

# *Chapter 2*

## *Literature survey*

*In this chapter, background information for this study is presented, with particular reference to air pollution (Par. 2.1.) and the types of pollutants (Par. 2.1.1.) that play a key role in atmospheric chemistry. The sources (Par. 2.1.2.), sinks, composition and impacts of atmospheric gaseous species and aerosols will be discussed, with an emphasis on pollutant species (Par. 2.2.) that are currently considered to be criteria species by South African and European legislation (Par. 2.4.). The main anthropogenic activities in the western Bushveld Igneous Complex are also discussed (Par. 2.5.). In the last section, the meteorology of the South African interior is described (Par. 2.6.).*

### **2.1. Air pollution**

The atmosphere can be divided into five different layers based on rapid temperature and pressure fluctuations with increasing altitude (Atkinson, 2000). These five layers are the troposphere, stratosphere, mesosphere, thermosphere and exosphere. The troposphere is the closest to the surface of the earth and is the densest of these layers. It contains approximately 80% of the total mass of the atmosphere. The troposphere is chemically composed of 78.08% nitrogen (N<sub>2</sub>), 20.95% oxygen (O<sub>2</sub>), 0.93% argon (Ar), 0.036% carbon dioxide (CO<sub>2</sub>), varying amounts of water vapour (altitude, temperature and weather dependent), as well as trace amounts of other gaseous species (Atkinson, 2000).

Air pollution can be defined as a change in the natural composition of the atmosphere that is harmful or injurious to human life and the environment (Kampa & Castanas, 2008). Pollution affects the troposphere and the stratosphere (Lourens, 2008; Atkinson, 2000). Pollution disturbs the natural cycles in the atmosphere responsible for weather

patterns and chemical reactions, which affects planetary health (Jacobson, 2002). Chemical elements are circulated through the global environment within a biogeochemical cycle; which can be described as fluctuations between reservoirs i.e. atmosphere, terra firma and oceans. Some pollutant chemical species have long resident times in the atmosphere and can be transported for great distances (Swap *et al.*, 2003).

Apart from health effects, air pollution causes several environmental problems, which include the increase of tropospheric oxidants, changes in the self-cleaning ability of the atmosphere, perturbation of biogeochemical cycles, acidic precipitation, radiative effects caused by an increase in greenhouse gases and aerosols, the depletion of stratospheric ozone, as well as related environmental impacts that force a change in the global environment (Brasseur *et al.*, 1999). The introduction of new chemical compounds into the atmosphere, in addition to the continued release of large quantities of already existing pollutants (natural and anthropogenic), will adversely affect all processes of the biogeochemical cycle of atmospheric species, leading to significant impacts on both human health and the sustainability of the environment.

### **2.1.1. *Types of air pollutants***

There is a considerable number of pollutant species present in the atmosphere, which have different sources, chemical compositions, transformations, as well as impacts on the environment and its inhabitants. Pollutants are categorised mainly into two types of species, i.e. gaseous species and aerosols. The physical and chemical properties of these particles determine their impact on human health, the environment and climate (Engelbrecht, 2009).

Gaseous pollutant species consist of organic and inorganic compounds. The main atmospheric organic compounds include Volatile Organic Compounds (VOCs), CH<sub>4</sub> (methane), non-methane hydrocarbons (NMHC) and halogenated organic species. SO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, O<sub>3</sub>, CO and CO<sub>2</sub> are considered to be the most important inorganic gaseous compounds present in the atmosphere. CO<sub>2</sub>, CO, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O and halogenated carbons are regarded as greenhouse gases that contribute to climatic changes (Martins, 2008).

Aerosols, or particulate matter (PM), are a complex mixture of solid and liquid particles suspended in the atmosphere (Kampa & Castanas, 2008). The most common examples of aerosols present in the atmosphere are clouds, smoke and wind-blown dust. Aerosols are categorised according to their aerodynamic particle diameter into *ultra fine* ( $< 0.1 \mu\text{m}$ , viz.  $\text{PM}_{0.1}$ ), *fine* ( $0.1 \mu\text{m} > 1 \mu\text{m}$ , viz.  $\text{PM}_1$ ) and *coarse* particles ( $> 1 \mu\text{m}$ , viz.  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ). Aerosols also consist of organic and inorganic compounds. The main components of atmospheric aerosols are usually dust, sea salt (NaCl), elemental/black carbon (EC/BC), organic carbon (OC), sulphate and nitrate (Engelbrecht, 2009).

A special type of pollutant is smog, which is a mixture of fog and smoke that causes problems in urban areas with high combustion emissions. Smog can be formed from  $\text{SO}_2$ ,  $\text{NO}_x$ , VOCs, peroxyacyl nitrates and aldehydes in the atmosphere (EPA, 2011).

### **2.1.2. Sources**

Gaseous and particulate pollutant species can be emitted directly into the atmosphere from natural and anthropogenic sources, i.e. primary pollutants. Secondary pollutant species are formed through chemical reactions occurring in the atmosphere. Natural sources of atmospheric chemical species include vegetation (plant surfaces), soil surfaces, oceanic and other aqueous surfaces, volcanic eruptions, biomass burning (such as wild and forest fires), dust storms, decomposition of animal and plant material, as well as spray from sea waters. Typical anthropogenic sources include the combustion of fossil fuels, biomass burning (veld fires and household combustion for space heating and cooking), vehicular emissions, chemical and petrochemical industries, agricultural activities, high-temperature combustion processes (e.g. pyrometallurgical industries) and mining activities.

Fossil fuel combustion is considered to be the largest anthropogenic source of atmospheric pollutants.  $\text{NO}_x$ ,  $\text{SO}_2$ , CO,  $\text{CO}_2$ , VOCs and heavy metals are emitted into the atmosphere from the combustion of fossil fuels (Crawford *et al.*, 2003). Coal, gas and oil are the main fossil fuels utilised for electricity generation, with coal accounting for ca. 40%, gas ca. 20% and oil ca. 6% of the total global electricity generation (Höök, 2007).

In South Africa, coal-fired power stations are the primary source of electricity. The petrochemical industry is also a major source of pollutants associated with fossil fuels. Coal combustion is considered to be the major source of CO<sub>2</sub> in the world (Höök, 2007). Sulphur and nitrogen are also major constituents of coal. The desulphurisation (de-SO<sub>x</sub>) of most coal-fired power plants in the world has led to a reduction of sulphur emissions (Höök, 2007). NO<sub>x</sub> formation is generally prevented (de-NO<sub>x</sub>) in modern combustion power plants by various methods such as selective or non-selective catalytic reduction (SCR / NSCR) (Höök, 2007). However, de-SO<sub>x</sub> and de-NO<sub>x</sub> are not yet standard practice in South Africa.

Oil-related products are mainly combusted in vehicles. Vehicular emissions contribute significantly to the total air pollution load in many urban areas (Singh, 2008). The energy required for vehicles is generated through the incomplete combustion of fossil fuels in internal combustion chambers. Some of the partially combusted fuel is released from the system leading to the formation of a variety of impurities. In the presence of air, these impurities are oxidised to form NO<sub>x</sub> and carbon monoxide. PM is also emitted from exhaust gases (Singh, 2008). NO<sub>x</sub> emitted from vehicles and hydrocarbons is the main constituent of photochemical smog. In South Africa, transportation is largely by road with most of the vehicles being privately owned, as public transport is ineffective. The current vehicular fleet is aging and uses outdated automotive technologies. Road and fleet upkeep is costly resulting in above normal emissions (Singh, 2008).

High-temperature industries such as pyrometallurgical smelters are also an important source of atmospheric pollutants. Depending on the specific process, temperatures up to 3000°C can be achieved resulting in the production of various pollutants being released as off-gas. Low concentrations produced from furnaces and intermittent production from converters makes it challenging to capture the pollutant gas species in some of these processes, therefore it is commonly discharged to the atmosphere through a tall stack (Jones, 1999). Ash handling and treatment of flue gases are also important for reducing the environmental impact. Since the introduction of particulate filters, the amount of fly ash released has been decreased in the USA, the European Union and South Africa. This

is still a major problem in more undeveloped parts of the world, where the fly ash is released directly.

Biomass burning is generally defined as the open combustion of any non-fossilised vegetative or organic fuel. Veld fires, domestic and industrial biofuel use, tropical forest fires, extratropical (mostly boreal) forest fires, as well as crop residue burning are regarded to account for most of the global biomass consumption (Akagi *et al.*, 2011). Biomass burning is the second largest source of trace gases and the largest source of primary fine carbonaceous particles in the global troposphere (Bond *et al.*, 2004). Biomass burning in tropical and subtropical regions is a significant source of NO<sub>x</sub> as well as other pollutant species such as CO<sub>2</sub>, CO, CH, NMHC, N<sub>2</sub>O and aerosols (Crawford *et al.*, 2003). Smoke particles from biomass burning are composed of ca. 50-60% organic carbon and ca. 5-10% black carbon and ca. 12-15% other inorganic species (Reid *et al.*, 2005). It is also well documented that approximately 90% of the carbon released during biomass burning is oxidised to CO or CO<sub>2</sub> (Ferek *et al.*, 1998).

Agriculture also leads to the presence of nitrous-containing compounds in the atmosphere. Most of these compounds are produced from agricultural activities such as fertilisers used, manure use, rice cultivation, as well as veld and field burning of agricultural residues. Agriculture is also a large source of methane emissions. Most of the methane emissions are due to enteric fermentation from livestock, with a small amount from the handling of livestock wastes (Rees & Ball, 2011).

### **2.1.3. Removal**

Dry deposition refers to the removal of trace substances from the atmosphere without the aid of precipitation, i.e. the direct uptake of atmospheric species on the surface of the earth. Dry deposition is a slow continuous process and is profoundly affected by the physical, chemical and biological properties of the surface (Wesely, 2003). It occurs through convective transport, diffusion and adhesion to the earth's surface (Pöschle, 2005; Engelbrecht, 2009). Atmospheric gas molecules can react with surface materials or dissolve in them when the atmosphere comes in contact with surface elements. Vertical

transfer of particles in the atmosphere is primarily accomplished by turbulent mixing; for particles with diameters greater than 1 to 2  $\mu\text{m}$ , which is also aided by gravitational settling. Particles can be captured by interception or impaction with the surface elements (Pöschle, 2005).

Atmospheric pollutant species are also removed from the atmosphere through wet deposition. Certain pollutants are readily removed from the atmosphere by dissolving in cloud water, which are then precipitated from the atmosphere. In cloud-free air, small amounts of condensable species such as sulphates, ammonia and nitrates coagulate with water vapour to form small atmospheric aerosol particles (Walcek, 2003). Through gaseous diffusion and aerosol coagulation, smaller aerosols generally grow in size, while continuously maintaining an approximate equilibrium with water vapour and other surrounding condensable trace gases. Some aerosols eventually become large enough to develop an appreciable fall speed that overcomes frictional air drag, therefore slowly settling towards the surface. However, well before particles grow to sizes where gravitational settling becomes important, larger aerosol particles are readily incorporated into clouds (Walcek, 2003). In the immediate vicinity of precipitation systems, soluble gases and a large fraction of soluble aerosols are efficiently removed from the atmosphere on a time scale of an hour or less. Chemical species that are rapidly removed by precipitation include gaseous  $\text{HNO}_3$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$ . Soluble constituents of cloud condensation nuclei (CCN), including aerosol sulphates, nitrates, and sea salts are also rapidly scavenged from the atmosphere under most precipitating conditions (Walcek, 2003). Wet deposition is the main sink of atmospheric aerosol particles.

## ***2.2. Selection of species measured***

$\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ , CO and  $\text{PM}_{10}$  are considered to be criteria pollutants in the new South African Air Quality Act, for which legislative standards have been set (NEM:AQA, 2004). The ambient concentrations of these species were measured in this investigation in order to assess air quality in the western Bushveld Igneous Complex. The significance of

this region is discussed in Section 2.5. In the subsequent paragraphs in this section the afore-mentioned criteria pollutant species are discussed.

### **2.2.1 Sulphur dioxide**

SO<sub>2</sub> is described as a colourless gas that is emitted mainly from stationary sources that burn fossil fuels, such as power plants, ore smelters and refineries (Elsom, 1987). It is also naturally emitted from volcanic eruptions (Martins, 2008). Other sulphur-containing compounds in the atmosphere include carbonyl sulphide, carbon disulphide, dimethyl sulphide, H<sub>2</sub>S and SO<sub>3</sub>. Some of these species can also lead to the formation of atmospheric SO<sub>2</sub>.

Figure 2.1 indicates the world sulphur emission trends from 1850 up to 2000 (IPCC, 2001). A rapid increase in SO<sub>2</sub> emissions since the late eighteenth century is noticeable, which coincides with the beginning of the industrial revolution and increased power generation. In the late twentieth century, global awareness of air quality increased, which forced industries and governments to take drastic measures. More recently, the ambient concentrations, especially in first-world countries, have started to decrease. This phenomenon is mainly attributed to the use of lower sulphur-containing fuel and desulphurisation of stack emissions from plants (IPCC, 2007b). However, an upward trend has been observed for South Africa, which is considered to be the 9<sup>th</sup> highest sulphur emitting country (Stern, 2006).

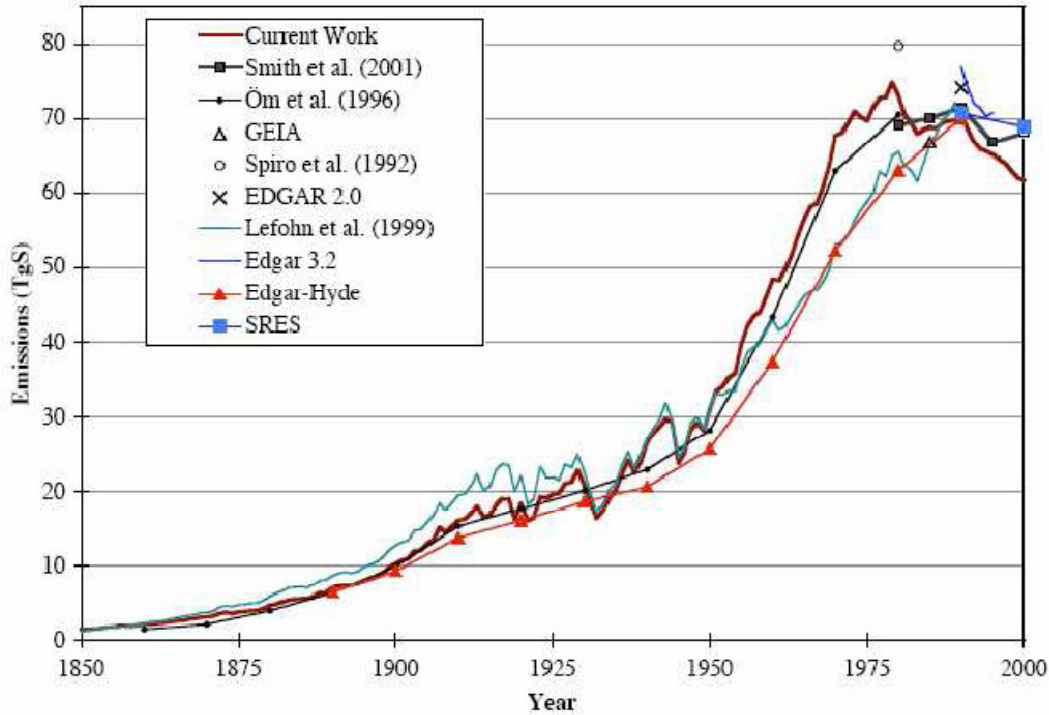


Figure 2.1: The world sulphur emissions trend (IPCC, 2001)

Atmospheric  $\text{SO}_2$  leads to the formation of sulphuric acid aerosols.  $\text{H}_2\text{SO}_4$  formation can also take place through direct sulphate ( $\text{SO}_4^{2-}$ ) emissions.  $\text{SO}_2$  can also form other sulphate aerosol particles. The properties of these sulphate aerosols differ according to the process of formation; while the production thereof can be in the gas or aqueous phase (Houghton *et al.*, 2001). These particles build up in size to form molecular clusters, which subsequently form ultra-fine aerosols that grow to larger diameters.

In the production of  $\text{H}_2\text{SO}_4$  in the atmosphere,  $\text{SO}_2$  reacts with oxygen to form  $\text{SO}_3$ :



This direct reaction of  $\text{SO}_2$  with  $\text{O}_2$  is extremely slow under atmospheric conditions. Therefore,  $\text{SO}_3$  is more readily produced via the more favourable hydroxyl radical ( $\text{HO}^\bullet$ ) abstraction reaction:







with A representing a vibrational exchange species.

Sulphuric acid is then formed when  $\text{SO}_3$  reacts with water:



As mentioned previously,  $\text{SO}_2$  can also be secondarily formed in the atmosphere. Dimethyl sulphide undergoes a few reactions to also form  $\text{SO}_2$ , which can enter the aerosol formation cycle:



Hydrogen sulphide undergoes  $\text{HO}\cdot$  abstraction to form the SH radical that undergoes a series of reactions to form  $\text{SO}_2$  (Seinfeld & Pandis, 1998):

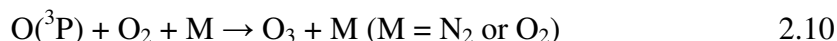


The residence time of  $\text{SO}_2$  in the atmosphere ranges between twelve hours and six days (Kellogg *et al.*, 1972).

### 2.2.2 Nitrogen oxides

Nitrogen oxides ( $\text{NO}_x$ ) (total concentration of NO and  $\text{NO}_2$ ) are produced anthropogenically from traffic, coal-fired power plants, biomass burning and agricultural processes (EPA, 2000), or naturally by the oxidation of  $\text{NH}_4^+$  and the reduction of  $\text{NO}_3^-$  in the biosphere. High  $\text{NO}_2$  levels have been found in urban areas in the morning and late afternoon, due to increased motor vehicle activities. NO is usually emitted from the source, which is rapidly oxidised to  $\text{NO}_2$ . Nitrogen dioxide is the most prominent nitrogen-containing atmospheric pollutant. It is one of the most important species in the troposphere since it absorbs radiation over the entire visible and ultraviolet solar spectrum range (Seinfeld & Pandis, 2006).  $\text{NO}_x$  can react with water to form nitric acid,

which leads to the formation of acid rain. South Africa is well known for the NO<sub>2</sub> hotspot over the Mpumalanga Highveld. The tropospheric NO<sub>2</sub> column density of this area is comparable to that observed for central and northern Europe, eastern North-America and south-east Asia. The most well-known sources in this area are a large array of coal-fired power stations and a large petrochemical plant (Lourens *et al.*, 2011(b)). NO<sub>2</sub> is the precursor for the formation of O<sub>3</sub> that influences the oxidative capacity of the atmosphere. Should the photolysis of O<sub>3</sub> be considered the start of tropospheric chemistry, NO<sub>2</sub> must then be regarded as the precursor for all chemistry in the troposphere (Pienaar & Helas, 1996). Once released into the atmosphere, this abundant species undergoes a series of chemical reactions (Fellenberg, 1997).



These reactions interconvert NO, NO<sub>2</sub> and O<sub>3</sub>, shown in Figure 2.2, below.

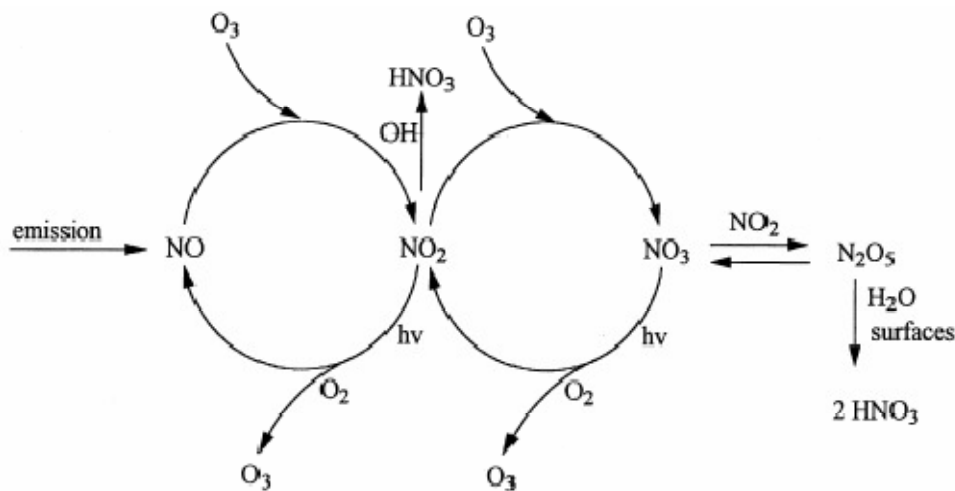
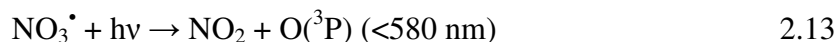
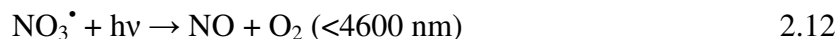


Figure 2.2: Tropospheric NO cycle (Atkinson, 1998)

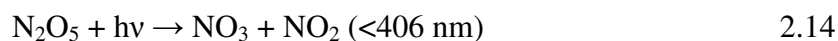
Furthermore, the reaction of NO<sub>2</sub> and O<sub>3</sub> leads to the formation of the nitrate radical NO<sub>3</sub><sup>•</sup>



which reacts rapidly (lifetime of 5s) with NO in the presence of sunlight to form NO again, as well as NO<sub>2</sub>:



Photolysis of other nitrogen oxides in the troposphere is:



The reaction of NO<sub>2</sub> with the HO<sup>•</sup>-radical is considered to be the major depleting chemical process for NO<sub>x</sub> during daytime hours (Atkinson, 2000). NO<sub>x</sub> is extremely reactive and therefore has very short residence times in the lower troposphere, while it can have relatively long lifetimes in the upper troposphere (Brasseur *et al.*, 1999).

### 2.2.3 Ozone

Tropospheric ozone is a secondary pollutant, which is formed from the chemical reactions between O<sub>2</sub>, NO<sub>x</sub> and VOCs in the presence of sunlight (Brasseur *et al.*, 1999). It is argued that tropospheric O<sub>3</sub> is the most widely occurring gaseous pollutant species, especially in regions with high incidences of sunlight. Most studies indicate that daytime ozone levels correlate strongly with temperature, i.e. higher temperatures coincide with higher O<sub>3</sub> levels (IPCC, 2007b). A 33-year study of ozone data from Japan showed ozone in the lower troposphere to have increased from 1970 to 2002 (Soloman *et al.*, 2007). From relatively recent studies in South Africa, it is evident that almost the entire interior of South Africa has elevated O<sub>3</sub> levels (Lourens *et al.*, 2011(a); Josipovic *et al.*, 2010).

As discussed in Lourens (2008), photolysis of low ozone levels (at wavelengths < 319nm), present in the troposphere, is considered to be the start of all atmospheric oxidation reactions. Both ground state (O) and excited singlet (O(<sup>1</sup>D)) atoms are produced (Lourens, 2008)



The singlet O(<sup>1</sup>D) oxygen atom reacts with water vapour and generates two HO<sup>•</sup>-radicals:



Once the HO<sup>•</sup>-radical is formed, it reacts virtually with all the atmospheric trace species present in the troposphere. The gaseous species that do not react with the HO<sup>•</sup>-radical have longer lifetimes and are transported into the stratosphere, where they are photochemically destroyed (Seinfeld & Pandis, 1998). The key to understanding tropospheric chemistry begins with understanding the role of the HO<sup>•</sup>-radical. This short-lived radical is the most important species in tropospheric chemistry. Although O<sub>2</sub> and O<sub>3</sub> are the most abundant oxidants in the atmosphere, they have large bond energies and are generally unreactive. This implies that the HO<sup>•</sup>-radical is the primary oxidising species in the atmosphere. The oxidation of atmospheric species can be very complex (Lourens, 2008).

#### 2.2.4 Carbon monoxide

Carbon monoxide (CO) is the main pollutant released into the atmosphere due to the incomplete combustion of carbon-based fuels. Petroleum powered vehicles are an important source of CO emissions and contribute to more than 90% of CO in most urban areas (Elsom, 1996). CO is also released by the industrial sector, especially from coal-fired power stations (Höök, 2007). In South Africa, household combustion also contributes significantly to CO emissions due to the large amount of low-income groups living in informal settlements. The inefficient combustion of coal or biofuels less than two meters above the ground in residential areas causes high levels of human exposure to CO. Elevated CO levels are also observed at the end of winter and beginning of spring in Southern Africa, due to extensive biomass burning events (Laakso *et al.*, 2008).

In the troposphere, hydroxyl free radicals ( $\cdot\text{OH}$ ) oxidise CO to form hydroperoxy radicals ( $\text{HO}_2\cdot$ ) (Levy, 1971) that catalyse tropospheric  $\text{O}_3$  formation:



As indicated by Crutzen and Zimmermann (1991), in a  $\text{NO}_x$ -rich environment, these reactions produce ozone. Within the atmosphere, the major CO source is oxidation of methane by  $\cdot\text{OH}$ , producing formaldehyde ( $\text{CH}_2\text{O}$ ) and then carbon monoxide. This methane reaction, in combination with equation 2.21, consumes most  $\cdot\text{OH}$  radicals in the troposphere. The tropospheric abundances of CO and  $\text{CH}_4$  therefore become important indices of the tropospheric oxidising capacity, represented most specifically by the concentrations of ozone and hydroxyl free radicals (Crutzen & Zimmermann, 1991).

### 2.2.5. *Particulate matter*

Atmospheric PM or aerosols consist of a complex mixture of inorganic and organic compounds. Atmospheric aerosols range in size from 0.01-100  $\mu\text{m}$ . Airborne particulate PM changes in size and composition, while they also interact with other particles. The lifetime of aerosols can range from a few hours up to several weeks (Pöschle, 2005). Aerosol particles have a short residence time in the atmosphere compared to gases, suggesting lower concentrations per unit mass emitted. This, however, does not influence their impact on the environment, which may be comparable to that of the long-lived gases due to their indirect effects on the concentrations of other pollutants through the heterogeneous chemistry that takes place on aerosol surfaces (Dentener *et al.*, 1996). Aerosols are important for the energy balance of the earth, atmospheric circulation, the hydrological cycle, as well as the abundance of greenhouse and reactive gaseous species in the atmosphere (Pöschle, 2005). The impacts of aerosols on the atmosphere are closely related to their chemical composition and physical properties, which are very complex due to their chemical diversity and evolution in the atmosphere (Cousin *et al.*, 2005). Aerosols have an impact on gaseous chemistry (Ravishankara, 1997) and are essential for the closure of radiative budgets (Charlson *et al.*, 1992; Penner *et al.*, 1996; Adams *et al.*, 2001).

Aerosols are emitted directly into the atmosphere as primary pollutants or are formed as secondary pollutants through chemical reactions in the atmosphere. Primary aerosols can be emitted naturally from the dispersal of solids from the surface of the earth, e.g. through volcanoes, biomass burning and erosion, as well as anthropogenically, e.g. industrial activities. The production of secondary aerosols is a result of transformation reactions between individual primary aerosols and/or gaseous species in the atmosphere (Houghton *et al.*, 1999). Gaseous precursor species lead to new particle formation by nucleation and condensation, i.e. gas-to-particle conversion (Pöschle, 2005). Recent studies in South Africa have indicated that the frequency and rate of new particle formation in South Africa is among the highest measured in the world (Laakso *et al.*, 2008; Vakkari *et al.*, 2011).

In Figure 2.3, the cycle of aerosols from their emission into the atmosphere until their final removal is shown. A number of studies have indicated that the emissions from natural sources exceed emissions from anthropogenic sources on a global scale by a factor of 4 to 5 (Hobbs, 2000). It is, however, estimated that in 2040 the emissions from anthropogenic sources will equal the level of the natural emissions. This is due to the increase in the combustion of fossil fuels, especially in fast-developing countries such as China and India (EEA, 2003).

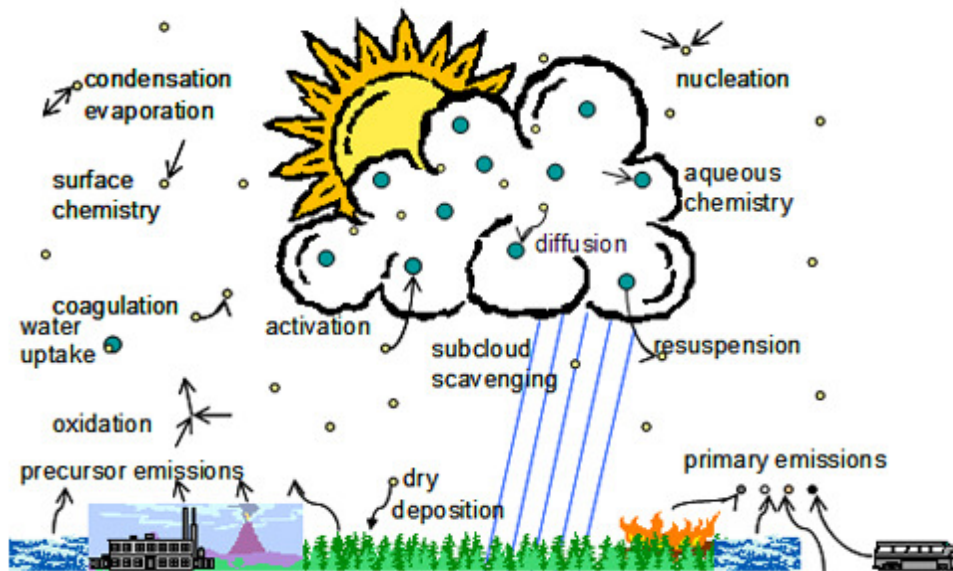


Figure 2.3: Schematic diagram illustrating the many interactions of aerosols in the environment – from emission to deposition (Ghan, 2011)

Aerosols are also important for the formation of clouds, since they are CCN and ice nuclei (IN), which leads to the formations of droplets or ice in the atmosphere. The best known example of aerosols in the atmosphere is clouds. In atmospheric chemistry, a distinction is made between water droplets and suspended particles that contain a large proportion of condensed matter other than water (Pöschle, 2005).

## **2.3. *Impacts of atmospheric pollutants***

The impacts of atmospheric pollutants can be divided into two main impacts, i.e. effects on air quality (human health and the environment) and the influence on climate change.

### **2.3.1 *Air quality***

Air pollutants can cause serious health-related problems depending on their chemical composition, physical properties and concentrations in the atmosphere. Various studies have also revealed that an increase in air pollution is associated with an increase in mortality and hospital admissions (Brunekreef & Holgate, 2002; Suwa *et al.*, 2002). For gases, solubility controls removal from the air stream. Highly soluble gases such as SO<sub>2</sub> are absorbed in the upper airways, whereas less soluble gases such as NO<sub>2</sub> and O<sub>3</sub> may penetrate to the pulmonary region. Irritant gases are thought to stimulate neuro-receptors in the respiratory walls and cause a variety of responses, including sneezing, coughing, broncho-constriction and rapid, shallow breathing. The dissolved gas may be eliminated by biochemical processes or may diffuse to the circulatory system (Vallero, 2008).

High concentrations of atmospheric pollutant species can also be detrimental to ecological systems. Atmospheric pollutants can have significant environmental impacts on a local, regional and global scale – depending on their chemical composition and physical properties. Major changes include global climate change, the ozone hole, acid rain, El Niños and air pollution. These, in turn, affect the weather and climate, upsetting the natural habitat of the plant and animal kingdom that is in delicate balance and is needed to sustain life.

SO<sub>2</sub> is normally removed from the upper respiratory system due to its solubility in watery fluids. Absorption and adsorption of SO<sub>2</sub> on particles provide a transport mechanism for SO<sub>2</sub> into the pulmonary system, where SO<sub>2</sub> toxicity occurs. Consequently, particles can potentiate the effect of SO<sub>2</sub>. Harmful aerosols such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) can be produced as a result of the interaction of gaseous pollutants with the moist environment of the lungs (Godish, 2004). In the environment, SO<sub>2</sub> shifts the atmospheric acidity and is



one of the major precursors of acid rain, which has acidified soils, lakes and streams, and accelerated the corrosion of buildings and monuments. Sulphur dioxide is also a major precursor of fine particulate soot that leads to reduced visibility (EPA, 2011).

According to Last *et al.* (1994), acute exposure of humans to NO<sub>2</sub> at concentrations above about 150ppm (282 mg/m<sup>3</sup>) causes death, either rapidly due to pulmonary oedema or after a few weeks due to bronchiolitis obliterans with severe fibrosis. In animal experiments, exposure of rats to about 25ppm (47 mg/m<sup>3</sup>) for several days was lethal to more than half of the animals. Exposure of rats to concentrations between approximately 4 and 20ppm of NO<sub>2</sub> for several days causes mild oedema, increased protein content of lung lavage fluid, inflammation, damage to airway epithelial cells, and bronchiolitis (Last *et al.*, 1994). Nitrogen oxides contribute to ozone formation and can have adverse effects on both terrestrial and aquatic ecosystems. Nitrogen oxides in the air can significantly contribute to a number of environmental effects such as acid rain and eutrophication in coastal waters. Eutrophication occurs when a body of water suffers an increase in nutrients that leads to a reduction in the amount of oxygen in the water, producing an environment that is destructive to fish and other animal life (EPA, 2011).

In the troposphere, O<sub>3</sub> exposure is destructive as it is highly reactive with tissues, leading to ecological degeneration, such as forest damage and reduced crop production, as well as human health effects, especially cardio-pulmonary diseases. Environmental impacts induced by ozone are visible by the distinctive brown-coloured lesions on leaves of exposed foliage. Plants have a decrease in growth rate and seed production (Scheepers *et al.*, 2009).

The most important impacts associated with atmospheric PM are (Slanina & Zang, 2004):

- The impact on human health. Aerosols do not only exacerbate heart and lung diseases, but also contribute to asthma and bronchitis.
- The occurrence of acid deposition and eutrophication caused by sulphates and nitrates present in aerosols.

- The formation of ozone through heterogeneous reactions on the surface of aerosols.
- The reflection and absorbance of incoming sunlight, which affects the radiative balance of the earth and, hence, the global climate (discussed in Section 2.3.2).

There are many human health problems associated with particulate matter, which renders this one of the major environmental concerns in the world (WHO, 2007). These health effects are related to the specific surface area of the aerosol and the presence of certain chemical species such as transition metals and organic compounds (Bernstein *et al.*, 2004). The adverse health impacts are also determined by the size of aerosols, i.e. coarse (PM<sub>10</sub>), fine (PM<sub>2.5</sub>) and ultra fine (PM<sub>1</sub> and PM<sub>0.1</sub>). According to certain investigations, thoracic coarse particles may affect the airways and lungs, while fine particles affect the cardiovascular system. Ultra fine particles can also migrate through the lungs to other locations in the human body, such as the liver, brain, spleen and placenta (WHO, 2007). Statistics on health effects associated with PM estimate that atmospheric PM causes about 8% of trachea, bronchus, and lung cancer; 5% of cardio respiratory diseases; and 3% of respiratory infections, globally (WHO, 2007). Environmental damage occurs when particles are carried over long distances by wind and then settle on ground or water. The effects of this settling include acidifying lakes and streams; changing the nutrient balance in coastal waters and large river basins; depleting the nutrients in soil; damaging sensitive forests and farm crops; and affecting the diversity of ecosystems (EPA, 2011).

Since the ambient atmosphere in a community is usually contaminated with complex mixtures of gaseous species and PM, it is possible that these species may interact with each other and modify the physiological effects and impacts on the environment. A comprehensive understanding of the sources, chemical composition, physical properties, atmospheric interactions and sinks of hazardous pollutants is required for proper air quality control and the reduction of the concomitant detrimental health effects. Without this recognition, the introduction of new laws, regulations and technical solutions aimed at protecting the environment could be ineffective and in some instances cause actual harm through unwanted side-effects (Pöschle, 2005).

### 2.3.2 *Climate change*

An important consequence of atmospheric pollution is its effects on climate change (IPCC, 2007b). The earth's climate is a complex system that is influenced by the interaction of the atmosphere, land and water surfaces (e.g. terra firma, snow and ice, oceans), as well as all living organisms (IPCC, 2007b). The climate system evolves over time under the influence of its own internal dynamics together with external factors that also affect climate. External forcings include natural phenomena such as volcanic eruptions and solar variations, as well as human-induced changes in the atmospheric composition. The IPCC (fourth assessment) reports an increase in the rate of climate change due to anthropogenic activities (IPCC, 2007b).

Greenhouse gases contribute significantly to global climate change, since they effectively absorb infrared radiation, i.e. solar radiation reflected from the surface of the earth, causing the atmospheric temperature to rise (IPCC, 2007b). Godish (2004) describes the greenhouse effect to be primarily caused by the sorption and re-radiation of thermal energy by CO<sub>2</sub> and H<sub>2</sub>O vapour. Other atmospheric gaseous species are also considered to be greenhouse gases, which include CH<sub>4</sub>, N<sub>2</sub>O, tropospheric O<sub>3</sub>, CFCs, perfluorocarbons and sulphur hexafluoride.

The increases in global atmospheric CO<sub>2</sub> since the industrial revolution are mainly due to CO<sub>2</sub> emissions from the combustion of fossil fuels. Other sources include emissions due to land use changes such as deforestation (Houghton, 2003) and biomass burning (Andreae & Merlet, 2001).

CH<sub>4</sub> and N<sub>2</sub>O absorb infrared radiation 21 and 206 times more effectively than CO<sub>2</sub>, respectively (Godish, 2004). Their contribution as greenhouse gases compared to that of CO<sub>2</sub> and H<sub>2</sub>O vapour was historically relatively limited (Godish, 2004). However, the concentrations of these species in the atmosphere are increasing. CH<sub>4</sub> concentrations in the atmosphere have increased 150% from pre-industrial times, while atmospheric N<sub>2</sub>O levels have increased ca. 16%, since 1750. Tropospheric O<sub>3</sub> also has the potential to significantly absorb thermal radiation, with a radiative effectiveness 2000 times larger than CO<sub>2</sub>. Tropospheric O<sub>3</sub> levels have increased by ~36% since 1750 (Godish, 2004).

Although these species absorb infrared radiation more effectively than CO<sub>2</sub>, their concentrations are much lower in the atmosphere.

The radiative balance of the earth can be changed in three ways: 1) changing the incident solar radiation, 2) changing the fraction of solar radiation that is reflected (direct and indirect aerosol effects) and 3) altering the long wave radiation from the surface of the earth back to space (greenhouse gases) (IPCC, 2007b). Radiative forcing (RF) is a measurement of how the energy balance of the earth's atmospheric system is influenced when factors that affect climate are altered (IPCC, 2007b). Radiative forcing is measured in Watts per square meter (W.m<sup>-2</sup>). A positive value indicates that the energy of the earth-atmosphere system will increase and will lead to warming, whereas a negative radiative forcing value indicates a decrease in energy and consequent cooling of the system (IPCC, 2007b). In Figure 2.4, the estimated changes in RF from 1750 to 2005 are presented. It is evident that CO<sub>2</sub> has the largest positive RF values, while the combined impact of the other gaseous species also contributes significantly to the warming of the atmosphere. The level of scientific understanding (LOSU) of the contribution of these species to climate change is also high.

Atmospheric aerosols can absorb or scatter solar and infrared radiation in the atmosphere. These properties of aerosols can lead to positive or negative RF, i.e. heating or cooling. Aerosol particles may lead to heating of the lower atmosphere if they contain species such as elemental carbon that absorbs radiation (Andreae, 2001), while particles such as SO<sub>4</sub><sup>-</sup> reflects radiation causing the cooling of the atmosphere. Atmospheric aerosols also indirectly affect RF through the cloud albedo effect. Aerosols potentially modify cloud size, lifetime, brightness, precipitation (IPCC, 2007b), and the concentrations of trace gases (Dentener *et al.*, 1996). The 'first indirect effect' – the 'Cloud albedo effect' or the 'Twomey effect' – is the effect on the cloud droplet number concentration; therefore the cloud droplet size with the liquid water content held fixed. The effect on the liquid water content, cloud height and lifetime of clouds has been called the 'second indirect effect', the 'Cloud lifetime effect', or the 'Albrecht effect' (IPCC, 2007b). Figure 2.4 indicates that aerosols primarily cause cooling of the atmosphere. It is, however, also evident that

there is a low LOSU of the impacts of aerosols on climate change with the most uncertainties in this field of research associated with these species. The radiative impacts of aerosols depend on their concentrations, as well as their physical and chemical properties that cause difficulty to exactly determine their impacts (IPCC, 2007b; Ramanathan *et al.*, 2001; Andrea *et al.*, 2002). Until the mechanisms leading to background and anthropogenic aerosol formation and the removal thereof are fully understood within a theoretical framework (model), their influence on atmospheric chemistry and therefore climate will not be fully understood (O'Dowd *et al.*, 1999).

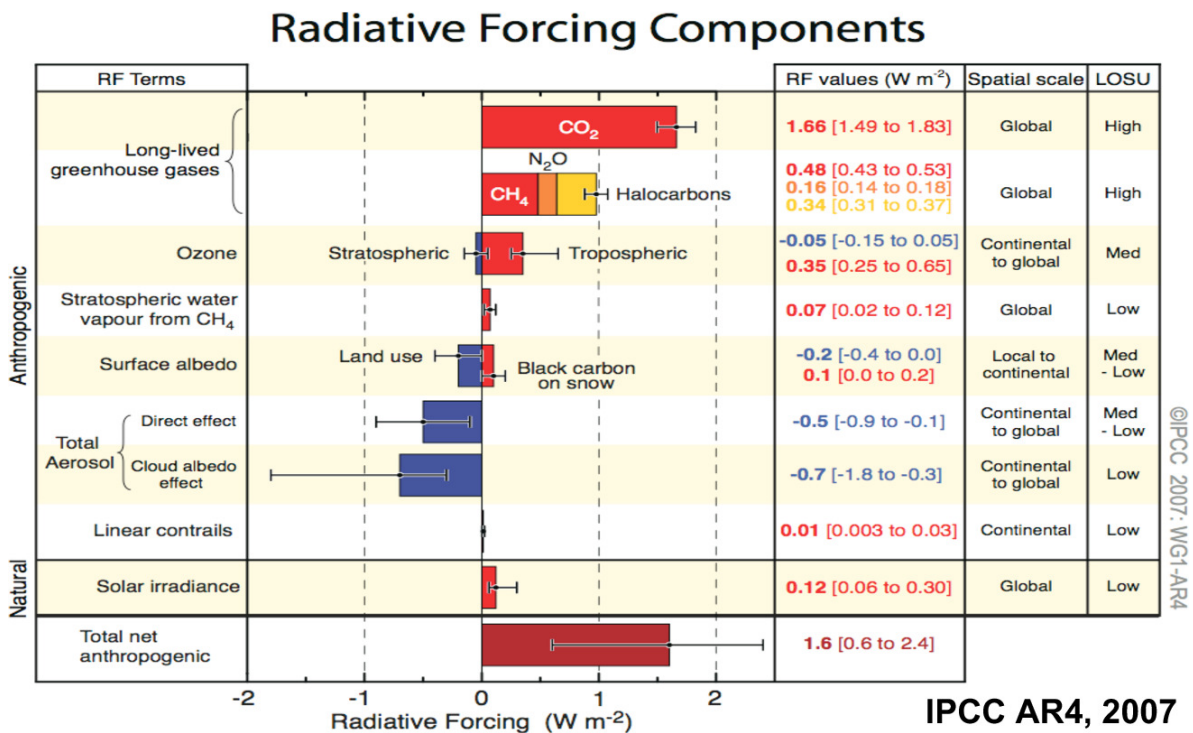


Figure 2.4: Changes in radiative forcing between 1750 and 2005 as estimated by the IPCC (IPCC, 2007b)

## 2.4. *Air quality standards*

The direct and indirect adverse effects caused by atmospheric pollution on the environment and human health necessitate the measurement and reporting of air quality on local, regional and global scale. In order to improve the air quality worldwide, federal and state agencies (such as EPA, WHO) have developed standards and guidelines to reduce pollutant emissions. These standards and guidelines are intended to protect the public against severe health effects.

Measurement and improvement of air quality in developed countries are considered a priority. In developing countries, less emphasis is placed on environmental issues, since resources are mostly utilised for economic growth. South Africa is regarded as a developing country with elements of a developed country. Globally, southern Africa is a significant source region of atmospheric pollutants, due to biomass burning emissions (Swap *et al.*, 2003) and the presence of the “NO<sub>2</sub> hotspot” over the Highveld (Wenig *et al.*, 2003).

In the last decade, South African ambient air quality standards were revised (NEM:AQA, 2004) and are now in line with ambient air quality standards in developed countries. In addition, South African legislation makes provision for the identification and declaration of geographical air pollution “hotspot” areas termed Priority Areas. In these areas, South African ambient air quality standards are frequently exceeded, hence improvement is required. Two priority areas have been declared in South Africa, i.e. the Vaal Triangle Airshed Priority Area (VTAPA) and the Highveld Priority Area (HPA) (DEAT, 2007). Major atmospheric pollutant point sources in these areas are petrochemical and metallurgic industries, as well as coal-fired power stations.

The US EPA (United States Environmental Protection Agency) regards SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, Pb, CO and PM<sub>10</sub> (i.e. particulate matter with an aerodynamic diameter less than or equal to 10µm) as criteria pollutants. A criteria pollutant is a pollutant for which there is a set NAAQS (National Ambient Air Quality Standard) (Regulations, 1974). South Africa has also incorporated standards for all the above-mentioned species. These are the most

important and commonly monitored species in the atmosphere due to their importance in atmospheric chemistry influencing human health and the environment. Of these criteria pollutants, gases of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, CO and PM<sub>10</sub> were selected for monitoring in this study. The actual South African standards for each of these species will be indicated and discussed within the context of the results presented in Chapter 4.

## **2.5. *Bushveld Igneous Complex***

South Africa has the largest industrialised economy in Africa, with significant mining and metallurgical activities. A large fraction of the South African mineral assets is concentrated in the Bushveld Igneous Complex. The BIC, which covers an area of 66 000km<sup>2</sup>, holds approximately 70% the world's viable chrome resources, as well as large deposits of vanadium, cobalt, nickel, tin and copper. 80% of the platinum group metals (PGMs) of the world are also produced in the BIC (Cramer *et al.*, 2004; Xiao & Laplante, 2004; Beukes *et al.*, 2010). Globally, PGMs play an important role in atmospheric pollutant mitigation, since they are mainly used in catalytic converters of vehicular exhaust systems. The BIC is geographically subdivided into five limbs, of which the western limb is the most exploited and industrially developed.

The BIC region is 700 to 1100m above sea level and receives between 300 and 500mm of rain per annum. The land in this region is quite flat, but has several mountain ranges of which the Waterberg are the best known. The BIC is a layered igneous intrusion – igneous because it is composed of solidified magma that erupted from the earth's mantle and intrusion because molten magma was forced between pre-existing subterranean rock formations. The molten homogeneous mass cooled and physical and chemical differentiation occurred (Reader, 1999).

The South African government is currently considering declaring the western BIC an national Priority Area (Scott, 2010). However, due to a deficiency of past measurements in this area, no baseline data exist. In contrast, numerous studies have been conducted and published for the Vaal Triangle and Highveld priority areas (Bornman *et al.*, 2010; Collett *et al.*, 2010; Lourens *et al.*, 2011(a)). Recent changes in South African legislation

have forced local authorities to initiate measurements of ambient priority pollutants in the western BIC (Scott, 2010). Problems associated with the development of these monitoring networks, capacity limitations and the lack of quality assurance procedures make it difficult to evaluate the data quality. Most of these datasets are also not published in peer-reviewed journals. To at least partially address this knowledge gap, a comprehensive air quality monitoring station was operated for more than two years in the western BIC. In Chapter 4, an air quality assessment of criteria pollutants in this globally important area is presented.

A study conducted in 2001 (Pulles *et al.*, 2001), on behalf of the Rustenburg Air Quality Forum (RAQF), attempted to quantify emissions from all sources in the region. Although emission levels from each of the sources were obtained directly from the persons responsible for the sources, the data are incomplete and do not include all pollution sources (Pulles *et al.*, 2001) such as those from natural occurring processes.

Table 2.1: Estimated emission source contribution in the Rustenburg area (Pulles *et al.*, 2001)

Sulphur dioxide		Oxides of nitrogen		Particulate Matter			
Source	Percentage	Source	Percentage	Source	Percentage	Source	Percentage
Industrial	99.25	Domestic	65.85	Unpaved roads	62.14	Domestic	1.54
Domestic	0.41	Industrial	25.98	Industrial	28.55	Veld fires	1.27
Small Boilers	0.31	Vehicular	6.46	Paved roads	3.47	Tailing dams	0.45
Vehicular	0.03	Small boilers	0.99	Small boilers	2.26	Vehicular	0.13
		Veld fires	0.75				

## 2.6. Meteorology of the South African interior

Air quality is always influenced by transport and removal processes, hence a brief overview of the meteorological conditions influencing the area under consideration is



presented. Southern Africa is situated in the subtropical high-pressure belt (which circles the globe between 25°S and 30°S), where it is influenced by several high-pressure cells. The circulation of South Africa's atmosphere is anti-cyclonic throughout the year. This can be due to the dominance of three high pressure cells, i.e. the South Atlantic high-pressure cell off the west coast, the South Indian high-pressure cell off the east coast and the continental high-pressure cell over the interior (Liebenberg-Enslin *et al.*, 2007). In the summer months, the anti-cyclonic belt weakens and shifts southwards, allowing the tropical easterly flow to resume its influence over South Africa. Low air pressure conditions prevail over the interior of South Africa with generally unstable meteorological conditions, which increase the vertical motion and dispersion of pollutants in the atmosphere (Tyson *et al.*, 1996).

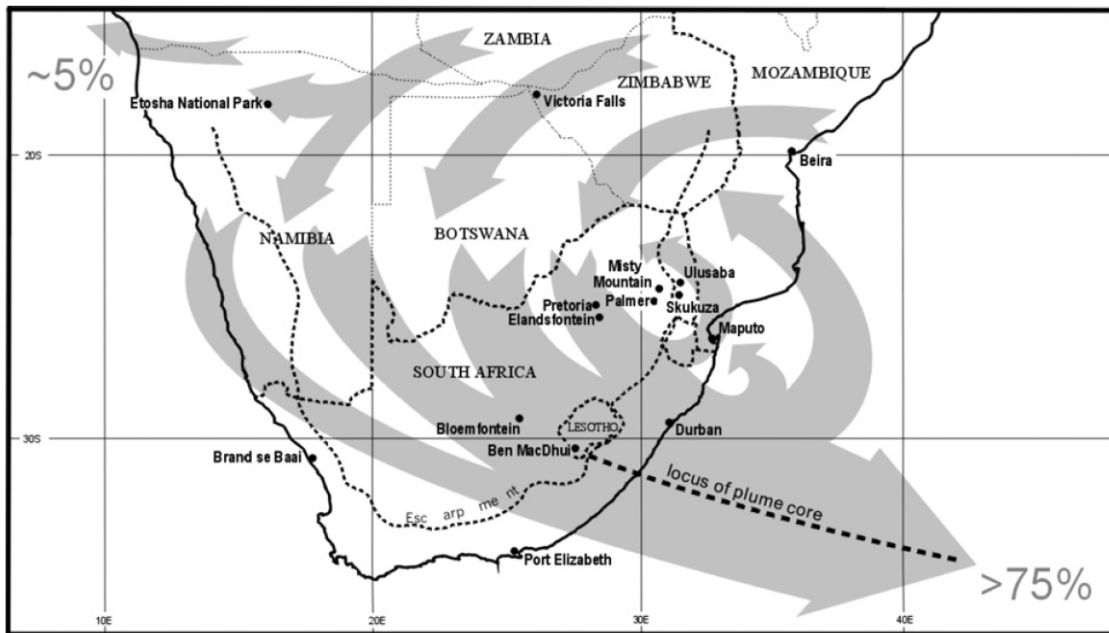


Figure 2.5: Average atmospheric transport pathways over southern Africa (Reason *et al.*, 2006)

In the winter months, the weather of South Africa is largely dominated by perturbations in the westerly circulation. These perturbations take the form of a succession of cyclones or anti-cyclones that move eastwards around the coast or across the country (Liebenberg-

Enslin *et al.*, 2007). During the winter, however, stable conditions with low wind speeds prevail over most parts of the interior of the country. Winters are characterised by the formation of inversion layers inhibiting vertical atmospheric mixing, and in general, weaker removal processes, effectively trapping pollutants between these layers. The temperature inversion layer traps the air pollution in the lower atmosphere, increasing pollutant concentrations and contributing to poor air quality (Preston-Whyte & Tyson, 1988). Cloudlessness (experienced for most winter months over the region) ensures full intensity of incoming solar radiation, which enhances photochemistry and results in the accumulation of photochemical smog in some areas (Liebenberg-Enslin *et al.*, 2007). A haze layer blankets southern Africa for most of the year on non-raining days to the level of the frequently occurring, sporadic ubiquitous ending stable layers observed at the 500hPa level at an altitude of 5-6km (Cosijn & Tyson, 1996). These thick aerosol layers covering most of southern Africa are visible from space during the dry season in September (Schmid *et al.*, 2003).

## **2.7. Conclusion**

Criteria pollutants, such as gases and aerosols adversely affect human health. The South African government is currently considering declaring the western BIC an Airshed Priority Area (Scott, 2010). However, due to a deficiency of past measurements in this area, very little baseline data exist. However, considering the global importance of this area (e.g. supply of PGMs utilised in automotive catalytic converters), there certainly is a need for more peer-reviewed studies published in the public domain on air quality for the western BIC. To at least partially address this knowledge gap, a comprehensive air quality monitoring station was operated for more than two years in the western BIC.