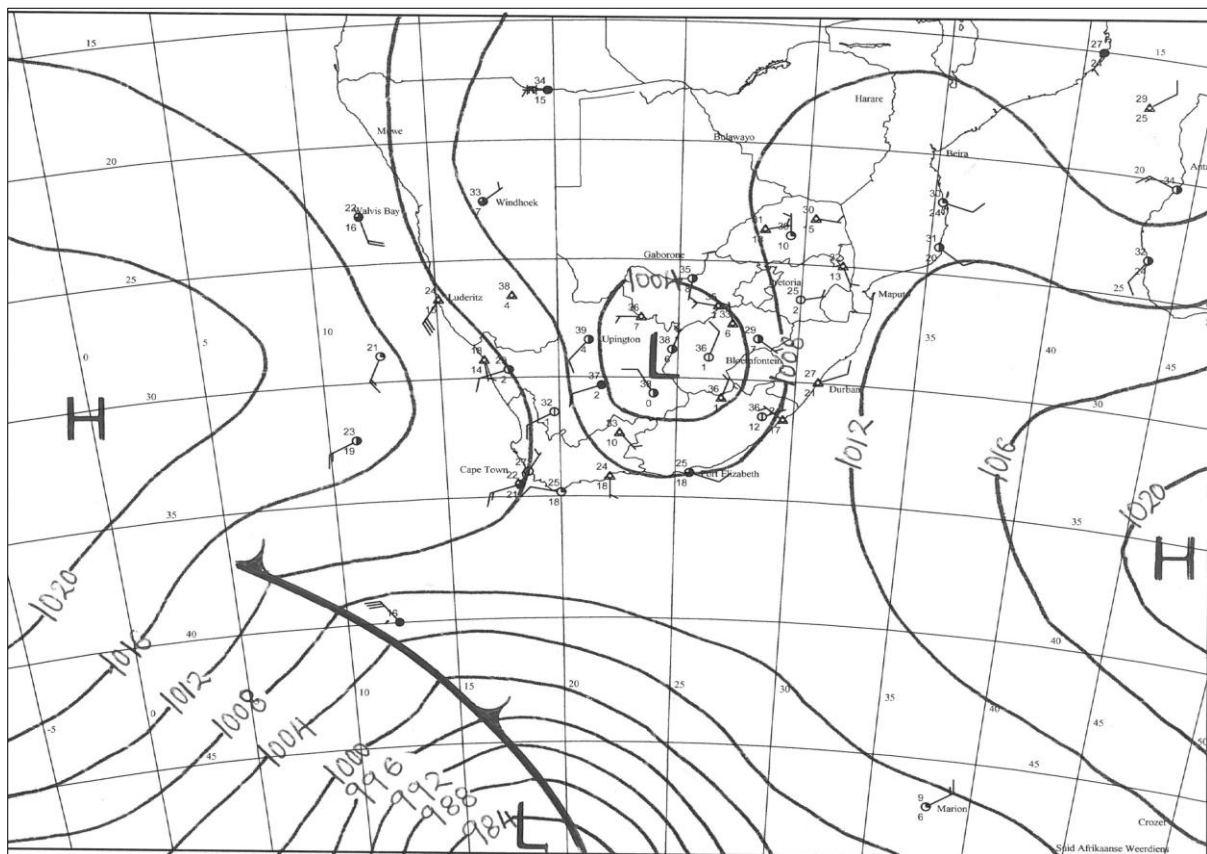


Figure 4.35: Synoptic chart showing the dominant circulation patterns for the January 2018 sampling period (2018/01/14) (Weathersa.co.za, 2017).

Although the section focused on the regional circulation patterns over the specified period, there is a need to discuss in detail the conditions over the study site. The synoptic circulations discussed have an influence on the climatic conditions that prevailed during the various sampling periods. The following section will highlight the climatic conditions that were recorded at all the monitoring sites.

4.5. Weather Conditions over Study Site

4.5.1. Alberton

The climatic conditions recorded around the Alberton station for the various sampling periods are presented in Table 4.28. The average daily maximum temperature was highest in January 2018 with a reading of 29 °C and the lowest was 16 °C measured in June 2016.

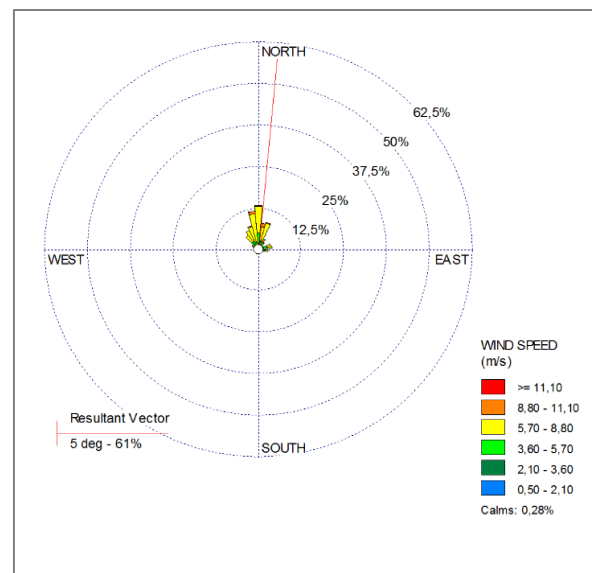
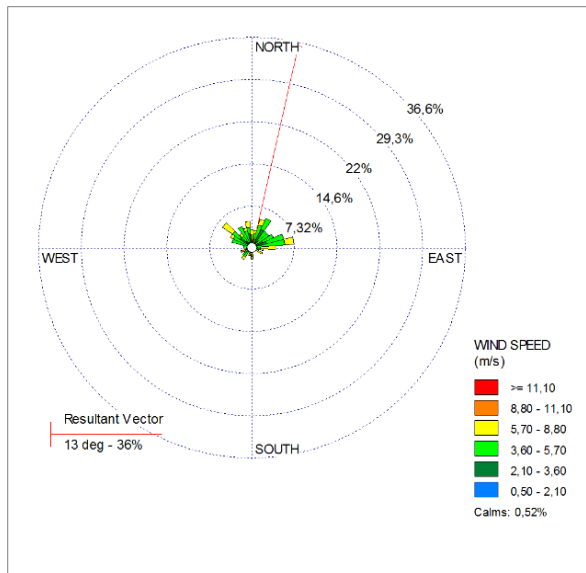
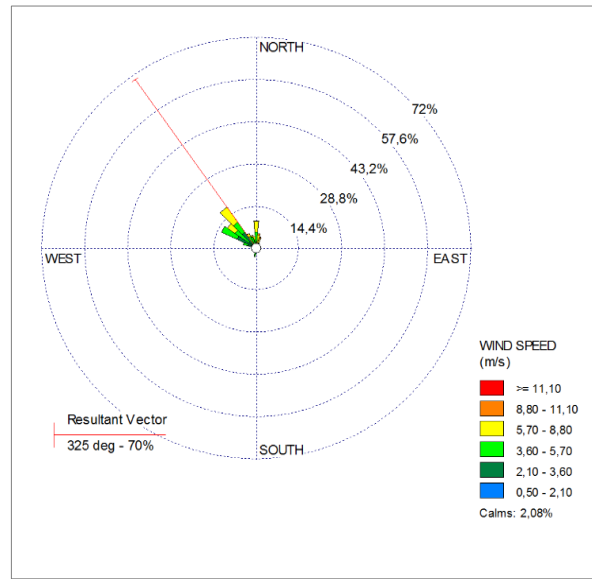
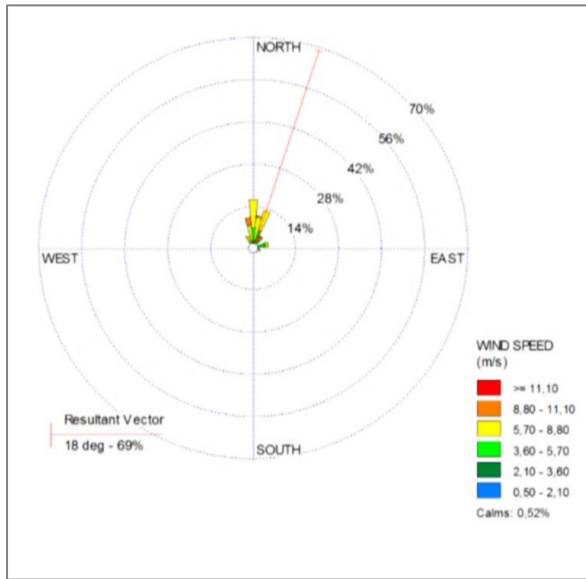
Table 4.10: Weather conditions over Alberton Site

	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	28	27	16	25	23	25	19	21	29
Average Daily Minimum Temperature	13	15	7	11	15	14	10	10	15
Average Pressure	836.69	834.15	838.55	834.69	832.44	837.83	838.89	831.7	833.7
Average Wind direction	142.50	201.25	252.50	239.74	136.37	196.67	260.10	212	14.,28
Average Wind speed	5.16	4.55	4.03	6.13	4.91	3.14	3.74	4.8	4.2

The highest average wind speed was 6.13 m/s recorded during October 2015 sampling period and the lowest was 3.14 m/s recorded during the April 2017 sampling period. The wind direction was dominantly from the southeast direction during the October 2015 and January 2017 sampling periods. During the February 2016, April 2017 and October 2017 periods, the dominant wind direction was south-southwest. In June and October 2016 the wind was from the west-southwest direction. Figure 4.36, 4.37 and 4.38 illustrate the wind direction and speed over the different sampling periods at the Alberton site.

October 2015

February 2016

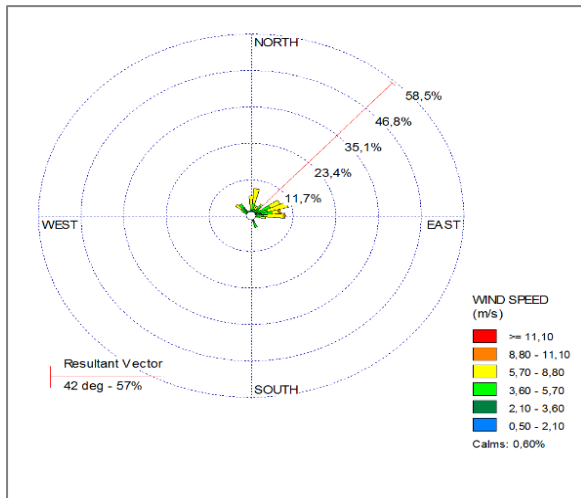


June 2016

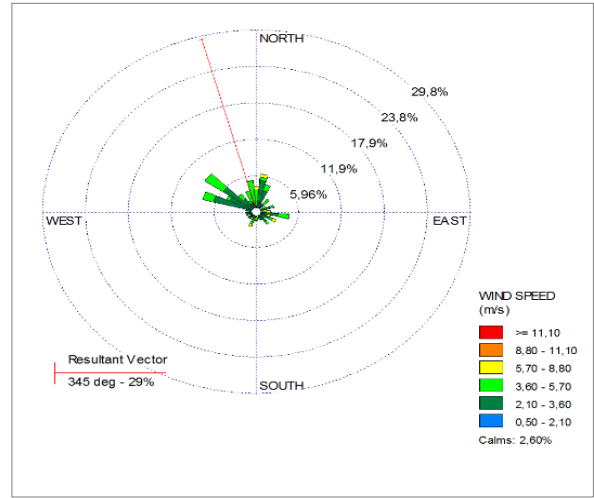
October 2016

Figure 4.36: Windroses for Alberton Depot during the October 2015, February 2016, June 2016 and October 2016 sampling periods.

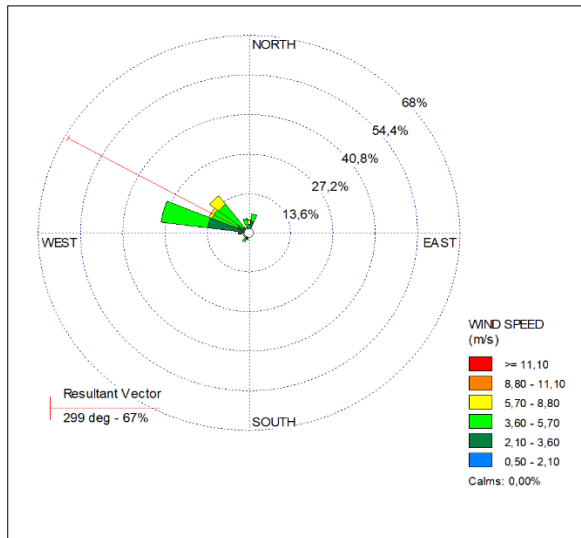
January 2017



April 2017



July 2017



October 2017

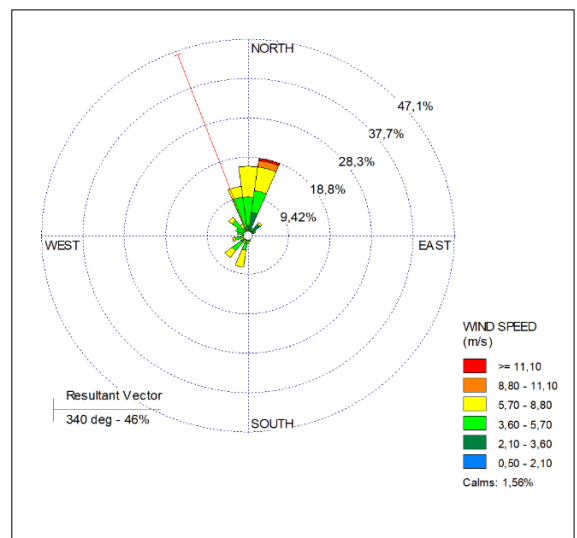


Figure 4.37: : Windroses for Alberton Depot during the January 2017, April 2017, July 2017 and October 2017 sampling periods.

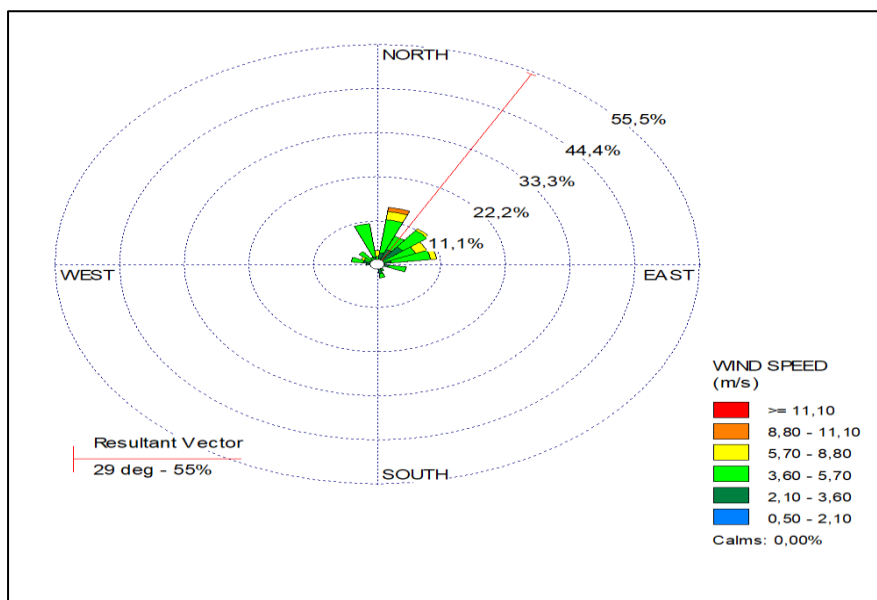


Figure 4.38: Windrose showing wind speed and direction at Alberton depot for the January 2018 sampling period.

4.5.2. Witbank

The average climatic conditions around the Witbank depot in Emalahleni showed variations with the different seasons. The conditions recorded at the Witbank weather station are showed in Table 4.29. The average daily maximum temperature was highest in January 2018 with 29 °C and lowest in June 2016 with a value 18 °C. The average daily minimum temperature was highest in the February 2016 while the lowest was recorded in June 2016 and July 2017.

Table 4.11: Weather conditions over Witbank site

	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	26	27	18	25	24	27	20	23	29
Average Daily Minimum Temperature	12	15	6	12	14	13	6	11	14
Average Pressure	851.75	848.20	746.23	849.16	846.40	851.75	853.89	845.8	847.6
Average Wind direction	112.50	203.75	15.00	210.47	142.98	153.07	179.06	204	139.22
Average Wind speed	2.94	3.25	1.18	4.35	3.90	2.19	2.34	3.2	3.1

The wind speed was strongest in October 2016 at 4.35 m/s and weaker in June 2016 at 1.18 m/s. The dominant wind direction was south-southwest which prevailed in February 2016 and October 2016 with direction ranges between 203.75 and 210.47. In October 2016 the wind direction was east-southeast, while in June 2016 it was north-northeast, in February 2017 the wind direction was southeast and in April 2017 it was south-southeast. Figure 4.39, Figure 4.40 and Figure 4.41 shows the prevailing wind speed and direction at Witbank depot during the different sampling periods.

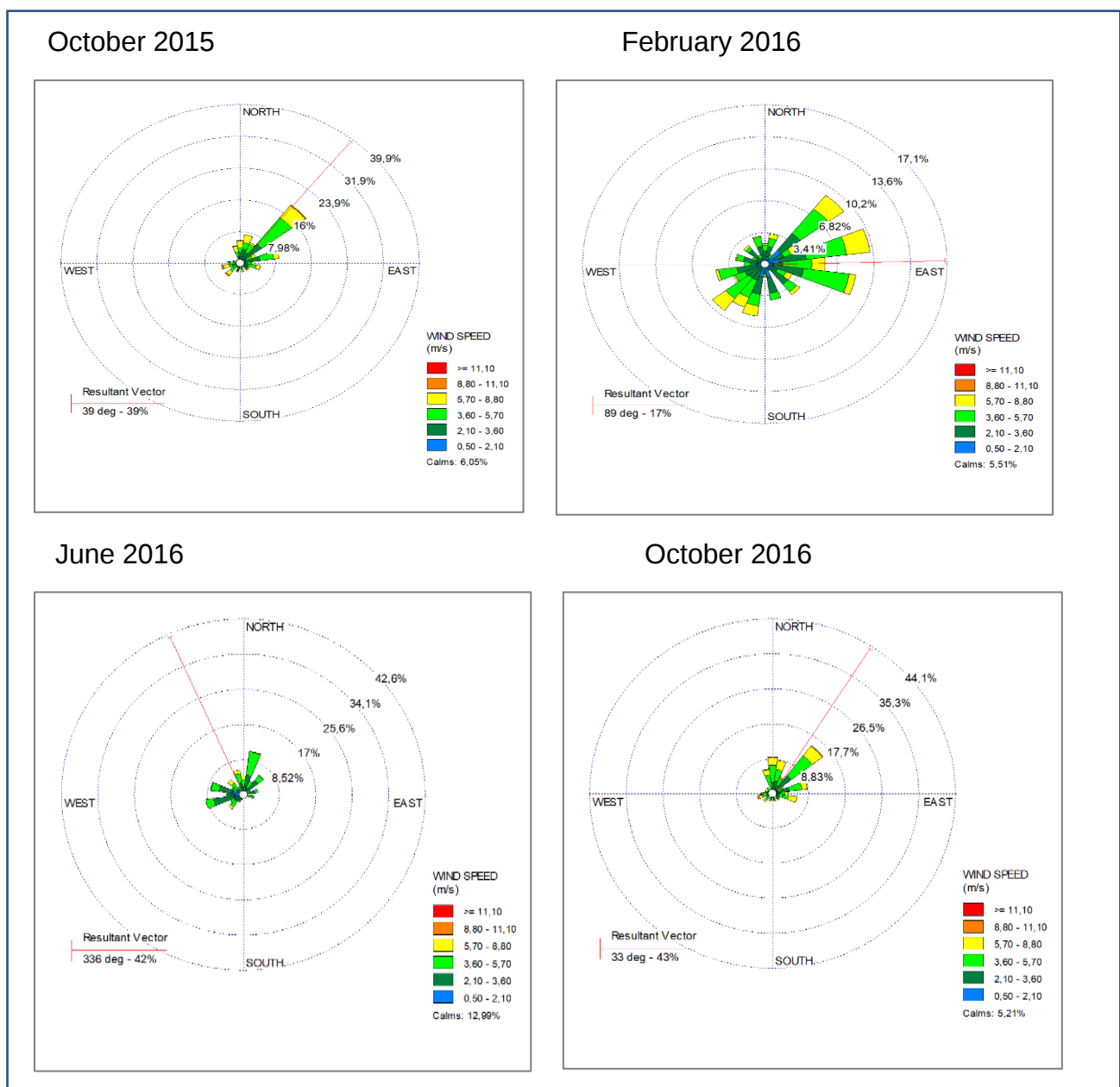
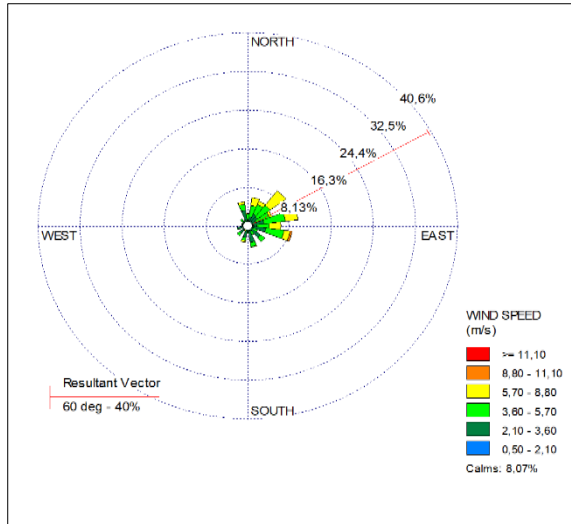
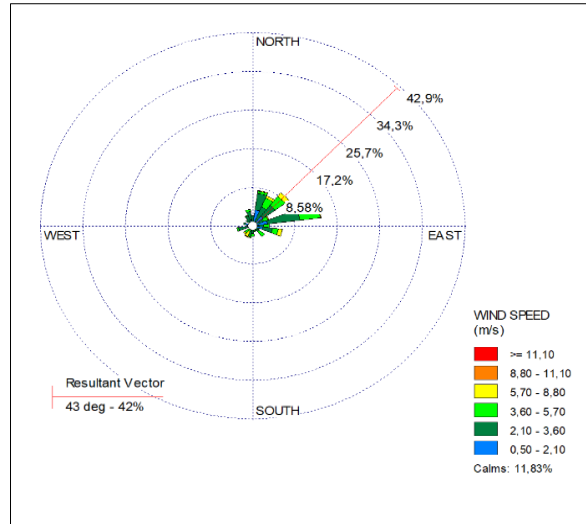


Figure 4.39: Windroses indicating wind speed and direction over Witbank depot for the October 2015, February 2016, June 2016 and October 2016 sampling periods.

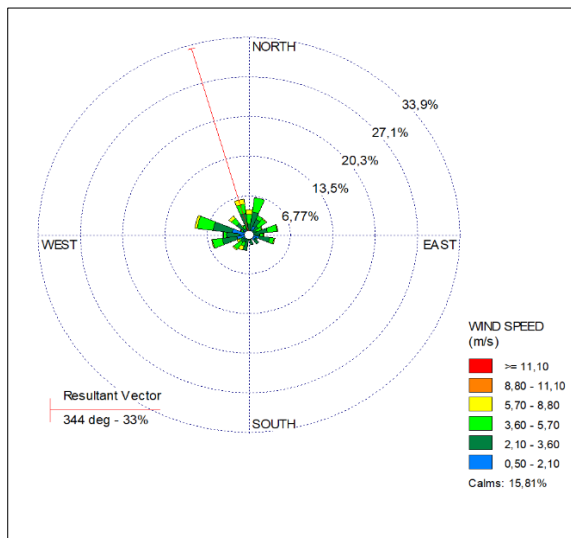
January 2017



April 2017



July 2017



October 2017

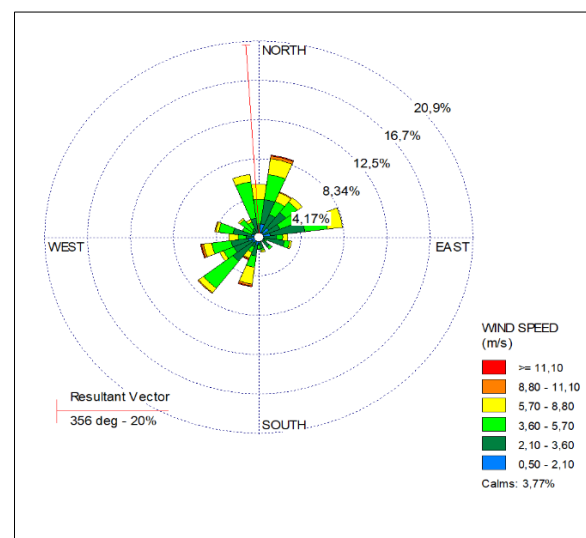


Figure 4.40: Windroses indicating wind speed and direction over Witbank depot for the January 2017, April 2017, July 2017 and October 2017 sampling periods.

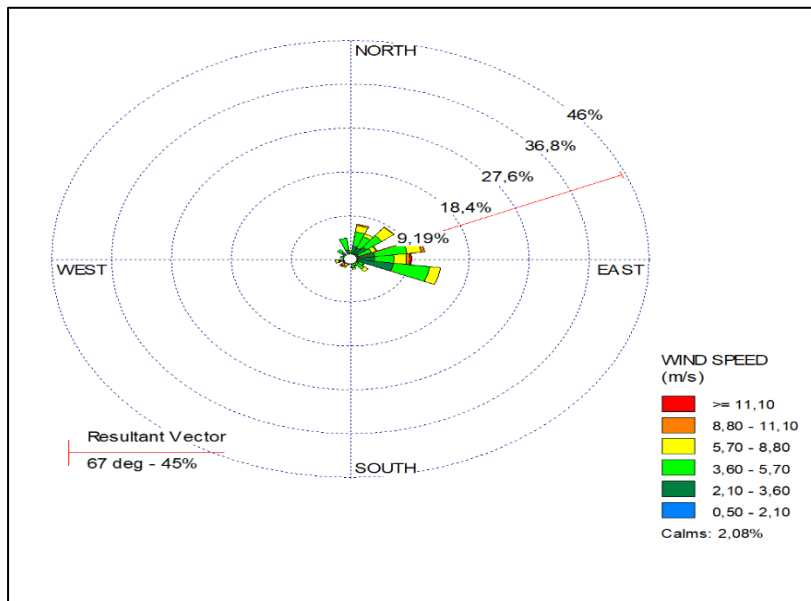


Figure 4.41: Windrose indicating wind speed and direction over Witbank depot January 2018 sampling periods.

4.5.3. Kroonstad

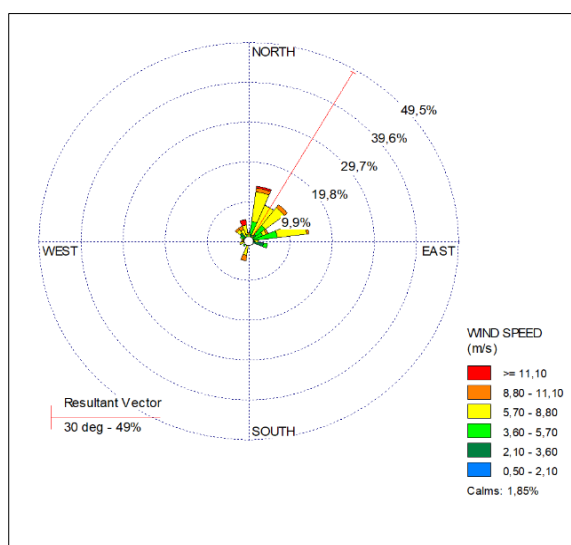
The average daily maximum temperatures were slightly high in Kroonstad with the lowest temperature at 20 °C in June 2016 and the highest at 33 °C in February 2016 and January 2018. The average daily minimum temperatures ranged between 5 °C and 17 °C. Table 4.30 shows the weather conditions over the Kroonstad site.

Table 4.12: Weather conditions over Kroonstad site

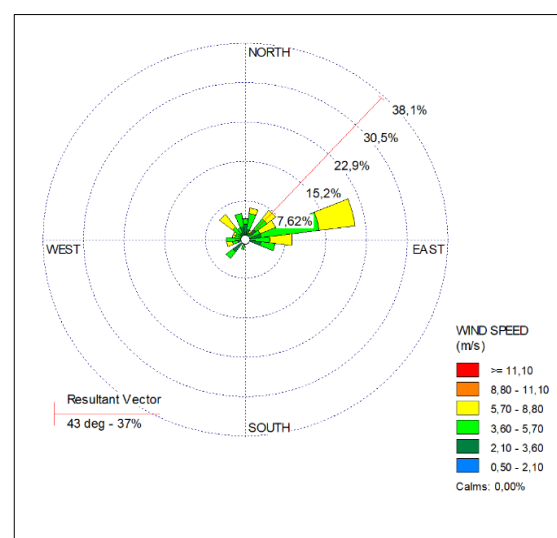
	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	30	33	20	28	26	23	22	23	33
Average Daily Minimum Temperature	14	16	5	8	17	14	5	9	16
Average Pressure	861.19	859.14	865.22	857.96	857.94	860.68	864.36	856.9	859.2
Average Wind direction	72.50	48.75	64.44	171.15	143.15	166.00	175.21	171	116.25
Average Wind speed	6.46	5.03	2.80	4.30	4.10	2.74	3.46	3.7	4.3

The average wind speed ranged between 2.74 m/s and 6.46 m/s with higher speeds during the October 2015 and February 2016 periods (Figure 4.42). The most dominant wind direction the NE direction during the February 2016 sampling period. The site mostly experienced wind from the south direction which prevailed in October 2016, July 2017 and October 2017 (Figure 4.43). Wind from the southeast and south-southeast direction were experienced in January 2017 and April 2017 respectively.

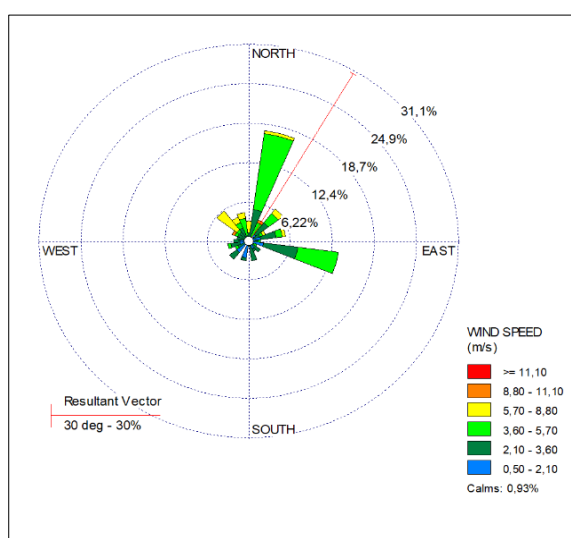
October 2015



February 2016



June 2016



October 2016

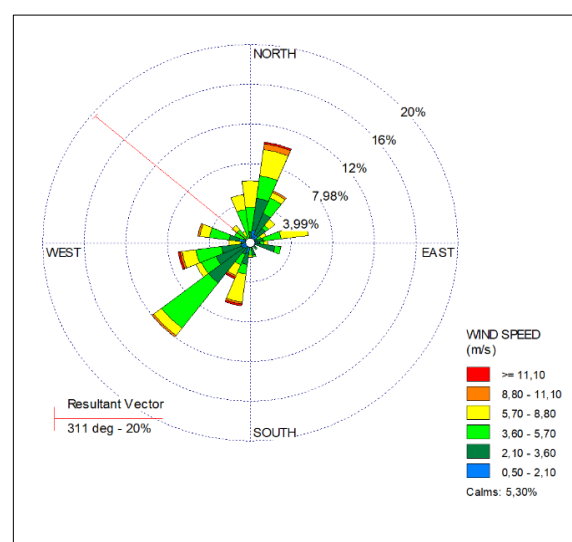


Figure 4.42: Windroses for Kroonstad Depot during the October 2015, February 2016, June 2016 and October 2016 sampling periods.

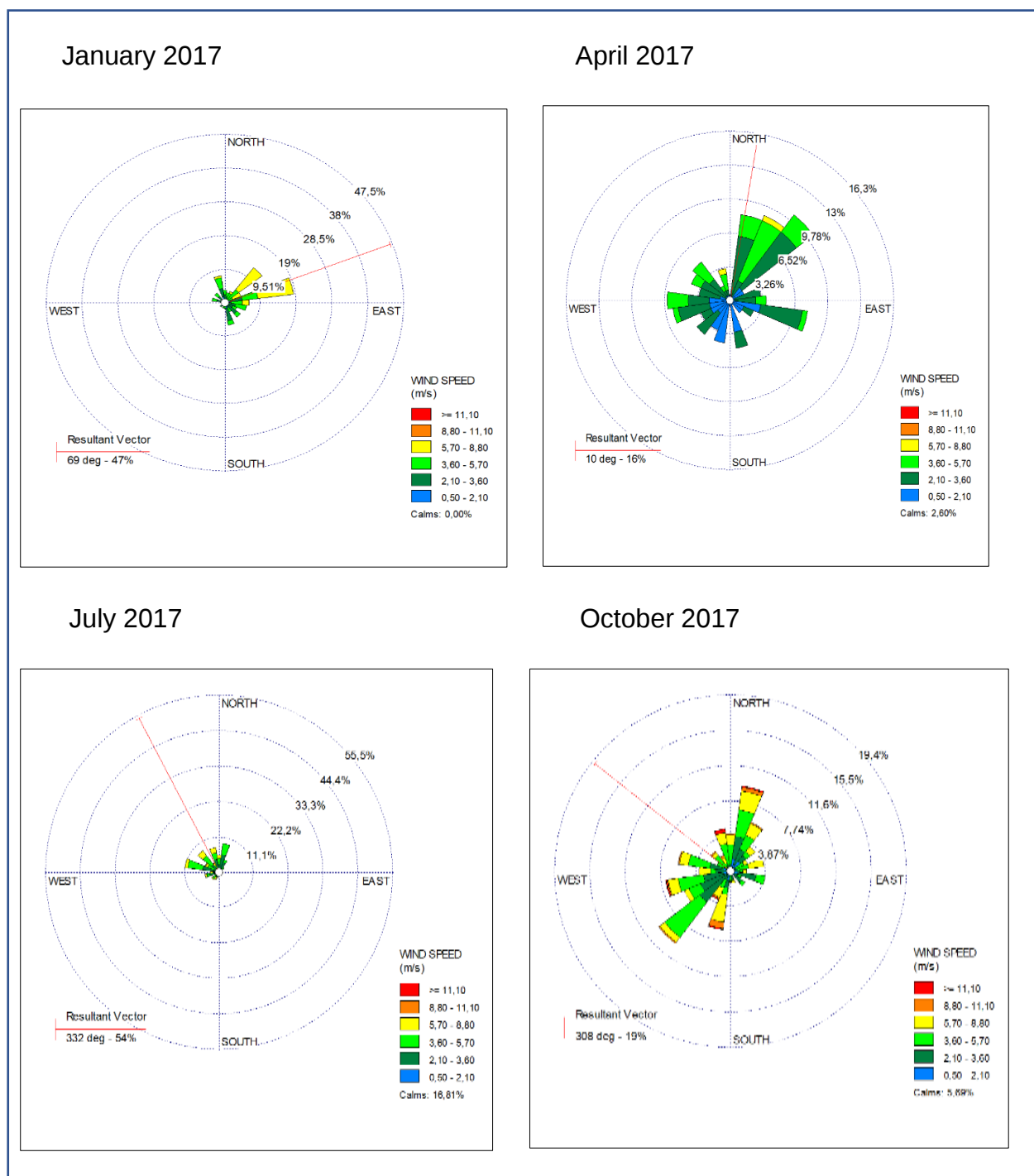


Figure 4.43: Windroses for Kroonstad Depot for the January 2017, April 2017, July 2017 and October 2017 sampling periods.

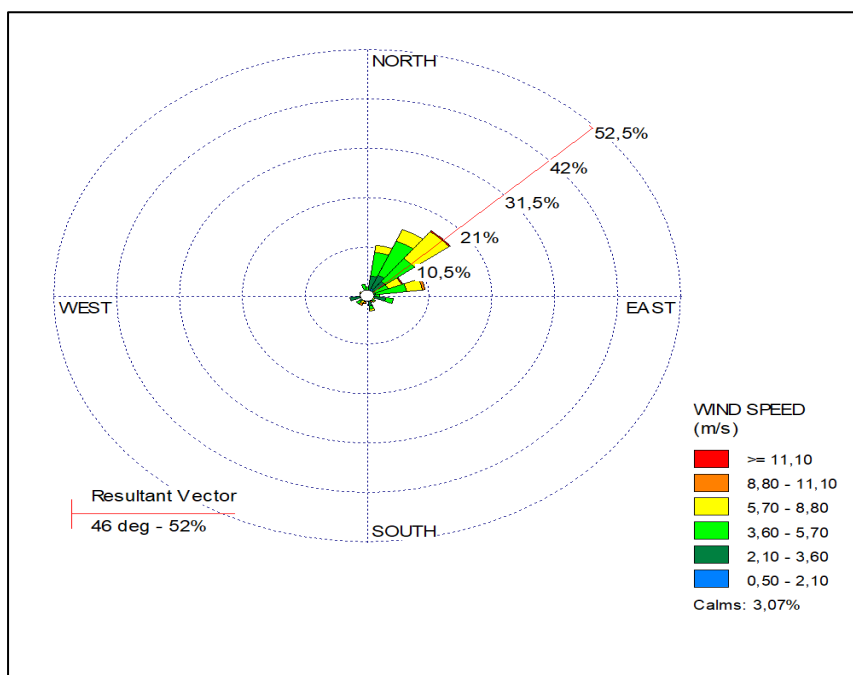


Figure 4.44: Windrose showing the wind speed and direction at Kroonstad site during the January 2018 sampling period.

4.5.4. Rocky's Drift

The average daily maximum temperature was highest in February 2016 and January 2018 while the lowest was 23 °C in July 2017 sampling period (Table 4.31). The average daily minimum temperatures were between 11.10 °C and 18.74 °C. The prevailing wind was dominantly from the east, east-southeast, southeast and southerly direction. The average wind speed was strongest during the October 2016 sampling period at 3.53 m/s and lowest in June 2016 at 1.16 m/s.

Table 4.13: Weather conditions over Rocky's Drift site

	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	25	29	25	25	25	27	23	24	29
Average Daily Minimum Temperature	16	19	12	11	17	17	11	14	16
Average Pressure	923.27	919.91	922.15	919.41	918.29	921.55	925.18	916.8	919.4

Average Wind direction	92.86	128.75	177.50	108.33	116.61	86.20	154.11	110	107.26
Average Wind speed	1.36	1.25	1.16	3.53	2.63	2.55	3.48	3	3.1

The wind speed was strongest in October 2016 at 3.53 m/s and lowest in June 2016 at 1.16 m/s. The most dominant wind direction was ESE which prevailed in October 2016, January 2017 and October 2017 with direction ranging between 108.33 and 116.61. During the October 2015 and April 2017 sampling period the wind was from the easterly direction. In February 2016, June 2016 and October 2017 the wind direction was from southeast, south, and south-southeast respectively. Figure 4.45, 4.46 and 4.47 show the variations in wind speed and direction at Rocky's Drift depot during the different sampling periods.

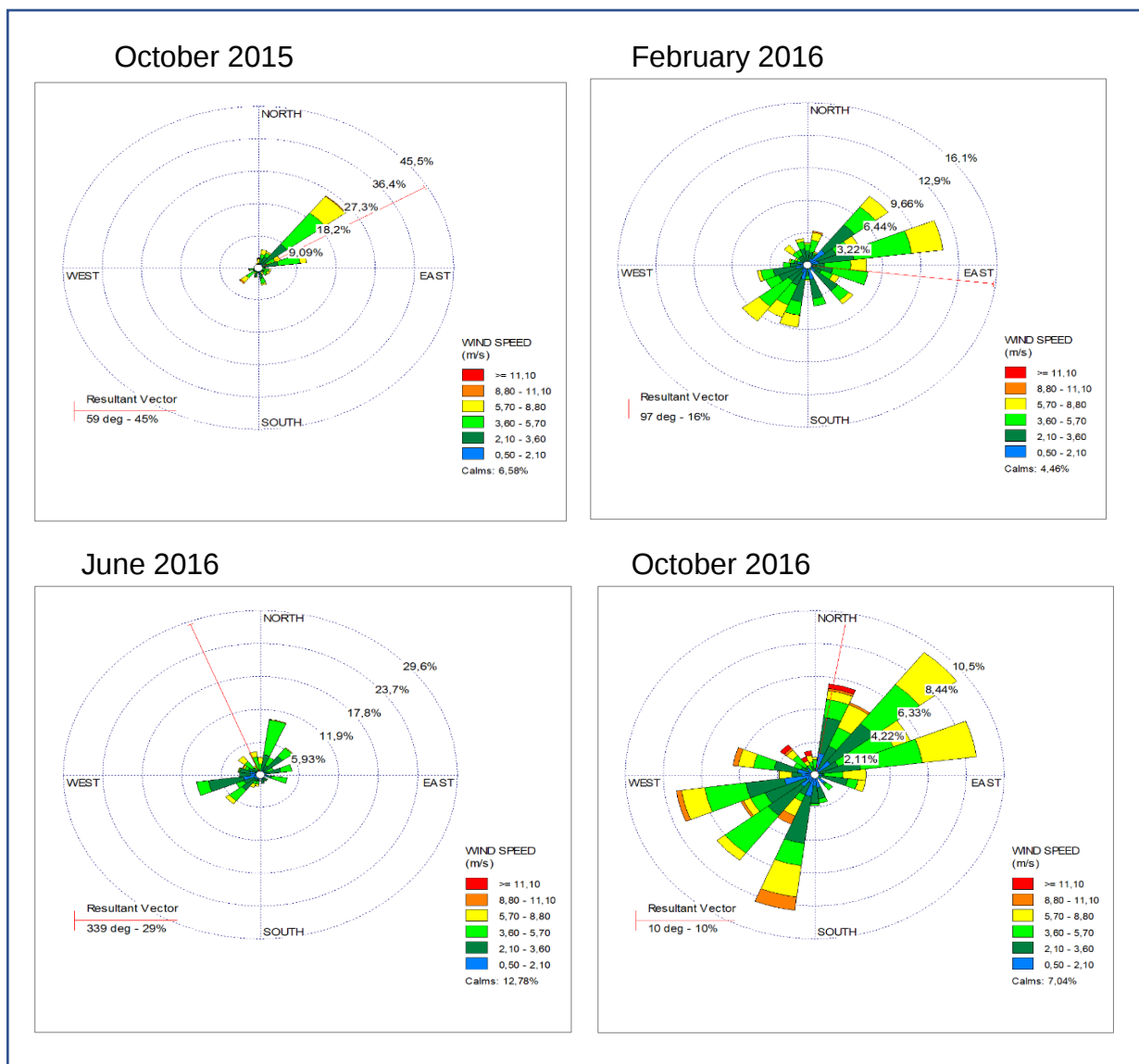


Figure 4.45: Windroses indicating wind speed and direction over Rocky's Drift depot for the October 2015, February 2016, June 2016 and October 2016 sampling periods.

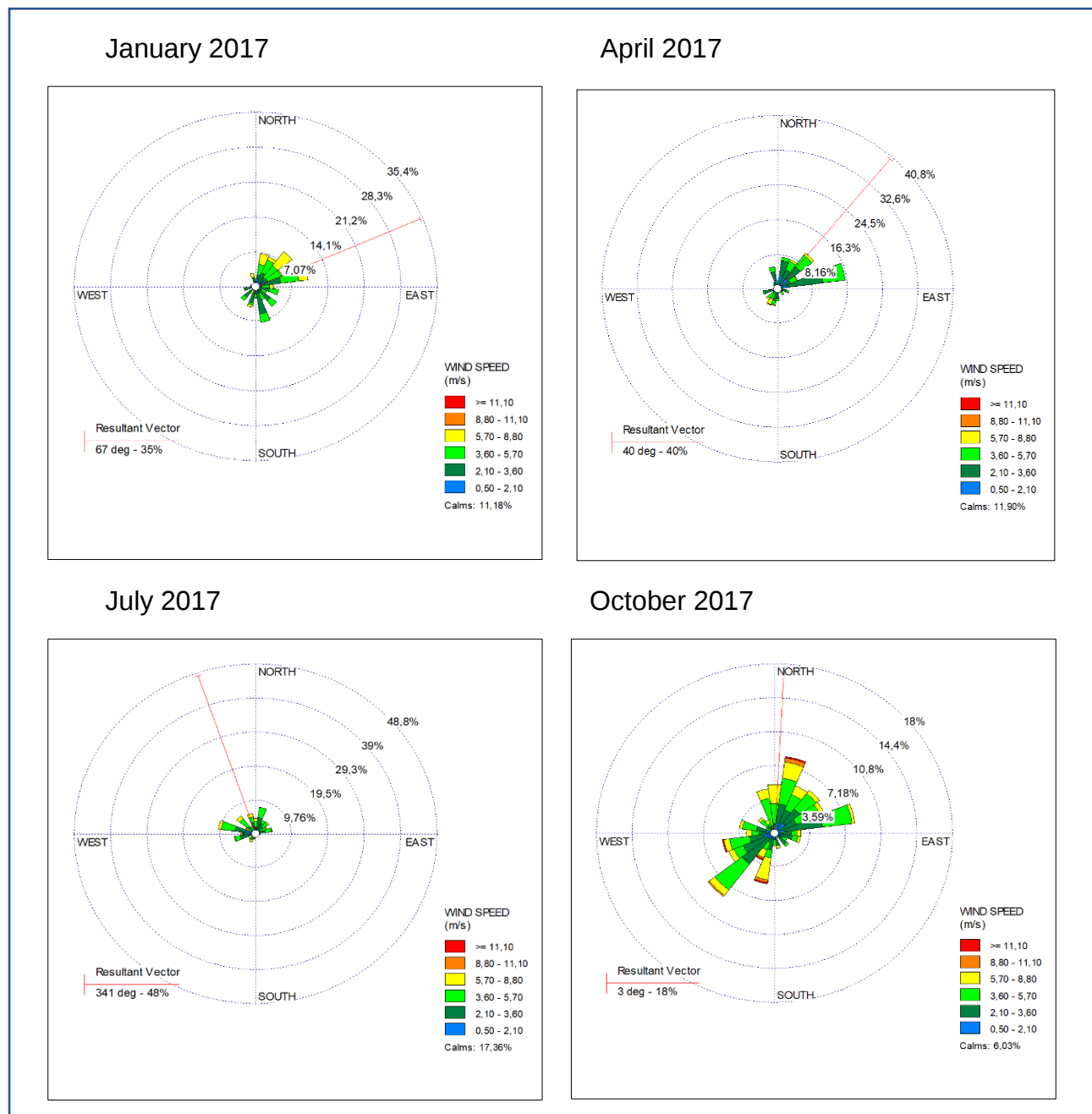


Figure 4.46: Windroses indicating wind speed and direction over Rocky's Drift depot for the January 2017, April 2017, July 2017 and October 2017 sampling periods.

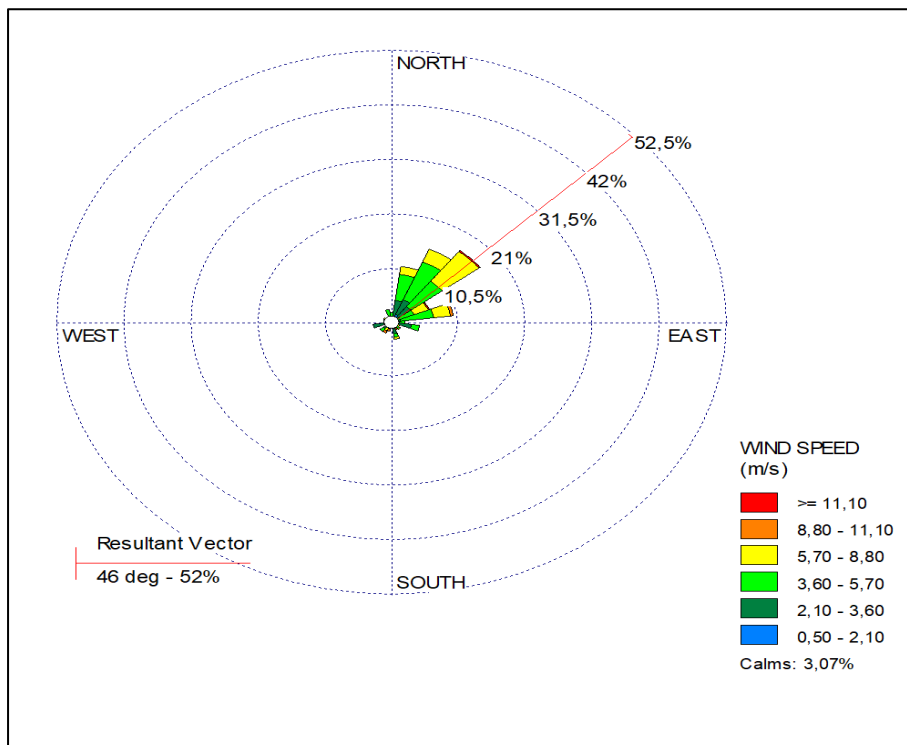


Figure 4.47: Windrose indicating wind speed and direction over Rocky's Drift depot for the January 2018 sampling period.

4.5.5. Island View

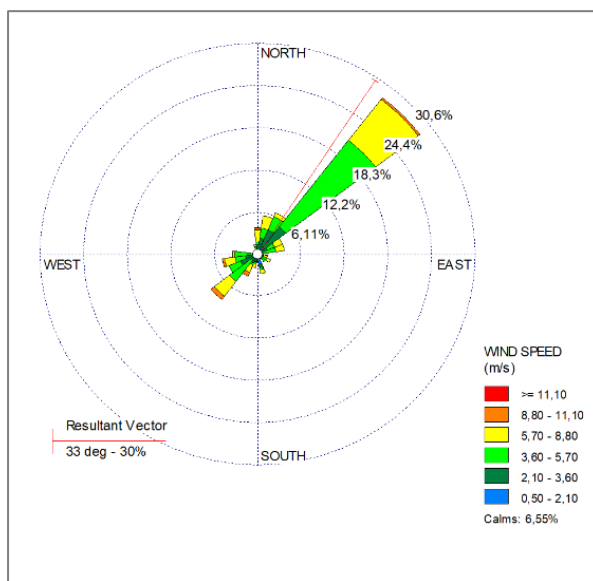
At the Island View depot, the average daily maximum temperatures were slightly high ranging between 21 °C and 29 °C. The average daily minimum temperatures ranged between 12 °C and 21 °C as presented in Table 4.32.

Table 4.14: Weather conditions over Island View site

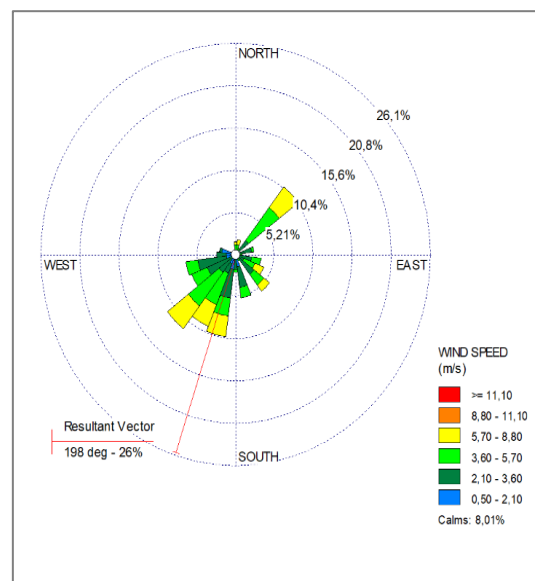
	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	25	28	23	22	26	27	24	21	29
Average Daily Minimum Temperature	18	20	20	14	20	20	12	15	21
Average Pressure	1019.81	1013.59	1021.93	1016.00	1012.90	1016.80	1019.90	1014	1013.1
Average Wind direction	88.75	180.00	107.78	109.68	108.63	114.88	73.28	157	76.96
Average Wind speed	3.21	3.20	1.61	3.33	2.80	3.06	1.41	3.4	3.9

The most dominant wind was from the east-southeast direction experienced during the June 2016, October 2016, January 2017 and April 2017. The average wind direction was ranging between 1.41 m/s and 3.9 m/s, and was strongest in January 2018 and weaker in July 2017. The average wind speed was above 3 m/s for majority of the sampling periods indicating it was light to gentle (Figure 4.48, 4.49 and 4.50).

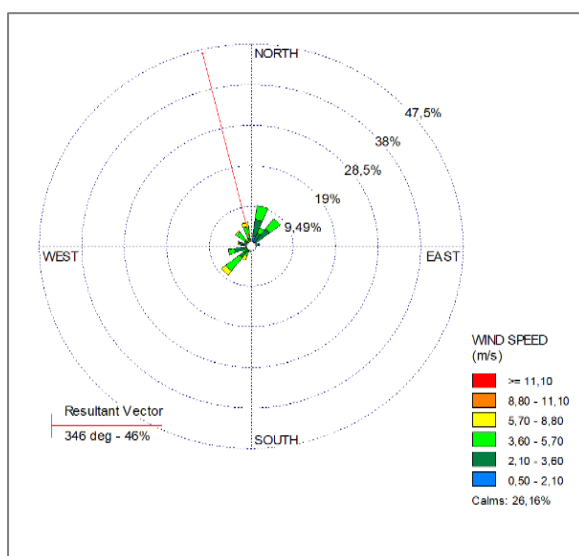
October 2015



February 2016



June 2016



October 2016

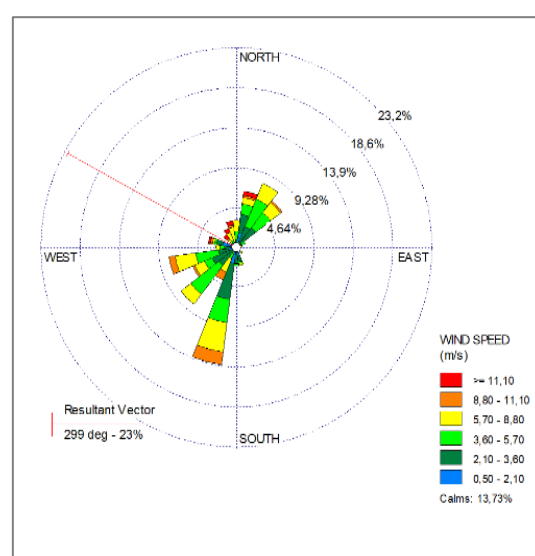


Figure 4.48: Windroses indicating wind speed and direction over Island View depot for the October 2015, February 2016, June 2016 and October 2016 sampling periods.

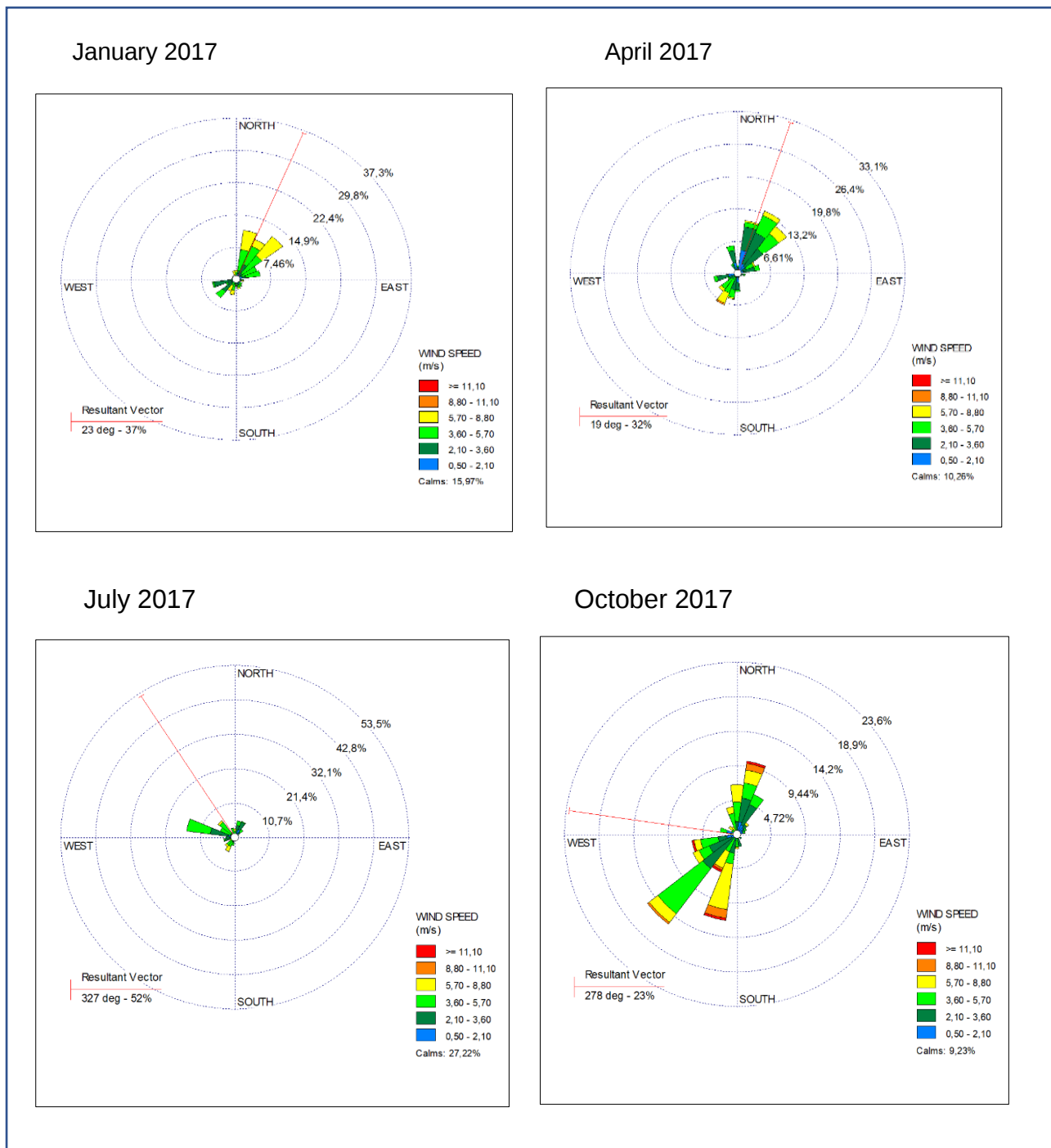


Figure 4.49: Windroses showing the wind speed and direction over Island View depot for the January 2017, April 2017, July 2017 and October 2017 sampling period.

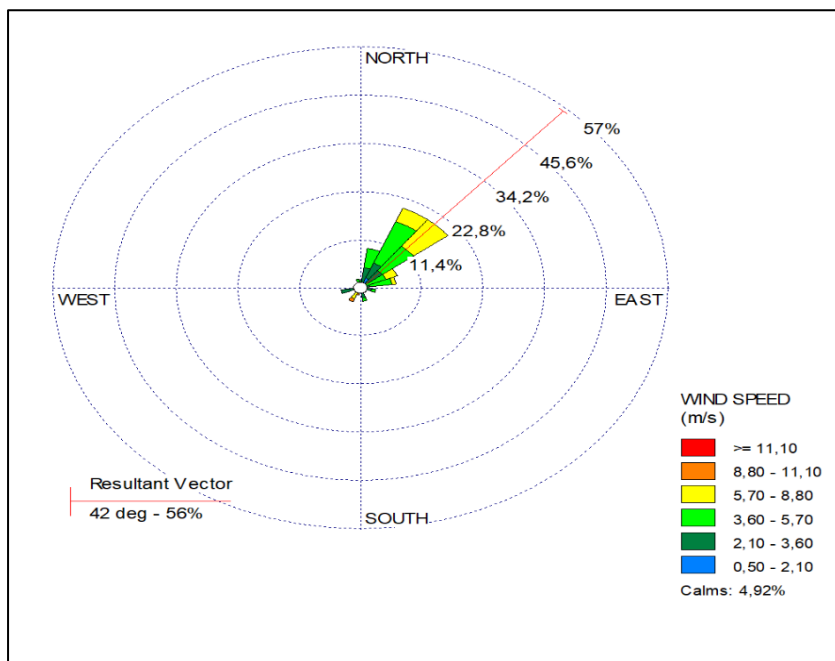


Figure 4.50: Windrose indicating wind speed and direction over Island View depot for the January 2018 sampling period.

4.5.6. Port Elizabeth

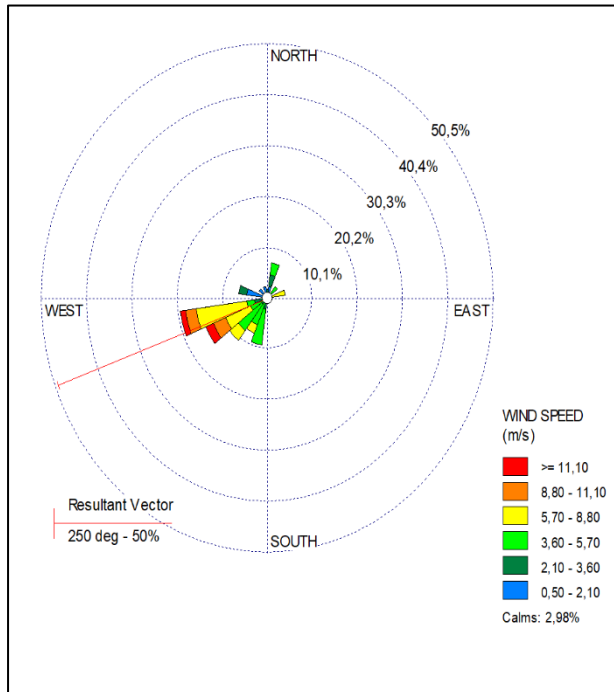
The climatic conditions recorded at the Port Elizabeth depot during the passive sampling program are presented in Table 4.33. The average daily maximum temperature ranged between 21 °C and 27 °C, while the average daily minimum temperature was ranging between 9 °C and 19 °C. The most dominant wind was from the southeast direction and the least dominant was from the south-southeast direction. The average wind speed was between 2.28 m/s and 7.53 m/s.

Table 4.15: Weather conditions over Port Elizabeth site

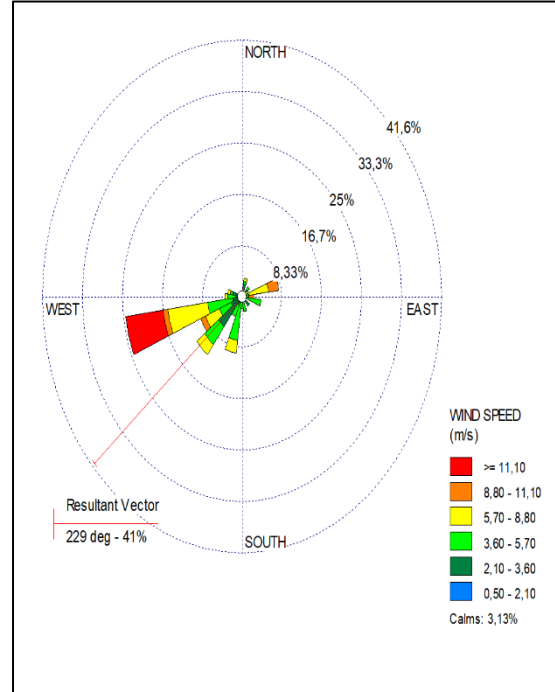
	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017	October 2017	January 2018
Average Daily Maximum Temperature	23	27	21	21	26	25	25	19	27
Average Daily Minimum Temperature	13	18	9	11	16	16	9	10	19
Average Pressure	1012.76	1006.38	1012.05	1010.60	1008.30	1156.20	1012.60	1010.5	1006.7
Average Wind direction	124.29	145.00	182.50	183.18	140.16	161.67	249.27	203	144.17
Average Wind speed	3.21	2.99	2.28	7.53	5.53	5.15	4.03	4.9	6.1

The wind speed was strongest in October 2016 at 7.53 m/s and weaker in June 2016 at 2.28 m/s. The most dominant wind was from the southeast direction which prevailed in October 2015, January 2017, January 2018 and February 2016. During the June 2016 and October 2016 sampling period the wind was from the southerly direction. Figure 4.51, 4.52 and 4.53 show the variations in wind speed and direction at Port Elizabeth depot during the different sampling periods.

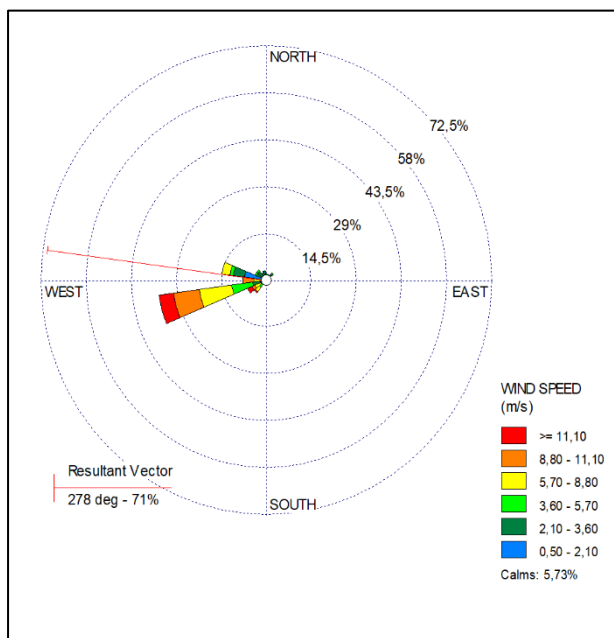
October 2015



February 2016



June 2016



October 2016

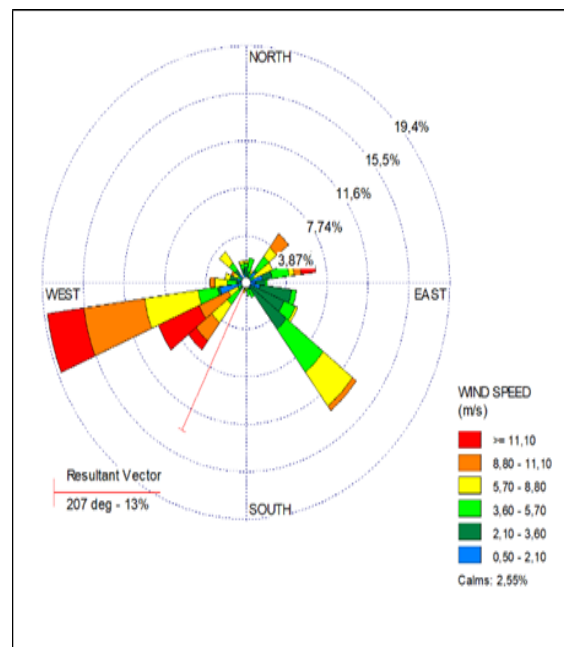
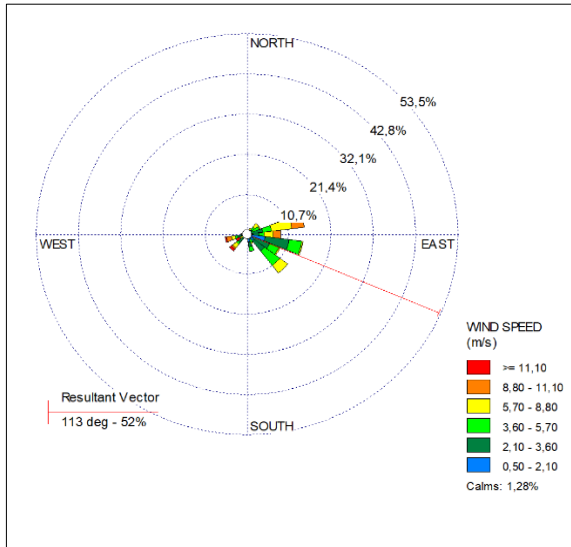
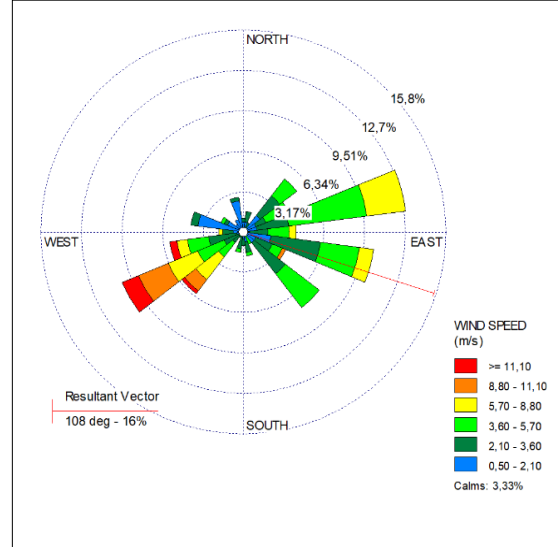


Figure 4.51: Windroses indicating wind speed and direction over Port Elizabeth depot for the October 2015, February 2016, June 2016 and October 2016 sampling periods.

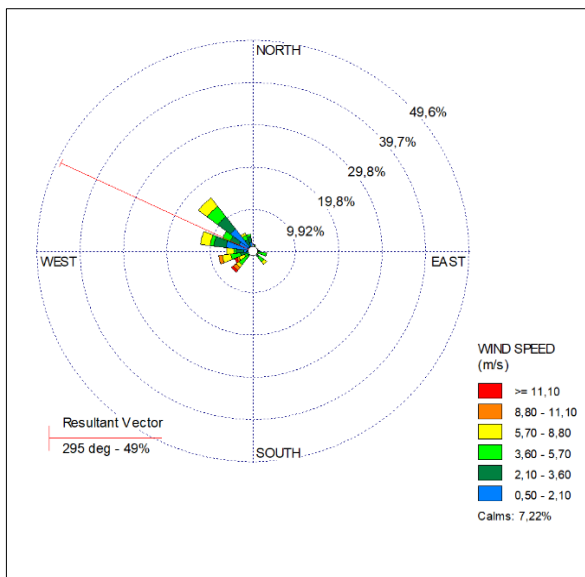
January 2017



April 2017



July 2017



October 2017

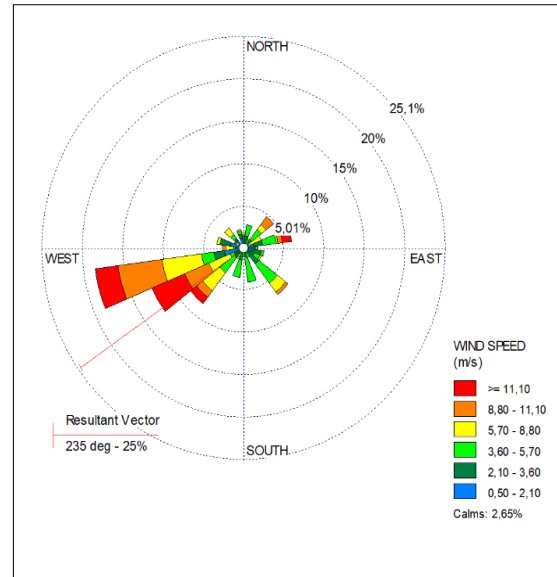


Figure 4.52: Windroses for Port Elizabeth depot for October 2016, January 2017, April 2017, July 2017 and October 2017 sampling periods.

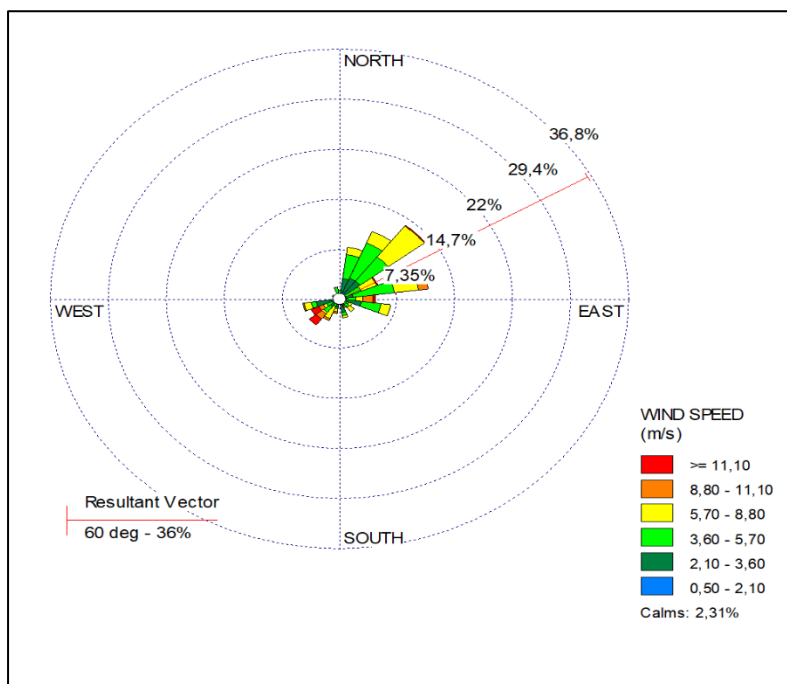


Figure 4.53: Windrose indicating wind speed and direction over Port Elizabeth depot for the January 2018 sampling period.

4.5.7. Kimberley

The average daily maximum temperature, daily minimum temperature, pressure, wind direction and speed recorded at Kimberly site for the different sampling periods are presented in Table 4.34. The average daily maximum temperatures were high in Kimberly, ranging between 20 °C and 37 °C. The average daily minimum temperatures were ranging between 2 °C and 19 °C.

Table 4.16: Weather conditions over Kimberley site

	October 2015	February 2016	June 2016	October 2016	January 2017	April 2017	July 2017
Average Daily Maximum Temperature (°C)	31	37	20	28	29	24	24
Average Daily Minimum Temperature (°C)	13	19	2	8	18	14	4
Average Pressure (hPa)	884.61	882.19	889.59	883.51	880.55	884.96	886.5
Average Wind direction	108.75	66.25	176.67	201.81	137.50	172.80	223.06
Average Wind speed (m/s)	5.78	3.93	2.59	4.27	3.86	2.71	3.2

The highest average wind speed was 5.78 m/s recorded during October 2015 sampling period and the lowest was 2.59 m/s recorded during the June 2016 sampling period. The wind direction was dominantly from the southerly direction during the June 2016 and April 2017 sampling periods. Throughout the other sampling periods the wind direction and speed varied. Figure 4.54 and Figure 4.55 illustrate the various wind directions and speed that were experienced during the different sampling periods.

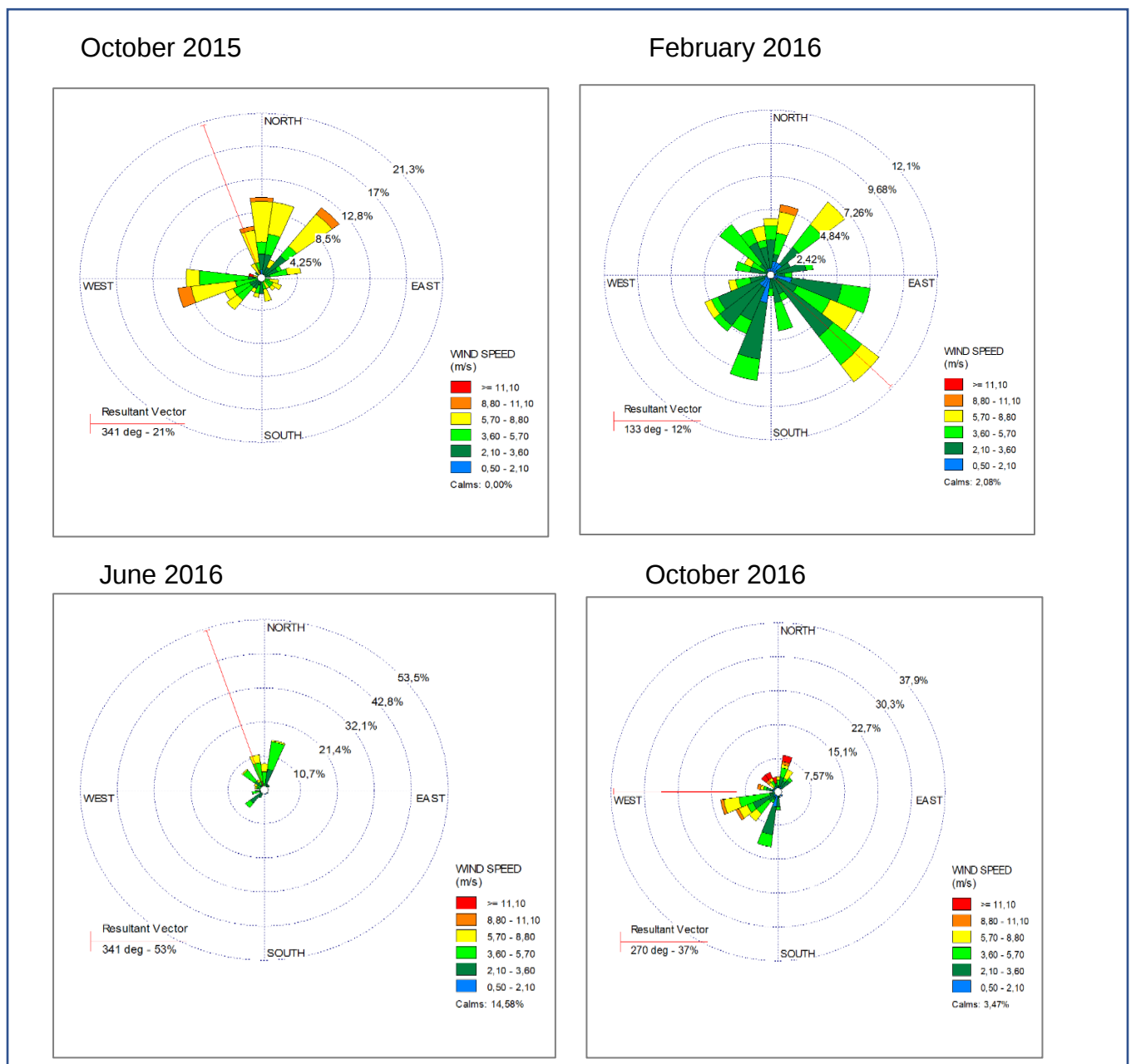
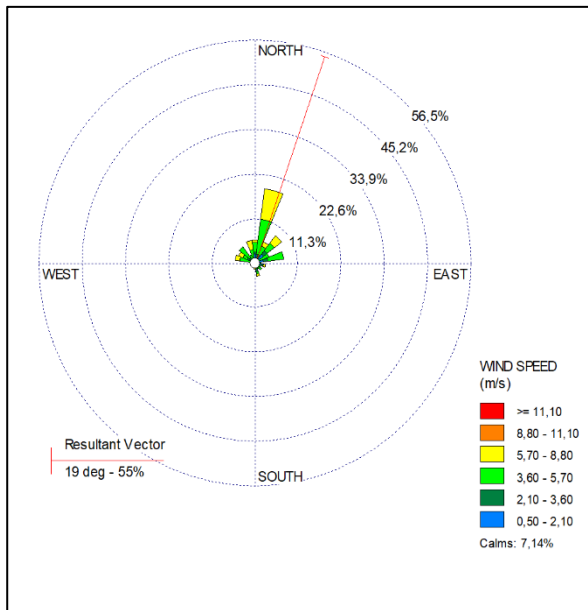
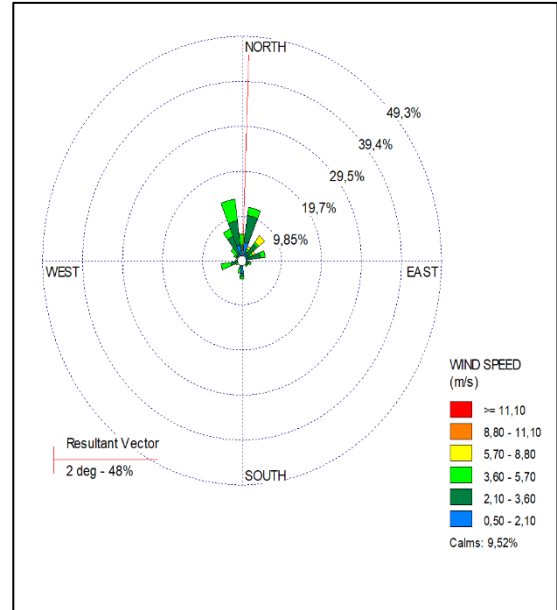


Figure 4.54: Windroses for Kimberley depot for October 2015, February 2016, June 2016 and October 2016 sampling periods.

January 2017



April 2017



July 2017

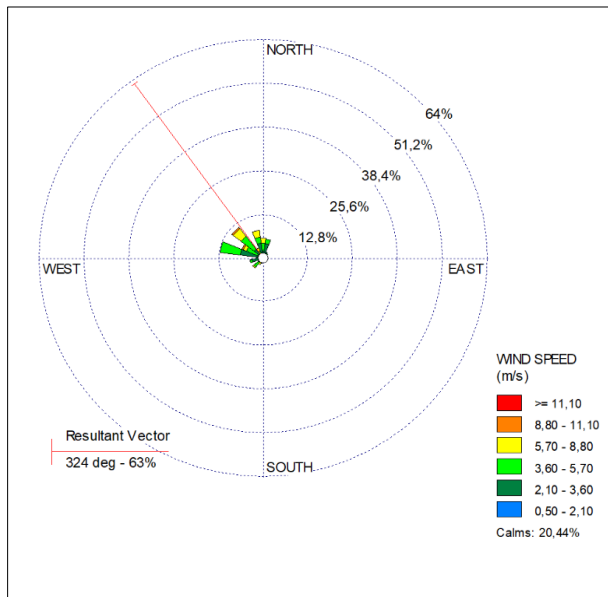


Figure 4.55: Windroses for Kimberley depot over January 2017, April 2017 and July 2017 sampling periods.

4.5.8. Ladysmith

The climatic conditions recorded at the Ladysmith site are showed in Table 4.35. The average daily maximum temperature was highest in October 2015 and lowest in June 2016. The average daily minimum temperature was highest in the February 2016 and lowest in June 2016.

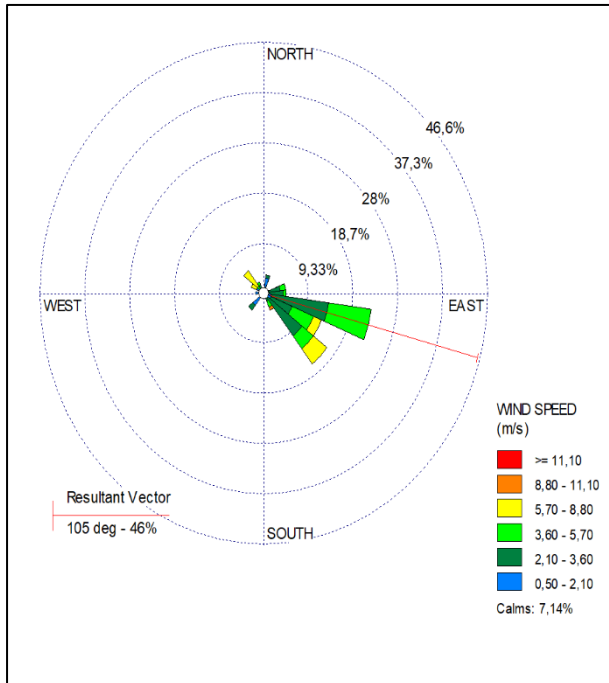
Table 4.17: Weather conditions over Ladysmith site

	October 2015	February 2016)	June 2016	October 2016	January 2017	April 2017	July 2017
Average Daily Maximum Temperature (°C)	29	27	21	28			24
Average Daily Minimum Temperature (°C)	13	17	7	11			5
Average Pressure (hPa)	901.14	898.47	902.66	897.42	896.16	898.89	901.35
Average Wind direction	100.00	108.33	130.00	158.80	118.93	162.40	210.72
Average Wind speed (m/s)	1.77	2.23	4.20	3.48	2.59	2.33	2.71

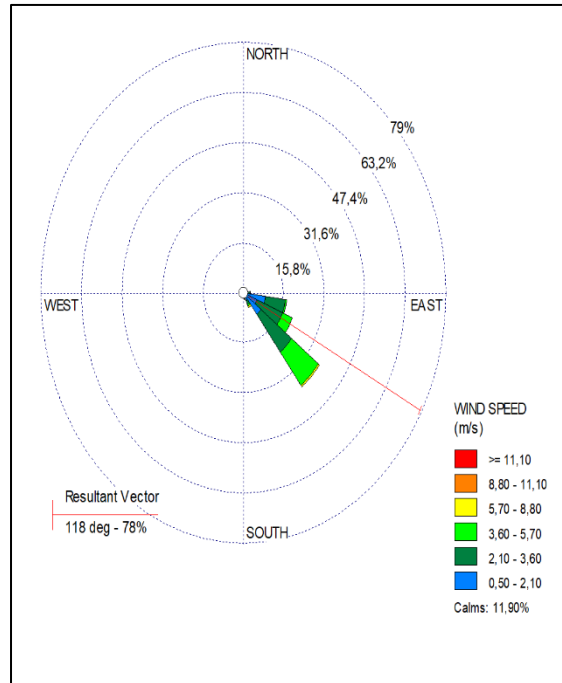
*Yellow- Data Not Available

The dominant winds were from the east-southeast and south-southeast directions which prevailed in February 2016, June 2016, January 2017, October 2016 and April 2017. The wind speed was strongest in June 2016 at 4.20 m/s and weaker in October 2015 at 1.77 m/s. The wind was light for the majority of the sampling periods with average speed lower than 3 m/s then during the June 2016 and October 2016 sampling periods became gentle with average speed higher than 4 m/s. the recorded wind speed and direction for the Ladysmith depot are illustrated in Figure 4.56 and 4.57.

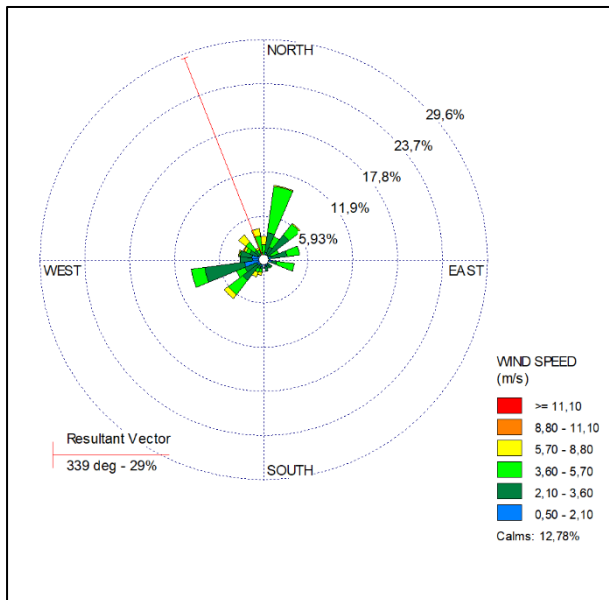
October 2015



February 2016



June 2016



October 2016

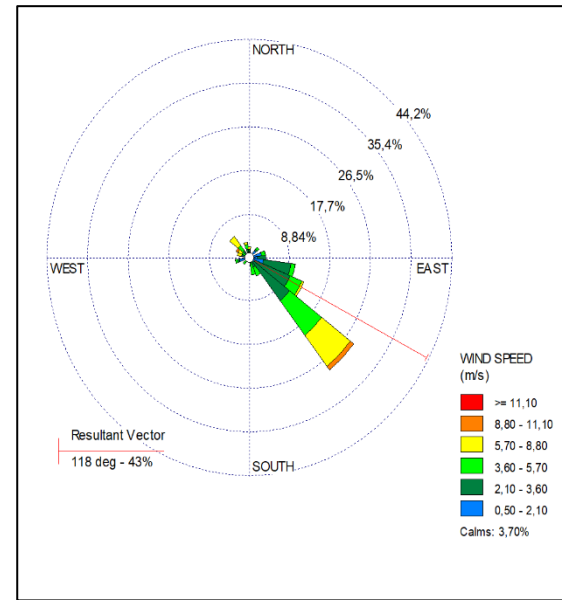
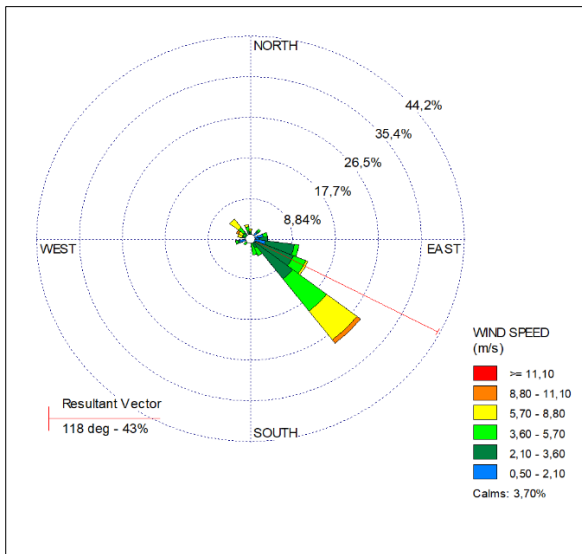
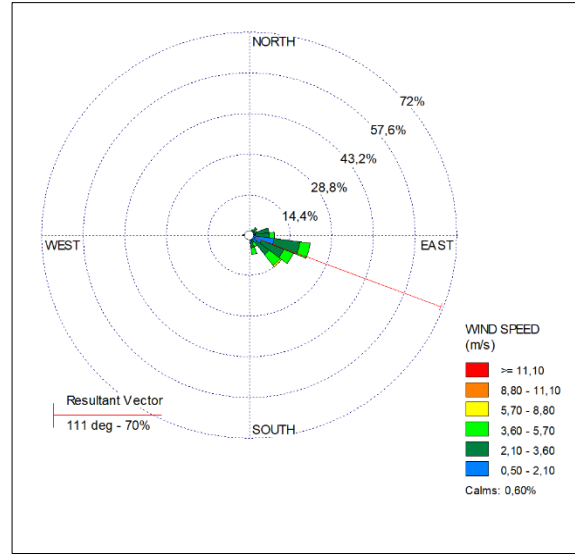


Figure 4.56: Windroses for Ladysmith depot for October 2015, February 2016, June 2016 and October 2016 sampling periods.

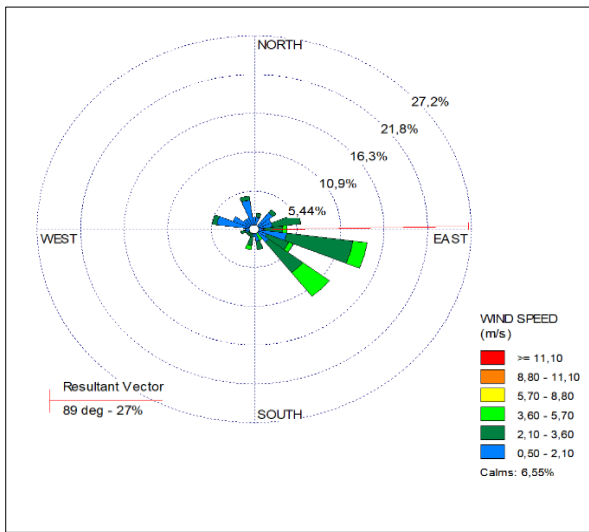
January 2017



April 2017



July 2017



October 2017

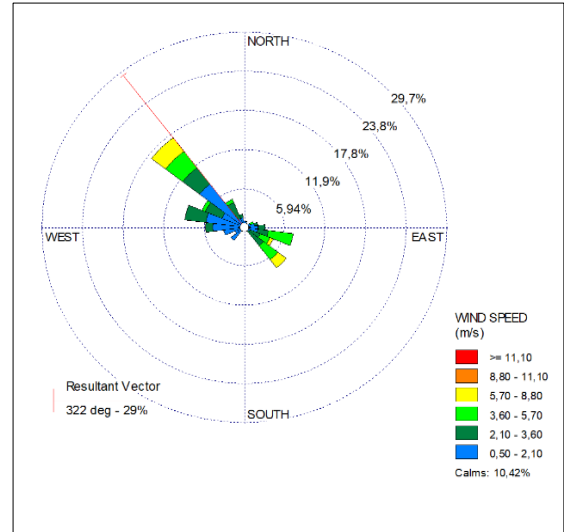


Figure 4.57: Windroses indicating wind speed and direction over Ladysmith depot for January 2017, April 2017, July 2017 and October 2017 sampling periods.

5. Discussions

The study area consisted of sites situated in industrial areas and mixed-use urban areas therefore the consideration of the differences in the location was essential for the BTEX concentrations measured. The sites located in industrial areas were Rocky's Drift, Island View and Port Elizabeth while those within the urban mixed use areas were Alberton, Witbank, Ladysmith, Kimberley, Kroonstad site 1 and site 2. This chapter is a discussion of the significance of the results relating up to the relevant literature and previous studies. The observed synoptic circulations and climatic conditions will be related to the BTEX concentrations that were recorded during the different sampling periods at all the monitoring sites.

5.1. BTEX Concentrations and Sources

According to Tiwari et al (2010), benzene and toluene have longer atmospheric lifetimes of 12.5 and 2.0 days respectively and are relatively stable compared to xylene which has a lifetime of 7.8 hours and does not remain in the atmosphere for long. Therefore, benzene and toluene are expected to be found in the atmosphere in higher concentrations as compared to xylene. The measured concentrations showed that toluene was the most abundant compound among the BTEX group followed by benzene and the toluene concentrations were higher compared to benzene across the majority of sites except Witbank (Table 4.2). The toluene concentrations were elevated with average highest during June 2016, October 2016 and October 2017 in Alberton, Ladysmith, Island View and Port Elizabeth as illustrated in Table 5.2. At the Witbank site the toluene concentrations were lower compared to those of benzene at the various sampling points. The benzene concentrations had high average values during the June 2016, October 2016 and October 2017. The remaining sites and sampling periods had lower concentrations of both toluene and benzene with the concentrations of toluene also higher compared to those of benzene.

The abundance of toluene and benzene concentrations at the majority of site may be attributed to the longer lifetimes of toluene and benzene, which allows the compounds to remain in the atmosphere for long periods after emission. The sensitivity of benzene and toluene to photochemical reactions could also be considered as the reactions contribute to how long the compounds remain in the

atmosphere depending on the other conditions such as temperature (Gallego et al., 2008; Król et al., 2012). Toluene reacts faster than benzene with hydroxyl radicals during the day in the presence of sunlight therefore this may be another factor influencing the variation between the concentrations of the two compounds throughout the sampling periods (Singh *et al.*, 2016). The weather conditions of an area have been noted to also have an impact on BTEX concentrations and this will be discussed in details in section 5.3. It could also be considered that the industrial process and storage facilities use more petrol and toluene is more abundant in it than benzene.

The measured concentrations of ethyl-benzene and xylene illustrated a trend of xylene concentrations being higher than those of ethyl-benzene at all monitored sites during the October 2015, February 2016, June 2016, October 2016, January 2017, April 2017, July 2017, October 2017 and January 2018 sampling periods. Although the different sites showed a similar trend, there were sites that had significantly higher concentrations of xylene such as Alberton, Ladysmith, Island View and Port Elizabeth with concentrations ranging between 2.11-179.97 $\mu\text{g}/\text{m}^3$, 2.4-77.14 $\mu\text{g}/\text{m}^3$, 2.45-75.12 $\mu\text{g}/\text{m}^3$ and 0.83-43.77 $\mu\text{g}/\text{m}^3$ (Section 4.2.2). The sampling points that had higher concentrations of toluene also had slightly elevated benzene concentrations compared to the BTEX compounds. Xylene is usually used in solvents and similar to toluene, it is more abundant in petrol. Petrol contains approximately 7 to 8 percent of xylene and approximately 1 to 2 percent of ethylbenzene, therefore the use of petrol in the depots also contributed to the higher concentrations of xylene (Scottish Environmental Protection Agency, 2012).). Although both BTEX compounds are constituents of petrol, diesel and also present in other fuel oils, the abundance of each specific compound differs (Scottish Environmental Protection Agency, 2012).

The sites located within industrial areas were surrounded by other petrochemical facilities, manufacturing plants and refineries in their surroundings such as Total, PetroSA, Sapref and Fynnlads refinery, therefore the emissions from the neighbouring sites may also contribute to the recorded BTEX concentrations. The industrial processes, surrounding facilities and mobile sources have been noted as

the major sources of the BTEX concentrations in the atmosphere around depots. The Rocky's Drift site was dominated by wind blowing from the north-easterly direction for the most of the sampling periods (Figures 4.35 and 4.36) and there were manufacturing plants and industries in that direction whose emissions may be transported by wind towards the fuel depot thereby contributing to the BTEX concentrations. In Island View, the depot was surrounded by other petrochemical facilities to the west and during the February 2016, October 2016, July 2017 and October 2017 sampling periods the dominating wind was from the north-westerly and south-westerly direction as indicated in Figure 4.37 and Figure 4.38 while the BTEX concentrations were high compared to those measured in other sampling periods. In a study conducted in Yokohama, Japan the maximum average concentrations of BTEX were observed at an industrial site of Shiohama while the minimum at residential locations where the impact of other sources except vehicles is minimal (Tiwari *et al.*, 2010). The high concentrations of toluene around the industrial site may be due to the petrochemical industrial activities which include petrochemical refining and storage, paints, solvent and varnish (Tiwari *et al.*, 2010). In most studies the highest BTEX concentrations were observed close to photochemical plants, refinery followed by industrial areas and places with heavy traffic (Perkey and Yilmaz, 2010, Tiwari *et al.*, 2010). In this study, toluene was the most abundant compound followed by benzene and xylene for the majority of sites. The sites located in industrial areas also showed more elevated concentrations of toluene and xylene in comparison to the sites within urban mixed areas.

Jaars *et al* (2014), established that toluene was the most abundant aromatic hydrocarbon in a study conducted at the Welgegund measurement station which is occasionally impacted by anthropogenic sources from various regions in the interior of South Africa (Jaars *et al.*, 2014). Similarly, the toluene concentrations were significantly higher than those of benzene over the interior of South Africa (Lourens *et al.*, 2011). Toluene and xylenes are widely used in solvents and they are also more abundant in gasoline than benzene (Gallego *et al.*, 2008). The presence of gasoline in the fuel stored and handled at monitored depots and the possibility of other surrounding facilities using it may justify the recorded concentrations of toluene, xylene and benzene in sites located within industrial areas. The differences in toluene concentrations in the depots located in the industrial and urban mixed-use

areas indicate that around the industrial areas the surrounding facilities contribute to the emissions as the depots store the same products. The evaporation of fuel from leaks and emissions may also contribute to the high concentrations observed around the different sites. The leak detection and repair programme results from the October 2017 campaign conducted at the depots reveal that there were leaking components identified at Witbank, Rocky's Drift and Island View depot (Appendix 3). The discussed results show a trend that was identified in other studies locally and internationally with regards to BTEX concentrations around various sites (Gallego *et al.*, 2008; Tiwari *et al.*, 2010; Lourens *et al.*, 2011; Jaars *et al.*, 2014). Although there may be less facilities or point sources around the mixed-use urban areas, mobile sources may also influence the BTEX concentrations in the atmosphere.

The results presented in section 4.2.1 are in agreement with previous studies that indicated that toluene concentrations were higher than benzene in industrial, urban and mixed-use areas (Liu *et al.*, 2008; Choi *et al.*, 2009; Perkey and Yilmaz, 2010; Jaars *et al.*, 2014). Choi *et al.* (2009) revealed that the BTEX concentrations recorded in industrial areas were different from those that were measured in commercial and residential areas which had similar emission sources, the highest concentrations were recorded in industrial, followed by commercial and residential areas in Dageu, Korea. Toluene and xylene concentrations had high levels in the sampling sites which included industrial areas and it reflected the industrial processes conducted at the emission sources (Choi *et al.*, 2009). Other studies also found toluene to be the most abundant compound in the urban areas including India, Iran, Spain, Mexico, Hong Kong and Algiers (Ho *et al.*, 2004; Parra *et al.*, 2006; Hoque *et al.*, 2008; Kerchich and Kerbach, 2012; Cerón-Bretón *et al.*, 2014; Rad *et al.*, 2014).

5.2. Toluene to Benzene Ratio

Interspecies ratios were mostly used to estimate the air photochemical reactivity based on the assumption that BTEX compounds had varying degradation rates in the atmosphere (Lovino *et al.*, 2008). Due to the differences in reaction rates of VOCs with the hydroxyl radical, the ratios may be used to gain information regarding the different origin source in the environment (Tiwari *et al.*, 2010). During the day,

the abundance of highly reactive VOC species decreases as they undergo photochemical reactions whereas the abundance of the relatively less reactive species increases during the day due to accumulation (Tiwari *et al.*, 2010). The calculated T/B ratios indicated that the BTEX concentrations measured around the fuel depots in the study area are influenced by various sources such as traffic emission and manufacturing plants (Section 4.3).

Toluene was the most abundant compound in the majority of sites in the study therefore the high T/B ratios calculated can be attributed to the use of petrol in fuel depots, which emits large amounts of toluene as compared to the other compounds. The T/B ratios showed a variation throughout the different sampling period as illustrated in Table 5.1. During the June 2016 sampling period, the ratios were higher and in January 2017 the ratios were lowest. The high calculated ratios could be attributed to the significant difference between the measured concentrations of benzene and toluene at a particular sampling point. In June 2016, sampling point PE-2 recorded a higher toluene concentration and a low benzene concentration which led to the highest calculated ratio. During the January 2017 sampling period the concentrations of benzene and toluene were slightly different therefore leading to low ratios. Industrial process that use more petrol and solvents that contain higher amounts of toluene could have influenced the higher concentrations of toluene. The highest T/B ratio was observed in June 2016 at the Port Elizabeth site on sampling point PE-2 which had the highest toluene concentration of $110.30 \mu\text{g}/\text{m}^3$ and a low benzene concentration of $6.39 \mu\text{g}/\text{m}^3$. The toluene concentration was unexpectedly higher in comparison to the benzene, xylene and ethylbenzene for the same sampling point and other points within the same depot. As indicated before, the longer lifetime of toluene may also contribute to its longer presence in the atmosphere as compared to benzene.

Table 5.1: The T/B ratio range over the different sampling periods.

Sampling Periods	T/B ratio ranges
October 2015	0.56-2.93
February 2016	0.21-5.67
June 2016	0.70-17.28
October 2016	0.51-3.14
January 2017	0.62-2.08
April 2017	0.62-5.17
July 2017	0.67-4.02
October 2017	0.72-4.11
January 2018	0.79-4.20

The maximum T/B ratios for all sampling periods were found at the depots located within industrial areas. In October 2015, February 2016, October 2016, April 2017 and July 2017 the site with the highest T/B ratio was Island View, while Port Elizabeth had the highest T/B ratio in June 2016 and Rocky's Drift had the highest T/B ratio in January 2017, October 2017 and January 2018. The Island View depot is surrounded by petrochemical storage facilities such as Total, PetroSA, Sapref and Fynnlads refinery therefore the recorded T/B ratios may be influenced by the emissions from the surrounding facilities. The samplers with high T/B ratios were Island View-3 and Island View-4 which were located near the loading gantry next to storage tanks and the loading gantry after the site entrance respectively. The two loading gantries are towards the fence of the site and therefore it is easier for the samplers to be affected by emissions from surrounding sources. At the Rocky's Drift depot, the sampler with the high T/B ratio during the January 2017 sampling period was Rocky's Drift-1 which was installed near the storage tanks and closer to the gate towards the Axis industrial park, brick farm, Timbercity, Oasis water, granite designs and Bird machines manufacturing plants. The other sampler which is RCD-4 was installed close to the loading gantry therefore the emissions from loading gantry and the surrounding manufacturing plants can be considered to justify the recorded ratio.

The majority of the sites located in the urban mixed-use areas had T/B ratios which were less than 3 (influenced by emission from traffic or mobile source) except a few points that had higher ratios in the February 2016 and June 2016 sampling periods. In October 2015, October 2016, January 2017 and April 2017 all the depots within urban mixed-use areas had T/B ratios which were less than 3 indicating their concentrations were from traffic and mobile sources. The Kroonstad and Witbank sites had T/B ratios 4.20 and 3.35 respectively for the February 2016 sampling period indicating the influence of industrial facilities and evaporative sources respectively. In June 2016, the Kroonstad site 2 had a high T/B ratio of 4.60 at sampling point Kroonstad-6 indicating that the ratio may be attributed to industrial facilities and point sources.

Ho *et al* (2004) indicated that high T/B ratios may be related to high emission sources or the use of fuel which emits large amounts of toluene. As indicated the high T/B ratios were observed in sites that were surrounded by other industrial facilities and plants which may also contribute to the emissions. According to Kerchich and Kerbachi (2012), the T/B ratios decrease as the distance from the pollution source increases therefore the high T/B ratios calculated may indicate that sites were close to the emission sources. Previous studies revealed that the T/B ratios increase with an increase in the traffic and number of industrial emission sources around the monitored sites (Lee *et al.*, 2002; Choi *et al.*, 2012). In a study conducted in Dageu, the T/B ratios were highest around the industrial estates as compared to those observed in the commercial and residential areas (Choi *et al.*, 2012).

In the majority of industrial cities, the emissions may not be attributed to industrial sources only but also to surrounding traffic sources that contribute to the emissions (Liu *et al.*, 2008). According to Choi *et al* (2012), the high T/B ratios in Dageu may be related to VOCs that were emitted from automobiles and industrial estates with the influence of topographic and meteorological conditions in comparison to T/B from other cities. The climatic conditions of an area are therefore essential in establishing

the relationship between the sources of emissions with the observed T/B ratios. The benzene content in gasoline and motor vehicle exhaust is lower than the toluene levels, the evaluation of T/B ratios considers this to be certain about pollutant sources (Liu *et al.*, 2008). While T/B species are not the only ones used to understand the information about sources together with atmospheric chemistry, the ratios of other species were not considered in this study such as that of xylene and ethylbenzene as it also depends on the sampling technique adopted and the consideration of their isomers (Joumard *et al.*, 2004).

5.3. Influence of Weather Conditions on BTEX Concentrations

The regional circulatory patterns have been noted to control the dispersion of pollutants in the atmosphere as they control the prevailing weather (Ahrens, 2009). Dispersion of pollutants in the atmosphere is influenced by the large-scale circulation activities (Garsteng, *et al.*, 1996; Jagathlal, 2002). In South Africa particularly, the dominance of anticyclones and also the presence of mid-latitude cyclones have an impact of the transportation of pollutants in the atmosphere. Wind speed influences the transportations, rate of dilution and distribution of the BTEX compounds, therefore a decrease in wind speed causes an increase in concentrations (Ahrens, 2009). According to Cetin *et al.* (2003), wind speed greater than or equal to 5 m/s can be considered strong wind while wind speed lower than 5 m/s can be classified as weak wind. Therefore, it is essential to comprehend the synoptic scale circulation that prevailed during the passive sampling program to investigate their impact on the BTEX concentrations over the study area.

During the October 2015 sampling period, the presence of surface troughs with associated anticyclones and cold fronts influenced conditions over the monitoring sites with average maximum temperatures that ranged between 23 °C and 31 °C. High BTEX concentrations were measured in Island View and Alberton while the temperatures measured at both sites were high. In Island View, the wind speed was low which may have influenced the high concentrations as the dispersion of pollutants was lower. The Kimberley and Kroonstad sites had high average maximum temperature of 31 °C and 30 °C together with strong wind speed of 5.78 m/s and 6.46 m/s respectively. The measured BTEX concentrations were slightly

high in Kroonstad and lowest in Kimberley as compared to those of other sites for the same sampling period. The Kimberley and Kroonstad sites showed a significant relationship between the measured BTEX concentrations and the weather conditions around the site as the measured temperature and wind speed were high causing faster distribution of the compounds and dispersion which resulted in lower BTEX concentrations. The BTEX concentrations in Kroonstad and the other site could also be influenced by the weather conditions that prevailed in the area.

The February 2016 sampling period was mostly dominated by surface troughs over the interior accompanied by anticyclones. The circulation indicated in Figure 4.20 influenced warm and hot conditions over the country with high average maximum temperatures of 37 °C in Kimberley and 33 °C in Kroonstad while the other sites had temperatures ranging between 27 °C and 29 °C. The highest BTEX concentrations were measured in Island View, Alberton and Witbank and the average wind speeds were 3.20 m/s, 4.55 m/s and 3.25 respectively. The wind experienced at the Island View, Alberton and Witbank was considered to be weak therefore may lower the horizontal dispersion of BTEX compounds. The low wind speed recorded may have influenced the increase in BTEX concentrations. Extremely high temperatures were recorded in Kimberley and Kroonstad with gentle and strong wind respectively and the BTEX concentrations recorded were slightly lower compared to other sites. The high temperatures could have caused photochemical reactions which influence faster degradation of BTEX compounds.

In June 2016, cold fronts were dominant with associated anticyclones west and east of the country causing cloudy and cold conditions over the country with average daily maximum temperatures ranging between 16 °C and 25 °C. The Kalahari anticyclone was also present along the north-eastern part of the country restricting rainfall over the interior of the country. The average maximum temperatures were lower in Alberton and Witbank due to the influence of the cold front and the measured BTEX concentrations were high for these sites. The wind speed ranged between 1.16 m/s and 4.20 m/s, which is considered to be light and gentle. The other sites had high average maximum temperatures and calm wind. Among the remaining sites, high concentrations of BTEX were recorded in Ladysmith and Port Elizabeth. The

Kimberley, Rocky's Drift and Island View sites recorded low concentrations while the temperatures measured were high and wind speed was low. The sites which recorded high BTEX concentrations had moderate temperatures and lower wind speed.

During the October 2016 sampling period, the circulations were dominated by anticyclones and cold fronts which influenced cool to warm conditions over the country. The average maximum temperatures ranged between 21 °C and 28 °C while the average wind speed ranged between 3.33 m/s and 7.53 m/s for the October 2016. The high BTEX concentrations were measured in Alberton, Island View and Witbank while the lowest concentrations were measured in Kimberley. The temperature and wind speed recorded around the sites with high concentrations were fairly warm with gentle to moderate wind therefore this may attribute to the elevated BTEX concentrations measured. The results from the Kimberly site were different from the observed pattern as temperature was high with moderate wind however the BTEX concentrations were very low in comparison to other sites. The Kimberley site showed distinct influence of weather conditions on the recorded BTEX concentrations.

The January 2017 sampling period was dominated by surface troughs over the central and western interior accompanied by anticyclones. The prevailing circulations influenced partly cloudy to cloudy and cool and warm conditions with isolated showers over the country and high temperatures around Kimberley and Port Elizabeth. The recorded temperatures were ranging between 23 °C and 29 °C while the wind speed ranged between 2.59 m/s and 5.53 m/s. The sites with higher BTEX concentrations were Alberton and Island View which also had high temperatures and gentle wind. Low BTEX concentrations were measured in Kimberley and Port Elizabeth, while these sites had high temperatures due to the influence of the surface trough.

During the April 2017 sampling period, surface troughs dominated the circulation pattern together with associated anticyclones (Figure 4.24). There was also a cold

front for two days during the sampling period. The conditions experienced were partly cloudy, cool to warm conditions with rain over most parts of the country for about two days and there were very hot conditions in Kimberley, Port Elizabeth, Ladysmith and Island View. The average maximum temperature was ranging between 23 °C and 27 °C while the average minimum temperature ranged between 13 °C and 21 °C. The average wind speed ranged between 2.19 m/s and 5.15 m/s. High BTEX concentrations were measured at Alberton and Island View while the temperatures were high and wind speed was gentle. In Kimberley and Ladysmith, the BTEX concentrations were low whereas the temperatures were high and wind speed was gentle.

In July 2017, the circulation was dominated by cold fronts with associated anticyclones influencing partly cloudy to cloudy, cold to cool conditions with light rain over the country. The average daily maximum temperatures ranged between 19 °C and 25 °C while wind speed ranged between 1.41m/s and 4.03 m/s over the various sites. The highest concentrations of BTEX were measured at Alberton and Island View where the recorded temperatures were high and wind speed was calm. The site with low BTEX concentrations was Kimberley and it had high temperature and low wind speed during the sampling period.

In October 2017, the weather conditions were partly cloudy, cool to warm over most part of the country with light rain. The average maximum temperatures were lowest in Port Elizabeth with 19 °C and high in Rocky's Drift with 24 °C. The average wind speed ranged between 3 m/s recorded in Rocky's Drift and 4.9 m/s recorded in Port Elizabeth. The highest BTEX concentrations were measured in Island View and Alberton where average maximum temperatures were 21 °C and 21 °C, with wind less than 5 m/s at both sites. The lowest BTEX concentrations were measured in Kroonstad, where average maximum temperature was 23 °C while the average wind speed was 3.7 m/s. Although the recorded BTEX concentrations and weather conditions showed a variation at the different sites, no clear relationship was determined between weather conditions of the sites and their influence on recorded BTEX concentrations.

During the January 2018 sampling period, surface troughs were dominant with anticyclones and the prevailing circulations influenced partly cloudy and cool to warm or hot conditions with isolated showers over most parts of the country. There were hot conditions at most of the monitored sites due to the influence of the dominant circulation. The average maximum temperatures were high as they range between 27 °C and 33 °C recorded in Port Elizabeth and Kroonstad respectively. The average wind speed ranged between 3.1 m/s and 6.1 m/s. The highest BTEX concentrations were measured in Alberton, Island View and Kroonstad while the temperatures at these sites were also high and wind speed was moderate. The Witbank and Rocky's Drift sites had low BTEX concentrations while the temperatures were high and wind speed was low. The high temperatures at Witbank and Rocky's drift could have influenced the low concentrations measured as high temperature increases photochemical reactions of the BTEX compounds in the atmosphere.

5.4. Seasonal Variations

The sampling was done at different time periods so there could be a representation of the various seasons of the year. The sampling periods represent the seasons as follows: October presents spring, January and February present summer, April presents autumn while June and July presents winter. As indicated in the previous sections, there were different weather conditions experienced through the different sampling periods. The concentrations of the BTEX compounds showed a variation over the different sampling periods as illustrated in Section 4.2.1 and 4.2.2. Although there was a noted variation in the total BTEX and also the compounds ranges, the relationship between the concentrations and weather conditions was significant in Kimberley depot throughout the sampling periods while the other sites showed no clear relationship between measured concentrations and prevailing weather conditions. The highlighted weather conditions over the different season had no notable influence on the recorded BTEX concentrations. The total BTEX was low in January 2017, followed by April 2017, October 2015, July 2017, October 2017 while it was high in January 2018, February 2016, June 2016 and October 2017 (Table 5.2).

Table 5.2: The averages for BTEX compounds

Sampling Periods	Average Benzene ($\mu\text{g}/\text{m}^3$)	Average Toluene ($\mu\text{g}/\text{m}^3$)	Average Ethyl-benzene ($\mu\text{g}/\text{m}^3$)	Average Xylene ($\mu\text{g}/\text{m}^3$)
October 2015	8.04	11.74	2.85	10.43
February 2016	9.17	15.37	2.73	12.70
June 2016	14.59	27.42	3.89	16.67
October 2016	13.44	22.18	3.40	15.81
January 2017	6.59	8.92	1.75	6.38
April 2017	5.73	9.34	1.76	7.63
July 2017	10.39	19.83	4.60	13.33
October 2017	11.61	20.35	3.05	13.73
January 2018	6.76	13.55	2.26	11.77

6. Conclusions

The aim of the study was to investigate the average BTEX concentrations, seasonal variations and relationship between concentrations and the climatic conditions of the areas. This was achieved by monitoring of sites through radiello samplers in October 2015, February 2016, June 2016, October 2016, January 2017, April 2017, July 2017, October 2017 and January 2018 together with analysis of synoptic circulation around the sites and the prevailing weather conditions. The results obtained from the passive sampling showed that toluene was the most abundant compound amongst the BTEX group followed by benzene at majority of the sites except Witbank. The sites with elevated toluene concentrations were Alberton, Ladysmith, Island View and Port Elizabeth. The concentrations of xylene were higher compared to those of ethyl-benzene at all monitored throughout all the sampling periods. The observed trend with regards to toluene and benzene concentrations was in agreement with previous studies (Gallego *et al.*, 2008; Tiwari *et al.*, 2010; Lourens *et al.*, 2011; Jaars *et al.*, 2014).

The sources of BTEX in the study area were also investigated as the depots were located within differing land-use areas. The site that had highest toluene concentration was located within an industrial area while the one with the lowest concentration was located within an urban mixed-use area. The xylene concentrations were also higher amongst the depots located in industrial areas. The higher concentrations of toluene and xylene around the depots within industrial areas could be influenced by their wide use as solvents and that they are more abundant in gasoline than the other compounds (Gallego et al., 2008). It was noted that in most industrial areas there were other petrochemical storage facilities and refineries such as Totalsa, Sapref and Fynnlands around the Island View depot, which may have contributed to the recorded BTEX concentrations. The evaporation of fuel from leaks was also noted to contribute to the anomalously high concentrations observed at some sampling points. The different lifetimes of the BTEX compounds and the atmospheric chemistry was also noted for the variation in the recorded concentrations across the monitored sites.

The calculated T/B ratios indicated that the concentrations measured around the fuel depots in the study area were influenced by sources such as traffic emission, mobile and evaporative sources together with industrial facilities. The maximum T/B ratios were recorded in depots located within industrial areas for all sampling periods. The consideration of the specific sampling points which had high T/B ratios revealed the influence of surrounding facilities and activities such as loading of fuel. The prevailing weather conditions had an influence on the recorded BTEX concentrations for majority of the sampling period except in October 2017. The Kimberley site revealed a more significant influence of weather conditions on BTEX concentrations as compared to the other sites. There were noted variations of total BTEX throughout the sampling periods however no distinct seasonal relationship was established.

6.1. Recommendations

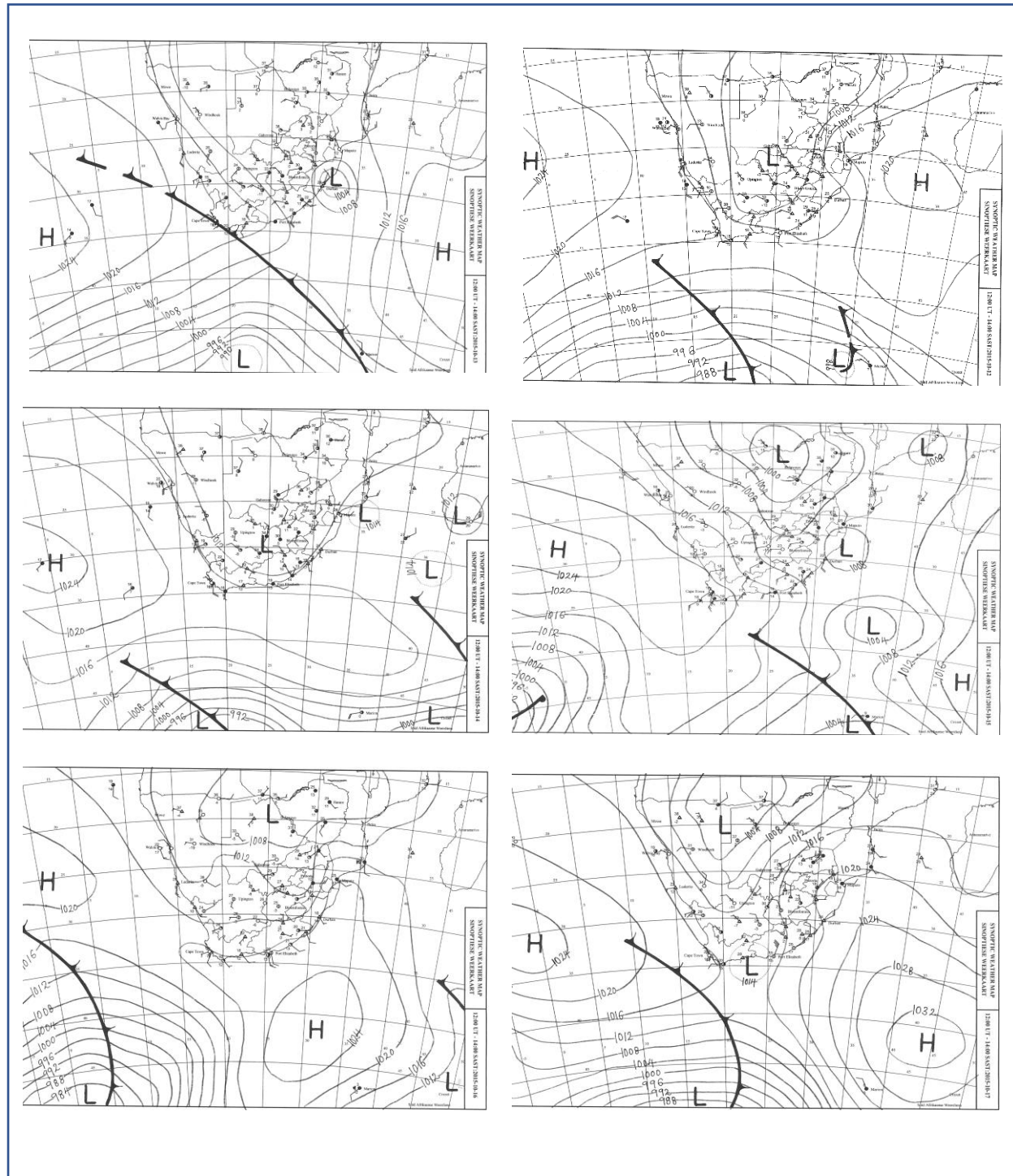
There is certainly a need for more investigations around the seasonal variations of concentrations. An in-depth investigation into the seasonal variations of BTEX concentrations would provide a clearer understanding of the reactions of the BTEX compounds in the atmosphere with other compounds. It is also important to have studies that take into consideration the temporal variations i.e. day-time and night-time monitoring of BTEX concentrations as the weather conditions are different. The change in frequency of monitoring i.e. monthly and weekly, would also improve the investigation around variation of BTEX concentrations as it would be easier to trace the changes in weather conditions and operations in relation to recorded concentrations at certain periods. The inclusion of other sampling techniques such as active monitors would also enhance the results obtained as the concentrations can be compared and analysed further.

More research needs to be done on seasonality with regards to the BTEX concentrations taking into consideration the temporal distribution of the compounds within the fuel depots. It is also important to have studies that will consider other sources of BTEX in industrial and mixed-use urban areas in order to correctly quantify the amount of BTEX emitted by the various sources. The consideration of other additional programs such as leak detection and repair that can contribute to establishing the sources of BTEX within the sites is essential. Leak detection and repair conducted together with air quality monitoring could improve the understanding of how leaks within the depots also contribute to the BTEX concentrations measured.

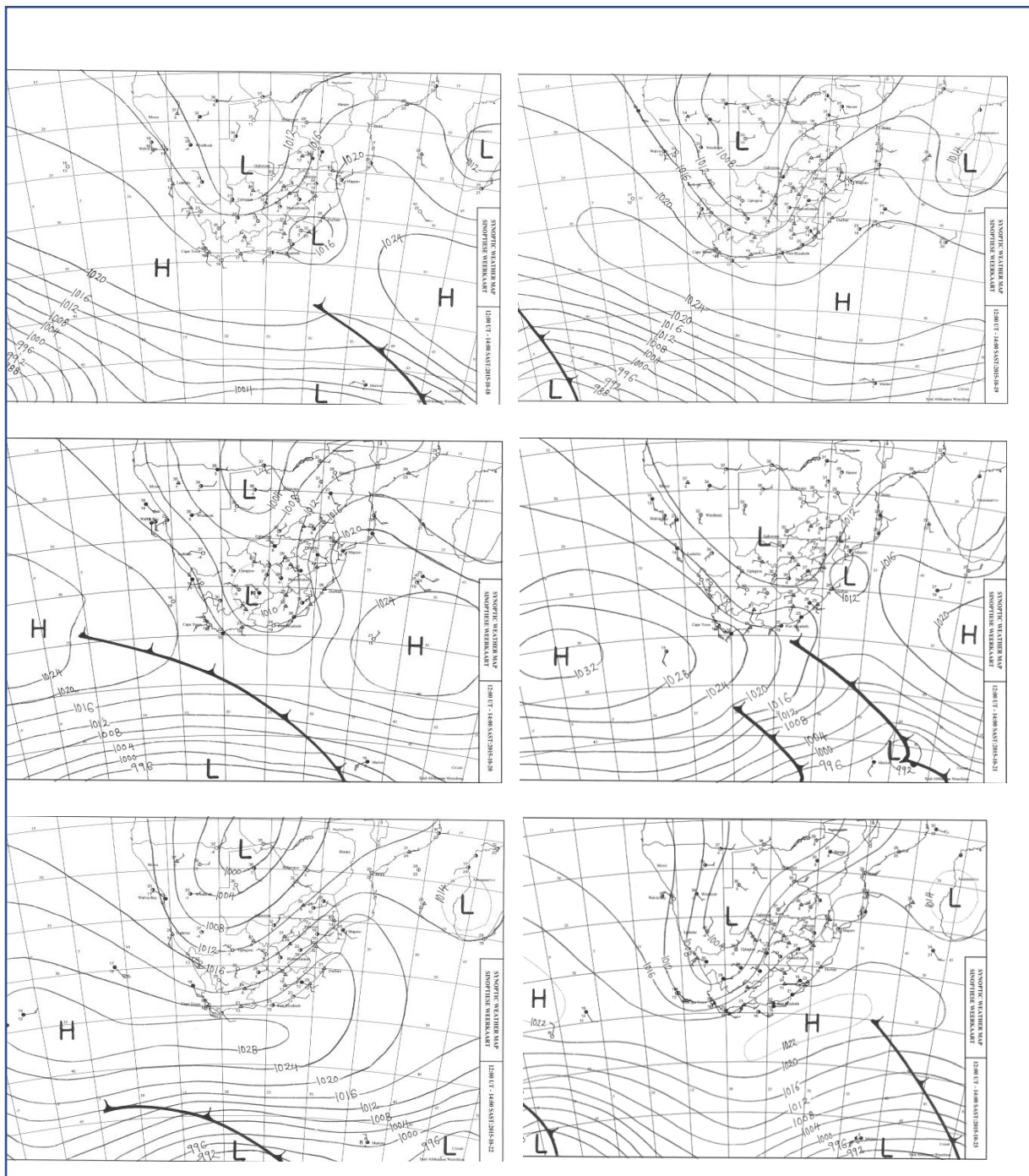
7. Appendices

7.1. Appendix 1-Synoptic Charts

7.1.1. October 2015

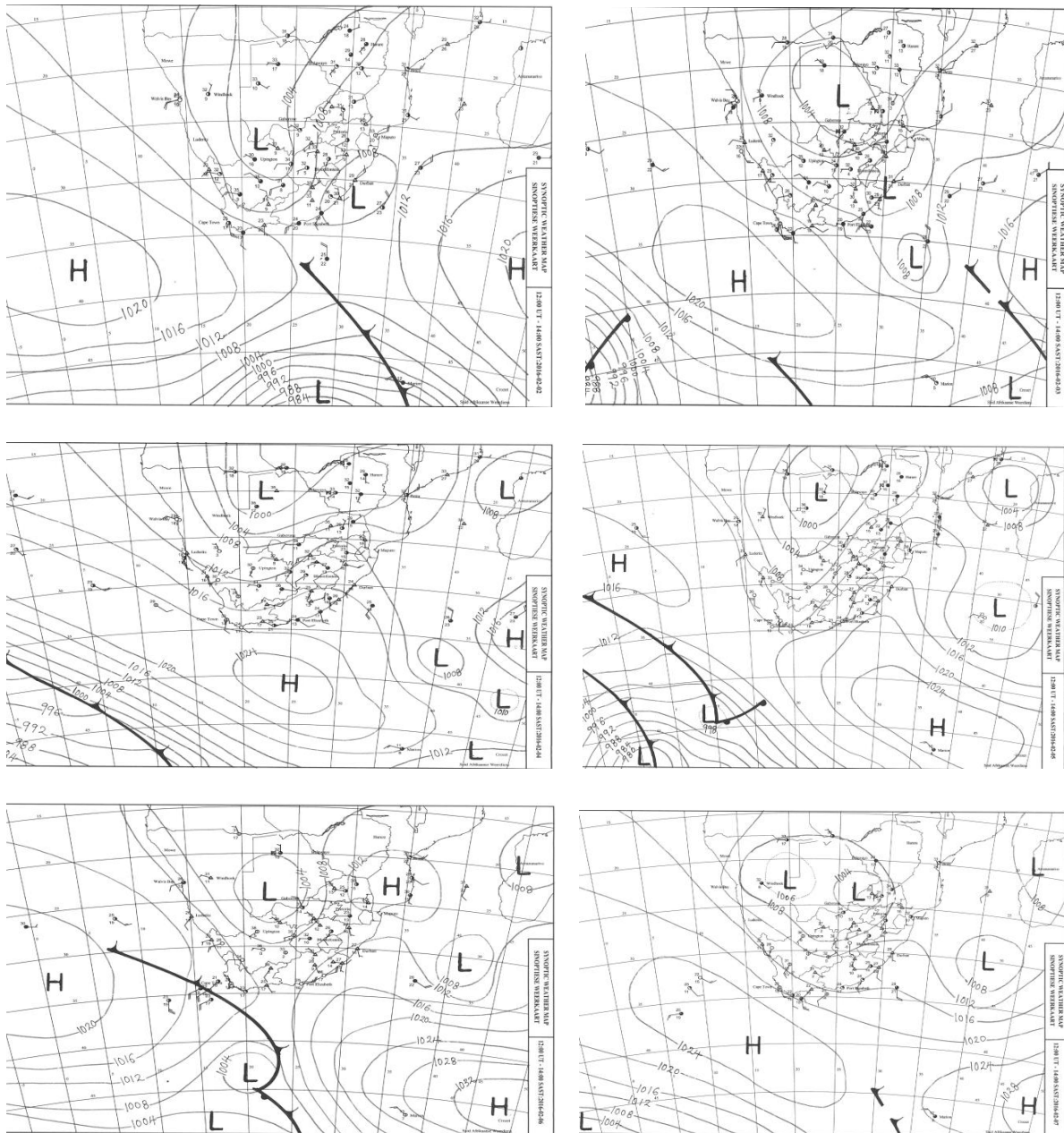


Synoptic Charts indicating circulation patterns during the October 2015 sampling period (12/10/2015-19/10/2015) (Weathersa, 2017)

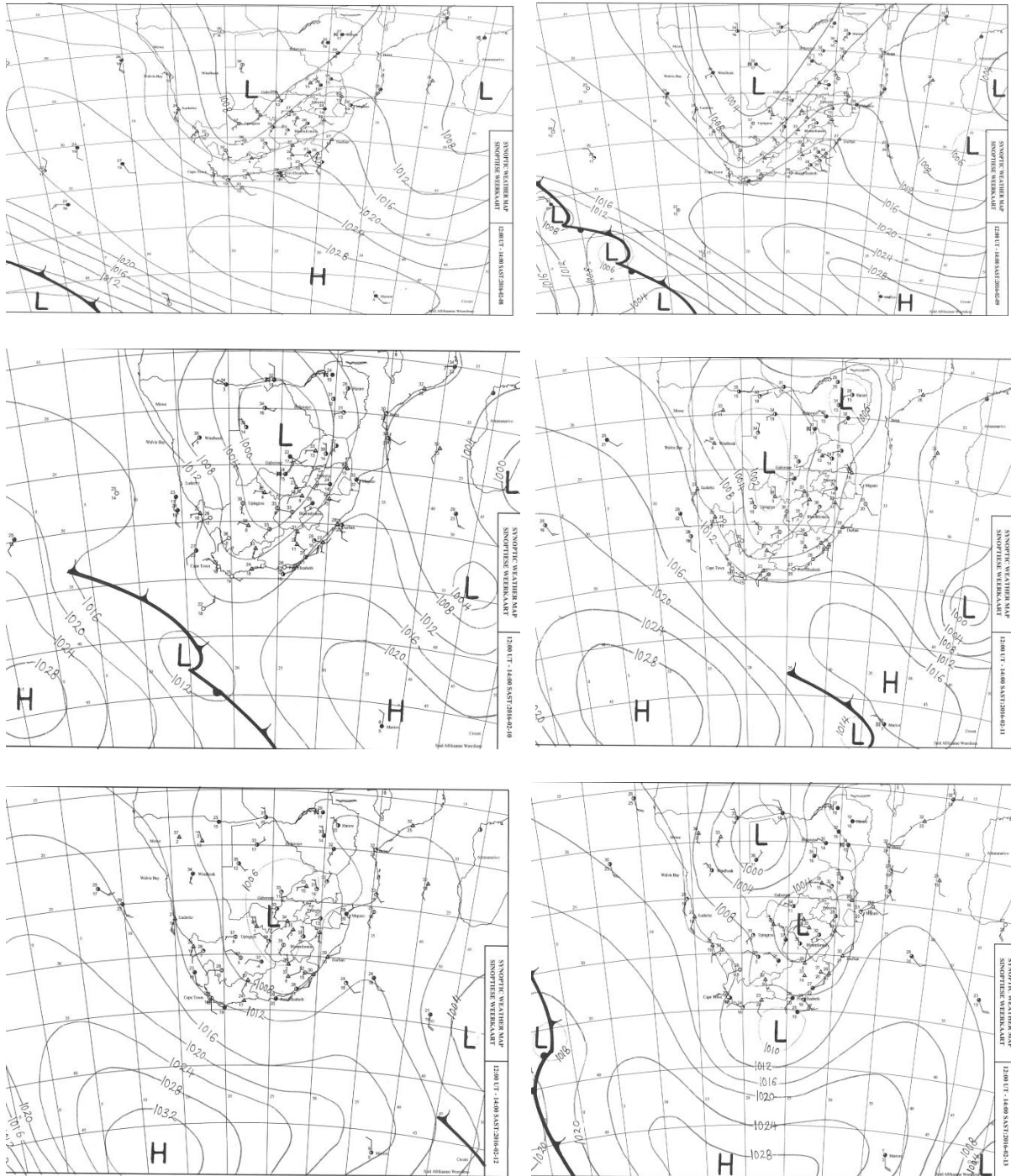


Synoptic charts showing the circulation patterns for the last four days of the October 2015 sampling period (18/10/2015-23/10/2015) (Weathersa, 2017)

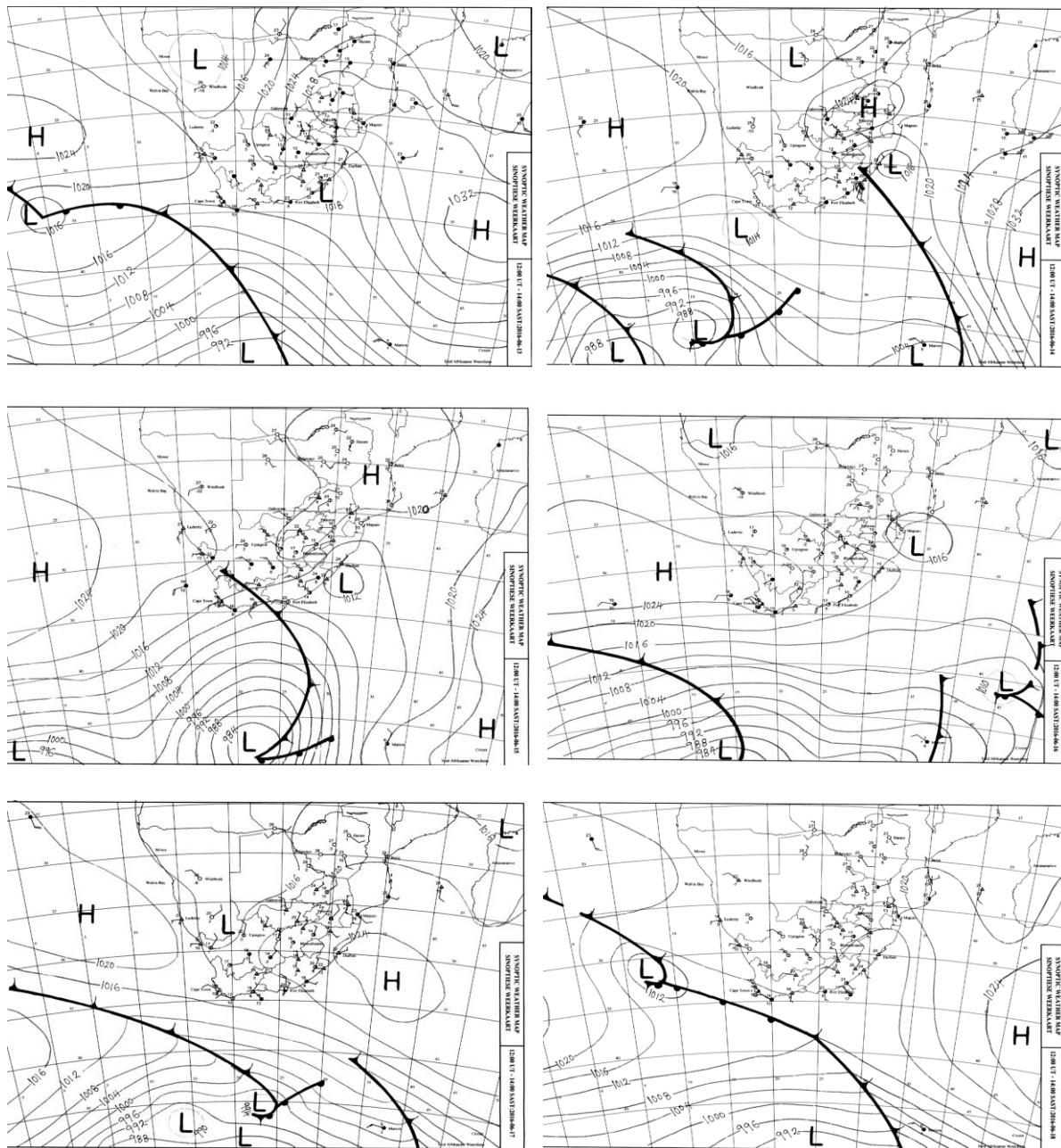
7.1.2. February 2016



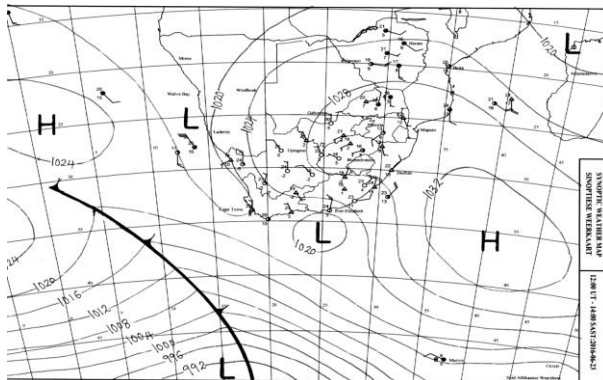
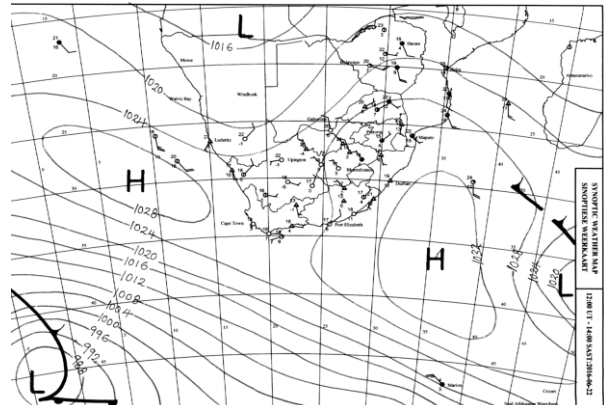
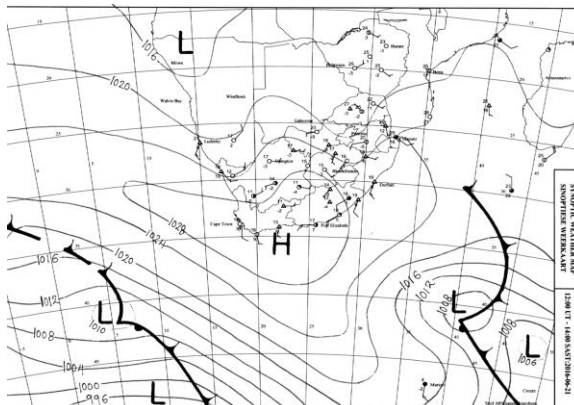
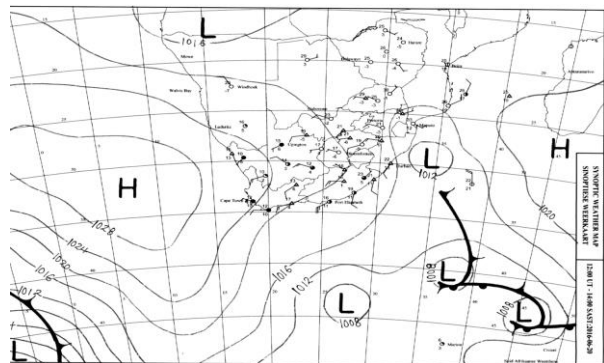
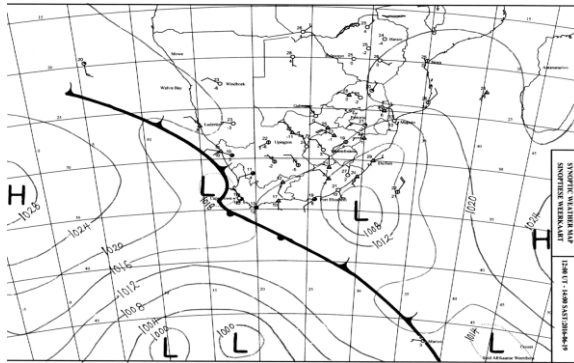
Synoptic charts showing the circulation patterns for the last four days of the February 2016 sampling period (02/02/2016-07/02/2016) (Weathersa, 2017)



Synoptic charts showing the circulation patterns for the February 2016 sampling period (08/02/2016-13/02/2016) (Weathersa, 2017)

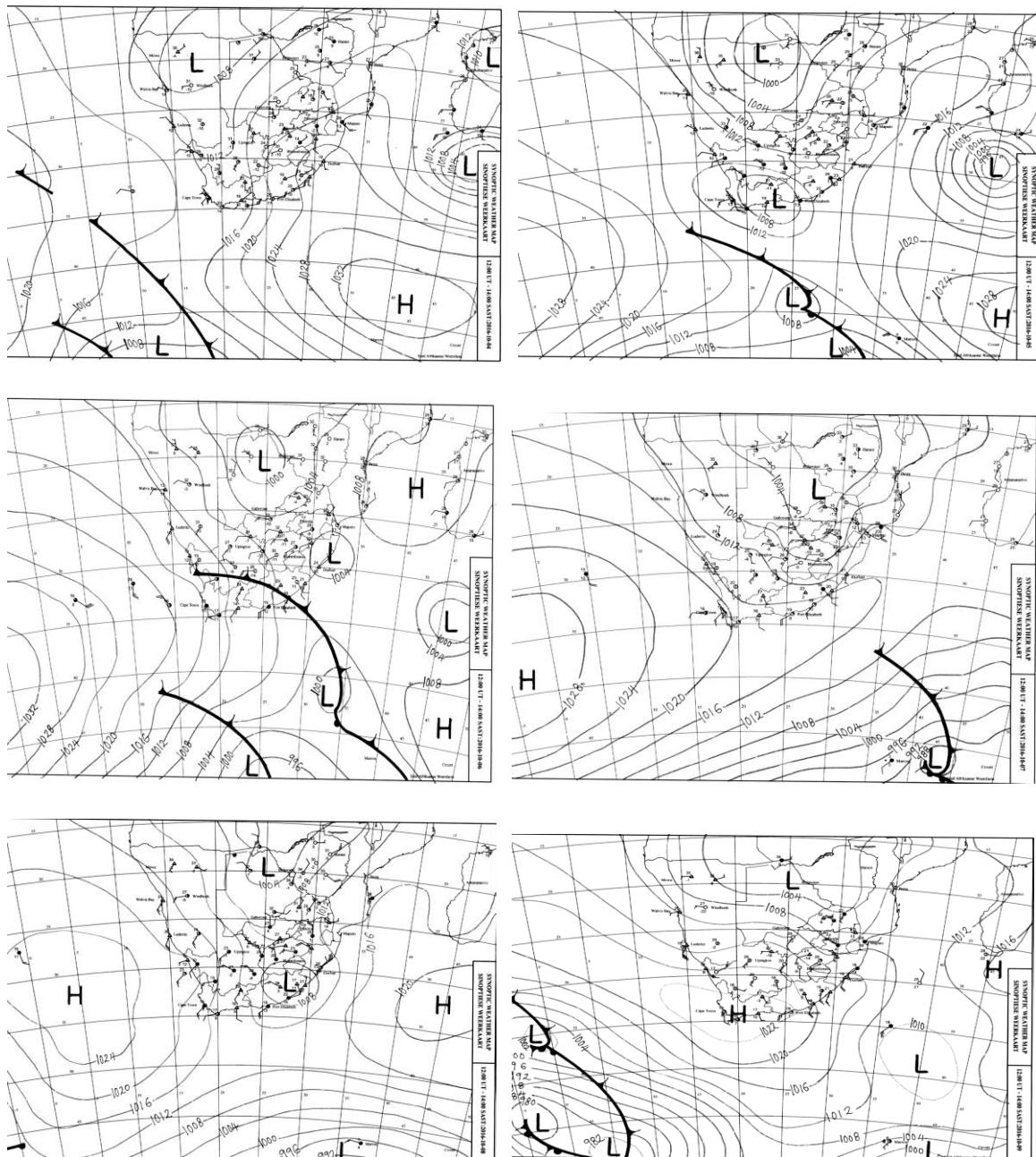


Synoptic charts showing the circulation patterns for the last four days of the June 2016 sampling period (13/06/2016-18/06/2016) (Weathersa, 2017)

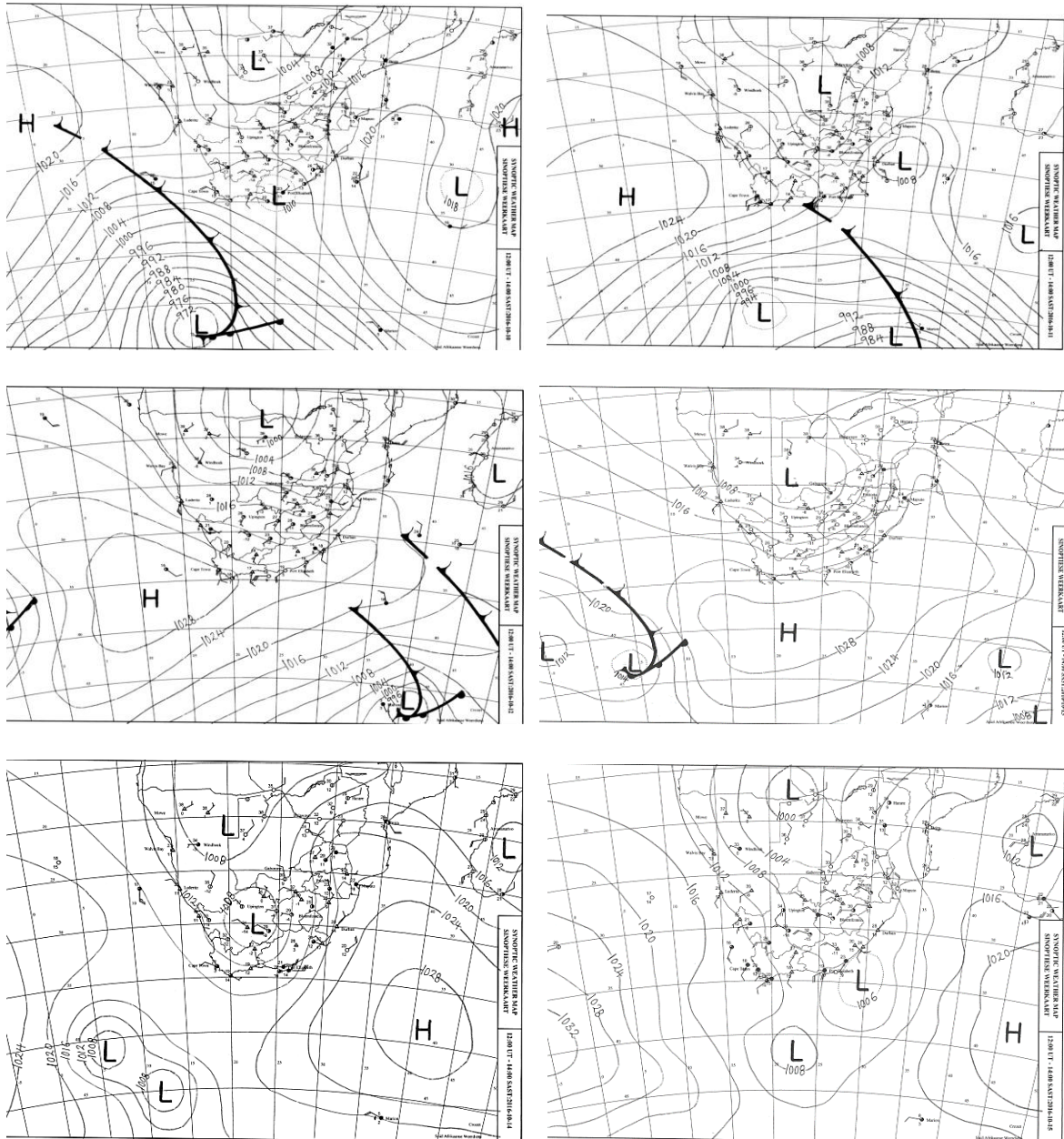


Synoptic charts showing the circulation patterns for the last three days of the June 2016 sampling period (19/06/2016-23/06/2016) (Weathersa, 2017)

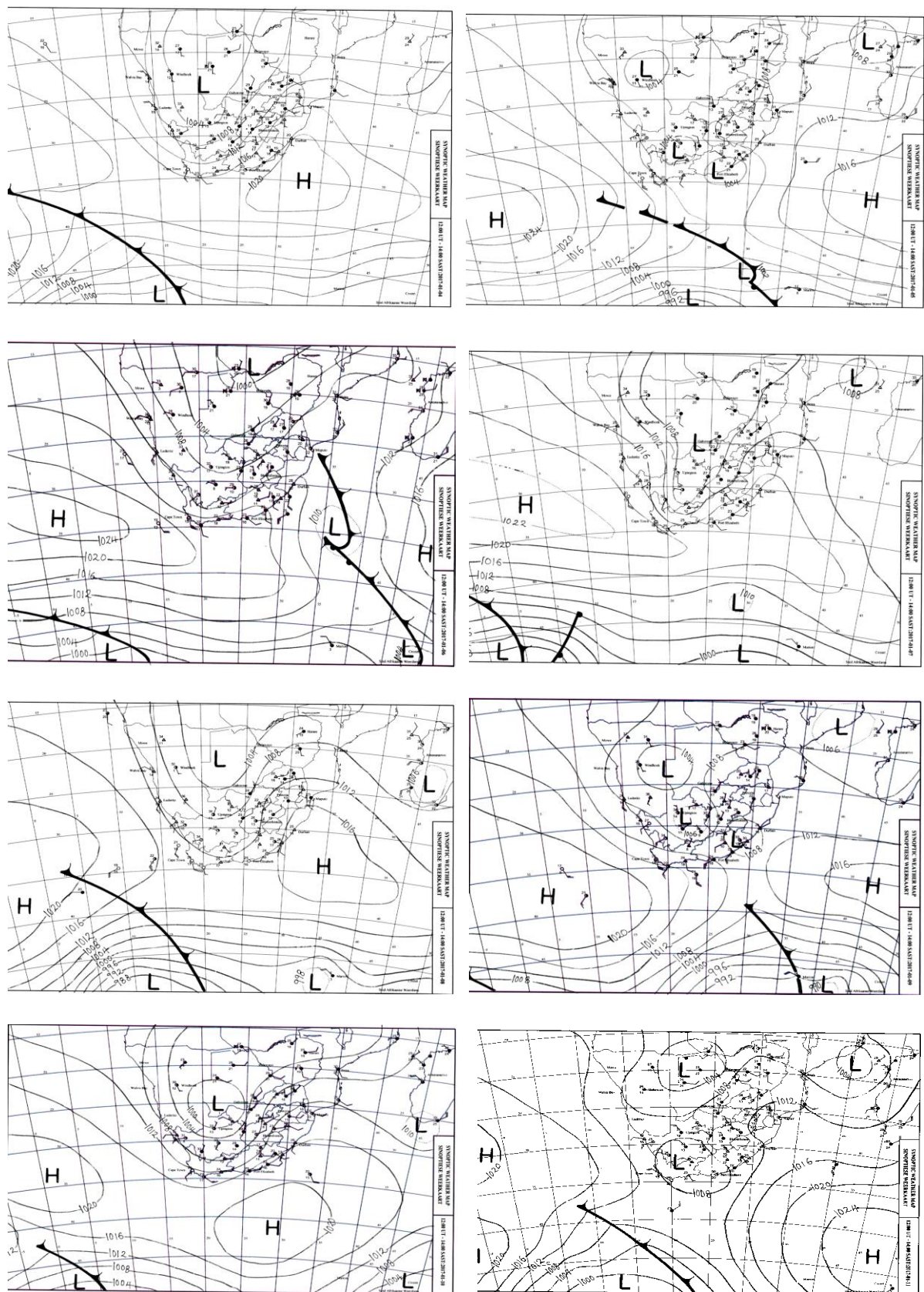
7.1.4. October 2016



Synoptic charts showing the circulation patterns for the October 2016 sampling period (04/10/2016-09/10/2016) (Weathersa, 2017)

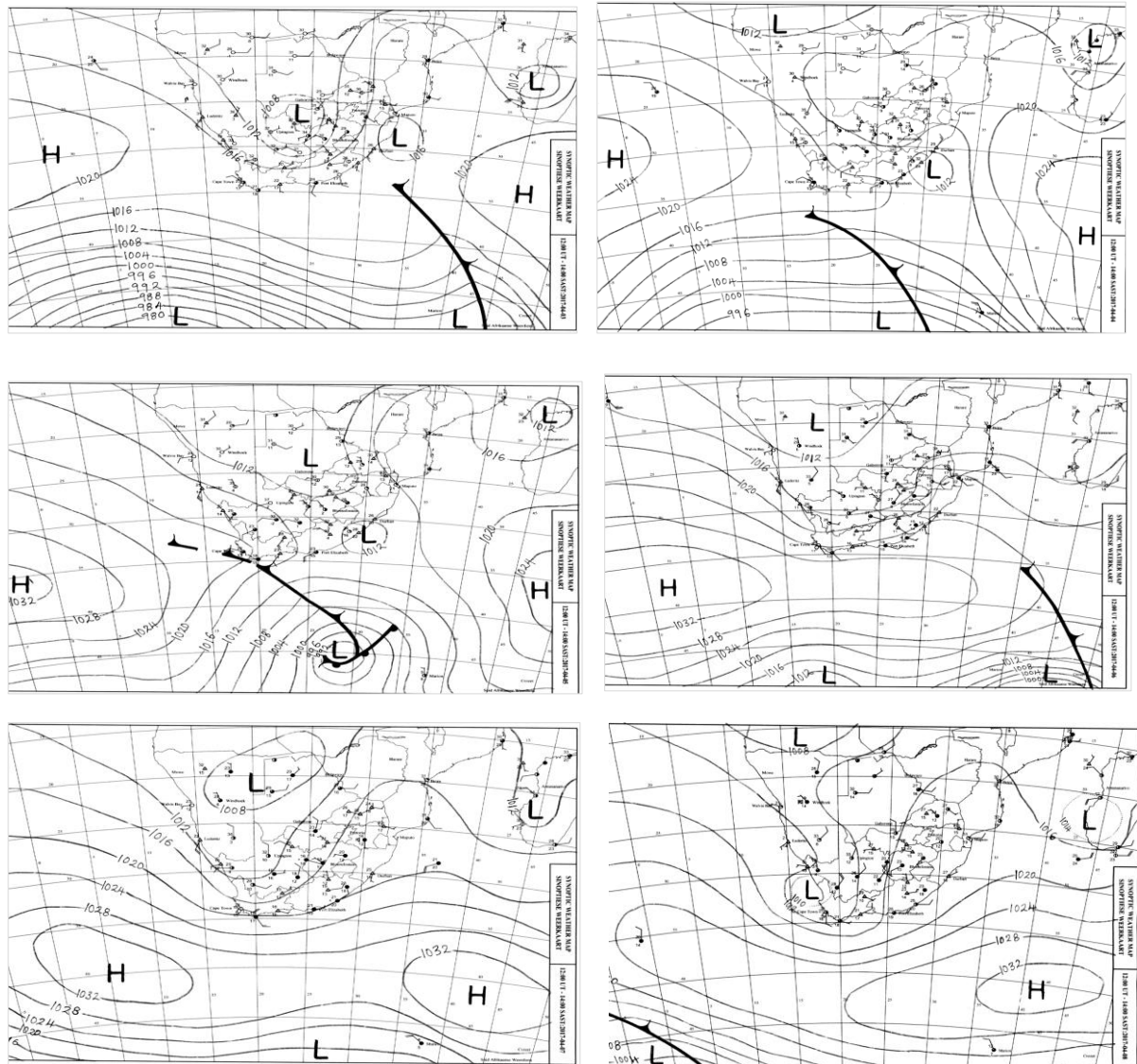


Synoptic charts showing the circulation patterns for the last four days of the October 2016 sampling period (10/10/2016-15/10/2016) (Weathersa, 2017)

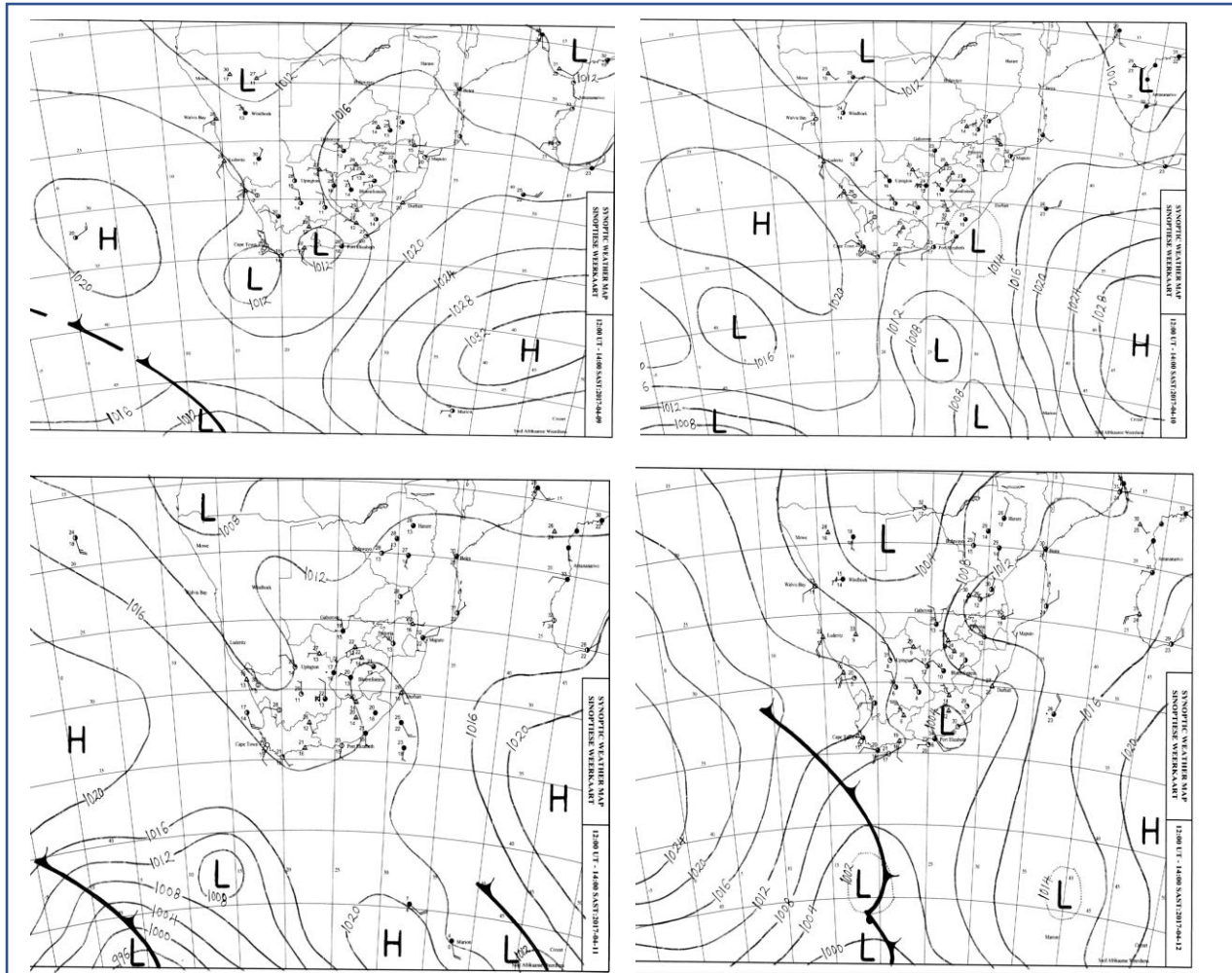


Synoptic charts showing the circulation patterns for the January 2017 sampling period (03/01/2017-10/01/2017) (Weathersa, 2017)

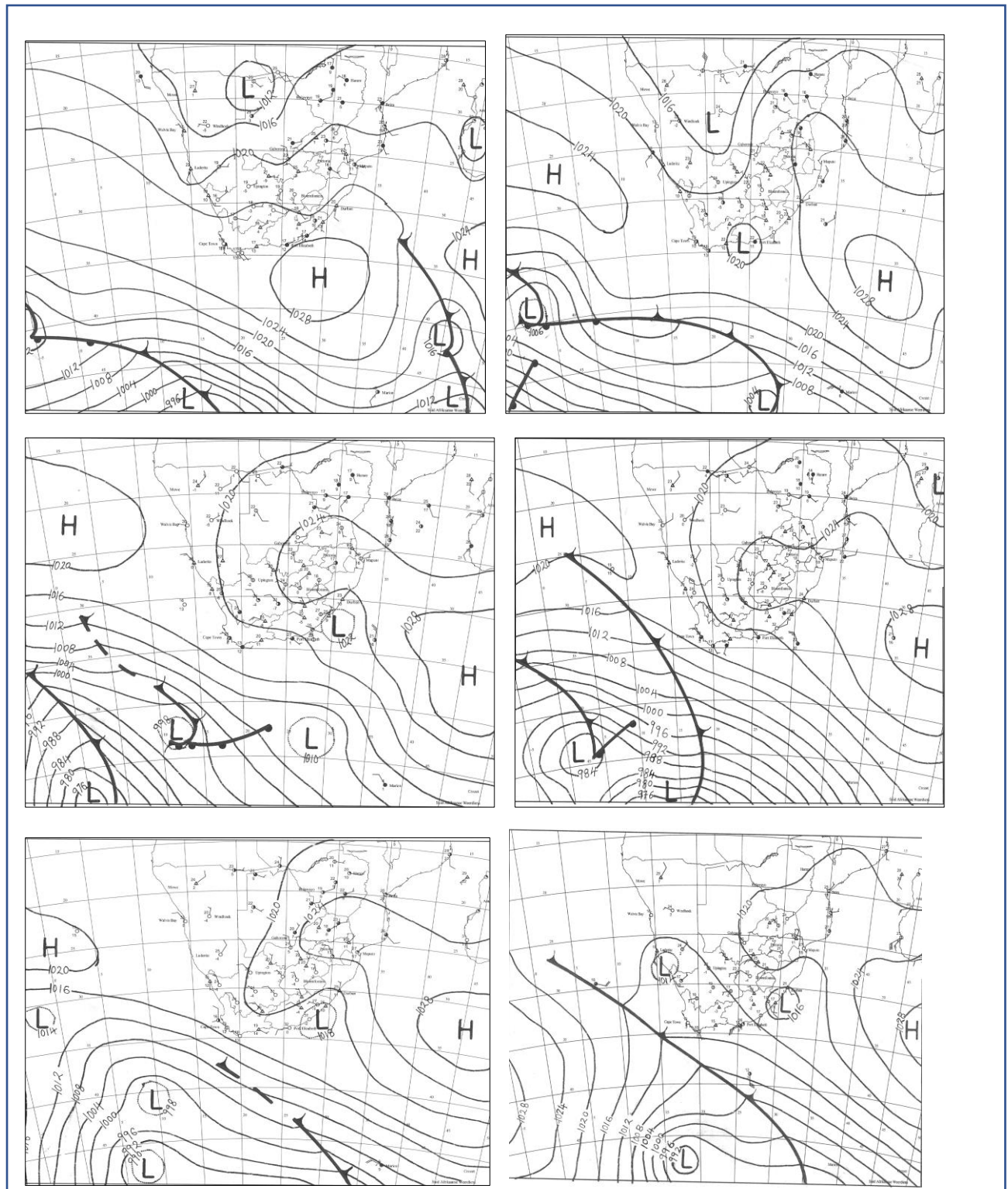
7.1.6. April 2017



Synoptic Charts for April 2017 Sampling period (03/04/2017-08/04/2017) (Weathersa, 2017)



Synoptic Charts for April 2017 Sampling period (09/04/2017-12/04/2017) (Weathersa, 2017)



Synoptic Charts for April 2017 Sampling period (03/07/2017-08/07/2017) (Weathersa, 2017)

7.2. Appendix 2- Laboratory Certificates



TEST REPORT

DATE OF REPORT : 31 October 2017

REFERENCE NO : CLS173995

CLIENT REFERENCE NO :

CLIENT ORDER NO :

CONTACT PERSON : Adri Cowley

CLIENT : Mamadi & Company

CLIENT ADDRESS : 1 Newton Avenue
Kilarney
Johannesburg

CLIENT CONTACT PERSON : Neo Molomo

CLIENT TELEPHONE NO : 078 245 2881

CLIENT FAX NO :

CLIENT e-MAIL ADDRESS : neo@mamadi.co.za

ANALYSIS REQUIRED : Analysis for BTEX.

METHOD USED : Radiello Method D1.

Chemtech Laboratory Services CC. Reg. No: (1998/37710/23), V.A.T. No: 4730185131. Members: Mr. E Cowley, Mrs. A Cowley
Physical: 732 Makou Street, Monument Park, Pretoria. Postal: P.O. Box 25825, Monument Park, 0105
Telephone/Facsimile: +27(0) 12 347 4979, E-Mail: info@chemtechlab.co.za, Web: www.chemtechlab.co.za



TEST RESULTS

Table 1–Analysis for BTEX.

TEST ITEM DESCRIPTION	TEST ITEM CONDITION	DATE RECEIVED	DATE OF ANALYSIS
Radiello Passive Monitors	Sealed in glass tubes. Received at ambient temperature.	18/10/2017	28/10/2017

RESULTS: ($\mu\text{g}/\text{m}^3$)

	PE-1	PE-2	PE-3	PE-4
Compound	B502P	B503P	B499P	B504P
Benzene	2.77	7.59	10.98	2.68
Toluene	3.75	9.61	13.25	4.15
Ethyl benzene	0.76	1.58	1.66	0.89
Xylene	3.85	7.26	7.21	3.80

	MSB-1	MSB-2	MSB-3	MSB-4
Compound	B498P	B501P	B500P	B497P
Benzene	3.28	9.42	7.11	4.98
Toluene	4.14	15.60	12.74	6.49
Ethyl benzene	0.67	2.07	2.12	1.00
Xylene	3.34	10.52	9.51	5.78

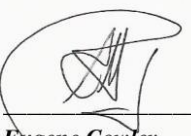
Detection Limit (μg)

Compound	Detection Limit	Compound	Detection Limit
Benzene	0.20	Ethyl benzene	0.26
Toluene	0.23	Xylene	0.24

Specific Test Conditions	Samples stored at $< 5^{\circ}\text{C}$ prior to analysis. Results confirmed using Gas Chromatography/Mass Spectrometry.
Comments	None.

WORK APPROVED BY:


Adri Cowley
 (Laboratory Manager)
 (Technical Signatory)


Eugene Cowley
 (Technical Manager)
 (Technical Signatory)

31/10/2017
 Date

TEST RESULTS

Table 1 – Analysis for BTEX.

TEST ITEM DESCRIPTION	TEST ITEM CONDITION	DATE RECEIVED	DATE OF ANALYSIS
Radiello Passive Monitors	Sealed in glass tubes. Received at ambient temperature.	18/10/2017	27/10/2017

RESULTS: ($\mu\text{g}/\text{m}^3$)

	IV-1	IV-2	IV-3	IV-4
Compound	B516P	B507P	B510P	B513P
Benzene	37.79	73.80	19.41	20.30
Toluene	67.87	118.29	48.53	47.56
Ethyl benzene	8.81	14.63	8.25	5.55
Xylene	40.09	75.12	38.70	25.52

	WIT-1	WIT-2	WIT-3	WIT-4
Compound	I63YX	I64YX	I65YX	I66YX
Benzene	7.32	8.31	25.03	10.40
Toluene	5.66	6.01	20.54	8.46
Ethyl benzene	1.00	0.97	3.25	1.52
Xylene	3.94	3.85	13.23	5.98

	ALB-1	ALB-2	ALB-3	ALB-4
Compound	B8800	B8810	B8670	B8820
Benzene	10.39	11.30	8.59	5.24
Toluene	23.11	34.95	18.39	11.40
Ethyl benzene	5.22	5.89	3.31	2.11
Xylene	21.08	24.20	14.91	9.45

Detection Limit (μg)

Compound	Detection Limit	Compound	Detection Limit
Benzene	0.20	Ethyl benzene	0.26
Toluene	0.23	Xylene	0.24

Specific Test Conditions	Samples stored at $< 5^{\circ}\text{C}$ prior to analysis. Results confirmed using Gas Chromatography/Mass Spectrometry.
Deviations	None.

TEST RESULTS

Table 1–Analysis for BTEX.

TEST ITEM DESCRIPTION	TEST ITEM CONDITION	DATE RECEIVED	DATE OF ANALYSIS
Radiello Passive Monitors	Sealed in glass tubes. Received at ambient temperature.	1/02/2018	02/02/2018

RESULTS: ($\mu\text{g}/\text{m}^3$)

Compound	AIB1	AIB2	AIB3	AIB4	WIT 1	WIT 2
Benzene	4.14	17.33	12.74	8.17	6.58	6.30
Toluene	11.94	53.93	24.15	16.85	5.20	5.30
Ethyl benzene	2.48	15.79	3.47	2.51	< 0.73	< 0.73
Xylene	12.00	98.74	15.26	11.81	2.49	2.86

Compound	WIT 3	WIT 4	ROCKY 1	ROCKY 2	ROCKY 3	ROCKY 4
Benzene	5.53	13.74	1.16	7.34	2.99	5.47
Toluene	5.37	11.66	4.87	12.58	5.90	10.66
Ethyl benzene	< 0.73	1.63	< 0.85	1.46	0.85	1.45
Xylene	2.85	7.83	1.89	7.15	2.74	6.60

Compound	MSB 1	MSB 2	MSB 3	MSB 4	PE 1	PE 2
Benzene	2.68	2.84	5.37	4.78	3.36	5.46
Toluene	4.83	5.50	8.34	7.72	6.99	9.47
Ethyl benzene	0.64	0.64	0.89	0.64	0.73	1.22
Xylene	1.62	1.85	5.76	2.45	4.57	5.22

Compound	PE 3	PE 4	ISV 1	ISV 2	ISV 3	ISV 4
Benzene	1.38	5.12	9.60	6.65	3.32	9.31
Toluene	5.09	9.97	24.43	23.03	13.72	21.50
Ethyl benzene	1.28	0.98	3.18	4.40	3.14	2.63
Xylene	8.35	4.24	16.28	23.26	17.82	12.99

Compound	KRN 1	KRN 2	KRN 3	KRN 4	KRN 5	KRN 6
Benzene	10.50	9.25	8.16	3.66	4.47	4.03
Toluene	17.66	14.89	14.15	6.57	9.42	6.95
Ethyl benzene	1.97	1.58	1.52	0.91	1.50	1.01
Xylene	8.83	7.04	7.00	5.03	8.17	4.92

Detection Limit (μg)

Compound	Detection Limit	Compound	Detection Limit
Benzene	0.20	Ethyl benzene	0.26
Toluene	0.23	Xylene	0.24

Specific Test Conditions	Samples stored at $< 5^{\circ}\text{C}$ prior to analysis.
Comments	Results confirmed using Gas Chromatography/Mass Spectrometry.
	None.

WORK APPROVED BY:



Adri Cowley
(Laboratory Manager)
(Technical Signatory)



Eugene Cowley
(Technical Manager)
(Technical Signatory)

03/04/2018

Date

This report relates to the specific sample(s) tested as identified herein, it does not imply Chemtech Laboratory Services approval of the quality and/or performance of the item(s) in question and the test results do not apply to any similar item that has not been tested.

This report may only be reproduced in full, with the written approval of Chemtech Laboratory Services.

The acceptance of an item for test and the issue of a test report are subject to Chemtech Laboratory Services condition of test. This document is available on request.

Chemtech Laboratory Services does not accept responsibility for errors that might have arisen during sampling and transport of samples by external parties.

Results express in ppm, ppb, mg/m^3 or $\mu\text{g/m}^3$ were calculated using data supplied by the client.

7.3. Appendix 3- Leak Detection and Repair Results

7.3.1. Rocky's Drift

Component Tested	Count	Near Leak	Leaking
Flanges	112 (37% of Total Count)	0	0
Valves	35 (12% of Total Count)	0	0
Pump Valve	38 (12% of Total Count)	0	1
Pump Flange	119 (39% of Total Count)	0	0
Total	304	0	1

7.3.2. Witbank

Component Tested	Count	Near Leak	Leaking
Flanges	325 (83% of Total Count)	0	0
Valves	63 (15% of Total Count)	1	1
Pumps	11 (2% of Total Count)	0	0
Total	426	1	1

7.3.3. Island View

Component Tested	Count	Near Leak	Leaking
Flanges	392 (83% of Total Count)	0	0
Valves	64 (13% of Total Count)	1	1
Pumps	19 (4% of Total Count)	2	0
Total	474	3	1

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