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Analysis of trace gas emissions from spontaneous coal combustion at a South African colliery

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ABSTRACT

Atmospheric pollution resulting from an open-cast coal mine situated 10 km south-west of Witbank (Mpumalanga, South Africa) was investigated during summer and winter 2004. Industrial and urban activities in and around Witbank release large amounts of toxic and criteria pollutants into the atmosphere. Spontaneous combustion from the many collieries in the Witbank area contributes to this problem. Direct, automated, and continuous *in situ* measurements of trace gas concentrations and prevailing meteorological parameters were carried out by a mobile monitoring unit and an automatic weather station. The data collected show that spontaneous combustion is a source of CO, NO, SO_2 and H_2S. Summer daily averages of SO_2, NO, NO_2 and O_3 concentrations ranged between 1 and 18 ppb, 0.3 and 40 ppb, 12 and 75 ppb and 0.9 and 19 ppb respectively. Winter daily concentrations of SO_2 and O_3 were much higher, ranging between 15 and 180 ppb and 14 and 30 ppb respectively. NO and NO_2, in contrast, were lower in winter (0.8 to 15 ppb and 2 to 28 ppb for daily means). Winter daily average concentrations of H_2S, CO and CO_2 ranged between 16 and 217 ppb, 2100 and 5100 ppb and 322 and 436 ppm). Synoptic circulations over the Highveld were found to affect pollutant concentrations. During winter, temperature inversions played a significant role in increasing the pollutant concentrations in the early morning hours until about 10:00. Although considerable amounts of NO, NO_2 and O_3 were captured; their concentrations were within the South African Department of Environmental Affairs and Tourism's permissible levels as contained in the National Environmental Management: Air Quality Act (2004). SO_2 concentrations during winter 2004 exceeded the allowed standards. Elevated concentrations of pollutants were mostly observed when the wind blew from the SE, SSE, S and WSW directions, implicating the 2A south pits of the open-cast mine investigated as the major source of the emissions.

KEY WORDS: spontaneous coal combustion, coal combustion gas emissions, emissions open-cast colliery, weather impact on emissions.

DECLARATION

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

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Thabile S. Dlamini

_____October 2007

To my family

PREFACE

Since the industrial revolution, the need for natural resources to supply increasing industrial demands for energy has had adverse effects on the environment and humans. World-wide, coal is used industrially for manufacturing and processing purposes. In South Africa, coal is mainly extracted and used for electricity generation, with most of the power stations situated in the Mpumalanga Highveld, where the coal reserves and mines are located. This region is also a major source of air pollutants in South Africa. South Africa's dependence on coal-based energy makes it the largest emitter of air pollutants in southern Africa.

Spontaneous combustion in coal mines has been reported in many countries, including South Africa. The emissions released during these fires have altered the chemical composition of the atmosphere. Since the first reporting of a spontaneous coal fire at the Witbank coalfield in 1947, spontaneous coal fires have continually emitted noxious gases into the atmosphere. Measuring and reporting such emissions and the effects they potentially have on the environment and human health is important, particularly if these emissions exceed known toxic concentrations. SO_2, NO, NO_2, O_3, H_2S, CO, and CO_2 affect the environment either directly or indirectly. Their concentrations in the atmosphere are affected by prevailing weather conditions. The emission of trace gases into the atmosphere has implications for the global climate due to their long residence times in the atmosphere.

The purpose of this research report is to discuss the impact of an open-cast coal mine located 10 km south-west of Witbank (Mpumalanga, South Africa) on local air quality. The specific objectives are to:

i. Characterise trace gas emissions within a mine where spontaneous coal combustion occurs.

ii. Determine seasonal differences in air pollution concentrations and their impact on air quality.

This research report is sub-divided into five chapters. **Chapter 1** discusses the problem of coal mine fires in South Africa. It reports what South African mines have done to contribute to air quality management and states the objectives of the report.

In **Chapter 2** the role of trace gases in pollution, their regional transport and air pollution regulations in South Africa are discussed. A review is presented of existing literature about spontaneous coal combustion and associated emissions.

Chapter 3 describes the study area and its general climate. The equipment, methods used in collecting data, calibration of the instruments and the handling of data are discussed in this chapter.

Chapter 4 contains a presentation and discussion of the findings obtained.

A summary of the conclusions drawn from the study is presented in **Chapter 5**.

Sections of this research report have been presented at the South African Society for Atmospheric Sciences (20 to 24 May 2004), the Durban student workshop (20 to 21 July 2004) and at the South African Society for Atmospheric Sciences (26 to 28 September 2005). Parts of this report were also used in the compilation of the CoalTech 2020 Report (Otter *et al*., 2005) for Anglo Coal South Africa.

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ABBREVIATIONS AND ACRONYMS

ACSA	Anglo Coal South Africa
AQA	Air Quality Act
CH	Continental anticyclone (high pressure system)
CO	carbon monoxide
CO_2	carbon dioxide
DEAT	Department of Environmental Affairs and Tourism
EW	Easterly low (low pressure system)
H_2O	water
H_2S	hydrogen sulphide
NO	nitrogen oxide
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen (being NO and NO_2)
O_3	ozone
ppb	parts per billion
ppm	parts per million
ppmv	parts per million by volume
RH	Ridging anticyclone (high pressure system)
RSA	Republic of South Africa
SO_2	sulphur dioxide
US	United States (of America)
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WW	Westerly low (low pressure system)

CHAPTER 1:
BACKGROUND

Chapter 1 of this report introduces the problems that spontaneous combustion of coal poses to the environment. The occurrence of spontaneous fires in South African coal mines is discussed and the objectives of the project are outlined.

Introduction

The extraction of natural resources from the earth depletes them, and impacts the environment. Atmospheric trace gas composition has undergone significant changes over the past 100 years due to anthropogenic and economic activities (Wenig *et al.*, 2002). Coal mining and coal usage are two such activities. Atmospheric pollution resulting from coal-mining activities is produced mainly during combustion processes (United States (US) Department of Energy, 1993). The increase in coal production has been accompanied by a concomitant rise in environmental problems (Hayashi, 1999; Ghose and Majee, 1999), mainly from coal fires. Historically, coal fires occur naturally but coal mining has exacerbated their proliferation, resulting in a global problem characterised by the emission of enormous quantities of noxious gases and particulate matter into the atmosphere, land subsidence, soil and water pollution (Stracher and Taylor, 2004; Heffer and Coates, 2004).

Studies of fires in South African collieries indicate that spontaneous combustion is a major cause of large amounts of trace gases and aerosols being released into the atmosphere, significantly affecting the global chemistry of the atmosphere and its radiative properties, and degrading the air quality (Wang *et al*., 2003; Walsh-Paton *et al*., 2004). The changing composition of natural and anthropogenic trace gases in

the atmosphere has important consequences for global warming (Tyson and Preston-Whyte, 2000).

Coal is the main fuel processed and burned in South Africa, and is one of the largest sources of foreign exchange (Johnson, 2003). This author notes that coal mining in South Africa will continue for the next 200 years. The same author further states that the high usage of readily available cheap coal makes the South African economy a major emitter of greenhouse gases per capita. The benefits of having affordable energy outweigh the possible impact of its contribution to global warming. The present focus in developing countries such as South Africa is on economic development and industrial growth, with slow (and inadequate) environmental change policies, and this allows trace gas emissions to continue to increase (Streets *et al*., 2000). It is noteworthy that in countries like the United Kingdom, sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) from coal mines still remain significant within and around emission sources despite stringent legislation on emission reduction (McGonigle *et al*., 2004).

Open-cast mining produces spoil piles that consist of overburden partings, unrecovered coal and carbonaceous shale, siltstones and mudstones. The carbon content of these materials makes them liable to spontaneous combustion with consequent emission of heat energy, fine particles and gases (Carras, 2001). Spontaneous combustion causes open and smouldering fires that can emit carbon dioxide (CO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), SO_2 and other organic emission compounds associated with incomplete combustion (Carras *et al*., 1997).

Under suitable conditions, spontaneous coal combustion manifests itself in all major aspects of coal mining, coal handling and utilisation (namely, underground coal mining, sea-borne transport (ships' holds), stacking of reject material (discard dumps), stockpiling (tips, stacks and silos) of coal at the pithead and power stations and ports) (Uludag, 2001; Spencer *et al.*, 2000). It has been observed that

spontaneous coal fires are more common where coal is or was actively mined (Clarke *et al*., 1997; Kaymakci and Didari, 2000; Prakash, 2003). Spontaneous combustion has been reported in many countries including the United States of America, Canada, China, Australia, India, Indonesia, South Africa, England, Germany, Poland, Czech Republic, Russia, Ukraine, Turkey and Thailand (Finkelman, 2003). Lloyd (2002) notes that burning in abandoned mines is probably the worst horror that the South African coal-mining industry has inherited.

Spontaneous combustion in South African coal mines

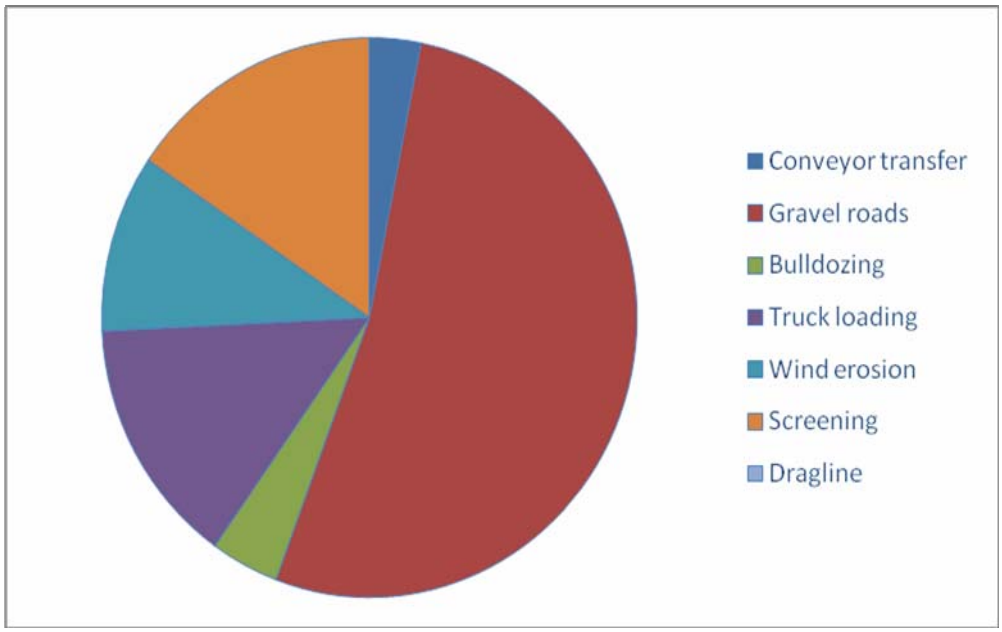
Spontaneous combustion was first reported in 1947 at the Witbank Coalfield (Bell *et al*., 2000). The Kleinkopje Colliery was found to have the most extensive occurrences of spontaneous fires (Uludag, 2001). The extent of the existing potential problems in the Witbank area was such that, in 1986, the Coal Mining Research Council approved funding for research on fires in shallow mines. This work was initiated by the Department of Mining Engineering at the University of the Witwatersrand before being undertaken by the Coal Mining Laboratory of the Chamber of Mines of South Africa (ACSA, 2002). Measures have been taken to bring the fires under control and manage them, but they continue to burn, injecting more pollutants into an already polluted atmosphere.

Anglo Coal South Africa's air quality management

Anglo Coal South Africa (ACSA) is in the process of developing an air quality management system for its mining operations (ACSA, 2002). The company believes in assessing the impacts of emissions from different activities throughout the life-cycle of its products. According to the above report, particulate emissions are monitored on all ACSA mines for occupational and public health reasons. Furthermore, a programme to characterise emissions such as CH_4, SO_2 and CO_2 and model the concentrations contributed by the company's operations is under way and

it includes the quantification of greenhouse gas emissions from spontaneous combustion.

One such project involved undertaking an emission inventory at the Keinkopje Colliery in 2002 to develop an account of particulate emissions and their associated sources from mining activities (ACSA, 2002). That research indicates that gravel roads contributed the highest emissions (51 %). Screening and conveyor transfer had the smallest contributions (3 % each) (Figure 1.1). Spontaneous combustion, although it emits aerosols into the atmosphere (Figure 1.2), was not listed in these activities, despite it (which is continuous and difficult to control), worsening the problem of ground level accumulation of pollutants.



(Source: ACSA, 2002:32)

Figure 1.1: Percentage contribution of operation activities to particulate emissions at the Kleinkopje colliery

Figure 1.2: Spontaneous combustion particulate emissions are highly visible, particularly when trapped under an inversion layer (left). Once the inversion layer lifts, the pollutants are dispersed and become less apparent (right)

Significance of the study

A thorough search of the literature available revealed no documented information on emissions from spontaneous coal combustion in South Africa, with the result that the present study could well provide the first data set. Determining the ongoing effects of coal mining on South Africa's air quality is necessary and could be used to support effective control measures. With the current shift in South Africa's air quality legislation from a source-based approach to an ambient air quality paradigm, it is important to determine the contribution of individual pollution sources to the air quality of an area (Scorgie *et al*., 2005). These authors also suggest that measuring gaseous pollutant concentrations at different locations downwind of emission sources is, therefore, necessary and is believed to be appropriate in addressing the current effects of air pollution in the South Africa.

In this study, a wide range of gas concentrations (SO_2, nitrogen oxide (NO), NO_2, O_3, hydrogen sulphide (H_2S), CO and CO_2 was measured simultaneously with prevailing weather parameters. The continuous measurement of gas concentrations enabled the determination of their transformations during the day and the effects of changing weather conditions on their atmospheric concentrations. It also provided time-

resolved data with short time averages. *In situ* measurements reduce the probability of chemical and physical reactions of the gas samples between sampling and analysis time.

Objectives of the study

The overall goal of this research is to quantify the concentrations of trace gases near a source of spontaneous combustion in an open-cast coal mine situated 10 km south-west of Witbank, in the Mpumalanga Highveld. Its specific objectives are to:

i. Characterise trace gas emissions within a mine where spontaneous coal combustion occurs.
ii. Determine seasonal variations in air pollution concentrations and their impact on air quality.

CHAPTER 2:
LITERATURE REVIEW

This chapter reviews the findings obtained from similar previous studies. It discusses the mechanism and causes of spontaneous coal combustion. An overview of air pollution in the South African Highveld and the effects of trace gases are outlined.

Trace gases as air pollutants

Air pollution affects humans directly as a consequence of inhalation or contact and indirectly by affecting the environment which, in turn, impacts on man's well-being (Held *et al*., 1996). Knowledge of ambient atmospheric pollution levels is essential for assessing air quality and exposure risk for man and the environment (Balamanti *et al.,* 2001). Trace gases play an important role in the thermodynamics of the atmosphere by virtue of their properties as greenhouse gases by absorbing outgoing long-wave, infra-red radiation from the earth and atmosphere to produce the greenhouse effect (Tyson and Preston-Whyte, 2000). O_2, O_3, H_2O and CO_2 are the most significant absorbing gases in the atmosphere (Seinfeld and Pandis, 1998). Spontaneous combustion of coal has been recognised by the Inter-governmental Panel on Climate Change as a potential source of greenhouse gas emissions but it has been excluded from greenhouse gas inventories (Carras *et al.,* 2001). This is because it is considered that there is no acceptable method for estimating the emissions which is partly due to the lack of accurate data on the extent of burning in different areas (Prakash, 2003).

At a global scale, the emissions of large volumes of greenhouse gases from burning coal (including spontaneous combustion) – if present in sufficient amounts – have important consequences for climate change and global warming, which alter ecosystems and patterns of disease occurrence (Merrick, 1984; Gouws, 1993; Kirkman, 1998; Tyson and Preston-Whyte, 2000; Gabbard, 2000; Finkelman, 2003). CO_2 is the most contributory gas to the greenhouse effect (55 %), while CO accounts for 5 % (Gow and Pidwirny, 1996). Methane (CH_4), another product of coal combustion, is 21 times more potent than CO_2 in its greenhouse effect (Lloyd, 2002; Innovations Report, 2005). NO_2 and SO_2 are important criteria pollutants that impact on air quality and are the most important constituents of acid rain (Gabbard, 2000).

Concern about emissions of trace elements from coal combustion also arises from the known toxic, carcinogenic and mutagenic effects that have been observed in individuals exposed to high doses of these elements (Merrick, 1984). These adverse health effects have been known for a long time (Kjellstrom *et al*., 2002). There is, however, no clear cause-and-effect relationship between a particular air-borne pollutant and a corresponding health disorder (Lyons and Scott, 1990; Kjellstrom *et al*., 2002). The same authors note that toxic trace gases are particularly dangerous because they are invisible and show unpredictable physical behaviour. Spontaneous combustion of coal, in particular, releases a wide range of air-borne pollutants which, in high concentrations and with sufficient exposure, may be hazardous to health (Freudenstein *et al.*, 2000; Carras, 2001). Recent studies suggest that even at the substantially lower levels of air-borne pollution experienced today, compared to the 1950s, there are still associations with premature mortality, chronic illness and discomfort (Evans and Bennett, 1998; Mishra, 2003). Health impacts of air pollution depend on the pollutant type, its concentration in the atmosphere, length of exposure, other pollutants in the atmosphere and individual susceptibility (Mishra, 2003).

Exposure to SO_2 can cause breathing difficulties, respiratory illness, wheezing and aggravate existing heart disease (United States Environmental Protection Agency (USEPA), 2005; Longo *et al.*, 2005). Sulphate particles formed from SO_2 are a major

cause of reduced visibility, whereas the toxicity of NO_2 relates to its ability to form nitric acid when combined with water in the eyes, lungs, mucous membranes and skin (Kjellstrom *et al*., 2002). High concentrations of NO_2 can, therefore, result in lung irritation and potential damage to the respiratory system. Nitrate particles and NO_2 can block the transmission of light in the atmosphere, contributing to reduced visibility (USEPA, 2005). O_3 (also known as smog) exposure leads to itchy and watery eyes and has been associated with respiratory disorders such as asthma (USEPA, 2005). Other ill-health effects resulting from O_3 are pneumonia, bronchitis and reduced lung function. Prolonged exposure to CO could affect a developing foetus resulting in delivery of a low birth-weight baby to non-smoking mothers (USEPA, 2005). Reduction of delivery of oxygen to body organs may result in impairment of brain function and affect the cardiovascular system (USEPA, 2005).

Overview of air pollution in the South African Highveld

There are always background concentrations of naturally occurring gases in the atmosphere. These concentrations can, however, be significantly enhanced by emissions from the spontaneous combustion of coal. The Highveld of South Africa, where Witbank is located, has several sources of primary pollutants (Tyson *et al*., 1988). This region contributes about 90 % of South Africa's emissions of dust, SO_2 and NO_2, with power stations being a principal source of moderate ground-level SO_2 concentrations (Held *et al*., 1996; Freiman and Piketh, 2002). Witbank, in particular, has ground-level concentrations of trace gases elevated by emissions from industries and power stations, dumps of discard coal, domestic combustion, motor vehicles and veld-burning (Tyson *et al*., 1996; Ryerson *et al*., 2001). Near-ground-level sources of emissions from spontaneous combustion in coal dumps are important since the region has a weak dispersion potential in the lower atmosphere (Tyson *et al*., 1988).

According to Held *et al*. (1996), ozone (O_3) concentrations in the mixing layer over the Highveld are high (40 ppb). Annual mean concentrations of O_3 range between 20 and 38 ppb. Hourly mean concentrations exceed 20 ppb with only a few occurrences

above 60 ppb (Held *et al*., 1996). NO is the main form of nitrogen oxides emitted from combustion processes and it quickly oxidises to form NO_2 (Tyson *et al*., 1988). Monthly mean values of NO are lower in summer, reaching a minimum of 20 ppb, while they rise to as much as 120 ppb in winter (Held *et al.,* 1996). H_2S, if allowed to escape into the atmosphere, is oxidised to SO_2 and adds to the SO_2 load of the area (Held *et al*., 1996). In rural areas, SO_2 peaks during daylight hours while, in locations close to coal dumps, low-level SO_2 emissions peak at night or during the early morning hours (Held *et al*., 1996). SO_2 monthly means show low values of around 9 ppb in summer, increasing to about 35 ppb in winter (Held *et al.,* 1996).

Air pollution regulations in South Africa

For environmental protection, ambient air quality guidelines have been established internationally and in South Africa. These provide a basis for protecting the public from the adverse effects of air pollution and aim to eliminate or reduce air pollutants that are hazardous to human health and well-being (van Niekerk, 2001). The USEPA and the World Health Organisation (WHO) have published air quality standards (USEPA, 2005; WHO, 2000) (Table 2.1) that have been adopted by many countries.

According to the South African Minister of Environmental Affairs and Tourism, Marthinus van Schalkwyk, South Africa accounts for 1.4 % of global greenhouse gas emissions and ways of reducing these are necessary (Louw, 2005). The same author notes that in February 2005 South Africa passed the National Environmental Management: Air Quality Act (AQA) 39 of 2004 (RSA, 2004), which came into effect on 11 September 2005. This Act replaces the Atmospheric Pollution Prevention Act 45 of 1965 (RSA, 1965) and introduces an objectives-based approach in dealing with pollution in South Africa by providing national norms and standards for regulating air quality monitoring, management and control (DEAT, 2005). Unlike dealing with individual emission sources, its use of ambient air quality as a point of reference will enable Government to set tighter emission standards in areas with multiple sources of pollutants (Louw, 2005). This will be effective in dealing with the

cumulative impacts of air pollution on the environment (Groenewald, 2004). Minister van Schalkwyk also stated that the new Act establishes a scientific basis for identifying South Africa's most polluted air and guilty polluters (Groenwald, 2004) and sets standards (Table 2.1) that provide a benchmark for air quality management in South Africa (Stanford, 2005). The SO_2 ambient standard setting initiative (completed in 2002) was instrumental in the setting of standards for other gases (DEAT, 2005).

Table 2.1: International and South African ambient air quality standards at 25 °C and normal pressure

Pollutant	Averaging time	DEAT standards (ppb)	USEPA standards (ppb)	WHO standards (ppb)
O_3	Instant peaks	250		
	1 hour	120	120	60
	8 hours	-	80	-
SO_2	Instant peaks	191		
	1 hour	-	-	-
	24 hours	48	140	40
	1 month	50	-	-
	1 year	19	30	20
NO_2	Instant peaks	5000		
	1 hour	200	128	100
	24 hours	100	-	-
	1 month	80	-	-
	1 year	50	53	20
CO (ppm)	1 hour	9	9	9
	8 hours	35	3 to 5	26

Note: There are no NO, H_2S and CO_2 guidelines.

Source: WHO, 2000; Scorgie *et al*., 2003; DEAT, 2005; USEPA, 2005.

Air pollution transport and meteorology

Although atmospheric pollutants may be produced at a small scale, their impacts are often felt thousands of kilometres away due to atmospheric transport and meteorology. For example, noxious gases and particulate emissions released by combustion associated with one spontaneous fire, the Liu Huangou coal fire, were blown by winds to Urumqi city, one of the ten worst polluted cities in the world (Stracher *et al*., 2004). Trace gases have relatively long atmospheric lifetimes enabling them to be transported over great distances, resulting in complaints about dust generation and health concerns (Evans and Bennett, 1998). CO_2 has a residence life in the atmosphere of up to 150 years, while CO resides for 30 to 90 days (Seinfeld and Pandis, 1998). NO has a lifetime of a few hours (Seinfeld and Pandis, 1998), making its distribution more confined to its source region

Pollution transport depends on the height pollutants reach in the atmosphere, their particle sizes and meteorological conditions (stability, wind direction and speed) (Alloway and Ayres, 1997; Querol *et al.*, 1998; Jonsson *et al.*, 2004). Although the routes of transport of atmospheric pollutants have been well established, the amounts of material in each identified transport route remain uncertain (Simukanga *et al.*, 2004). During transport in the atmosphere, some of the air pollutants are subject to physical and chemical transformations resulting in more toxic species than the primary emissions (Arutyunyan and Aloyan, 1997). The general trend, however, is that the concentrations of the pollutants decrease as they travel from the source and are dispersed by wind and other natural processes (Preston-Whyte and Tyson, 1989; USEPA, 2004).

The impact of pollution on ambient air quality depends on the micro-meteorological conditions (Ghose and Majee, 1999) since pollution concentrations are strongly dependent on the atmosphere into which they are being emitted. The rate of pollutant accumulation and dispersion in the atmosphere depends on the state of the atmosphere, particularly the earth's boundary layer where thermal and mechanical

turbulence are dominant processes (Tyson *et al*., 1988). Circulations in the atmospheric conditions are major determinants of the low-level field during the night and in winter when they control the transport and dispersion of low-level concentrations of pollutants (Lyons and Scott, 1990; Held *et al*., 1996). Pollution concentrations vary significantly among air mass types and there is evidence that air pollution can be modified according to the presence or absence of specific weather conditions (Rainham *et al.*, 2004).

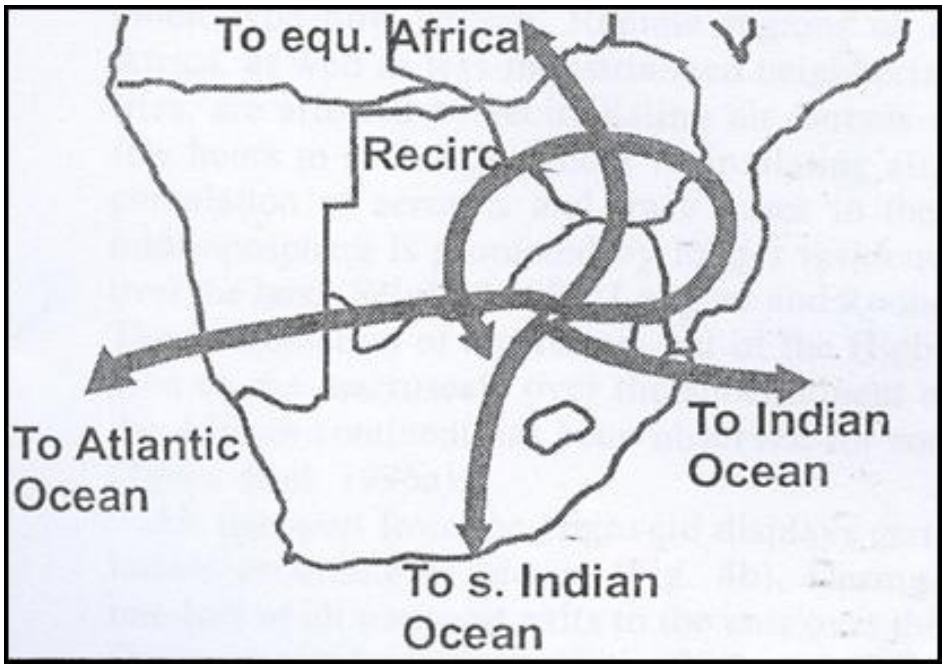
Establishing a link between weather conditions and emission patterns to pollutant concentrations is important, as pollution concentration levels fluctuate in response to the changing state of the atmospheric stability (Tyson and Preston-Whyte, 2000). The stability of the air – as determined by the vertical variation of temperature – influences how quickly the pollutants are diluted by mixing with air (Neiburger *et al*., 1977). Atmospheric concentrations are, therefore, not only a function of emissions and production but also meteorology, transport and mixing (Tyson *et al*., 1996; Querol *et al.*, 1998).

Meteorological factors that affect pollutant concentrations in the lower atmosphere are mainly wind velocity, vertical temperature profile, mechanical turbulence as well as the rate and height of emissions (Wicking-Baird *et al*., 1997). Accurate definition of these is, therefore, one of the chief requirements in understanding air quality (Seaman, 2002). Since the gas-to-particle conversion processes controlling the secondary particulate emissions are also dependent on the meteorological conditions (insolation and humidity are major parameters controlling sulphate and nitrate formation), there are significant seasonal variations in the levels of secondary particulate pollutants (Querol *et al.,* 1998). The chemical reactions occurring in the atmosphere between the different gases are also affected by weather conditions. McGonigle *et al*. (2004) report that increases in relative humidity increase the rates of aqueous reactions in the atmosphere. The presence of sunlight (solar radiation) accelerates the photolysis reaction that forms O_3 (Eatough *et al.*, 1984; Seinfeld and Pandis, 1998).

Regional scale transport over southern Africa

The nature of the export of aerosols and trace gases out of the industrial Highveld region is an essential starting point towards understanding the nature and chemistry of air transport over southern Africa (Held *et al*., 1996; Freiman and Piketh, 2002). Trajectory analysis has been used by Freiman and Piketh (2002) to establish the transport pathways into and out of the Highveld. Backward trajectories have shown that there are four main transport pathways into the Highveld. These are from the Atlantic Ocean, subtropical Africa, Indian Ocean and over southern Africa. About 43 % of air reaching the Highveld is clean marine air advected with westerly disturbances over the southern parts of South Africa (Freiman and Piketh, 2002). Southern African transport reaching the Highveld frequently carries previously polluted air (D'Abreton and Tyson, 1996; Piketh *et al*., 1998; Freiman and Piketh, 2002).

Air masses, trace gases and aerosols from the Highveld of South Africa are either directly transported or recirculated on various scales over the subcontinent (Tyson *et al.*, 1997; Tyson and D'Abreton, 1998). Air is advected directly in westerly, easterly, northerly and southerly transport modes and is also recirculated towards its point of origin (Figure 2.1) (Freiman and Piketh, 2002). Up to 41 % of all transport from the Highveld affects neighbouring countries (Gatebe *et al*., 1999; Freiman and Piketh, 2002). Of this, transport to Mozambique occurs on about one-third of the time (Piketh, 2000). Botswana is affected by one out of three trajectories exiting the Highveld while Swaziland is affected by one out of four trajectories (Piketh, 2000).



(Drawing created after Tyson *et al*., 1996)

Figure 2.1: The major air transport pathways out of the Highveld

Spontaneous combustion and its emissions

The mechanism of spontaneous combustion

Coal is one of the carbonaceous materials which, under certain conditions, can combust spontaneously as a result of its oxidation with atmospheric oxygen (Sevil, 1995). Spontaneous combustion is a process that usually begins as 'hot spots', which appear when coal absorbs oxygen from the air (US Department of Energy, 1993). Coal's reaction with atmospheric oxygen liberates heat which accumulates, resulting in temperature rise and leading to an ignition (Carras, 2001; Lyman and Volkmer, 2001).

Although spontaneous combustion has been studied extensively, the mechanism by which it occurs is not well understood (Kaymakci and Didari, 2000). Several theories

have been used to describe the spontaneous combustion phenomenon (bacterial, oxidation, humidity and pyrite). The oxidation theory has had a great deal of support compared with the others (Gouws, 1993). It suggests that oxygen is adsorbed onto the surface of coal under ambient conditions, followed by a temperature rise (Spencer *et al*., 2000). The oxidation of coal is a complex process due to the heterogeneous nature of coal. In simplified terms, this reaction can be summarised as:

C + O_2 = CO_2 + Heat (Lyman and Volkmer, 2001)

This chemical reaction is exothermic and the rate of reaction doubles for every 10 °C temperature rise (Goodarzi and Gentzis, 1991; Speight, 1983). If the heat does not escape and is allowed to accumulate, it raises the temperature of the coal past its ignition point and a spontaneous fire occurs. It has been established that low-rank, high-moisture coals exhibit self-ignition at temperatures as low as 30 °C (Goodarzi and Gentzis, 1991; Carras, 2001; Lyman and Volkmer, 2001).

Once the coal's temperature rises above ambient (65 to 149 °C), coal begins to give off minute but measurable quantities of gas, aerosols, hydrogen and CO_2, which are precursors of combustion (US Department of Energy, 1993). As the temperature increases further (to about 371 °C) relatively large, visible particles are emitted. If the temperature continues to rise, combustion and eventually self-ignition and flames occur (US Department of Energy, 1993).

Causes of spontaneous combustion

Spontaneous combustion can result from both external and internal factors. The external conditions are mining operations and atmospheric conditions. The internal characteristics that affect the susceptibility of a particular coal to self-heating include temperature, rank, exposed surface area, inherent moisture content and pyrite content (Fierro *et al*., 1999; Bell *et al*., 2000). The impacts that these factors have on the susceptibility of coal to combust spontaneously are explained by Lyman and Volkmer (2001) and Kaymakci and Didari (2000):

- Air flow rate: Air provides oxygen necessary for the oxidation process and a means to dissipate the heat as it is generated.
- Particle size: The smaller the particle size, the greater the surface area available for oxidation to take place.
- Temperature: The higher the temperature, the faster the reaction of coal with oxygen.
- Pyrite content: The presence of sulphur minerals (pyrite and marscasite) may accelerate spontaneous heating. These minerals may swell upon heating, causing the coal to disintegrate and reducing the size of particles involved in the reaction. The concentration of pyrite must be greater than 2 % for it to have a significant effect.
- Geological factors: Rocks are poor conductors of heat. Faults and fractures in the overburden can allow water and air to enter a coal seam. This influx is the reason that abandoned mines, especially those that have suffered subsidence events, are often sites of spontaneous coal fires.
- Coal rank, which depends on volatile matter, fixed carbon, moisture and oxygen. It increases with an increase in the amount of carbon and a decrease in volatile matter (Neiburger *et al*., 1977; Smith and Glasser, 2004): As the rank decreases, the tendency for coal to self-heat increases.

Coal seams can also be susceptible to self-burning as a result of external sources of ignition, such as forest fires or lightning strikes (Gentzis and Goodarzi, 2000). Other incidents of spontaneous combustion are likely to occur when the roofs of old workings collapse. This gives rise to sink holes which may extend from the surface to the coal seam, creating fractures that may expose the coal and, where present, the carbonaceous shale resulting in combustion (ACSA, 2002).

In areas of active and abandoned mines, mining activities result in breaking or crushing of coal and spreading small fragments of coal, carbonaceous materials and

coal dust in the vicinity of the main coal seam. This porous coal rubble is more prone to spontaneous combustion than a thick coal seam would be (Prakash, 2003).

Spontaneous combustion emissions

Air pollution research has been fairly extensive over the South African Highveld region and numerous pollution sources in this region have been identified. However, the amounts of trace gases contributed by each of the source categories have not been established (Piketh, 2000). Spontaneous combustion in coal dumps has been identified as one of the sources that is contributing to the degradation of air quality in the Highveld (Held *et al*., 1996).

Research on spontaneous combustion tends to focus on modelling (Svanas, 1987; Bradshaw, 1989; Uludag, 2001) and determining the propensity of coal samples to combust spontaneously (Kutcha *et al*., 1980; Clarke *et al.,* 1997; Gouws, 1993; Wade, 1997). Few measurements of the gases emitted during the process have been conducted and, as far as can be ascertained, there are no documented measurements for South Africa. Other studies aimed at determining the emission rates and pollution from various open-cast mining operations have omitted spontaneous combustion from their list of sources (Chakraborty *et al*., 2001; Chaulya, 2004). Finkelman (2003), quoting the USEPA, confirms that few studies have monitored effluents from domestic coal-burning, and fewer still have tried to determine the pollutants from burning coal beds and waste piles.

CO is the main gas released in the initial stages of coal combustion (incomplete combustion). As the temperature rises, CO_2 is also given off and the coal begins to burn (Spencer *et al.,* 2000; Gabbard, 2000). Other elements released on coal combustion are NO, NO_2, SO_2 and volatile organic compounds (methane, ethane, propane, butane and toluene) (Merrick, 1984; Chagger *et al*., 1999; Lloyd 2002). In addition to the primary emissions, the gas-to-particle conversion processes also give rise to considerable volumes of highly reactive, secondary particulate emissions

which could be more harmful (Querol *et al*., 1998; Seinfeld and Pandis, 1998). Other chemical reactions between gases produce O_3 as the main secondary product.

A study conducted in China established that the incomplete combustion of 1 ton of coal with 720 kg carbon, emits an equivalent of 4.9 tons of CO_2 (Timko and Derick, 1989). Another study concluded that the amount of CO_2 from spontaneous fires in Northern China alone accounts for as much as 2 to 3 % of the annual world emissions of atmospheric CO_2 from burning fossil fuels (Ottl *et al*., 2002; Stracher and Taylor, 2004; Gould, 2003; Van der Meer, 2005).

An air quality survey, where ambient air samples were collected at five locations in the Jharia Coalfield of Bharat, India, indicated that suspended particulate matter concentrations for all the stations exceeded the permissible limits specified by the Central Pollution Control Board during all but the rainy season (Ghose and Majee, 1999). These authors also note that SO_2 and NO_x concentrations exceeded their limits at different occasions.

Monitoring of the hydrocarbons ethylene (C_2H_4), propylene (C_3H_6) and acetylene (C_2H_2) showed that they were coal-fire detector gases because they were released sequentially as the temperature increased during heating (Stracher and Taylor, 2004). When analysing gases from the Langgu Colliery in a laboratory coal oxidation experiment, Lu *et al.* (2004) established that CH_4 was the main gas emitted. In this experiment, ethane (C_2H_6) appeared at temperatures of 30 to 40 °C (normal ambient temperature), while C_2H_4 was detected at 64.3 to 75.3 °C, and its increased concentration indicated that self-heating was developing. The appearance of ethyl hydride (C_2H_5H) showed no particular regularity. The discrepancies between the findings of Stracher and Taylor (2004) and Lu *et al.* (2004) could be attributed to the fact that Lu *et al*. (2004) conducted a laboratory experiment while Stracher and Taylor (2004) took gas samples from the mine vents, where oxidation occurs under natural and not controlled conditions.

Laboratory analysis, conducted in Israel by Davidi *et al*. (1995), on the organic volatile emissions accompanying low-temperature coal combustion in stock-piles revealed that hydrocarbons (C_{1-4}) and molecular hydrogen were present in significant quantities. Despite originating from different countries, the coal samples had similar emission trends. However, high concentrations of hydrocarbons were not necessarily associated with areas of higher temperatures. The same study concluded that the concentrations of hydrocarbon emissions were in the order: methane > ethane > propane (Table 2.2). Davidi *et al*.'s finding that CH_4 is the main gaseous product of spontaneous combustion was consistent with Lu *et al*. (2004).

Table 2.2: Emissions of saturated hydrocarbons by oxidation of coals from four countries

Country of Origin	Size Fraction (µm)	CH_4 (ppmv)	C_2H_6 (ppmv)	C_3H_8 (ppmv)
South African	<74	770	79	16
	250 to 315	970	102	26
Colombian	<74	550	102	5
	250 to 315	549	104	6
American	<74	974	195	83
	250 to 315	1080	389	189
Australian	250 to 315	550	102	4
Source: Davidi *et al*., 1995.				

According to Carras (2001), the Australian Coal Research carried out two projects to explore methods of establishing greenhouse gas emissions from spontaneous

combustion. The first project (C8059) sought to provide methods, supported by direct measurements, to quantify the emissions. Measurements of emissions from spoil piles, coal rejects and tailings were conducted at 11 mines in the Hunter Valley and the Bowen Basin using the chamber technique. This project significantly advanced the knowledge of emissions from spontaneous combustion in open-cast mines, but there were practical problems in applying the results to estimate greenhouse gas emissions from operating mines. A key finding was that emission rates of greenhouse gases from spoil piles, where there was no spontaneous combustion but only low-temperature oxidation, had similar emission rates to those from biological activity in vegetated surfaces (Carras, 2001). This suggests that spoil piles with no spontaneous combustion have a minimal net contribution to greenhouse gas emissions.

The second project (C9062) used air-borne infra-red thermography to monitor the long-term behaviour of spoil piles subject to spontaneous combustion (Carras, 2001). However, due to the complexity of the processes involved in producing heat, its surface manifestation and the associated emissions of greenhouse gases, the estimates were subject to high uncertainty. Of particular interest were the concentrations of hydrocarbons, which are known to be carcinogenic if present in high concentrations (Carras, 2001). The main conclusion from this project was that air-borne infra-red data could be used to monitor the long-term behaviour of spoil piles subject to spontaneous combustion (Carras *et al*., 1997). These investigations in the Upper Hunter Valley have shown that spontaneous combustion can give rise to significant trace gas concentrations at ground level (Carras, 2001).

The US Bureau of Mines examined spontaneous combustion episodes in coal mine pillars in an active underground mine using six different methods. Gas detection devices were used to measure emissions from the atmosphere surrounding the pillars. They measured daily oxygen, CH_4 and CO levels (Rosema *et al*., 1999). The detection of CO emissions from the pillars provided an indication that spontaneous heating was taking place. The same authors indicate that oxygen concentrations were below-

ambient, which indicated that oxygen was being used up in the coal oxidation reaction.

An open-cast mine accumulated 700 tons of coal over a 5-week period in England in December, 1998. Villagers living downwind from the mine complained of strong, unpleasant odours. Later, skin and airway irritations were reported, suggesting that SO_2 was unlikely to be the only gas present (Freudenstein *et al*., 2000). This led to a hazard assessment which included measurements of weather conditions being conducted but no SO_2 was detected. This could have been because the detection threshold for the equipment used was ~100 ppm higher than the level at which health effects would be expected (~125 ppb) (Freudenstein *et al*., 2000). In a similar incident, a stack survey conducted in May 1994 in Coalstrip, Montana verified that particulate emissions, SO_2, NO_x, CO, total hydrocarbons and H_2S were emitted from spontaneous combustion (Sheldon and Frank, 1995). The concentrations of these emissions were, nevertheless, within permissible levels of the United States Environmental Protection Agency.

Several studies have been done in French mines (Ferreux *et al*., 2000; Gabbard, 2000) to improve the understanding of the processes mobilising arsenic from mine tailings. The field data suggest that arsenic is released into the hydrological cycle where mine tailings have undergone spontaneous combustion (Ferreux *et al*., 2000). These authors note that almost three times more arsenic is released by the burnt samples. In contrast, sulphate concentrations were much higher in the unburnt samples. These results suggest that arsenic is more mobile after combustion (Ferreux *et al.*, 2000). Naturally-occurring radioactive materials (uranium and thorium) have also been released from coal combustion, although their emissions are not as well known (Gabbard, 2000).

Carbon monoxide as a tracer for spontaneous combustion

Studies have shown that CO time-based trends are the most accurate indicators of spontaneous combustion (Timko and Derick, 1989; Davison and Hewitt, 1997). Its temporal variation in concentration is normally due to meteorological factors rather than chemical transformation. A study conducted by Glen *et al*. (1996) showed that meteorological factors rather than emissions explained most of the CO seasonal behaviour between 15 sites. This is because CO is stable in the atmosphere and variations in its concentration indicate variations in the weather conditions. Sulphur, although also considered to be typical of coal combustion emissions (Cyrys *et al.*, 2002), differs from CO in that SO_2 is quite reactive in the atmosphere. It quickly forms other atmospheric species including sulphate aerosols. It, therefore, could not be used the same way as CO because its variability results from more complex processes.

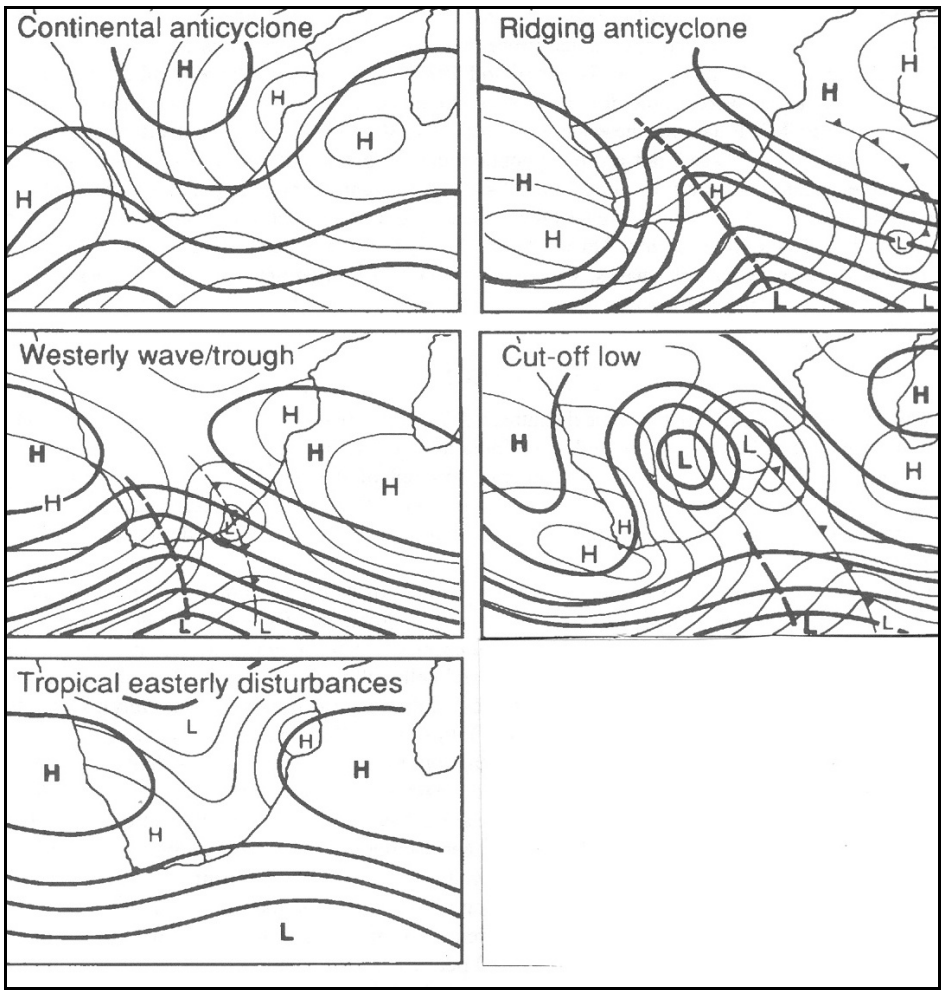
CHAPTER 3:
METHODOLOGY

This chapter describes the study area and its general climate, the equipment and methods used to collect data. Methods used in data manipulation for analysis are also explained.

Description of the study area

Witbank is located in the Mpumalanga Highveld of South Africa, which is part of the Mpumalanga province (Figure 3.2) and is a major source of pollutants in South Africa. The industrial and urban activities taking place in the Highveld have released large amounts of pollutants into the atmosphere, where dispersion of pollutants is unfavourable (Tyson *et al*., 1988).

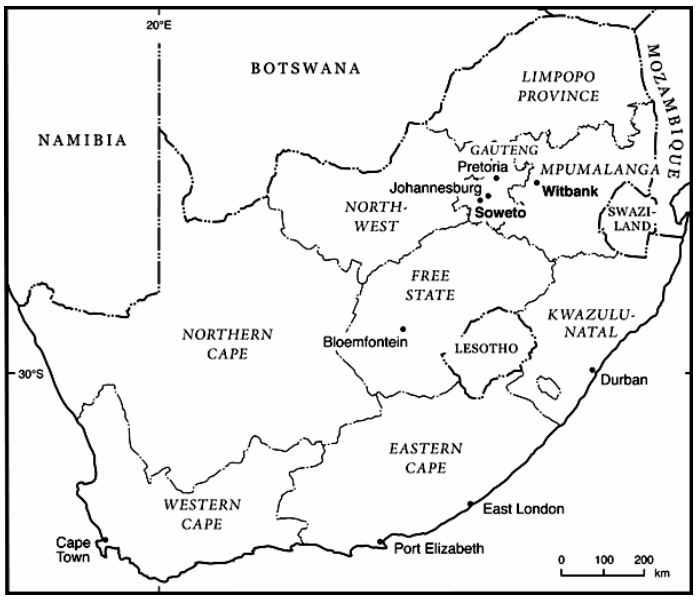
The Mpumalanga Highveld is characterised by high atmospheric stability, clear skies and low wind speeds associated with high pressure systems and circulation is generally anticyclonic throughout the year (Tyson, 1986; Tyson *et al*., 1988). Four major air circulation types (Figure 3.1), which occur at different frequencies throughout the year, dominate over southern Africa (Tyson *et al*., 1996) affecting the Highveld. Semi-permanent subtropical anticyclones (continental anticyclones) are most frequent in winter, while barotropic quasi-stationary tropical easterly waves occur mostly in summer (Tyson *et al.*, 1996). Transient mid-latitude ridging anticyclones show a little annual variation, whereas westerly baroclonic disturbances show a maximum in spring (Tyson *et al*., 1996).



Source: Tyson *et al*., 1996

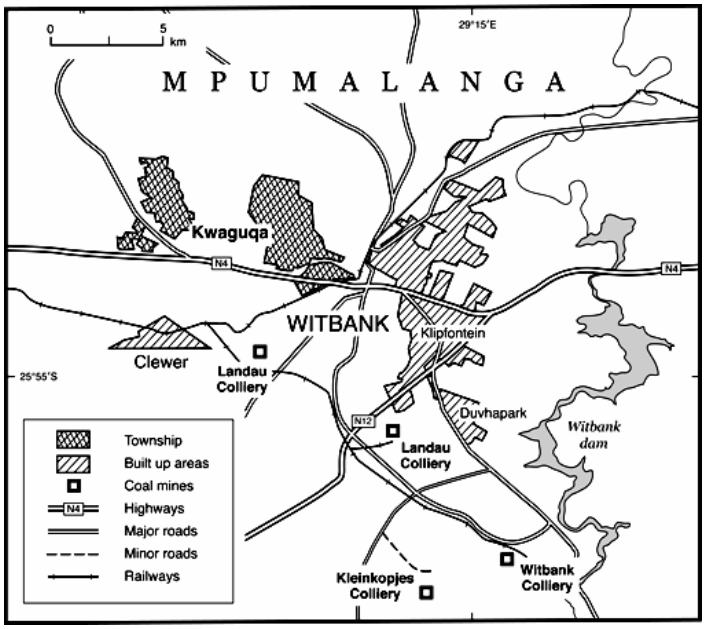
Figure 3.1: Major circulation types affecting southern Africa

The present study was carried out on a small scale with only one sampling site (mobile monitoring station) within the boundary of the colliery. The monitoring station was located on latitude 25° 59' 07.06" S and longitude 29° 13' 23.5" E at 1588 m above sea level. The air quality monitoring site was surrounded by actively mined pits. The closest of these (2A South) pits were located 500 m to the south and south east of the air quality monitoring station (Figure 3.4) (Otter *et al*., 2005).



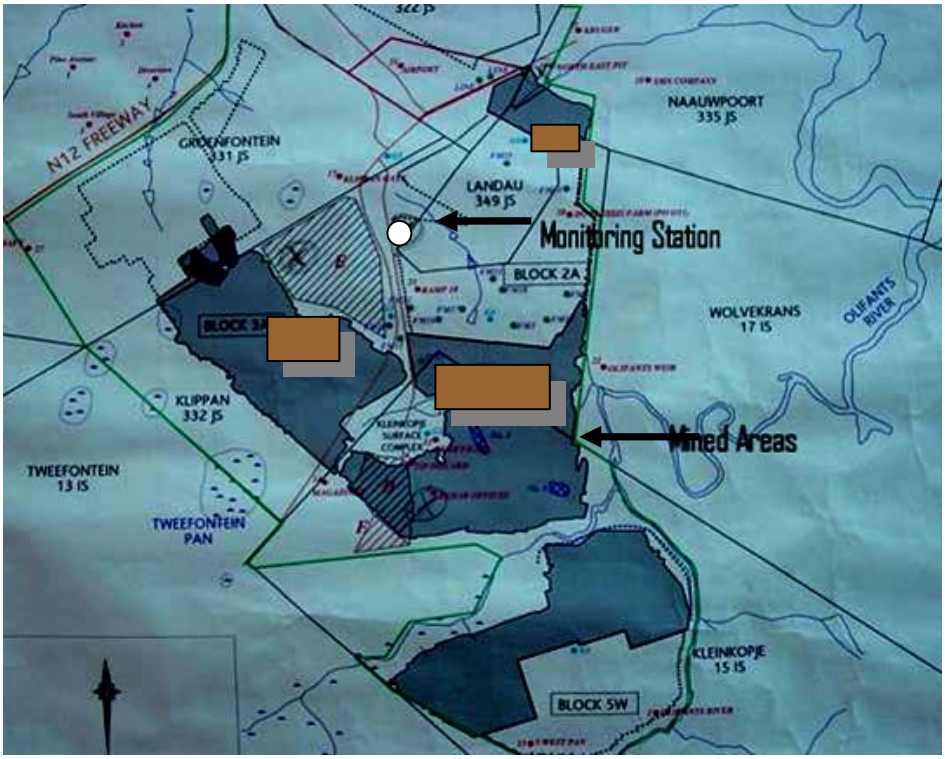
Source: University of the Witwatersrand, School of Geography, Archaeology and Environmental Studies, Cartography Unit

Figure 3.2: Map of South Africa showing the location of Witbank



Source: University of the Witwatersrand, School of Geography, Archaeology and Environmental Studies, Cartography Unit

Figure 3.3: Map of the study area (Witbank) showing open-cast collieries



Source: Colliery map library

Figure 3.4: Map of the colliery showing the active pits and the location of the air quality monitoring station

The air quality monitoring station was positioned within the mine property to site it as close as possible to the sources of spontaneous combustion. The proximity of the monitoring station to the mine workings was to minimise the influence of other pollution sources. Carras *et al.* (2001) suggest that monitoring sites should be located sufficiently close to the spontaneous combustion source to obtain a large measurement signal. The site also had suitable wind direction and topography for capturing pollutants. Another advantage was that there were no obstacles that could affect sampling. Security and availability of power at the site were also considered when selecting the location for the caravan, because the caravan contained expensive equipment and electricity was required during the period of sampling.

Data collection

Data collection was carried out in two field campaigns. The first took place between 16 February and 9 March 2004 (representing the summer season). The second took place between 3 June and 2 July 2004 (representing the winter season). Regular weekly visits to the monitoring station were undertaken throughout the sampling period to download data and ensure that the instruments were operating correctly. Thermo-Environmental Instruments (analysers) were used to sample ambient concentrations of SO_2, NO, NO_2, O_3, H_2S, CO and CO_2 continually at 5-minute average intervals and were recorded on a CR10 Campbell Scientific data logger. Calibration of each instrument was done before and after each campaign. The ambient gas analysers (Figure 3.5) were housed in a caravan. Through the inlet probes (Figure 3.6) ambient air was pumped into a cylindrical manifold to which the separate analysers were connected, and drew the air samples.

Co-located was a meteorological station (Figure 3.6), which was equipped to measure wind speed and direction, solar radiation, temperature, relative humidity, rainfall and barometric pressure. These instruments sampled meteorological data at 10-minute intervals.

Figure 3.5: Ambient gas analysers housed in the mobile monitoring station

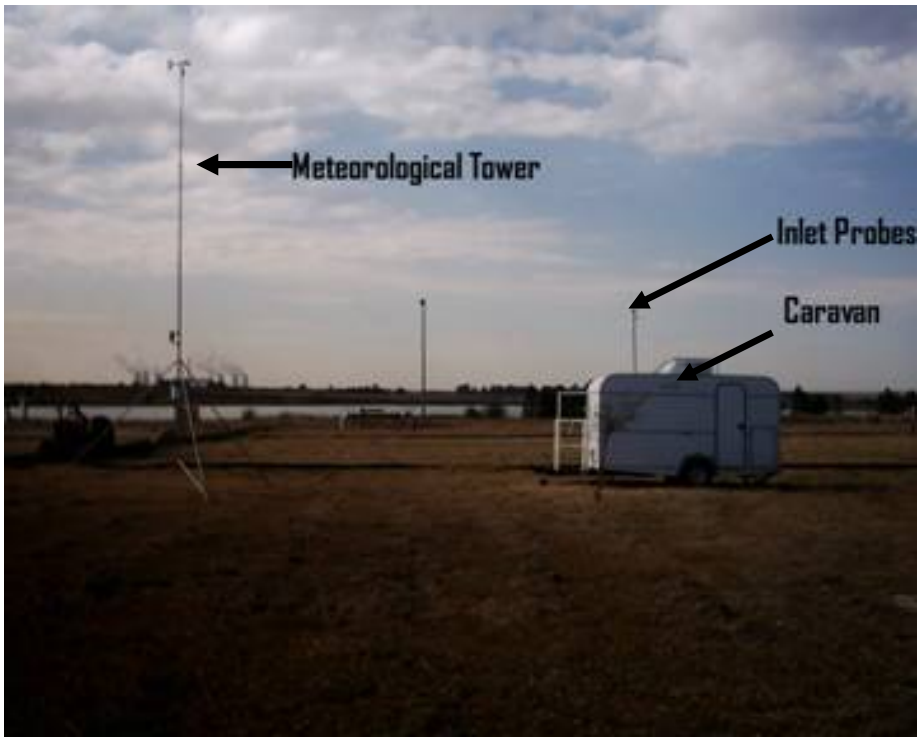


Figure 3.6: Monitoring station; caravan with inlets into analysers and meteorological station

Advantages of continuous analysers

Automatic samplers produce high time-resolution measurements (low averages) in real time at a single point for pollutants. This enables the determination of short-term variations in concentrations. These analysers have the advantage of real atmosphere analysis and, therefore, direct determination of pollution impacts on ambient air. This means that no subsequent laboratory analyses are required. The analysers need high maintenance (such as changing the chemical traps during the weekly visits and identifying non-functional instruments) to increase their reliability.

Instrument calibration

The ambient gas analysers have user-programmable software to allow selection of zero/span activation and instrument calibration with traceable gas standards. This enabled standard routine zero, span and range settings, which were done – according to the manufacturers' specifications – before each campaign to ensure the production of quality data. Temperature and pressure corrections were also made to ensure accurate instrument readings. Instrument flow-rates were adjusted as per the equipment manufacturer's specification and the analysers were checked during the calibration period to ensure that there were no leaks. Instrument ranges were set as follows:

SO_2:	0 to 500 ppb
NO - NO_2 - NO_x:	0 to 200 ppb
O_3:	0 to 200 ppb
H_2S:	0 to 500 ppb
CO:	0 to 7000 ppb
CO_2:	0 to 500 ppm

Data analysis

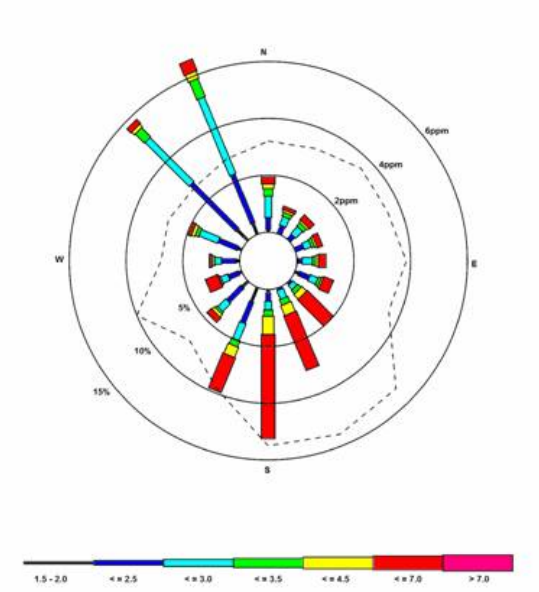
The data were imported from the data logger into Microsoft Excel spreadsheets, where they were first screened for erroneous data, caused by equipment failure, power failures and warm-up phases. Thereafter, the trace gas data collected at 5-minute intervals were averaged into 10-minute averages so that they correlated with the 10-minute meteorological data. Due to instrument failures, data capture during the summer campaign was affected.

The local weather conditions were used to interpret the trace gas data. Wind data (direction and speed) were particularly useful in determining the transport routes of the pollutants from their sources. This information was essential for determining the origins and sources of polluted air. Pollution roses for all the gases measured during both seasons were constructed to show the relationship between pollution concentrations and the prevailing wind direction. A pollution rose can be described as a presentation of the average pollutant concentration when wind blows from a given direction (Husar and Renard, 1998). In this way, the concentration levels that arrive at the monitoring station from different directions are evaluated such that directional sectors that show high values point towards the sources with high concentration levels (Husar and Renard, 1998).

Each arc of a pollution rose represents a 5 % concentration frequency and the average concentrations measured from each direction are denoted by the dotted lines around the pollution rose. The width of the different segments indicates varying concentrations as shown by the scale. The length of each concentration segment is associated with its frequency of occurrence such that a particular concentration only makes a marked effect on the average when its frequency is high.

From the CO pollution rose (Figure 3.7), concentrations of up to 7 ppm were measured from all directions. High average concentrations of up to 5.5 ppm were

only recorded from the SE to S due to the high occurrence (7 to 13 %) of 7 ppm concentrations from these directions. It was, however, noted that at various times measurements went over the 7ppm mark, which was the maximum to which the instrument was set.



CO concentration in ppm

Figure 3.7: An example of a pollution rose

Wind roses for the duration of each campaign were constructed to bring out the differences in seasonal wind speeds and directions at the monitoring station. For all the trace gases, hourly averages were calculated. Then for each clock hour, the concentrations were averaged across all the days for each of the seasons to give a 24-hour (diurnal) trend for each gas and season. Day-to-day variations in trace gas concentrations were obtained by calculating the daily average concentrations for each gas. This helps eliminate the effects of diurnal variations in the pollutant concentrations (Held *et al*., 1996).

CHAPTER 4:
RESULTS AND DISCUSSION

This chapter presents the ambient trace gas concentrations measured during the two-month campaign at a South African open-cast colliery. The results are discussed in terms of the effects that spontaneous combustion can have on the air quality in the vicinity of a coal mine.

Diurnal variation in measured trace gas emissions

Variability, at different times of the day, in atmospheric concentrations of the trace gases was observed. The measured gases underwent transformations and chemical reactions during the day such that their concentrations did not remain uniform throughout the day. This variability is mainly attributed to source strength, meteorological conditions, chemical reactions and time of day.

In winter peak SO_2 concentrations were observed during the night and early morning hours. The same observation was made by Held *et al*. (1996). Measured SO_2 concentrations steadily increased from about 22:00 and reached a maximum at 04:00, with a secondary maximum at 10:00 (Figure 4.1). According to Held *et al*. (1996), peak SO_2 concentrations close to elevated sources occur at times of greatest insolation. In contrast, for ground-level sources (such as in coal discard dumps), peaks are observed at night or during the early morning hours. This confirms that spontaneous combustion was the major source of SO_2 at the monitoring station during winter.

NO_2 levels were almost steady in the morning hours until 07:00 when concentrations started to decline slowly, with a sharper decrease towards noon. Thereafter, NO_2 concentrations increased again until about 18:00. NO_2 decrease during the day is due

to its depletion during the photochemical reaction that forms O_3. This cyclic reaction can be summarised as:

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3 + M$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

where $h\nu$ is ultra-violet light

(Seinfeld and Pandis, 1998)

The daily pattern of NO showed a peak towards 07:00 and a secondary peak at 15:00 (Figure 4.1). The second NO peak was associated with the disappearance of NO_2 as depicted by the reaction ($NO_2 + h\nu \rightarrow NO + O$). Pienaar and Helas (1996) made the observation that the formation of NO from NO_2 requires the presence of ultra-violet light. So this rise in ambient NO concentrations during daylight was attributed to its formation from NO_2.

Due to the same reaction, O_3 concentrations, increased throughout the day, peaking at 16:00 (Figure 4.1). Thereafter, O_3 levels decreased in the late afternoon due to dry deposition and other reactions (Cheng, 2001). During the night, O_3 is predominantly scavenged by NO (Cheng, 2001; Seinfeld and Pandis, 1998) such that O_3 concentrations remain low until the morning when sunlight promotes its formation.

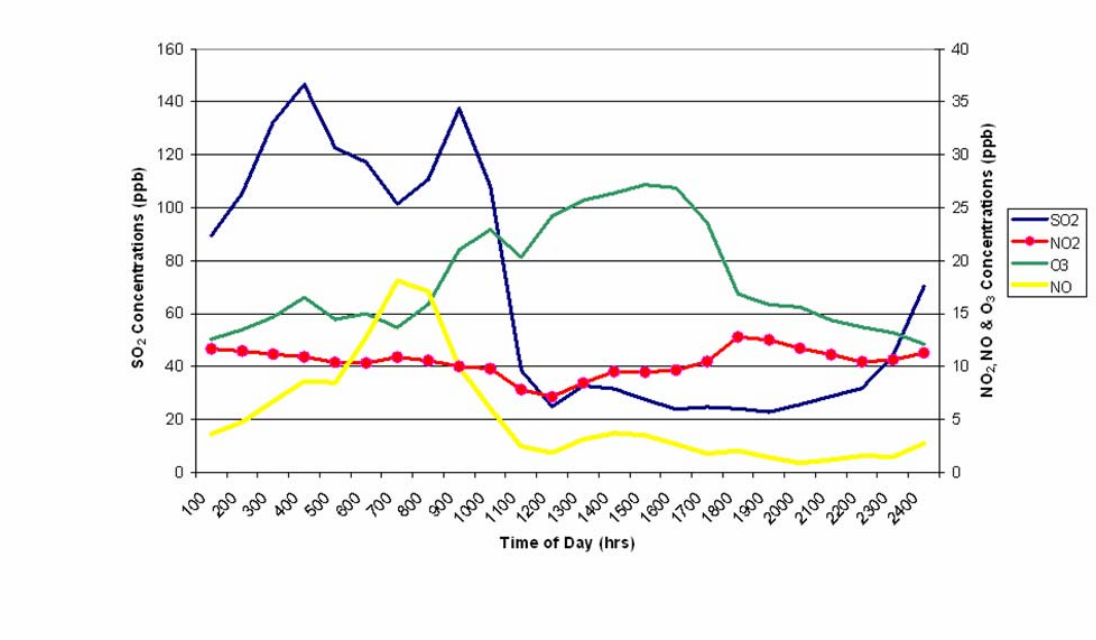


Figure 4.1: Diurnal pattern of SO_2, NO, NO_2 and O_3 observed in winter 2004

During summer the same interaction between NO_x and O_3 was observed. NO_2 concentrations increased in the morning, reaching a maximum at around 07:00 (Figure 4.2), thereafter steadily decreasing with a minimum at 13:00. NO displayed a peak in the morning and another in the afternoon. O_3 diurnal levels were directly proportional to the intensity of solar radiation, resulting in a maximum at around 15:00 after its formation from the demise of NO_2.

SO_2 showed higher variability than the other gases during summer, with its concentrations peaking at 14:00 (coinciding with the maximum vertical mixing in the atmosphere) with another smaller peak at around 06:00.

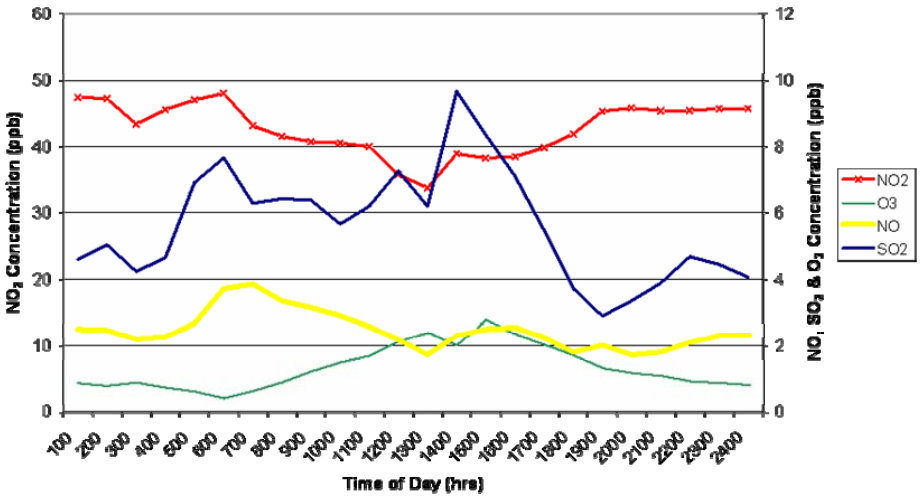


Figure 4.2: Diurnal pattern of SO_2, NO, NO_2 and O_3 observed in summer 2004

Temperature inversions, which are normally experienced in the early morning hours of winter, also had a significant effect on the daily variation of pollutant concentrations. During a temperature inversion, stagnant conditions occur beneath the nocturnal surface layer leading to a build-up of pollutants near the surface (Held *et al.*, 1996). The pollutants then dispersed as the day progressed after the inversion had lifted.

SO_2 and H_2S show a similar temporal diurnal signature (Figure 4.3) since they are both sulphur compounds and, therefore, have common sources. They both showed peak concentrations in the morning, during the inversion. CO displayed a similar pattern to SO_2 and H_2S. This confirms that the elevated morning concentrations resulted from a combination of emissions from the spontaneous combustion of coal and the development of a surface inversion. Glen *et al*. (1996) report that the elevated morning concentrations of CO are due to nocturnal inversions and are not a function of the time of day. The lifting of the temperature inversion resulted in improved atmospheric dilution and dispersion associated with reduced concentrations of H_2S,

SO_2 and CO. The concentrations of SO_2 and CO dropped significantly to 35 ppb and 2000 ppb respectively during the daytime.

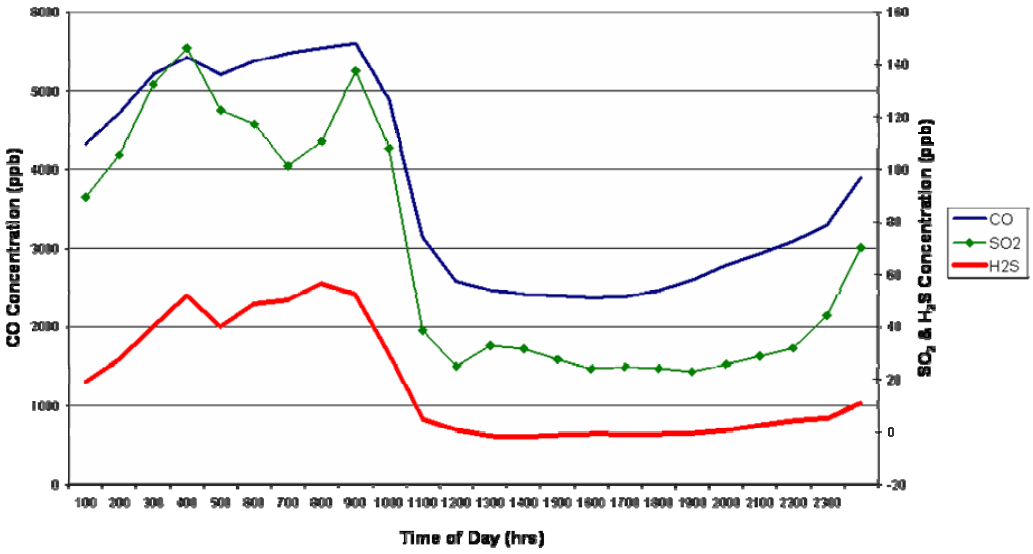


Figure 4.3: Diurnal pattern of CO, SO_2 and H_2S observed in winter 2004

Seasonal differences

Seasonal differences in pollutant concentrations are mainly governed by meteorological controls. Summer experienced higher temperatures, solar radiation, rainfall and relative humidity than recorded during the winter (Figure 4.4). These parameters have effects on the measured pollutant concentrations and among themselves, resulting in complex relationships. Fewer and weaker temperature inversions occurred in summer and the air was mostly well mixed, dispersing pollutants more effectively.

The summer campaign began with moist tropical air flowing southwards, resulting in partly cloudy and warm to hot conditions. Showers resulted from cloudy conditions during this season. In winter high pressure systems, leading to fine and mild

conditions, were experienced. Influx of moisture resulted in partly cloudy to cloudy conditions with little rain. Temperatures were generally low, with cold fronts experienced on the 7, 27 and 30 June, causing cold conditions.

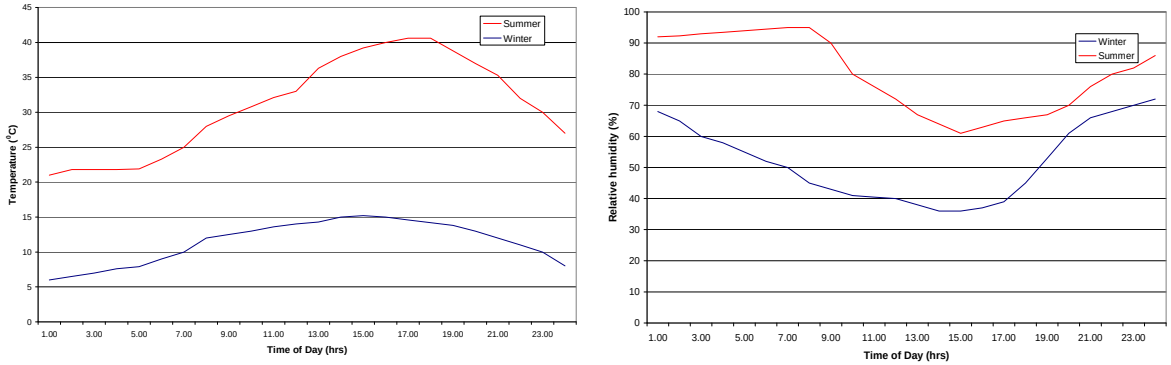
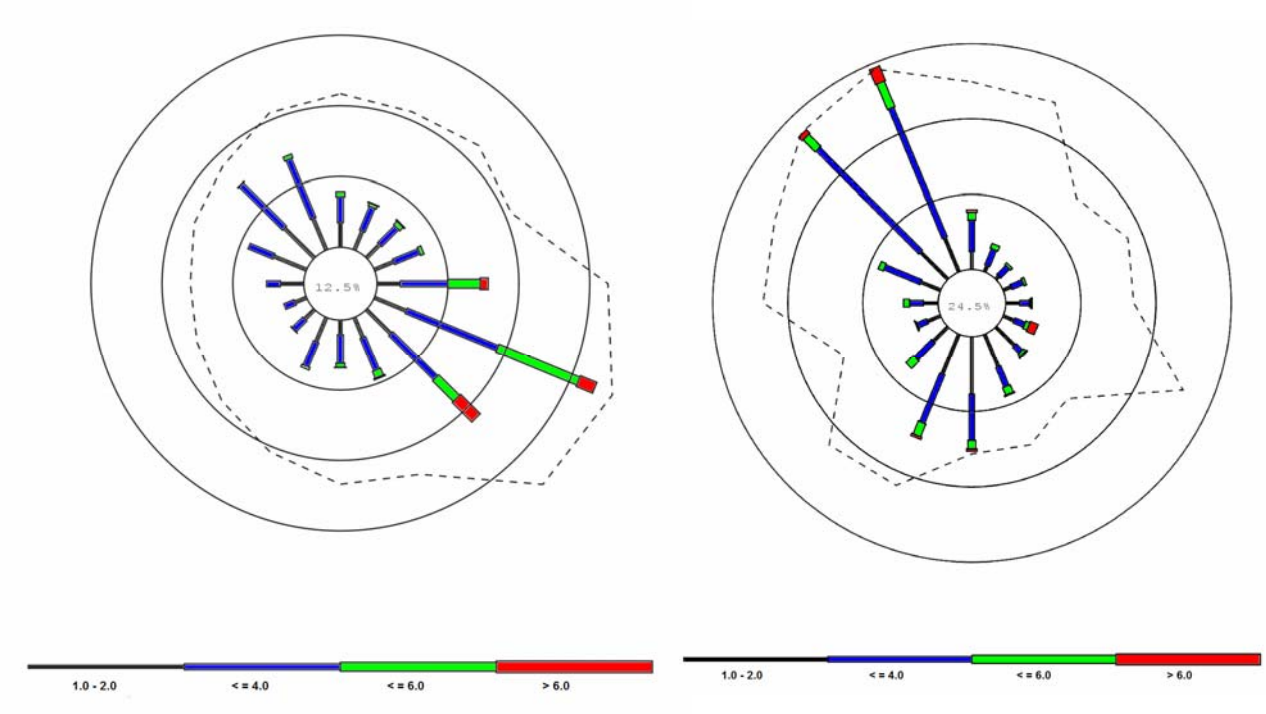


Figure 4.4: Average diurnal trend for temperature (left) and relative humidity (right) for summer and winter 2004

More calm days were experienced at the monitoring station during the winter campaign (24.5 %) than during summer (12.5 %) (Figure 4.5). Higher wind speeds in summer have been previously observed by Held *et al.* (1996). The dominant wind direction in summer was ESE-SE while it was NNE-NE in winter (Figure 4.5).



Wind speed in m/s

Note: Arcs represent 5 % frequency intervals and 1 m/s.

Figure 4.5: Wind roses from the monitoring station for the summer (left) and winter (right) campaign

Held *et al.* (1996) have documented the average trace gas concentrations for the Highveld (Table 4.1). The monthly averages for each of the campaigns during this study were calculated and considered representative of each season sampled: February/March for summer and June for winter. Measured winter concentrations of SO_2, CO and CO_2 were much higher than the average concentrations of the same gases for the region. However, winter NO and NO_2 concentrations were lower. The generally higher winter concentrations were consistent with the findings of Held *et al*. (1996) for the Highveld. The measured average SO_2 in winter was 67 ppb, while it was 11 ppb in summer.

Table 4.1: Comparison of measured with documented seasonal averages

Gas	Summer	Winter	Documented*
	Measured (ppb)	Measured (ppb)	(ppb)
SO_2	11	67	9 to 35
NO	12	5	20 to 120
NO_2	43	11	-
O_3	7	18	20 to 38
H_2S	-	87	-
CO	-	3700	2000
CO_2	-	397 (ppm)	350 (ppm)
Held *et al*., 1996.			

Winter and summer SO_2 concentrations displayed variations in their diurnal patterns. Winter SO_2 concentrations were much higher than during summer. The morning peak observed in winter was associated with the occurrence of surface inversions during winter mornings, whereas in summer there were peaks in the morning and the afternoon (Figure 4.6). These two peaks in summer were likely to depict a combined effect of both ground level (morning peak) and elevated emissions emitted from tall stacks (daylight peak).

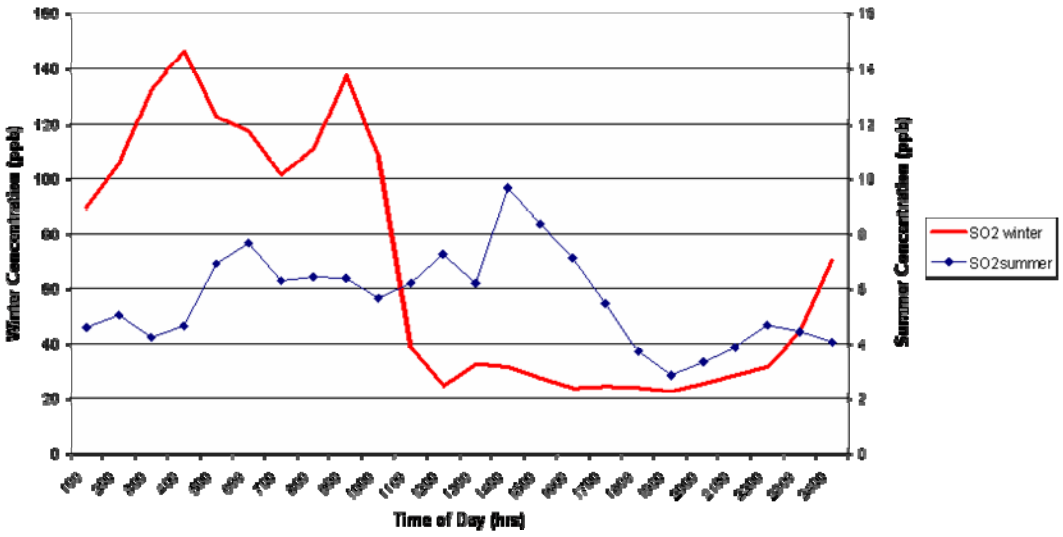


Figure 4.6: SO_2 diurnal trend for summer and winter 2004

The diurnal patterns of NO_x during both seasons were similar. Higher NO concentrations were captured in summer compared to the winter concentrations (Figure 4.7), with averages of 12.3 ppb and 5.3 ppb for summer and winter respectively. The high morning peak in NO concentrations resulted from spontaneous combustion, while the afternoon peak was associated with NO formation from NO_2.

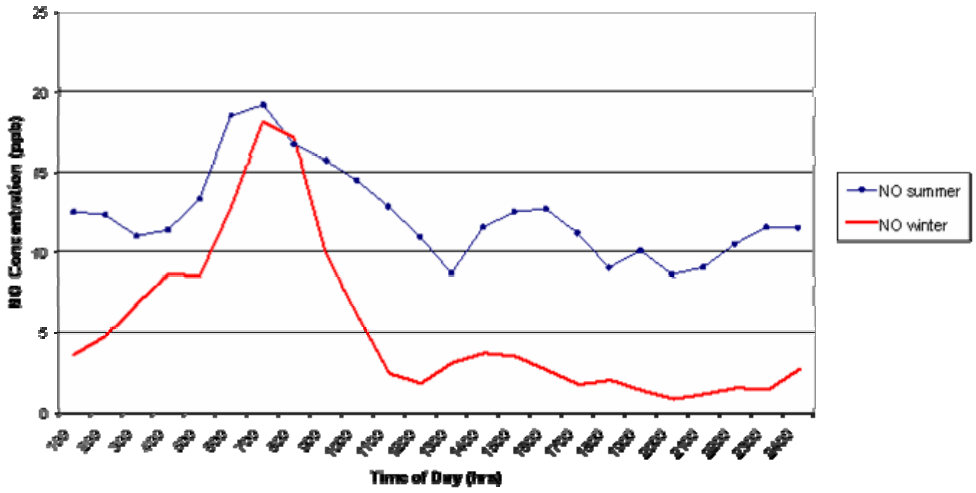


Figure 4.7: NO diurnal trend for summer and winter 2004

NO_2 concentrations were higher during summer than in winter (Figure 4.8). NO_2 displayed similar diurnal patterns during both seasons with concentrations slightly decreasing from the morning and reaching a minimum between 13:00 and 14:00. This decrease was associated with the consumption of NO_2 during the formation of O_3 and NO. The higher NO_x in summer than winter could have been caused by less efficient conversion of NO_x into O_3.

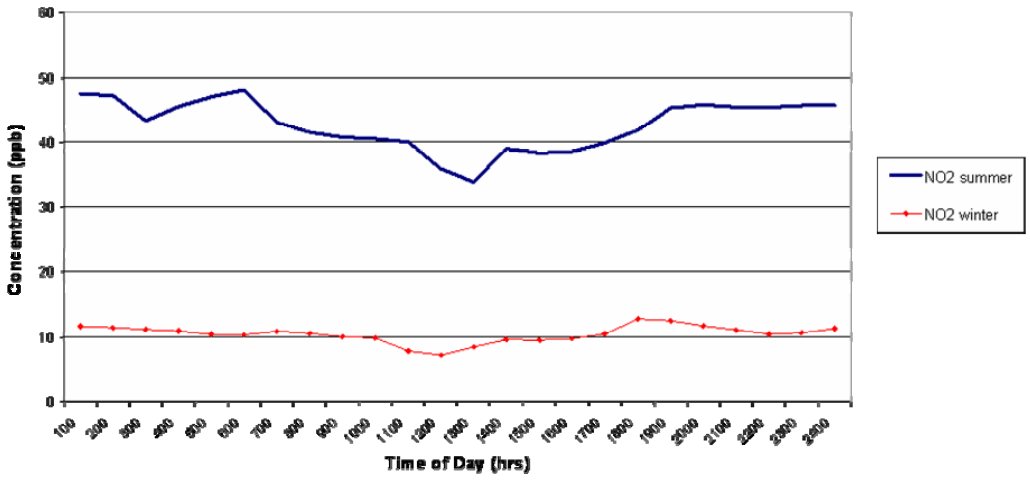


Figure 4.8: NO_2 diurnal trend for summer and winter 2004

O_3 is a secondary pollutant formed from the reaction of NO_x and volatile organic compounds with sunlight. Its concentrations are thus expected to be higher in summer when there is more intense solar radiation (Held *et al*., 1996; Seinfeld and Pandis, 1998). This observation was made in this study as well. O_3 levels in both seasons showed a minimum in the morning, progressively increasing and reaching their peak levels at about 16:00 (Figure 4.9), when the solar radiation was high. Measured summer and winter averages were 18 and 7 ppb respectively.

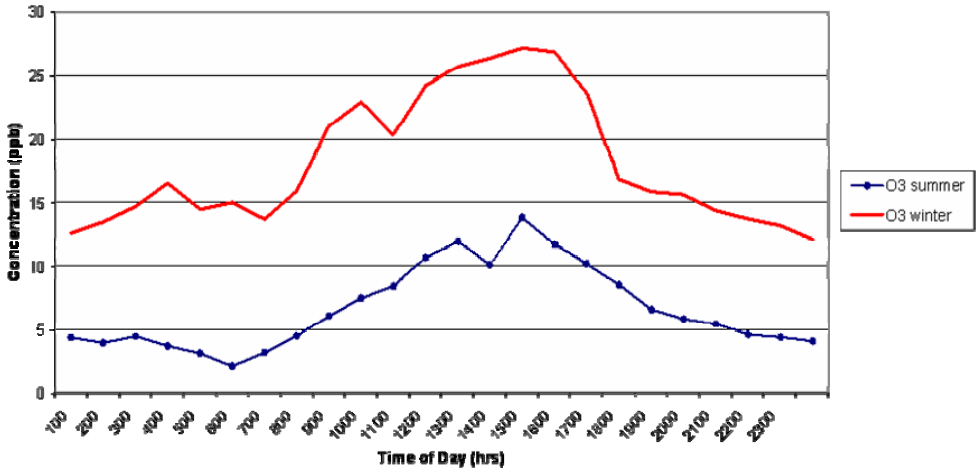


Figure 4.9: O_3 diurnal trend for summer and winter 2004

Measured trace gas concentrations with respect to DEAT standards

The measured trace gas concentrations were averaged into daily and hourly averages and compared with the standards in the National Environmental Management: Air Quality Act (RSA, 2004). Comparison indicated that NO, NO_2 and O_3 were all within permissible levels both in winter and summer. NO, NO_2 and O_3 mean daily maximums were 33 ppb, 76 ppb and 18 ppb respectively during summer. In winter daily averages were 15 ppb, 34 ppb and 34 ppb for NO, NO_2 and SO_2 respectively. DEAT has set the daily standard for NO at 400 ppb and 100 ppb for NO_2. The daily SO_2 standard (48 ppb) was exceeded on 17 out of the 28 days (61 %) during the winter campaign (Figure 4.10). The maximum daily mean recorded was 179 ppb on 14 June with the lowest on 8 June (13 ppb). The 10-minute SO_2 standard (191 ppb) was also exceeded during winter. The measured 10-minute average concentrations

rose to more than double the guideline (Figure 4.11), reaching a maximum of 496 ppb on six (6) out of the 28 days of the winter campaign.

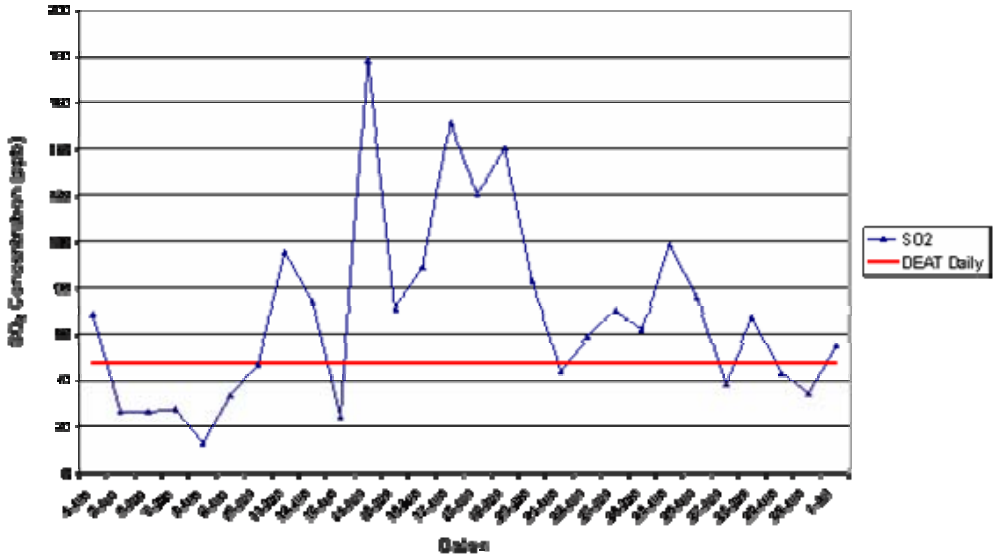


Figure 4.10: Mean daily SO_2 compared with the DEAT 24-hour standard in winter 2004

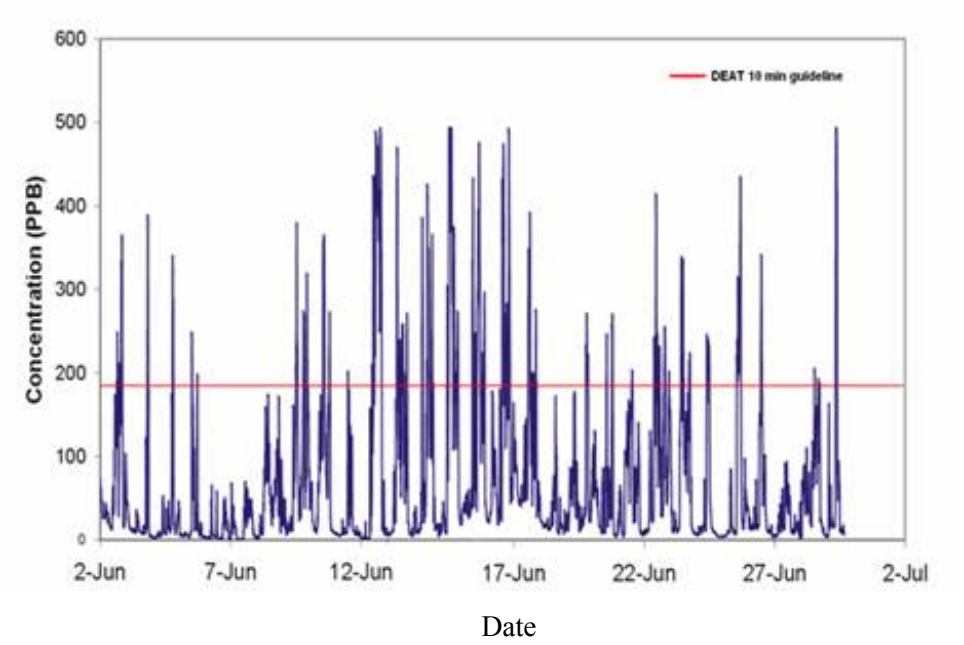


Figure 4.11: Mean 10-minute SO_2 compared with the DEAT 10-minute standard in winter 2004

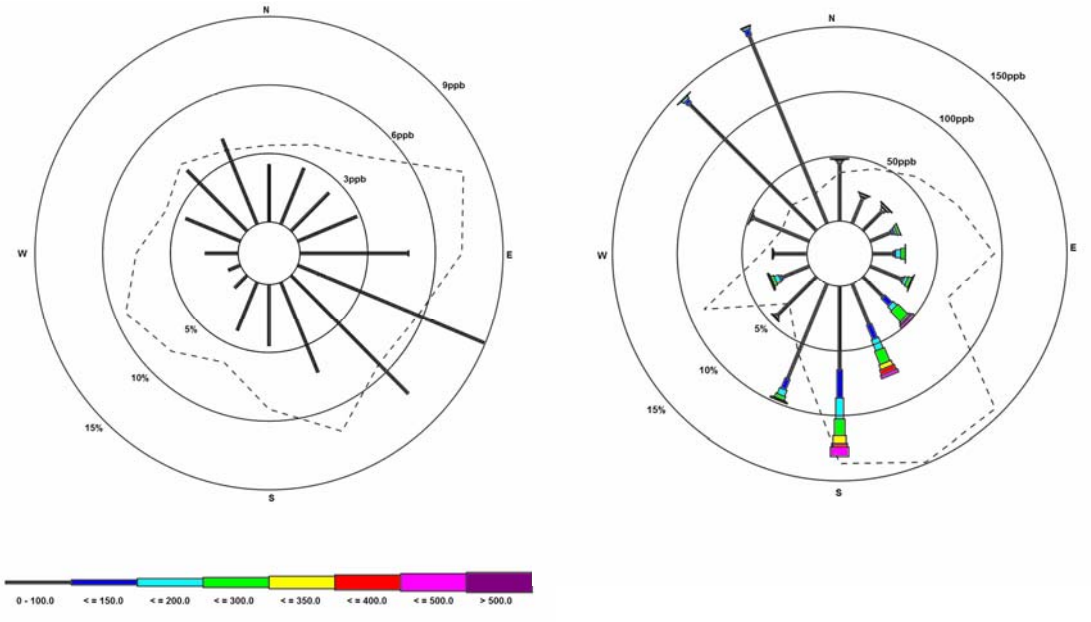
Wind direction and source identification of peak concentrations

Wind direction influences air quality at a particular site. The air transport regimes are useful in determining the pathways travelled by pollutants from their sources to the monitoring station. Estimating the wind direction that gives a maximum average concentration of an atmospheric species helps to find the directions of peak concentrations (Henry *et al*., 2001), which are taken as the directions of the sources from the receptor, assuming they are not far from the receptor. A combination of wind data and pollution concentrations, in the form of pollution roses, are used to establish transportation of pollutants from their sources to the receptors (Piketh, 1994) and this can be applied to source contributions from receptor models (Glen *et al*., 1996).

The pollution roses constructed exhibit seasonal variations in distribution of trace gases. Concentration intervals differed for each gas (as determined by the

concentration ranges) and are shown on the scales. Where concentrations showed little dependence on wind direction, it could be argued that their sources were dispersed within the area (Colbeck and Eleftheriadis, 1996), meaning that they were from several sources around the monitoring station. Since the mine was the nearest pollution source to the monitoring station, the assumption was that it caused the highest contribution of the measured pollutants.

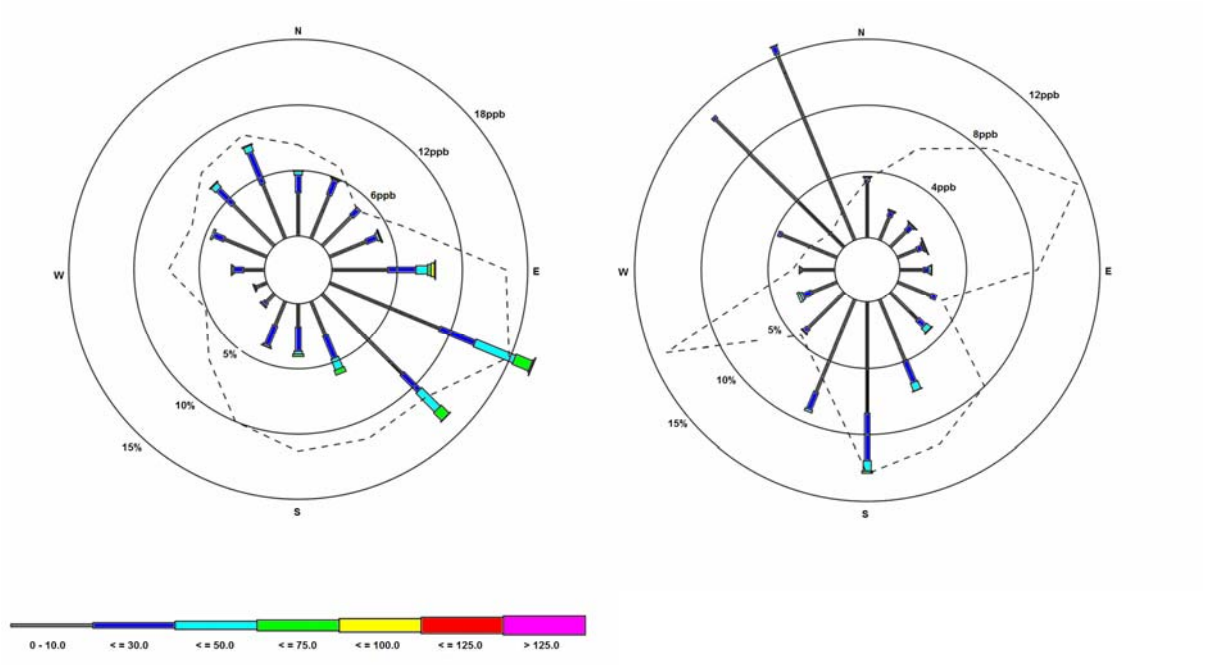
In summer the average SO_2 concentrations per direction were low (a maximum of 6 ppb) such that the small peaks observed were insignificant. During winter SO_2 concentrations showed high dependence on wind direction. Average SO_2 concentrations of up to 150 ppb were measured in winter from the SE to S directions (Figure 4.12). Spontaneous combustion of coal from the mine was the source of these high SO_2 levels.



SO_2 concentration in ppb

Figure 4.12: SO_2 pollution roses for summer (left) and winter (right) 2004

Elevated NO levels during both summer and winter were also captured from the SE and S respectively (Figure 4.13). In summer, maximum average concentrations of up to 18 ppb came from the SE. This was to be expected since NO is a coal combustion product (Glaister *et al.*, 1999). The peak (12 ppb) on the ENE during summer was not statistically important due to the low frequency (<5 %) of wind blowing from that direction.



NO concentration in ppb

Figure 4.13: NO pollution roses for summer (left) and winter (right) 2004

NO_2 concentrations during both winter and summer did not show any particular dependence on wind direction. The summer NO_2 pollution rose (Figure 4.14) shows that concentrations of up to 90 ppb measured from the SE occurred on a few occasions to make a significant effect on the overall average from that direction. A slight peak of 12 ppb was observed from the S in winter. This small dependence on

wind direction indicates that spontaneous combustion is not necessarily a significant source of NO_2.

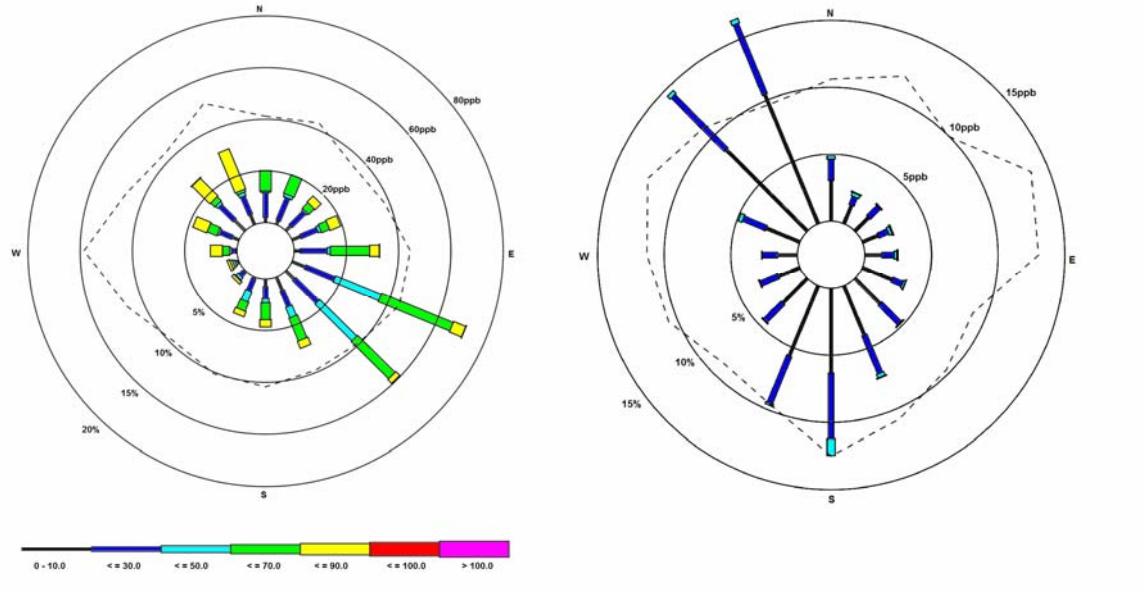
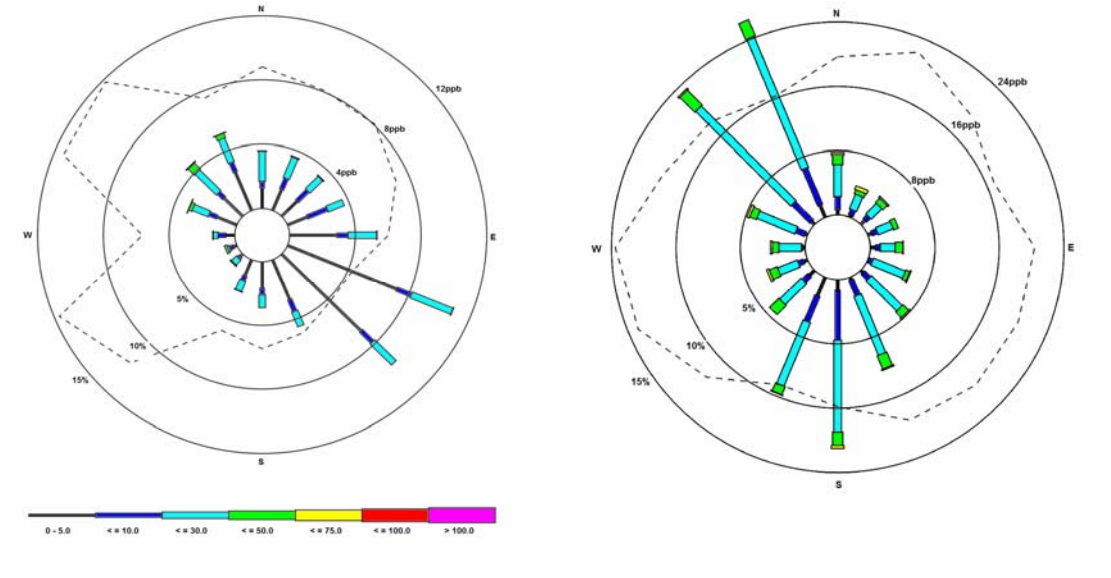


Figure 4.14: NO_2 pollution roses for summer (left) and winter (right) 2004

O_3, being a secondary pollutant, was not expected to be directly produced from spontaneous coal combustion. Its summer concentrations had high average concentrations of about 12 ppb from the SW and NW. No particular sources were attributed to these peaks. In winter there was no significant O_3 average peak, its concentrations were almost equally distributed.

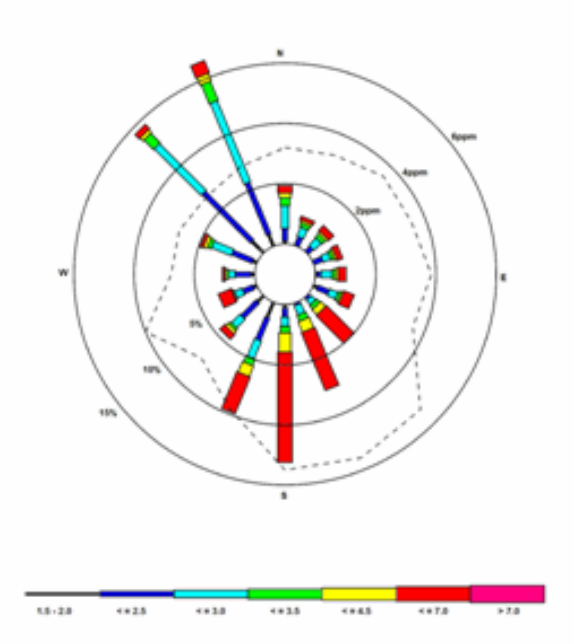


O_3 concentration in ppb

Figure 4.15: O_3 pollution roses for winter (left) and summer (right) 2004

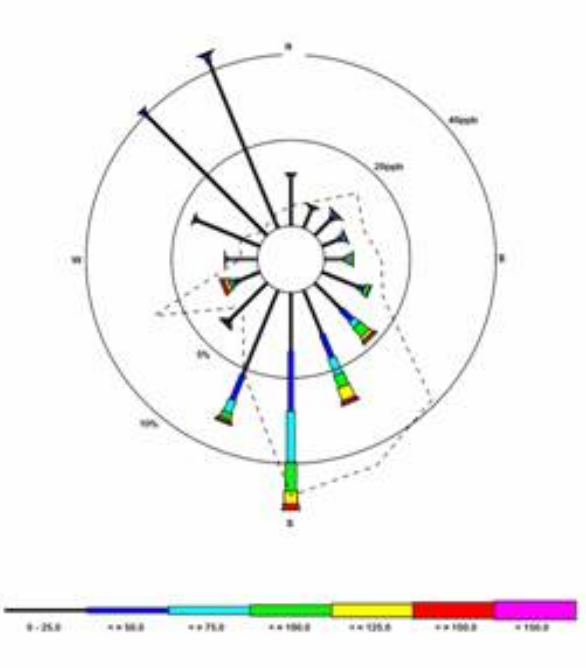
CO and H_2S concentrations in winter were moderately high and their elevated concentrations came from the SE to S directions. Average CO levels were as high as 5500 ppb (Figure 4.16) while average H_2S concentrations had a maximum of around 50 ppb (Figure 4.17). CO has been cited as one of the main products of spontaneous combustion and these high concentrations were evident.

CO_2 was distributed equally from all directions around the monitoring station (Figure 4.18) and its average concentrations from all directions were around 400 ppm.



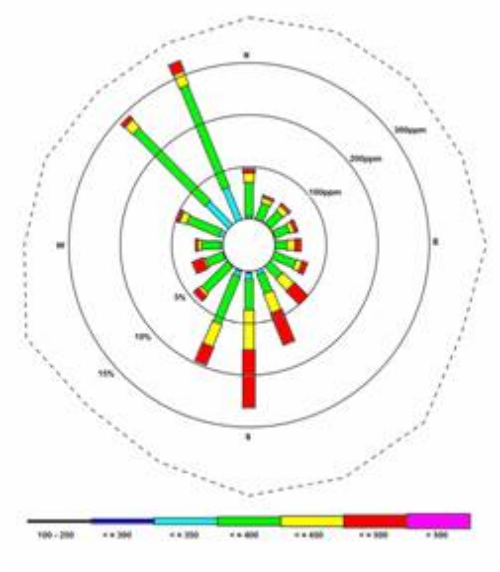
CO concentration in ppm

Figure 4.16: CO pollution rose for winter 2004



H_2S concentration in ppb

Figure 4.17: H_2S pollution rose for winter 2004



CO_2 concentration in ppm

Figure 4.18: CO_2 pollution rose for winter 2004

Relationship between prevailing synoptic conditions and pollutant concentrations

To establish the influence of prevailing synoptic conditions on the behaviour of atmospheric pollutants, synoptic systems on each day of the campaigns were divided into the four main types for the Southern African region: ridging anticyclone (RH), continental anticyclone (CH), easterly low (EW) and westerly low (WW). Continental anticyclones were the most prevalent synoptic circulation during winter (73 %), while easterly waves dominated in summer (55 %) (Figure 4.19). This was in agreement with previous observations for the Highveld (Tyson *et al*., 1996; Ross *et al*., 2001).

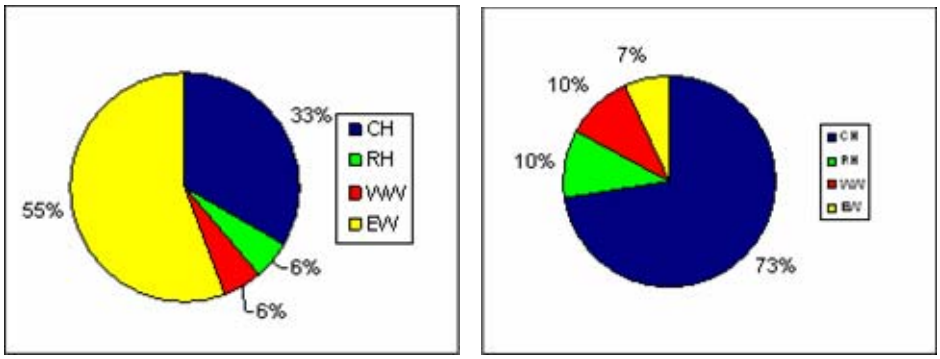


Figure 4.19: Frequency of occurrence of synoptic circulations for summer (left) and winter (right) 2004

Previous studies have reported that statistically there is no clear relationship between a single meteorological variable and pollutant concentrations (Liu *et al*., 1994; Cheng, 2001). Hence this study used the large-scale synoptic regimes over the Highveld to understand the effects of weather on atmospheric pollutant concentrations. Strong dependence of the measured pollutant concentrations on synoptic weather patterns was observed. Continental anticyclones over the Highveld caused accumulation of trace gases in the atmosphere. Under such conditions vertical mixing of air is restricted, causing pollution to build-up in the lower atmosphere.

During the winter campaign the periods from the 10 to 14 June and 22 to 26 June represented the strongest episodes of CO, NO, NO_2 and SO_2 (Figure 4.20) associated with the advection of high pressure systems over the preceding 5 days from 9 to 14 June and from 21 to 26 June. Mean wind speeds for 11, 12 and 13 June were 2.4 m/s, 1.5 m/s and 1.8 m/s respectively, which is relatively low and characteristic of high pressure systems. Ridging anticyclonic conditions, which are associated with steep pressure gradients and advection of unstable air, resulted in low average concentrations of pollutants. This was observed for CO, SO_2, NO and NO_2 in winter (Figure 4.20).

The passage of cold fronts replaced the high pressure system and advected clean marine air from the south over the region. Pollution concentrations dropped dramatically under cold front conditions due to high dilution (Unni *et al.*, 2002). The 7, 27 and 30 June experienced cold fronts with lower mean daily CO concentrations of 2100 ppb, 3400 ppb and 3800 ppb respectively than the preceding days. NO, NO_2 and SO_2 (Figure 4.20) also showed decreased concentrations on the same days. Elevated wind speeds were also recorded on these days, averaging 3.6 m/s, 2.3 m/s and 3.4 m/s for 7, 27 and 30 June respectively.

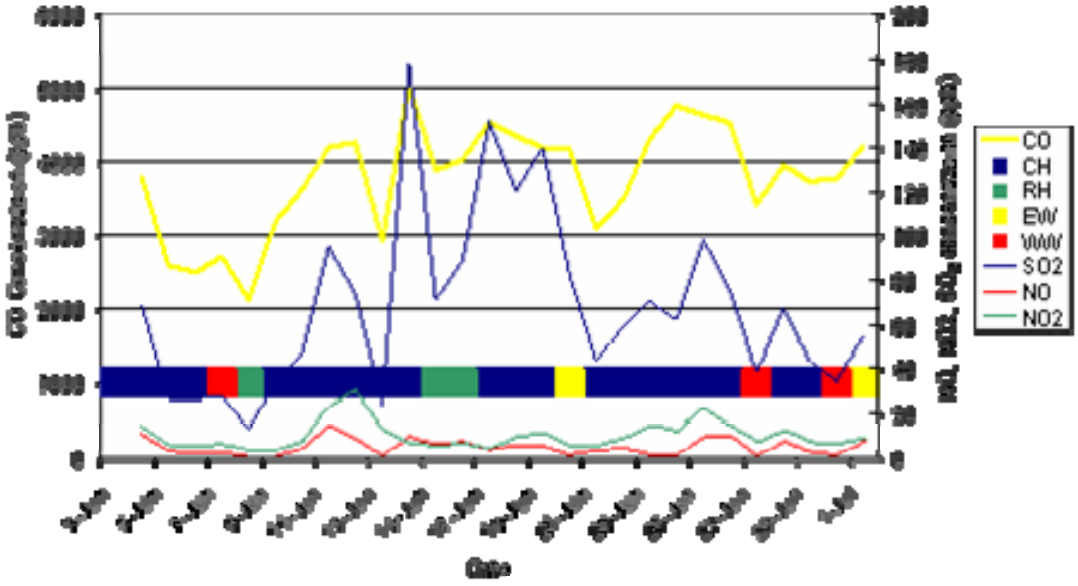


Figure 4.20: The effect of synoptic systems on CO, SO_2, NO and NO_2 concentrations in winter 2004

The effect of synoptic circulations was equally important in summer. NO and NO_2 concentrations remained low during the persistence of easterly lows (20 to 29 February). On 1 March a continental high pressure system developed and increased the concentrations of SO_2, NO and NO_2 (Figure 4.21) over the following four days. A reduction in NO, NO_2 and SO_2 concentrations was again recorded as a result of a westerly wave and a ridging anticyclone on 5 and 6 March. The re-

established high pressure system towards the end of the campaign (7 and 8 March) resulted in increased pollutant concentrations.

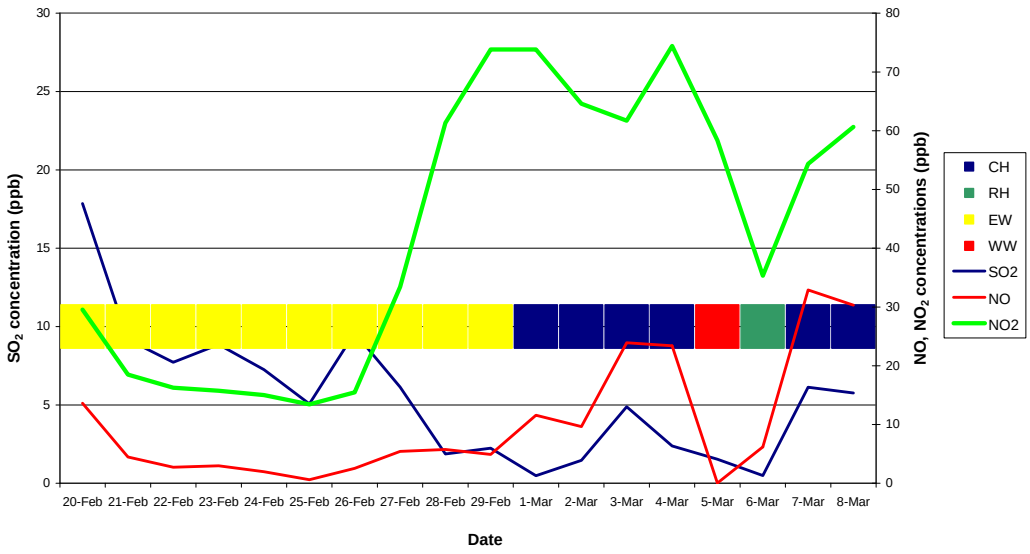


Figure 4.21: The effect of synoptic systems on SO_2, NO and NO_2 concentrations in summer 2004

CHAPTER 5:
SUMMARY AND CONCLUSIONS

This chapter summarises the findings of the study
and overall conclusions drawn from the study are presented.

Summary

Coal mining has been cited as a major source of pollutants in the form of trace gases and aerosols. SO_2, H_2S, CO, CO_2, NO, NO_2 and O_3 were measured at an open-cast coal mine experiencing spontaneous combustion for a month in winter and another in summer. The mine was the main source of the measured trace gases considering its proximity to the monitoring station.

From the presented results SO_2, CO and NO were emitted by the spontaneous combustion of coal. Elevated levels of these gases were seen to come from the direction of the mine in relation to the monitoring station. CO, NO and SO_2 are considered to be primary gaseous products of coal combustion, whereas O_3, NO_2 and CO_2 did not appear to be coming directly from spontaneous combustion.

The measured trace gases exhibited high temporal variability, both during the day and seasonally. The diurnal behaviour of gases showed how their concentrations changed with time of day. Seasonal variations were mainly due to differences in prevailing weather conditions. Substantially higher trace gas concentrations were measured during winter compared to summer, with the exception of NO and NO_2. The prevalence of stable conditions, coupled with the occurrence of nocturnal inversions during winter, was cited as major factors in increasing pollutant concentrations.

Findings from this study indicate that both emissions and meteorological conditions need to be considered when explaining the concentrations of pollutants from any

particular source as previously reported by Tyson *et al.* (1996). The dependence of pollutant concentrations on prevailing weather conditions was observed. Although individual weather parameters could not be directly linked to pollutant behaviour because of the complexity and interactions in the atmosphere, it was observed that pollutant concentrations strongly depend on the synoptic weather patterns over the Highveld. Of the four synoptic patterns examined, days with continental anticyclones had highest average concentrations of pollutants, while days experiencing ridging anticyclones and westerly waves showed a reduction in concentrations of pollutants.

NO, NO_2 and O_3 concentrations were found to be within permissible levels during both campaigns. SO_2 concentrations in winter, in contrast, were high – exceeding both its 10-minute and 24-hour average standards. This could have adverse implications with respect to the health risks of people living and working in the area.

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