Chapter 1

Introduction

1.1 Background

Atmospheric pollution and climate change are currently issues of major national and international concern. Efforts to measure and improve air quality have increased over the last decades and are considered priorities in developed countries. However, Africa is one of the least studied continents in terms of atmospheric sciences, although it is highly vulnerable to the impacts of air pollution and climate change, due to limited financial and infrastructural resources. South Africa has the largest industrialised economy in Africa (Rorich & Galpin, 1998) and is known for its diverse anthropogenic activities, which include agriculture, mining and metallurgical operations, power generation, petrochemical operations, coal dumps, large-scale biomass combustion (veld fires), household combustion and transportation (Lourens *et al.*, 2011; Venter *et al.*, 2012). The combination of relatively high atmospheric pollutant emissions and unique weather conditions, which include high temperatures, prolonged periods of high solar radiation and dominant anti-cyclonic recirculation climatology, causes the trapping of pollutant species and increased photochemical activity, especially over the interior of South Africa (Tyson *et al.*, 1996).

Various gaseous and aerosol species emitted directly from both anthropogenic and biogenic sources, as well as secondary formed species, are important within the context of atmospheric pollution and climate change. The focus of this study was on atmospheric volatile organic compounds (VOCs). These gaseous species that are emitted into the atmosphere from both biogenic and anthropogenic sources (Brasseur *et al.*, 1999; Hewitt, 1999; Bates *et al.*, 2000) have a wide range of atmospheric lifetimes (minutes to days) (Atkinson, 2000; Atkinson & Arey, 2003). Although it is estimated that biogenic volatile organic compounds (BVOCs), e.g. isoprenes and terpenes, make up 90% of the global atmospheric VOC budget (Guenther *et al.*, 1995), anthropogenic VOC might be the dominant species in highly industrialised regions. Typical anthropogenic VOCs include benzene, toluene, ethylbenzene and xylenes (BTEX).

VOCs and their reaction products are increasingly regarded as posing unacceptable risks to public and occupational health, as well as to biological and physical environments. Toxicological research indicated that many VOCs have various reversible and irreversible effects on human health, ranging from acute anaesthesia to long-term effects such as induction of carcinomas (WHO, 2007; Lippman, 1992). Benzene is a known genotoxic carcinogen and is associated with leukaemia, whereas toluene can cause foetal malformation (WHO, 2007). Ecotoxicological research indicated that the effects of VOCs on the environment range from changes in the population of terrestrial and aquatic ecosystems to the extinction of vulnerable species (EPA, 2001). All of these effects were found to be directly caused by atmospheric VOCs, although the active agent may be one or more metabolic compound(s) produced by the species impacted (IAQM, 2012).

In the troposphere, VOCs can also react with the hydroxyl radical ($^{\bullet}OH$) (the most important sink for VOCs), or to a lesser extent with the nitrate radical ($NO_3^{\bullet}$) and halogen radicals ($Cl^{\bullet}$, $Br^{\bullet}$, $I^{\bullet}$) (Koppmann, 2007) leading to the formation of higher molecular weight organic compounds, which produce carbon monoxide (CO), peroxyacytyl nitrate (PAN) and ultimately secondary organic aerosol (SOA) particles (Otter *et al.*, 2003) by nucleation and condensation. SOA particles directly impact air quality and visibility, and directly and indirectly the radiation balance of the earth that in turn contributes to the regulation of the climate system on both regional and global scales (Finessi *et al.*, 2012). VOCs are also precursor species for O_3 formation. It is well established that ozone (O_3) is formed *in situ* from the sunlight-initiated oxidation of VOCs, in the presence of nitrogen oxides (NO_x) (Hoque *et al.*, 2008; Atkinson & Arey, 2003). Tropospheric O_3 is considered a pollutant, with negative impacts on human health, the ecosystem (IPCC, 2007; NRC, 2008) and food security (Zunckel *et al.*, 2007). O_3 is also a short-lived greenhouse gas that affects regional climate (IPCC, 2007; NRC, 2008). Additionally, VOCs contribute directly and indirectly (through O_3 formation) to the formation of photochemical smog that could have adverse effects on human health and vegetation. It is evident that VOCs play an important role in the global carbon budget and radiation balance, regional oxidant balance, and in the distribution of O_3 and other reactive gases (Otter *et al.*, 2003).

1.2 Significance of the study

Notwithstanding the above-mentioned described relevance of atmospheric VOCs, very little has been published in the peer-reviewed scientific literature on atmospheric VOCs in South Africa. Otter *et al.* (2002) measured BVOCs at Nylsvley and modelled BVOC emissions over South Africa as part of the SAFARI 2000 campaign. Burger (2006) reported on BTEX active and passive measurements in the Vaal Triangle and in Cape Town, while Van der Walt (2008) discussed hydrocarbon emissions in a South African metropolitan area. Lourens *et al.* (2011) measured BTEX in the Mpumalanga Highveld and the Vaal Triangle with passive sampling techniques for a one-year period. Additionally, it is likely that much more VOC measurements have been conducted in South Africa, especially by industries conducting compliance monitoring and governmentally controlled measurement stations assessing air quality. However, none of this data have been published in the peer-reviewed public domain.

To at least partially address the above-mentioned knowledge gap, i.e. very little VOC data published in the peer-reviewed scientific realm in South Africa, VOCs were measured at a site in the North West Province, i.e. the Welgegund measurement station (Welgegund, 2010; Beukes *et al.*, 2012). The site is situated approximately 100km west of Johannesburg and is considered to be a regionally representative background site with no direct impacts from pollution sources within close proximity. The sector that lies west of the Welgegund measurement station has very few large anthropogenic activities (Beukes *et al.*, 2012). Air masses arriving from this region at Welgegund can therefore be considered to be representative of a region without anthropogenic emissions.

The Welgegund measurement station is, however, also impacted by plumes from major anthropogenic source regions in the interior of SA, i.e. the western Bushveld Igneous Complex (BIC), the eastern Bushveld Igneous Complex (BIC), the Johannesburg-Pretoria metropolitan conurbation (>10 million people), the Vaal Triangle and the Mpumalanga Highveld (Beukes *et al.*, 2012). In 2005, the Vaal Triangle and areas of southern Gauteng were proclaimed as a national air pollution hotspot, termed the Vaal Triangle Air-shed Priority Area (Government Gazette, 2005). In the last quarter of 2007, the Mpumalanga Highveld and parts of south-eastern Gauteng were proclaimed as a national air pollution hotspot, termed the Highveld Priority Area (Government Gazette, 2007). Due to current and possible future air quality considerations, the western BIC was included in the area that was recently declared as the Waterberg Priority Area (Government Gazette, 2012). The Johannesburg-Pretoria conurbation also seems to be relatively heavily polluted (Lourens *et al.*, 2012).

Due to the strategic positioning of Welgegund (Beukes *et al*., 2012), air mass that had passed over the various source regions can be sampled at Welgegund. Therefore, measurements of VOCs at this station will provide a good understanding of the influence of the major anthropogenic source regions on VOC concentrations, as well as the impacts from a relatively 'clean' sector. BVOC measurements at Welgegund will provide a proper understanding of BVOC cycles in the Dry Highveld Grassland Biome in which Welgegund is placed - a region for which no measured BVOC data exist.

1.3 Objectives

The specific objectives of this study were to:

1.3.1 conduct a comprehensive literature survey, to establish the importance of atmospheric VOC compounds and to assess the current state of knowledge on atmospheric VOCs for South Africa.

1.3.2 measure a comprehensive set of anthropogenic and biogenic VOCs at a site with high atmospheric variability in the North West Province (South Africa), i.e. Welgegund measurement station, for at least a full seasonal cycle.

1.3.3 determine temporal and other possible trends of the above-mentioned VOCs at this measurement site.

1.3.4 explain the observed trends by investigating possible sources, interspecies correlations and ratios, as well as correlations with other high resolution ancillary data measured at Welgegund, e.g. meteorological data and trace gas concentrations.

1.3.5 compare the measured VOC concentrations to published VOC data from previous measurements conducted in South Africa and internationally.