

**Measurement of organic compounds in
atmospheric aerosols collected at Welgegund,
South Africa**

W Booyens

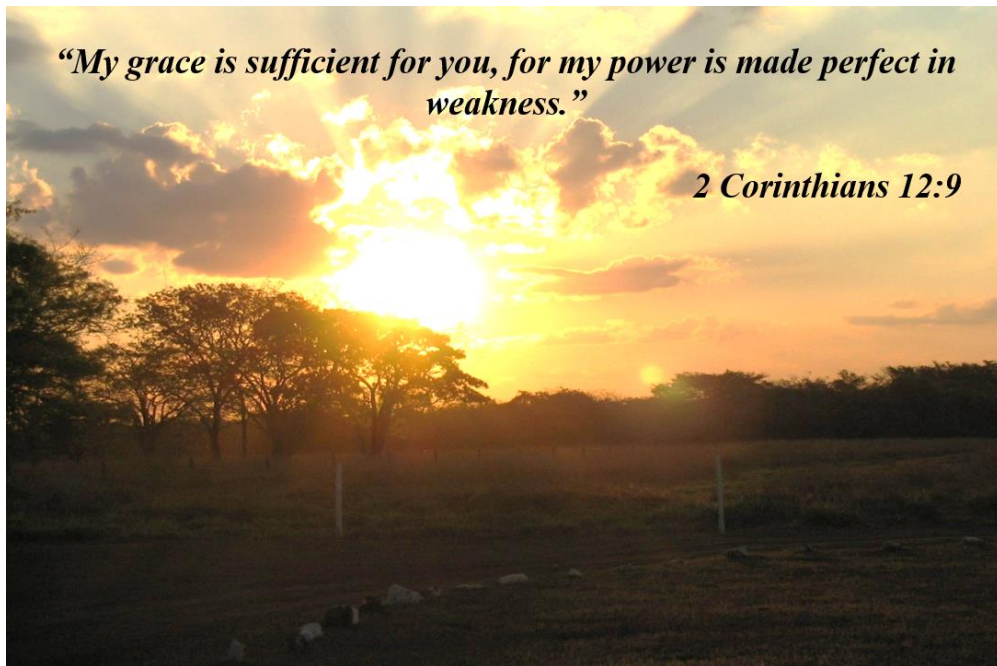
 **orcid.org 0000-0002-5422-403X**

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Promoter:	Prof PG van Zyl
Co-promoter:	Prof JP Beukes
Assistant Promoter:	Prof M-L Riekkola

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Thank you

Wanda

Preface

Introduction

This thesis was submitted in article format, as allowed by the Faculty of Natural Sciences in terms of the General Rules of the North-West University (NWU). This entails that the articles are added into the thesis as they were published, submitted or prepared for submission to the specific journals. The conventional results and discussions chapters were excluded, since the relevant information is summarised in the articles. Separate background, motivation and objectives (Chapter 1), literature survey (Chapter 2), methodology (Chapter 3) and project evaluation chapters (Chapter 7) were included in the thesis, even though some of this information was summarised in the articles. This will result in some repetition of ideas/similar text in some of the chapters and in the articles themselves. The fonts, numbering and layout of Chapters 4 to 6 (containing the research articles) are also not consistent with the rest of the thesis, since they were added in the formats published, submitted or prepared for submission as required by the journals.

Rationale in submitting thesis in article format

Currently, it is a prerequisite for submitting a PhD thesis at the NWU that a research article be submitted to a journal. In practice, many of these draft papers are never submitted to peer-reviewed journals. However, in this study, the candidate decided to submit this PhD thesis in article format, to ensure that most of the work is published. At the time when this thesis was submitted for examination, one article had already been published in the Journal of Atmospheric Chemistry, while the other two papers were ready for submission to ISI-accredited journals. Therefore, the prerequisite of the NWU was exceeded.

Contextualising the articles in the overall storyline

The topic of this PhD was associated with the chemical characterisation of atmospheric organic aerosols. Three articles are presented in this thesis, with each focusing on a different aspect related to the topic. In the first article (Chapter 4), the emphasis was on the characterisation and semi-quantification of atmospheric organic aerosols collected at Welgegund, while the second paper (Chapter 5) focused on the assessment of polar organic aerosols at a regional background site in South Africa. In the third paper (Chapter 6), atmospheric particulate organic nitrogen was specifically assessed. A summary of the research articles and relevant journal(s) to which they have been submitted to, prepared for, or where they have been published is provided below:

The co-authors of the above-mentioned articles were:

Article 1 (Chapter 4): **Wanda Booyens**, Pieter G. Van Zyl, Johan P. Beukes, Jose Ruiz-Jimenez, Matias Kopperi, Marja-Liisa Riekkola, Miroslav Josipovic, Andrew D. Venter, Kerneels Jaars, Lauri Laakso, Ville Vakkari, Markku Kulmala and Jacobus J. Pienaar. (2015). **Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa.** Published in **Journal of Atmospheric Chemistry**, 72: 43-64, DOI 10.1007/s10874-015-9304-6, a SpringerLink journal. The article is presented as the final published version.

Article 2 (Chapter 5): **Wanda Booyens**, Johan P. Beukes, Pieter G. Van Zyl, Jose Ruiz-Jimenez, Matias Kopperi, Marja-Liisa Riekkola, Miroslav Josipovic, Ville Vakkari, Lauri Laakso. **Assessment of polar organic aerosols at a regional background site in southern Africa.** Prepared for **Journal of Atmospheric Chemistry**, a SpringerLink journal. This article was formatted according to the guidelines for authors of the journal.

Article 3 (Chapter 6): **Wanda Booyens**, Pieter G. Van Zyl, Johan P. Beukes, Jose Ruiz-Jimenez, Matias Kopperi, Marja-Liisa Riekkola, Miroslav Josipovic, Ville Vakkari, Lauri Laakso. **Characteristics of particulate organic nitrogen at a savannah-grassland region in South Africa.**

Prepared for **Journal of Atmospheric Chemistry**, a SpringerLink journal. This article was formatted according to the guidelines for authors of the journal.

Other articles, to which the author contributed as co-author, which were published during the duration of this study, but not included for examination purposes, include:

1. Venter, A.D., Jaars, K., **Booyens, W.**, Beukes, J.P., Van Zyl, P.G., Josipovic, M., Hendriks, J., Vakkari, V., Hellén, H., Hakola, H., and Aaltonen, H., Plume characterization of a typical South African braai. *South African Journal of Chemistry*, 68, pp.181-194. **2015**

Abstract

Atmospheric aerosols or particulate matter (PM) are a complex mixture of solid and liquid particulates suspended in the atmosphere that originate from natural and anthropogenic sources. These species influence climate change and general air quality, while also having other detrimental impacts on the environment (e.g. acidification, eutrophication). These impacts of atmospheric aerosols are determined by their physical and chemical properties. Atmospheric aerosols consist of inorganic and organic chemical species, of which the organic fraction is estimated to contribute between 20 and 90 % of the total PM in the atmosphere. It is therefore important to characterise these organic species in atmospheric aerosols in order to establish the impacts of these species on the environment and human health.

Atmospheric aerosols consist of thousands of organic compounds with various chemical and physical properties. At present, little is known about the actual chemical composition of atmospheric organic compounds, which necessitates the development and employment of new methods to allow for more precise speciation of organic aerosol compounds. One such method is comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS), which is a powerful instrument used for the chemical characterisation of organic compounds in complex matrices. GCxGC-TOFMS has been successfully applied in characterising a wide range of organic compounds present in complex ambient atmospheric samples. Therefore, the aim of this study was to characterise and semi-quantify ambient organic aerosols collected in different size ranges at a regional background site in South Africa using GCxGC-TOFMS, which will be the first time that this technique has been used for analysis of ambient aerosols in South Africa. South Africa has the largest industrialised economy in Africa and is considered to be a significant source of atmospheric pollutants. However, the region is still considered to be understudied with regard to atmospheric measurements, especially relating to the characterisation of ambient atmospheric aerosols.

Aerosol samples were collected at the Welgegend atmospheric monitoring station, which is a comprehensively equipped atmospheric measurement station located 100 km west of Johannesburg.

Welgegund is considered to be a regional background site with no sources in close proximity. It is, however, impacted by major source regions in the north-eastern interior of South Africa. Size-resolved (PM_{10} , $\text{PM}_{2.5-1}$ and $\text{PM}_{10-2.5}$) 24-hour aerosol samples were collected once a week for one year from 12 April 2011 to 4 April 2012. This is the most comprehensive number of size-resolved ambient atmospheric aerosol samples collected in South Africa for the characterisation of organic compounds. The collected samples were analysed using a GCxGC-TOFMS, which detected a large number of peaks (approximately 8 000 compounds). Procedures and rules were applied in order to optimise the number of compounds identified, as well as to increase the reliability of organic compounds characterised. In order to characterise more organic compounds detected using the GCxGC-TOFMS for the samples, less restrictive positive characterisation parameters were applied and the compounds were therefore considered tentatively characterised. The concentrations of the large number of organic compounds that were tentatively characterised were expressed as response factors (RF) in relation to an internal standard, i.e. 1-1'-binaphthyl.

A combined total of 1 056 different organic compounds could be tentatively characterised. The largest number of organic compounds tentatively identified was associated with $\text{PM}_{2.5-1}$ (particles in the size range 1-2.5 μm), while this size fraction also had the highest total number of normalised response factors ($\sum\text{NRF}$). On average, 52 %, of species tentatively identified were oxygenated species, while 26 %, 6 %, 13 % and 3 % of the species tentatively characterised were hydrocarbons, halogenated compounds, N-containing compounds and S-containing compounds, respectively. Alkane and mono-aromatic species were the largest number of hydrocarbons tentatively identified with the highest $\sum\text{NRFs}$. The largest number of oxygenated species tentatively characterised were carboxylic acids and esters, while ether compounds had the highest $\sum\text{NRFs}$. Most of the halogenated compounds tentatively identified were chlorinated species with the highest $\sum\text{NRFs}$ in two size fractions. Iodate species had a significantly higher $\sum\text{NRF}$ in the $\text{PM}_{2.5-1}$ size fraction. The largest number of N-containing species tentatively characterised with the highest $\sum\text{NRFs}$ were amines. A small number of S-containing compounds with low $\sum\text{NRFs}$ were tentatively identified. The major sources of organic compounds measured at Welgegund were considered to be biomass burning and air masses moving over the anthropogenically impacted source regions.

An assessment of polar organic aerosol compounds, i.e. oxygenated species (alcohols, ethers, aldehydes, ketones, carboxylic acids, esters), halogenated compounds (Cl, Br, I, F), as well as nitrogen (N)- and sulphur (S)-containing organic compounds characterised at Welgegund was conducted in order to provide a more detailed picture of organic aerosol composition for southern Africa. The influence of meteorological conditions and major sources impacting air masses measured at Welgegund on polar organic compounds measured was assessed. No distinct seasonal pattern was observed for the total number of polar organic compounds tentatively characterised and their corresponding semi-quantified concentrations (Σ NRFs). There was, however, a period during late winter and early spring with a significantly lower total number of polar organic compounds and corresponding Σ NRFs, while it also seemed that the total numbers of polar organic compounds and the corresponding Σ NRFs for the period from mid-autumn to mid-winter were relatively higher compared to the period from late spring to mid-autumn. The influences of source regions, meteorology and open biomass burning were investigated in order to assess the temporal variability. A relatively lower total number of polar organic compounds and the corresponding Σ NRFs could be attributed to fresher plumes arriving at Welgegund from a source region relatively close to Welgegund, while a relatively higher total number of polar organic compounds and the corresponding Σ NRFs were associated with aged air masses passing over another source region and the regional background. Meteorological parameters indicated that the wet removal of aerosols during the wet season contributed to a lower total number of polar organic compounds and associated Σ NRFs, while increased anticyclonic recirculation and more pronounced inversion layers in winter contributed to a higher total number of polar organic compounds and corresponding Σ NRFs. The large-scale influence of biomass burning on organic aerosol compounds was also indicated by fire pixel counts. The period with significantly lower total number of polar organic compounds and the corresponding Σ NRFs was attributed to fresh biomass burning plumes from wild fires occurring within close proximity of Welgegund, consisting mainly of volatile organic compounds and non-polar hydrocarbons. Multiple linear regression (MLR) was performed in an effort to quantify the influence of each of these factors on the total number of polar organic compounds and their corresponding Σ NRFs, which supported the hypothesis that the temporal variations were related to a combination of the

influence of source regions, meteorology and the occurrence of wild fires within close proximity of Welgegund.

Although atmospheric organic N compounds are considered important within the global N cycle, these species are not that well understood, which can be attributed to the lack of consistency in sampling and measurement techniques, as well as their chemical complexity. Therefore, the characteristics of organic N compounds identified and semi-quantified using GCxGC-TOFMS in aerosol samples collected at Welgegund were assessed. 135 atmospheric organic N compounds were tentatively characterised and semi-quantified, which included amines, nitriles, amides, urea, pyridine derivatives, amino acids, nitro- and nitroso compounds, imines, cyanates and isocyanates, and azo compounds. Nearly half of the semi-quantified concentrations of organic nitrogen compounds was attributed to amines (51 %), while nitriles, pyridine derivatives and amides comprised 20 %, 11 % and 8 %, respectively, of the semi-quantified concentrations. The semi-quantified concentrations of the other organic N functional groups were very low. The temporal variations of amines, nitriles, amides and pyridine derivatives were similar to that observed for all the polar organic compounds, i.e. a period between 12 April 2011 and 12 July 2011 coinciding with the dry season with elevated semi-quantified concentrations of these species. These temporal variations were attributed mainly to meteorological parameters and the influence of local open biomass burning. Anthropogenic sources in the major source regions impacting air masses measured at Welgegund, as well as regional agricultural activities, were considered the major sources of amines. The regional influence of household combustion was considered the main sources of nitriles and amides. Most of the other organic N functional groups were most likely related to the influence of local and regional agricultural activities. This is the first time that atmospheric particulate organic N species were identified and semi-quantified for southern Africa, while, in general, only a few studies have been conducted globally utilising GCxGC-TOFMS to characterise atmospheric organic N.

Keywords: *Agricultural • Air pollution • Amines • Atmospheric aerosols • Biomass burning*

• Characterisation and semi-quantification • Climate change • GCxGC-TOFMS • Organic compounds

• Oxygenated organic compounds • Size-resolved • Welgegend

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List of abbreviations

AMS	Aerosol mass spectrometer
ARL	Air Resources Laboratory
BC	Black carbon
BSTFA	<i>N,O</i> -bis(trimethylsilyl)-trifluoroacetamide
CDNW	Cloud droplet number concentration
EBIC	Eastern Bushveld Igneous Complex
EDS	Energy dispersive spectrometer
EPA	Environmental Protection Agency
GC	Gas chromatography
GCXGC-TOFMS	Two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer
GDAS	Global data assimilation system
HYSPLIT	Hybrid single-particle Lagrangian integrated trajectory
<i>I</i>	Retention indices
IC	Ion chromatography
LWC	Liquid water content
MLR	Multiple-linear regression
MPH	Mpumalanga Highveld
MS	Mass spectrometer
NCEP	National Centre for Environmental Prediction
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NRF	Normalised response factor

o-VOCs	Oxygenated volatile organic compounds
PAH	Polycyclic aromatic hydrocarbons
PM	Particulate matter
RF	Response factor
RH	Relative humidity
RMSE	Root mean square error
S/N	Signal-to-noise
SOA	Secondary organic aerosols
SVOCs	Semi-volatile organic compounds
TIC	Total ion count
TMCS	Trimethylchlorosilane
VOCs	Volatile organic compounds
VT	Vaal Triangle
WBIC	Western Bushveld Igneous Complex

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Chapter 1: Background, motivation and objectives

1.1 Background and motivation

The quality of air and its impact on the environment is an issue of significant public and governmental concern in South Africa. Air pollution is diverse and has serious consequences for human health, plants and animals. Atmospheric pollutants consist of numerous gaseous species and particulate matter (PM), which could also be dissolved in the aqueous phase in the atmosphere. Atmospheric aerosols are solid and/or liquid particles suspended in air and are recognised as important contributors to global climate change, air quality (which relates to aspects such as visibility and human health) and other detrimental impacts on the environment (e.g. acidification and eutrophication) (Gozzi et al. 2016).

Atmospheric aerosols or PM are a complex mixture of solid and liquid particulates emitted from natural and anthropogenic sources. Volcanic eruptions, wind-blown mineral dust, pollen, sea-spray, biogenic emissions and natural occurring wild fires are common natural sources of aerosols, while the most significant anthropogenic sources include fossil fuel combustion and human-induced biomass burning (open biomass burning, as well as household combustion for space heating). PM can be emitted directly into the atmosphere as primary aerosols, while secondary formation of aerosols in the atmosphere through chemical reactions and gas-to-particle conversion are also considered another important source of atmospheric aerosols (Pöschl 2005). PM is classified according to its aerodynamic diameters into ultrafine PM₁ (particles $\leq 1 \mu\text{m}$), fine PM_{2.5-1} (particles between $1 \mu\text{m}$ and $2.5 \mu\text{m}$) and coarse PM_{10-2.5} (particles between $2.5 \mu\text{m}$ and $10 \mu\text{m}$) particles.

The impacts of atmospheric aerosols are determined by their physical (e.g. size, mass, optical density) and chemical properties, while their chemical composition also has an influence on certain physical properties. Lighter coloured particulates, such as sulphate (SO_4^{2-}) species and lightly coloured organic species, reflect incoming solar radiation resulting in a net cooling effect on the atmosphere, while dark particulates, such as black carbon (BC) and dark organic compounds, absorb radiative energy, leading to the warming of the near-surface atmosphere. These properties of PM are also related

to the impacts of these species on human health, which are usually associated with lung and heart diseases, as well as harmful effects on respiratory and cardiovascular systems (Dockery et al. 1993; Wichmann and Peters 2000). PM_{10} aerosols are generally filtered in the nose and throat and do not necessarily cause problems. Smaller particles ($PM_{2.5}$ and smaller) can penetrate through the gas-exchange regions of the lungs and affect other organs (Pope and Burnett 2002).

Atmospheric aerosols consist of inorganic and organic chemical species, of which the organic fraction is estimated to contribute between 20 and 90 % of the total PM in the atmosphere (Jimenez et al. 2009). It is important to chemically characterise these species in order to establish their impacts on climate change and air quality. The current state of knowledge relating to organic aerosols provide valuable information relating to the general chemical composition, oxidation state and reactivity of organic aerosols. However, limited information on the actual chemical character of individual organic compounds of which aerosols are comprised exists (Pöschl 2005), which comprises thousands of organic compounds (Goldstein and Galbally 2007). The chemical composition of atmospheric organic compounds is complex and currently not much information are available for these species (Ruiz-Jimenez et al. 2010). This state of affairs requires the development and employment of new methods with more detailed speciation of organic aerosol compounds of which one such method is comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS).

GCxGC-TOFMS is a powerful instrument used for the chemical characterisation of organic compounds in complex matrices (Lewis et al. 2000; Welthagen et al. 2003). The first to report on the use of GCxGC-TOFMS for atmospheric samples were presented by Lewis et al. (2000) who collected on aerosol samples on filters in an urban area. Since then, GCxGC-TOFMS has been successfully applied in numerous studies characterising an extensive range of organic compounds present in complex ambient atmospheric samples (Welthagen et al. 2003; Kallio et al. 2003; Hamilton et al. 2004; Schnelle-Kreis et al. 2005; Kallio et al. 2006; Laitinen et al. 2010; Arsene et al. 2011; Alam et al. 2013).

Southern Africa is one of the least investigated region in terms ambient atmospheric aerosols and their chemical composition (Laakso et al. 2012), which signifies that chemical characterisation and quantification of atmospheric aerosol species are of particular importance for this region. South Africa

has the largest industrialised economy in Africa, with a large number of anthropogenic activities that include mining, industry and agriculture (Lourens et al. 2011), which is therefore considered a significant source of atmospheric pollutants. Biomass burning is also an important source of atmospheric pollutants in South Africa through endemic open biomass burning (Vakkari et al. 2014; Strydom and Savage 2016), as well as household combustion for space heating and cooking (Venter et al. 2012). Aerosol mass spectrometer measurements (AMS) conducted recently by Tiitta et al. (2014) at Welgegund – a regional background site in South Africa – indicated that a large fraction ($\approx 50\%$) of chemical species identified in aerosols contains organic compounds. Africa is also generally considered one of the largest sources of organic aerosols and black carbon (Kanakidou et al. 2005).

1.2 Objectives

In view of the background and motivation presented above, the general aim of this study was to collect PM samples in different size fractions on filters at a background station in the interior of South Africa, which were analysed using GCxGC-TOFMS in order to identify and semi-quantify organic compounds in the atmosphere. Ambient aerosol filters were collected at the Welgegund measurement site, which is a comprehensively equipped atmospheric monitoring station, impacted by the major source regions in the interior of South Africa and at a relatively clean region in the south-western to northern sector. Part of this study also focused specifically on organic nitrogen species, which are considered to be important species in the atmosphere, especially with regard to the global N cycle, but are understudied due to their chemical complexity, i.e. large numbers of different organic N compounds (Cape et al. 2011). The results reported in this thesis were the first organic compounds characterised and semi-quantified using GCxGC-TOFMS for ambient atmospheric aerosol samples collected in South Africa, which were also the most comprehensive size-resolved identification of organic species in South African atmospheric PM.

The specific objectives of this study were to:

- I. collect ambient aerosols in the PM₁, PM_{2.5-1} and PM_{10-2.5} size fractions on filters for at least one year at the Welgegund measurement station;
- II. extract the collected aerosols from filters with a dynamic ultrasonic-assisted extraction approach;
- III. perform analysis of the extracted samples using a GCxGC-TOFMS;
- IV. characterise and semi-quantify organic compounds in atmospheric samples in the different size ranges;
- V. conduct an assessment of temporal variations of organic compounds characterised and semi-quantified, as well as determine possible sources of these species; and
- VI. specifically characterise and semi-quantify organic nitrogen compounds.

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Chapter 2: Literature survey

2.1 Air pollution

The earth's atmosphere is a complex and dynamic natural gaseous system that is essential for supporting life on the planet (Hamid et al. 2009). The atmosphere consists of different layers based on temperature and pressure fluctuations with increasing altitude. The troposphere is the primary layer wherein chemical species and reactions occur, as well as where local, regional and global weather manifestations are predominant. The stratosphere is the second layer of the atmosphere, just above the troposphere. Ozone heats the stratosphere; the temperature rises upwards causing little convection and mixing making stable layers of air. Due to these stable layers, particles that get into the stratosphere can stay there for months or years (UCAR 2011).

The impacts associated with air pollution include influences on climate change and contributions to poor air quality with the latter having detrimental effects on human health and other environmental problems such as acidification and eutrophication. Air pollutants comprise gaseous and aerosol species emitted from numerous natural and anthropogenic sources. The characterisation and quantification of these atmospheric pollutants are important and the emphasis of many research activities. Typical gaseous pollutants in the atmosphere include volatile organic compounds (VOCs), methane (CH_4), non-methane hydrocarbons, halogenated species, nitrogen oxides (NO_x), nitrous oxide (N_2O), sulphur dioxide (SO_2), ozone (O_3), carbon monoxide (CO) and carbon dioxide (CO_2) (Graedel and Crutzen 1997). Atmospheric aerosols or particulate matter (PM) are suspensions of solid and/or liquid particles in the atmosphere and comprise a large number of chemical species.

2.2 Atmospheric aerosols

Atmospheric aerosols play an important role in the chemistry of the atmosphere. These species are observed in the air as clouds, smoke, haze and dust. Atmospheric aerosols differ in physical and

chemical characteristics, which include differences in size, chemical composition, radiative properties and atmospheric lifetime. Aerosol particle size distribution is typically divided into three modes, i.e. Aitken, accumulation and coarse mode, as presented in Fig. 2.1 The size and chemical composition of particulates change in the atmosphere as these species interact with other particles, and also chemically and physically transform (Alfarra 2004; Seinfeld and Pandis 1998; 2006).

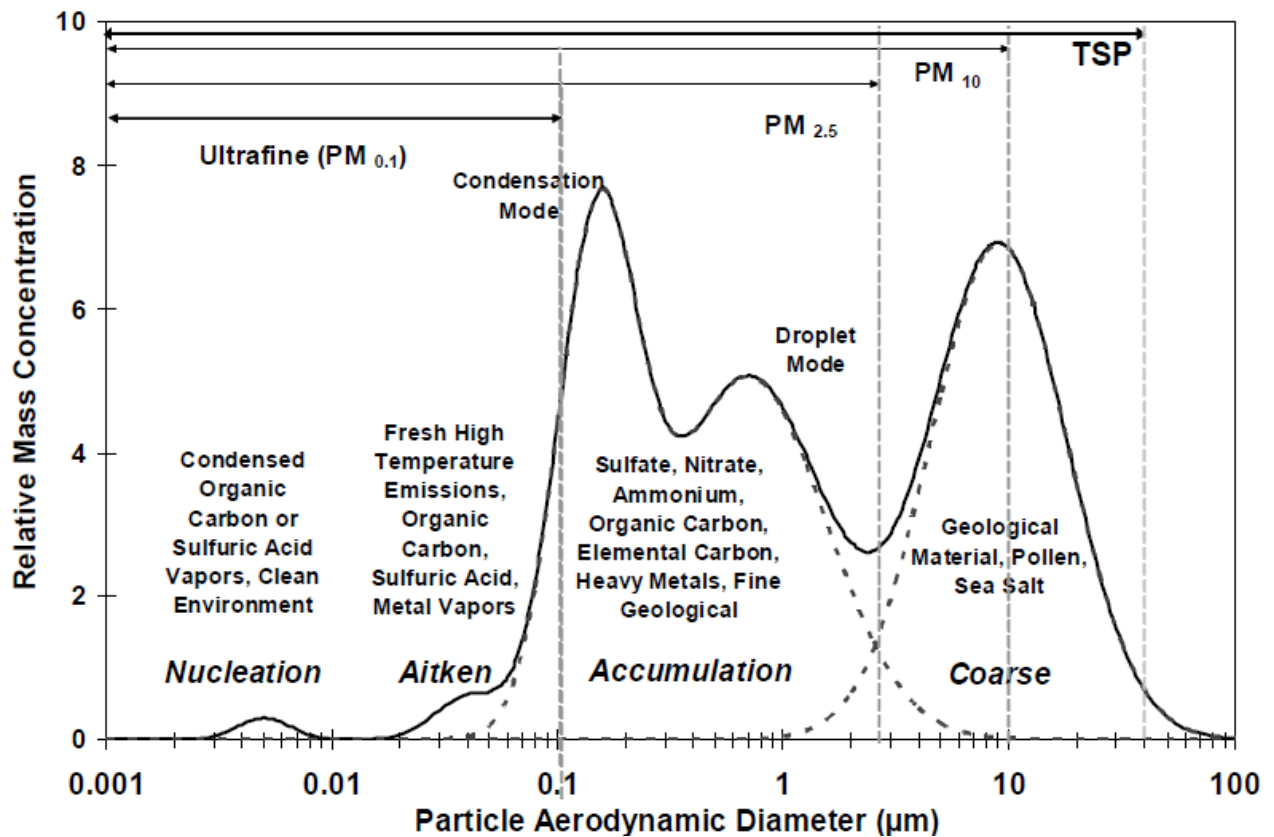


Figure 2.1: Typical atmospheric particle size distribution and the typical chemical composition in the three different modes, PM – Particulate matter, TSP – Total suspended particulate (Watson et al. 2010, with permission of Dr. J.G. Watson)

The Aitken mode includes particulates with diameters ranging between 0.01 μm and 0.1 μm. Aitken mode particles are generally produced by the condensation of hot vapour during combustion processes or are formed as secondary particles through gas-to-particle conversion. These particles have short atmospheric lifetimes and typically coagulate into accumulation mode sized particles. Accumulation mode particulates have diameters ranging between 0.1 and 1.0 μm. After these particles

are formed by the coagulation of Aitken mode particles, these particulates grow through the condensation of vapours onto existing particles. These particles have longer atmospheric lifetimes than Aitken mode particles, and are therefore removed less efficiently. Particulates in the coarse mode have diameters larger than $1.0\mu\text{m}$. These particles have large sedimentation velocities and short lifetimes. In addition, PM is generally classified into ultrafine $\text{PM}_{0.1}$ (particles $\leq 0.1\mu\text{m}$) and PM_1 (particles $\leq 1\mu\text{m}$), fine $\text{PM}_{2.5}$ (particles $\leq 2.5\mu\text{m}$) and coarse PM_{10} (particles $\leq 10\mu\text{m}$) particles (Bathmanabhan et al. 2010; Jiang et al. 2018; Kodzius et al. 2018).

The particle size of atmospheric aerosols relates to the following important aspects associated with air pollution: transport, distribution of chemical species, the effects on atmospheric reactions and physiological properties (Reeve 2002).

- Transport – The atmospheric lifetime of particles are dependent on their size, i.e. the greater the size, the more rapidly deposition from the atmosphere occurs. Particles with a diameter smaller than $0.1\mu\text{m}$ are capable of permanent suspension, although, as indicated above, these particulates coagulate into larger particles.
- Distribution of chemical species – PM from a specific industrial process often occurs within a narrow size range. Fractionation of the dust sample and particle size measurements will determine the pollution control which should be employed.
- Effects on atmospheric reactions – Many chemical reactions occur on the surface of the particles. The surface area per unit mass decreases with an increase in particle size.
- Physiological properties – Smaller particles have a greater possibility of entering the gas exchange region of the lungs, which increases their physiological effects. Particles smaller than $5\mu\text{m}$ are called the ‘respirable’ dust. The ‘total inhalable dust’ is the larger fraction entering the nose and mouth.

2.2.1 Sources and deposition

Atmospheric aerosols are primarily emitted into the atmosphere from various natural and anthropogenic sources, while secondary aerosols can also form in the atmosphere through chemical

reactions and gas-to-particle conversions (Pöschl 2005). Typical natural sources include volcanic eruptions, wind-blown dust, pollen, maritime, biogenic emissions and natural wild fires, while the most important anthropogenic sources are fossil fuel combustion and biomass burning. Biomass burning refers to human-induced wild fires, as well as household combustion for cooking and heating. Ultrafine and fine particles are usually associated with high-temperature combustion processes or are formed as secondary particles in the atmosphere (Salma et al. 2001), while coarse particles in the atmosphere are mostly dust emitted through the crushing, grinding and abrasion of surfaces (Tasic et al. 2006).

Atmospheric aerosols undergo various chemical and physical transformations, which lead to changes in composition, structure and particle size before being deposited from the atmosphere. Aerosols are removed from the atmosphere through wet and dry deposition as a function of their size and chemical characteristics. Approximately 80 to 90 % of aerosols are removed by wet deposition (Prospero 1981), which refers to the removal of aerosols through precipitation. Dry deposition refers to the direct uptake at the surface (without precipitation) and occurs through convective transport, diffusion and adhesion to the surface of the earth (Pöschl 2005; Engelbrecht 2009). Dry deposition is less significant on a global scale (Walcek, 2003).

2.2.2 Impacts

Atmospheric PM has impacts on climate change, as well as on general air quality, which has an influence on the environment and human health. The impacts of these species are determined by their physical and chemical properties. The chemical composition of aerosols also determines certain physical properties of aerosols. SO_4^{2-} species and certain organic species, for instance, are lightly coloured particles that reflect incoming solar radiation, which has a net cooling effect on the atmosphere. In contrast, dark particles, such as black carbon (BC) and certain organic species, absorb radiative energy, leading to the warming of the atmosphere. The impact of atmospheric aerosols on human health is also influenced by their physical and chemical properties.

2.2.3 *Climate*

Atmospheric aerosols play an important role in the earth's climate, as well as radiative balance through direct and indirect radiative effects (Levin et al. 1996; IPCC, 2001; Ramanathan et al. 2001). In Fig. 2.2, the various radiative mechanisms associated with aerosols and aerosol-modified clouds are presented. Direct effects include the scattering and absorption of solar radiation by atmospheric aerosols, which are dependent on their chemical composition or refractive index (Adams et al. 2001). A net cooling effect occurs when a solar radiation is scattered back, while a net warming effect occurs when solar radiation is absorbed. Indirect effects relate to the influence of aerosols on the cloud albedo. Aerosols act as nuclei for fog and cloud formation, which can also scatter and absorb solar radiation. Aerosols can therefore change the cloud albedo, the droplet concentration number, the lifetime of clouds and the frequency of the precipitation. According to the latest Intergovernmental Panel on Climate Change (IPCC) report (IPCC 2014), there are still relatively large uncertainties associated with the impacts of aerosols on radiative forcing. However, since the latest IPCC report in 2014, the level of scientific understanding relating to the impacts of aerosols has increased through a number of international initiatives such as the European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) (Kulmala et al. 2009) project.

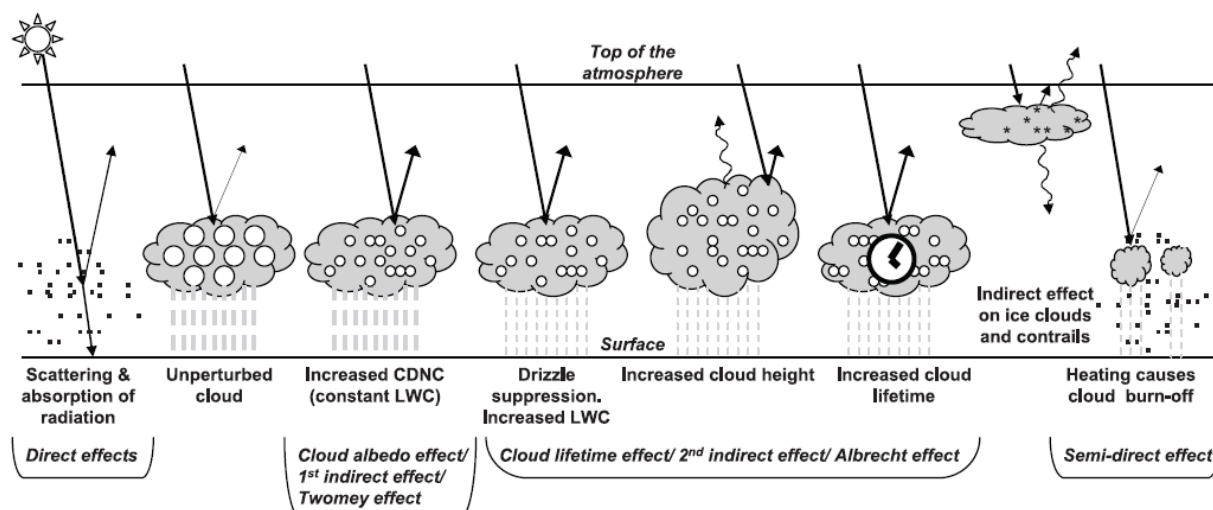


Figure 2.2: Schematic diagram showing the various radiative mechanisms associated with aerosols and aerosol-modified clouds. The black dots represent aerosol particles; the open circles cloud droplets and their relative size. Straight lines represent the incident and reflected solar radiation, and wavy lines represent terrestrial radiation. LWC refers to liquid water content and CDNC to cloud droplet number concentration (IPCC 2007, with permission of IPCC)

2.2.4 Human health

Epidemiological studies have proved that there are many health problems associated with atmospheric aerosols. Health problems related to these species are usually associated with lung and heart diseases, as well as damaging effects on respiratory and cardiovascular systems (Dockery et al. 1993; Samet et al. 2000; Wichmann and Peters 2000). Particles are retained within the respiratory system according to their size, i.e. larger particles are deposited in the upper respiratory tract, while smaller particles penetrate deeper into the lungs where they stay for longer periods (Heil 1998). Coarse particles (PM_{10}) are generally filtered in the nose and throat and do not necessarily cause problems. Smaller particles ($PM_{2.5}$ and smaller) can penetrate through the gas-exchange sections of the lungs and affect other organs (Pope and Burnett 2002). Particles that may contain polycyclic aromatic hydrocarbons (PAHs) can be carcinogenic in animals and mutagenic in *in-vitro* bioassays (Seinfeld and Pandis 2006). Very young and elderly people are especially at risk groups. PM_{10} and $PM_{2.5}$ are considered criteria pollutants with ambient concentrations and emissions thereof being regulated for

many years in most countries, especially in first-world countries in Europe and Northern America. In South Africa, PM₁₀ has been regulated in the past, with PM_{2.5} being added as a criteria pollutant to the list of National Air Quality Standards in 2015 (Final Air Quality Chapter 2018).

2.2.5 Composition

Atmospheric aerosols consist of a number of inorganic and organic chemical species. The main components of atmospheric aerosols are usually water, sulphates, nitrates, ammonium, BC, organic carbon (OC), sea salt, mineral dust, crustal elements and trace metals (Alade 2010). Atmospheric aerosols usually consist of variable amounts of main constituents and hundreds of minor and trace constituents (Pöschl 2005). The composition of aerosols depends on the particle sources and atmospheric ageing processes involved (coagulation, gas-particle partitioning, chemical reactions). It is important to determine the chemical composition of atmospheric aerosols in order to identify their sources and to address issues such as human health and global climate (Alfarra 2004). The accurate determination of the chemical composition of aerosols is a challenging analytical task. The main reasons why the identification and measurement of atmospheric aerosols are more complicated than for gaseous species are: (1) not all the aerosols are directly emitted into the atmosphere, since some are formed through secondary gas-phase processes, (2) aerosol sizes and composition properties vary across different locations, and (3) aerosols mix over time to form internally and externally mixed aerosols (Alfarra 2004). The potential re-equilibration of gas-particle partitioning during sampling also complicates this analysis due to the strong effect of temperature on the partitioning (Pankow and Bidleman 1991).

2.3 Atmospheric organic aerosols

Atmospheric organic aerosols contribute 20 to 90 % of the total particulate matter in the atmosphere (Jimenez et al. 2009). The composition and concentrations of atmospheric organic aerosols depend on the primary emissions and the photochemical conditions in the atmosphere. Primary emissions of organic aerosols include natural and anthropogenic sources such as biomass burning, fossil

fuel combustions and biological materials. Secondary organic aerosols (SOA) are produced by chemical reactions of gas phase compounds, through different pathways, including (Ervens et al. 2011):

- new particle formation, i.e. gas-phase reactions of volatile organic compounds (VOCs) resulting in the formation of semi-volatile organic compounds (SVOCs) from which new aerosol particles can be formed;
- gas-particle partitioning: formation of SVOCs by gas-phase reactions and absorption by a pre-existing aerosol particle; and
- heterogeneous multiphase reactions: chemical reaction between low-volatility or non-VOCs with VOCs and SVOCs at the surface or in the bulk of aerosol or cloud particles.

The principal parameters governing SOA formation include relative humidity, temperature, as well as the concentrations of organic and inorganic nucleating and condensing vapours, which, in turn, depend on atmospheric transport, as well as local sources and sinks such as photochemistry and pre-existing aerosol or cloud particles (Odum et al. 1996; Hoffmann et al. 1997; Kamens et al. 1999; Kamens and Jaoui 2001). On a global scale, SOA formation is dominated by the oxidation of biogenic VOCs (Schulze et al. 2017).

Current measurements of organic compounds provide valuable information relating to the general chemical composition, oxidation state and reactivity of organic aerosols. However, these methods provide limited information on the actual character of individual organic compounds (Pöschl 2005). Atmospheric aerosols consist of thousands of organic compounds with various differences in chemical and physical properties (Goldstein and Galbally 2007). Different functional groups characterised in previous studies include hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, esters and nitrogen-containing organic compounds (Alam et al. 2013), which include within these different functional groups various classes of compounds e.g. PAHs, oxygenated-PAHs, substituted aromatics alkan-2-ones, n-alkanoic acid methyl esters, acetic esters, n-alkanoic acid amides, nitriles, linear alkylbenzenes and 2-alkyl-toluenes, hopanes and PAHs (Schnelle-Kreis et al. 2005). The present knowledge on the chemical composition of atmospheric organic compounds is incomplete (Ruiz-Jimenez et al. 2010). Some of the reasons for the limited atmospheric monitoring, can also be attributed

to a lack of resources relating to funding, equipment and human capacity (Forbes and Rohwer 2008), which necessitates the development and employment of new methods to identify ambient organic aerosol species.

2.4 Analysis of atmospheric organic aerosols

Atmospheric organic aerosols are a complex mixture of chemical compounds, which consist of thousands of compounds with different thermodynamic and chemical properties (Saxena and Hildemann 1996). Measurements of atmospheric organic aerosols can occur through on-line or off-line measurement techniques.

2.4.1 On-line analysis

Online analysis entails the real-time measurements of atmospheric organic aerosols. Aerosol mass spectrometers (AMS) have been developed in recent times and deployed in numerous field campaigns in order to determine the chemical composition of aerosols (Jayne et al. 2000; Zhang et al. 2011). The components of a typical AMS include an aerodynamic lens, differential pump, aerodynamic sizer, thermal vaporiser, electron impact ioniser and a quadrupole mass spectrometer (Alfarra 2004). The sample and the carrier gas are typically heated to a temperature of 550 to 600 °C in a tungsten vaporiser. Material that is non-refractory flash-vaporises and the emerging vapour is electron-impact-ionised for analysis. Quantitative information on the chemical composition of the submicron fraction of aerosol particles has been studied using AMS in a number of studies (Jayne et al. 2000; Allan et al. 2003; Jimenez et al. 2003; Alfarra et al. 2004; Drewnick et al. 2004a; Drewnick et al. 2004b]. AMS instruments are generally expensive and require specialist field operators. Photo Ionization Detection (PID) instruments are used for the determination of ionized chemicals present in the air using a UV source through the ionization potential of each organic compound and are not used for the separation of compounds (KD Analytical Consulting 2016). Light detection and ranging (Lidar) sensors use the optical wavelength spectral range to check for aerosols and trace gases and the concentration thereof. The connections between electromagnetic radiation are strong (Collis and Russell 1976). Field portable

gas chromatography combined with a mass spectrometry (GC-MS) is used for the rapid identification of analytes as well as the time when these chemicals appear with a high certainty (Eckenrode 2001).

2.4.2 Off-line analysis

Off-line analysis refers to the collection of aerosol samples on filters with instruments such as cascade impactors, which are subsequently analysed in order to chemically characterise and quantify atmospheric organic compounds. These measurement techniques are more commonly applied to determine the chemical composition of aerosols, since they are less expensive, logistically more feasible and do not require specialised field operation. Typical analytical instruments utilised for the analysis of organic aerosol samples collected on filters include scanning electron microscopy (SEM), high performance liquid chromatography (HPLC), ion chromatography (IC) and gas chromatography (GC) (Alfarra 2004). SEM is a surface analytical technique, which provides valuable information on the morphology and physical characteristics of particulates. An energy dispersive spectrometer (EDS) coupled to a SEM can be utilised to chemically characterise samples. However, SEM-EDS cannot be used to quantify concentrations of chemical species and is also not ideal to chemically characterise organic compounds. HPLC and IC have been used in numerous studies to identify and quantify water-soluble organic particulates (Karthikeyan and Balasubramanian 2006; Zhang 2010), as well as to determine water-soluble organic acids in rain water (Zhang 2010; Hodgkins et al. 2011). HPLC and IC separate different mixtures of compounds and ions, respectively and the selectivity and sensitivity depends on the analysis type (Pelia 2012). For the separation of inorganic counter ions and ion exchange separation with a suppressed conductivity detection will be best, for the separation of organic counter ions and impurities, an IC system with suppressed conductivity will be best and for the simultaneous analysis of an active ingredient and its counter ion, a mixed-mode column on a HPLC will be best (Pelia 2012). Disadvantages for HPLC and IC is that in HPLC different polarities can exit at the same time causing coelution and IC can have long run times. In GC analysis, samples are vaporised and carried with a gas, i.e. mobile phase through a heated column containing the stationary phase. The stationary phase can either be a liquid or a solid phase in the column. As the gas carries the vaporised sample through the column, the time spent in the stationary phase differs for all the chemical components of

the sample i.e. different retention times, which consequently results in the separation of organic compounds. Each separated component is then detected with a detector (Stashenko and Martínez 2014). GC coupled with a mass spectrometer (MS) detector (GC-MS) analysis has been used in numerous studies for the characterisation and quantification of atmospheric organic aerosols (Sheesley et al. 2003; Morisson et al. 2006; Alves 2008; Forbes et al. 2012; Naudé and Rohwer 2012). Although the GC-MS method is valuable, the entire sample need to be exposed to all dimensions of the separation as well as to increase the resolution. The GCxGC increase resolution for complex samples in all dimensions.

2.4.3 GCxGC-TOFMS

Comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS) is a powerful instrument used for the chemical characterisation of organic compounds in complex matrices (Lewis et al. 2000; Welthagen et al. 2003). This technique subjects samples to a two-dimensional separation, wherein two gas chromatography columns with different selectivity are used and two chromatographic mechanisms are applied to separate organic compounds. In most instances, the first column contains a non-polar stationary phase and the second column a polar stationary phase. The first column separation is usually based on volatility, whereas compounds in the second column are separated according to their polarity. The two columns are connected normally before the thermal modulator, so that modulation occurs before the second column. The modulator cryogenically traps and compresses the effluent from the primary column and re-injects narrow bands of isolated compounds into the secondary column for rapid separation (Dimandja et al. 2003; Focant et al. 2003, 2004; Semard et al. 2009). Due to the different separation mechanisms in the two columns, compounds that co-elute from the first column are likely to separate in the second column. Compared to one-dimensional GC, two-dimensional GC has a much higher peak capacity, because the entire plane of a GCxGC chromatogram is used for separation. Other advantages of the GCxGC technique include enhanced sensitivity due to analyte refocusing, more reliable identification due to two retention times, and well-ordered bands of compound groups (Phillips and Xu 1995; Schomburg 1995; Beens et al. 1998; Phillips and Beens 1999). In Fig. 2.3, a schematic diagram of a typical GCxGC-TOFMS analytical setup is presented.

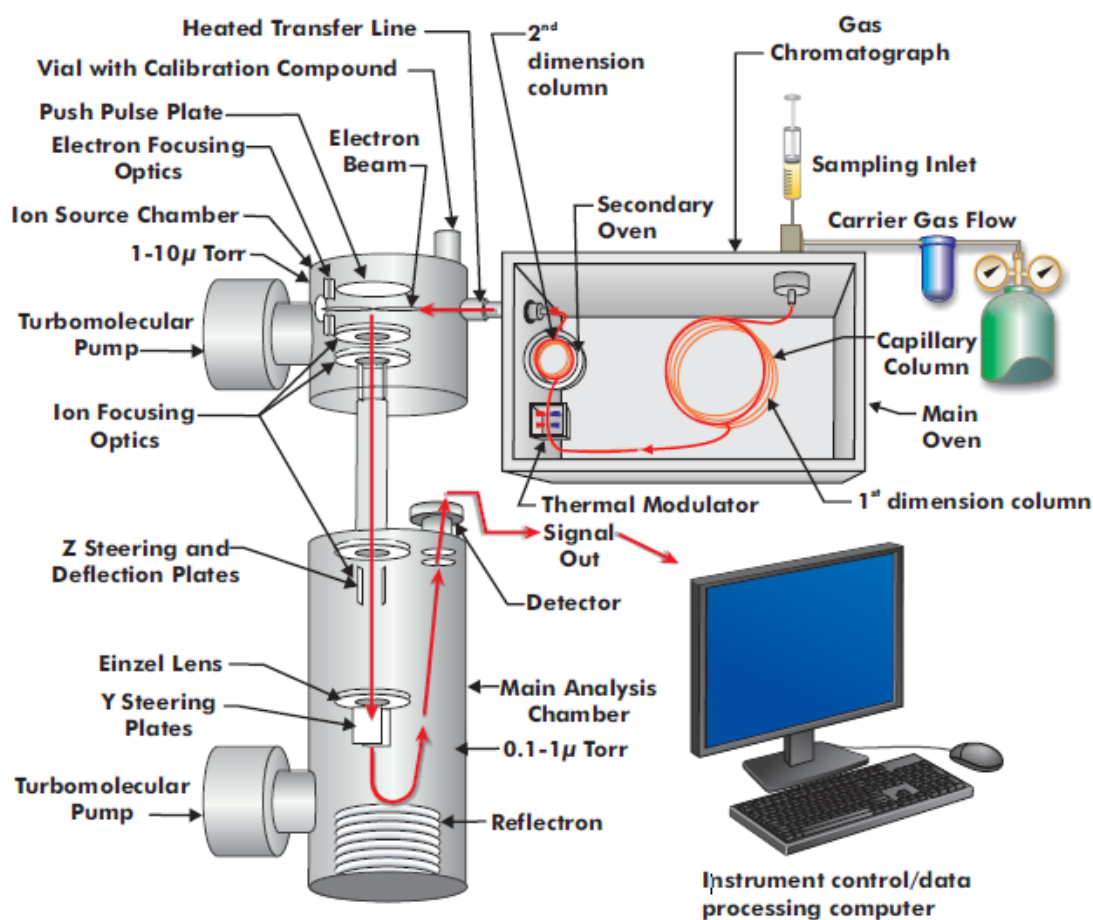


Figure 2.3: Schematic diagram of a GCxGC-TOFMS (LECO 2014, with permission of LECO Corporation)

The modulator is the most important component in GCxGC-TOFMS. The cryogenic four-jet nitrogen modulator uses two liquid nitrogen-cooled jets for trapping and two hot gas jets for remobilisation (Ledford and Billesbach 2000). The time between each pulse is called the modulation time, which is very fast (typically between 2 and 6 seconds).

The modulation period is generally between 2 – 5 ms, and peak widths in GCxGC are very narrow (50 – 200 ms) which necessitates a very fast detector. Time of Flight mass spectrometry, which can provide acquisition rates up to 500 spectra/s is the ideal detector providing fast acquisition and combining the improved analytical resolution of GCxGC with mass spectral information. The

fragmentation patterns obtained from mass spectral data can be used to identify and classify compounds separated by GCxGC.

GCxGC-TOFMS has proved to be useful in the identification of components in complex matrices such as in tobacco smoke where 150 compounds could be identified (Wu et al. 2003). Lewis et al. (2000) were the first to report the use of GCxGC-TOFMS for atmospheric samples collected on filters in urban air. Since then, GCxGC-TOFMS has been successfully applied in characterising a wide range of organic compounds present in complex ambient atmospheric samples (Welthagen et al. 2003; Kallio et al. 2003; Hamilton et al. 2004; Schnelle-Kreis et al. 2005; Kallio et al. 2006; Laitinen et al. 2010; Arsene et al. 2011; Alam et al. 2013). In South Africa, GCxGC-TOFMS was also used for the identification of semi-volatile organic compounds (SVOCs). A study on SVOCs in South Africa from Forbes et al. 2013, showed that the TD-GCxGC-MS is an appropriate analytical method for the identification of SVOCs.

Disadvantages of GCxGC, include the sensitivity enhancement in the separations compared to 1D GC (Górecki and Mostafa 2013), the trapping of volatile compounds at high temperatures by the modulator, as well as mobilizing of these trapped analytes (Górecki et al. 2014). Some disadvantages for TOFMS include the decrease in sensitivity, with an increase of the spectral production rate as well as the fact that single quadrupole MS devices were used for all MS spectral databases, resulting in low-quality results (Shimadzu 2018).

2.5 Synoptic-scale meteorology over southern Africa

Southern Africa, with its urban and industrial areas, is recognised as a country contributing to the hemispherical production and transportation of aerosols in the southern hemisphere (Sivertsen et al. 1995; Piketh et al. 1999). Southern Africa is situated in the sub-tropical high-pressure belt with the major atmospheric circulation pattern over this region being anticyclonic (Garstang et al. 1996). Three high pressure cells dominate the meteorological conditions in South Africa, i.e. the South Atlantic high-pressure cell of the west coast, the South Indian high-pressure cell of the east coast and the continental high-pressure cell over the interior as presented in Fig. 2.4 (Van Heerden and Hurry 1987). In the

summer, the tropical easterly flow is predominant over southern Africa due to the weakening of the anti-cyclonic belt that shifts southwards as indicated in Fig. 2.4 (a). During this time of the year, the pressure is low over the interior with unstable metrological conditions occurring, which increase the vertical motion and dispersion of pollutants in the atmosphere (Tyson et al. 1996). In the winter, more stable conditions with low wind speeds occur for most parts over southern Africa due to the prominence of the continental high-pressure cell over the interior (Fig. 2.4 (b)). More pronounced inversion layers are formed that prevent vertical atmospheric mixing. Together with weaker removal processes during winter, pollutants are effectively trapped between these layers. Pollutants emitted near the surface of the earth build up in the boundary layer, which results in increased concentrations of emitted pollutants (Cosijn and Tyson 1996; Garstang et al. 1996; Tyson and Preston-Whyte 2000). The first elevated inversion layer is located at an altitude of ~ 3 km over the plateau during winter, with the first elevated layer increasing to between 4 and 5 km over the plateau during summer.

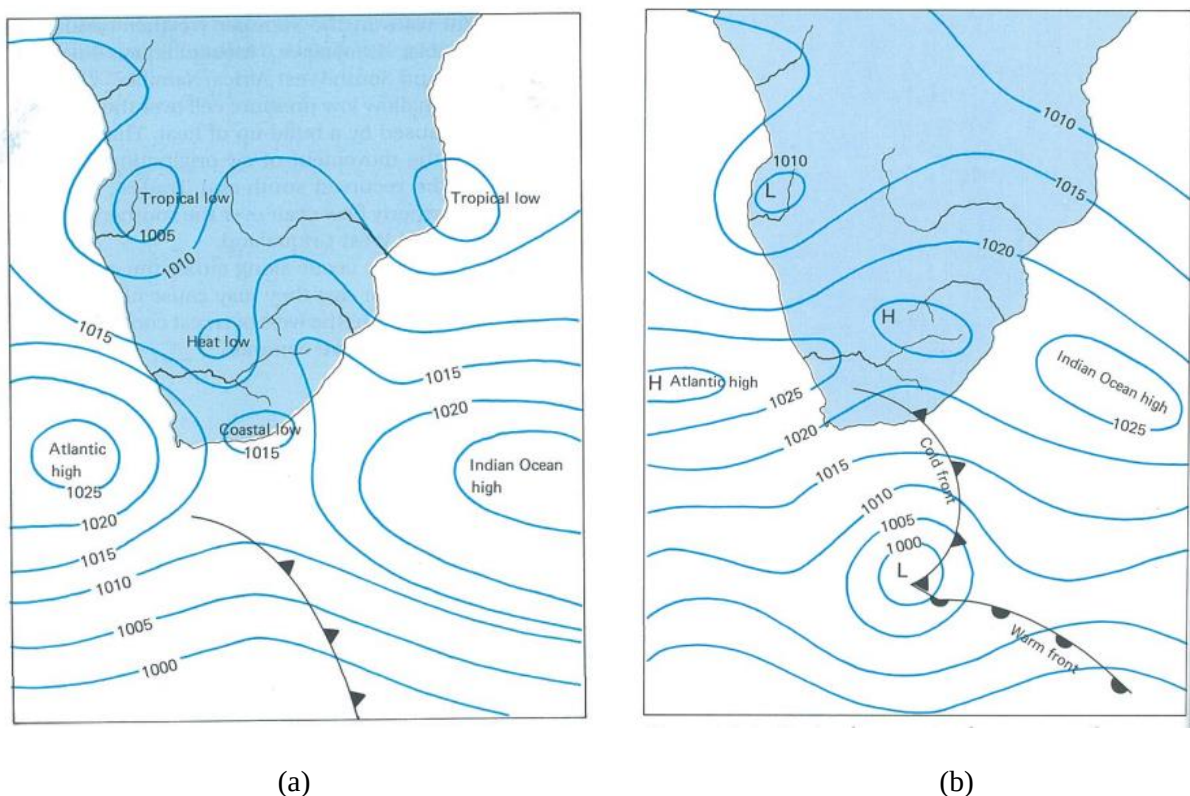


Figure 2.4: The seasonal circulation of air masses over southern Africa during (a) mid-summer and (b) mid-winter (Van Heerden and Hurry 1987, with permission of Van Schaik Publishers)

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Chapter 3: Methodology

3.1 *Measurement location*

3.1.1 *Site description*

The Welgegend monitoring station (Fig. 3.1) is situated approximately 100 km west from Johannesburg on the property of a commercial farmer (latitude 26°34'10"S, longitude 26°56'21"E, 1480 m AMSL (above mean sea level)). Welgegend is located on a farm where the immediate area is grazed by cattle and sheep, with crop fields (mostly maize and to a lesser degree sunflower) covering the areas that are not grazed. In Fig. 3.2, the location of the Welgegend station is indicated. Welgegend is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity. However, it is impacted by plumes from major anthropogenic source regions in the interior of South Africa, which include the western and eastern Bushveld Igneous Complex, the Johannesburg-Pretoria metropolitan conurbation, the Vaal Triangle, the Mpumalanga Highveld and also a region of anti-cyclonic recirculation of air mass over the interior of South Africa, as indicated in Fig. 3.2. Major sources of atmospheric pollutants in the western and eastern Bushveld Igneous Complex include pyrometallurgical smelters and mining activities – 11 pyrometallurgical smelters are located in the western Bushveld Igneous Complex mainly associated with the production of Cr, Fe, V and Ni. The Johannesburg-Pretoria metropolitan conurbation has a population of more than 10 million people (Johannesburg Population 2017). The Vaal Triangle region contains many petrochemical-related industries, while two coal-fired power stations and large pyrometallurgical smelters are also located in this region. The Mpumalanga Highveld region holds 11 coal-fired power stations, several pyrometallurgical smelters, a very large petrochemical plant and many coal mines (Venter et al. 2017). In addition to these source regions, Welgegend is also impacted by a relatively clean region in the north-west to south sector of Welgegend with no large point sources. The impacts of regional wild fires occurring mainly in the dry winters and spring are also measured at Welgegend

(Vakkari et al. 2014). A detailed description of the Welgegund measurement station was presented by Beukes et al. (2015).



Figure 3.1: The Welgegund monitoring station (www.welgegund.org)

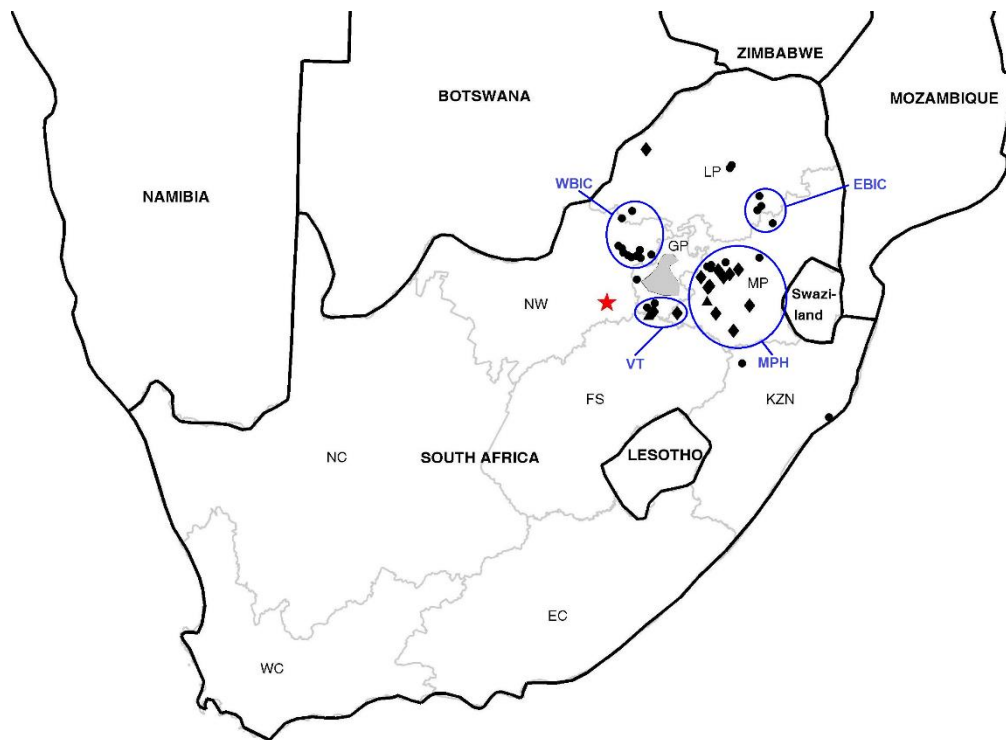


Figure 3.2: Map of South Africa indicating the Welgegund measurement site (red star), as well as source regions and large point sources in the north-eastern interior. The shaded grey polygon indicates the Johannesburg-Pretoria conurbation. EBIC – Eastern Bushveld Igneous Complex, WBIC – Western Bushveld Igneous Complex, VT – Vaal Triangle and MPH – Mpumalanga Highveld.

3.1.2 Geographical region

The Welgegund measurement site is geographically located within the South African Highveld, which accounts for approximately 30 % of the surface area of South Africa (Beukes et al. 2015). The Welgegund measurement station is located in the Vaal-Vet Sandy Grassland vegetation type that covers substantial parts of the North West and Free State Provinces of South Africa (provincial boundaries indicated in Fig. 3.2). Only 0.3 % of the Vaal-Vet Sandy Grassland is currently statutorily conserved, while the rest is mostly used for grazing and crop production (Jaars 2016). The main grass species in the immediate proximity of the measurement station are *Hyparrhenia hirta* and *Sporobolus pyramidalis*, while *Acacia sieberiana*, *Rhus rehmanniana*, *Walafrida densiflora*, *Spermacoce natalensis*, *Kohautia cynanchica* and *Phyllanthus glaucophyllus* are the main non-grassy plant species (Bredenkamp et al. 1989).

3.1.3 Regional meteorology

As indicated in section 2.5, the atmospheric circulation path over the South African Highveld is dominated by anti-cyclonic circulation, which is especially pronounced during winter (June to August). During the winter and early spring months, multiple inversion layers form on a regular basis at various altitudes, which significantly reduce the vertical mixing of atmospheric pollutant species and lead to significant increases in the concentrations of these species (Hobbs et al. 2003; Vakkari et al. 2014). The South African Highveld is also characterised by distinct wet and dry seasons, with almost all the rain events occurring from middle October to April, with nearly no precipitation occurring during May to middle October. This distinct precipitation cycle strongly affects the levels of atmospheric pollutant species. During the wet season, enhanced wet scavenging of pollutants occurs, while pollution levels increase during the dry season due to the occurrence of large-scale biomass burning (wild fires) (Vakkari et al. 2014). The mean annual rainfall between 1998 and 2014 was 540 mm, with a standard deviation of 112 mm (Räsänen et al. 2017). The average temperature at Welgegund is 18 °C, ranging between -3 and 28 °C in the winter, and 10 and 33 °C in summer.

3.2 Measurement methods

3.2.1 Sampling

24-hour samples were collected once a week for one year from 12 April 2011 until 4 April 2012. Samples were collected with a Dekati PM₁₀ cascade impactor at a flow rate of 30 L/min (Fig. 3.3). This impactor allows the collection of PM in different size ranges. Ambient aerosols in the size fractions PM₁ (particles smaller than 1 µm), PM_{2.5-1} (particles in the size range 1-2.5 µm) and PM_{10-2.5} (particles in the size range 2.5-10 µm) were collected. The PM_{2.5-1} and PM_{10-2.5} size fractions were collected on 25 mm quartz filters (Whatman), while a 47 mm quartz filter was used as a back filter in order to collect PM₁ particulates. After sampling, the filters were placed in petri dishes that were sealed off with parafilm, which were stored in a freezer until they were couriered to Finland for analysis. During the transport of the filters they were kept at temperatures below 25 °C in an air tight container. In Finland they were kept in freezer at -18 °C until analysis. In total, 52 samples were collected for each of the

three size fractions, which is the most comprehensive number of size-resolved atmospheric samples collected in South Africa for the characterisation of organic compounds. This sampling method has some artifacts including the volatilization of semi-volatile organic compounds (SVOCs) on the quartz filters, the overload of particles on the collection plates can cause bounce and blowoff of particles (Lamminen 2009), and gas-particle partitioning.



Figure 3.3: Dekati PM₁₀ three-stage cascade impactor (www.dekati.com, with permission of Dekati Ltd)

3.2.2 Analysis

Filter samples were extracted by using a dynamic ultrasonic-assisted extraction approach with a 1:1 v/v mixture of methanol and acetone and was completed within 40 min at a flow rate of 1 ml/min. The average volume of solvent used was 41.5ml per sample. The extraction time was considered to be adequate, based on previous studies by Ruiz-Jimenez et al. (2011a) and Ruiz-Jimenez et al. (2011b), where 20 and 30min extraction times were applied. This polar solvent mixture was validated by Ruiz-Jimenez et al. (2011a) for the extraction of acids, aldehydes, amine and polyols. Although this method was not validated for non-polar species, such as hydrocarbons, it was also used by Ruiz-Jimenez et al. (2011b) for the simultaneous extraction of polar and non-polar compounds. Three to four drops of toluene were added, after which the extracts were completely dried with a gentle stream of nitrogen and then reconstituted with 5 ml methanol. After extraction, the samples were analysed immediately or

stored in a freezer until used (Ruiz-Jimenez et al. 2011b). Three different aliquots (1 ml) from each sample were further pre-concentrated before analysis using a gentle nitrogen stream. In the first aliquot 5 ng 1-1'binaphthyl, used as the internal standard (Sigma-Aldrich) was added and analysed for volatile and semi-volatile compounds. Silylation with or without catalyser was used for the transformation of non-volatile hydroxyl-compounds into volatile species before GCxGC-TOFMS analysis. Hydroxyl-compounds with low molecular weight were directly analysed after ultrasound-assisted derivatisation at 35 °C and sonicated for 45 min using 25 µl *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) (Sigma-Aldrich) as reagent. The same procedure, but adding 25 µl pyridine as catalyser, was used for the derivatisation of high molecular weight hydroxyl compounds. In this case, an additional drying step with a gentle stream of nitrogen was necessary to remove pyridine from the sample before the analysis. In both silylated samples, 5 ng 1-1'binaphthyl was also added as the internal standard. Small differences in GCxGC conditions can produce large changes in the detector response (TOFMS). In this study, the internal standard was used to correct potential differences between injections, i.e. the internal standard enabled the comparison of the results obtained for different samples. It is well known that there are a correlation between the quantity of analyte (among other parameters such as ionisation efficiency and fragmentation) and the TOFMS response, which could be used for a rough estimation of analyte concentration, i.e. comparison of the results determined for different samples and the same analyte/s. The latter was the objective of the presented research and therefore a simple internal standard approach was used (a real concentration value is not employed in the text). However, for future research it is acknowledged that a more complex approach should be applied in order to semi-quantify the identified compounds (give a concentration value), such as the method utilised by Kopperi et al. (2013) that was based on the use of surrogates (different standards) and chemometry tools in order to quantify/semi-quantify the identified compounds by GCxGC-TOFMS.

Analysis was performed with a LECO Pegasus 4D GCxGC-TOFMS system equipped with an Agilent 7890 A GC and an Agilent 7683 B auto sampler (Fig. 3.4). The GCxGC-TOFMS method utilised was based on the method developed by Ruiz-Jimenez et al. (2011b). The system consists of two separation columns that are connected in series. The column set used in this investigation provided

primary volatility-based separation, followed by secondary polarity-based separation. The first column was an HP-1 (30 m x 0.25 mm i.d x 0.25 μ m film thickness) column with a non-polar 100 % dimethylpolysiloxane stationary phase, while the second column was a DB-17 (1 m x 0.1 mm i.d. x 0.1 μ m film thickness) column with a 50 % phenyl and 50 % methylsiloxane semi-polar stationary phase.



Figure 3.4: LECO Pegasus 4D GCxGC-TOFMS (www.leco.com, with permission of LECO Corporation)

The LECO Pegasus 4D is equipped with a secondary oven that allows independent column temperature controls. The temperature of the primary oven that housed the first column was continuously raised from 70 °C (2 min hold time) to 280 °C (5 min hold time) at a rate of 5 °C/min, while the temperature of the secondary oven with the second column was continuously raised from 75 °C (2 min hold time) to 285 °C (5 min hold time) at a rate of 5 °C/min. The modulator containing the heating jets was heated to 100 °C above oven temperatures and the pulse duration of the heated pulses was 600 ms. The cold pulses were only switched on during the heated periods. A modulation period

of 5 seconds was used. Helium (analytical grade 99.998%, supplied by AGA) was the carrier gas utilised at a flow of 1.3 ml/min. After GCxGC separation, the compounds were detected by the TOFMS. The TOFMS transfer line temperature was kept at 290 °C and the ion-source temperature was held constant at 200 °C. Data was acquired in the m/z ratio range between 50 and 450 amu.

3.2.3 Characterisation and semi-quantification

A large number of peaks were detected in this study using GCxGC-TOFMS. To optimise the number of compounds and the reliability of the organic compounds identified, some procedure and rules were applied. Detected peaks with a signal-to-noise (S/N) ratio larger than 10 were considered for characterisation. Unique mass was used for area/height calculations and the peak width was set at 0.5 seconds. Retention indices (I) were calculated for each compound by utilising linear hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), silylated polyols and carboxylic acids as reference compounds.

The first step in identifying organic compounds was spectral matching of the recorded mass spectra after deconvolution to spectra contained in the National Institute of Standards and Technology (NIST) library. Compounds with a normal and reverse spectral similarity fit ≥ 700 were kept in the peak table, a fit of 1000 would be a perfect match. An automated comparison of the experimental I values of these compounds was then performed with experimental or theoretical I values presented in literature with Guineu software (Castillo et al. 2011). A value of 150 units were selected as the maximum difference between experimental and literature I values, which is considered a good confidence interval when comparing experimental I values to literature I values calculated with the group theory (Ruiz-Jimenez et al. 2010). In most instances, the identified compounds had differences between the experimental and the theoretical I values smaller than 75 units. In instances where more than one compound was identified by applying the positive characterisation parameters, the compound with the lowest difference between the experimental and literature I value was selected. In order to identify organic compounds that are not included in the NIST library, experimental I values were analysed by using the Golm metabolome database, which contains mass spectra and I values for

biologically active metabolites (Hummel et al. 2010). Since the Golm database exclusively contains experimentally determined *I* values, a confidence interval of 25 units was chosen.

Validation of identified organic compounds with real standards and by applying more restrictive characterisation parameters, i.e. higher spectral fit similarities and lower *I* value confidence intervals, would result in the more accurate positive characterisation of organic compounds. However, these more restrictive conditions will allow only for the identification of a relatively small group (hundred or a couple of hundred) of organic compounds, but with more confidence. In order to characterise more organic compounds detected using the GCxGC-TOFMS for samples collected at Welgegund, less restrictive positive characterisation parameters were applied which could have led to false positives. Therefore, the compounds characterised in this study by the developed methodology, i.e. for NIST library similarity fits over 700 and *I* differences fewer than 150 are considered to be tentatively identified organic species.

The concentrations of the large number of organic compounds that were tentatively characterised were expressed as response factors (RF) in relation to the internal standard, i.e. 1-1'-binaphthyl. The RFs were calculated by:

$$RF = (A_{ci} / A_{IS}) \quad [1]$$

where A_{ci} is the peak area of the compound and A_{IS} is the peak area of the internal standard. In order to account for differences in sampling volumes, the RFs were also normalised (NRF) per volume of air sampled by:

$$NRF = RF / V \quad [2]$$

where V is the amount of air collected for each of the samples. The sum of the NRFs of different organic compounds with the same functional groups is presented by $\sum NRF$.

The organic compounds tentatively identified were categorised according to their functional groups in hydrocarbons (alkanes, alkenes, alkynes, aromatics), oxygenated species (alcohols, ethers,

aldehydes, ketones, carboxylic acids, esters), halogenated compounds (Cl, Br, I, F), nitrogen-containing compounds (amines, amides, amino acids, azo-compounds, imines, cyanates, isocyanates, nitriles, nitro, nitroso, pyridine derivatives, urea) and sulphur-containing compounds (sulphides, sulphones, sulphonic, sulphonamides, sulfoxides, thiols).

3.2.4 Ancillary measurements

Welgegund is a comprehensively equipped atmospheric monitoring station measuring a large number of physical and chemical properties of atmospheric pollutants. In this study, temperature (T), relative humidity (RH) (T and RH measured with a Rotronic MP 101A) and soil moisture measurements conducted at Welgegund were also utilised to interpret ambient atmospheric organic aerosol data. Soil moisture at different depths (5 and 20 cm) was measured with a Theta probe ML2x (Delta-T). Additional soil moisture information was obtained with a 100 cm PR2 soil moisture profile probe (Delta-T).

3.2.5 Quality control and -assurance

Quality control and -assurance were applied throughout the sampling and analytical procedures. Filters were handled with surgical gloves and stainless-steel forceps in order to prevent contamination. As mentioned previously, sampled filters were sealed off in petri dishes and extracted samples were analysed immediately or stored in a freezer at -18 °C. Samples were transported to Finland in an air tight container and kept at temperatures below 25 °C, arriving in Finland they were placed in a freezer at -18 °C. Field blanks were prepared and stored similar to the sampled filters for each week of sampling. The same extraction and analytical procedures were also applied to the field blanks. A small number of compounds were noticed on the blank filters that were below the detection limit of the analytical instrument.

3.3 Air mass history

The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (version 4.8) was used to calculate back trajectories of air masses arriving at Welgegund. Back-trajectory analysis uses interpolated measured or modelled meteorological data to calculate the most-likely central path of an air parcel over geographical regions, which provides the movement of air masses to an area at a given time. The model was developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess 2004). Meteorological data from the Global Data Assimilation System (GDAS) archive of the US National Weather Service's National Centre for Environmental Prediction (NCEP), archived from the ARL (Air Resources Laboratory 2009), is used to run the model. In this study, 96-hour back trajectories arriving every hour at a height of 100m were calculated for the entire sampling period. An arrival height of 100 m was chosen, since the orography in HYSPLIT is not very well defined. Lower arrival heights therefore could result in larger error margins on individual trajectory calculations (Jaars 2016).

3.4 Multiple-linear regression

Statistical analyses of the organic compounds tentatively characterised and their associated Σ NRFs were performed with multiple-linear regression (MLR). MLR attempts to model the relationship between two or more (n) independent variables ($x_1, x_2, x_3, \dots, x_n$) and a dependant variable (y) by fitting a linear equation to the observed data. Every value of the independent variable x is associated with a value of the dependent variable y . A MLR equation is obtained that can be utilised to calculate values for the dependent variable according to the dependencies of the dependent variable on the different independent variables. The following general equation is obtained:

$$y(x) = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \dots + \alpha_n x_n \quad [3]$$

where $\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_n$ are the coefficients calculated by the model for the independent variables ($x_1, x_2, x_3, \dots, x_n$) that minimises the root mean square error (RMSE), which compares the calculated values with the measured values as follows:

$$\chi^2 = [\sum_n y_n - \sum_n \alpha_n \times x_n]^2 \quad [4]$$

The optimum combination of independent variables is determined in order to derive an equation. α_0 accounts for factors that may have an influence on the model that are not considered in the MLR model.

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Chapter 4: Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa

4.1 Author list, contributions and consent

Wanda Booyens¹, Pieter G. Van Zyl¹, Johan P. Beukes¹, Jose Ruiz-Jimenez², Matias Kopperi², Marja-Liisa Riekkola², Miroslav Josipovic¹, Andrew D. Venter¹, Kerneels Jaars¹, Lauri Laakso^{1,3}, Ville Vakkari^{3,4}, Markku Kulmala⁴ and Jacobus J. Pienaar¹

¹Unit for Environmental Science and Management, North-West University, Private Bag X6001, 2520, Potchefstroom, South Africa

²Department of Chemistry, University of Helsinki, PO Box 55, 00014, University of Helsinki, Finland

³Finnish Meteorological Institute, PO Box 503, 00101, Helsinki, Finland

⁴Department of Physical Sciences, University of Helsinki, PO Box 64, 00014 University of Helsinki, Finland

Contributions to the article

Contributions of the various co-authors were as follows. The work was done by the author **Wanda Booyens**, i.e. sample analysis, data processing, research and writing of the scientific paper, with the supervisors of this study, Pieter G. van Zyl and Johan P. Beukes assisting in the interpretation of data, writing of the article and also made conceptual contributions. Jose Ruiz-Jimenez, Matias Kopperi and Marja-Liisa Riekkola were involved with the extraction and analysis of samples in the chemistry laboratory of the University of Helsinki. Miroslav Josipovic, Andrew D. Venter and Kerneels Jaars assisted in the sampling at the Welgegund site from April 2011-April 2012. Lauri Laakso and

Ville Vakkari assisted in establishing the Welgegund monitoring station and made conceptual contributions. Markku Kulmala and Jacobus J. Pienaar made conceptual contributions.

All the co-authors have been informed that the PhD will be submitted in article format and have given their consent.

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Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa

Wanda Booyens · Pieter G. Van Zyl · Johan P. Beukes · Jose Ruiz-Jimenez ·
Matias Kopperi · Marja-Liisa Riekkola · Miroslav Josipovic · Andrew D. Venter ·
Kerneels Jaars · Lauri Laakso · Ville Vakkari · Markku Kulmala · Jacobus J. Pienaar

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Abstract The organic fraction of atmospheric aerosols is 20 to 90 % of which only a small percentage has been chemically characterised. Two-dimensional gas chromatography with a time-of-flight mass spectrometer (GCxGC-TOFMS) is a powerful instrument used to chemically characterise organic compounds. Size-resolved characterisation and semi-quantification of ambient organic aerosol compounds were performed with a GCxGC-TOFMS for the first time in South Africa. Twenty-four-hour samples were collected for 1 year for three different size ranges. A combined total of 1056 different organic compounds could be tentatively characterised. The largest number of organic compounds tentatively identified was $PM_{2.5-1}$ (particles in the size range 1–2.5 μm), while this size fraction also had the highest total number of normalised response factors (ΣNRF). On average, 52, 26, 6, 13 and 3 % of species tentatively identified were oxygenated species, hydrocarbons, halogenated compounds, N-containing compounds and S-containing compounds, respectively. Oxygenated compounds were the most abundant species. Alkane and mono-aromatic species were the largest number of hydrocarbons tentatively identified with the highest ΣNRF s. The largest number of oxygenated species tentatively characterised were carboxylic acids and esters, while ether compounds had the highest ΣNRF s. Most of the halogenated compounds tentatively identified were chlorinated species with the highest ΣNRF s in two size fractions. Iodate species had a significantly higher ΣNRF in the $PM_{2.5-1}$ size fraction. The largest number of N-containing

W. Booyens · P. G. Van Zyl (✉) · J. P. Beukes · M. Josipovic · A. D. Venter · K. Jaars · L. Laakso ·
J. J. Pienaar
Unit for Environmental Science and Management, North-West University, Private Bag X6001,
2520 Potchefstroom, South Africa
e-mail: pieter.vanzyl@nwu.ac.za

J. Ruiz-Jimenez · M. Kopperi · M.-L. Riekkola
Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland

L. Laakso · V. Vakkari
Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland

V. Vakkari · M. Kulmala
Department of Physical Sciences, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

species tentatively characterised with the highest $\sum$ NRFs were amines. A small number of S-containing compounds with low $\sum$ NRFs were tentatively identified. The major sources of organic compounds measured at Welgegund were considered to be biomass burning and air masses moving over the anthropogenically impacted source regions.

Keywords Atmospheric aerosols · Organic compounds · Characterisation and semi-quantification · GCxGC-TOFMS · Size-resolved · Welgegund

1 Introduction

Atmospheric aerosols are a complex mixture of solid and liquid particulates suspended in the atmosphere, which originate from natural and anthropogenic sources. Typical natural sources include volcanic eruptions, wind-blown dust, pollen, maritime, biogenic emissions and natural wild fires, while the most important anthropogenic sources are fossil fuel combustion and biomass burning (human-induced wild fires, as well as household combustion for cooking and heating). Atmospheric aerosols are emitted directly into the atmosphere as primary aerosols, while secondary aerosols can also form in the atmosphere through chemical reactions (Pöschl 2005). Particulate matter (PM) can be classified according to its aerodynamic diameters into ultrafine PM_{0.1} (particles $\leq 0.1 \mu\text{m}$) and PM₁ (particles $\leq 1 \mu\text{m}$), fine PM_{2.5} (particles $\leq 2.5 \mu\text{m}$) and coarse PM₁₀ (particles $\leq 10 \mu\text{m}$) particles. Ultrafine and fine particles are usually associated with high-temperature combustion processes or are formed as secondary particles in the atmosphere (Salma et al. 2001), while coarse particles in the atmosphere are mostly dust emitted through the crushing, grinding and abrasion of surfaces (Tasic et al. 2006).

Atmospheric PM has impacts on climate change, as well as on general air quality, which has an influence on the environment and human health. The impacts of these species are determined by their physical (e.g. size, mass, optical density) and chemical properties. The chemical composition of aerosols also determines certain physical properties of aerosols. Sulphate (SO₄²⁻) species and certain organic species, for instance, are lightly coloured particles that reflect incoming solar radiation, which has a net cooling effect on the atmosphere. In contrast, dark particles, such as black carbon (BC) and certain organic species, absorb radiative energy, leading to the warming of the atmosphere. The impact of atmospheric aerosols on human health is also influenced by their physical and chemical properties. Health problems related to these species are usually associated with lung and heart diseases, as well as damaging effects on respiratory and cardiovascular systems (Dockery et al. 1993; Samet et al. 2000; Wichmann and Peters 2000). Coarse particles (PM₁₀) are generally filtered in the nose and throat and do not necessarily cause problems. Smaller particles (PM_{2.5} and smaller) can penetrate through the gas-exchange sections of the lungs and affect other organs (Pope and Burnett 2002).

Atmospheric aerosols consist of a number of inorganic and organic chemical species, of which the organic fraction contributes 20 to 90 % of the total particulate matter in the atmosphere (Jimenez et al. 2009). Because the chemical properties of organic compounds will have an influence on the effects of aerosols on radiation, as well as on the environment and human health, it is important to identify these organic species. Current measurements of organic compounds provide valuable information relating to the general chemical composition, oxidation state and reactivity of organic aerosols. However, these methods provide limited information on the actual character of individual organic compounds (Pöschl 2005). Atmospheric aerosols consist of thousands of organic compounds with various differences in chemical and physical properties (Goldstein and Galbally 2007). The present knowledge on

the chemical composition of atmospheric organic compounds is incomplete (Ruiz-Jimenez et al. 2010), which necessitates the development and employment of new methods to identify organic aerosols species. This is of particular importance in South Africa, which is one of the least studied regions with regard to atmospheric aerosols and the chemical composition thereof (Laakso et al. 2012, 2013). Africa is also considered to be a large source of organic aerosols and black carbon (Kanakidou et al. 2005). Tiitta et al. (2014) recently indicated with aerosol mass spectrometer measurements at Welgegund—a regional background site in South Africa—that a large fraction ($\approx 50\%$) of chemical species identified in aerosols consist of organic compounds.

Comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS) is a powerful instrument used for the chemical characterisation of organic compounds in complex matrices (Lewis et al. 2000; Welthagen et al. 2003). Lewis et al. (2000) were the first to report the use of GCxGC-TOFMS for atmospheric samples collected on filters in urban air. Since then, GCxGC-TOFMS has been successfully applied in characterising a wide range of organic compounds present in complex ambient atmospheric samples (Welthagen et al. 2003; Kallio et al. 2003, 2006; Hamilton et al. 2004; Laitinen et al. 2010; Arsene et al. 2011; Alam et al. 2013). The aim of this investigation was to collect ambient PM in different size fractions in the interior of South Africa for 1 year in order to analyse these samples with GCxGC-TOFMS in order to identify and semi-quantify organic compounds in the atmosphere. The results reported in this study present the first organic compounds characterised and semi-quantified with GCxGC-TOFMS for atmospheric aerosol samples collected in South Africa. In addition, this is also the most comprehensive size-resolved identification of organic species in South African atmospheric PM.

2 Measurement location and methods

2.1 Site description

The Welgegund monitoring station is situated approximately 100 km west from Johannesburg on the property of a commercial farmer (latitude $26^{\circ}34'10''\text{S}$, longitude $26^{\circ}56'21''\text{E}$, 1480 m AMSL). In Fig. 1, the location of the Welgegund station is indicated. Welgegund is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity. However, it is impacted by plumes from major anthropogenic source regions in the interior of South Africa, which include the Bushveld Igneous Complex, the Johannesburg-Pretoria metropolitan conurbation, the Vaal Triangle, the Mpumalanga Highveld and also a region of anti-cyclonic recirculation of air mass over the interior of South Africa. Sources of atmospheric pollutants in these different source regions include pyrometallurgical smelters, petrochemical and chemical industries, coal-fired power stations and emissions typically associated with a megacity (Beukes et al. 2014). It is also impacted by a relatively clean region in the north-west to south sector of Welgegund with no large point sources. The impacts of regional wild fires occurring mainly in the dry winters and spring are also measured at Welgegund (Vakkari et al. 2014). A detailed description of the Welgegund measurement station was presented by Beukes et al. (2014).

The Welgegund measurement site is geographically located within the South African Highveld, which accounts for approximately 30 % of the surface area of South Africa (Beukes et al. 2014). The Welgegund measurement station is located in the Vaal-Vet Sandy Grassland vegetation type that covers substantial parts of the North West and Free State Provinces of South Africa (provincial boundaries indicated in Fig. 1). Only 0.3 % of the Vaal-Vet Sandy

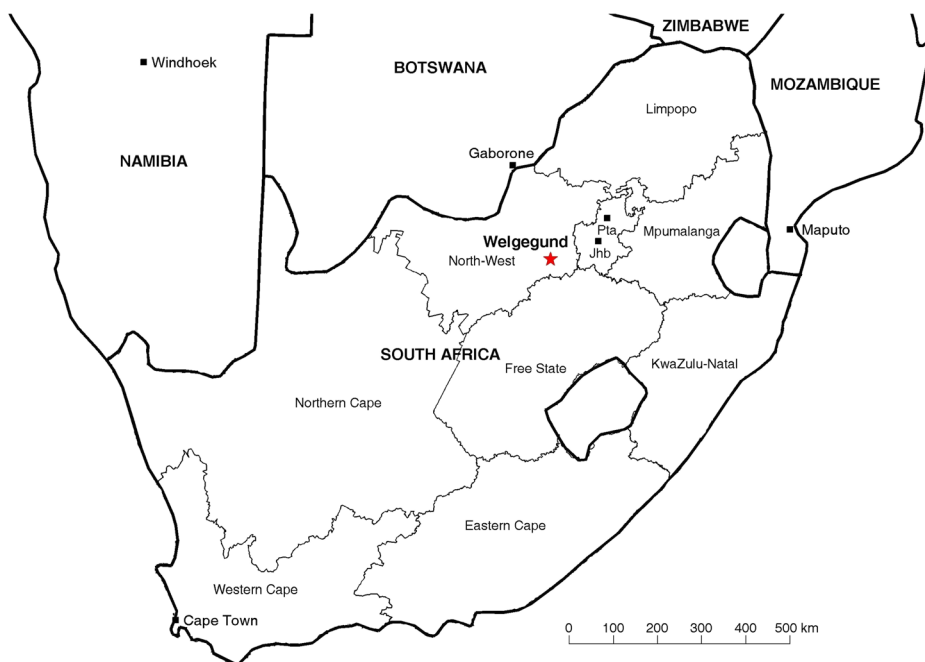


Fig. 1 Map of southern Africa with the Welgegund measurement site indicated with a red star. In order to contextualise where Welgegund is located, the South African provincial borders and names, as well as Cape Town, Johannesburg and Pretoria are also indicated

Grassland is currently statutorily conserved, while the rest is mostly used for grazing and crop production. Welgegund is located on a farm where the immediate area is grazed by cattle and sheep, with crop fields (mostly maize and to a lesser degree sunflower) covering the areas that are not grazed. The main grass species in the immediate proximity of the measurement station are *Hyparrhenia hirta* and *Sporobolus pyramidalis*, while *Acacia sieberiana*, *Rhus rehmanniana*, *Walafrida densiflora*, *Spermacoce natalensis*, *Kohautia cynanchica* and *Phyllanthus glaucophyllus* are the main non-grassy plant species (Bredenkamp et al. 1989).

A synopsis of meteorological conditions prevalent over the South African Highveld was recently presented by Laakso et al. (2012) with references therein. In general, the atmospheric circulation path over the South African Highveld is dominated by anti-cyclonic circulation, which is especially pronounced during winter (June to August). During the winter and early spring months, multiple inversion layers form on a regular basis at various altitudes, which significantly reduces the vertical mixing of atmospheric pollutant species and leads to significant increases in the concentrations of these species (Hobbs et al. 2003; Vakkari et al. 2014). The South African Highveld is also characterised by distinct wet and dry seasons, with almost all the rain events occurring from middle October to April, with nearly no precipitation occurring during May to middle October. This distinct precipitation cycle strongly affects the levels of atmospheric pollutant species. During the wet season, enhanced wet scavenging of pollutants occurs, while pollution levels increase during the dry season due to the occurrence of large-scale biomass burning (wild fires) (Vakkari et al. 2014). The average temperature at Welgegund is 18 °C, ranging between −3 and 28 °C in the winter, and 10 and 33 °C in summer.

2.2 Measurement methods

2.2.1 Sample collection

Twenty-four-hour samples were collected once a week from April 2011 until April 2012. Samples were collected with a Dekati PM₁₀ cascade impactor at a flow rate of 30 L/min. This impactor allows the collection of PM in different size ranges. Aerosols in the size fractions PM₁ (particles smaller than 1 µm), PM_{2.5-1} (particles in the size range 1–2.5 µm) and PM_{10-2.5} (particles in the size range 2.5–10 µm) were collected. The PM_{2.5-1} and PM_{10-2.5} size fractions were collected on 25 mm Quartz filters (Whatman), while a 47 mm quartz filter was used as a back filter in order to collect PM₁ particulates. After sampling, the filters were placed in petri dishes that were sealed off with parafilm, which were stored in a freezer until they were analysed. According to the knowledge of the authors, this is the most comprehensive number of size-resolved atmospheric samples collected in South Africa for the characterisation of organic compounds.

2.2.2 Analysis

Samples collected on filters were extracted with a 1:1 v/v mixture of methanol and acetone by using a dynamic ultrasonic-assisted extraction approach. This polar solvent mixture was validated by Ruiz-Jimenez et al. (2011a) for the extraction of acids, aldehydes, amine and polyols. Although this method was not validated for non-polar species, such as hydrocarbons, it was also used by Ruiz-Jimenez et al. (2011b) for the simultaneous extraction of polar and non-polar compounds. The extraction of the organic compounds present in the aerosol particles was completed within 40 min at a flow rate of 1 mL min⁻¹. The extraction time was considered to be adequate based on previous studies of Ruiz-Jimenez et al. (2011a, b), where 20- and 30-min extraction times were applied. Three to four drops of toluene were added, after which the extracts were dried with a gentle stream of nitrogen and then reconstituted with 5 ml methanol. After extraction, the samples were analysed immediately or stored in a freezer until used (Ruiz-Jimenez et al. 2011b). Three different aliquots (1 mL) from each sample were further pre-concentrated before analysis using a gentle nitrogen stream. Volatile and semi-volatile compounds were detected in the first aliquot, which was directly analysed after the addition of 5 ng 1-1'-binaphthyl used as the internal standard (Sigma-Aldrich). Silylation with or without catalyser was used for the transformation of non-volatile hydroxyl-compounds into volatile species before GCxGC-TOFMS analysis. Low molecular weight hydroxyl-compounds were directly analysed after ultrasound-assisted derivatisation at 35 °C and sonicated for 45 min using *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1 % trimethylchlorosilane (TMCS) (Sigma-Aldrich) as reagent. The same procedure, but adding pyridine as catalyser, was used for the derivatisation of high molecular weight hydroxyl compounds. In this case, an additional drying step was necessary to remove pyridine from the sample before the analysis. In both silylated samples, the internal standard 5 ng 1-1'-binaphthyl was also added as the internal standard. Small differences in GCxGC conditions can produce large changes in the detector response (TOF-MS). In this study, the internal standard was used to correct potential differences between injections, i.e. the internal standard enabled the comparison of the results obtained for different samples. It is well known that TOF-MS response is related to the quantity of analyte (among other parameters such as ionization efficiency and fragmentation), which could be used for a rough estimation of analyte concentration, i.e. comparison of the results determined for different samples and the same analyte/s. The latter was the objective of the presented research and therefore a simple

internal standard approach was used (a real concentration value is not employed in the text). However, the authors acknowledge that a more complex approach should be applied in future research in order to semi-quantify the identified compounds (give a concentration value), such as the method utilised by Kopperi et al. (2013) that was based on the use of surrogates (different standards) and chemometry tools in order to quantify/semi-quantify the identified compounds by GCxGC TOF-MS.

Analysis was performed with a LECO Pegasus 4D GCxGC-TOFMS system equipped with an Agilent 7890 A GC and an Agilent 7683 B auto sampler. The GCxGC-TOFMS method utilised was based on the method developed by Ruiz-Jimenez et al. (2011b). The system consists of two separation columns that are connected in series. The column set used in this investigation provided primary volatility-based separation followed by secondary polarity-based separation. The first column was an HP-1 (30 m×0.25 mm i.d.×0.25 µm film thickness) column with a non-polar 100 % dimethylpolysiloxane stationary phase, while the second column was a DB-17 (1 m×0.1 mm i.d.×0.1 µm film thickness) column with a 50 % phenyl and 50 % methylsiloxane semi-polar stationary phase.

The LECO Pegasus 4D is equipped with a secondary oven that allows independent column temperature controls. The temperature of the primary oven that housed the first column was continuously raised from 70 °C (2 min hold time) to 280 °C (5 min hold time) at a rate of 5 °C min⁻¹, while the temperature of the secondary oven with the second column was continuously raised from 75 °C (2 min hold time) to 285 °C (5 min hold time) at a rate of 5 °C min⁻¹. The modulator containing the heating jets was heated to 100 °C above oven temperatures and the pulse duration of the heated pulses was 600 ms. The cold pulses were only switched on during the heated periods. A modulation period of 5 s was used. Helium (supplied by AGA) was the carrier gas utilised at a flow of 1.3 ml/min. After GCxGC separation, the compounds were detected by the TOFMS. The TOFMS transfer line temperature was kept at 290 °C and the ion-source temperature was held constant at 200 °C. Data was acquired in the M/z ratio range between 50 and 450 amu.

2.2.3 Quality control and -assurance

Quality control and -assurance were applied throughout the sampling and analytical procedures. Filters were handled with surgical gloves and forceps in order to prevent contamination. As mentioned previously, sampled filters were sealed off in petri dishes and extracted samples were analysed immediately or stored in a freezer. Field blanks were prepared and stored similarly as the sampled filters for each week of sampling. The same extraction and analytical procedures were also applied to the field blanks. A small number of organic compounds were detected on the blank filters that were below the detection limit of the analytical instrument.

2.2.4 Characterisation and semi-quantification

A large number of peaks were detected in this study with GCxGC-TOFMS, which is generally the case for complex matrices such as atmospheric aerosols (Welthagen et al. 2003). Therefore, procedures and rules were applied in order to optimise the number of compounds identified, as well as to increase the reliability of organic compounds characterised. Detected peaks with a signal-to-noise (S/N) ratio larger than 10 were considered for characterisation. Unique mass was used for area/height calculations and the peak width was set at 0.5 s. Retention indices (*I*) were calculated for each compound by utilising linear hydrocarbons, polycyclic aromatic hydrocarbons (PAH), silylated polyols and carboxylic acids as reference compounds.

The first step in identifying organic compounds was mass spectral matching of the deconvoluted peaks in the NIST library. Compounds with a normal and reverse spectral similarity $\text{fit} \geq 700$ were kept in the peak table. An automated comparison of the experimental I values of these compounds was then performed with experimental or theoretical I values presented in literature with Guineu software (Castillo et al. 2011). A difference between experimental and literature I values of 150 units was selected as the maximum difference, which is considered a good confidence interval when comparing experimental I values to literature I values calculated with the group theory (Ruiz-Jimenez et al. 2010). In most instances, the identified compounds had differences between the experimental and the theoretical I values smaller than 75 units. In instances where more than one compound was identified by applying the positive characterisation parameters, the compound with the lowest difference between the experimental and literature I value was selected. In order to identify organic compounds that are not included in the NIST library, experimental I values were analysed by using the Golm metabolome database, which contains mass spectra and I values for biologically active metabolites (Hummel et al. 2010). Since the Golm database exclusively contains experimentally determined I values, a confidence interval of 25 units was chosen.

Applying more restrictive characterisation parameters, i.e. higher spectral fit similarities and lower I value confidence intervals, as well as verification of identified organic compounds with real standards, would result in the more accurate positive characterisation of organic compounds. However, these more restrictive conditions will allow only for the identification of a relatively small group (hundred or a couple of hundred) of organic compounds. In order to characterise more organic compounds detected with the GCxGC-TOFMS for samples collected at Welgegund, less restrictive positive characterisation parameters were applied. Therefore, the compounds characterised in this paper by the developed methodology, i.e. for NIST library similarity fits over 700 and I differences fewer than 150 are considered to be tentatively identified organic species.

The concentrations of the large number of organic compounds that were tentatively characterised were expressed as response factors (RF) in relation to the internal standard, i.e. 1-1'-binaphthyl. The RFs were calculated by:

$$\text{RF} = \left(A_{ci} / A_{IS} \right)$$

where A_{ci} is the peak area of the compound and A_{IS} the peak area of the internal standard. In order to account for differences in sampling volumes, the RFs were also normalised (NRF) per volume of air sampled by:

$$\text{NRF} = \text{RF} / V$$

where V is the amount of air collected for each of the samples. The sum of the NRFs of different organic compounds with the same functional groups is presented by $\sum \text{NRF}$.

3 Results and discussion

3.1 Chromatograms

A total of 52 aerosol samples for each of the size ranges were collected. Examples of typical total ion count (TIC) chromatograms obtained for samples collected in each of the three

different size ranges are presented in Fig. 2a, b and c. These example chromatograms were obtained for non-derivatised samples. Visual inspection of these three chromatograms presented indicates that more compounds were usually obtained in the $PM_{2.5-1}$ size fraction. This will be discussed in detail and statistically evaluated later in the paper when the total number of compounds tentatively identified with their corresponding Σ NRFs will be presented for each of the different size ranges.

It is evident from the chromatograms presented in Fig. 2 that the aerosol samples collected in South Africa were complex, with approximately 8000 compounds detected. Atmospheric aerosol samples analysed with GCxGC-TOFMS in other investigations showed similar complex chromatograms (Welthagen et al. 2003; Hamilton et al. 2004; Ruiz-Jimenez et al. 2011b; Özel et al. 2011; Alam et al. 2013). Welthagen et al. (2003) and Hamilton et al. (2004), for instance, detected 15,000 and 10,000 peaks, respectively of which only a small fraction (~2 %) could be identified. The large number of organic compounds present in aerosol samples can be attributed to the exponential increase of isomeric forms for compounds with higher carbon numbers. One of the benefits of comprehensive gas chromatography coupled with mass spectrometry is the possibility to form GCxGC contour plots for individual m/z ratios, which assist in the characterisation of complex matrices. In this study, the functional groups were

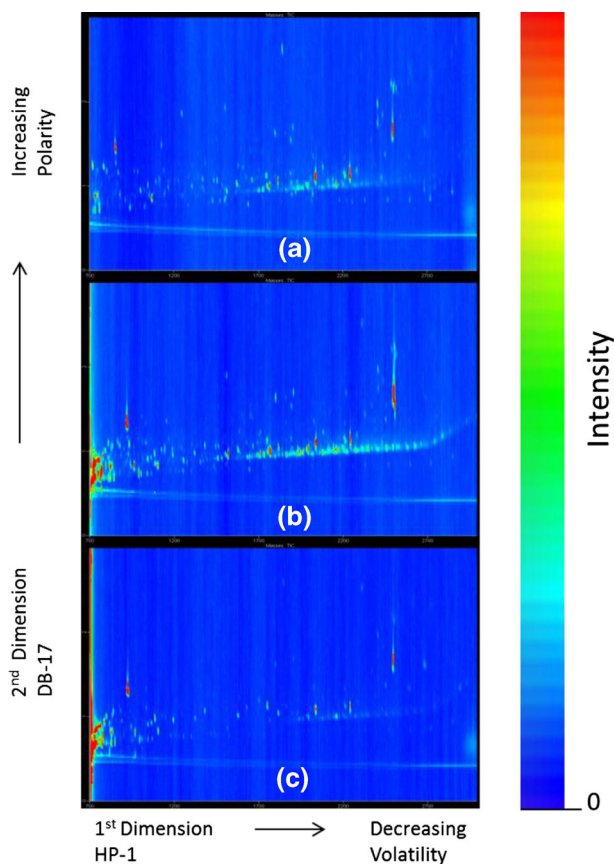


Fig. 2 Typical TIC chromatograms obtained with GCxGC-TOFMS for samples collected in three different size ranges, i.e. PM_1 (a), $PM_{2.5-1}$ (b) and $PM_{10-2.5}$ (c). Internal standard peaks are indicated with white circles

grouped by applying the selection rules for compound class identification described by Welthagen et al. (2003).

3.2 Characterisation and semi-quantification of organic compounds

Although a large number of peaks could not be identified (~87 %), a combined total of 1056 organic compounds were tentatively identified for all the samples analysed by applying the procedures and conditions described in Section 2.2.3, i.e. for NIST fits over 700 and I differences under 150 to positively tentatively identify organic species. The RFs of these organic compounds characterised ranged between several orders of magnitude. According to the knowledge of the authors, the 1056 organic compounds tentatively identified are the largest number of organic compounds chemically tentatively characterised in atmospheric samples utilising GCxGC-TOFMS. In previous studies, fewer organic compounds were characterised in atmospheric samples, although emphasis in those studies was placed on identifying and quantifying specific functional groups (Alam et al. 2013), such as oxygenated species (Hamilton et al. 2004) or N-containing compounds (Özel et al. 2011).

In Fig. 3, the combined total number (a) of organic compounds tentatively characterised in each of the size fractions, as well as the semi-quantified concentrations (b) of the organic compounds identified on all the sample filters is presented. It is evident that there is no significant difference between the total number of organic compounds tentatively identified in the three size fractions. The $PM_{2.5-1}$ size fraction at the highest mean value of 662 different species identified, while the lowest average of 608 species was tentatively identified in the $PM_{10-2.5}$ fraction. Although the statistical evaluation of the Σ NRF values indicates that the Σ NRFs of the $PM_{2.5-1}$ and $PM_{10-2.5}$ size fractions were comparable, the highest average Σ NRFs of the species tentatively identified were determined in the $PM_{2.5-1}$ size fraction. The $PM_{10-2.5}$ size fraction had the second highest mean Σ NRF value, while the $<PM_1$ fraction had the lowest average Σ NRF. In the PM_1 fraction, the blow-off of semi-VOCs (SVOCs) is likely to occur, which can contribute to an underestimation of the number of compounds and Σ NRFs of species in this fraction (Forbes et al. 2012). Quantification of the number of compounds and Σ NRF values, as indicated in Fig. 3, confirmed the visual observations that were already evident in Fig. 2. Although the lowest average number of different organic compounds was tentatively identified in the $PM_{10-2.5}$ size fraction, the concentrations of the organic species characterised in this size fraction were the second most abundant. This can be expected, since higher Σ NRFs of organic compounds would be detected if larger particles of specific compounds are present in the atmosphere. In addition, larger particles also present larger surface areas for organic compound adsorption.

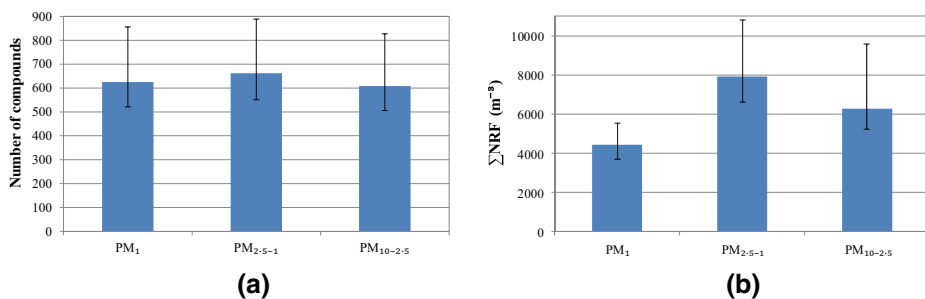


Fig. 3 Total number of compounds identified (a) and the summation of the normalised response factor (Σ NRF) (b) for every particle size for all the samples

The organic compounds tentatively identified were categorised according to their functional groups, i.e. hydrocarbons (alkanes, alkenes, alkynes, aromatics), oxygenated species (alcohols, ethers, aldehydes, ketones, carboxylic acids, esters), halogenated compounds (Cl, Br, I, F), as well as nitrogen (N)- and sulphur (S)-containing organic compounds. In Fig. 4, the combined total number of hydrocarbons, oxygenated species, halogenated compounds, as well as N- and S-containing organic compounds tentatively identified on all the sample filters with their corresponding Σ NRFs in the three size ranges is presented. Of the total number of compounds tentatively characterised in all three size ranges, 52 % were oxygenated, 26 % were hydrocarbons, 6 % were halogenated compounds, 13 % were N-containing compounds and 3 % were S-containing compounds according to mean values. The total Σ NRFs for all the compounds tentatively characterised consisted of 55 % oxygenated compounds, 16 % hydrocarbons, 16 % halogen compounds, 12 % N-containing organic compounds and 1 % S-containing organic compounds on average.

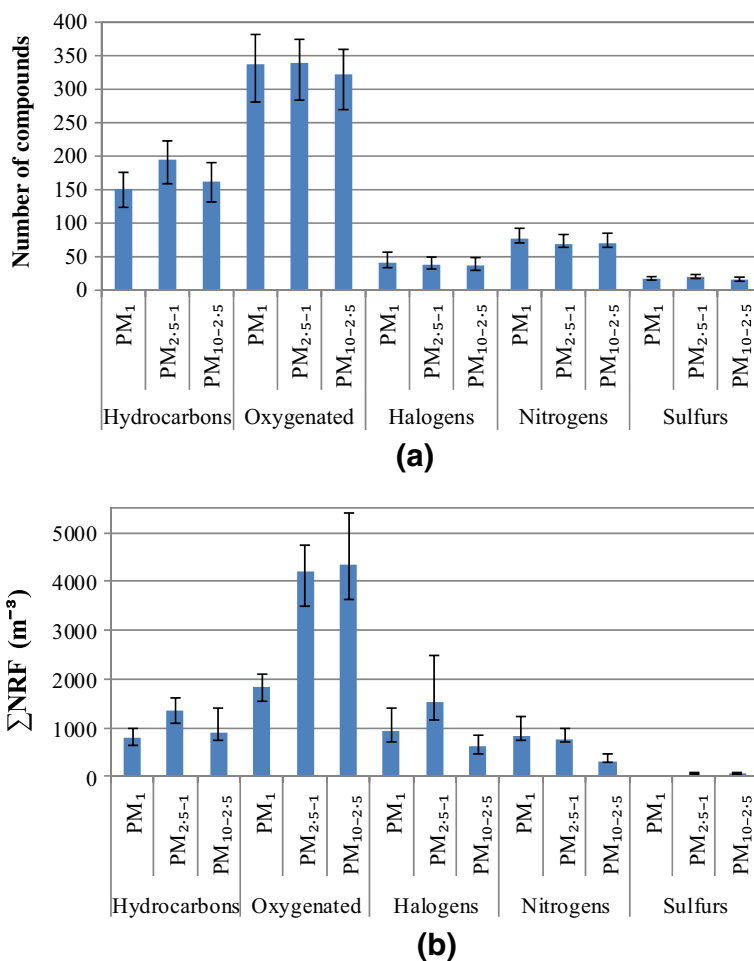


Fig. 4 Total number of compounds identified (a) with their associated Σ NRF (b) for each of the functional group categories in the three particle size ranges

The largest number of organic compounds tentatively characterised in all three size ranges were oxygenated species with more than 50 % of the species tentatively characterised in all three size ranges being oxygenated species. Oxygenated compounds also had significantly higher Σ NRFs in all three size ranges relative to the other organic compound groups, with the Σ NRFs of the tentatively identified peaks contributing on average 68, 52 and 40 % to the total Σ NRFs in the $PM_{10-2.5}$, $PM_{2.5-1}$ and $<PM_1$ size fractions, respectively. Oxygenated organic aerosols are usually considered to be present in the atmosphere as secondary aerosols and are usually indicative of aged air masses. The dominance of the oxygenated compounds can be expected since Welgegund is considered to be a regional background atmospheric monitoring station affected by aged air masses from different anthropogenic source regions in the interior of South Africa (Beukes et al. 2014). Aerosol mass spectrometry measurements (AMS) conducted by Tiitta et al. (2014) at Welgegund also indicated higher levels of oxygenated compounds. Furthermore, GCxGC-TOFMS analysis of aerosols collected from fresh plumes at Welgegund by Venter et al. (2014) indicated the higher occurrence of primary emitted hydrocarbon compounds, compared to oxygenated organic compounds. Ruiz-Jimenez et al. (2011b) determined the organic chemical composition of ultrafine (30 and 50 nm) and total suspended atmospheric particulates collected in the centre of a boreal forest in Finland. Their study also indicated a larger number of oxygenated species with higher Σ NRF values. Alam et al. (2013) collected aerosols in an urban background site in Birmingham, UK to indicate the diversity of the organic compounds in atmospheric aerosols and not focus on specific groups of compounds. A large number of oxygenated species was also determined in their study.

A relatively large number of hydrocarbon species was also tentatively identified in all the size fractions with mean percentage contributions of 32, 38 and 30 % in the $PM_{10-2.5}$, $PM_{2.5-1}$ and $<PM_1$ size fractions, respectively. The Σ NRFs of hydrocarbons and halogen compounds were comparable, although a smaller number of halogen species was tentatively identified. This indicates the presence of larger concentrations of specific halogen compounds. Slightly lower Σ NRFs were determined for N-containing species, tentatively characterised compared to the hydrocarbons and halogen compounds tentatively identified. However, a larger number of N-containing compounds was tentatively characterised compared to the halogen compounds, which indicates the presence of a larger number of different N-containing organic compounds at lower concentrations. The total number and the concentrations of S-containing species were much lower compared to the other groups of organic compounds tentatively identified.

As mentioned in Section 2.2.2, a polar solvent mixture was used in this study, which was not validated or non-polar species, such as hydrocarbons. However, Ruiz-Jimenez et al. (2011b) did apply this method for the simultaneous extraction of polar and non-polar compounds. Therefore, the higher number of oxygenated species tentatively identified in this study with their associated higher Σ NRFs compared to non-polar hydrocarbon species could be partially attributed to the extraction method utilised in this investigation.

3.2.1 Hydrocarbons

In Fig. 5, the total number of each of the different hydrocarbon functional groups tentatively characterised is presented with their corresponding Σ NRFs. The largest number of hydrocarbon species tentatively identified in all three size fractions was alkanes and mono-aromatic compounds, while a relatively large number of alkene compounds were also identified. The largest number of organic compounds tentatively characterised for each of the functional groups were in the $PM_{2.5-1}$ size fraction. Alkanes were the most abundant hydrocarbon species in the $PM_{2.5-1}$ and $PM_{10-2.5}$ size fractions, while mono-aromatics had the highest Σ NRF in the PM_1 size fraction. The total Σ NRF of alkane species in the $PM_{10-2.5}$ size fraction was

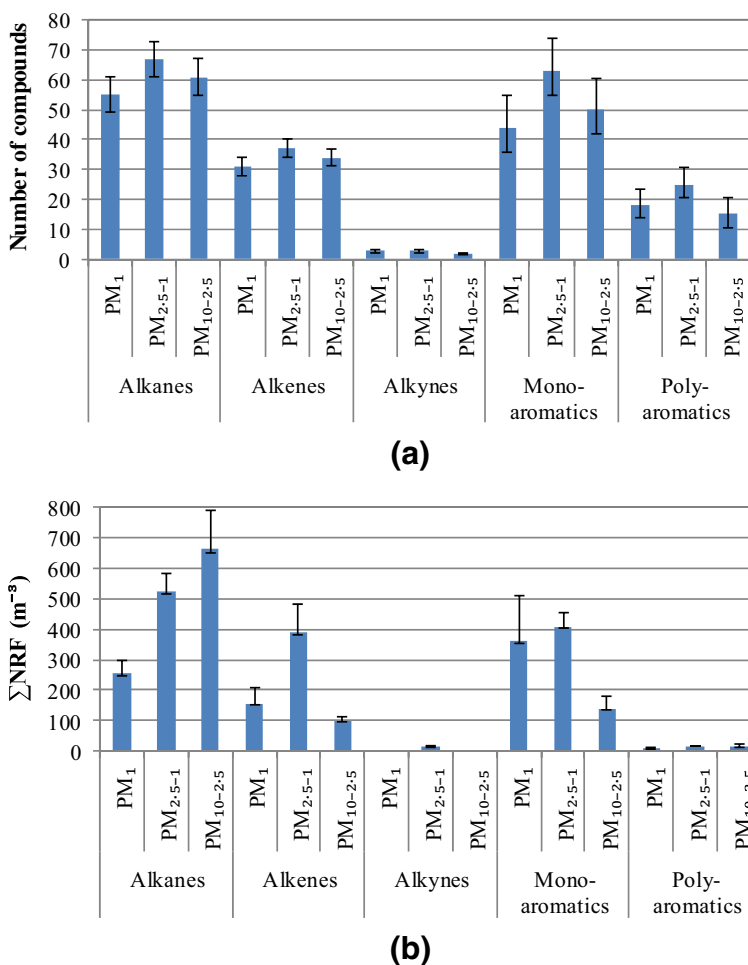


Fig. 5 Total number of compounds identified (a) with their associated Σ NRFs (b) for the different hydrocarbon functional groups

substantially higher (~72 %) compared to the concentrations of the other hydrocarbon species tentatively identified in this size fraction. The Σ NRFs values of mono-aromatics and alkenes were comparable in the PM_{2.5-1} size fraction. A small number of different alkyne species was also detected with very low concentrations in each of the size fractions.

The major sources of alkanes, alkenes and mono-aromatic species are usually the combustion of fossil fuels and biomass (Dewulf and Van Langenhove 2003; Barrero and Cantón 2007; Alves et al. 2009; Vakkari et al. 2014). Vakkari et al. (2014) indicated that biomass burning is the most important emission source in PM₁ during the dry season, while aerosol mass spectrometer (AMS) measurements of PM₁ at Welgegend also indicated biomass burning as a major source of hydrocarbons (Tiitta et al. 2014). The mono-aromatic groups also include the commonly measured benzene compounds and alkyl-substituted benzenes. In a study conducted by Jaars et al. (2014) on volatile aromatic hydrocarbons measured at Welgegend, significantly higher aromatic hydrocarbon concentrations were observed in air masses that passed over anthropocentrically impacted regions.

PAHs were also identified, although the relative Σ NRFs of PAHs detected were very low compared to the Σ NRFs of the other hydrocarbon species measured in this study. Atmospheric PAHs are prominent atmospheric pollutants present in particulate matter. These species are carcinogenic and have been investigated intensively due to their toxicity (Walgraeve et al. 2010). The main sources of PAHs are considered to be the primary emissions from combustion processes. The relatively low PAH levels measured could be expected, since Welgegend is not directly affected by pollution sources in close proximity. The low number of PAHs tentatively characterised could also be partially ascribed to the polar extraction solvent used in this study. A few oxygenated PAHs were also tentatively identified mainly in the $PM_{10-2.5}$ size fraction, which includes 9,10-anthracenedione, 9-fluorenone, 9H-xanthene and 1,8-naphthalic anhydride. Ringuet et al. (2012) also identified 9,10-anthracenedione and 9-fluorenone predominantly in the coarse fractions in measurements conducted in Paris, France. The sources of these species were attributed to non-combustion processes, such as deferment of surface soil and wind-generated dust particles.

3.2.2 Oxygenated organic compounds

Figure 6 presents the total number of each of the different functional groups of the oxygenated organic compounds tentatively characterised with their associated Σ NRFs. The largest number of oxygenated organic compounds tentatively identified in all three size fractions was carboxylic acids, while the second largest number of oxygenated compounds determined in all three size fractions was esters. However, a comparison of their Σ NRFs with the Σ NRFs of the other oxygenated species indicated that carboxylic acids and esters were not the most abundant oxygenated species. This indicates a large number of different carboxylic acid and ester compounds present at relatively low Σ NRFs. The total Σ NRFs of carboxylic acids are the highest in the $PM_{10-2.5}$ size fraction with one compound specifically contributing to a large peak area, i.e. formic acid. An increase in concentration with an increase in particle size is especially observed for carboxylic acids. Similar results for carboxylic acids and esters could be expected, since esters are chemical derivatives of carboxylic acids. Sources of these organic functional groups can be classified into primary and secondary sources. Primary sources include biomass burning, tobacco smoke, animal wastes, plastic combustions and chemical plant emissions (Graedel et al. 1986). The main secondary source of carboxylic acids and esters is the aging of volatile organic compounds primarily emitted into the atmosphere (Pöschl 2005).

A relatively large number of ketones were also tentatively identified in all the size fractions. The Σ NRF value of ketones was similar compared to the concentrations of carboxylic acids and esters. Although a large number of ketones in the $PM_{2.5-1}$ size fraction were tentatively characterised, cyclobutanone had a large contribution to the Σ NRF value with a large peak area. A small number of aldehydes with very low Σ NRFs were tentatively identified. The chemical properties of aldehydes and ketones are very similar and these species are usually associated with each other. A possible reason for the small amount of aldehydes identified could be attributed to their reactivity, i.e. aldehydes can be oxidised to acids, while ketones are more stable (George and Abbatt 2010; Chacon-Madrid et al. 2011). The oxidation of aldehydes could also contribute to carboxylic acid concentrations, especially in larger particles. Typical sources of ketones are spray painting, polymer manufacturing, printing and lacquer manufacturing, incinerator emissions and internal combustion engine exhausts (Subramanian 2000).

The number of alcohol species tentatively characterised was similar to the number of ketones detected. The Σ NRF values of alcohols in the $PM_{10-2.5}$ size fraction were lower compared to the

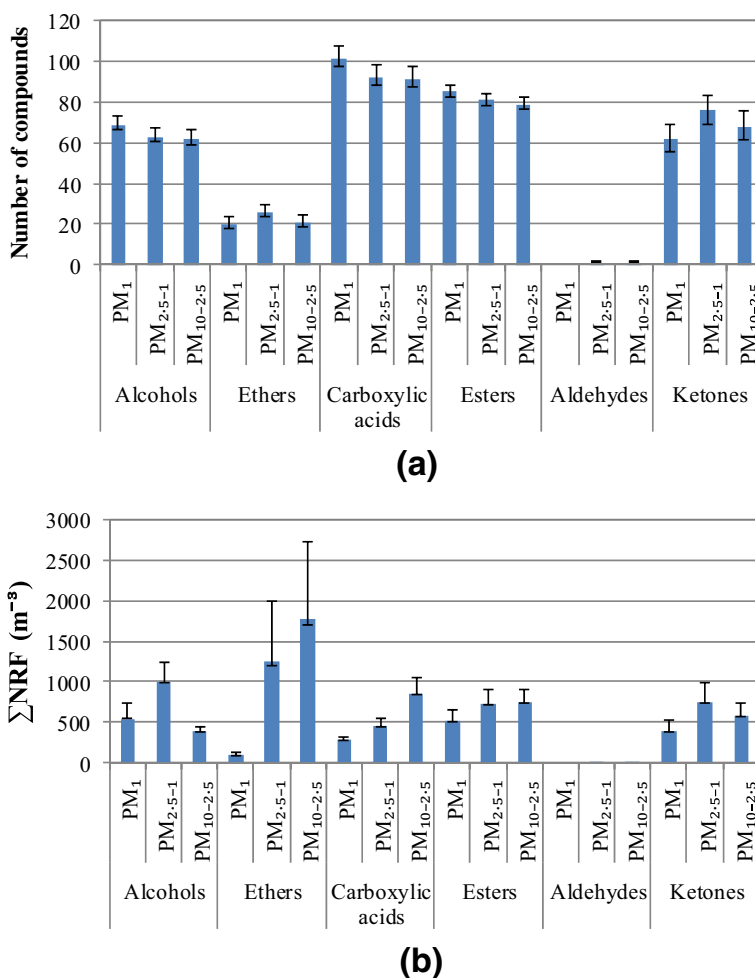


Fig. 6 Total number of compounds identified (a) with their associated ΣNRFs (b) for the different oxygenated functional groups

carboxylic acids, esters and ketones, while the ΣNRFs of alcohols in the PM_{2.5-1} size fraction were relatively higher compared to the afore-mentioned oxygenated species. The concentrations of alcohols in the PM₁ size fraction were also higher than the concentrations of carboxylic acids and ketones. Compounds contributing to the high concentrations of alcohol species in the PM₁ and PM_{2.5-1} size fractions include 2-butanol, 2-methyl-2-hexanol and 1-ethoxy-2-propanol. The higher levels of alcohols in the smaller size fractions could be attributed to the oxidation of alcohols to the carbonyl-containing functional groups present in larger particulates. Alcohols are used as preservatives for vehicle fuels, while natural sources of alcohols include vegetation, insects and microbes (König et al. 1995; Han et al. 2007).

With the exception of aldehydes, the lowest number of oxygenated species was determined for ethers. However, the concentrations of ether species in the PM_{2.5-1} and PM_{10-2.5} size fractions were significantly higher compared to the other oxygenated species, as well as to all the other organic compounds measured. This indicates the presence of large concentrations of

specific ether species. The $PM_{2.5-1}$ and $PM_{10-2.5}$ size fractions only had 26 and 21 compounds, respectively, but one compound had an extremely large peak area, i.e. 1,3,5-trioxepane in both size fractions. Other compounds also contributing to the large concentrations of $PM_{2.5-1}$ and $PM_{10-2.5}$ are 2-ethyl-1,3-dioxolane and 2-(1-methyl)-1,3-dioxolane, respectively. The $\sum NRFs$ for ethers contribute to approximately 28 % of the total $\sum NRFs$ calculated for all the organic compounds measured in the $PM_{10-2.5}$ size fraction. The concentrations of all the oxygenated species were the lowest in PM_1 size range.

In a study conducted by Hamilton et al. (2004) $PM_{2.5}$ aerosols were collected at a roadside in London in order to investigate oxygenated volatile organic compounds (o-VOCs) contained within urban aerosols. More than 10,000 individual compounds were isolated with GCxGC-TOFMS analysis, from which only 130 o-VOCs could be identified based on *I* and spectral matching. In addition, more than 100 other oxygenated species were observed that could not be identified, which also signifies the complexity of these atmospheric aerosol samples. Carboxylic acid species were one of the most abundant species, while a large number of furanones was also determined. The study of Hamilton et al. (2004) revealed oxygenated species that are typically found in the early stages of gas-to-particle formation. Alam et al. (2013) also indicated a large number of carbonyl containing oxygenated species for samples collected in an urban area.

As mentioned previously, oxygenated organic compounds are usually indicative of aged air masses from anthropogenic and natural sources of organic species. Primary emitted VOCs can be chemically transformed in the atmosphere through photo-chemical oxidation reactions with species such as ozone (O_3), the hydroxyl radical ($OH^\bullet$) and the nitrate radical ($NO_3^\bullet$) into secondary oxygenated particulates. These secondary organic aerosols can also further react through photolysis to form smaller oxygenated species. Furthermore, Welgegund is also affected by regional biomass burning events (Vakkari et al. 2014) that could be additional sources of oxygenated organic compounds. Tiitta et al. (2014) also found that oxygenated organic compounds correlated with biomass burning aerosols during the dry season.

3.2.3 Halogenated organic compounds

In Fig. 7, the total number of halogenated organic compounds, as well as their associated $\sum NRFs$, is presented. No clear trend is observed between the amounts of halogenated compounds determined in the different size fractions. The largest number of halogenated species detected was chlorinated organic species, while a smaller number of fluorinated compounds were determined. The smallest number of halogenated species identified were brominated and iodinated compounds. Iodinated organic compounds in the $PM_{2.5-1}$ size fraction were the most abundant halogenated compounds with a much higher total concentration, which is similar to that of the total ether concentration in the $PM_{2.5-1}$ size fraction. This large concentration consisted of only three iodinated species with, especially, very high concentrations determined for ethyl iodoacetate. These three iodinated species were not present in all the samples and were only observed on certain days. A possible source for these iodinated species could be the combustion of fossil fuel from land-based sources, as the main source of iodine in the atmosphere is considered to be the ocean (ATSDR 2004). However, it is not possible to completely attribute these iodinated species observed to a specific source. The second most abundant halogenated species were chlorinated compounds in the $PM_{10-2.5}$ and PM_1 size fractions, which consisted of the concentrations of a larger number of different chlorinated organic species. However, there was one compound in each size fraction that contributed to more than half of the total $\sum NRF$ value, i.e. chloromethyl chloroacetate and 2-chloroethenyl-1,3-butadiene in $<PM_1$ and $PM_{10-2.5}$, correspondingly. According to O'Doherty and Carpenter (2007), chlorine is the most abundant halocarbon in the atmosphere and sources of

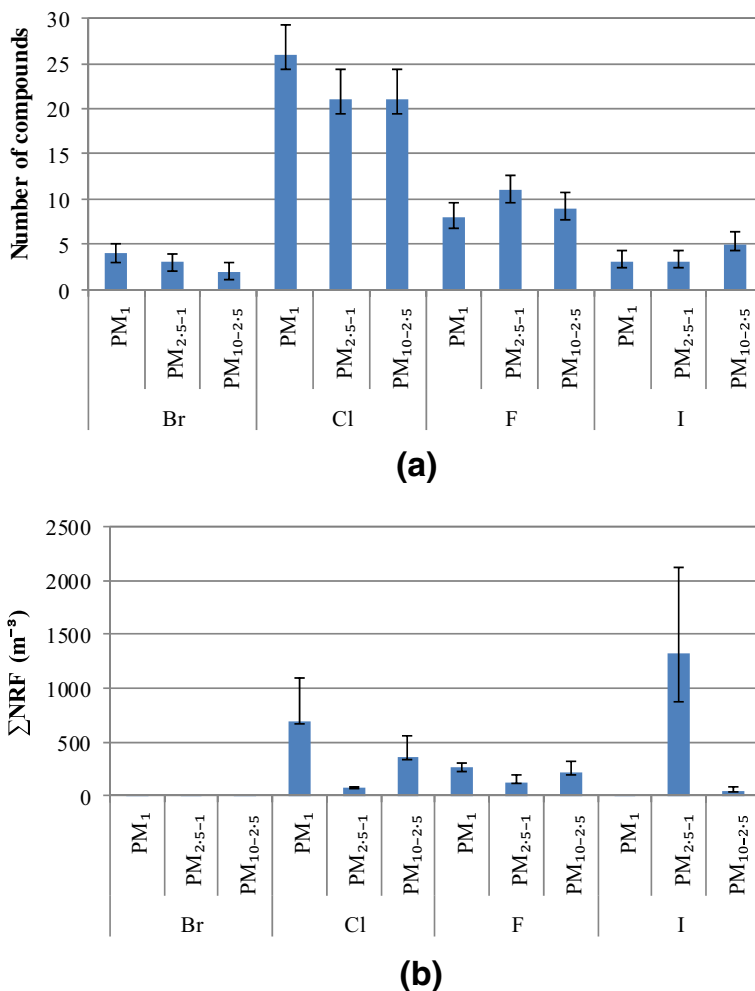


Fig. 7 Total number of compounds identified (a) with their associated ΣNRFs (b) for the different halogenated functional groups

these compounds can be natural and anthropogenic. Natural sources of chlorine consist of sea salt, whereas anthropogenic sources are primarily manufactured compounds, mainly chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), hydrochlorofluorocarbon (HCFC) and methyl chloroform (WMO/UNEP 1998). Biomass burning is also considered to be a source of atmospheric chlorine (Akagi et al. 2011, 2012; Vakkari et al. 2014), which could most likely be the predominant source of chlorine compounds measured at Welgegend. Lower ΣNRFs were observed for fluorinated compounds, while very small concentrations were determined for brominated species.

3.2.4 N- and S-containing organic compounds

In Fig. 8, the total number of each of the N-containing organic functional groups tentatively identified is presented with their respective ΣNRFs . The pyridine compounds identified in the

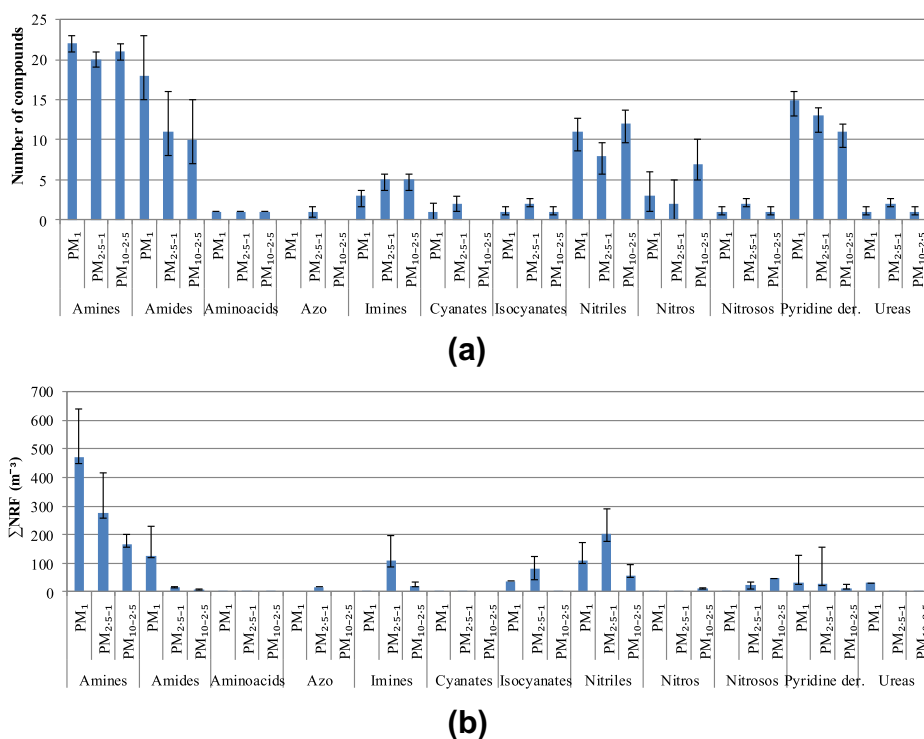


Fig. 8 Total number of compounds identified (a) with their associated Σ NRFs (b) for the different nitrogen-containing functional groups

samples derivatised with pyridine were excluded. The largest number of species tentatively identified containing nitrogen functional groups in all size fractions was amines, which also had the highest Σ NRFs. The total number of amide species tentatively identified in the <PM₁ size fraction were comparable to the number of amine compounds characterised in all the size ranges. However, the Σ NRF of the amide compounds was significantly lower compared to the Σ NRF of the amines. The Σ NRFs of amines in the PM₁ size fraction are especially significant since it contributes approximately 10 % to the total Σ NRFs of all the organic compounds measured in the PM₁ size fraction. In addition, one specific amine compound, i.e. 2-methyl-2-propanamine contributed to 40 % of the total Σ NRF in this size fraction. In a recent paper (Almeida et al. 2013), the importance of amines with regard to atmospheric nucleation during secondary aerosol formation was indicated. Vakkari et al. (2013) and Hirsikko et al. (2012) indicated record-high frequencies of nucleation events in the Highveld region. Cloud chamber experiments showed that trimethyl amine increased particle growth formation rates more than 1000 fold compared with ammonia. A trimethyl amine compound identified in this study was 1-methyl-2-tert-butylpyrrole. Considering the afore-mentioned, it is recommended that when the impact of anthropogenic activities on particle formation is assessed in future, amines should also be considered. Anthropogenic sources dominate the emissions of amines, although biomass burning (which can be natural or anthropogenic), as well as emissions from soil and marine organisms also contribute (Murphy et al. 2007; Ge et al. 2011).

The number of nitrogen organic compounds tentatively characterised in the PM_{2.5-1} and PM_{10-2.5} size fractions of the amides, as well as in all three size fractions of the pyridine derivatives and nitriles were comparable. However, the associated Σ NRFs of the amides in the

PM_{2.5-1} and PM_{10-2.5} size fractions were very low. Nitrile compounds had relatively higher Σ NRFs compared to the other N-containing compounds. Approximately five imines were detected with relatively higher Σ NRFs in the PM_{2.5-1} fraction, while two isocyanates were identified with slightly elevated levels in the PM_{2.5-1} fraction. The concentrations of all the other nitrogen-containing organic compounds were very low. In general, sources of these species are the burning of fossil fuels, fertiliser and animal excretion (Jiang et al. 2013). Özel et al. (2010) characterised between 17 and 57 organic nitrogen compounds in urban aerosols, which included mainly amines, nitriles, amides and nitro compounds.

The total number and the Σ NRFs of each of the different S-containing organic compounds determined are presented in Fig. 9. Compared to the other functional groups, a small number of S-containing compounds were detected with very low Σ NRFs. The largest numbers of S-containing compounds measured were sulphides (6 compounds in each of the PM_{2.5-1} and PM_{10-2.5} size fractions) and sulphonic acids (7 and 6 species in the PM_{2.5-1} and PM₁,

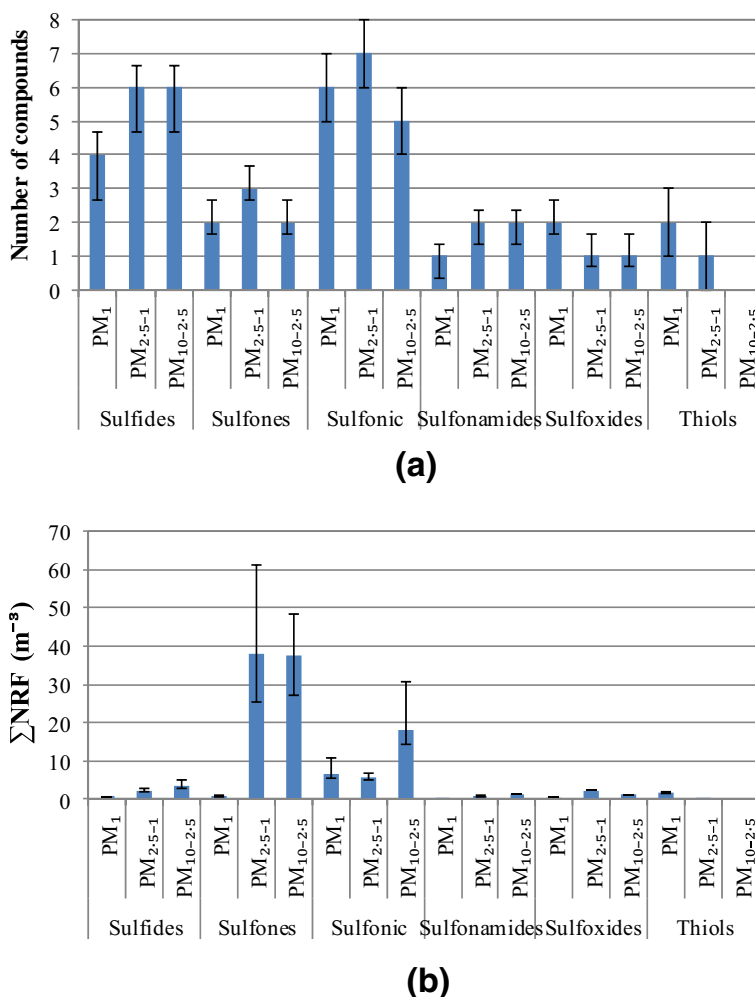


Fig. 9 Total number of compounds identified (a) with their associated Σ NRFs (b) for the different sulphur-containing functional groups

respectively) in all three size fractions. However, concentrations of these functional groups were very low. The highest Σ NRFs were determined for the sulphones in the $\text{PM}_{2.5-1}$ and $\text{PM}_{10-2.5}$ size fractions. Seinfeld and Pandis (2006) presented some of the sources of sulphur into the atmosphere, which include the combustion of fossil fuels, biomass burning, oceans, wetlands, plants and soils, and volcanoes.

4 Conclusions

In this study, GCxGC-TOFMS was used to tentatively identify and semi-quantify organic compounds in aerosols collected on filters in ambient air for the first time in South Africa. Twenty-four-hour samples were collected for 1 year with impactors for three different size fractions, i.e. PM_1 , $\text{PM}_{2.5-1}$ and $\text{PM}_{10-2.5}$, which is the most comprehensive number of size-resolved ambient atmospheric aerosol samples collected in South Africa for the characterisation of organic compounds. Approximately 8000 peaks were detected of which a combined total of 1056 different compounds could be tentatively characterised by applying the positive characterisation parameters, i.e. NIST library similarity fit of 700 and I differences under 150 compared to theoretical I values. No significant difference between the total number of organic compounds tentatively identified in the three size fractions was observed. The total numbers of organic compounds tentatively identified were on average 662, 625 and 608 in the $\text{PM}_{2.5-1}$, PM_1 and $\text{PM}_{10-2.5}$ size fractions, respectively. Semi-quantification of the organic compounds tentatively identified indicated that the $\text{PM}_{2.5-1}$ size fraction had the highest Σ NRF, while the $\text{PM}_{10-2.5}$ size fraction was the second most abundant. Categorisation of the organic compounds tentatively characterised according to their functional groups revealed that of the total number of compounds tentatively characterised on average, 52 % were oxygenated, 26 % were hydrocarbons, 6 % were halogenated compounds, 13 % were N-containing compounds and 3 % were S-containing compounds. Oxygenated compounds were also the most abundant species and contributed on average 55 % to the total Σ NRF for all the compounds tentatively characterised in all the size fractions, while, according to mean values, hydrocarbons, halogen compounds, N-containing species and S-containing compounds contributed to 16, 16, 12 and 1 %, respectively.

The largest numbers of hydrocarbons tentatively identified were alkane and mono-aromatic species, which also had the highest Σ NRFs in all the size fractions. Of the oxygenated species tentatively characterised, the largest number of species were carboxylic acids and esters, while ether compounds, especially in the $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5-1}$ size fractions, had significantly higher Σ NRFs. Most of the halogenated compounds tentatively identified were chlorinated species, with the highest Σ NRFs in the $<\text{PM}_1$ and the $\text{PM}_{10-2.5}$ size fractions. Iodate species, however, had a significantly higher Σ NRF in the $\text{PM}_{2.5-1}$ size fraction, which was attributed mainly to the presence of one compound. The largest number of N-containing species tentatively characterised were amines, which also had the highest Σ NRFs in all size fractions. A relatively small number of S-containing compounds were tentatively identified, which also had very low Σ NRFs.

The large number of oxygenated species was expected, since Welgegund is a regional background station that is affected by aged air masses. Tiitta et al. (2014) also indicated with AMS measurements at Welgegund that the largest number of organic aerosols was oxygenated species. The major sources of organic compounds measured at Welgegund could be considered to be biomass burning (Vakkari et al. 2014), as well as air masses moving over the anthropogenically impacted source regions (Jaars et al. 2014). The higher levels of oxygenated species tentatively identified compared to non-polar species, such as hydrocarbons, could also

be partially attributed to the polar solvent extraction mixture utilised in this study. Optimisation of the solvent extraction procedure by varying the solvent with non-polar solvents such as hexane is required in future work to determine the impacts of solvents on the chemical profile of compounds extracted.

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Compliance with ethical standards Conflict of interest: The authors declare that they have no conflict of interest. Disclosure of potential conflict of interest forms was signed by all the authors. The research did not involve any human participants and/or animals.

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Chapter 5: Assessment of polar organic aerosols at a regional background site in southern Africa

5.1 Author list, contributions and consent

Wanda Booyens¹, Johan P. Beukes¹, Pieter G. Van Zyl¹, Jose Ruiz-Jimenez², Matias Kopperi², Marja-Liisa Riekkola², Miroslav Josipovic¹, Ville Vakkari³, Lauri Laakso^{1,3}

¹Unit for Environmental Science and Management, North-West University, Private Bag X6001, 2520, Potchefstroom, South Africa

²Department of Chemistry, University of Helsinki, PO Box 55, 00014, University of Helsinki, Finland

³Finnish Meteorological Institute, PO Box 503, 00101, Helsinki, Finland

Contributions to the article

Contributions of the various co-authors were as follows. The work was done by the author **Wanda Booyens**, i.e. sample analysis, data processing, research and writing of the scientific paper, with the supervisors of this study, Pieter G. van Zyl and Johan P. Beukes assisting in the interpretation of data, writing of the article and also making conceptual contributions. Jose Ruiz-Jimenez, Matias Kopperi and Marja-Liisa Riekkola were involved with the extraction and analysis of samples in the chemistry laboratory of the University of Helsinki. Miroslav Josipovic assisted in the sampling at the Welgegund site. Lauri Laakso and Ville Vakkari assisted in establishing the Welgegund monitoring station and made conceptual contributions.

All the co-authors have been informed that the PhD will be submitted in article format and have given their consent.

5.2 *Formatting and current status of article*

The article was formatted in accordance with the journal specifications, to which it will be submitted, i.e. the **Journal of Atmospheric Chemistry**, a SpringerLink journal. The guide for authors that was followed in preparation of the article is available at http://www.springer.com/earth+sciences+and+geography/atmospheric+sciences/journal/10874?detailsPage=pltpci_1060574 [Accessed 12 November 2017]. At the time when this PhD was submitted for examination, this article had not yet been submitted for review, but the intention was to submit it soon thereafter.

Assessment of polar organic aerosols at a regional background site in southern Africa

Wanda Booyens¹, Johan P. Beukes¹, Pieter G. Van Zyl^{1*}, Jose Ruiz-Jimenez², Matias Kopperi², Marja-Liisa Riekkola², Miroslav Josipovic¹, Ville Vakkari³, Lauri Laakso^{1,3}

¹Unit for Environmental Science and Management, North-West University, Private Bag X6001, 2520, Potchefstroom, South Africa

²Department of Chemistry, University of Helsinki, PO Box 55, 00014, University of Helsinki, Finland

³Finnish Meteorological Institute, PO Box 503, 00101, Helsinki, Finland

* Corresponding author: Pieter G. van Zyl, e-mail: pieter.vanzyl@nwu.ac.za, tel: +27 (0) 18 299 2353, fax: +27 (0) 18 299 2350.

Abstract

Although southern Africa is a significant source of atmospheric pollutants, the region is still considered understudied with regard to atmospheric measurements, especially relating to the characterisation of ambient atmospheric aerosols. A recent paper reported GCxGC-TOFMS analysis used for the first time in southern Africa to tentatively characterise and semi-quantify 1 056 organic compounds in ambient aerosols in three different size fractions collected for one year at Welgegund – a regional background atmospheric monitoring station in South Africa. The aim of this paper was to further assess ambient polar organic aerosol compounds characterised at Welgegund in relation to the influence of meteorological conditions and major sources impacting Welgegund. No distinct seasonal pattern was observed for the total number of polar organic compounds tentatively characterised and their corresponding semi-quantified concentrations (Σ NRFs). There was, however, a period during late winter and early spring with significantly lower total number of polar organic compounds and

corresponding Σ NRFs, while it also seemed that the total numbers of polar organic compounds and the corresponding Σ NRFs for the period from mid-autumn to mid-winter were relatively higher. Therefore this temporal variability was assessed by investigating the influences of source regions, meteorology and open biomass burning. Relatively lower total numbers of polar organic compounds and corresponding Σ NRFs could be attributed to fresher plumes arriving at Welgegund from a source region relatively close to Welgegund. Meteorological parameters indicated that wet removal of aerosols during the wet season contributed to lower total numbers of polar organic compounds and associated Σ NRFs as expected, while increased anticyclonic recirculation and more pronounced inversion layers in winter typical in this region contributed to higher total numbers of polar organic compounds and corresponding Σ NRFs. The period with significantly lower total number of polar organic compounds and the corresponding Σ NRFs was attributed to fresh biomass burning plumes from wild fires occurring within close proximity of Welgegund, consisting mainly of volatile organic compounds and non-polar hydrocarbons. Multiple linear regression substantiated that the temporal variations in polar organic compounds were related to a combination of the factors investigated in this study.

Keywords: Atmospheric aerosols; organic compounds; Welgegund; GCxGC-TOFMS; biomass burning; multiple linear regression

1. Introduction

Southern Africa is considered to be a significant source of atmospheric pollutants, which include atmospheric gaseous species and aerosols species. South Africa has the largest industrialised economy in Africa, with a large number of mining, industrial and agricultural activities (Lourens et al. 2011; Laakso et al. 2012). In addition, biomass burning is also a significant source of atmospheric pollutants in the region through the prevalent occurrence of household combustion for space heating and cooking (Wichmann and Voyi 2006; Venter et al. 2012; South Africa Environmental Outlook 2012), as well as the widespread incidences of wild fires (Alade 2010; Vakkari et al. 2014; Strydom

and Savage 2016). The influence of biomass burning plumes from southern Africa on South America and Australia is well documented (Swap et al. 2003). There has been a substantial increase in atmospheric measurements in southern Africa during the last few years through various endeavours, which include legislative compliance monitoring by government and industries (Collett et al. 2010; Pretorius et al. 2016), as well as through numerous scientific initiatives and programmes (Kulmala et al. 2011; Laakso et al. 2012; Venter et al. 2012; Tiitta et al. 2014; Conradie et al. 2016). However, the region is still considered to be understudied with regard to atmospheric measurements (Laakso et al. 2012), especially relating to the characterisation of atmospheric aerosols (Booyens et al. 2015).

Atmospheric aerosols or particulate matter (PM) are directly emitted from various natural (e.g. wind-blown dust, wild fires) and anthropogenic (e.g. incomplete fossil fuel combustion, household biomass burning) sources. In addition, atmospheric aerosols are also formed through chemical reactions and physical processes in the atmosphere. It is important to chemically and physically characterise PM, since the influence of these species on air quality and climate is determined by their physical and chemical properties. Some species, such as sulphate (SO_4^{2-}) and certain organic compounds, for instance, scatter incoming solar radiation that has a cooling effect on the atmosphere, while absorbing compounds, such as black carbon (BC), have a warming effect on the atmosphere. Atmospheric aerosols are frequently classified according to their aerodynamic diameters (size) as coarse PM_{10} (particles $\leq 10 \mu\text{m}$), fine $\text{PM}_{2.5}$ (particles $\leq 2.5 \mu\text{m}$) and ultra-fine $\text{PM}_{0.1}$ (particles $\leq 0.1 \mu\text{m}$) and PM_1 (particles $\leq 1 \mu\text{m}$) particulates, which is important with regard to the impact of these species on human health. Larger PM_{10} species are usually filtered in the nose and throat, while smaller $\text{PM}_{2.5}$, PM_1 and $\text{PM}_{0.1}$ particulates penetrate through the respiratory system and affect other organs (Pope and Burnett 2002).

Atmospheric aerosols comprise a large number of inorganic and organic compounds. It has been indicated that the organic content of atmospheric aerosols can range between 20 and 90 % of the total PM in the atmosphere (Jimenez et al. 2009). Tiitta et al. (2014) recently indicated that a large fraction ($\approx 50 \%$) of chemical species identified in aerosols at a regional background site in South

Africa, i.e. Welgegund, were organic compounds. Furthermore, Vakkari et al. (2015) also indicated the importance of organic compounds in the growth of newly formed particles measured at Welgegund, while Chiloane et al. (2017) indicated that organic aerosols comprise a significant fraction of aerosol measurements conducted in the north-eastern interior of South Africa, where major anthropogenic sources in South Africa are located. This organic fraction of atmospheric aerosols consists of thousands of organic compounds with different chemical and physical properties (Goldstein and Galbally 2007). However, current organic compound measurements, e.g. aerosol mass spectrometry (AMS), provide limited insight into the actual chemical species, and the present knowledge on the chemical composition of atmospheric organic compounds is incomplete (Ruiz-Jimenez et al. 2010). Therefore, observations with more precise speciation are needed. One such method entails the characterisation of organic atmospheric aerosols with comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS) (Lewis et al. 2000, Welthagen et al. 2003, Alam et al. 2013, Booyens et al. 2015), which is a powerful instrument for the chemical characterisation of organic compounds in complex matrices.

Booyens et al. (2015) recently utilised GCxGC-TOFMS for the first time in South Africa to tentatively identify and semi-quantify 1 056 ambient organic compounds in aerosols collected on filters for three different size fractions (PM_1 , $PM_{2.5-1}$ and $PM_{10-2.5}$) at a regional background site, i.e. Welgegund. This was considered to be the largest number of ambient organic compounds tentatively characterised in atmospheric samples utilising GCxGC-TOFMS. Furthermore, the ambient aerosol samples collected were also the most comprehensive number of size-resolved ambient atmospheric aerosol samples collected in Southern Africa for the characterisation of organic compounds. The organic compounds characterised were categorised according to their functional groups as oxygenated, hydrocarbons, halogenated compounds, N-containing compounds and S-containing compounds. However, Booyens et al. (2015) indicated that the polar solvent extraction mixture utilised was not validated for non-polar species, which could have contributed to lower values related to the number of hydrocarbon species tentatively characterised and their associated semi-quantified concentrations. Therefore, the aim of this paper was to conduct an assessment of ambient polar

organic aerosol compounds characterised at Welgegund by Booyens et al. (2015) in order to determine the influence of meteorological conditions, as well as major sources and source regions impacting air masses measured at Welgegund in order to provide a more detailed picture of ambient polar organic aerosol composition for southern Africa. Furthermore, organic aerosols in southern Africa are affected by globally important sources such as (primary and secondary) biomass burning aerosols (and secondary organic aerosols in general) (Vakkari et al. 2014; Tiitta et al. 2014).

2. Measurement location and methods

2.1 Site description and meteorological conditions

The Welgegund monitoring station (www.welgegund.org) is a comprehensively equipped atmospheric measurement site located within the South African Highveld approximately 100 km west of Johannesburg on a commercial farm (latitude 26°34'10"S, longitude 26°56'21"E, 1480 m AMSL) (Fig. 1). Welgegund is considered to be a regionally representative background site with no direct impacts from large pollution sources in close proximity. It is, however, impacted by plumes passing over the major anthropogenic source regions in the interior of South Africa, which include the Western Bushveld Igneous Complex (WBIC), the Eastern Bushveld Igneous Complex (EBIC), the Johannesburg-Pretoria metropolitan conurbation, the Vaal Triangle and the Mpumalanga Highveld, as well as a region of anticyclonic circulation of air mass over the interior of South Africa as indicated in Fig. 1. The western sector (from north-west to south-east) contains no significant point sources, which can therefore be considered as representative of a relatively clean regional background (Fig. 1). The impacts of widespread regional wild fires that mainly occur during the dry winters and early spring are also observed at Welgegund (Vakkari et al. 2014). A number of papers have been published on atmospheric measurements conducted at Welgegund, wherein detailed descriptions of measurements conducted (Petäjä et al. 2013; Beukes et al. 2015; Räsänen et al. 2016), geographical and bioregion location (Booyens et al. 2015; Jaars et al. 2016), and the major source regions affecting Welgegund (Beukes et al. 2013; Jaars et al. 2014) have been presented.

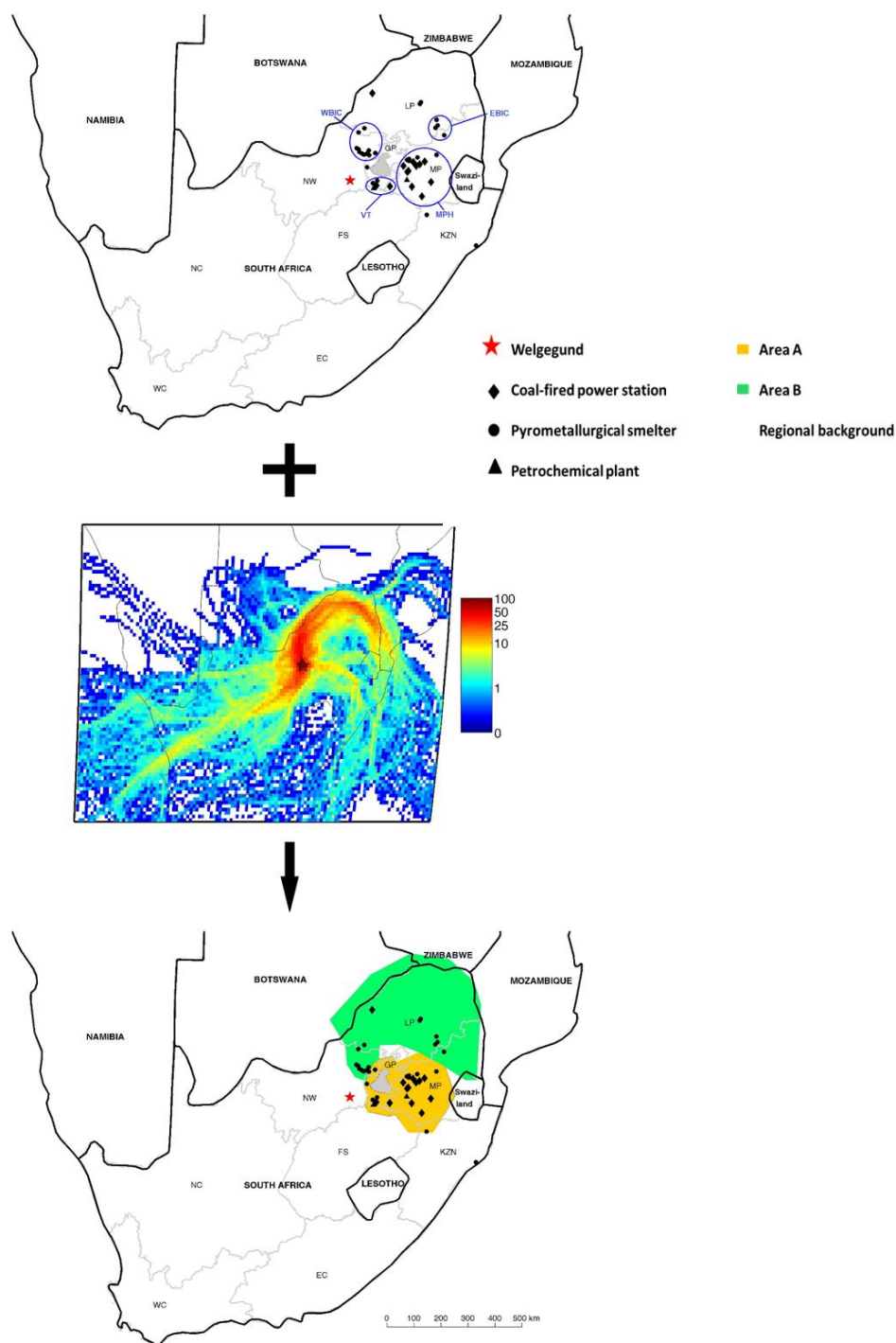


Fig. 1 Map of South Africa indicating the Welgegund measurement site, the major large point sources in the north-eastern interior of South Africa, the source regions defined in this study and the 96-hour overlay trajectories for the entire period. The colour scale for the overlay back trajectories indicates the percentage of trajectories passing over $0.2^\circ \times 0.2^\circ$ grid cells, with blue to yellow to red indicating the lowest to highest frequency of air mass movement

Laakso et al. (2012) with references therein presented a synopsis of meteorological conditions prevalent over the South African Highveld, which was summarised by Booyens et al. (2015). In short, anti-cyclonic circulation dominates the atmospheric circulation path over the South African Highveld, especially during the winter months (June to August). During winter and early spring, multiple inversion layers form on a regular basis at various altitudes, which significantly reduce the vertical mixing of atmospheric pollutant species and lead to significant increases in the concentrations of atmospheric pollutants (Hobbs et al. 2003; Vakkari et al. 2014; Giannakaki et al. 2015). The South African Highveld is also characterised by distinct wet and dry seasons with the wet season generally occurring from middle October to April. Wet scavenging during the wet season contributes to lower concentrations of atmospheric pollutants, while levels of atmospheric species increase during the cold and dry season due to large-scale open biomass burning (Vakkari et al., 2014), as well as increased household combustion for space heating and cooking (Vakkari et al., 2014). The average temperature measured at Welgegund during the sampling period was 18 °C, ranging between -3 and 28 °C in the winter, and 10 and 33 °C in summer.

2.2 Sample collection and analysis

Detailed descriptions of the sample collection, analysis, and quality control and -assurance procedures are presented by Booyens et al. (2015). In short, 24-hour ambient aerosol samples in three size ranges, i.e. PM₁, PM_{2.5-1} and PM_{10-2.5} were collected on quartz filters once a week from 12 April 2011 until 4 April 2012 with a Dekati PM₁₀ cascade impactor at a flow rate of 30 L/min. The mean volume of air sampled was 46 023 L ranging between 50 223 and 29 599 L. A polar solvent mixture of methanol and acetone utilising dynamic ultrasonic-assisted extraction was used to extract samples from filters, after which three to four drops of toluene were added, the extracts dried with a gentle nitrogen stream and reconstituted with 5 ml methanol. Three separate aliquots (1 ml) from each sample were further pre-concentrated and an internal standard (1-1'binaphthyl) was added. The first aliquot was directly analysed, while the other two aliquots were derivatised in order to transform non-volatile compounds into volatile compounds. Analysis was performed with a LECO Pegasus 4D

GCxGC-TOFMS system equipped with an Agilent 7890 A GC and an Agilent 7683 B auto sampler. The GCxGC-TOFMS method utilised was based on the method developed by Ruiz-Jimenez et al. (2011B), i.e. a two-separation column setup providing primary volatility-based separation, followed by secondary polarity-based separation.

2.3 Characterisation and semi-quantification

Detailed descriptions of characterisation and semi-quantification methods performed are presented by Booyens et al. (2015). To summarise, certain procedures and rules were applied in order to optimise the number of compounds identified and to increase the reliability of organic compounds characterised. Organic compounds were identified through mass spectral matching of deconvoluted peaks in the NIST library (normal and reverse spectral similarity fit ≥ 700), while the automated comparison of experimental and theoretical retention indices (I) (difference of 150 units between experimental and literature I values) was also performed. Additional organic compounds not included in the NIST library were identified with the Golm metabolome database, which contains mass spectral data for biologically active metabolites (Hummel et al. 2010). Compounds characterised are considered to be tentatively identified organic species due to the less restrictive positive characterisation parameters applied as indicated in Booyens et al. (2015). Polar compounds characterised include oxygenated species (alcohols, ethers, aldehydes, ketones, carboxylic acids, esters), halogenated compounds (Cl, Br, I, F), as well as nitrogen (N)- and sulphur (S)-containing organic compounds. The concentrations of the organic compounds tentatively characterised were expressed as response factors (RF) in relation to the internal standard, i.e. 1-1'-binaphthyl, which was also used by Ruiz-Jimenez et al. (2011A) and Ruiz-Jimenez et al. (2011B) to semi-quantify polar and non-polar organic compounds. The RFs for the different polar organic compounds were calculated in relation to the internal standard, i.e. peak area of the compound (A_{ci}) / peak area of the internal standard (A_{IS}). The RFs were also normalised per volume of air sampled (V), i.e. RF/V , which is presented as the sum of the normalised RFs ($\sum NRF$).

2.4 Air mass history analysis

Back trajectories were calculated with the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (version 4.8), which was developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Stein et al. 2015). The model runs with meteorological data from the Global Data Assimilation System (GDAS) archive of the US National Weather Service's National Centre for Environmental Prediction (NCEP), which is archived by the ARL. For each 24-hour sampling period, individual hourly arriving 96-hour (4 days) back trajectories were calculated at an arrival height of 100 m.

2.5 Ancillary measurements

The numbers of polar organic compounds tentatively characterised and semi-quantified were related to temperature (T) and relative humidity (RH) (Rotronic MP 101A), as well as soil moisture measured at different depths (5 and 20 cm) with a Theta probe ML2x (Delta-T) at Welgegund. Additional soil moisture information was obtained with a 100 cm PR2 soil moisture profile probe (Delta-T).

3. Results

3.1 Temporal variations

In Fig. 2, the total numbers of polar organic compounds tentatively identified and their corresponding $\sum$ NRFs in the three size ranges for each sample collected during the entire sampling period are presented. From Fig. 2, it is evident that although the total number of polar organic compounds tentatively characterised and the $\sum$ NRFs were different for each of the samples collected, no distinct seasonal pattern for the total number of polar organic compounds and their semi-quantified concentrations is observed. There is, however, a period from 2 August 2011 to 4 October 2011, coinciding with austral winter and spring, during which total numbers of polar organic compounds and corresponding $\sum$ NRFs were significantly lower. In addition, it also seems that the total number of polar organic compounds and the corresponding $\sum$ NRFs were more consistent and relatively higher

during the sampling period 12 April 2011 to 12 July 2011 compared to the sampling period between 11 October 2011 and 4 April 2012. These occurrences will be explored in subsequent sections in this paper. Furthermore, in most instances, the size distribution in each of the samples also resembled the combined total size distribution for all the samples collected indicated by Booyens et al. (2015), i.e. no significant difference between the total number of organic compounds tentatively identified in the three size fractions, while relatively higher $\sum$ NRFs of the species tentatively identified were determined in the PM_{2.5-1} size fraction.

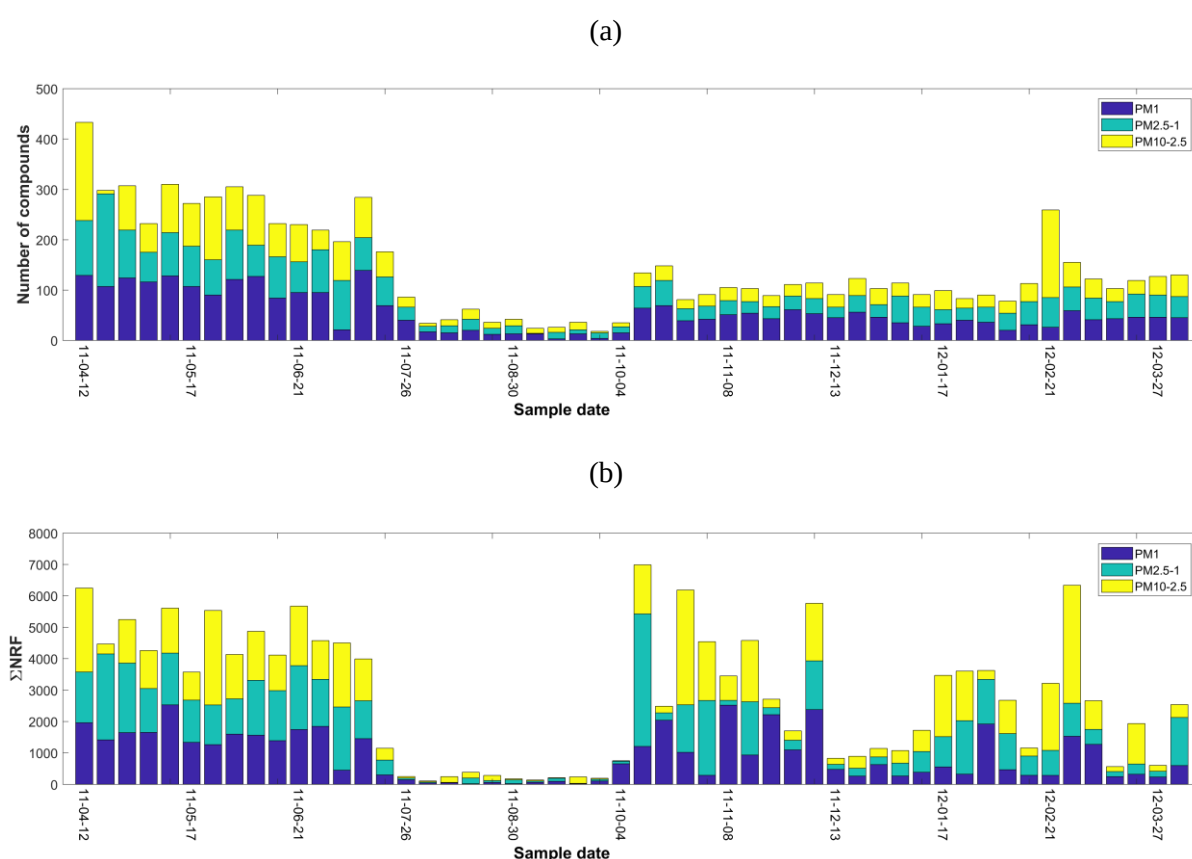
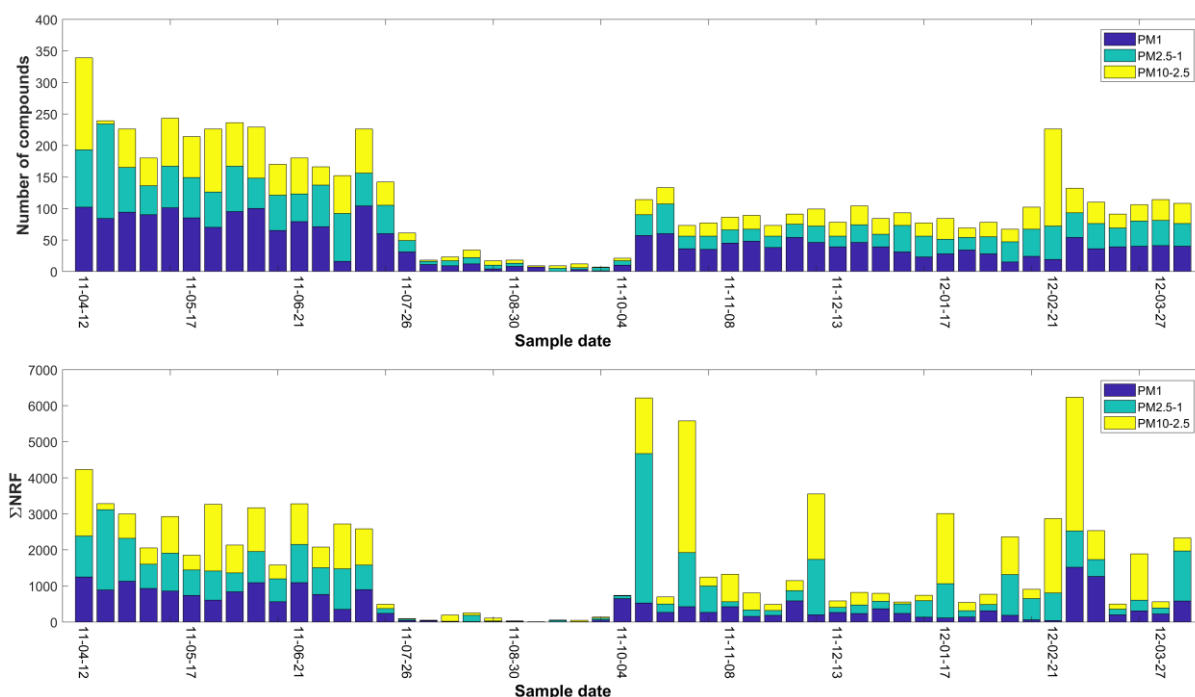


Fig. 2 Total number of polar organic compounds identified (a) and the sum of the normalised response factors ($\sum$ NRF) (b) for the three particle size ranges for each sample collected

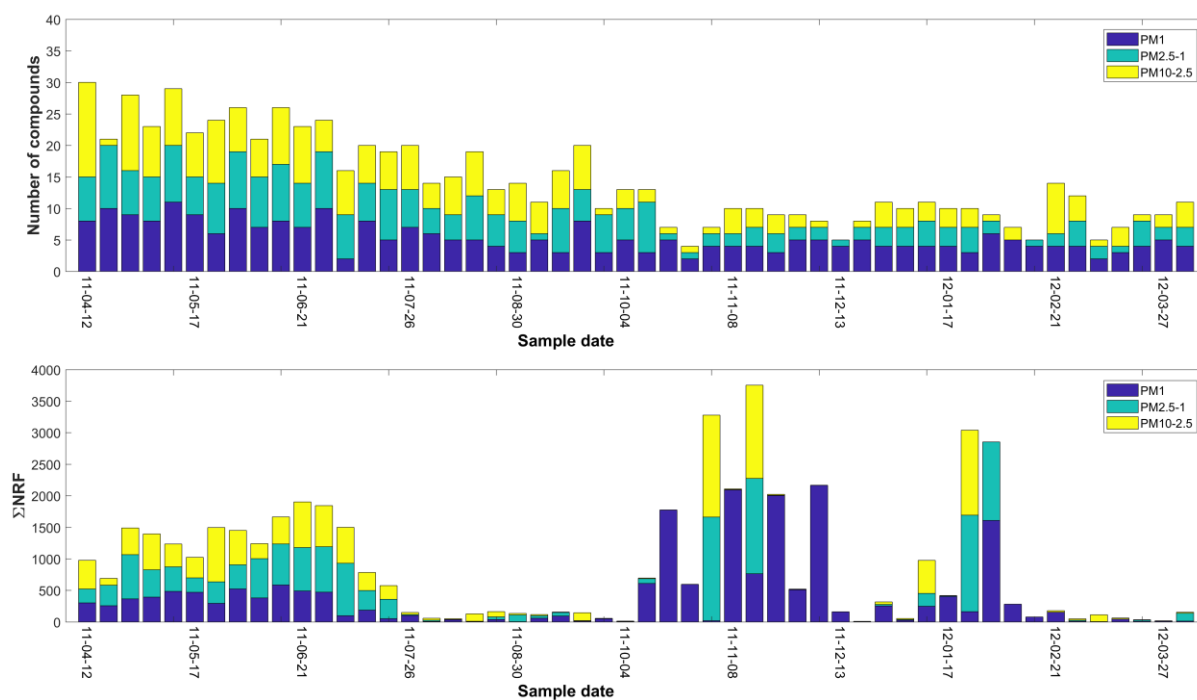
In Fig. 3, the total numbers of oxygenated species, (a) halogenated compounds, (b) as well as N- (c) and S-containing (d) organic compounds tentatively identified with their corresponding $\sum$ NRFs

in the three size ranges for each sample collected are presented. Booyens et al. (2015) indicated that oxygenated species were the most abundant species (~55 % of the Σ NRFs), which is reflected by each of the samples collected. Similar to the total number of polar organic compounds tentatively characterised and their associated Σ NRFs determined in the different size ranges in each sample (Fig. 2), no distinct temporal variations are observed for the total number of species tentatively characterised for each functional group and their corresponding Σ NRFs. However, the total numbers of species tentatively characterised for each of the functional groups and their corresponding Σ NRFs do reflect the period between 2 August 2011 and 4 October 2011 with significantly lower total numbers of species and corresponding Σ NRFs, as well as relatively higher total numbers of polar compounds and corresponding Σ NRFs for the sampling period 12 April 2011 to 12 July 2011 compared to the sampling period between 11 October 2011 and 4 April 2012.

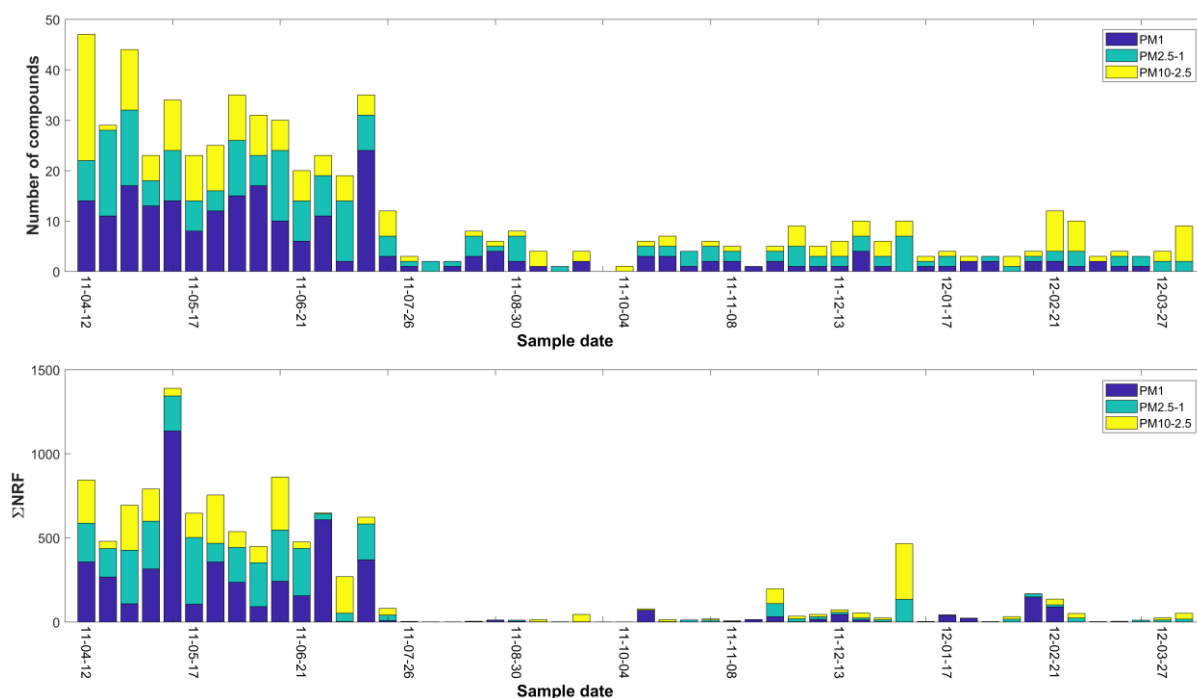
(a)



(b)



(c)



(d)

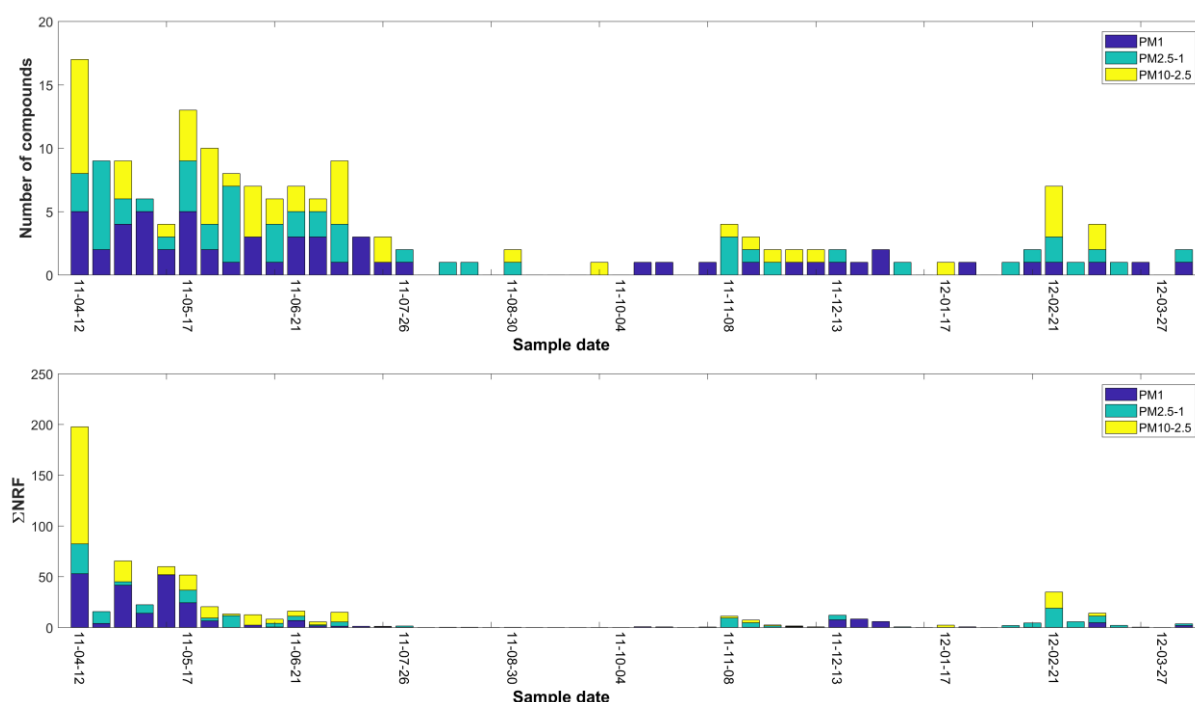


Fig. 3 The total number of oxygenated species (a), halogenated compounds (b), as well as N- (c) and S-containing (d) compounds identified and the sum of the normalised response factors (ΣNRF) in the three particle size ranges for each sample collected

3.2 Elucidation of temporal variations

In an effort to explain the temporal variations observed for the polar organic compounds, as well as the occurrence of significantly lower total number of polar organic compounds and corresponding ΣNRFs determined for the sampling period from 2 August 2011 to 4 October 2011, the influences of different source regions impacting Welgegend, meteorological conditions, and fire counts over the interior of southern Africa were explored.

3.2.1 Source region influence

Beukes et al. (2013) classified the major source regions impacting Welgegend according to air mass history as the regional background, Western Bushveld Igneous Complex, the Johannesburg-

Pretoria megacity, the Vaal Triangle, the Mpumalanga Highveld and the combined Anticyclonic Recirculation-Eastern Bushveld Igneous Complex. However, since only 24-hour ambient aerosol samples were collected once a week, the allocation of hourly back trajectories to air masses passing over all of these source regions defined by Beukes et al. (2013) was not feasible. Therefore, similar to Jaars et al. (2014), the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld source regions, which were identified as the regions with the highest anthropogenic impacts, were grouped together and are referred to as Area A in this paper. The Western and Eastern Bushveld Igneous Complex, as well as the anti-cyclonic source regions that lie on the anti-cyclonic recirculation path of air masses moving towards Welgegend (Fig. 1), were grouped together, which are referred to as Area B. The regional background source region was kept as defined by Beukes et al. (2013). In Fig. 1, the different source regions considered in this paper are presented. It is also evident from Fig. 1 that the major large point sources in Area A include coal-fired power stations and petrochemical plants, while pyrometallurgical smelters are major large point sources in Area B.

In total, 1 248 (52 samples $\times$ 24 hours) back trajectories were generated for the entire sampling period. Back trajectories were classified as passing over the different source regions defined in Fig. 1. Only back trajectories that had passed over one of the defined source regions were considered. Therefore, back trajectories that had passed over both anthropogenic source regions (Areas A and B) were not considered, while back trajectories were allocated as passing over the regional background if such trajectories did not pass over either Area A or B, or both Area A and B. According to these criteria, 69 % of all back trajectories could be classified as passing over just one of the three source regions defined. The back trajectories of air masses passing over the different source region are presented in Fig. 4. 19 % of the air mass back trajectories could be classified as passing over Area A, while 27 % and 23 % of the air mass back trajectories could be classified as passing over Area B and the regional background, respectively, for the entire sampling period. The reason for the lower percentage of air masses passing over Area A can be attributed to the persistence of the anti-cyclonic

circulation pattern over the interior of South Africa, which favours the arrival of air masses at Welgegund from the north to north-eastern sector.

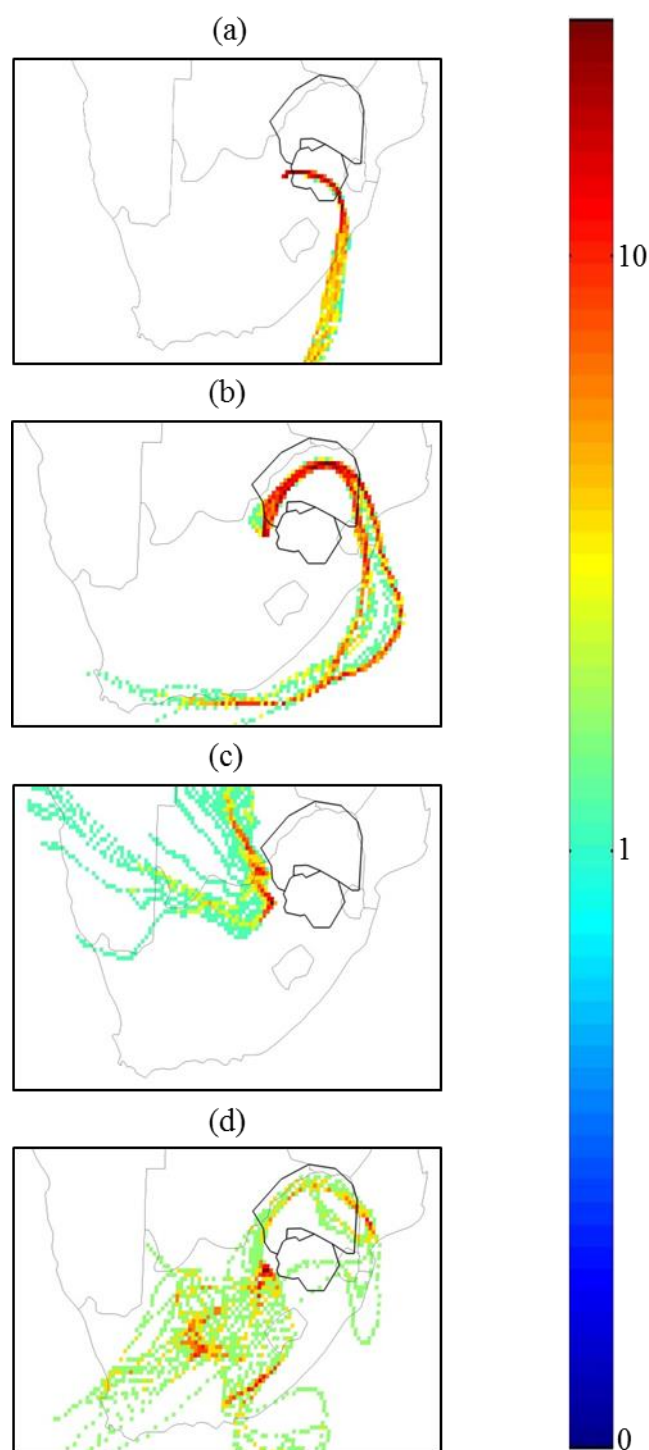


Fig. 4 Back trajectories of air masses passing over the defined source regions, i.e. (a) Area A, (b) Area B and (c) regional background; (d) indicates back trajectories for air masses passing over different source regions. The percentage of trajectories passing over $0.2^\circ \times 0.2^\circ$ grid cells are presented with colours, with red the highest percentage

In Fig. 5, the percentages of hourly arriving air masses passing over the different source regions during each 24-hour sampling period are presented. The influence of source regions on the total number of polar organic compounds and the corresponding Σ NRFs is not that evident. However, in section 3.1, it was indicated that it seems that the total numbers of polar organic compounds and the corresponding Σ NRFs were more consistent and relatively higher during the sampling period 12 April 2011 to 12 July 2011 compared to the sampling period 11 October 2011 to 4 April 2012. A comparison of the percentage of hourly arriving air masses passing over the different source regions for the sampling period between 12 April 2011 and 12 July 2011 and the sampling period between 11 October 2011 and 4 April 2012 does indicate more frequencies of air masses passing over Region A between 11 October 2011 and 4 April 2012. Therefore, it seems that a relatively higher total number of polar organic compounds and the corresponding Σ NRFs are associated with air masses passing over Area B and the regional background.

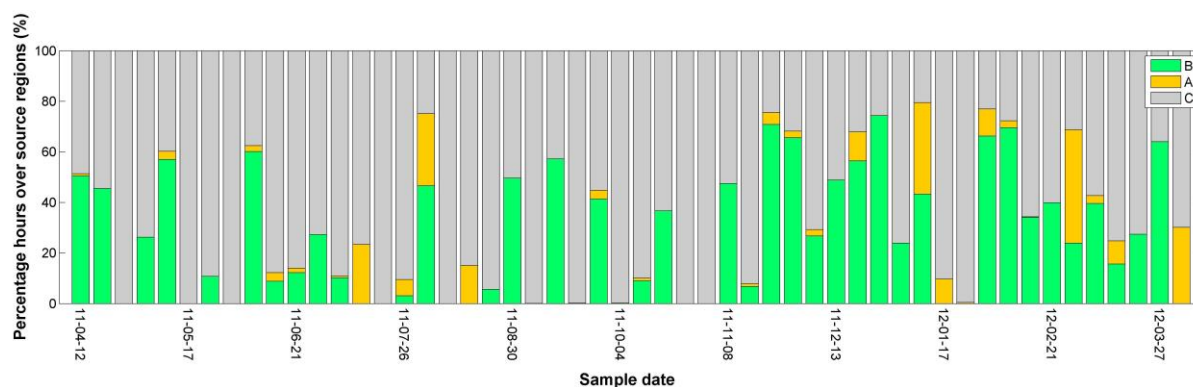


Fig. 5 Percentage of hourly back trajectories of air masses passing over source regions for each sample collected with A, B and C representing Area A, Area B and the regional background, respectively.

In Fig. 6, the total number of organic compounds and the corresponding Σ NRFs measured for air masses passing over the three source regions are presented. It is evident that the total number of polar organic compounds and the corresponding Σ NRFs were the highest in air masses passing over

Area B, second highest for the regional background and the lowest for air masses passing over Area A, which were between 20 and 40 % lower than the total number of polar organic compounds and the corresponding $\sum$ NRFs determined for Area B. The higher number of organic compounds and their associated higher concentrations associated with Area B can be attributed to the aging of air masses during the anti-cyclonic recirculation of primary emissions. Booyens et al. (2015) indicated that the highest number of organic compounds with the highest corresponding $\sum$ NRFs were oxygenated species that were considered to be indicative of secondary organic aerosol formation occurring in aged air masses influencing Welgegund. The relatively high concentrations of polar organic compounds in the regional background can also be attributed to secondary aerosol formation from natural emissions of VOCs, as well as to smaller cities and agricultural activities in this region. Furthermore, Welgegund is also affected by regional biomass burning events (Vakkari et al. 2014), and it was indicated that oxygenated organic particulates measured with an aerosol mass spectrometer correlated with biomass burning aerosols during the dry season (Tiitta et al. 2014). This will be further explored in a subsequent section.

The lower number of polar organic compounds with their corresponding $\sum$ NRFs in Area A can be attributed to fresher plumes from Area A arriving at Welgegund. Jaars et al. (2014) indicated that the highest aromatic VOC concentrations were associated with this source region, which was attributed to anthropogenic emissions in this region. Lourens et al. (2012) indicated that the Johannesburg-Pretoria megacity is relatively heavily polluted, while both the Vaal Triangle and the Mpumalanga Highveld source regions have been included in areas declared as pollution hotspots (national priority areas) by the South African government (Government Gazette 2005; Government Gazette 2007). However, due to this source region being in close proximity of Welgegund, these primary emitted VOCs have less time to form secondary organic aerosols (Özel et al., 2010). It is also evident from Figs. 2 and 3(a) that during the period characterised by relatively lower $\sum$ NRFs (11 October 2011 to 4 April 2012) instances of higher $\sum$ NRFs were associated with higher $\sum$ NRFs of oxygenated species. In addition, higher $\sum$ NRFs during this period were also associated with higher

Σ NRFs of halogenated compounds (Fig. 3(b)), which are also oxidised organic compounds indicative of aged air masses.

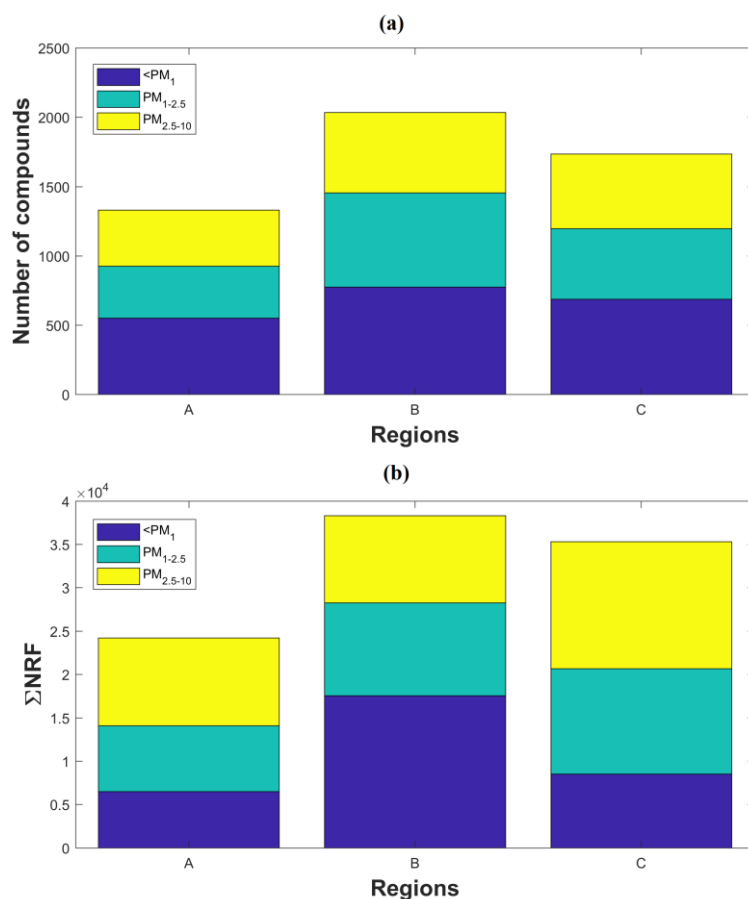


Fig. 6 (a) The total number of organic compounds and (b) the corresponding Σ NRFs for each of the defined source regions

From the discussion above, the total number of organic compounds and corresponding Σ NRFs for each sample presented in Fig. 2 can partially be attributed to differences in air mass histories. There is, however, no clear connection between the different source regions and the occurrence of a significantly lower total number of polar organic compounds and corresponding Σ NRFs determined for the sampling period from 2 August 2011 to 4 October 2011.

3.2.2 Meteorological conditions

As indicated in section 2.1, this region is characterised by distinct wet (middle October to April) and dry (May to middle October) seasons, while multiple inversion layers and anti-cyclonic recirculation are more pronounced during the winter months (June to August). Therefore, in an effort to evaluate the influence of meteorological conditions on the number of organic compounds determined and their corresponding $\sum$ NRFs, box-and-whisker plots of the temperature, relative humidity and soil moisture for each 24-hour sampling period were compiled, which are presented in Fig. 7. Since one 24-hour sample was collected once a week, precipitation events could not be directly correlated to the number of organic compounds determined and their corresponding $\sum$ NRFs. Therefore, soil moisture and relative humidity were considered to be indicative of precipitation. The meteorological data indicate the typical seasonal patterns for this region, i.e. higher temperatures observed for the period between late spring and early autumn, while relative humidity and soil moisture related to the distinct wet and dry seasons.

As indicated in sections 3.1 and 3.2.1, the total number of polar organic compounds and the corresponding $\sum$ NRFs were relatively higher during the sampling period 12 April 2011 to 12 July 2011, which coincides with late autumn and early winter. As previously mentioned, the colder months in this region are characterised by more pronounced inversion layers trapping pollutants near the surface, while an increase in emissions occurs due to an increase in household combustion and the occurrence of wild fires. Furthermore, the anti-cyclonic recirculation of air masses is also more pronounced, which could lead to an increase in pollutants from source regions. The sampling period 11 October 2011 to 4 April 2012, which had relatively lower total number of polar organic compounds and corresponding $\sum$ NRFs, coincided with the period between late spring and early autumn, which corresponds with the wet season. Although this period is characterised by higher temperatures, as well as increased relative humidity and soil moisture that can lead to increased biogenic emissions of organic compounds, it seems that the wet scavenging of polar organic particulates is more pronounced during this period. However, there were certain sampling days during this period when higher polar organic compound concentrations were measured, which could be

attributed to fewer occurrences of rain events. In addition, lower total number of polar organic compounds and corresponding Σ NRFs associated with higher temperatures, can also be attributed to increased blow-off sampling artifacts at higher temperatures (Geldenhuis et al. 2015). There is no clear correlation between the meteorological data and the occurrence of significantly lower total number of organic compounds and corresponding Σ NRFs determined for the sampling period from 2 August 2011 to 4 October 2011. This period, however, does coincide with the lowest relative humidity and soil moisture measurements.

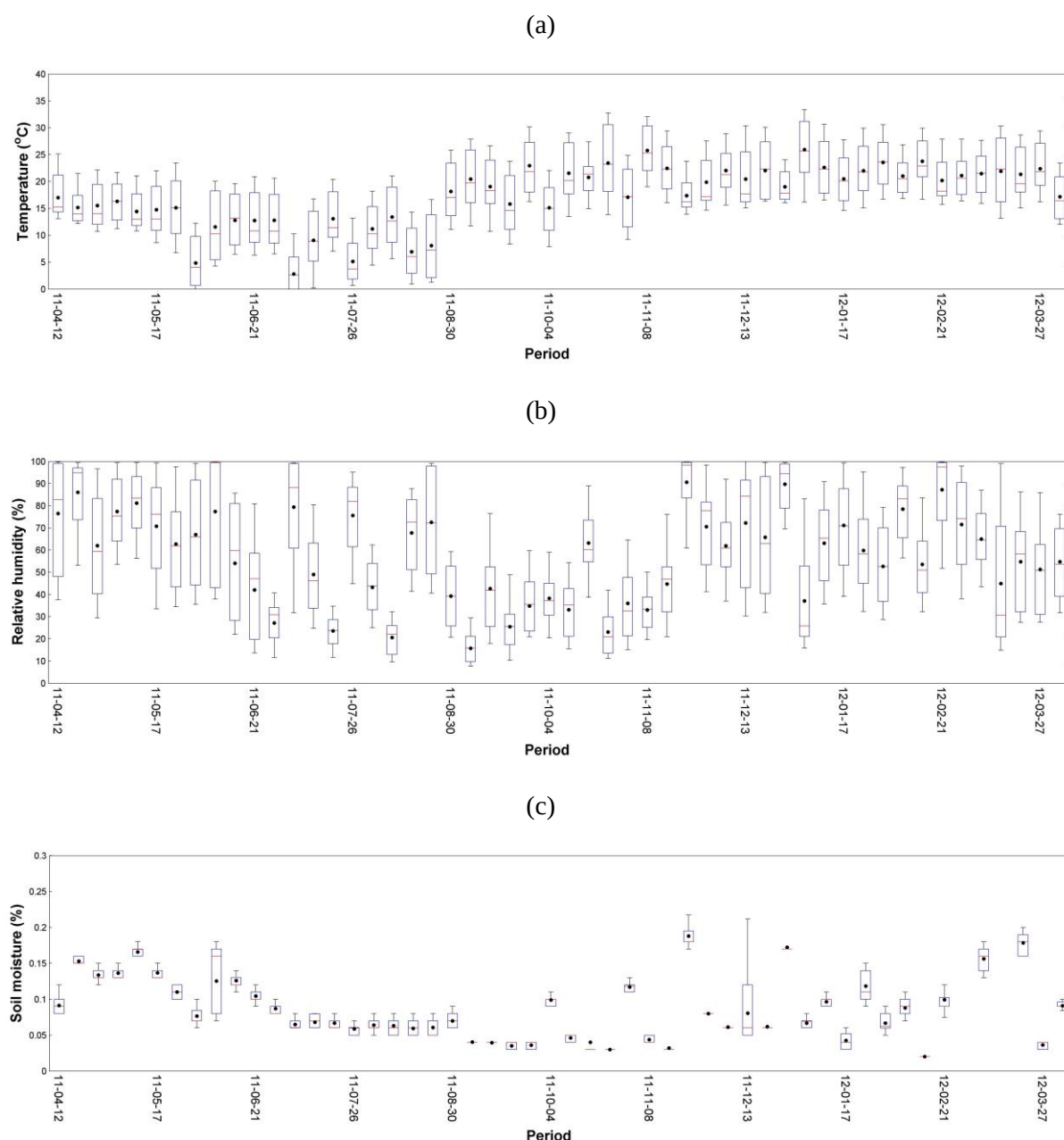


Fig. 7 Monthly variation of (a) temperature, (b) relative humidity, and (c) soil moisture for the entire measurement period. The red line of each box is the median, the blue dots the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers $\pm 2.7 \sigma$ (99.3 % coverage if the data has a normal distribution)

3.2.3 Fire counts

In Fig. 8, a map of MODIS burned area observations in southern Africa within a 1000 km radius of Welgegund for the entire sampling period is presented, which indicates the widespread

occurrence of wild fires for this region. Wild fire occurrences are predominant in the sector north-west to south of Welgegund, with significant wild fire occurrences in the eastern part of South Africa. It is evident that wild fires will have a significant impact on air masses arriving at Welgegund. In addition, it is also evident that within close proximity of Welgegund, i.e. a 100 km radius, wild fires occurring in all directions from Welgegund can have an influence on air masses arriving at Welgegund. In Fig. 9, the monthly numbers of fire counts (fire pixels) within a 1 000 km radius of Welgegund for a five-year period (a), i.e. 2009 to 2013 are presented in order to contextualise the number of fire counts during the sampling period in this study, while the number of fire counts within a 1 000 km radius of Welgegund during each 24-hour sampling period (b) are presented. Fig. 9 clearly indicate a significant number (MODIS fire pixels ranging in the orders of 10^4 and 10^5) of wild fires occurring within a 1 000 km radius of Welgegund. From the five-year period, it is evident that these wild fires mainly occur from May to October, which coincides with the dry season. It is also apparent that the number of wild fires peaked in August and September, i.e. the end of winter and beginning of spring, for the five-year period. Therefore, as indicated in section 3.2.1, the widespread occurrence of wild fires can be a significant source of organic compounds measured at Welgegund. Tiitta et al. (2014) indicated that biomass burning is the most important emission source in PM_{10} during the dry season.

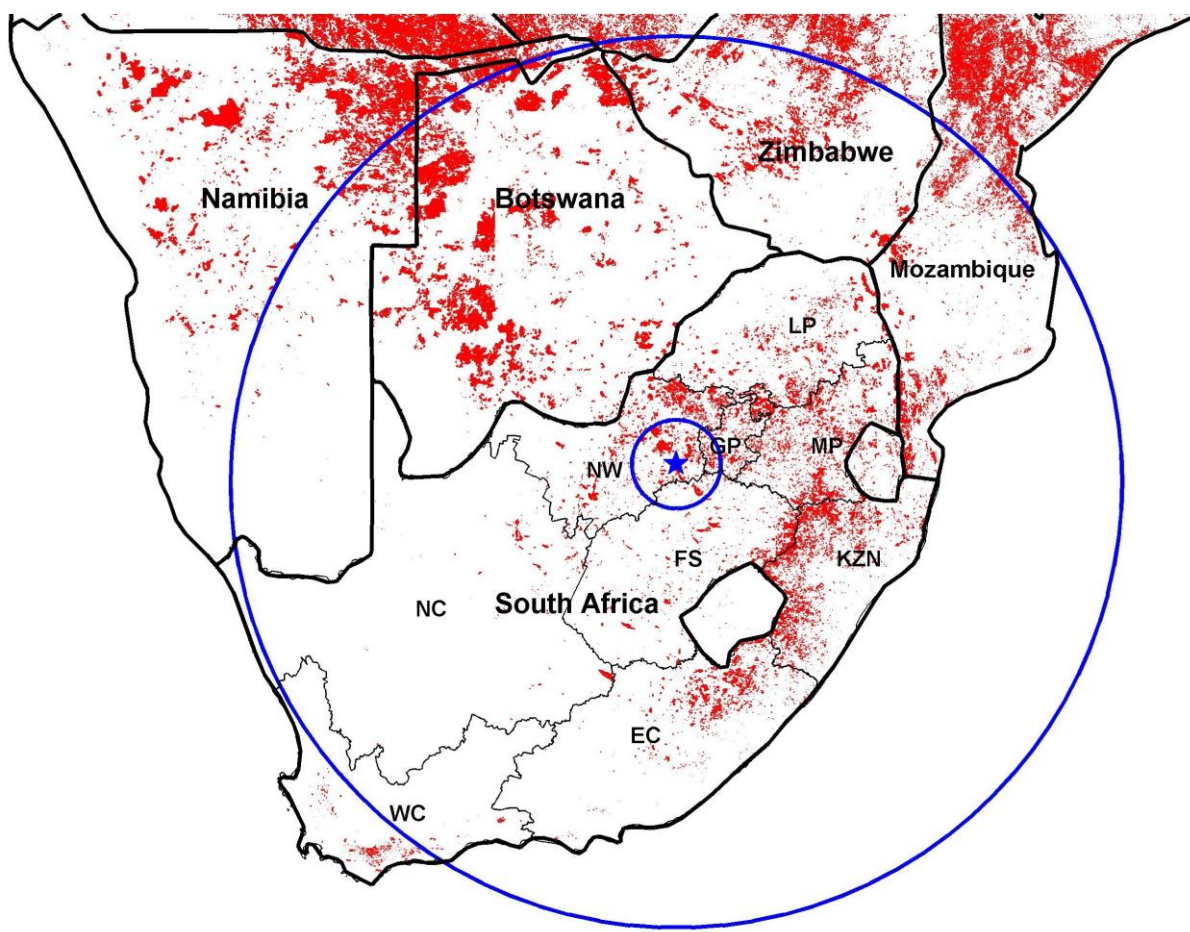


Fig. 8 Map of MODIS burned area observations in South Africa for the sampling period, with the blue star indicating the Welgegund measurement site, the larger circle the 1 000 km radius and the smaller circle the 100 km radius

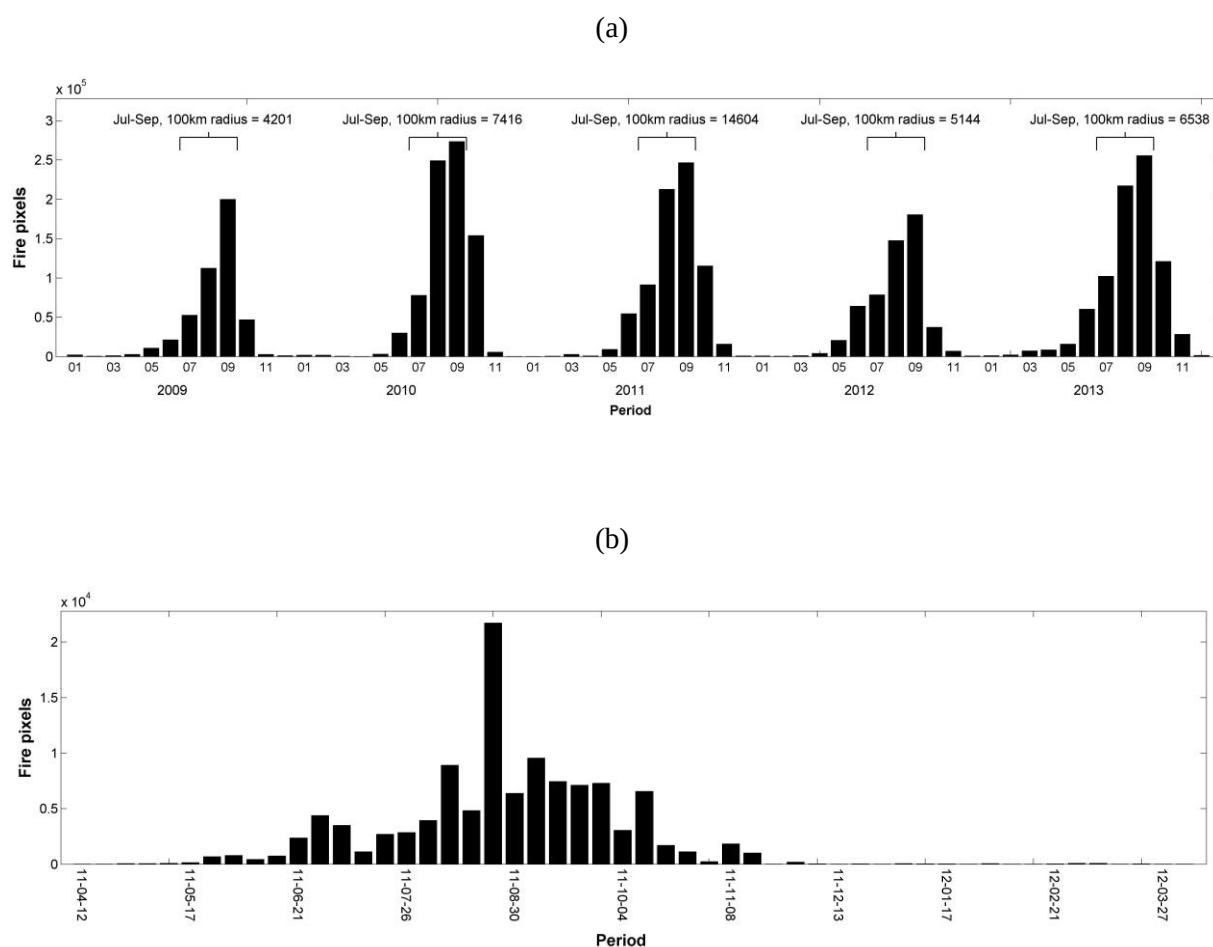


Fig. 9 Fire pixel counts representing the number of fires within a 1000 km radius from the Welgegund monitoring station (a) over a period of five years (2009 to 2013) and (b) for the entire sampling period

From Fig. 9(b), it is evident that the 2 August 2011 to 4 October 2011 period during which significantly lower total numbers of polar organic compounds and corresponding $\sum$ NRFs were measured (Fig. 2), coincided with the peak burning season months in August and September. There is, in particular, a significantly large number of fire counts observed for the 24-hour sample collected on 23 October 2011, during which the fire counts were more than double the fire counts determined for the other 24-hour samples collected during August and September. This concurrence between the period with significantly lower total number of polar organic compounds and corresponding $\sum$ NRFs, and the peak burning season months alludes to Welgegund being impacted by fresh biomass burning plumes, i.e. wild fires occurring in close proximity of Welgegund. From Fig. 8, it is evident that a

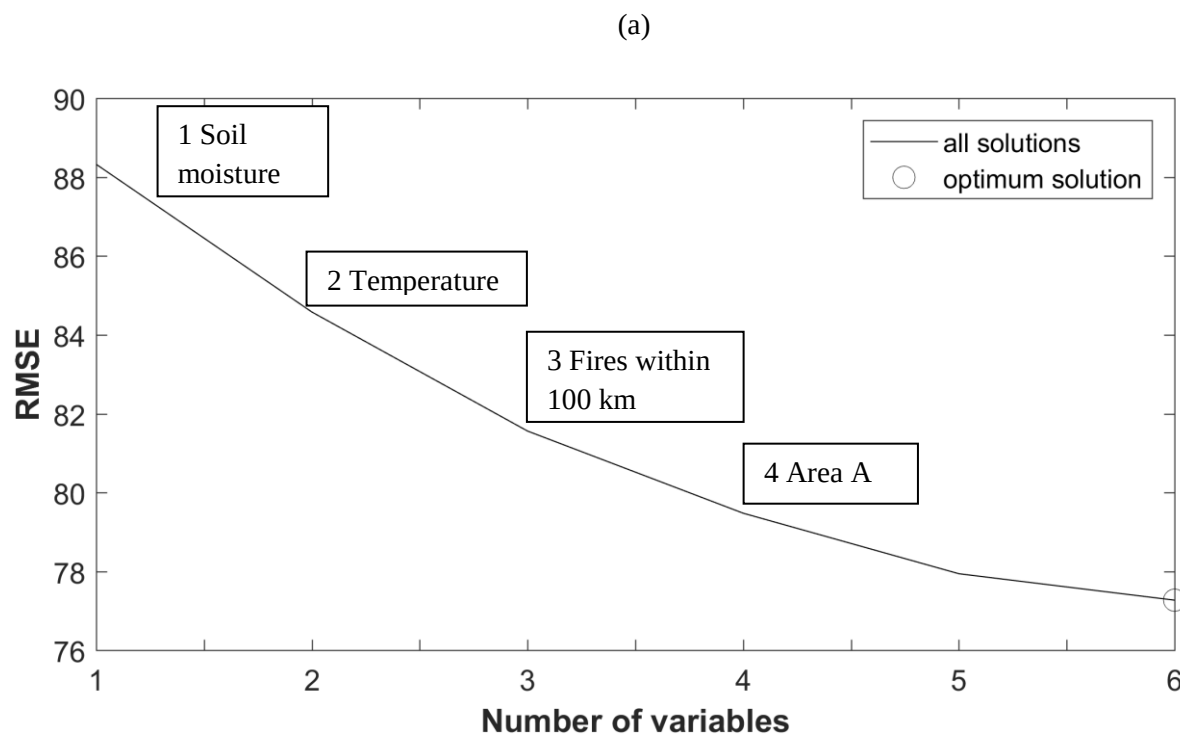
large number of wild fires occurred within close proximity of Welgegund (100 km radius,), while Fig. 9(a) also indicates that the numbers of fire counts within a 100 km radius of Welgegund for July to September in 2011 were significantly higher compared the number of fire counts during these months for the other four year presented in Fig. 9(a). It is expected that fresh biomass burning plumes would be characterised by a smaller number of secondary (oxidised) organic aerosols, since most of the VOCs associated with biomass burning would not have been transformed to secondary organic aerosols. Furthermore, it is also expected that organic aerosol compounds in fresh biomass burning plumes will mainly consist of non-polar hydrocarbon species that have not yet been oxidised to oxygenated-, halogenated-, N-containing or S-containing species (Özel et al. 2010). From Fig. 3(b), it is also evident that, although the corresponding Σ NRFs of halogenated compounds were lower from 2 August 2011 to 4 October 2011, the total number of halogenated compounds was not significantly lower during this period. This can possibly be attributed to the occurrence of potassium chloride (KCl) in the fresh smoke of burning savannah grass, which can react to form halogenated organic compounds (Aurela et al. 2016; Venter et al. 2017).

3.2.4. Multiple linear regression

From the discussions in the previous sections, it seems that the observed temporal variations for the total number of polar organic compounds and their corresponding Σ NRFs cannot be related to a specific single influencing factor, and depend on a combination of the influences of source regions, meteorology and wild fires. Furthermore, none of these factors could conclusively explain the occurrence of significantly lower total number of polar organic compounds and corresponding Σ NRFs determined for the sampling period from 2 August 2011 to 4 October 2011. Therefore, in an effort to quantify the influence of these factors on the total number of polar organic compounds and their associated Σ NRFs, multiple linear regression (MLR) was performed as an explorative tool by using the source regions (Region A, Region B and regional background), meteorological parameters (temperature, relative humidity, soil moisture) and fire counts as input data in order to indicate parameter interdependencies on the total number of polar organic compounds characterised. In Fig.

10(a), the root mean square error (RMSE) difference between the experimentally characterised and calculated total number of polar organic compounds, as a function of the number of interdependent variables included in the optimum MLR solution, is presented. The interdependence between six parameters resulted in the optimum decrease in RMSE, with soil moisture (as a proxy for precipitation), temperature and fire pixel counts within a 100 km radius and source region A resulting in more significant decreases in RMSE differences. The measure of optimisation was taken as at least 1 % contribution to the overall reduction of RMSE. In Fig. 10(b), the experimentally characterised total numbers of polar organic compounds are compared to the calculated total numbers of polar organic compounds, which indicate very good correlations between the experimentally characterised and the calculated total numbers of polar organic compounds. Differences between measured and calculated values could partially be ascribed to the exclusion of non-polar hydrocarbons in this study due to the polar extraction solvent utilised. The total number of polar organic compounds calculated from MLR mimics the differences observed for sampling periods identified in sections 3.2.1 to 3.2.3, i.e. 12 April 2011 to 12 July 2011, 2 August 2011 to 4 October 2011 and 11 October 2011 to 4 April 2012. The relatively good correlations for the 2 August 2011 to 4 October 2011 period with significantly lower total number of organic compounds, especially, indicate relatively high level of confidence in the statistical evaluation of the total number of polar organic compounds dataset. Therefore, according to MLR analyses of the dataset, the predominant parameters influencing the temporal variations observed can be ascribed to soil moisture (as a proxy for precipitation), temperature, the occurrences of wild fires within a 100 km radius and air mass movement over source region A. This statistical analysis substantiates the deductions made in sections 3.2.1 to 3.2.3 where it was indicated that the total numbers of polar organic compounds and associated semi-quantified concentrations were related to a combination of the influence of source regions, meteorology and the occurrence of wild fires within close proximity of Welgegund. In addition, negative correlations were calculated between the total numbers of polar organic compounds, and temperature, fires within a 100 km radius and air masses passing over source region A, which agree with the deductions made in sections 3.2.1 to 3.2.3. Lower total numbers of polar organic compounds were associated with air

masses passing over source regions A, higher temperatures (late spring to mid-autumn) and increases in wild fires occurring within close proximity of Welgegund.



(b)

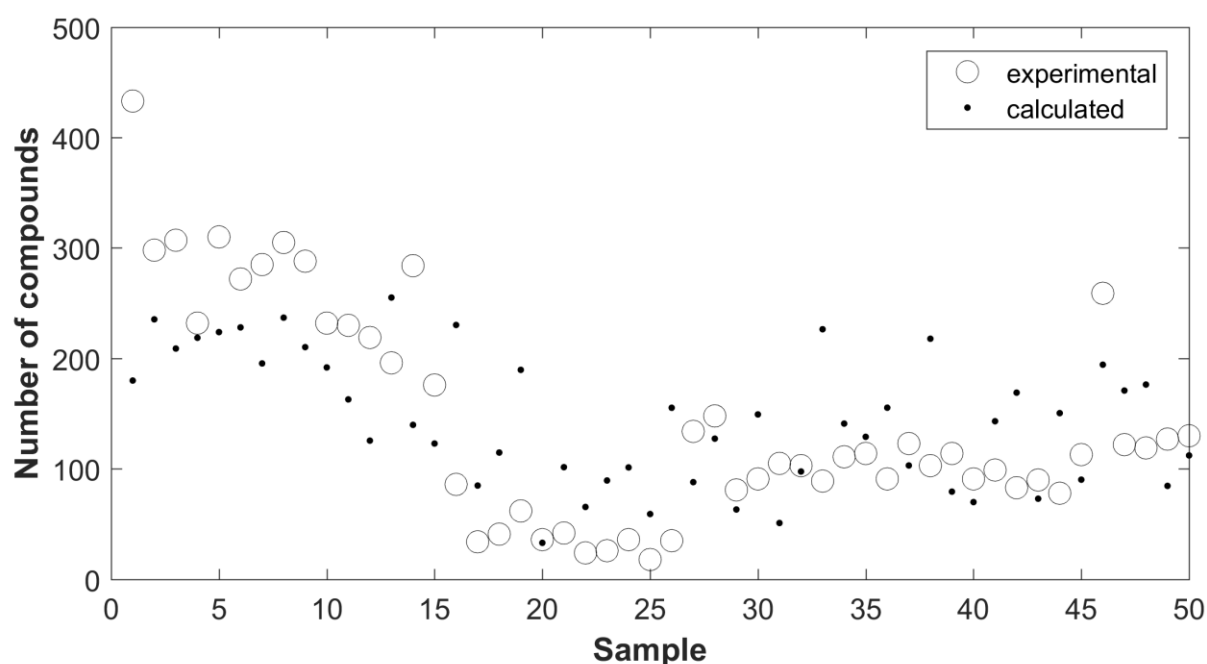


Fig. 10 (a) The optimum combination of independent variables to include in an MLR equation to calculate the dependant variable (total number of organic compounds) indicated by the root mean square error (RMSE) difference between the calculated and experimentally characterised total number of organic compounds, and (b) comparison between total number of polar organic compound calculated with MLR and experimentally characterised

4. Summary and conclusions

No distinct seasonal pattern was observed for the polar organic compounds tentatively characterised and their corresponding $\sum$ NRFs (semi-quantified concentrations), as well as for the total number of species tentatively characterised for each of the functional groups and their corresponding $\sum$ NRFs. However, there was a period coinciding with late winter and early spring with a significantly lower total number of polar organic compounds and corresponding $\sum$ NRFs, while it also seemed that the total numbers of polar organic compounds and their associated $\sum$ NRFs for the period coinciding with mid-autumn to mid-winter were relatively higher compared to the period from late spring to mid-autumn. Therefore, in an effort to elucidate the temporal variations, the influences of source regions, meteorology and burnt area pixels were investigated. Three source regions were identified, which

indicated that the relatively lower total number of polar organic compounds and corresponding Σ NRFs could be attributed to fresher plumes arriving at Welgegund from a source region comprising the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld, while relatively higher total numbers of organic compounds and the corresponding Σ NRFs were associated with aged air masses passing over the other source region and the regional background. Meteorological parameters indicated that the wet removal of aerosols contributed to lower total numbers of polar organic compounds and corresponding Σ NRFs, while increased anticyclonic recirculation and more pronounced inversion and stable stratified layers in winter contributed to the pollution entrapment and consequently higher total number of polar organic compounds and the corresponding Σ NRFs. Fire counts indicated large-scale biomass burning as an important source of polar organic aerosol compounds. The period with a significantly lower total number of organic compounds and corresponding Σ NRFs, which coincided with the peak burning months, was attributed to the influence of wild fires in close proximity of Welgegund. Fresher biomass burning plumes impacting Welgegund would mainly contain primary emitted VOCs and non-polar hydrocarbon aerosols.

Since the temporal variations observed could not be related to a specific influencing factor, but rather seemed to depend on a combination of the influences of source regions, meteorology and fire counts, MLR analysis was performed in an effort to quantify the influence of each of these factors on the total number of polar organic compounds and corresponding Σ NRFs. Furthermore, none of these factors could conclusively explain the period with a significantly lower total number of organic compounds and corresponding Σ NRFs. MLR indicated that the total numbers of polar organic compounds and associated semi-quantified concentrations were related to a combination of the influence of source regions, meteorology and the occurrence of wild fires within close proximity of Welgegund.

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Chapter 6: Characteristics of particulate organic nitrogen at a savannah-grassland region in South Africa

6.1 Author list, contributions and consent

Wanda Booyens¹, Johan P. Beukes¹, Pieter G. Van Zyl¹, Jose Ruiz-Jimenez², Matias Kopperi², Marja-Liisa Riekkola², Miroslav Josipovic¹, Ville Vakkari³, Lauri Laakso^{1,3}

¹Unit for Environmental Science and Management, North-West University, Private Bag X6001, 2520, Potchefstroom, South Africa

²Department of Chemistry, University of Helsinki, PO Box 55, 00014, University of Helsinki, Finland

³Finnish Meteorological Institute, PO Box 503, 00101, Helsinki, Finland

Contributions to the article

Contributions by the various co-authors were as follows. The work was done by the author **Wanda Booyens**, i.e. sample analysis, data processing, research and writing of the scientific paper, with the supervisors of this study, Pieter G. van Zyl and Johan P. Beukes assisting in the interpretation of data, writing of the article and also making conceptual contributions. Jose Ruiz-Jimenez, Matias Kopperi and Marja-Liisa Riekkola were involved with the extraction and analysis of samples in the chemistry laboratory of the University of Helsinki. Miroslav Josipovic assisted in the sampling at the Welgegund site. Lauri Laakso and Ville Vakkari assisted in establishing the Welgegund monitoring station and made conceptual contributions.

All the co-authors have been informed that the PhD will be submitted in article format and have given their consent.

6.2 *Formatting and current status of article*

The article was formatted in accordance with the journal specifications, to which it will be submitted, i.e. the **Journal of Atmospheric Chemistry**, a SpringerLink journal. The guide for authors that was followed in preparation of the article is available at http://www.springer.com/earth+sciences+and+geography/atmospheric+sciences/journal/10874?detailsPage=pltpci_1060574 [Accessed 12 November 2017]. At the time when this PhD was submitted for examination, this article had not yet been submitted for review, but the intention was to submit it soon thereafter.

Characteristics of particulate organic nitrogen at a savannah-grassland region in South Africa

Wanda Booyens¹, Pieter G. Van Zyl^{1*}, Johan P. Beukes¹, Jose Ruiz-Jimenez², Matias Kopperi², Marja-Liisa Riekkola², Miroslav Josipovic¹, Ville Vakkari^{3,4}, Lauri Laakso^{1,3}

¹Unit for Environmental Science and Management, North-West University, Private Bag X6001, 2520, Potchefstroom, South Africa

²Department of Chemistry, University of Helsinki, PO Box 55, 00014, University of Helsinki, Finland

³Finnish Meteorological Institute, PO Box 503, 00101, Helsinki, Finland

⁴Department of Physical Sciences, University of Helsinki, P.O. Box 64, 00014 University of Helsinki, Finland

*Corresponding author: Pieter G. van Zyl, e-mail: pieter.vanzyl@nwu.ac.za, tel: +27 (0) 18 299 2353, fax: +27 (0) 18 299 2350.

Abstract

Although atmospheric organic N compounds are considered important within the global N cycle, these species are not that well understood, as indicated by recent reviews. This can be attributed to a lack of consistency in sampling and measurement techniques, as well as their chemical complexity. Comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS) is an analytical technique that is utilised for the characterisation of complex samples. Therefore, the aim of this study was to assess the characteristics of organic N compounds identified and semi-quantified using GCxGC-TOFMS in ambient aerosol samples collected at a savanna-grassland background region and to determine possible sources. 135 atmospheric organic N compounds were

tentatively characterised and semi-quantified, which included amines, nitriles, amides, urea, pyridine derivatives, amino acids, nitro- and nitroso compounds, imines, cyanates and isocyanates, and azo compounds. Nearly half of the semi-quantified concentrations of organic nitrogen compounds was attributed to amines (51 %), while nitriles, pyridine derivatives and amides comprised 20 %, 11 % and 8 %, respectively, of the semi-quantified concentrations. The semi-quantified concentrations of the other organic N functional groups were very low with each contributing less than 2% to the semi-quantified concentrations. The temporal variations of amines, nitriles, amides and pyridine derivatives were similar to that observed for all the polar organic compounds, i.e. a period between 12 April 2011 and 12 July 2011 coinciding with the dry season was characterised by elevated semi-quantified concentrations of these species. These temporal variations were attributed mainly to meteorological parameters and the influence of local open biomass burning. Anthropogenic sources in the major source regions impacting air masses measured at Welgegund, as well as regional agricultural activities, were considered the major sources of amines, while the regional influence of household combustion was considered the main sources of nitriles and amides. Most of the other organic N functional groups were most likely related to the influence of local and regional agricultural activities.

Keywords: Atmospheric aerosols; organic aerosols; amines; agricultural; GCxGC-TOFMS; Welgegund

1. Introduction

Nitrogen (N) is one of the most important elements in the environment of the earth, which, together with carbon (C) and oxygen (O), is crucial for life (Keeney and Hatfield 2008). N is present in terrestrial- and marine ecosystems, as well as in the atmosphere. 78 % of the atmosphere consists of dinitrogen (N₂), which is the largest source of N. However, it has limited availability for biological processes and organisms (Galloway et al. 2004). N is converted into different chemical forms in

ecosystems through the biogeochemical cycle of N (or N cycle), which includes biological (e.g. microbial activity) and physical (e.g. reaction with O) processes (Kingston et al. 2000). The N cycle is very important for the N-uptake by ecosystems and the rate of important ecosystem processes (e.g. primary biogenic production and decomposition of biomass) (Butterbach-Bahl and Gundersen 2011). The natural N cycle, however, has been drastically disturbed by anthropogenic activities such as fossil fuel combustion and the use of artificial N fertilisers (Galloway et al. 2004). Typical N species in the environment include nitrogen oxide (NO), nitrogen dioxide (NO₂), ammonia/ammonium (NH₃/NH₄⁺), nitrate (NO₃⁻), nitrous oxide (N₂O) and organic nitrogen. N species of particular interest in the atmosphere that are well studied and understood include N₂O, due to its contribution to global warming, as well as NO and NO₂ that are usually associated with potential health impacts, acid deposition (oxidised NO₂ to NO₃⁻) and photochemical O₃ production (Yamulki et al. 1997, Ng et al. 2017; Laban et al. 2017). In addition, NH₄⁺ in particulate matter (PM), which is an important acid-neutralising species in the atmosphere, is also well quantified (Lee et al. 2003). However, although atmospheric organic N compounds are considered important, these species are not that well understood (Cape et al. 2011) and not routinely assessed (Cornell 2011).

Reviews by Neff et al. (2002) and Cornell et al. (2003) indicated the significance of organic N to total atmospheric N. Atmospheric organic N compounds occur in the gas, particulate and aqueous phases. A few gaseous organic N species are considered significant (e.g. peroxyacyl nitrates, HCN, HNCO, CH₃CN and alkyl nitrates with low molecular weights), while organic N in the particulate and aqueous phases is considered to be the main organic N species important to the global atmospheric N budget (Altieri et al. 2009; Cape et al. 2011; Jickells et al. 2013). Organic N plays an important role in regulating the environmental nutrient supply, while an excess can be toxic (Özel et al. 2011). The impacts of organic N on biogeochemistry, ecosystems and human health are well documented (Cornell 2011). Numerous studies have been conducted that indicate the importance of organic N to new particle formation and particle growth, especially studies relating to the role of amines in secondary particulate

formation (Facchini et al. 2008; Ge et al. 2011; Almeida et al. 2013). Organic N species are also considered to be important to the long-range transport of N (Gorzelka and Galloway 1990; Neff et al. 2002) due to their removal process being less effective compared to NO_3^- and NH_4^+ that are usually deposited closer to their sources, (Cornell 2011). Certain organic N compounds, such as isocyanates, nitroamines and nitrosamines are also considered toxic and carcinogenic, presenting serious health concerns, while it is generally considered that the addition of N to a hydrocarbon compound, e.g. polycyclic aromatic hydrocarbons (PAHs), can increase its carcinogenic effects (Arey et al. 1988; Özel et al. 2010). Lee and Wexler (2013) also recently presented a comprehensive review on the toxicity associated with atmospheric amines. In addition, organic N compounds, e.g. amines and amino acids, are important precursor species in the formation of atmospheric brown carbon (Galloway et al. 2008; Nozière et al. 2009). The importance of atmospheric brown carbon has been indicated in various recent studies (Andreae and Gelencsér 2006; IPCC 2013; Laskin et al. 2014), due to its influence on light scattering and the subsequent impacts on climate change. A recent modelling study indicated that 20 to 70 % of black carbon forcing can be attributed to brown carbon forcing (Lin et al. 2014).

Atmospheric particulate organic N compounds are primarily emitted from numerous natural and anthropogenic sources (as indicated by Cape et al. 2011 and references therein) or can be formed in the atmosphere as secondary pollutants, e.g. photochemical reactions of hydrocarbons and nitrogen oxides (Roberts 1990; Borduas 2015). Jickells et al. (2013) indicated that, according to air mass history, four particular sources are considered to be important, i.e. soil dust (e.g. Mace et al. 2003a), biomass burning (e.g. Zamora et al. 2011), marine emissions (e.g. Mace et al. 2003b), as well as anthropogenic and agricultural sources (Mace et al. 2003a; Chen et al. 2010). In addition, vegetation (biogenic emissions) can also be an important source of organic N (Ge et al. 2011). The size distribution of particulate organic nitrogen can also be related to sources. Coarse mode particulates ($>1\ \mu\text{m}$) are usually associated with primary sources (e.g. soil dust and marine emissions), while fine fraction PM ($<1\ \mu\text{m}$) typically results

from secondary aerosol formation, i.e. gas-to-particle conversion associated with combustion (e.g. biomass burning and coal-fired power plants) (Raes et al. 2000).

Important factors relating to atmospheric organic N species being understudied relate to the lack of consistency in sampling and measurement techniques, as well as their chemical complexity, i.e. large number of different organic N compounds (Cape et al. 2011). At present, there is a great diversity in sampling and analytical methods for organic N in aerosols (Cornell 2011), while PM comprises thousands of organic compounds with various differences in chemical and physical properties (Goldstein and Galbally 2007) with only very few compounds identified (Booyens et al. 2015). These factors cause major difficulties in addressing the biogeochemical and ecological role of atmospheric organic N (Cape et al. 2011). In general, two strategies are applied, i.e. analysis of specific organic N species or performing bulk analysis. Compounds analysed previously in individual studies include amines, amino acids, urea, nitrophenols, alkyl amides, N-heterocyclic alkaloids and organic nitrates (Jickells et al. 2013). In bulk analysis, which includes filter sampling or near real-time sampling, e.g. aerosol mass spectrometry (AMS), the total concentrations of organic N is determined. This measurement technique gives information relating to the general chemical composition, oxidation state and reactivity of these species (Cape et al. 2011). However, the bulk analysis of aerosol samples provides limited information on the actual character of individual organic N compounds, sources of these species and their impacts on the environment. Furthermore, filter sampling of aerosols with subsequent offline analysis provides detailed analysis of some classes of organic N and has not been able to identify or quantify the full range of material identified (Cape et al. 2011). Therefore, analytical techniques with more precise speciation are required for bulk samples. One such method entails the characterisation of organic atmospheric aerosols collected on filters with comprehensive two-dimensional gas chromatography coupled with a time-of-flight mass spectrometer (GCxGC-TOFMS) (Lewis et al. 2000; Welthagen et al. 2003; Alam et al. 2013), which is a powerful instrument for the chemical characterisation of organic compounds in complex matrices.

Most studies conducted on atmospheric organic N are related to the water-soluble organic N fraction in aerosols and precipitation with, especially, organic N deposition associated with precipitation being studied extensively (Özel et al. 2010; Cornell 2011). Limited studies have been conducted utilising GCxGC analysis (or GC analysis in general) to determine organic N in aerosols (Özel et al. 2011). Booyens et al. (2015) and Booyens et al. (2017) recently utilised GCxGC-TOFMS for the first time in South Africa to tentatively identify and semi-quantify organic compounds in ambient aerosols collected on filters for three different size fractions (PM_{10} , $PM_{2.5-10}$ and $PM_{2.5}$) at a regional background site, i.e. Welgegund situated in the grassland-savannah region. In view of the importance of atmospheric organic N, and considering that these species are currently understudied as indicated above, the aim of this study was to assess the characteristics of organic N compounds in ambient aerosols collected at Welgegund and to determine possible sources. In addition, according to the knowledge of the authors, this is the first study in which a comprehensive number of particulate organic N compounds are tentatively characterised and semi-quantified in southern Africa.

2. Measurement location and methods

2.1 Site description

The Welgegund monitoring station (latitude 26°34'10"S, longitude 26°56'21"E, 1480 m AMSL) is a comprehensively equipped atmospheric monitoring located within the South African Highveld approximately 100km west of Johannesburg on a commercial farm. The site is a regionally representative background site with no direct impacts from large pollution sources in close proximity. It is, however, impacted by plumes passing over the major anthropogenic source regions in the interior of South Africa. A number papers on atmospheric measurements conducted at Welgegund have been published, wherein detailed descriptions of measurements conducted (Petäjä et al. 2013; Beukes et al. 2015; Räsänen et al. 2016), geographical and bioregion location (Booyens et al. 2015; Jaars et al. 2016),

and the major source regions affecting Welgegund (Beukes et al. 2013; Jaars et al. 2014) have been presented.

2.2 Sampling and analysis

The methodology developed by Booyens et al. (2015) and Ruiz-Jimenez et al. (2011A) was applied for the determination of organic N compounds in 52 ambient atmospheric aerosol samples collected at Welgegund. Briefly, 24-hour ambient aerosol samples in the PM₁, PM_{2.5-1} and PM_{10-2.5} size ranges were collected on quartz filters once a week from 12 April 2011 until 4 April 2012 with a Dekati PM₁₀ cascade impactor at a flow rate of 30 L/min. Filters were extracted utilising dynamic ultrasonic-assisted extraction and analysed with a LECO Pegasus 4D two-dimensional gas chromatograph coupled to a time-of flight mass spectrometer (GCxGC-TOFMS). The characterisation and semi-quantification of organic compounds are discussed in detail in Booyens et al. (2015). Organic N compounds characterised are considered to be tentatively identified species due to the less restrictive positive characterisation parameters applied (Booyens et al. 2015). The concentrations of the organic N compounds tentatively characterised were expressed as response factors (RF) in relation to the internal standard (1-1'binaphthyl), which were calculated by: $RF = (A_{ci} / A_{IS})$ (A_{ci} = peak area of the compound; A_{IS} = peak area of the internal standard). RFs were normalised per volume of air sampled and presented as the sum of the normalised RF of different organic (N) compounds ($\sum NRF$). The 1-1'binaphthyl internal standard was also used by Ruiz-Jimenez et al. (2011A) and Ruiz-Jimenez et al. (2011B) to semi-quantify N organic compounds.

3. Results and discussion

In Fig. 1, the total number of organic N species tentatively identified for all the samples collected with their corresponding $\sum NRF$ s in the three size ranges are contextualised in relation to the other functional group categories. In total, 135 organic N compounds could be tentatively characterised in all

three size ranges that contributed 13 % of the total number of compounds tentatively characterised in all three size ranges, while organic N compounds contributed to 12 % of the total $\sum$ NRFs for all the compounds tentatively identified. In the zoomed-in figure, the total numbers of each of the organic N functional groups, i.e. amines, amides, amino acids, azo-compounds, imines, cyanates, isocyanates, nitriles, nitro, nitroso, pyridine derivatives and urea, tentatively identified, are presented with their respective $\sum$ NRFs. As indicated by Booyens et al. (2015), all the pyridine compounds identified in the samples derivatised with pyridine were excluded. The largest number of organic N species tentatively identified in all size fractions was amines (29 % of total number of organic N species), which were also the most abundant species as indicated by their respective combined $\sum$ NRFs (51 % of total $\sum$ NRFs of all organic N species). According to the $\sum$ NRFs, nitriles were the second most abundant species (20 % of total $\sum$ NRFs of all organic N species), while pyridine derivatives and amides also have relatively higher $\sum$ NRFs (11 and 8 % of total $\sum$ NRFs of all organic N species, respectively). In addition, a relatively large number of pyridine derivatives (20 % of total number of organic N species) species was tentatively characterised. The semi-quantified concentrations of all the other organic N species were very low. Each of these organic N functional groups tentatively characterised will be discussed in detail in subsequent sections.

In a study conducted by Özel et al. (2010) that characterised and semi-quantified organic N compounds in PM_{2.5} samples collected in an urban area in Birmingham, England using DTD(direct thermal desorption)-GCxGC-TOFMS, 114 organic N compounds were identified. Of the total number of organic samples detected in each sample, 2 to 7 % of the species were organic N. Özel et al. (2010) indicated that ~33 % of organic N were nitriles, 14 % were amides, 7 % were amines and 6 % were nitro compounds. Ochiai et al. (2007) tentatively characterised 15 organic N species with TD-GC×GC-NPD(-nitrogen phosphorous detector)/qMS(quadropole MS) for aerosol samples collected in the 0.058 µm size range at a roadside crossing in Kawasaki, Japan, which included five nitriles, four alkaloids, two quinolines, one amide, one amine, one pyridine and one azole. In addition, Schnelle-

Kreis et al. (2005) utilised DTD-GC_xGC-TOFMS to characterise and semi-quantify a series of nitriles among other organic compounds for PM_{2.5} samples collected in Augsburg, Germany.

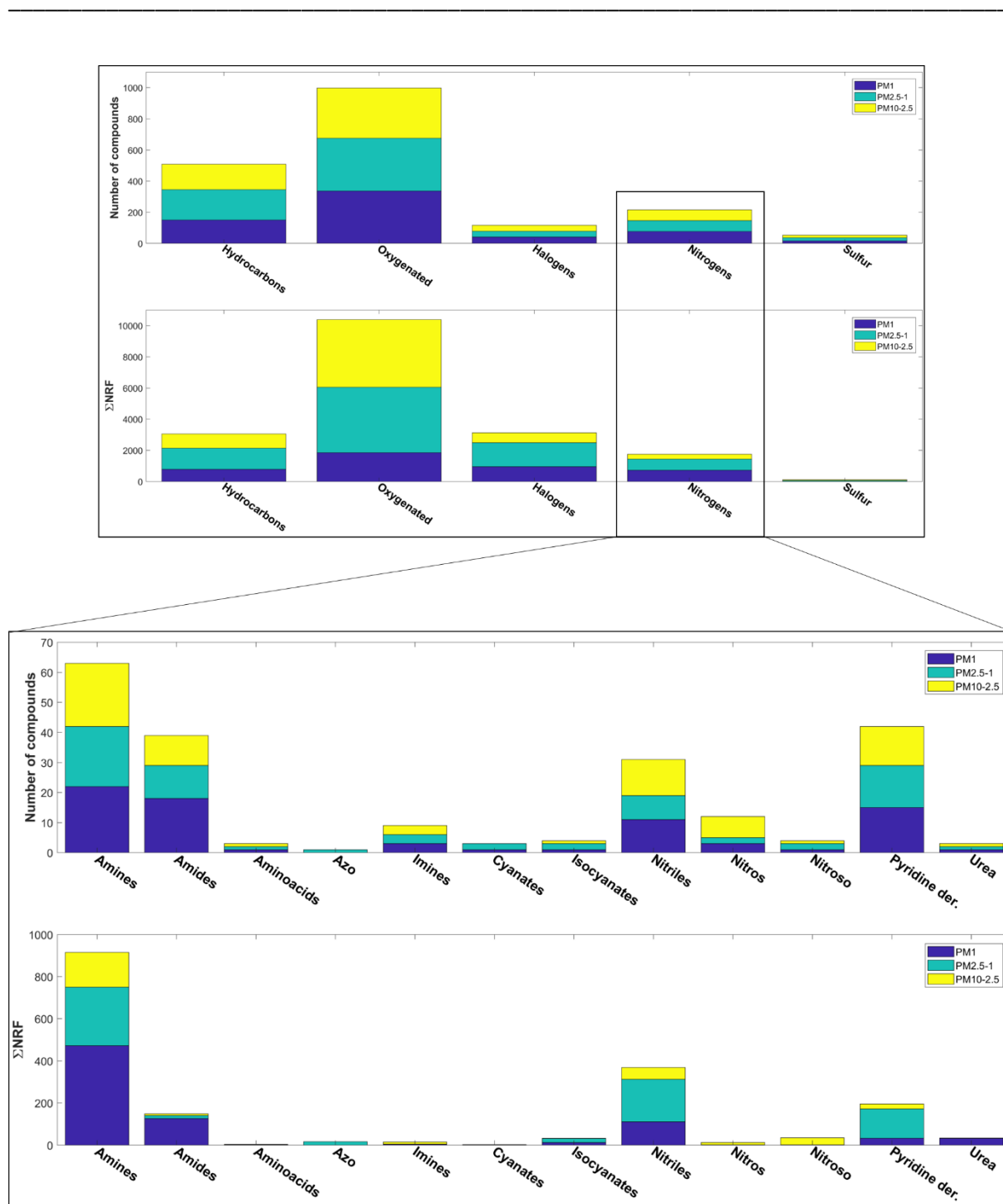


Fig. 1 Total number of compounds tentatively identified with their associated ΣNRF s for each of the functional group categories in the three particle size ranges with the extracted figure concentrating on the different nitrogen-containing functional groups (Booyens et al. 2015)

3.1 Amines

Although atmospheric amine species have been studied more extensively compared to other atmospheric organic N species, as indicated by a comprehensive review by Ge et al. (2011), these species are still considered understudied, especially studies related to their atmospheric chemistry. The amine functional group is considered to be the organic derivative of inorganic NH_3 with at least one hydrogen atom replaced by an alkyl group. Similar to the basic character of NH_3 , due to the lone pair of electrons on the N atom, which dominates the chemistry of NH_3 , amines are also basic compounds (Murphy et al. 2007). Therefore, atmospheric amine species are also important to neutralise acidic species in the atmosphere (Ge et al. 2011). In addition, as mentioned previously, atmospheric amines play an important role in secondary organic aerosol (SOA) formation (Murphy et al. 2007). Almeida et al. (2013), for example, recently indicated that dimethyl amine increased particle growth formation rates by more than 1 000 fold compared to ammonia. Therefore, considering that Conradie et al. (2016) indicated an increase in the acidity in rain water samples collected over the north-eastern interior of South Africa (which included the Highveld) during the last decade, as well as studies by Vakkari et al. (2013) and Hirsikko et al. (2012) indicating record-high frequencies of nucleation events in the Highveld region, these species are important for this region.

Anthropogenic sources dominate the emissions of amines. The main anthropogenic sources of atmospheric amines, as identified by Ge et al. (2011), include livestock and animal husbandry, industry and combustion, composting operations, automobiles and other human activities (e.g. sewage, cooking and charbroiling, corrosion inhibitors, tobacco smoke, indoor textile, pesticides). Major natural sources identified include the ocean, soil, biomass burning and vegetation. As mentioned above, Welgegund is influenced by the major anthropogenic source regions in the interior of South Africa, with many of the anthropogenic activities listed here occurring in these source regions. Furthermore, since Welgegund is located on a commercial farm, animal husbandry/livestock (cattle and sheep) could also be a local source of amine species measured.

In total, 63 amines were tentatively characterised in all three size fractions. As indicated above, the largest number of organic N species identified were amine compounds, for which their respective combined Σ NRFs also indicated significantly higher semi-quantified concentrations compared to the other organic N species characterised in this study. Booyens et al. (2015) indicated that the Σ NRFs of amines in the PM₁ size fraction are especially significant since it contributes approximately 59 % to the total Σ NRFs of all the organic compounds measured in the PM₁ size fraction. One specific amine compound, i.e. 2-methyl-2-propanamine, contributed 25 % of the total Σ NRF of amines in the PM₁ size fraction, which occurred in the PM₁ size fraction of many of the samples collected.

In Fig. 2, the total number of amines tentatively identified and their corresponding Σ NRFs in the three size ranges for each sample collected during the entire sampling period are presented. No distinct seasonal pattern for the total number of amines and their Σ NRFs is observed in Fig. 2. The temporal variations of amines do, however, correspond with the three different periods indicated by Booyens et al. (2017) for all polar organic aerosols, as well as for all N-containing organic compounds, i.e. the period between 2 August 2011 and 04 October 2011 (late winter to early spring) with a significantly lower total number of amines and corresponding Σ NRFs, as well as a relatively higher total number of amines and corresponding Σ NRFs for the sampling period 12 April 2011 to 12 July 2011 (mid-autumn to mid-winter) compared to the sampling period between 11 October 2011 and 4 April 2012 (late spring to mid-autumn). Booyens et al. (2017) attributed these temporal variations to source region influence, meteorological parameters and the influence of open biomass burning. The period with a significantly lower total number of amines and corresponding Σ NRFs correspond with the peak open biomass burning season in this region. Booyens et al. (2017) ascribed these significantly lower concentrations of polar organic compounds to Welgegund being impacted by fresher biomass burning plumes containing mainly primary emitted VOCs and non-polar hydrocarbon aerosols. Furthermore, meteorological parameters indicated that the period with a relatively higher total number of polar organic compounds and corresponding Σ NRFs was attributed to a decrease in wet removal during the

dry season, which can be especially significant for amine compounds that are generally considered to be water-soluble. In addition, the occurrence of more pronounced inversion layers could also contribute to the build-up of possible local amine emissions from sources such as animal husbandry.

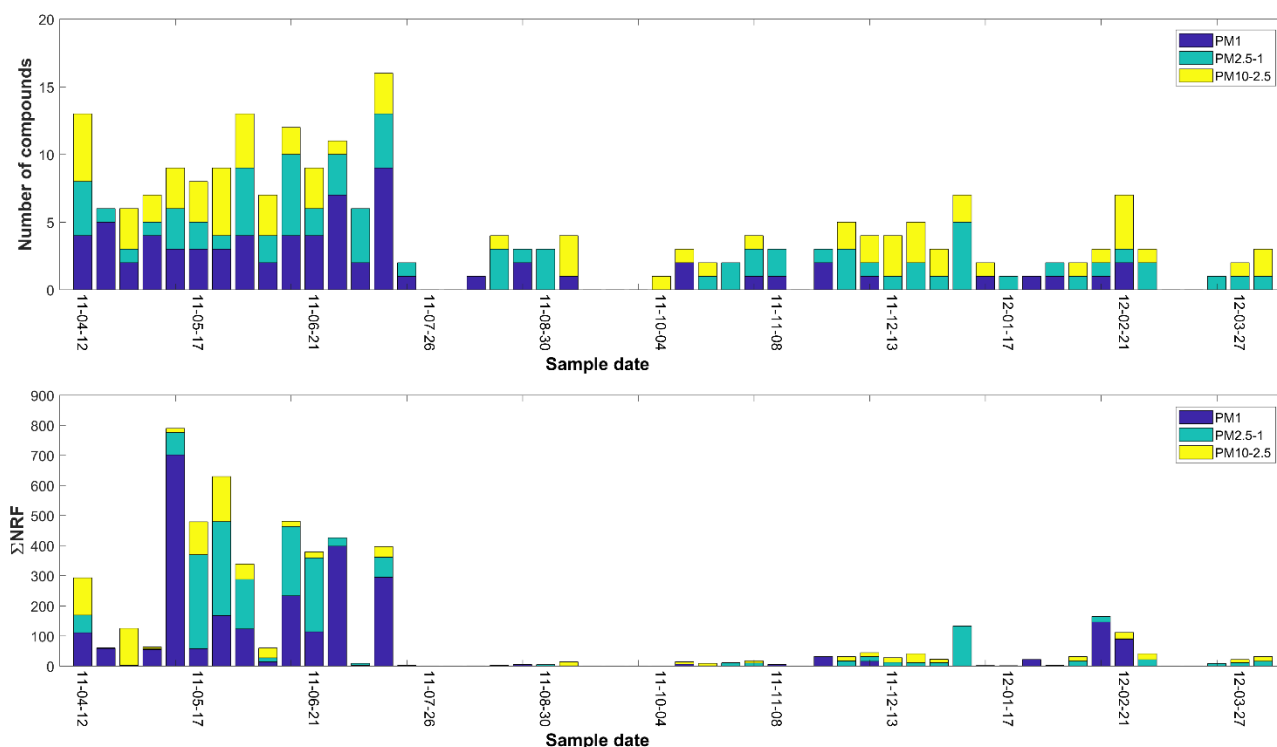


Fig. 2 Total number of amines identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

3.2 Nitriles, amides and urea

The main sources of organic nitriles and amides in the atmosphere are considered to be biomass burning and cooking (Simoneit et al. 2003; Cape et al. 2011), while Özel et al. (2011) also attributed additional sources of these species in air masses measured in a city centre in England. Additionally, amides can also be formed from atmospheric accretion reactions (reactions of organic compounds with each other and/or other atmospheric species to form products that are higher in molecular weight and lower in volatility) of organic acids with amines and ammonia (Barsanti and Pankow, 2006) and the

degradation processes of amines (Nielsen et al. 2012). As mentioned above, nitriles were the second most abundant species, while amides also had relatively higher $\sum$ NRFs. In total, 31 nitrile and 39 amide compounds were tentatively characterised in all three size fractions. Although more amide species were characterised compared to nitrile compounds, the $\sum$ NRFs of amides were significantly lower. According to the semi-quantified concentrations, amides occurred predominantly in the PM₁ size fraction, while nitriles had relatively higher concentrations in the PM_{2.5-1} size fraction.

In Fig. 3 and 4, the total number of nitriles and amides tentatively identified in the three size ranges for each sample collected during the entire sampling period are presented, respectively, with their corresponding semi-quantified concentrations. Similar to amines, the temporal variations of nitriles and amides also correspond with three periods observed for all polar organic aerosols and all N-containing organic compounds (Booyens et al. 2017). However, the total number of amides and nitriles with their corresponding $\sum$ NRFs were significantly lower for the period between 11 October 2011 and 4 April 2012 (wet season) than the period from 12 April 2011 to 12 July 2011 (dryer period), with no nitriles and amides being detected in a few samples collected during the wet period. Household combustion for space heating and cooking is a major source of atmosphere pollutants in South Africa. Chiloane et al. (2017) recently indicated the regional impact of household combustion on black carbon in the north-eastern interior of South Africa, while Venter et al. (2012) indicated the influence of household combustion on PM₁₀ measured in the industrialised Western Bushveld Igneous Complex that is also one of the major source regions impacting Welgegund. Furthermore, the regional impacts of household combustion from towns and cities within a 50 to 100 km radius will also influence air masses measured at Welgegund. Therefore, household combustion could be a major source of nitrile and amide compounds measured at Welgegund.

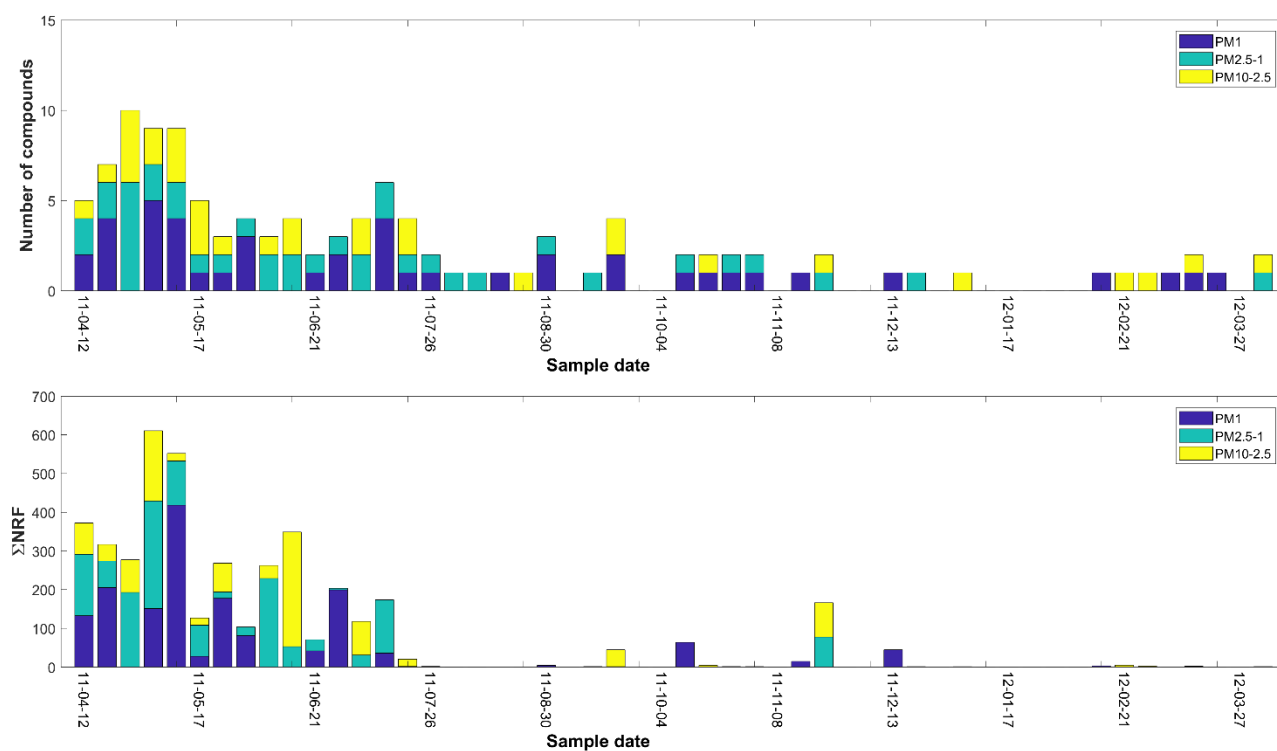


Fig. 3 Total number of nitriles identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

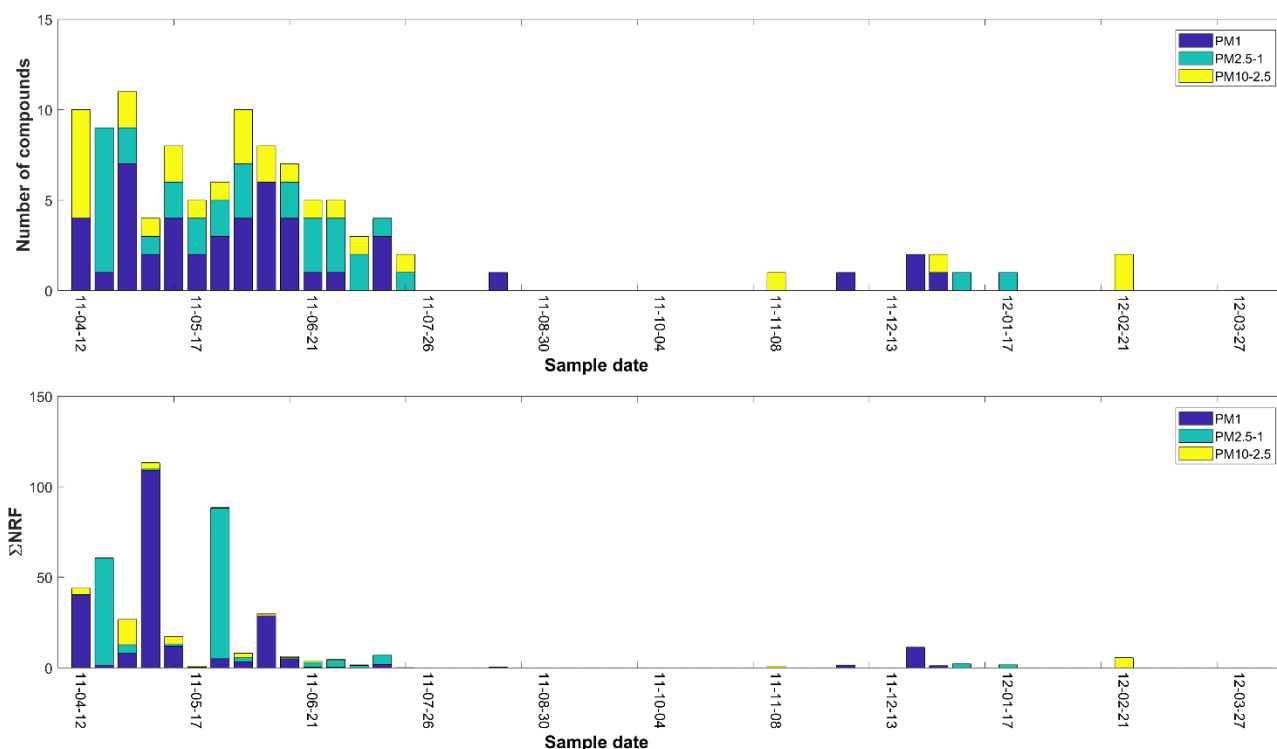


Fig. 4 Total number of amides identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

The Σ NRFs of two specific nitrile compounds, i.e. 2,4-pentandinitrile and cyanogen were significantly higher in the PM_1 size fraction in the sample collected on 10 May 2011. These species were also identified throughout the sampling period. Cyanogen is a toxic compound, while Graedel et al. (1986) indicated that possible sources of cyanogen in the environment are vehicles, waste incineration and tobacco smoke. 2,4-pentandinitrile is an aliphatic nitrile. Özel et al. (2011) also identified a number of aliphatic nitriles using GCxGC-TOFMS in aerosol samples collected in an urban area, although 2,4-pentandinitrile was not specifically characterised.

For the sample collected on 3 May 2011, the Σ NRF of amides in the PM_1 size fraction was significantly higher, which was attributed to one specific amide compound, i.e. acetamide. Acetamide is the simplest amide species, which is generally used as an industrial solvent. This compound is listed by the US EPA as a hazardous pollutant and was also characterised by Özel et al. (2011). Relatively

high semi-quantified concentrations were also determined for N-methoxy-formamide in the PM_{2.5-1} size fraction in the sample collected on 24 May 2011. Formamides have a number of industrial and commercial uses, which include the manufacturing of agrichemical (fungicides) and pharmaceutical products.

Urea is an amide compound with two NH₂ groups bonded to the carbonyl functional group. According to Cornell et al. (2003), the general ambient concentration of urea is 18 nmol N m⁻³ in aerosols, while its concentration ranges between <0.4 and 10 µmol N dm⁻³ in precipitation. The major anthropogenic sources of urea are agricultural fertiliser and animal husbandry, while the end-product of mammalian metabolism is the main natural source of urea (Cornell et al. 1998). As indicated in Fig. 1, very low semi-quantified concentrations of urea were determined using GCxGC-TOFMS analysis. In Fig. 5, the samples in which urea was tentatively characterised in the different size fractions and its corresponding ΣNRFs are presented. Urea was only tentatively identified in 13 samples collected, while mainly occurring in the PM_{2.5-1} and PM_{10-2.5} size fractions. Very low semi-quantified concentrations were determined in all the samples in which urea was tentatively characterised. Cornell et al. (1998) indicated that urea is generally a minor component of aerosol organic nitrogen. However, urea can be a major component in rain water and water-soluble aerosols depending on region (Cornell et al. 2001).

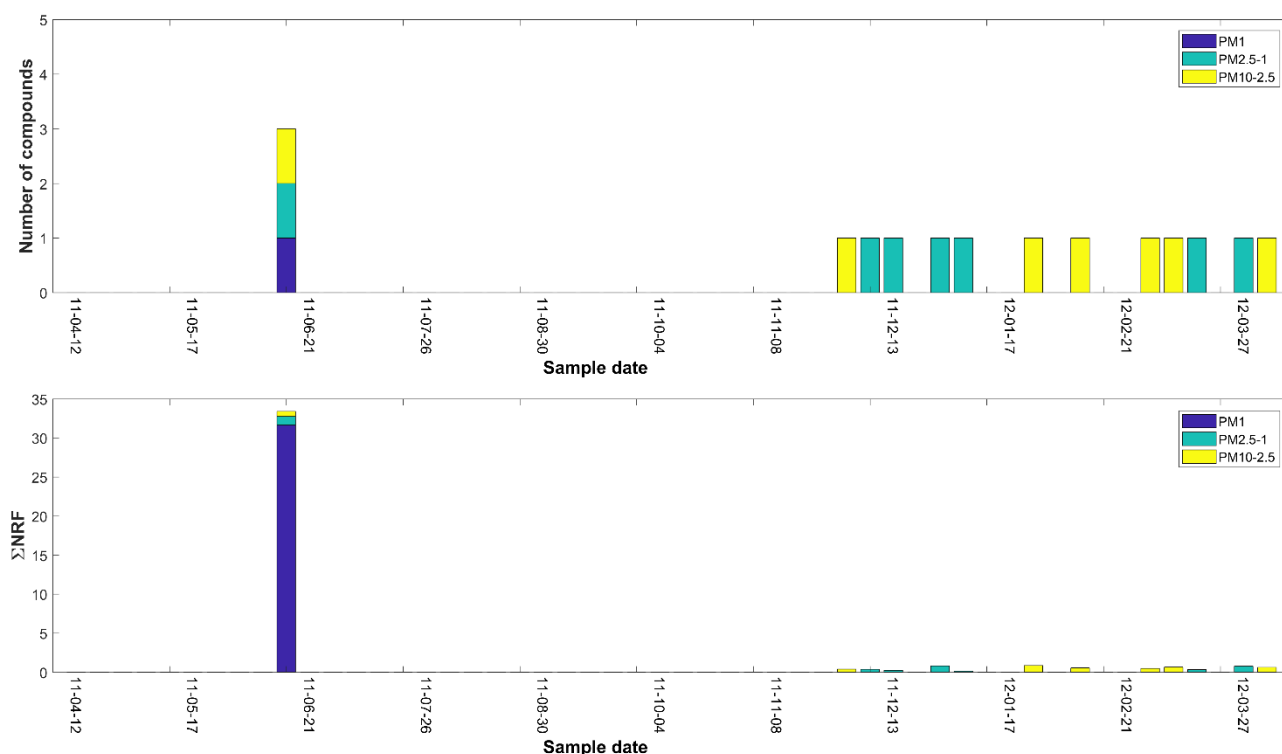


Fig. 5 Identification of urea in the different size fractions and its corresponding semi-quantified concentrations (Σ NRFs) for each sample collected

3.3 Pyridine derivatives and other aromatic heterocyclic compounds

42 heterocyclic pyridine derivatives and one other aromatic heterocyclic compound, i.e. 1,3,4-oxadiazole, were tentatively characterised, which was the second most number of species identified for an organic N functional group. In Fig. 6, the total number of pyridine derivatives (and 1,3,4-oxadiazole) tentatively characterised and their corresponding Σ NRFs in the three size ranges for each sample collected during the entire sampling period are presented. 1,3,4-oxadiazole was only characterised in the sample collected on 5 July 2011, which contributed to the relatively higher Σ NRFs in the $PM_{2.5-1}$ size fraction. Oxadiazole isomers are considered derivatives from furans (Bala et al. 2014). There are a number of sources of atmospheric furans (and dioxins), which include combustions processes (e.g. biomass burning), metal smelting and processing, chemical manufacturing, as well as biological and photochemical processes (Relvas, et al. 2013). It is evident from Fig. 6 that the total number of pyridine

derivatives characterised and their associated Σ NRFs were, similar to amines, nitriles and amides, also higher during the period from 12 April 2011 to 12 July 2011. With the exception of three samples, no pyridine derivatives were tentatively characterised for samples collected from 19 July 2011 to 4 April 2012. The significantly higher Σ NRFs determined for pyridine derivatives in samples collected on 29 April 2011 were attributed mainly to two species, i.e. 2,3,6-trimethyl-pyridine and 2-hydrazinopyridine. Ma and Hays (2008) characterised and quantified 14 heterocyclic aromatic N compounds using GCxGC-TOFMS, which included pyridine derivatives from biomass burning aerosols. Aerosol samples were collected from a simulated agricultural fire with rice crop residue. No pyridine compounds were characterised during the peak burning period in the study of Ma and Hays (2008), which can be attributed to completely different biomass that is burned in this region. Pyridine compounds could also be associated with pesticides (Atkinson 1987), which could be a possible source of the pyridine derivative measured at Welgegund. Forbes (2012) indicated relatively high concentrations of heterocyclic N-containing compounds in particulate emissions from household combustion in South Africa characterised with TD-GCxGC-TOFMS.

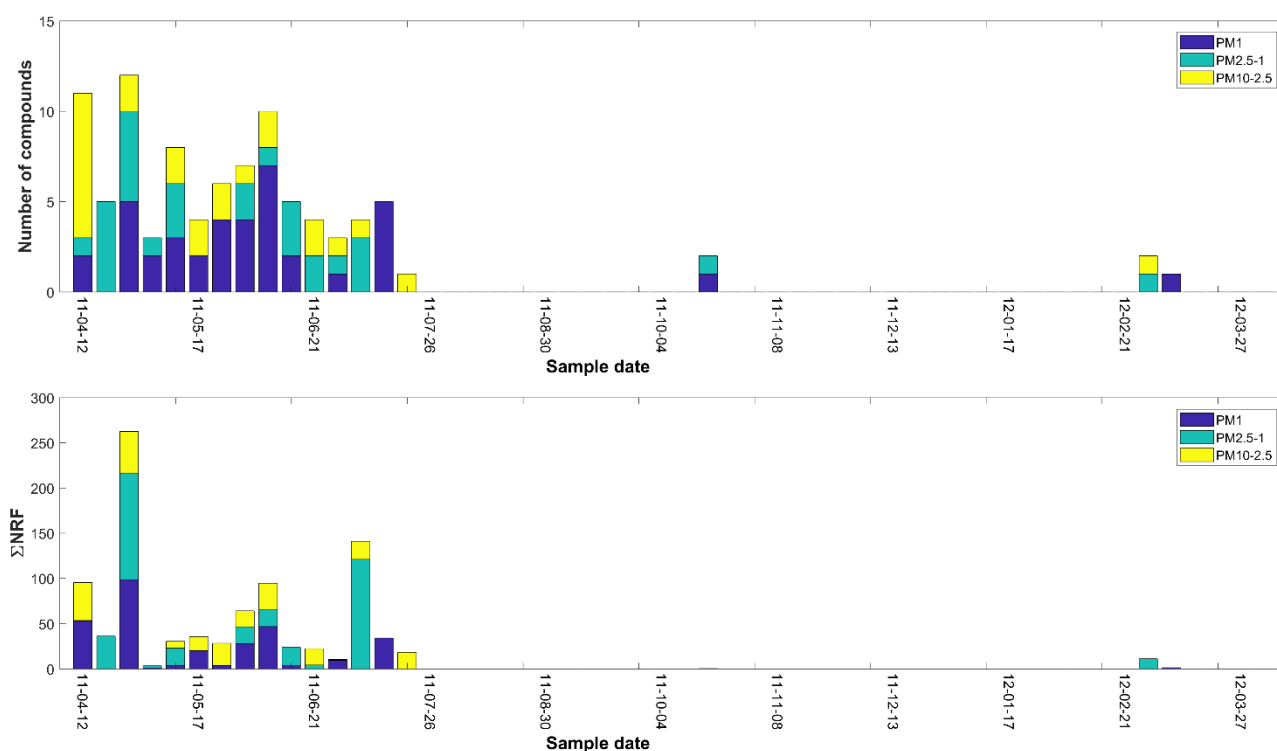


Fig. 6 Total number of pyridine derivatives identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

3.4 Amino acids

Amino acids are also considered an important group of atmospheric organic nitrogen compounds. These species predominantly occur in condensed phase in the atmosphere due to their low vapour pressures (Ge et al. 2011) and are typically present in rainwater (Cornell et al. 2003), fog (Zhang and Anastasio 2001) and dew (Scheller 2001). Zhang et al. (2002), for instance, indicated that amino acids contributed <1 % of total $PM_{2.5}$ mass at Davis, California, while Mace et al. (2003c) indicated that amino acids contribute ~53 % of organic N in rain water. Milne and Zika (1993) presented a review on atmospheric amino acids, and indicated that proteinaceous matter associated with terrestrially dust and marine environments is the major source of these species. It is evident from Fig. 7 that only one amino acid, i.e. glycine, was tentatively identified in eight aerosol samples collected at Welgegund. The corresponding Σ NRF of glycine was also very low, with the exception of slightly higher Σ NRF for one

sample collected on 4 April 2012. Glycine is commonly used in animal feed, which could be a possible source thereof on a commercial farm.

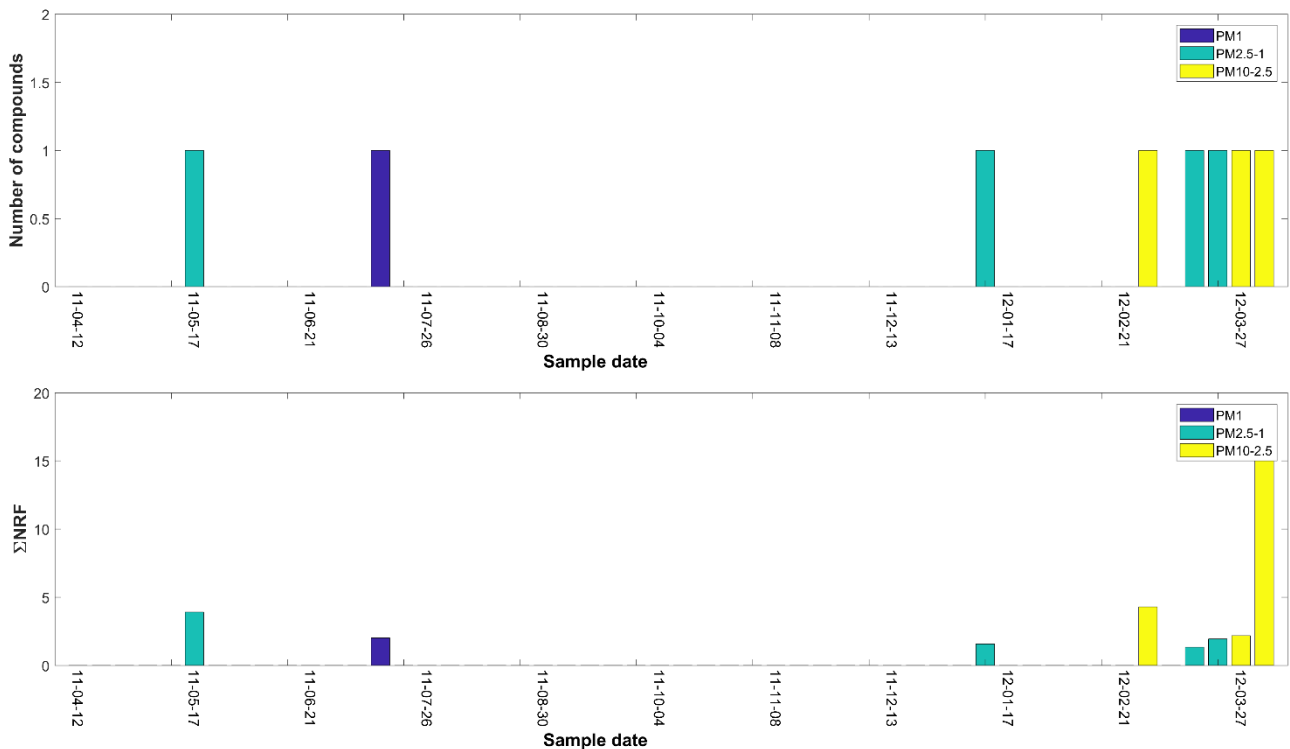


Fig. 7 Total number of amino acids identified and their corresponding semi-quantified concentrations (ΣNRFs) in the three particle size fractions for each sample collected

3.5 Nitro- and nitroso compounds

Nitro- and nitroso compounds are secondary pollutants, which can be formed in the atmosphere through the photochemical gas phase reactions between volatile organic compounds, NO_x and ozone (Ding et al. 1998a). These species could potentially be of toxicological importance with a few nitro- and nitroso compounds being listed on the hazardous air pollution list of the Environmental Protection Agency (EPA) (Ding et al. 1998b, Özel et al. 2010). In Fig. 8 and 9, the total number of nitro- and nitroso compounds tentatively characterised are presented, respectively, with their associated semi-quantified concentrations (ΣNRFs) in the three particle size fractions for each sample collected. With

the exception of two samples collected during the first three weeks, only one nitro-organic species was tentatively identified in a few samples collected thereafter, while also only one nitroso species was tentatively characterised in each of three collected samples throughout the sampling campaign. The corresponding Σ NRFs of the nitro species tentatively identified in samples collected after the first sampling week were also very low. The Σ NRFs of the nitro compounds tentatively identified on 12 April 2011 were significantly higher, which was mainly attributed to the species 2-nitrobutane. Two nitroso species were tentatively identified, i.e. N-nitroso-N-methyl-(1-phenyl)-ethylamine and N-nitroso-methyl-ethylamine. For the samples collected on 24 and 31 May 2011, significantly higher Σ NRFs were determined for N-nitroso-methyl-ethylamine in the $PM_{10-2.5}$ size fraction. Most nitrosamine species are considered carcinogenic and N-nitroso-methyl-ethylamine is listed on the US EPA hazardous pollutant lists. According to the Encyclopaedia of Toxicology (Wexler 2005), N-nitroso-methyl-ethylamine can be formed during night-time in the atmosphere through the reaction of atmospheric amines with nitrous acid. In addition, very high levels of N-nitroso-dimethylamine, which is related to N-nitroso-methyl-ethylamine, have been determined in soils, which was attributed to the use of triazine herbicides that react with nitrogenous fertilisers (Wexler 2005). Özel et al. (2011) characterised N-nitroso-dimethylamine using GCxGC-TOFMS. Atmospheric concentrations of nitro and nitroso species are generally low (Ding et al. 1998b), with most of these species considered to be semi-volatile organic compounds (Ding et al. 1998a). No organic nitrate species were tentatively characterised, which could be attributed to thermal decomposition during analysis (Özel et al. 2010).

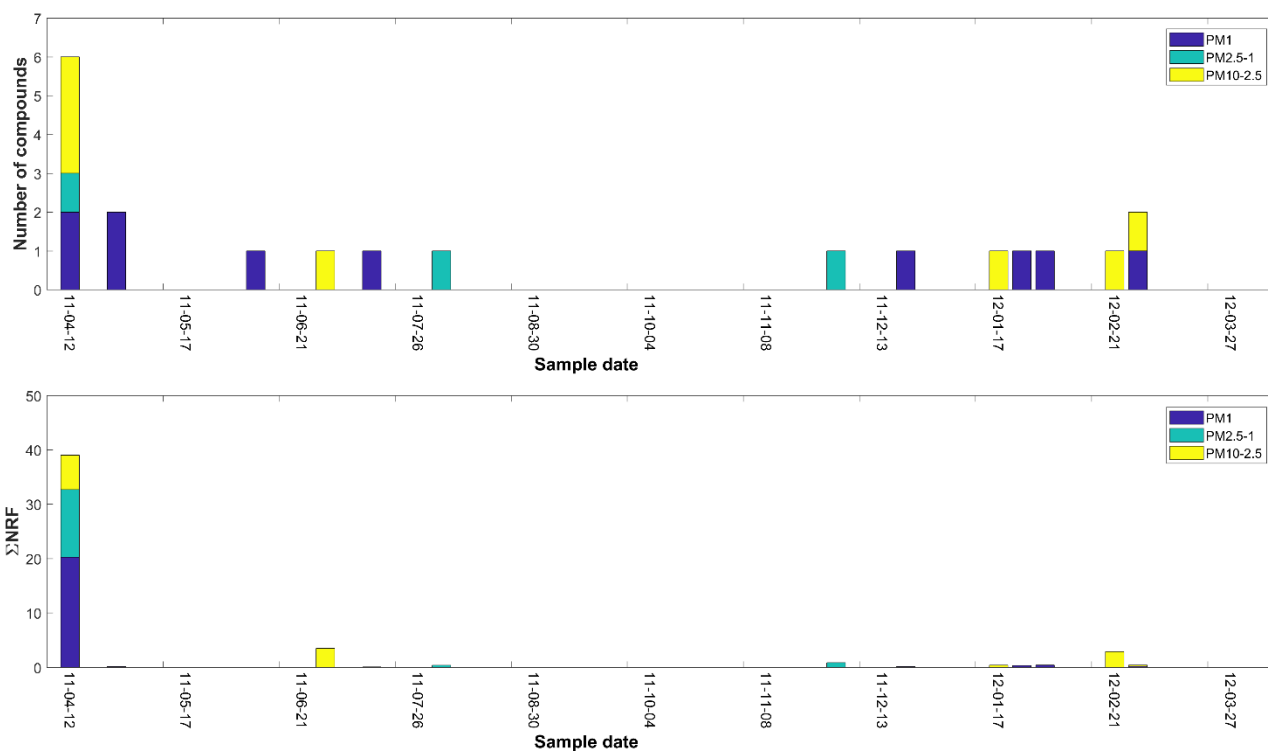


Fig. 8 Total number of nitro compounds identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

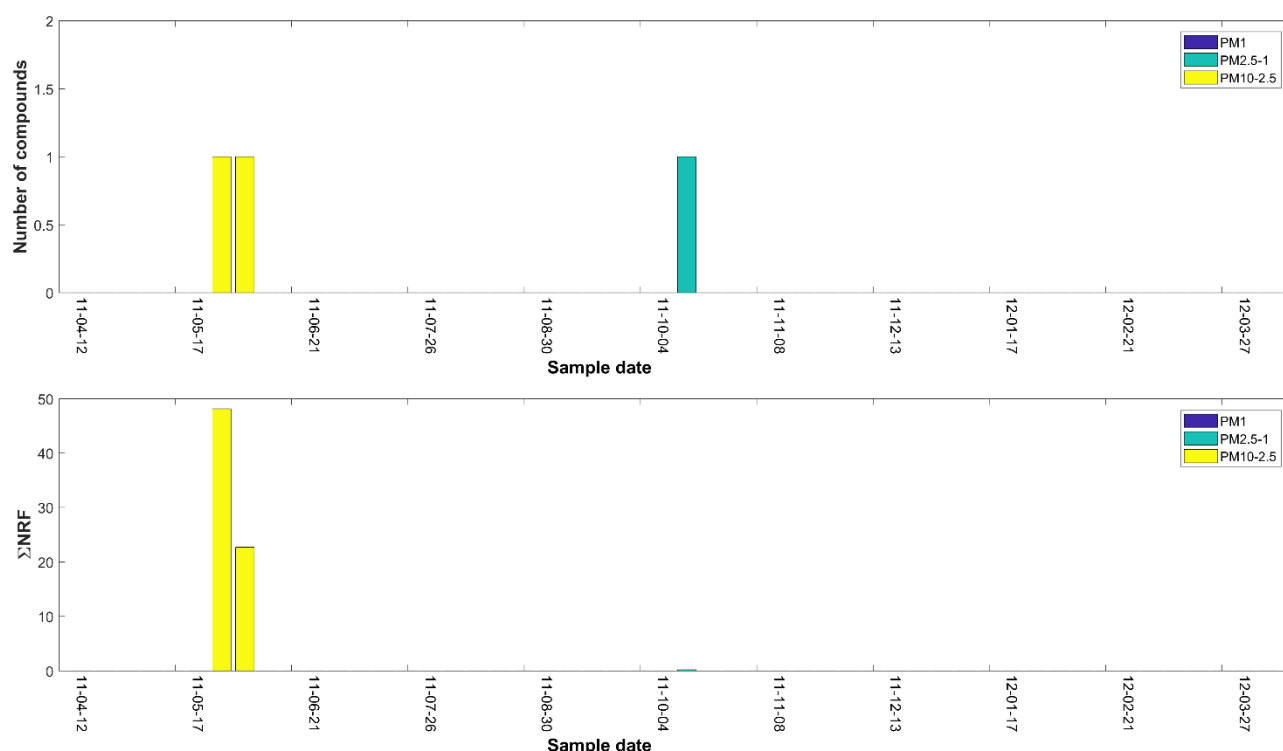


Fig. 9 Total number of nitroso compounds identified and their corresponding semi-quantified concentrations (Σ NRFs) in the three particle size fractions for each sample collected

3.6 Imines

According to Laskin et al. (2015), imines are formed in the atmosphere through the reaction of ammonia with carbonyls that form the intermediate primary imines and amines products, which react further with carbonyls to form more stable secondary imines. Imine species occur in the formation mechanism of brown carbon, but have not been observed in ambient measurements (Zhao et al. 2015; Kampf et al. 2016). From Fig. 10 presenting the total number of imines tentatively identified and their corresponding Σ NRFs in each sample collected during the sampling campaign, it is evident that only one imine compound, i.e. N-(1,2-Diphenylethyl) methanimine was tentatively identified in each of the size fractions for most of the 15 samples wherein imine species were tentatively characterised. The Σ NRFs of imines were very low throughout the sampling campaign.

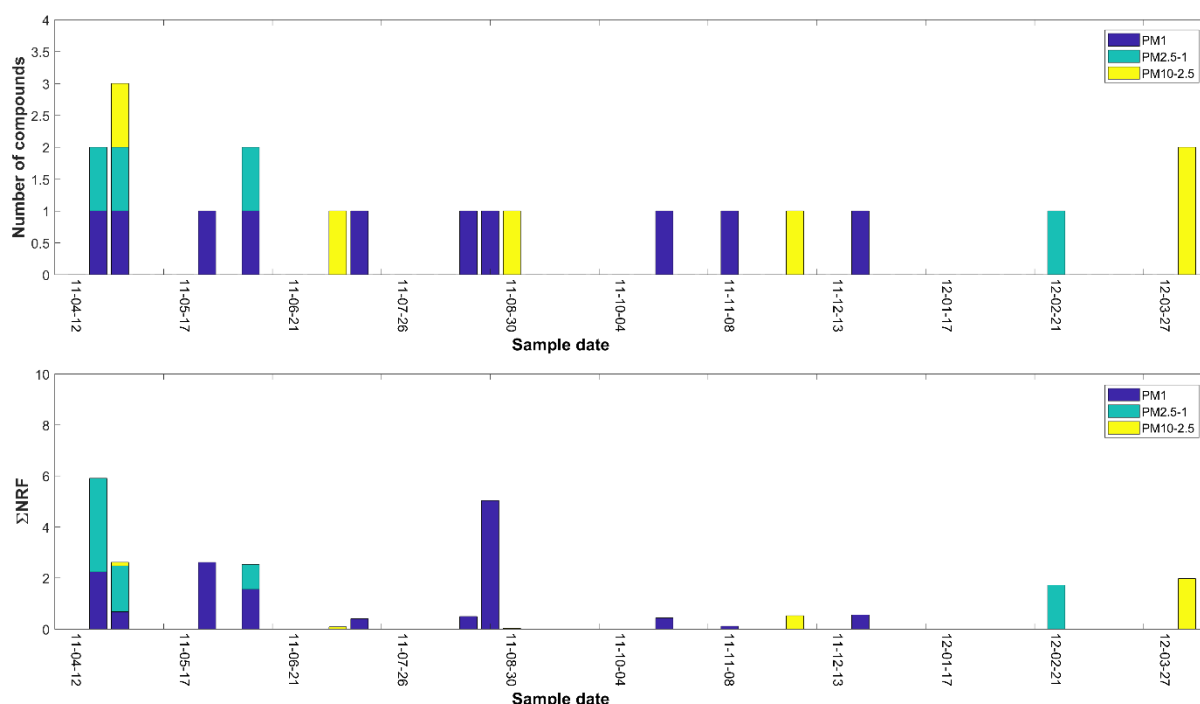


Fig. 10 Total number of imines identified and their corresponding semi-quantified concentrations (ΣNRFs) in the three particle size fractions for each sample collected

3.7 Cyanates and isocyanates

In Fig. 10 and 11, the total number of cyanates and isocyanates tentatively identified are presented, respectively, and their corresponding semi-quantified concentrations for each sample collected. Only one cyanate compound, i.e. ethyl ester cyanic acid, was found in each of three samples collected with very low ΣNRFs. One isocyanate species was tentatively characterised in four samples collected, i.e. cyclohexyl isocyanate. The samples collected on 12 July 2011 and 17 January 2012 had significantly higher ΣNRFs of cyclohexyl isocyanate in the PM_{2.5-1} and PM₁ size fractions, respectively. Cyclohexyl isocyanate is used in the manufacturing of pharmaceutical and agricultural chemicals. Isocyanates are generally considered to be harmful to the respiratory system, while exposure to isocyanate is identified as one of the most common causes of occupational asthma (Bernstein 1996; Redlich and Karol 2002).

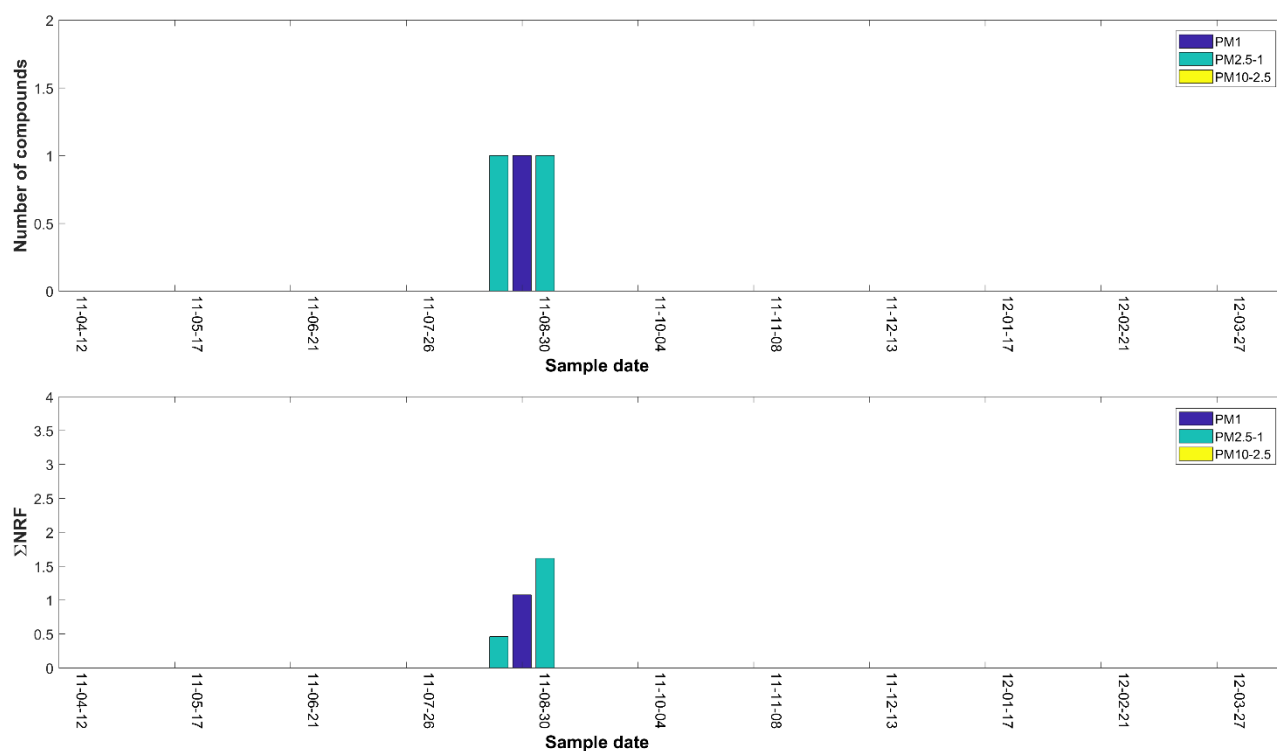


Fig. 11 Total number of cyanates identified and their corresponding semi-quantified concentrations (ΣNRFs) in the three particle size fractions for each sample collected.

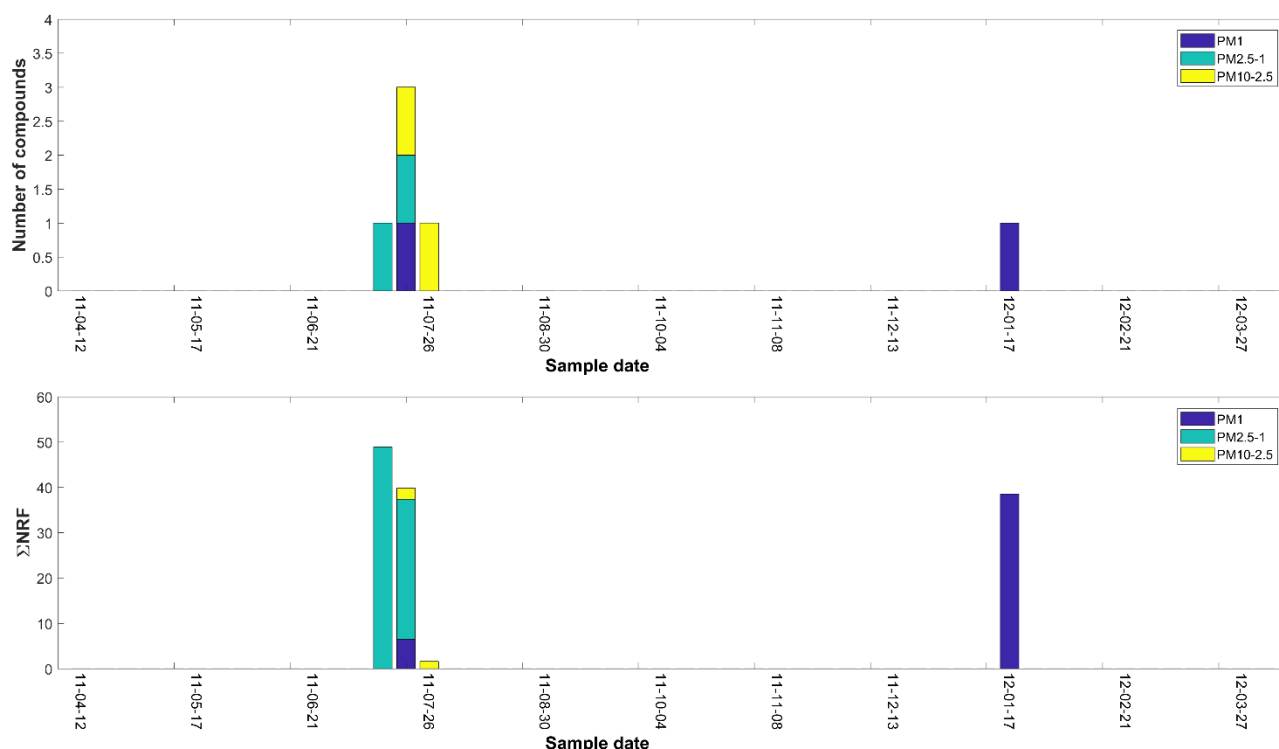


Fig. 12 Total number of isocyanates identified and their corresponding semi-quantified concentrations (ΣNRFs) in the three particle size fractions for each sample collected

3.8 Azo compounds

Only one azo compound was tentatively identified in a sample collected on 27 December 2011, i.e. 1,2,3-thiadiazole in the PM_{2.5-1} size fraction, which had a ΣNRF of ~17. Thiadiazole derivatives have numerous applications in agricultural, pharmaceutical and material chemistry. These compounds are widely used in pesticides, which include herbicides, fungicides, insecticides, bactericides and plant-growth regulators (Hu et al. 2014).

4. Summary and Conclusions

In total, 135 atmospheric organic N compounds were tentatively characterised and semi-quantified using GCxGC-TOFMS for ambient atmospheric aerosols collected at a savanna-grassland region in the interior of South Africa for one year. According to the knowledge of the authors, this is

the first time that atmospheric particulate organic N species were identified and semi-quantified for southern Africa, while, in general, only a few studies have been conducted globally utilising GCxGC-TOFMS to characterise atmospheric organic N. In this study, amines, nitriles, amides, urea, pyridine derivatives, amino acids, nitro- and nitroso compounds, imines, cyanates and isocyanates, and azo compounds were tentatively characterised and semi-quantified. The most abundant species tentatively identified were amines, while nitrile compounds were the second most abundant species. Relatively higher semi-quantified concentrations were also determined for amides and pyridine derivatives. The semi-quantified concentrations of the other organic N functional groups were very low, with most of these organic N groups consisting only of one species in each of the samples collected. The temporal variations of amines, nitriles, amides and pyridine derivatives were similar to that observed for all the polar organic compounds, i.e. a period between 12 April 2011 and 12 July 2011 (mid-autumn to mid-winter) coinciding with the dry season, with elevated semi-quantified concentrations of these species. These temporal variations were attributed mainly to meteorological parameters and the influence of local open biomass burning. Anthropogenic sources in the major source regions impacting air masses measured at Welgegund, as well as regional agricultural activities, were considered the major sources of amines, while the regional influence of household combustion was considered the main source of nitriles and amides. Most of the other organic N functional groups were most likely related to the influence of local and regional agricultural activities.

Although a large number of N compounds could be tentatively characterised and semi-quantified, it is recommended that future studies should attempt to characterise even more particulate organic N species with increased certainty, as well as to absolutely quantify compounds or at least specific compounds identified as problematic.

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Chapter 7: Project evaluation and future perspectives

7.1 Introduction

The objectives indicated in Chapter 1 were addressed through three research articles presented in this thesis. Each article provides an overview of the literature, describes the relevant experimental methods, presents the results obtained and makes concluding remarks. In the subsequent section, the successes and shortcomings of this project are evaluated in view of the objectives listed in Chapter 1, while future perspectives are also presented.

7.2 Project evaluation

Objective I: Collect ambient aerosols in the PM₁, PM_{2.5-1} and PM_{10-2.5} size fractions on filters for at least one year at the Welgegund measurement station.

PM₁, PM_{2.5-1} and PM_{10-2.5} ambient aerosol samples were collected successfully for one year at the regional background measurement station Welgegund. 24-hour samples were collected once a week with a Dekati PM₁₀ cascade impactor equipped with quartz filters. In total, 52 samples were collected, which are representative of each week during the one-year sampling period. This is the most comprehensive number of size-resolved ambient atmospheric aerosol samples collected in South Africa for the characterisation of organic compounds. However, limitations of this sampling technique include volatilisation of semi-volatile organic compounds collected on filters, collected compounds chemically reacting with other atmospheric species, blowoff occurring at higher concentration and temperatures (Geldenhuys et al. 2015) and gas-particle partitioning effects.

Objective II: Extract the collected ambient aerosols from filters with a dynamic ultrasonic-assisted extraction approach.

Ambient aerosol samples were effectively extracted from quartz filters with dynamic ultrasonic-assisted extraction within 40 min at a flow rate of 1ml/min utilising a 1:1 v/v mixture of methanol and acetone. This extraction solvent mixture utilised was, however, polar, which was not validated for non-polar species, such as hydrocarbons. Although this solvent mixture was used by Ruiz-Jimenez et al. (2011) for the simultaneous extraction of polar and non-polar compounds, it would have contributed to a lower number of hydrocarbon species being extracted and identified with lower corresponding semi-quantified concentrations.

Objective III: Perform analysis of the extracted samples using a GCxGC-TOFMS.

Analysis was successfully performed with a LECO Pegasus 4D GCxGC-TOFMS system equipped with an Agilent 7890 A GC and an Agilent 7683 B auto sampler. The GCxGC-TOFMS method utilised was based on the method developed by Ruiz-Jimenez et al. (2011). The system consisted of two separation columns that were connected in series with the primary column providing volatility-based separation and the secondary column polarity-based separation. After GCxGC separation, the compounds were detected by the TOFMS and data was acquired in the m/z ratio range between 50 and 450 amu.

Objective IV: Characterise and semi-quantify organic compounds in atmospheric samples in the different size ranges.

GCxGC-TOFMS was successfully used to tentatively identify and semi-quantify organic compounds in ambient aerosols collected on filters in ambient air for the first time in South Africa. Approximately 8 000 peaks were detected, which were similar to other studies where atmospheric samples were analysed using GCxGC-TOFMS (Welthagen et al. 2003; Hamilton et al. 2004; Schnelle-Kreis et al. 2005; Ruiz-Jimenez et al. 2011; Özel et al. 2011; Alam et al. 2013). A combined total of 1 056 different compounds could be tentatively characterised by applying the positive characterisation parameters (NIST library similarity fit of 700 and *I* differences under 150 compared to theoretical *I*

values). The compounds were considered to be tentatively identified, since less restrictive positive characterisation parameters were applied in order to characterise more organic compounds. Semi-quantified concentrations of the organic compounds tentatively characterised were expressed as normalised response factors (NRF) in relation to an internal standard.

These 1 056 organic compounds tentatively identified are the largest number of organic compounds chemically tentatively characterised in atmospheric samples utilising GCxGC-TOFMS. The tentatively identified and semi-quantified organic compounds could be categorised according to their functional groups into oxygenated (alcohols, ethers, aldehydes, ketones, carboxylic acids, esters), hydrocarbons (alkanes, alkenes, aromatics), halogenated compounds (Cl, Br, I, F), N-containing compounds and S-containing compounds. The largest number of organic compounds tentatively characterised with the highest semi-quantified concentrations were oxygenated species, which was also indicated by aerosol mass spectrometry (AMS) measurements conducted at Welgegund (Tiitta et al. 2014). These higher concentrations of oxygenated species were attributed to aged air masses passing over source regions impacting Welgegund, as well as the influence of widespread regional biomass burning. The contribution of each functional group within an organic compounds category to the total number of organic compounds tentatively characterised and to the combined semi-quantified concentrations could also be assessed.

Objective V: Conduct an assessment of temporal variations of organic compounds characterised and semi-quantified, as well as determine possible sources of these species.

Since it was indicated that the polar solvent extraction mixture utilised was not validated for non-polar species, which could have contributed to lower values associated with the number of hydrocarbon species tentatively characterised and their associated semi-quantified concentrations, temporal variations and possible sources of hydrocarbon species could not be assessed. Therefore, only polar organic aerosol compounds characterised were assessed in order to determine the influence of meteorological conditions, as well as major sources and source regions influencing air masses measured at Welgegund on these species.

Although no distinct seasonal pattern was observed, three periods could be identified corresponding to different characteristics in polar organic concentrations, i.e. a period coinciding with late winter and early spring with a significantly lower total number of organic compounds and corresponding $\sum$ NRFs, while it also seemed that the total number of organic compounds and the corresponding $\sum$ NRFs for the period coinciding with mid-autumn to mid-winter were relatively higher compared to the period from late spring to mid-autumn.

The influence of source regions, meteorology and burnt area pixels was investigated in order to elucidate the temporal variations. Three source regions could be identified, from which it could be established that a relatively lower total number of organic compounds and the corresponding $\sum$ NRFs were associated with fresher plumes arriving at Welgegund from a source region in close proximity of Welgegund. Temperature, relative humidity and soil moisture measurements indicated that the wet removal of aerosols contributed to a lower total number of organic compounds and the corresponding $\sum$ NRFs, while increased anticyclonic recirculation and more stable stratified layers in winter contributed to a higher total number of organic compounds and the corresponding $\sum$ NRFs. Burnt area pixels indicated large-scale regional biomass burning as an important source of organic aerosol compounds. However, the period with significantly lower total number of organic compounds and the corresponding $\sum$ NRFs coincided with the peak burning months. It could be indicated that open biomass burning occurring in close proximity of Welgegund during this period contributed to significantly lower total numbers of organic compounds and the corresponding $\sum$ NRFs due to fresher plumes impacting Welgegund that mainly contain primary emitted VOCs and non-polar hydrocarbon aerosols. However, temporal variations could not be related to a specific influencing factor with none of these factors conclusively explaining the period with significantly lower semi-quantified concentrations. Multiple linear regression (MLR) analysis was successfully deployed in an effort to quantify the influence of source regions, meteorology and burnt area pixels, which indicated that soil moisture, temperature and the occurrences of wild fires within a 100 km radius, were the most important factors influencing temporal variations.

Objective VI: Specifically characterise and semi-quantify organic nitrogen compounds.

A total of 135 atmospheric organic nitrogen compounds could be tentatively characterised and semi-quantified using GCxGC-TOFMS, which contributed 13 % of the total number of organic compounds characterised and 12 % of the semi-quantified concentrations of all the compounds tentatively identified. This was the first time that ambient atmospheric particulate organic nitrogen species were identified and semi-quantified for southern Africa. Amines, nitriles, amides, urea, pyridine derivatives, amino acids, nitro- and nitroso compounds, imines, cyanates and isocyanates, and azo compounds were tentatively characterised and semi-quantified. It was indicated that amines were the most abundant species tentatively identified, while nitrile compounds were the second most abundant species. Relatively higher semi-quantified concentrations were also determined for amides and pyridine derivatives, while $\sum$ NRFs of the other organic nitrogen species were low. The temporal variations of amines, nitriles, amides and pyridine derivatives were similar to that observed for all the polar organic compounds. Anthropogenic sources in the major source regions impacting air masses measured at Welgegund, as well as regional agricultural activities, were considered the major sources of amines, while the regional influence of household combustion was considered the main sources of nitriles and amides. Most of the other organic N functional groups were most likely related to the influence of local and regional agricultural activities.

Although N compounds were successfully tentatively characterised, the GCxGC-TOFMS conditions were not optimised for each of the compound classes and the differences in ionization efficiencies were not considered.

Based on the above evaluation of each of the objectives of this study, it can generally be concluded that this research project was successfully completed and that the general aim of this study was achieved. A few shortcomings were, however, indicated, which could be improved in future studies.

7.3 *Future perspectives*

From the results presented in this study, a few future perspectives can be drawn. Recommendations for future studies include:

- The optimisation of the solvent extraction procedure by varying the solvent with a non-polar solvent mixture, such as hexane, is required in future work to determine the impacts of solvents on the chemical profile of compounds extracted. The use of non-polar extractants could also elucidate the influence of local biomass burning on the emissions of hydrocarbons. Furthermore, atmospheric polycyclic aromatic hydrocarbons (PAH), which are considered important environmental pollutants, could also possibly be better characterised.
- The collection of ambient aerosol samples at Welgegund should be continued in order to improve the assessment of temporal patterns of organic compounds and specific organic functional groups. The collection of more than one sample per week could also contribute to an improved source apportionment of organic species. Future studies should also include continuous chemical measurements of atmospheric aerosols, such as AMS, which would contribute to an improved understanding of the chemical characteristics and temporal variability of organic aerosols.
- Although a large number of N compounds could be tentatively characterised and semi-quantified, it is recommended that future studies should attempt to characterise even more particulate organic N species with increased certainty, as well as to absolutely quantify compounds or at least specific compounds identified as problematic.
- In this study, a large dataset was obtained from the analysis of 52 ambient aerosol samples collected for one year using GCxGC-TOFMS analysis. It is therefore recommended that the dataset should be further mined in future studies in order to characterise more of the ~8 000 organic compounds detected using GCxGC-TOFMS. Similar to the results presented in this study on organic nitrogen, studies on all the other functional groups, especially the polar organic species, should be conducted.

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- It is also recommended that more restrictive characterisation parameters, i.e. higher spectral fit similarities and lower I value confidence intervals, as well as verification of identified organic compounds with real standards are applied that would result in the more accurate positive characterisation of organic compounds.

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Appendix

List of nitrogen compounds tentatively identified

<i>Metabolite name</i>	<i>RT1</i>	<i>RT2</i>	<i>Similarity</i>	<i>PM₁</i>	<i>PM_{2.5-1}</i>	<i>PM_{10-2.5}</i>
(-)-Norephedrine	1015,0	0,44	967		√	√
(E)-3-Phenyl-2-propenenitrile	1122,5	1,47	763	√	√	
(S)-3-(1-Methyl-2-pyrrolidinyl)-pyridine	1133,8	1,47	853	√	√	√
(S)-N,N'-Dimethyl-1,2-propanediamine	452,5	1,13	762	√		
(Z)-13-Docosenamide	2685,0	1,75	803			√
1-(6-Methyl-3-pyridinyl)-ethanone	850,0	1,60	772	√		
1,2,3-Thiadiazole	408,0	0,88	764		√	
1,2,3-Trimethylpiperidin-4-one	781,7	1,15	795	√	√	
1,2-Benzisothiazole	946,7	1,53	763	√	√	
1,2-Dimethylaziridine	337,5	2,24	733		√	
1,3,4-Oxadiazole	313,0	0,08	902		√	
1,3-Dimethyldiaziridine	341,0	2,60	833	√	√	√
1,5-Dihydro-5-methoxy-3,5-dimethyl-2H-pyrrol-2-one	755,0	1,70	859	√		
1,2-Diacetylhydrazine	925,0	1,68	761	√		
1-Azabicyclo[3.1.0]hexane	577,5	0,72	758	√	√	
1-Butanamine	503,1	1,57	780	√	√	√
1-Butylpyrrolidine	880,0	1,98	886	√		
1H-1,2,4-Triazole	590,0	0,82	873			√
1H-Pyrrole-2,5-dione	620,0	1,18	786			√
1-Methyl-2-pyrrolidinone	737,6	1,36	860	√	√	√
1-Methyl-2-tert-butylpyrrole	505,9	1,11	747	√	√	√
1-Methyl-3-(1,1-dimethylethyl)-pyrrole	495,0	1,12	746		√	√
1-n-Butoxy-2,3-dimethyldiaziridine	655,0	1,44	748	√		
1-Oxa-3,4-diazacyclopentadiene	313,3	0,09	914			√

<i>Metabolite name</i>	<i>RT1</i>	<i>RT2</i>	<i>Similarity</i>	<i>PM₁</i>	<i>PM_{2,5-1}</i>	<i>PM_{10-2.5}</i>
2-(1-Methyl-2-pyrrolidinyl)-pyridine	1158,8	1,40	812	√	√	√
2,2'-Bipyridine	1239,6	1,86	883	√	√	√
2,2-Diethyl-N-ethylpiperidine	938,4	1,61	894	√	√	√
2,2-Dimethyl-aziridine	331,7	4,18	789		√	√
2,2-Dimethyl-propanenitrile	377,8	0,47	834		√	√
2,3,6-Trimethyl-pyridine	722,0	0,96	872	√	√	√
2,3-Dimethyl-quinoline	1200,0	1,82	868	√		
2,4,6-Trimethyl-pyridine	727,8	0,99	895	√	√	√
2,4'-Bipyridine	1370,0	2,02	852	√	√	
2,4-Dimethyl-pyridine	657,5	1,00	841	√	√	√
2,4-Dimethyl-quinoline	1265,0	1,68	807	√	√	√
2,4-Pentandinitrile	378,3	1,68	790	√	√	√
2,5-Dimethyl-1-propylpyrrole	932,5	1,53	767			√
2,5-Dimethyl-pyridine	680,6	1,04	786	√	√	√
2,6-Diphenylpyridine	2195,0	2,16	822			√
2-Aminocynoacetamide	500,0	3,75	939			√
2-Ethyl-4,6-dimethyl-pyridine	792,5	1,04	880	√	√	√
2-Ethyl-6-phenyl-1,3,4-thiadiazolo(3,2-a)(1,3,5)-triazine-5,7-dione	2415,0	1,78	935	√		
2-Hydrazinopyridine	897,5	1,36	702	√	√	
2-Methoxy-ethanamine	406,8	1,10	860	√	√	√
2-Methyl-1H-indole	1155,0	1,90	863			√
2-Methyl-2-propanamine	430,4	0,97	888	√	√	√
2-Methyl-pyridine	445,0	0,88	822	√		
2-Nitro-butane	515,8	0,87	945	√	√	√
2-n-Propylaziridine	325,0	4,46	721	√		
2-Pentyl-pyridine	900,0	1,24	912		√	
2-p-Tolylpyridine	1490,4	1,93	852	√	√	√
2-Pyridinecarbonitrile	582,5	1,66	817	√		√
3-(Phenylsulfonyl)-2-propenenitrile	1845,0	2,70	807			√
3,3-Dimethyl-2-azetidinone	345,0	3,18	801	√		
3,4-Dimethyl-pyridine	601,3	1,12	841	√	√	√

Metabolite name	RT1	RT2	Similarity	PM₁	PM_{2,5-1}	PM_{10-2,5}
3,5-Dimethyl-pyridine	660,2	1,05	812	√	√	√
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1685,0	1,30	802	√		
3-Methyl-pyridine	455,0	0,86	730		√	
3-Metoxypyridine	769,9	1,07	778	√	√	√
3-Octanamine	475,0	1,08	729	√		
3-Pyridinecarbonitrile	490,0	1,66	871			√
4,7-Dimethyl-benzo[c]cinnoline	1985,0	2,10	756			√
4-Amino-4,5(1H)-dihydro-1,2,4-triazole-5-one	450,0	0,66	936			√
4-Benzoyl-benz[b]1,4-oxazin-3(2H)-one	2415,0	2,06	941	√		
4-Ethyl-pyridine	702,5	1,00	760	√	√	
4H-1,2,4-Triazol-4-amine	396,3	0,59	954		√	
4-Methyl-3-(O-methylbenzyl)pentanenitrile	1600,0	1,20	819			√
4-Methyl-3,5-pyridinedicarbonitrile	1100,0	1,70	784	√		
4-Methyl-N-(4-methyl-furazan-3-yl)-benzamide	2065,0	1,64	737			√
4-Methyl-pyridine	445,0	0,86	808	√		
4-Pyridinecarbonitrile	486,4	1,65	812	√	√	
5-(4-Hydroxy)-benzyl-2-thioxo-imidazolin-4-one	1980,0	2,06	859		√	
5H-1-Pyridine	805,0	1,48	722		√	√
5-Methyl-2-hexanamine	640,0	1,18	890		√	
5-Phenyl-1H-pyrazole-3-carboxaldehyde	1355,0	2,30	716			√
6-Methoxy-4-methyl-quinoline	1505,0	1,90	800	√		
Acetamide	493,1	1,09	846	√	√	√
Acetohydroxamic Acid	390,0	0,98	716	√		
N-Methyl-benzeneethanamine	780,0	1,82	888		√	
Aminoacetaldehyde dimethyl acetal	470,0	0,54	733	√		
Ammonia	424,0	0,71	841	√	√	√
Azetidine	335,0	1,35	777	√	√	
Caffeine	1743,3	2,55	757	√	√	√
Caprolactam	922,9	2,13	824	√		√
Cis-1-(1,1-dimethylethyl)-2,3-dimethyl-aziridine	670,0	1,40	795	√	√	√
Cyanogen	384,7	1,49	821	√	√	√

Metabolite name	RT1	RT2	Similarity	PM₁	PM_{2,5-1}	PM_{10-2.5}
Cyclohexyl isocyanate	921,5	1,36	875	√	√	√
Cycluron	1275,0	2,38	701		√	
Decanenitrile	1042,5	1,21	836		√	√
Diphenylamine	1463,3	2,00	779	√	√	
Ethyl ester cyanic acid	336,7	4,07	755	√	√	
Glycine	524,4	0,64	787	√	√	√
Heptadecanenitrile	2075,0	1,29	858	√		√
Heptanenitrile	715,0	1,18	774	√		
Hexadecanenitrile	1848,3	1,27	803	√	√	
Indole	955,0	2,52	828			√
Indolizine	815,0	1,46	805	√		
Isatin-3-oxime	1675,0	1,34	835			√
Isoquinoline	940,0	1,72	913	√		
Isoxazolidine	515,0	0,92	720		√	
Methenamine	871,3	1,63	870	√	√	√
Morpholine	561,3	0,97	926		√	
N-(1,2-Diphenylethyl)methanimine	858,4	1,61	789	√	√	√
N,1-Dimethylhexylamine	475,0	1,08	808	√		
N,N-Bis(1-methylethyl)-2-propen-1-amine	689,8	1,30	773	√	√	√
N,N-Dibutyl-formamide	1075,0	1,28	808		√	
N,N-Dimethyl-1-pentanamine	442,5	1,17	944	√		
N,N-Dimethyl-2-propyn-1-amine	335,0	0,52	812	√		√
N,N-Dimethylbutyramide	660,7	1,07	810	√	√	√
N-Dimethyl-2-propanamine	605,0	1,14	797	√		
N-Ethenyl-N-methyl-acetamide	520,0	1,39	809	√		
N-Ethyl-ethanamine	450,0	1,24	793	√		
N-Formylmorpholine	733,0	1,98	797	√	√	√
N-Formyl-N-methyl-formamide	610,0	1,10	754	√		
N-Isopropylcyclohexylamine	837,5	1,33	707		√	
N-Methoxy-formamide	340,4	0,59	823	√	√	
N-methyl-1-phenyl-cyclopropanamine	1075,0	0,52	737			√

Metabolite name	RT1	RT2	Similarity	PM₁	PM_{2,5-1}	PM_{10-2.5}
N-nitroso-methyl-ethylamine	310,0	2,61	731			√
N-nitroso-N-methyl-(1-phenyl)-ethylamin	1750,0	1,54	747		√	
Nonanenitrile	905,0	1,16	856			√
Norpseudoephedrine	1063,8	0,44	991	√	√	√
N-Phenyl-acetamide	1127,5	2,04	849		√	√
o-2-Methylpropyl-hydroxylamine	335,0	2,31	762		√	
Octanenitrile	852,5	1,12	832	√	√	
Oxamide, N-(methylthio)carbonyl-	1490,0	1,24	733	√		
Oxime cyclobutanone	430,0	1,04	715		√	
Pentadecanenitrile	1845,0	1,28	892		√	
Phenazine	1705,0	2,20	716		√	
Phenylpropanolamine	1029,8	0,45	939	√	√	√
Phthalimide	1392,6	1,74	795	√	√	√
Propiolonitrile	302,5	2,61	790	√	√	√
Pyridine	1005,6	0,57	754	√	√	√
Tridecanenitrile	1595,0	1,28	922	√		√
Trolamine	1566,8	0,90	874	√	√	√
Urea	954,3	2,07	802	√	√	√