Volatile organic compound measurements at a grazed savannah grassland in South Africa

K Jaars

20162750

MSc in Environmental Sciences

BSc Industrial Sciences

Thesis submitted in fulfilment of the requirements for the degree *Philosophiae Doctor* in *Environmental Sciences* at the Potchefstroom Campus of the North-West University

Supervisor: Dr PG van Zyl

Co-supervisor: Prof JP Beukes

July 2016

ACKNOWLEDGEMENTS

Now that I found myself at the conclusion of this thesis, I experience the feeling of fulfilment. I realised though only my name appears on the cover of this thesis, many people, including my family members, well-wishers, my friends, colleagues and various institutions and organisations have aided me in the completion of this huge task.

It was during my fourth year of my undergraduate studies that my journey began, when I had to choose a project to work on for my final year. Most of my undergraduate studies had focused on the more well-known traditional chemistry in a laboratory, where you mix different chemicals in a test tube and see what you get. So to say my knowledge of atmospheric chemistry at that time was inadequate was an understatement, especially biogenic volatile organic compounds (VOCs). However, my supervisors, Paul Beukes and Pieter van Zyl, soon convinced me to focus on these very limited, under-studied organic compounds in the South African environment. The enticement was evident and I have not regretted the choice since. In the early stages of my research, I felt like an absolute novice. The fact that I came so far, from a four-year project to PhD project, was due to my supervisors, who have supported and encouraged me on a daily basis throughout my postgraduate studies. They guided me through a world unknown to me, atmospheric chemistry, which enabled me to develop an in-depth understanding of the field. I would like to thank them for the many years of support, advice and for their friendship and laughs. They have been far more influential in my life than they will ever know. More than anything, it is their constant faith in me that fuelled the determination necessary to complete this PhD journey. I could not have wished for better supervisors. I am forever indebted to them for their unrelenting support and patience and for bringing out the best in me.

I am enormously grateful, appreciative and acknowledge the support received from Dr Heidi Hellén and Prof Hannele Hakola of the Finnish Meteorological Institute. This PhD project would not have been possible without their help with the identification and quantification of the VOCs. I want to thank them for always giving me a prompt and clear answer to all my questions, for all the ideas you have shared with me and for teaching me so many things about VOCs. I am equally thankful to Prof Janne Rinne for teaching me how to set up biogenic VOC emission measurements and for inviting me to attend the 2014 Biogenic Hydrocarbons and the Atmosphere Gordon Research Conference in Girona, Spain.

I am extremely thankful to Drs Lauri Laakso and Ville Vakkari for their sound advice, patience, support, feedback and useful comments, especially when it came to maintaining the Welgegund measurement station.

I wish to express my gratitude to all my co-authors for the help they have given. I am also grateful to all my colleagues and friends in the Atmospheric Chemistry Research and Chromium Technology Groups for their support, interest and encouragement. They were always beside me during the happy and hard moments to push me and motivate me. No research is possible without infrastructure and requisite materials and resources; therefore, I would like to thank the Welgegund measurement team for all the time they dedicated to helping me with my VOC measurements and also maintaining the other instruments every week.

This research would not have been possible without the necessary funding and support from the Atmospheric Research and Chromium Technology Groups at the North-West University, The Finnish Meteorological Institute and the University of Helsinki.

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF.

And then, of course, there is, and always has been, the home front. I am very fortunate to be surrounded by loving, caring and interested family members. My sincerest appreciation to my family, not only for their constant encouragement, but also for their never-ending love, prayers, support and understanding during my studies. My deepest gratitude goes to my parents, Isak and Els Jaars, for having faith in me and giving me liberty to choose what I desired. I salute you for the selfless love, care, pain and sacrifice you did to shape my life. Although you hardly understood what my research was about, you were willing to support me in any decision I made. I would never be able to pay back the love and affection showered upon by my parents. Furthermore, I express my thanks to my brothers and sisters for their support. It is difficult to find words to express my gratitude to them. Without their encouragements, I would not have finished this degree.

Finally, I owe thanks to a very special person, Rosa Gierens, for her continued and unfailing love, support and understanding during the final stages of this PhD. I wish to thank her for everything we have experienced together and for everything that is waiting for us. Thank you for showing me the meaning of life. You were always around at times I thought that it was impossible to continue; you helped me to keep things in perspective, personally and professionally. I greatly value her contribution and deeply appreciate her belief in me. Words would never say how grateful I am to you. "*Kiitos pullasta".*

It is also to my family and Rosa Gierens I would like to dedicate this work.

Thank you

Kerneels Jaars

At the end of the movie, Book of Eli, there is this prayer I like to quote with some adaptations: "***Dear Lord, thank you for giving me the strength and conviction to complete this huge task you entrusted to me. Thank you for guiding me straight and true through the many obstacles in my path. And for keeping me resolute when all around seemed lost. Thank you for your protection and for your many signs along the way. Thank you for the good that I may have done. I am so sorry about the bad. Thank you for the friends I made during this journey. Please watch over them as you watched over me. I fought the good fight. I finished the race. I kept the faith***."

PREFACE

The article model adopted by the Faculty of Natural Sciences in terms of the General Rules of the North-West University (NWU) has been followed as the research component of this post-graduate study. This entails that research articles are added into the thesis as they were published, submitted or prepared for submission to the specific journals. Therefore, the conventional 'Results and discussions' chapter was replaced by the respective articles. Separate background and motivation (Chapter 1), literature (Chapter 2), experimental (Chapter 3) and project evaluation chapters (Chapter 7) were included in the thesis, even though some of this information had already been summarised in the research articles. This will result in some repetition of ideas/similar text in the thesis. 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 for submitting thesis in article format

Currently, it is a prerequisite for submitting a PhD thesis at the NWU that one research article is submitted to a journal. Many draft articles prepared by post-graduate students are never submitted to internationally accredit peer-reviewed journals. Therefore, the author 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 *Atmospheric Chemistry and Physics*, while another paper was submitted and a third paper is ready for submission to an ISI-accredited journal. Therefore, the prerequisite of the NWU was exceeded.

Contextualising the articles in the overall storyline

The topic of this PhD was associated with ambient volatile organic compounds (VOCs). 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 author focused on anthropogenic ambient aromatic hydrocarbon measurements at Welgegund, South Africa, while the second article (Chapter 5) focused on measurements of biogenic volatile organic compounds at Welgegund, i.e. a grazed savannah-grassland-agriculture landscape in South Africa. In the third paper (Chapters 6), the author performed receptor modelling (source apportionment) and conducted a risk assessment study on all the ambient VOCs measured at Welgegund. 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:

1. **Article I: Jaars, K.,** Beukes, J.P., van Zyl, P.G., Venter, A.D., Josipovic, M., Pienaar, J.J., Vakkari, V., Aaltonen, H., Laakso, H., Kulmala, M., Tiitta, P., Guenther A., Hellen, H., Laakso, L., Hakola, H., **Ambient aromatic hydrocarbon measurements at Welgegund, South Africa**. Published in ***Atmospheric Chemistry and Physics***, a journal of the European Geosciences Union. (Atmospheric Chemistry and Physics, 14, 7075–7089, **2014** www.atmos-chem-phys.net/14/7075/2014/ doi:10.5194/acp-14-7075-2014). The article is presented as the final published version.
2. **Article II: Jaars, K.,** van Zyl, P.G., Beukes, J.P., Hellen, H., Vakkari, V., Josipovic, M., Venter, A.D., Räsänen, M., Knoetze, L., Cilliers, D. P., Siebert, S. J., Kulmala, M., Rinne, J., Guenther A., Laakso, L., Hakola, H., **Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa**. Submitted to ***Atmospheric Chemistry and Physics***, a journal of the European Geosciences Union. The article was formatted according to the guidelines for authors of the journal.
3. **Article III: Jaars, K.,** Vestenius, M., van Zyl, P.G., Beukes, J.P., Hellen, H., Vakkari, V., Venter, M., Hakola, H., **Receptor modelling and risk assessment of volatile organic compounds measured at Welgegund, South Africa.** Prepared for ***Atmospheric Chemistry and Physics***, a journal of the European Geosciences Union. The 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. Räsänen, M., Aurela, M., Vakkari, V., Beukes, J. P., Van Zyl, P. G., Josipovic, M., Venter, A. D., **Jaars, K.**, Siebert, S. J., Laurila, T., Tuovinen, J.-P., Rinne, J., and Laakso, L.: Carbon balance of a grazed savanna grassland ecosystem in South Africa, Biogeosciences Discuss., doi:10.5194/bg-2016-268, in review, **2016**.

2. Venter, A.D., Beukes, J.P., van Zyl, P.G., Josipovic, M., **Jaars, K.**, Vakkari, V., Regional atmospheric Cr (VI) pollution from the Bushveld Complex, South Africa. Accepted in *Atmospheric Pollution Research*. **2016**

3. Vakkari, V., Tiitta, P., **Jaars, K.**, Croteau, P., Beukes, J.P., Josipovic, M., Kerminen, V.M., Kulmala, M., Venter, A.D., Zyl, P.G., and Worsnop, D.R., 2015. Reevaluating the contribution of sulfuric acid and the origin of organic compounds in atmospheric nanoparticle growth. *Geophysical Research Letters*, *42*(23). **2015**

4. Booyens, W., Van Zyl, P.G., Beukes, J.P., Ruiz-Jimenez, J., Kopperi, M., Riekkola, M.L., Josipovic, M., Venter, A.D., **Jaars, K.**, Laakso, L. and Vakkari, V., Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa. *Journal of Atmospheric Chemistry*, *72*(1), pp.43-64. **2015**

5. Sundström, A.-M., Nikandrova, A., Atlaskina, K., Nieminen, T., Vakkari, V., Laakso, L., Beukes, J. P., Arola, A., Van Zyl, P. G., Josipovic, M., Venter, A. D., **Jaars, K.**, Pienaar, J. J., Piketh, S., Wiedensohler, A., Chiloane, E. K., De Leeuw, G., and Kulmala, M. Characterization of satellite-based proxies for estimating nucleation mode particles over South Africa. *Atmospheric Chemistry and Physics, 15*(9), pp.4983-4996. **2015**

6. 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**

7. Vakkari, V., Kerminen, V.M., Beukes, J.P., Tiitta, P., Zyl, P.G., Josipovic, M., Venter, A.D., **Jaars, K.**, Worsnop, D.R., Kulmala, M., and Laakso, L., Rapid changes in biomass burning aerosols by atmospheric oxidation. *Geophysical Research Letters*, *41*(7), pp.2644-2651. **2014**

8. Tiitta, P., Vakkari, V., Croteau, P., Beukes, J.P., Van Zyl, P.G., Josipovic, M., Venter, A.D., **Jaars, K.**, Pienaar, J.J., Ng, N.L., and Canagaratna, M.R., Chemical composition, main sources and temporal variability of PM 1 aerosols in southern African grassland. *Atmospheric Chemistry and Physics, 14*(4), pp.1909-1927. **2014**

9. Beukes, J.P., Vakkari, V., Van Zyl, P.G., Venter, A.D., Josipovic, M., **Jaars, K.**, Tiitta, P., Kulmala, M., Worsnop, D., Pienaar, J.J., and Virkkula, A., Source region plume characterization of the interior of South Africa, as observed at Welgegund. *National Association for Clean Air, The Clean Air Journal, 23*(1), pp.7-10. **2013**

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

1. Beukes, J.P., Venter, A.D., Josipovic, M., Van Zyl, P.G., Vakkari, V., **Jaars, K.**, Dunn, M., and Laakso, L. Automated continuous air monitoring, In: Monitoring Of Air Pollutants – Sampling, Sample, Preparation And Analytical Techniques, editor P Forbes, Elsevier, **2015** (ISBN: 9780444635532)

2. Lauri Laakso, Johan Paul Beukes, Pieter Gideon Van Zyl, Jacobus Pienaar, Miroslav Josipovic, Andrew Venter, **Kerneels Jaars**, Ville Vakkari, Casper Labuschagne, Kgaugelo Chiloane, and Juha-Pekka Tuovinen. Ozone concentrations and their potential impacts on vegetation in southern Africa, Developments in Environmental Science, Chapter 20, Vol. 13. Elsevier Ltd. **2013**, http://dx.doi.org/10.1016/B978-0-08-098349-3.00020-7

ABSTRACT

Various gaseous and aerosol species that are emitted directly from anthropogenic and biogenic sources, as well as secondary formed species, are present and mixed in the giant reactor of the atmosphere, where multiple complex chemical and physical interactions occur. The focus of this thesis was on volatile organic compounds (VOCs) – these compounds are ubiquitous, ranging from strong-smelling monoterpenes and sesquiterpenes emitted from vegetation to various anthropogenic VOCs that have been associated with toxicological effects on human health, e.g. benzene. It has been estimated that the total VOC emissions globally are approximately 1 300 Tg C yr^{-1}. Most of these emissions are from terrestrial ecosystems (~1 000 Tg C yr^{-1}), of which approximately 50 % consist of isoprene and 15 % of monoterpenes. It is estimated that biogenic VOC (BVOC) emissions exceed anthropogenic VOC emissions by eight times. However, in highly-industrialised regions, which include parts of South Africa, anthropogenic VOCs (e.g. benzene, toluene, ethylbenzene and xylene, combined abbreviated as BTEX) might dominate.

Once VOCs are emitted, their lifetimes depend on removal processes, such as dispersion, transformation, photolysis, wet and dry deposition (including deposition on aerosol particles) or oxidation. The chemistry of the atmosphere is strongly influenced by VOCs due to their ability to scavenge oxidants such as ozone (O_3), hydroxyl radicals ($^{\bullet}OH$, referred to from here on as OH) and nitrate radicals ($NO_3^{\bullet}$, referred to from here on as NO_3). VOCs contribute to net tropospheric production and the destruction of O_3 through catalytic reactions between oxidised VOC derivatives (peroxy radicals) and NO. The oxidation of VOCs produces structurally different organic oxygenates, which possess a wide range of properties (e.g. reactivity, volatility and aqueous solubility) and different susceptibilities to undergo gas-to-particle conversion. The vapour pressures of these new species tend to be lower than their precursor compounds, which enables them to condense onto already existing atmospheric particles and thereby contributing to secondary organic aerosol (SOA) formation and particle growth processes. Therefore, VOCs have an indirect regional influence on cloud condensation nucleus (CCN) budget and on the properties of the clouds. In addition to the climatic effects, VOCs and their reaction products are increasingly regarded as posing unacceptable risks to human health, as well as to biological and physical environments. VOCs also have a secondary impact on human health through their participation in the formation of photochemical smog, which is characterised by high concentrations of O_3 and SOA.

Despite VOCs playing a significant role in many different atmospheric processes, very few papers have been published in the peer-reviewed literature on VOC measurements in South

Africa. In an effort to at least partially address this knowledge gap, measurements of anthropogenic and biogenic VOCs were conducted at the Welgegund measurement station in South Africa, which is situated on a commercial farm in an area regarded as a grazed savannah-grassland-agriculture landscape. Welgegund is considered to be a regionally representative background site with few local sources, which is impacted by the major source regions in the interior of South Africa, i.e. the Bushveld Igneous Complex, the Johannesburg-Pretoria conurbation, the Mpumalanga Highveld and the Vaal Triangle. The site is also frequently affected by air masses passing over a relatively clean western sector. VOC samples were collected with an automated sampler on Tenax-TA and Carbopack-B adsorbent tubes with a heated inlet to remove O_3. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays for a period of more than two years, i.e. through a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. Individual VOCs were identified and quantified using a thermal desorption instrument, connected to a gas chromatograph and a mass selective detector.

In this thesis, three research articles are presented, each focusing on a different aspect related to the topic. The first article focused on anthropogenic aromatic VOCs, the second paper on BVOCs, while the third paper presented a receptor modelling and risk assessment study conducted on all the VOCs measured at Welgegund.

In article one, results indicated that the monthly median (mean) total aromatic hydrocarbon concentrations ranged between 0.01 (0.011) and 3.1 (3.2) ppb. Benzene levels did not exceed the local air quality standard limit, i.e. annual mean of 1.6 ppb. Toluene was the most abundant compound, with an annual median (mean) concentration of 0.63 (0.89) ppb. No statistically significant differences in the concentrations measured during daytime and night-time were found, and no distinct seasonal patterns were observed. Air mass back trajectory analysis indicated that the lack of seasonal cycles could be attributed to patterns determining the origin of the air masses sampled. Aromatic hydrocarbon concentrations were in general significantly higher in air masses that passed over anthropogenically impacted regions. Inter-compound correlations and ratios gave some indications of the possible sources of the different aromatic hydrocarbons in the source regions defined in the paper. The highest contribution of aromatic hydrocarbon concentrations to ozone formation potential was also observed in plumes passing over anthropogenically impacted regions.

In article two, the annual median concentrations of isoprene, 2-methyl-3-butene-2-ol (MBO), monoterpenes and sesquiterpenes (SQT) during the first campaign were 14, 7, 120 and 8 pptv, respectively and during the second campaign, 14, 4, 83 and 4 pptv, respectively. The sum of the concentration of the monoterpenes, with α-pinene being the most abundant species, was at

least an order of magnitude higher than the concentrations of other BVOC species during both sampling campaigns, which was also similar to atmospheric monoterpene levels in other environments. The highest BVOC concentrations were observed during the wet season, with elevated soil moisture also associated with increased BVOC concentrations. However, comparisons with measurements conducted at other landscapes in southern Africa and the rest of the world that have more woody vegetation indicated that BVOC concentrations were, in general, significantly lower. Furthermore, the total BVOC concentrations were an order of magnitude lower compared to total aromatic concentrations measured at Welgegund. An analysis of concentrations by wind direction indicated that isoprene concentrations were relatively higher from the western direction, while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. Statistical analysis indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpenes and SQT concentrations, while temperature had the greatest influence on isoprene levels. The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1 162 and 1 022 pptv, respectively. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured for all of the months during both sampling campaigns.

In manuscript three, positive matrix factorisation (PMF) analysis was performed on VOC data collected at a regional background atmospheric monitoring station affected by the major sources in the interior of South Africa in order to conduct a source apportionment study. In addition, a risk assessment study was also performed in view of the major source regions affecting Welgegund in order to quantify the impacts of anthropogenic VOCs measured at Welgegund on human health. PMF analysis revealed ten meaningful factor solutions, of which five factors were associated with biogenic emissions and five with anthropogenic sources. Three of the biogenic factors were characterised by a specific biogenic species, i.e. isoprene, limonene and 2-methyl-3-buten-2-ol (MBO), while the other two biogenic factors comprised mixtures of biogenic species with different tracer species. The temporal factor contribution for the isoprene, limonene and MBO factors correlated relatively well with the seasonal wet pattern. Wind roses indicated that Welgegund was affected by biogenic species from all wind directions in the surrounding environment. Two anthropogenic factors were associated with emissions from a densely populated anthropogenic source region to the east of Welgegund (Johannesburg-Pretoria conurbation and Mpumalanga Highveld) with a large number of industrial activities. An anthropogenic factor was also identified that reflected the influence of solvents on atmospheric VOC concentrations, while two anthropogenic factors were determined that indicated the influence of farming activities in close proximity to Welgegund. A non-cancer

(hazard ratios) and cancer-risk (lifetime cancer risks) assessment study conducted for VOCs measured at Welgegund in relation to three source regions identified, indicated that the non-cancerous influence of VOCs measured in the source regions is significantly lower compared to the cancerous influence of these species on human health, which poses a significant cancer risk. An assessment of the OH reactivity of anthropogenic VOCs indicated that OH reactivity was higher for VOCs in air masses passing over a highly industrialised source region, while the highest OH reactivity was determined for species for which high ozone formation potential was determined in previous studies.

Keywords: Volatile organic compounds (VOCs), aromatic hydrocarbons, biogenic VOCs, BTEX, positive matrix factorisation (PMF), health risk assessment, Welgegund

LIST OF ABBREVIATIONS

AMMA	African Monsoon Multidisciplinary Analyses
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	benzene, toluene; ethylbenzene, o-, m- and p-xylene
BVOC	biogenic volatile organic compound
CALEPA	California Environmental Protection Agency
EBIC	eastern Bushveld Igneous Complex
EXPRESSO	EXPeriment for the REgional Sources and Sinks of Oxidants
GPP	gross primary production
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
Jhb-Pta	Johannesburg-Pretoria
MBO	2-methyl-3-butene-2-ol
MDL	method detection limit
MIR	maximum incremental reactivity
MT	monoterpenes
NAAQS	National Ambient Air Quality Standards
NEE	net ecosystem exchange
OFP	ozone formation potential
PMF	Positive Matrix Factorisation
ppbv	parts per billion (10^{-9})
pptv	parts per trillion (10^{-12})
SOA	secondary organic aerosol
SQT	sesquiterpenes
VOC	volatile organic compound
WBIC	western Bushveld Igneous Complex
WHO	World Health Organization

TABLE OF CONTENTS

ACKNOWLEDGEMENTS ..... **I**

PREFACE ..... **IV**

ABSTRACT ..... **VIII**

LIST OF ABBREVIATIONS ..... **XII**

CHAPTER 1 ..... **1**

THESIS MOTIVATION, OBJECTIVES AND OVERVIEW **1**

1.1 INTRODUCTION **1**

1.2 OBJECTIVES **9**

1.3 THESIS OVERVIEW **10**

CHAPTER 2 ..... **11**

LITERATURE REVIEW ON THE FORMATION OF OXIDISING AGENTS, REACTION OF VOCS AND LIFETIMES **11**

2.1 INTRODUCTION **11**

2.2 FORMATION OF OXIDIZING AGENTS OF THE TROPOSPHERE **11**

2.3 REACTIONS OF VOCS IN THE TROPOSPHERE **14**

2.3.1 Reactions of alkanes 16

2.3.2 Reactions of alkenes 18

2.3.3 Reactions of aromatics 20

2.3.4 Lifetimes of VOCs 22

2.4 CONCLUSION **23**

CHAPTER 3 ..... **24**

MEASUREMENT LOCATION, TECHNIQUES AND DATA ANALYSIS **24**

3.1 MEASUREMENT LOCATION **24**

3.1.1 Site description 24

3.1.2 Vegetation 27

3.2 MEASUREMENT TECHNIQUES **30**

3.2.1 VOC measurements and analysis 31

3.2.2 Ancillary measurements 33

3.3 DATA ANALYSIS **34**

3.3.1 Positive matrix factorisation analysis 34

3.3.2 Reactivity of VOCs 35

3.3.3 Risk assessment 35

3.3.4 Air mass back trajectory analysis 37

CHAPTER 4 ..... **38**

AMBIENT AROMATIC HYDROCARBON MEASUREMENTS AT WELGEGUND, SOUTH AFRICA **38**

4.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT **38**

4.2 FORMATTING AND CURRENT STATUS OF ARTICLE **39**

CHAPTER 5 ..... **55**

MEASUREMENTS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS AT A GRAZED SAVANNAH-GRASSLAND-AGRICULTURE LANDSCAPE IN SOUTH AFRICA **55**

5.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT **55**

5.2 FORMATTING AND CURRENT STATUS OF ARTICLE **56**

CHAPTER 6 ..... **93**

RECEPTOR MODELLING AND RISK ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS MEASURED AT WELGEGUND, SOUTH AFRICA **93**

6.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT **93**

6.2 FORMATTING AND CURRENT STATUS OF ARTICLE **94**

CHAPTER 7 ..... **133**

PROJECT EVALUATION AND FUTURE PERSPECTIVES **133**

7.1 PROJECT EVALUATION **133**

7.2 FUTURE PERSPECTIVES **138**

APPENDIX A **140**

A.1 Temporal patterns of anthropogenic VOCs **140**

A.2 Monthly contributions of aromatic VOCs to OH reactivity **148**

BIBLIOGRAPHY **150**

LIST OF TABLES

Table 2-1: Calculated lifetimes of some of VOCs studied in this thesis according to literature with respect to reaction with the OH radical, reaction with the NO_3 radical and reaction with O_3 (Atkinson, 2000, Atkinson and Arey, 2003b)..... 23

Table 3-1: Non-cancer reference concentrations, cancer unit risks of the VOCs found during the campaigns and their carcinogenic classifications in the IARC at Welgegund. Risk probability values (inhalation reference concentration and unit risk) were obtained through the risk model calculator, established by the University of Tennessee ((RAIS, 2016) and reference therein), by giving priority to the most recent available data..... 36

LIST OF FIGURES

Figure 1-1: Schematic diagram of various processes involved in the cycle of atmospheric VOCs, which include sources, sinks and atmospheric pathways of VOCs (Koppmann, 2007) 2

Figure 1-2: An overview of volatile-mediated plant interactions with the surrounding environment (Dudareva et al., 2006) 3

Figure 1-3: Components affecting radiative forcing. The red rectangles highlight the sections showing the effect of O_3 and aerosols on radiative forcing, which can directly or indirectly be formed from VOCs. Adapted from (IPCC, 2013) 6

Figure 2-1: A schematic illustration of the formation of Criegee Intermediates and their destiny in the atmosphere. Figure adapted from Mogensen (2015) 14

Figure 2-2: Simplified schematic of the OH-initiated degradation of generic VOCs to form first-generation products (Hallquist et al., 2009) 16

Figure 2-3: Schematic representation of the major radical propagation pathways of the OH-initiated degradation of butane, also illustrating the sequential formation of the intermediate products MEK, CH_3CHO, HCHO and CO. The schematic is from Pinho et al. (2005); therefore, the electron balance is not shown. 18

Figure 2-4: Schematic representation of the atmospheric degradation of isoprene by OH radical (a) and (b) NO_3 radical (Atkinson and Arey, 2003b) 19

Figure 2-5: Schematic representation of the OH-initiated oxidation of p-xylene to first generation products. The schematic is from Jenkin et al. (2003); therefore, the electron balance is not shown. 21

Figure 3-1: Southern African map indicating the location of the Welgegund measurement station (blue star), total SO_2 emissions based on SAFARI 2000 emission inventory (Fleming and van der Merwe, 2002), large point sources in the industrial hub of South Africa and anthropogenic source regions affecting Welgegund. The figure was reproduced with permission from Vakkari (2013) 25

Figure 3-2: Population density over southern Africa. The measurement site is indicated with a blue star. The population hot-spot north-east of the measurement site is the JHB-PTA megacity and the Vaal Triangle. The figure was reproduced with permission from Vakkari (2013). 26

Figure 3-3: Air mass history at Welgegund. The trajectories have been calculated for arrival height of 100 metres and length of 96 hours backwards. The figure was reproduced with permission from Vakkari (2013). 27

Figure 3-4: The International Geosphere-Biosphere Programme (IGBP) vegetation classification for southern Africa for 2010 based on MODIS collection 5 land cover type product. The blue star indicates Welgegund. The figure was reproduced with permission from Vakkari (2013). 28

Figure 3-5: General vegetation map for 60 km radius of Welgegund measurement station. Figure is from Article II (Chapter 5). 29

Figure 3-6: Welgegund atmospheric research station indicating some of the measurements conducted 31

Figure 3-7: Thermal desorption instrument connected to a gas chromatograph and a mass selective detector 33

CHAPTER 1

THESIS MOTIVATION, OBJECTIVES AND OVERVIEW

1.1 INTRODUCTION

The passing decades have seen environmental politics and decision-making becoming a more prominent feature on the socio-political and economic agendas that focus on protecting our health and preserving our environment (Panel, 2015). This doctoral thesis is partially motivated by the primary legislation governing air quality in South Africa, specifically section 24 of the Constitution, which states that everyone has the right to an environment (including ambient air) that is not harmful to their health and well-being. In 2004, a new air quality act, the National Environmental Management Act: Air Quality Act 39 of 2004 (NEMA: AQA 39, 2004), was promulgated, repealing the out-dated Air Pollution Prevention Act 45 of 1965. In line with other environmental quality-related legislation, e.g. the Water Act, NEMA: AQA takes the Constitution as its foundation by providing for national quality and performance standards. Zunckel et al. (2007) stated that this approach ensures the holistic philosophy of air quality management at national, regional and local scales. Despite this, according to Laakso et al. (2008), Africa is still one of the least studied continents in terms of atmospheric sciences, although it is highly vulnerable to the impacts of air pollution and climate change. According to Chutel (2016), South Africa has the third largest economy in Africa after Egypt and Nigeria and is known for its diverse anthropogenic emission sources, which include agriculture, mining and metallurgical operations, power generation, petrochemical industries, coal dumps, large-scale biomass combustion (veld and bush fires), household combustion and transportation.

Various gaseous and aerosol species that are emitted directly from both anthropogenic and biogenic sources, as well as secondary formed species, are present and mixed in the giant reactor of the atmosphere, where multiple complex chemical and physical interactions occur. The focus of this thesis was on organic trace gases whose atmospheric concentrations are at low levels varying from some ten parts per billion down to a few parts per trillion. The acronym, VOCs (volatile organic compounds), includes a broad spectrum of atmospheric hydrocarbons with different structures and functional groups, e.g. terpenoids, alkenes, amines, alcohols, aldehydes and ketones (Kesselmeier and Staudt, 1999). VOCs are often defined as organic compounds having 15 or less carbon atoms in their structure, whose vapour pressure is over 10 Pa at 25 °C and whose boiling point at atmospheric pressure is up to 260 °C (Koppmann, 2007). VOCs are ubiquitous, ranging from the

strong-smelling mono- and sesquiterpenes emitted from vegetation (Kesselmeier and Staudt, 1999) to compounds that have been associated with toxicological effects on human health, e.g. benzene (Aguilera et al., 2007, Durmusoglu et al., 2010, Hellén et al., 2002, Hoque et al., 2008) emitted from human activities. As can be seen from Figure 1-1, these gaseous species can be classified according to sources thereof as either biogenic VOCs (BVOCs) (e.g. isoprene and monoterpenes) or anthropogenic VOCs (e.g. benzene) (Atkinson, 2000, Atkinson and Arey, 2003b). However, certain VOCs, e.g. isoprene, can originate from biogenic and anthropogenic sources (Hellén et al., 2012b, Wagner and Kuttler, 2014).

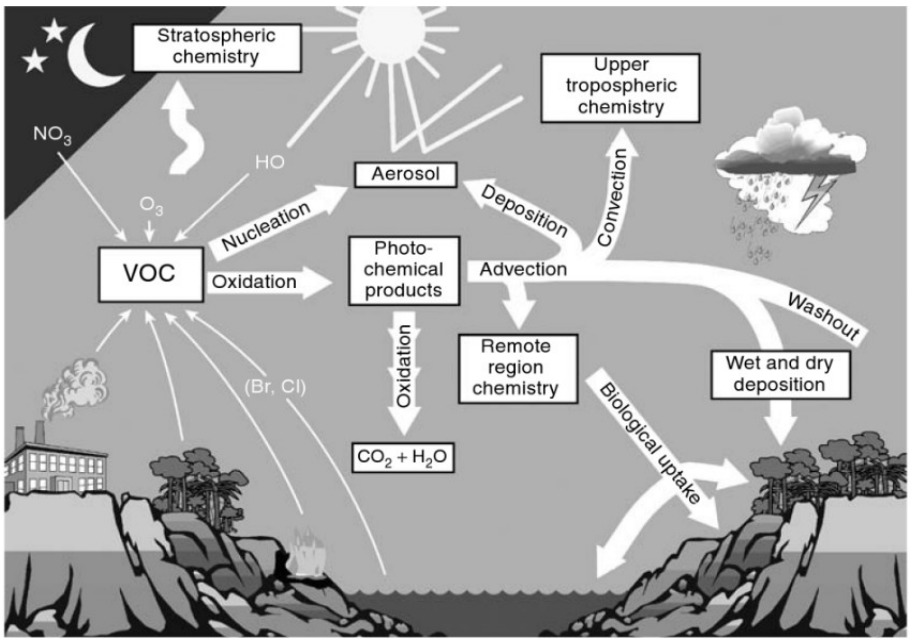

Figure 1-1: Schematic diagram of various processes involved in the cycle of atmospheric VOCs, which include sources, sinks and atmospheric pathways of VOCs (Koppmann, 2007)

As is evident from Figure 1-2, ecosystems produce and emit a large number of BVOCs that are involved in plant growth and reproduction, as well as acting as defensive compounds, e.g. preventing the colonisation of pathogens after wounding, deterring insects or recruiting natural enemies of herbivores (Smolander et al., 2014, Dudareva et al., 2006). The BVOC production rate in an ecosystem depends on several physical (e.g. temperature, precipitation, moisture, solar radiation and CO_2 concentration) and biological parameters (e.g. plant species, plant-specific emission capacity, phenology, biotic and abiotic stresses, attraction of pollinators) (Smolander et al., 2014, Dudareva et al., 2006), with typically 0.2 to 10% of the carbon uptake in photosynthesis being converted to BVOCs (Kesselmeier et al., 2002).

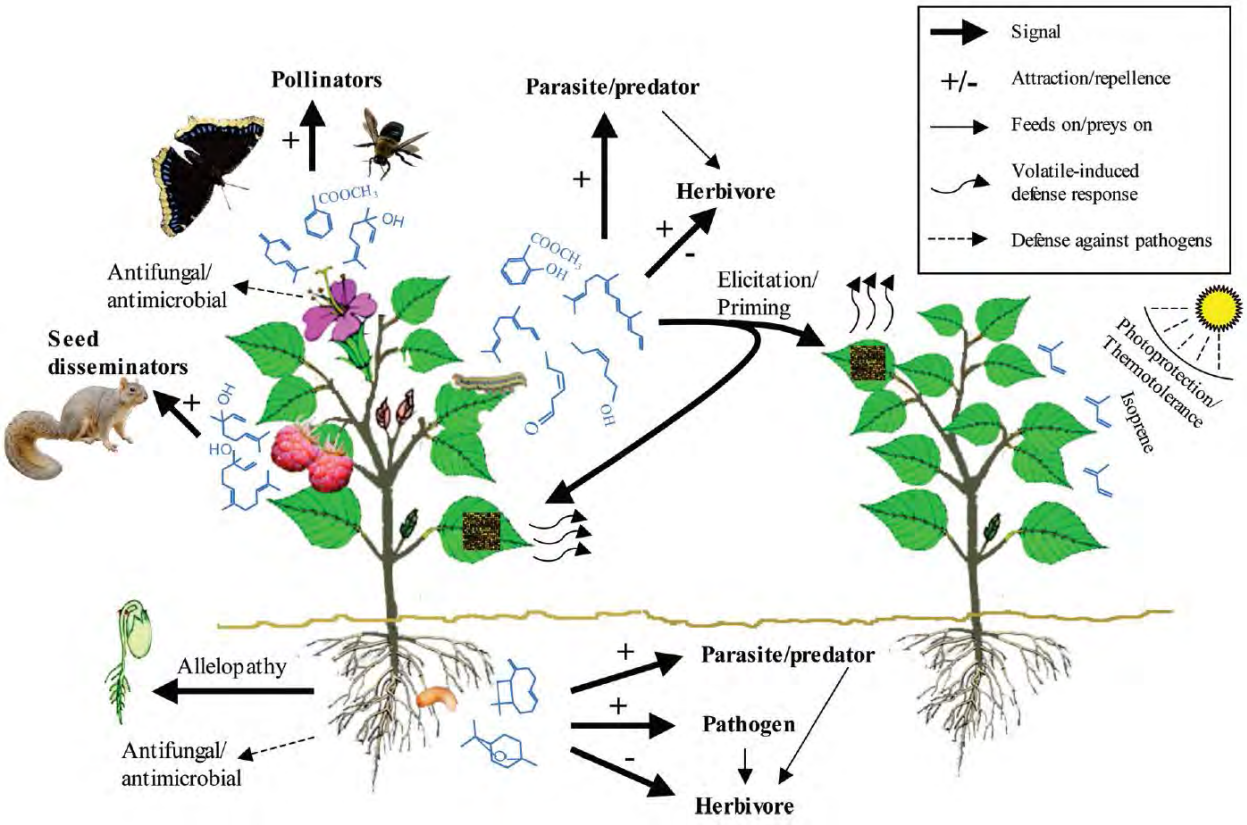

Figure 1-2: An overview of volatile-mediated plant interactions with the surrounding environment (Dudareva et al., 2006)

Guenther (2002) estimated that the total VOC emissions globally to be approximately 1 300 teragrams of carbon per year (Tg C yr^{-1}, 1 teragram = 10^{12} g). Most of these emissions are by terrestrial ecosystems (~1000 Tg C yr^{-1}), of which approximately 50 % is isoprene and 15 % is monoterpenes (Guenther et al., 2012). These estimates are dependent upon several factors, including climate, vegetative cover, as well as the emission characteristics of individual species and vegetation types within the vegetation cover. According to Lamarque et al. (2010), BVOC emissions exceed anthropogenic VOCs by eight times, which are estimated to be approximately 130 Tg C yr^{-1}. In view of the afore-mentioned, intensive studies have been conducted to investigate BVOC emissions and oxidation processes (Nakashima et al., 2014). However, few such studies have been conducted for South Africa, which will be discussed later. Additionally, South Africa is known for its diverse anthropogenic activities. Therefore, in contrast to the global trend, the South African atmospheric VOC budget could be dominated by the anthropogenic VOC emissions. The estimated total BVOC emissions for southern Africa are 80 Tg C yr^{-1}, with isoprene and monoterpenes contributing 56 and 7 Tg C yr^{-1}, respectively (Otter et al., 2003). Accoring to Otter et al. (2003) woodlands are the dominant vegetation type, covering 23% of southern Africa, and are the largest annual source of isoprene (20 Tg C), monoterpenes (3 Tg C), and other BVOCs (4 Tg C). It is estimated that the main anthropogenic sources of VOCs globally are the production and use of

fossil fuels (77.4 Tg C yr^{-1}), industrial processes, e.g. paints, adhesives and pharmaceuticals (26.7 Tg C yr^{-1}), biofuel combustion, e.g. electrical power generation (30 Tg C yr^{-1}) and waste management (2.7 Tg C yr^{-1}) (Reimann and Lewis, 2007). Furthermore, emissions from biomass burning are also an important source of VOCs that can be considered to be either from anthropogenic (household combustion for space heating, man-made wild fires) or natural activities (wild fires). Andreae and Merlet (2001) attributed 60 Tg C yr^{-1} of global VOC emissions to biomass burning, i.e. from savannah and grassland (26 Tg C yr^{-1}) and tropical forest (34 Tg C yr^{-1}) fires. Lourens et al. (2011) indicated several potential anthropogenic sources of VOCs in the South African Highveld.

Once VOCs are emitted, their lifetimes depend on removal processes, such as dispersion, transformation, photolysis, wet and dry deposition (including deposition on aerosol particles), or oxidation. Dry and wet deposition are more relevant for the chemically long-lived compounds, e.g. methanol, due to their slow chemical oxidation (Atkinson and Arey, 2003a). However, significant deposition has also been reported for the very reactive short-lived compounds, e.g. mono- and sesquiterpenes (Bamberger et al., 2011, Ruuskanen et al., 2011). The chemistry of the atmosphere is strongly influenced by VOCs due to their ability to scavenge oxidants such as ozone (O_3), hydroxyl radicals ($^{\bullet}OH$, referred from here on as OH for simplicity) and nitrate radicals ($NO_3^{\bullet}$, referred to from here on as NO_3 for simplicity) (Atkinson and Arey, 2003b). OH is the most important sink for VOCs (Atkinson and Arey, 2003b). In polluted, high nitrogen oxide (NO_x) environments (Lourens et al., 2012), VOCs contribute to net tropospheric O_3 production and destruction processes through catalytic reactions between oxidised VOC derivatives (peroxy radicals) and NO (Lelieveld et al., 2008, Atkinson and Arey, 2003b, Atkinson, 2000, Chameides et al., 1992, Vogel et al., 1995) (see **Section 2.2** for a more detail discussion). Recently, Criegee Intermediates (CIs) have also been suggested as important atmospheric oxidants (Mauldin III et al., 2012, Welz et al., 2012). The lifetime of reactivity of VOCs with all the afore-mentioned oxidants can be very short (minutes to hours) for compounds of biogenic origin, e.g. β-caryophyllene and α-pinene, or very long (several days) for compounds of anthropogenic origin and secondary formation, e.g. benzene and some oxygenated VOCs (Atkinson, 2000, Atkinson and Arey, 2003b, Kesselmeier and Staudt, 1999, Koppmann, 2008), depending on the structure of the VOC and the ambient conditions (Atkinson and Arey, 2003b). The long-lived VOCs are oxidised relatively slowly and they can therefore be transported over long distances. The very reactive short-lived BVOCs are oxidised quickly and this occurs locally.

The oxidation of VOCs produces structurally different organic oxygenates, which possess a wide range of properties (e.g. reactivity, volatility and aqueous solubility) and different propensities to undergo gas-to-particle conversion (Kulmala et al., 2004, Tunved et al., 2006). Moreover, the

vapour pressure of these new species tend to be lower than their precursor compounds, which enables them to condense onto already existing particles and in so doing partake in particle growth processes (Ehn et al., 2014, Hao et al., 2011, VanReken et al., 2006) and secondary organic aerosol (SOA) formation, interchangeably referred to as new particle formation (NPF) (Andreae and Crutzen, 1997, Claeys et al., 2004, Kiendler-Scharr et al., 2009, Kulmala et al., 2014, Went, 1960, Laakso et al., 2008, Vakkari et al., 2011, Vakkari et al., 2015). NPF has been observed in several environments around the world (Kulmala et al., 2004). VOCs are not the only component that can explain the occurrence of NPF. According to several studies (Kirkby et al., 2011, Kulmala et al., 2000, Lauros et al., 2011, Paasonen et al., 2010, Sipilä et al., 2010, Zhao et al., 2010), sulphuric acid (H_2SO_4) is one of the initial or required molecules in the nucleation mechanism. Recently, Vakkari et al. (2015) found that depending on the gaseous precursors and size of the newly formed particles, the growth was dominated by either H_2SO_4 accompanied by ammonium, or organic compounds originating either from biogenic emissions or savannah fires. These authors also observed that the contribution of H_2SO_4 was larger during the early phases of the growth, but in clean conditions organic compounds dominated the growth. Laakso et al. (2008) reported NPF was frequent in a relatively clean southern African savannah environment with formation and growth rates among the highest observed in continental environments. The afore-mentioned authors concluded that NPF is likely to have a regional effect on the cloud condensation nucleus (CCN) budget and on the properties of the clouds. Atmospheric water vapour can use the CCN as seeds and condense onto those; in so doing, cloud droplets are formed. Clouds alter the earth's radiation budget by scattering and the absorption of solar light; therefore, aerosol particles, and their sources, e.g. VOC oxidation products, particulate phase sulphate, nitrate and ammonium, directly affect our climate (Makkonen et al., 2012, Ehn et al., 2014). However, according to the Intergovernmental Panel on Climate Change (IPCC), the level of understanding of these processes is low (Figure 1-3).

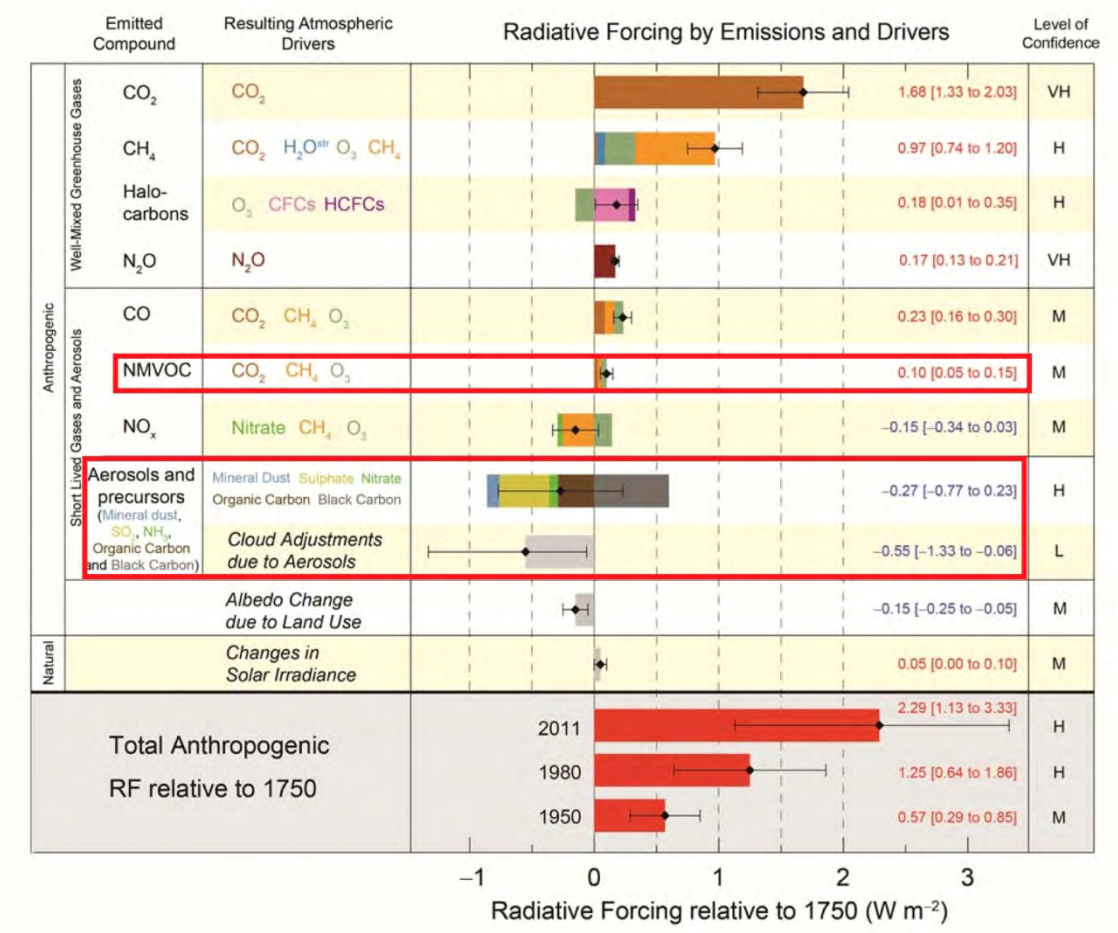

Figure 1-3: Components affecting radiative forcing. The red rectangles highlight the sections showing the effect of O_3 and aerosols on radiative forcing, which can directly or indirectly be formed from VOCs. Adapted from (IPCC, 2013)

In addition to climate effects, VOCs also have other significant effects on our lives. One obvious consequence is that VOCs and their reaction products are increasingly regarded as posing unacceptable risks to public and occupational health, as well as to biological and physical environments. Numerous studies suggest that ambient air exposure to certain VOCs can lead to potential chronic and acute health effects, e.g. acute and chronic respiratory effects, neurological toxicity, lung cancer, and eye and throat irritation (Delfino et al., 2003, Kim et al., 2002, Otto et al., 1992, Payne-Sturges et al., 2004, Wichmann et al., 2009). VOC species, such as benzene, have been designated as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) (IARC, 2012) and toxic as defined under the United States Agency for Toxic Substances and Disease Registry (ATSDR) (ATSDR, 2015). It has been estimated that a lifetime exposure of 0.3 ppbv of benzene leads to approximately six cases of leukaemia per 1 000 000 inhabitants (World Health Organization, 2000). Therefore, specific limits and standards have been set for benzene, which should not be exceeded, or only exceeded a set amount of times in order to minimise associated health and/or environmental impacts. For example, an annual limit of 1.6 ppbv

was set for benzene in ambient air by South Africa (Government Gazette Republic of South Africa, 2009), the European Union (European Union, 2008), India and South Korea (The Gazette of India, 2009, Korean Ministry of Environment, 2011), while the Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10 000) of 4.0 ppbv was established by ATSDR (ATSDR, 2016).

VOCs also have secondary effects on human health by participating in the formation of photochemical smog, which is characterised by high concentrations of O_3 and SOA (World Health Organization, 2006). Photochemical smog and haze pollution generally take place simultaneously and are of great concern in many cities around the world. The notorious 1952 air pollution disaster in London is a classic example (Brimblecombe, 2008). More recent examples are the photochemical smog in Beijing, China (Wang et al., 2013, Zhang et al., 2013, Sun et al., 2006), Los Angeles, USA (Pollack et al., 2013, Haagen-Smit, 1952, Heo et al., 2015), Delhi, India (Tiwari et al., 2015, George et al., 2013) and Mexico City, Mexico (Castro et al., 2001, Jaimes-Palomera et al., 2016, Hernández et al., 2016). Haze pollution is also common in South Africa. Piketh et al. (1999) wrote that the southern African haze layer is a ubiquitous sub-continental-scale feature of the lower atmosphere that extends to a depth of ~5 km (~500 hPa level) on non-rain days, particularly in winter. They go further to state that aerosols derived from biomass burning are commonly thought to contribute substantially to the total background aerosol loading within the layer. According to Diab et al. (2004), and references therein, within the haze layer, trace gases and aerosols are recirculated until they exit the sub-continent toward the east as a giant plume, approximately 1 000 km wide. Stein et al. (2003) said this phenomenon was first described with respect to a plume of anomalously high ozone concentrations as measured by the TOMS (Total Ozone Mapping Spectrometer) satellite platform. Similarly, Chiloane (2006) studied the brown haze that forms over Cape Town in winter months under inversion conditions and found that VOCs are an important component of the haze layer, particularly because of their reactivity. Gwaze et al. (2007) also studied the intense brown haze episodes over Cape Town during winter by characterizing the physical, chemical and optical properties of aerosol particles. Wicking-Baird et al. (1997) have shown that vehicles account for up to 67% of the Cape Town brown haze pollution. O_3, one of the main reactive oxidants in photochemical smog or haze, is particularly relevant for South Africa, with various studies indicating that O_3 is currently the most problematic pollutant in South Africa (Zunckel et al., 2004, Martins et al., 2007, Lourens et al., 2011, Laakso et al., 2012, Josipovic et al., 2010, Laban et al., 2015). This secondary formed pollutant can have negative impacts on human health, the ecosystem and food security (Zunckel et al., 2006, Townsend et al., 2003).

Despite the fact that VOCs play a significant role in many different atmospheric processes (see Figures 1-1 and 1-2), very few papers have been published in the peer-reviewed literature on VOCs in South Africa. Some industries do conduct anthropogenic VOC measurements for compliance

purposes, as do various governmentally controlled air quality measurement stations. According to Forbes and Rohwer (2008), VOCs (specifically benzene, toluene, ethylbenzene and xylenes, collectively referred to as BTEX) are monitored at nine sites across three provinces by local municipalities in South Africa. However, none of this data have been published in the peer-reviewed public domain. Brunke et al. (2001) reported interesting results for non-methane hydrocarbons monitored at Cape Point within the context of biomass burning episodes. Burger (2006) reported passive BTEX measurements in the Vaal Triangle and in Cape Town, whereas Van der Walt (2008) presented hydrocarbon emissions in a South African metropolitan area. Lourens et al. (2011) measured BTEX in the Mpumalanga Highveld and the Vaal Triangle with passive sampling techniques for a one-year period. Furthermore, VOCs have been studied within the context of emissions from spontaneous combustion of coal (Pone et al., 2007) and the Cape Town brown haze (Burger et al., 2004, Chiloane, 2006).

Zunckel et al. (2007), with references therein (especially studies by Otter et al. (2002), Otter et al. (2003) and Guenther et al. (1996)), indicated that limited research has been conducted on BVOC emissions in southern Africa, which comprised mainly brief campaigns measuring BVOC emission rates. On an international level, long-term ambient BVOC measurements to establish seasonal cycles of emissions and concentrations have been conducted extensively, which include boreal forest (Hakola et al., 2009, Hakola et al., 2000, Rinne et al., 2000, Rinne et al., 2005, Räisänen et al., 2009, Lappalainen et al., 2009, Eerdekens et al., 2009, Rantala et al., 2015), hemiboreal mixed forest (Noe et al., 2012), temperate (Spirig et al., 2005, Stroud et al., 2005, Mielke et al., 2010, Fuentes et al., 2007), Mediterranean (Harrison et al., 2001, Davison et al., 2009) and tropical ecosystems (Rinne et al., 2002). Shorter campaigns have also been conducted in Western and Central Africa, which include several different studies in the framework of African Monsoon Multidisciplinary Analyses (AMMA) (Grant et al., 2008, Saxton et al., 2007) and EXPeriment for the REgional Sources and Sinks of Oxidants (EXPRESSO) (Serca et al., 2001).

Detailed VOC inventories for South Africa are important in order to improve the understanding of regional and global atmospheric chemistry. The combination of relatively high atmospheric pollutant emissions and unique weather conditions necessitates that more comprehensive VOC measurements are conducted in South Africa. These unique weather conditions include relatively high temperatures, prolonged periods of high solar radiation and dominant anti-cyclonic recirculation climatology causing the trapping of pollutant species, which leads to the increased photochemical aging of pollutants, especially over the interior of South Africa (Tyson et al., 1996).

In an effort to at least partially address the above-mentioned knowledge gap, VOCs were measured at the Welgegund measurement station (Booyens et al., 2015, Tiitta et al., 2014, Beukes et al., 2015). The site is situated approximately 100 km west of Johannesburg and is considered to be a

regionally representative background site with no direct impacts from pollution sources within close proximity. The Welgegund measurement station is, however, affected by plumes from major anthropogenic source regions in the interior of South Africa, i.e. the western Bushveld Igneous Complex (BIC), the eastern BIC, the Johannesburg-Pretoria metropolitan conurbation (>10 million people), the Vaal Triangle and the Mpumalanga Highveld (Beukes et al., 2013). These source regions include the three national air pollution priority areas as declared by the South African government. In addition, Welgegund is also affected by air masses passing over a relatively clean sector in the western region with very few large point sources (Beukes et al., 2013). Measurements of VOCs at Welgegund will provide a good understanding of the influence of the major anthropogenic source regions on VOC concentrations, as well as the impacts from a relatively 'clean' sector (Beukes et al., 2013). In addition, BVOC measurements at Welgegund will provide a better understanding of ambient BVOC levels and processes in the Dry Highveld Grassland Biome in which Welgegund is positioned. Most of South Africa's maize, the local staple food, originates from this biome. Therefore, measurements at this site also contribute to ensuring future food security.

1.2 OBJECTIVES

The general objective of this investigation is to determine the ambient VOC concentrations at the Welgegund atmospheric measurement station, as well as the identification of sources and better understanding of processes in which VOCs participate in the interior of South. The specific objectives of this study include:

1. The collection of ambient anthropogenic and biogenic VOCs with an appropriate sampling technique for at least a full seasonal cycle;
2. The identification and quantification of atmospheric VOC species;
3. To contextualise VOC concentrations measured at Welgegund to published VOC data from previous measurements conducted in South Africa and internationally;
4. To determine the possible temporal trends of the atmospheric anthropogenic and biogenic VOC species;
5. To determine the general transport patterns of VOCs; and
6. To explain the observed trends by investigating the reactivity of VOCs, ozone formation potential, inter-compound correlations and ratios, as well as correlations with other high resolution ancillary data measured at Welgegund, e.g. meteorological data and trace gas concentrations.

7. Source apportionment of VOCs measured at Welgegund using positive matrix factorisation;
8. To evaluate the potential health risk when exposed to VOCs in the plumes passing over the identified source regions;

1.3 THESIS OVERVIEW

In order to achieve the above-mentioned objectives, this thesis composes of seven chapters, i.e.:

1. Chapter 1 provides the background and the major research objectives of this study
2. Chapter 2 presents a brief literature review on the formation of oxidizing agents, reaction of VOCs and lifetimes
3. Chapter 3 describes the methodology used in this study, including the description of the sampling site, measurement techniques, data analysis, quality control and assurance
4. Chapter 4, which is related to ambient aromatic hydrocarbon measurements at Welgegund, South Africa
5. Chapter 5, which is related to measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa
6. Chapter 6, which is related to receptor modelling and risk assessment of volatile organic compounds measured at Welgegund, South Africa
7. Chapter 7 contains the conclusions, project evaluation and future perspectives

CHAPTER 2

LITERATURE REVIEW ON THE FORMATION OF OXIDISING AGENTS, REACTION OF VOCS AND LIFETIMES

2.1 INTRODUCTION

This chapter is devoted to a discussion of the chemistry of VOCs, to compliment the information already presented in Chapter 1. As mentioned in Chapter 1, once released into the atmosphere, VOCs are involved in various chemical reactions and are removed from the atmosphere through different reaction mechanisms and at different rates. A number of excellent reviews of reaction mechanisms for the process of degradation of VOCs have been presented by Seinfeld and Pandis (2006), Atkinson (2000), Atkinson and Arey (2003a), Calvert et al. (2002) and Mellouki et al. (2003).

2.2 FORMATION OF OXIDIZING AGENTS OF THE TROPOSPHERE

As indicated in Chapter 1, VOCs are linked to the oxidation of the most important oxidising agents in the troposphere. The main source of tropospheric O_3 is the photo-dissociation ($\lambda \leq 430$ nm) of NO_2 to yield NO and ground state oxygen, O (^3P), which reacts with molecular oxygen to form O_3 in the presence of a third species M (Seinfeld and Pandis, 2006). The O_3 will quickly oxidise NO back to NO_2, and a steady state concentration of O_3 will be obtained as a balance of reactions 2.1, 2.2 and 2.3

$$NO_2 + h\nu\ (\lambda \leq 430\ nm) \rightarrow NO + O\ (^3P) \qquad (2.1)$$

$$O\ (^3P) + O_2 + M \rightarrow O_3 + M\ (M = air) \qquad (2.2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (2.3)$$

However, NO_2 is also formed by means of the reaction of NO with other oxidants, i.e. hydroperoxy (HO_2) and alkylperoxy radicals (RO_2). These free radicals are formed in the degradation reactions of VOCs (Figure 2-2 in Section 2.3), which may compete with and replace O_3 in the oxidation of NO.

This in combination with sufficient NO_x can increase the formation of tropospheric O_3; therefore, VOCs are important in tropospheric O_3 formation.

Degradation of VOCs → R → RO_2 + HO_2 (peroxy radicals) (2.4)

$RO_2 + NO \rightarrow NO_2 + RO$ (2.5)

$HO_2 + NO \rightarrow NO_2 + HO$ (2.6)

Only 10% of all atmospheric O_3 is located in the troposphere. Nevertheless, its presence is of fundamental importance to atmospheric chemistry, as it is the main source of OH radicals. It is now well recognised that the OH radicals, in terms of its reactivity, are the most important oxidant for several VOCs in the troposphere (Atkinson and Arey, 2003a, Calvert et al., 2002, Calvert et al., 2000, Atkinson, 1997). OH radicals do not only oxidise most VOCs very efficiently, but also recycle NO_x (NO + NO_2) and HO_x (OH + HO_2, in some studies, RO_2 are also included) radicals, while producing secondary pollutants such as O_3 and SOA (Atkinson, 2000, Atkinson and Arey, 2003a). Therefore, the key to understanding tropospheric chemistry begins with understanding the role of the OH radical. These ubiquitous short-lived radical concentrations are strongly affected by O_3 and, in turn, they substantially affect the O_3 concentration. In the troposphere, OH radicals are highly reactive, with a lifetime of less than 1 s. They are formed by the photo-dissociation (at wavelengths < 319 nm) of gaseous O_3 by solar ultraviolet (UV) radiation in the presence of water vapour (Rohrer and Berresheim, 2006). The photo-dissociation produces both ground state (O) (combines with O_2 to reproduce O_3) and high excess energy singlet (O (^{1}D)) oxygen atoms, which are important in both the troposphere and stratosphere:

$O_3 + hv\ (\lambda \leq 319\ nm) \rightarrow O_2 + O\ (^1D)$ (2.7)

In the troposphere, this excess energy causes the singlet oxygen atom to every so often react with N_2 and O_2, removing its energy and quenching O (^{1}D) to its ground state, thereby, in turn, replenishing O_3 through reaction 2.9:

$O\ (^1D) + M \rightarrow O\ (^3P) + M\ (M = N_2 \text{ or } O_2)$ (2.8)

$O\ (^3P) + O_2 + M \rightarrow O_3 + M$ (2.9)

Sometimes, O (^{1}D) reacts with water vapour and produces two OH radicals:

$O\ (^1D) + H_2O \rightarrow 2OH$ (2.10)

Other sources of OH radicals in the troposphere include the photolysis of nitrous acid (HONO), the photolysis of formaldehyde and other carbonyls in the presence of NO, and the night-time reactions

of O_3 with alkenes (Atkinson, 2000). From the above reactions, we can infer that once the OH radical is formed, it reacts effectively with most trace species present in the troposphere. However, since its formation is dependent on light, this is only true during daytime. The daytime concentration of OH is approximately 10^6 molecules cm^{-3} (Seinfeld and Pandis, 2006). Gaseous species that do not react with the OH radical have longer lifetimes (e.g. chlorofluorocarbons) and are transported into the stratosphere, where they are photochemically destroyed (Seinfeld and Pandis, 2006).

Furthermore, NO_3 radicals are also very important oxidants for several VOCs in the troposphere. The NO_3 radicals are typically important during evening and night-time hours, because they are photolysed (decomposed) in the presence of sunlight. In the troposphere, NO emitted from both natural and anthropogenic sources will react with O_3 leading to the formation of the NO_3 radical (Atkinson, 2000).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2.11)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2.12)$$

All the abovementioned radicals are generally considered to be the dominant oxidants that initiate the removal of pollutants (e.g. VOCs) from the atmosphere. However, recently, Welz et al. (2012) and Mauldin III et al. (2012) suggested that the Criegee intermediate radicals can play a crucial role in tropospheric oxidation. Boy et al. (2013) say that the Criegee intermediate formation mechanism starts from the reaction of ozone with unsaturated hydrocarbons (e.g. alkene), with the addition of ozone to the double bond of the alkene, thereby forming a primary ozonide with high excess energy. The excess energy causes the primary ozonide to decompose instantaneously to the CI, which will still possess excess energy. In order to release its excess energy, the Criegee intermediate either decomposes into different products or collisionally stabilises (we refer to the latter as a stabilised Criegee intermediate). The stabilised Criegee intermediate can then react with various atmospheric compounds, particularly H_2O, SO_2, VOCs and many others (Figure 2-1). The reaction with SO_2 is important relative to SOA formation, because this reaction forms sulphuric acid (H_2SO_4), which, in turn, initiates new particle formation (Kulmala et al., 2013). Therefore, it is not only oxidants such as O_3, OH and NO_3 radicals that may have a substantial contribution to the atmospheric oxidation capacity, but also the stabilised Criegee intermediate (Taatjes et al., 2008, Boy et al., 2013, Mauldin III et al., 2012, Sipilä et al., 2014, Berndt et al., 2014).

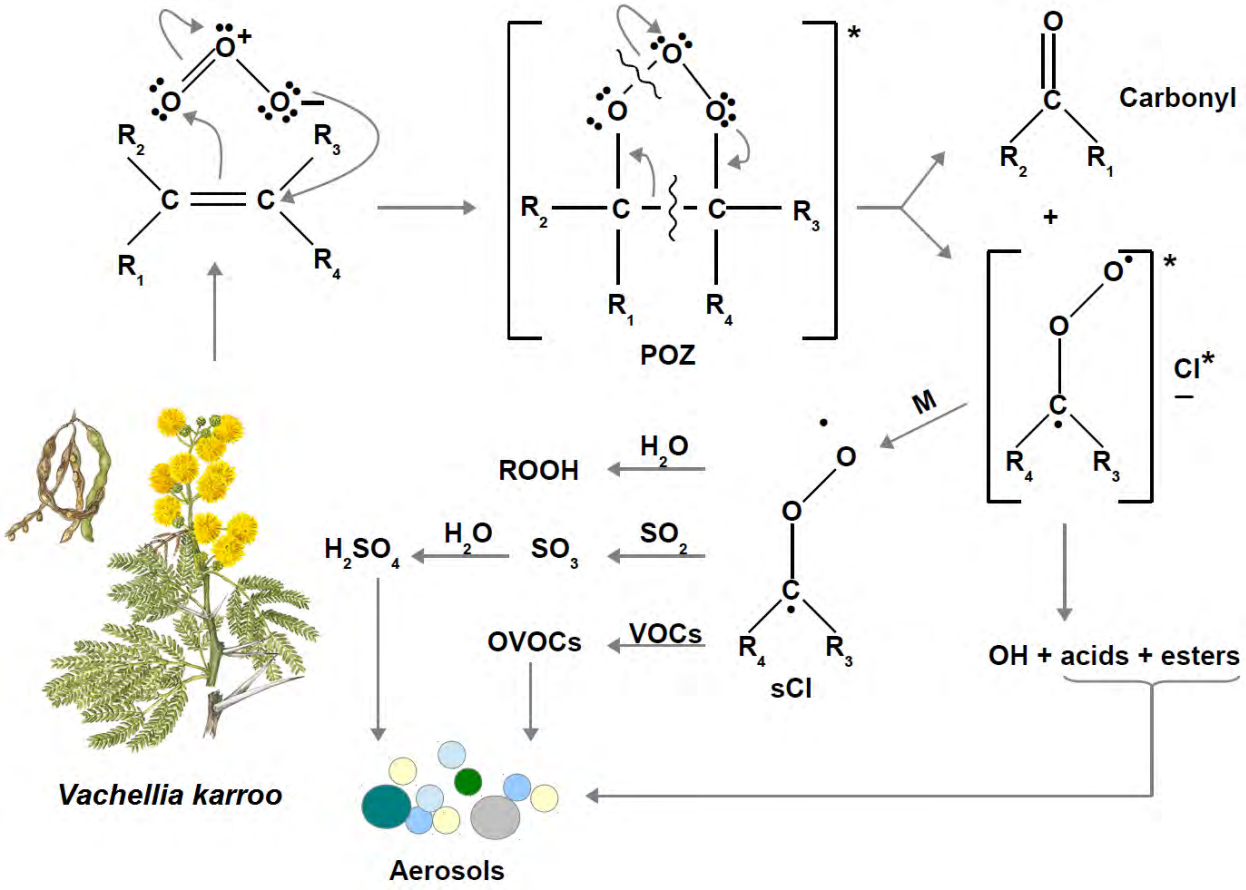

Figure 2-1: A schematic illustration of the formation of Criegee Intermediates and their destiny in the atmosphere. Figure adapted from Mogensen (2015)

2.3 REACTIONS OF VOCS IN THE TROPOSPHERE

The most studied aspect of VOC degradation in the troposphere is the OH-initiated chemistry, for which a simplified schematic is shown in Figure 2-2. OH, NO_3 radicals and O_3 react with VOCs by either addition to a carbon-carbon double bond or by hydrogen abstraction from carbon-hydrogen bonds (and to a much lesser extent, from O-H bonds), resulting in the formation of highly reactive alkyl or substituted alkyl radical (R) and water. Since this alkyl radical that formed is very reactive, it is immediately further oxidised by oxygen (O_2), generating an alkyl peroxy radical (RO_2). As indicated in Figure 2-2, the formed RO_2 can further react with either hydroperoxyl radicals (HO_2), nitrogen dioxide (NO_2), nitrogen oxide (NO) or other alkyl peroxy radicals.

As discussed by Hallquist et al. (2009), at high NOx levels, the RO_2 is efficiently converted to an alkoxy radical (RO) via the oxidation of NO to NO_2. According to Atkinson (2007), under atmospheric conditions, RO can decompose by C-C bond scission (leading to a smaller carbonyl product and an organic radical), isomerize by a 1,5-H shift through a six-membered transition state (leading ultimately to a hydroxycarbonyl product and HO_2), and react with O_2 to form a carbonyl

product and HO_2. In addition, the reactions of RO_2 with NO also have terminating channels that form organic nitrate products ($RONO_2$). The reaction with NO_2 terminates the reaction sequence by forming peroxynitrates (RO_2NO_2), e.g. peroxyacetyl nitrate (PAN), which can be transported long range. Therefore, the outcome of VOC degradation at high NO_x levels is the formation of carbonyls, hydroxycarbonyls, organic nitrates and PAN.

Hallquist et al. (2009) further write that at lower NO_x levels, the reactions of RO_2 with HO_2 and with the RO_2 radical become competitive, leading to a progressive change in the product distribution with changing NOx levels. As shown in Figure 2-2, the reaction of simple RO_2 radicals with HO_2 is known to be dominated by termination reactions to form hydroperoxide products (ROOH). The reactions with the RO_2 radical are partially propagating, to generate RO radicals (and therefore carbonyls and hydroxycarbonyls), and partially terminating to generate alcohol and carbonyl products. As a result, VOC degradation at very low NO_x levels tends to generate a product distribution that is dominated by the formation of hydroperoxides, carbonyls, hydroxycarbonyls and alcohols. Therefore, in the subsequent sections, the specific oxidation of alkanes, alkenes and aromatics is discussed.

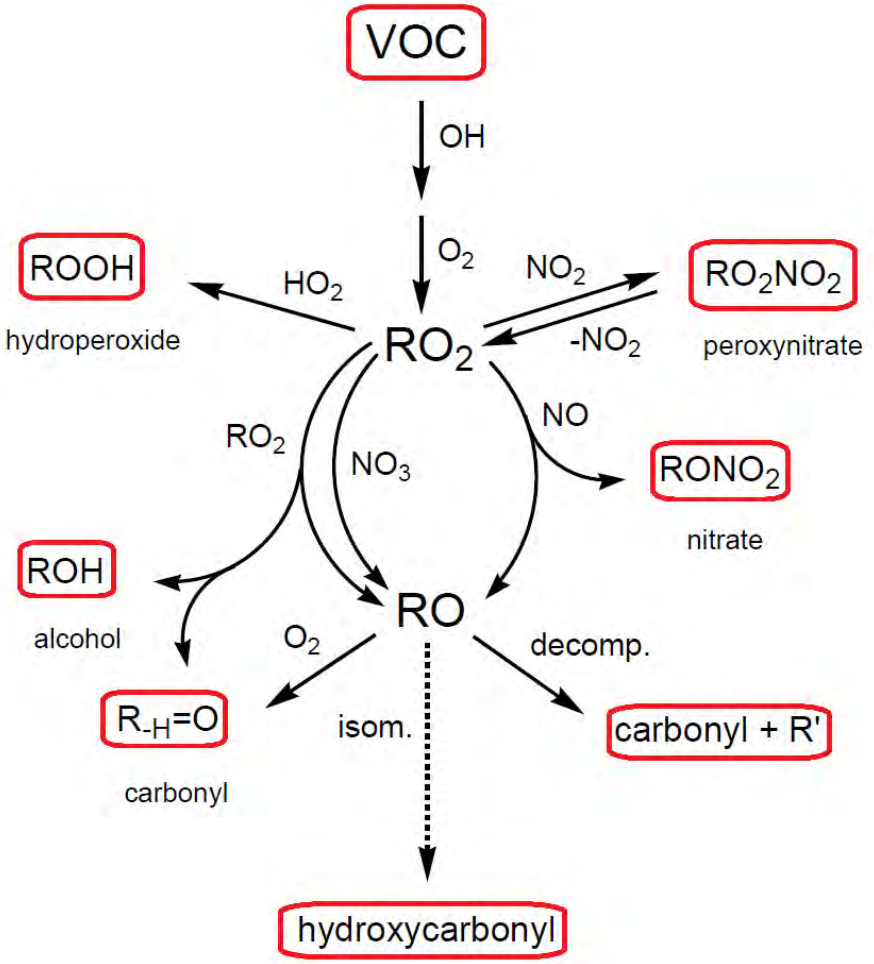

Figure 2-2: Simplified schematic of the OH-initiated degradation of generic VOCs to form first-generation products (Hallquist et al., 2009)

2.3.1 Reactions of alkanes

In the troposphere, alkanes react predominately with OH radicals and to a lesser extent with NO_3 radicals and Cl atoms. Alkanes do not absorb in the actinic region (i.e. at wavelengths > 290 nm) or react significantly with O_3 (Atkinson and Arey, 2003a). The reaction mechanisms of the OH-initiated degradation of butane, when NO_x is present, are summarised in Figure 2-3. The figure also illustrates the sequential formation of the intermediate products methyl ethyl ketone (MEK), acetaldehyde (CH_3CHO) and formaldehyde (HCHO). As indicated in the figure, the initial oxidation of butane (C_4H_{10}) to MEK is represented in the mechanism, but not shown, and therefore it will be discussed here. The C_4H_{10}-OH reaction proceeds via the hydrogen atom abstraction from the carbon-hydrogen bonds forming an alkyl (C_4H_9) radical (reaction 2.13). The alkyl radical (C_4H_9) reacts rapidly with O_2 to yield an alkyl peroxy radical ($C_4H_9O_2$) (reaction 2.14).

$$C_4H_{10} + OH \rightarrow C_4H_9 + H_2O \qquad (2.13)$$

$C_4H_9 + O_2 \rightarrow C_4H_9O_2 + M$ (M = N_2 or O_2) (2.14)

$C_4H_9O_2 + NO \rightarrow C_4H_9O + NO_2$ (2.15a)

$\rightarrow C_4H_9ONO_2$ (2.15b)

$C_4H_9O + O_2 \rightarrow$MEK + HO_2 (2.16)

In polluted environments, the main reaction of the $C_4H_9O_2$ radicals with NO yields NO_2 and alkoxy (C_4H_9O) radical (Reaction 2.15a), or the corresponding alkyl nitrate ($C_4H_9ONO_2$) (reaction 2.15b). At very high NO_2 concentrations, the alkyl peroxy radical can react with NO_2 to yield peroxynitrate ($C_4H_9O_2NO_2$). Furthermore, the produced NO_2 can undergo photolysis and in so doing promote tropospheric O_3 formation. The alkoxy (C_4H_9O) radical has several possible atmospheric fates, which include reactions with O_2 to yield MEK plus hydrogen peroxy radical (HO_2) and decomposes to form CH_3CHO and C_2H_5O. As shown in Figure 2-3, the further degradation of MEK, CH_3CHO and HCHO, initiated by the reaction with OH, leads to further NO-to-NO_2 conversion and therefore O_3 formation. As a result, the number of NO-to-NO_2 conversions at each oxidation step, and the lifetimes of butane and the product carbonyl compounds (which are partially determined by their OH reactivity), have an important influence on the rate of NO oxidation and O_3 formation.

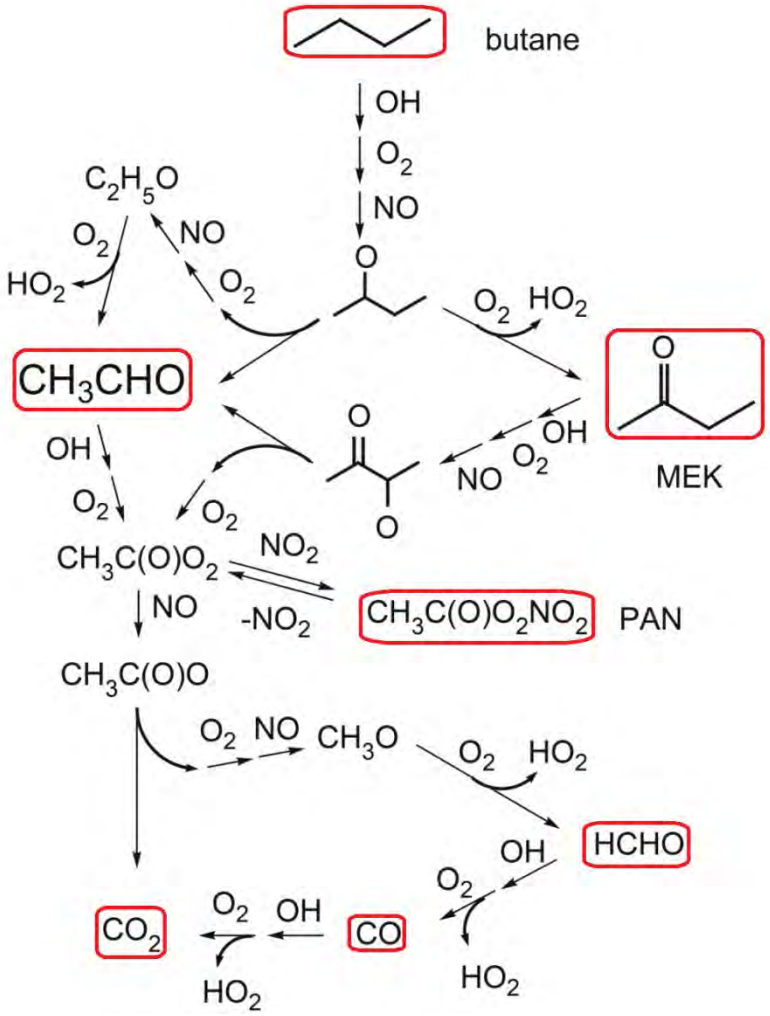

Figure 2-3: Schematic representation of the major radical propagation pathways of the OH-initiated degradation of butane, also illustrating the sequential formation of the intermediate products MEK, CH_3CHO, HCHO and CO. The schematic is from Pinho et al. (2005); therefore, the electron balance is not shown.

2.3.2 Reactions of alkenes

Alkenes can be classified according to sources as either biogenic or anthropogenic and they are highly reactive towards OH radicals, NO_3 radicals and O_3 (Atkinson, 1997, Atkinson, 2000, Calvert et al., 2000). During daytime and night-time, reactions with O_3 can be an important transformation process, which leads to the production of OH radicals, often in high yields (Atkinson, 1997, 2000). Furthermore, these reactions may also lead to the formation of SOA (see Figure 2-1) (Boy et al., 2013, Mogensen, 2015). Reaction rates with NO_3 radicals are fast and, according Hakola et al. (2003), NO_3 radicals can be the foremost oxidant for at least BVOCs during the night.

In Figure 2-4, the atmospheric degradation of isoprene by OH radicals and NO_3 radicals is presented. In Figure 2-4a, the reaction between isoprene and OH radical occurs by OH-addition to the >C=C< bonds. There are six different possible hydroxyalkyl radicals that can form from this reaction, after which the addition of O_2 may occur. The reaction of the hydroperoxy radicals with NO results in either the formation of nitrates or the formation of hydroxyalkoxy radicals, along with the conversion of NO to NO_2. The subsequent reaction of hydroxyalkoxy radicals involves competition between decomposition, isomerisation or reaction with O_2, leading to the formation of various oxygenated organic compounds. In Figure 2-4b, the reaction of the NO_3 radical with isoprene proceeds by NO_3-addition to the >C=C< bonds, yielding nitrooxyalkyl radicals, with subsequent O_2 addition leading to nitrooxyalkyl peroxy radicals. If NO_3 radicals are present in the troposphere, then NO will be at low concentrations due to the rapid reaction of NO with the NO_3 radical (and of NO with O_3). Therefore, as indicated in Figure 2-4b, the nitrooxyalkyl peroxy radicals formed will then either react with HO_2 or other RO_2 radicals. In Figure 2-1, the O_3 reaction with an alkene was presented. This reaction is very competitive with the daytime OH radical reaction and the night-time NO_3 radical reaction.

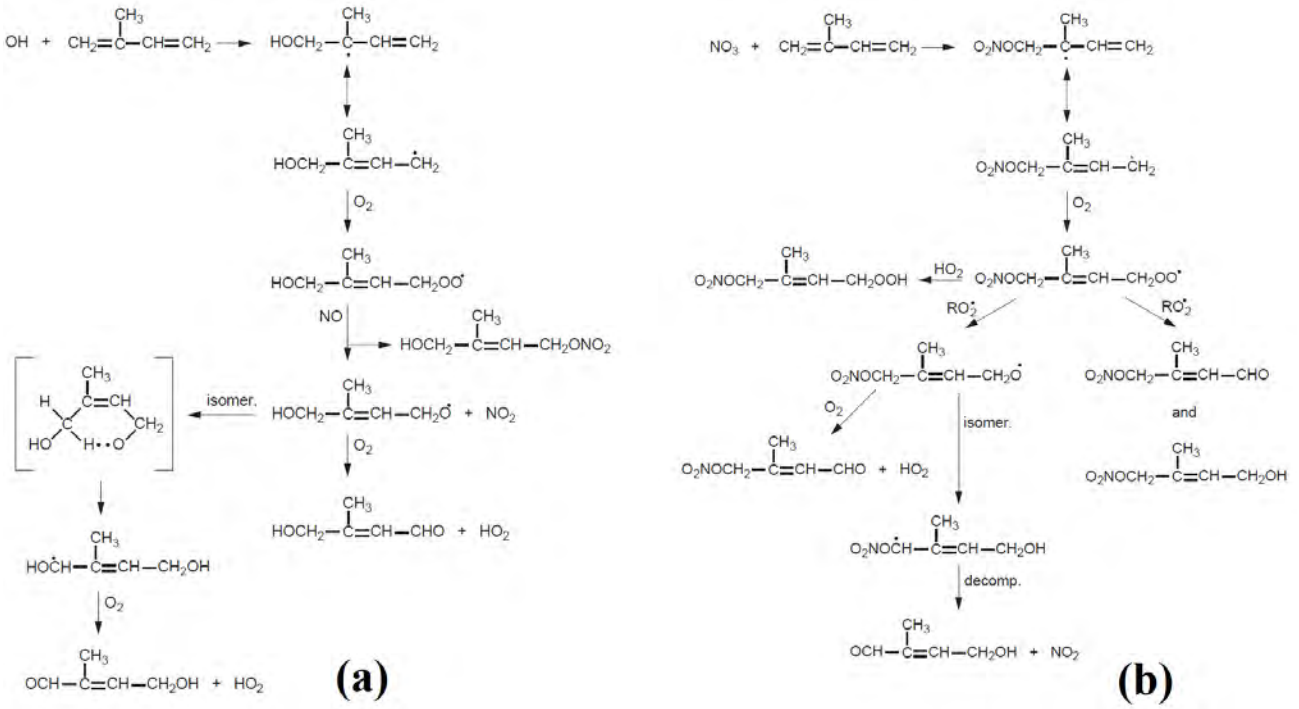

Figure 2-4: Schematic representation of the atmospheric degradation of isoprene by OH radical (a) and (b) NO_3 radical (Atkinson and Arey, 2003b)

2.3.3 Reactions of aromatics

Under atmospheric conditions, the aromatics are oxidised by OH and NO_3 radicals, with the OH radical reactions dominating as the tropospheric removal process. In Figure 2-5, the *p*-xylene-OH reaction proceeds by means of two different pathways: (a) a minor one (≤ 10%) involving H-atom abstraction from C-H bonds and (b) a major reaction pathway (≥ 90%) involving OH radical addition to the aromatic ring (Atkinson, 2000). The H-atom abstraction leads to the formation of aromatic aldehydes, while the second pathway generates an OH-xylene adduct (Seinfeld and Pandis, 2006). The reactions of benzyl and alkyl-substituted benzyl radicals formed from the H-atom abstraction are analogous to those for the alkyl radicals discussed above. OH-aromatic adducts react with O_2 and NO_2. Depending on the symmetry of the aromatic hydrocarbon, there can be up to six distinct points for OH addition. However, literature indicates that the positions on the aromatic ring favoured for OH attack in relation to substituents vary in the general order ortho- > para- > ipso- > meta- (Jenkin et al., 2003).

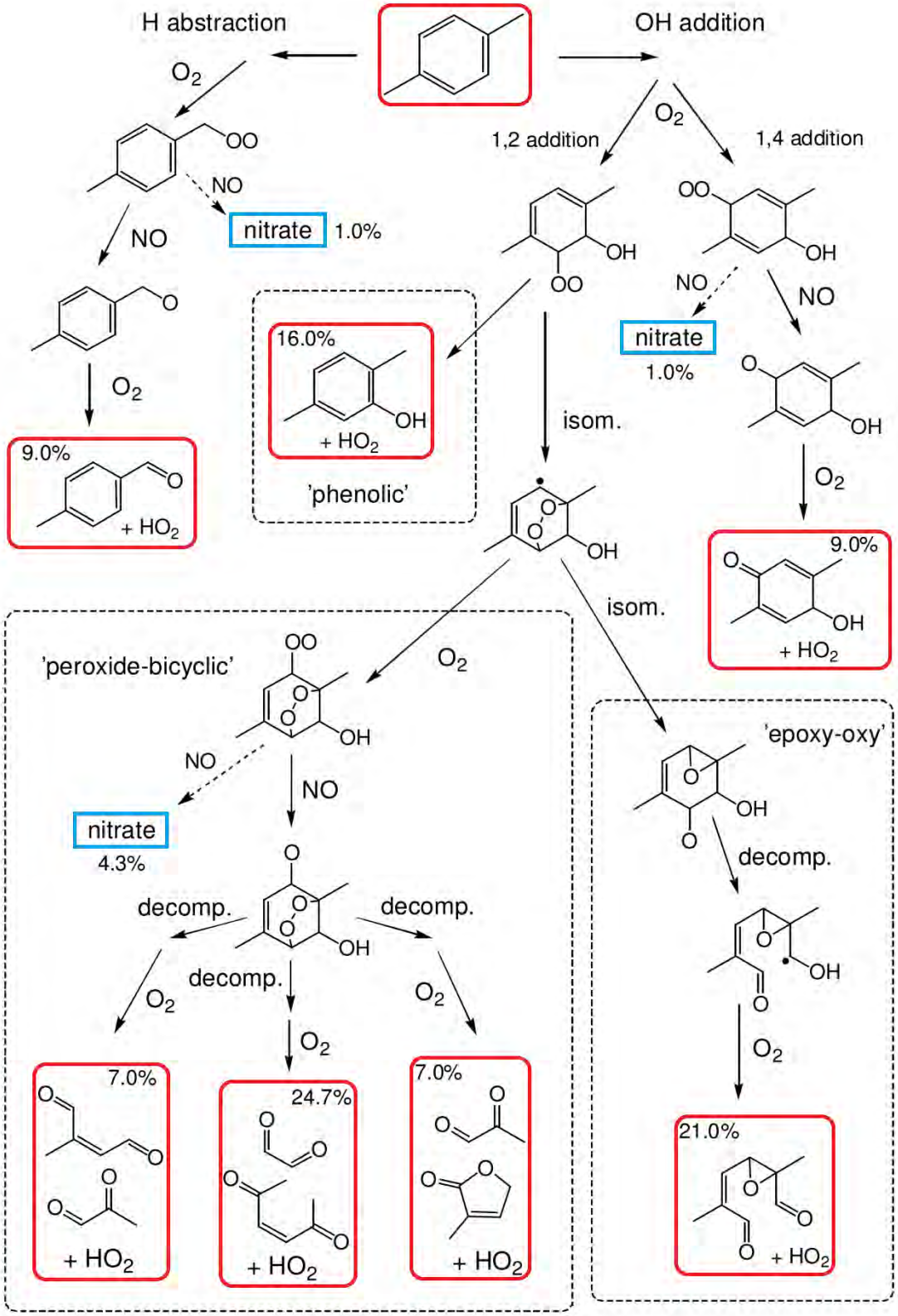

Figure 2-5: Schematic representation of the OH-initiated oxidation of p-xylene to first generation products. The schematic is from Jenkin et al. (2003); therefore, the electron balance is not shown.

2.3.4 Lifetimes of VOCs

As already mentioned in the previous sections, the foremost tropospheric oxidising agents are O_3, OH radicals (the most important sink for VOCs) and NO_3 radicals, whereas some VOCs can also undergo photolysis (Atkinson, 2000, Atkinson, 2007, Atkinson and Arey, 2003b). The lifetime of an organic compound can be defined as the time elapsed for 36.8 % (1/e) of the initial concentration of compound to be left in the atmosphere (Steiner and Goldstein, 2007). Reaction rate coefficients for gas-phase reactions of VOCs with the tropospheric oxidising agents have been elucidated over the past two decades (Atkinson, 2000, Atkinson, 1997, Atkinson and Arey, 2003b, Calvert et al., 2000). These rate constants can be combined with assumed ambient tropospheric concentrations of the oxidising agents to calculate the VOC lifetime using the equation

$$\tau = (k_{OH}[OH] + k_{O3}[O_3] + k_{NO3}[NO_3] + photolysis)^{-1} \quad (2.17)$$

where k_{OH} is the reaction rate coefficient for the VOC towards the OH radical, k_{O3} is the reaction rate coefficient for the VOC towards O_3, and k_{NO3} is the reaction rate coefficient for the VOCs towards NO_3 radical. In Table 2-1, the lifetimes of VOCs studied in this thesis according to literature are listed (Atkinson, 2000, Atkinson, 1997, Atkinson and Arey, 2003b, Calvert et al., 2000). The data in Table 2-1 indicate that the lifetimes of VOCs associated with anthropogenic emissions, i.e. alkanes and aromatics, are usually in the order of days. The lifetimes of VOCs associated with biogenic emissions, i.e. isoprene, mono- and sesquiterpenes, are typically a few hours or less. The BVOCs studied in this thesis, e.g. α-humulene, react so rapidly with O_3 (Table 2-1) that if these particular BVOCs are emitted from vegetation, they will be rapidly removed by reaction, even at a 'clean' remote site such as Welgegund. Furthermore, since there are such huge variations in lifetimes of the VOCs, it can be used to determine the probable source, as well as the age of the pollution plume, based on ratios of the compounds (Hoque et al., 2008, Guo et al., 2007, Holzinger et al., 2001, Kerbachi et al., 2006, Khoder, 2007).

Table 2-1: Calculated lifetimes of some of VOCs studied in this thesis according to literature with respect to reaction with the OH radical, reaction with the NO_3 radical and reaction with O_3 (Atkinson, 2000, Atkinson and Arey, 2003b)

	Lifetime due to		
	OH radical	NO_3 radical	O_3
Isoprene	1.4 hr	1.6 hr	1.3 day
MBO	2.4 hr	7.7 day	1.7 day
α-Pinene	2.6 hr	11 min	4.6 hr
Camphene	2.6 hr	1.7 hr	18 day
β-Pinene	1.8 hr	27 min	1.1 day
Δ^3-Carene	1.6 hr	7 min	11 hr
1,8-Cineol	1 day	1.5 year	>110day
Limonene	49 min	5 min	2 hr
Terpinolene	37 min	0.7 min	13 min
iso-Longifolene	2.9 hr	1.6 hr	>33day
α-Humulene	28 min	2 min	2 min
Benzene	9.4 day	>4 yr	>4.5 yr
Toluene	1.9 day	1.9 yr	>4.5 yr
(m,p)-Xylene	5.9 hr	200 day	>4.5 yr
Styrene	2.4 hr	3.7 hr	1.0 day
1,2,4-TMB	4.3 h	26 day	>4.5 yr
2,2,4-Trimethylpentane	3.2 day	1.4 yr	
Octane	1.3 day	240 day	

2.4 CONCLUSION

The general chemistry for VOCs is relatively well understood (as indicated in Chapter 2). However, limited VOC studies have been done for South Africa (as indicated in Chapter 1). Therefore, the concentration levels, sources, impacts and contribution of VOCs to various tropospheric processes are relatively poorly estimated in South Africa. The results presented in this study (Chapters 4-6) will make a contribution to address this knowledge gap.

CHAPTER 3

MEASUREMENT LOCATION, TECHNIQUES AND DATA ANALYSIS

3.1 MEASUREMENT LOCATION

3.1.1 Site description

Measurements were conducted at the Welgegund measurement station (26.57°S, 26.94°E, 1480 meters above mean sea level, www.welgegund.org), which is located approximately 100 km west of Johannesburg on the property of a commercial maize and cattle farmer. The distances to the nearest blacktop road and nearest town are approximately 10 and 30 km, respectively. The station is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity. Welgegund is, however, affected by plumes from several different anthropogenic source regions in the interior of South Africa, i.e.:

- pyrometallurgical smelters in the western and the eastern Bushveld Igneous Complexes (BIC), from which most of the world's ferrochrome and platinum group metals (PGMs) are produced. This region has recently been incorporated into the newly declared Waterberg Priority Area (Department of Environmental Affairs, 2012).

- Johannesburg-Pretoria (JHB-PTA) metropolitan conurbation with more than 10 million inhabitants (cf. the population density map in Figure 3-1), which Lourens et al. (2012) indicated as being relatively heavily polluted.

- petrochemical industries, conglomeration of large coal-fired power plants and metallurgical smelters in the Vaal Triangle. This area, together with part of southern Gauteng, was the first area to be declared a priority area, i.e. the Vaal Triangle Airshed Priority Area (Department of Environmental Affairs, 2005).

- coal-fired power plants, large petrochemical industries and several pyrometallurgical smelters in the Mpumalanga Highveld. This area, together with parts of Gauteng, was declared a priority area in 2007, i.e. the Highveld Priority Area (Department of Environmental Affairs, 2007).

In Figure 3-1, the position of Welgegund (indicated with a blue star), in relation to most of the major point sources occurring in the abovementioned anthropogenic source regions, is presented. From Figure 3-1, it is also evident that most of the industrial activities are concentrated around the JHB-PTA megacity as seen in the total emissions of SO_2 based on the SAFARI 2000 emission inventory (Fleming and van der Merwe, 2002). In addition, a prominent NO_2 hotspot seen in global maps from satellite retrievals is visible over the South African Highveld (Lourens et al., 2011, Lourens et al., 2012). Furthermore, because of the lure of employment, the JHB-PTA megacity and surrounding areas are very populated, as shown in Figure 3-2. The population density is an indicator of non-industrial human activities, as well as the propitiousness of local ecosystem for human living.

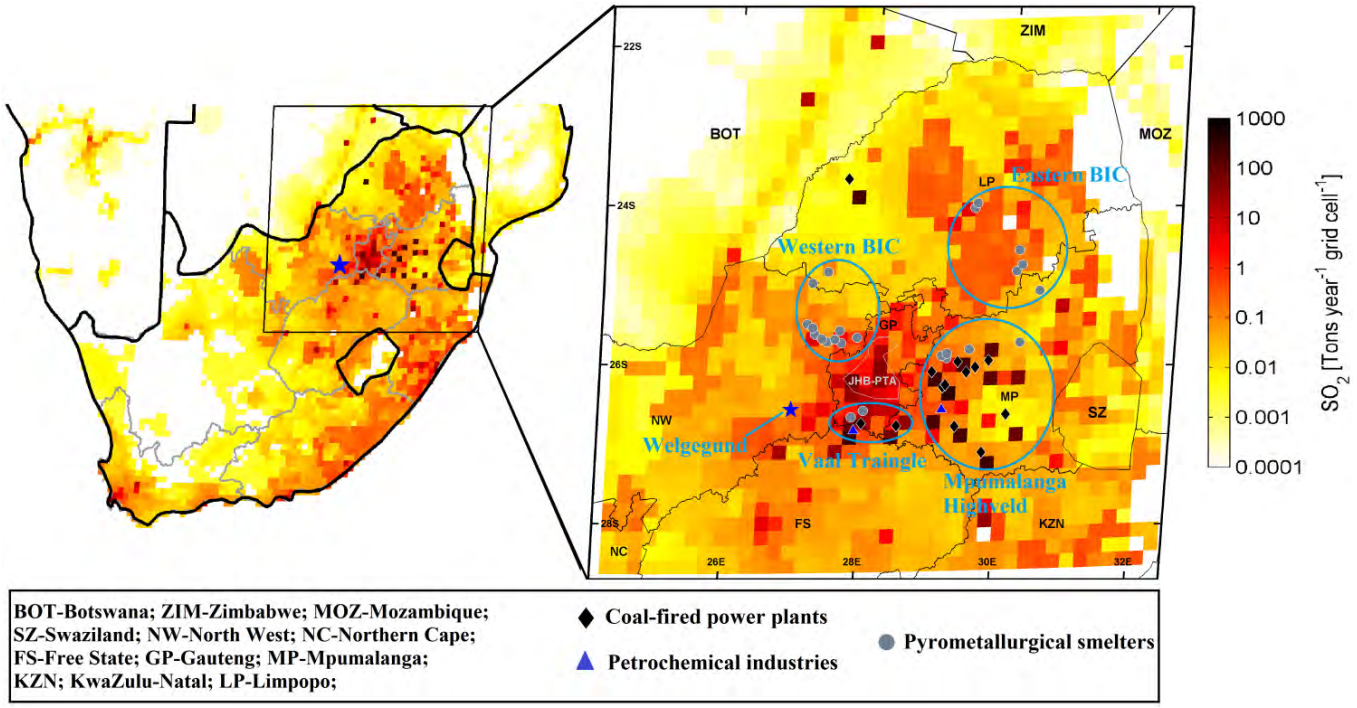

Figure 3-1: Southern African map indicating the location of the Welgegund measurement station (blue star), total SO_2 emissions based on SAFARI 2000 emission inventory (Fleming and van der Merwe, 2002), large point sources in the industrial hub of South Africa and anthropogenic source regions affecting Welgegund. The figure was reproduced with permission from Vakkari (2013).

It is also evident from Figures 3-1 and 3-2 that to the west of Welgegund both anthropogenic SO_2 emissions and population density decrease quite rapidly, which indicates that much fewer anthropogenic sources occur there. Therefore, the site has a wide, clean sector to the west. However, the clean sector cannot be directly comparable to other directions because the vegetation type also changes from west to east (Figure 3-4). The western sector has large areas where vegetation is sparse and consequently BVOC emissions are also lower than in the northern and

eastern sectors (Otter et al., 2002, Otter et al., 2003, Harley et al., 2003, Greenberg et al., 2003, Guenther et al., 1996).

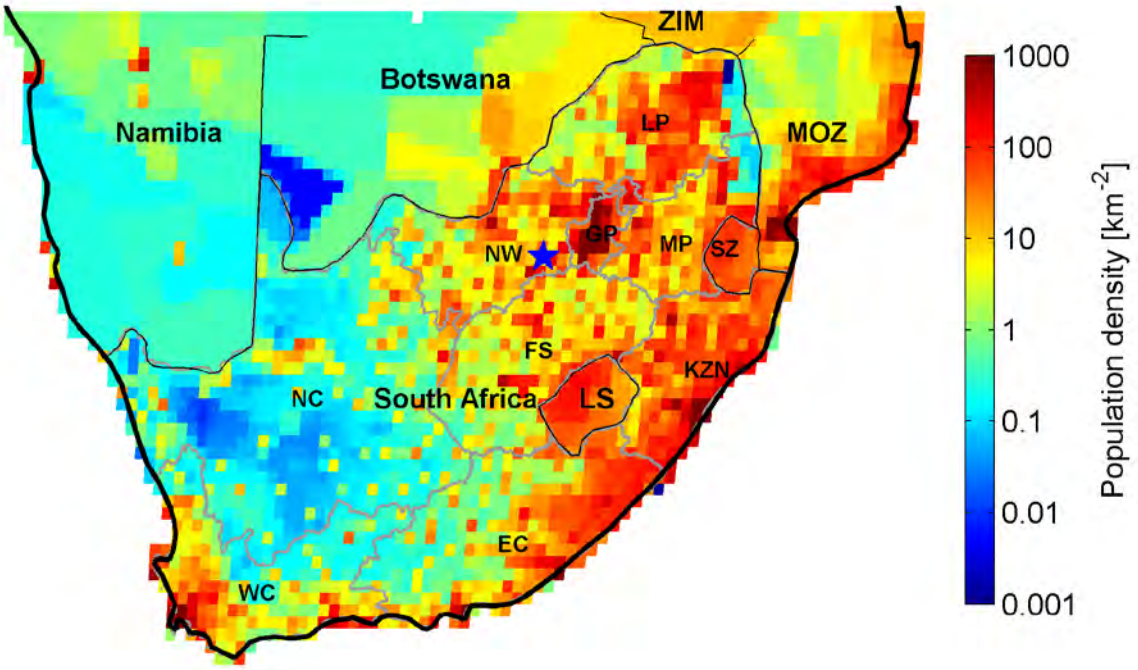

Figure 3-2: Population density over southern Africa. The measurement site is indicated with a blue star. The population hot-spot north-east of the measurement site is the JHB-PTA megacity and the Vaal Triangle. The figure was reproduced with permission from Vakkari (2013).

Welgegund is geographically located on the Highveld, a plateau approximately 1 500 metres above sea level in central southern Africa. Seasons in the southern African interior can roughly be divided into two distinct seasonal periods, i.e. a dry season from May to September that predominantly coincides with winter (June to August), and a wet season during the warmer months from October to April. The dry period is characterised by low relative humidity, while the wet season is associated with higher relative humidity and frequent rains that predominantly occur in the form of thunderstorms. The mean annual precipitation is approximately 500 mm with approximately >80% of rain events occurring during the wet season. During the sampling period, the coldest temperature recorded in winter at Welgegund was -5.1 °C in June 2011, while the highest temperature recorded in summer was +35.6 °C in October 2011. At the end of the dry season, wind speeds increase, which provide favourable conditions for the development of both dust storms and wild fires (Tyson and Preston-Whyte, 2000).

The prevailing feature in horizontal air mass movement over the South African interior is dominated by anticyclonic circulation (Garstang et al., 1996), which is also seen in the back-trajectory overlay graphics for Welgegund in Figure 3-3. These recirculated air masses are usually not representative

of the clean regional background, since they represent aged air masses that had passed over/around the industrial hub of South Africa. The back trajectories have been calculated for Welgegund from 20 May 2010 to 15 April 2012, i.e. coinciding with the first campaign of VOC measurements. The trajectories have been calculated with the HYSPLIT 4.8 model (Draxler and Hess, 2004) using GDAS meteorological data (Air Resources Laboratory, 2016) for arrival height of 100 metres and length of 96 hours backwards. Back trajectories were calculated for each hour, i.e. 24 trajectories per day. Individual back trajectories generated in HYSPLIT were superimposed and further analysed in MATLAB to form overlay back trajectory maps. In these overlay back trajectory maps, a colour code indicates the percentage of trajectories passing over 0.2º x 0.2º grid cells, with red being the highest percentage. Air masses that indicate the afore-mentioned characteristic anticyclonic circulation therefore have to be considered as a separate source region, since the composition of these air masses is likely to differ from that of the previously discussed anthropogenic source regions.

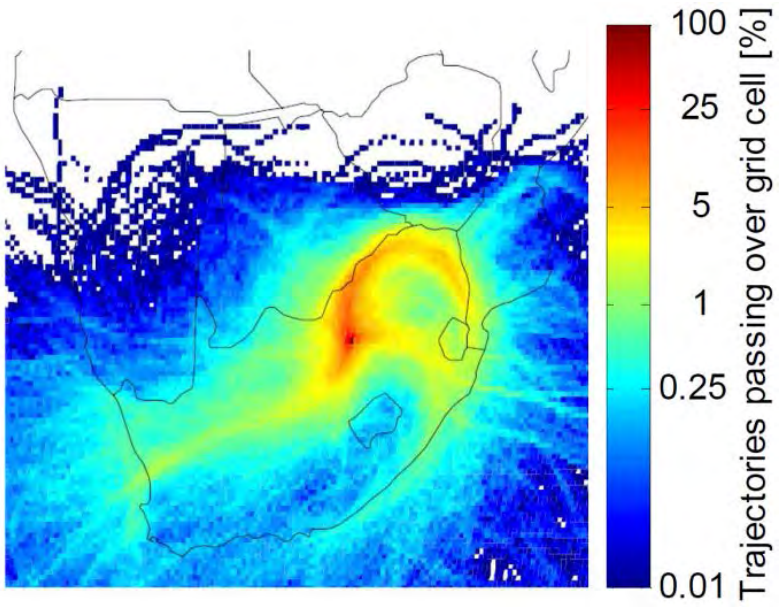

Figure 3-3: Air mass history at Welgegund. The trajectories have been calculated for arrival height of 100 metres and length of 96 hours backwards. The figure was reproduced with permission from Vakkari (2013).

3.1.2 Vegetation

Apart from anthropogenic sources affecting Welgegund, biogenic sources are also important at this background site. Welgegund is located in the Grassland Biome (Figure 3-4), which covers 28% of South Africa's land surface (Mucina and Rutherford, 2006). This biome has been significantly transformed, primarily as a result of cultivation, forestry, urbanisation and mining (Daemane et al.,

2010), while it has also been severely degraded by erosion and agricultural development. The station is situated within the Vaal-Vet Sandy Grassland with Andesite Mountain Bushveld of the Savannah Biome prominent on nearby ridges (< 1 km). At present, only 0.3 % of the Vaal-Vet Sandy Grassland is statutorily conserved, while the rest is mostly used for grazing and crop production.

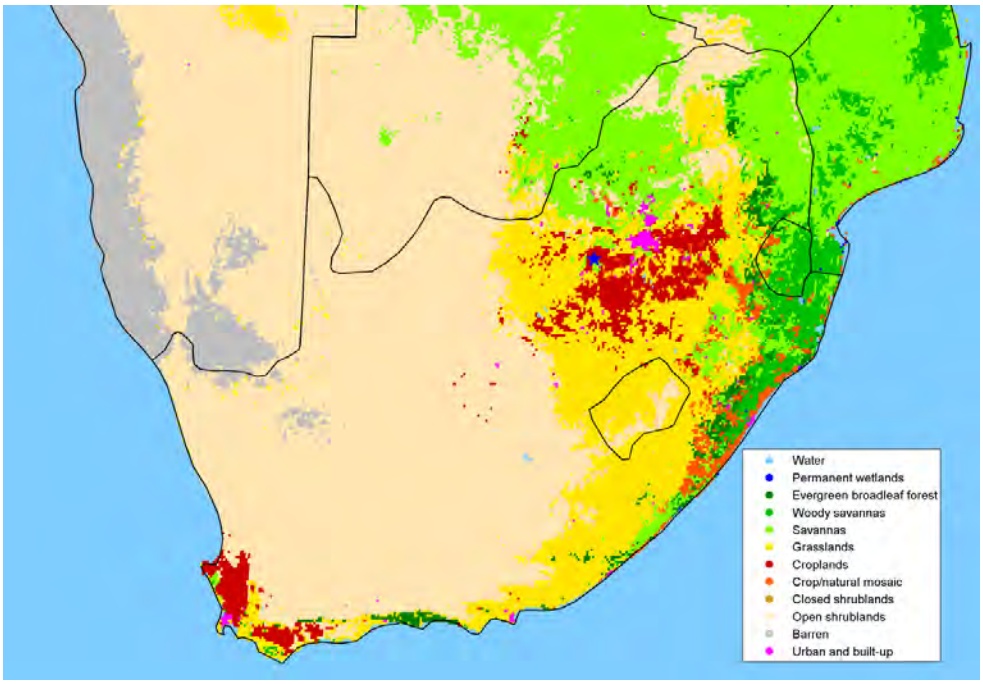

Figure 3-4: The International Geosphere-Biosphere Programme (IGBP) vegetation classification for southern Africa for 2010 based on MODIS collection 5 land cover type product. The blue star indicates Welgegund. The figure was reproduced with permission from Vakkari (2013).

In Figure 3-5, a land cover map within a 60 km radius from Welgegund is presented indicating the extent of cultivation in this region. The land cover survey was performed within a region that was estimated to represent the BVOC footprint at Welgegund, which was calculated from typical atmospheric lifetimes of the species measured (Atkinson, 2000, Atkinson and Arey, 2003b) and the general wind speed(s) at Welgegund. The immediate area surrounding Welgegund is grazed by livestock, with the remaining area being covered by crop fields (mostly maize and to a lesser degree sunflower). In the demarcated 60 km radius, a further three vegetation units of the Dry Highveld Grassland Bioregion (Grassland Biome) and another two of the Central Bushveld Bioregion (Savannah Biome) are also present. In addition, alluvial vegetation is found associated with major rivers and inland saline vegetation in scattered salt pans.

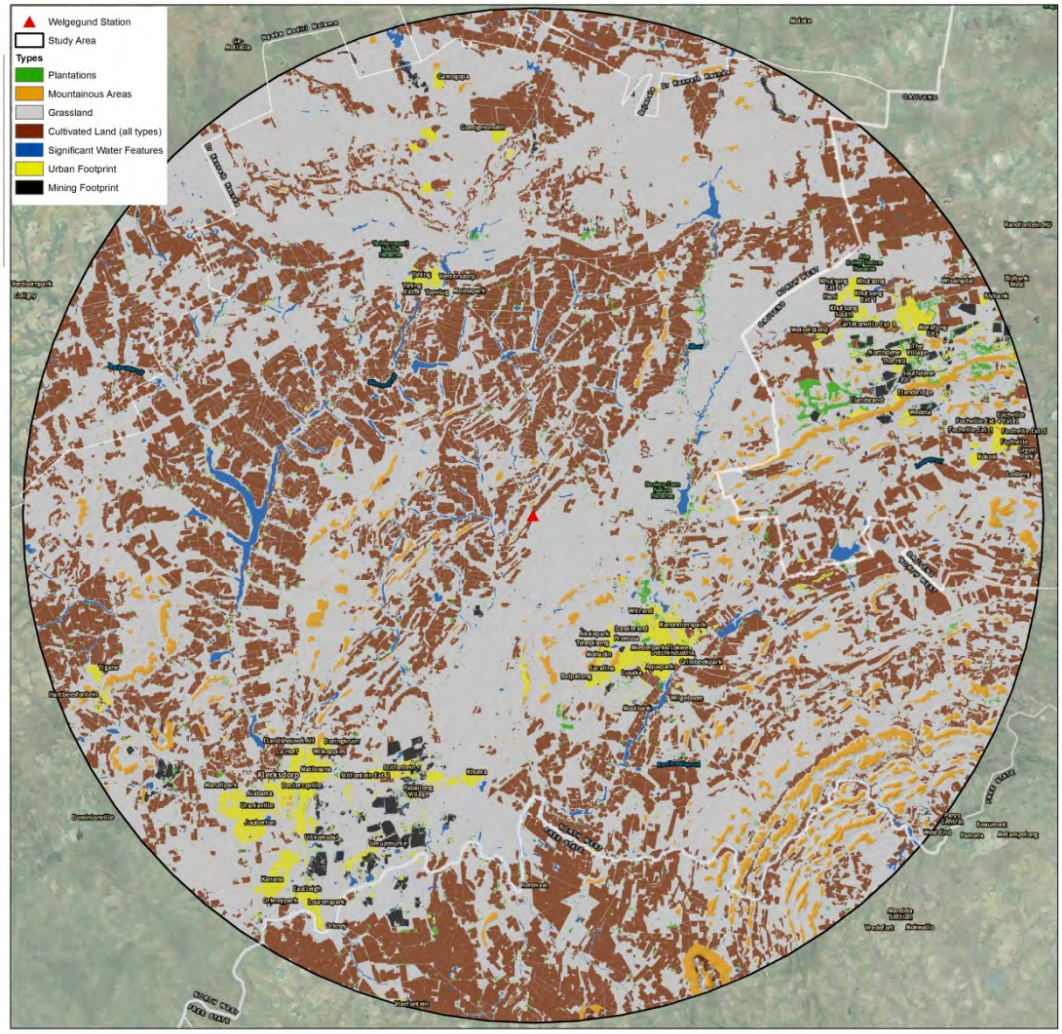

Figure 3-5: General vegetation map for 60 km radius of Welgegund measurement station. Figure is from Article II (Chapter 5).

The study area comprises a highly variable landscape with scattered hills and sloping, slightly irregular, undulating plains that are dissected by prominent rocky ridges. Soil in the catchment area is heterogeneous and rocky, varying from sandy to clayey depending on the underlying rock types, such as andesite, chert, dolomite, mudstone, quartzite, sandstone and shale.

Land use within the surrounding area is divided into six major land cover types, i.e. cultivated land, grasslands, mountainous areas, plantations, urban areas and water bodies, as indicated in Figure 3-5. Mountainous areas, grassland and water bodies (riparian areas) comprise many different vegetation units. The other homogenous areas were anthropogenically altered and no longer representative of the surrounding natural vegetation. The study area is characterised by a grassland-woodland vegetation complex, dominated by various grass and woody species, and recognised by the presence of non-native species in altered environments.

The most dominant woody species of the entire study area include the trees *Celtis africana*, *Searsia pyroides*, *Vachellia karroo* and *Ziziphus mucronata*, and the thorny shrub *Asparagus laricinus*. Tree diversity increases where there are patches of deep sand, characterised by *Gymnosporia buxifolia* and *Vachellia erioloba*, or in mountainous areas, where *Euclea undulata*, *Grewia flava* and *Senegallia caffra* become most prominent. Woody vegetation occurs sparsely in grasslands and when present are found on isolated ridges, including the small trees *Pavetta zeyheri*, *Vangueria infausta* and *Zanthoxylum capense*. In anthropogenically altered environments, native species decrease and introduced species dominate, such as *Eucalyptus camaldulensis*, *Pinus roxburghiana* and *Populus canescens* in plantations; *Gleditsia triacanthos*, *Pyracantha coccinea* and *Salix babylonica* along rivers and water bodies; and *Celtis sinensis*, *Melia azedarach* and *Robinia pseudoacacia* in the urban footprint.

The most dominant species of the grass sward in the entire study area include *Cynodon dactylon*, *Eragrostis chloromelas*, *Heteropogon contortus*, *Setaria sphacelata* and *Themeda triandra*. The dry, western grassland (Vaal-Vet Sandy Grassland specifically) is characterised by *Anthephora pubescens*, *Cymbopogon caesius*, *Digitaria argyrograpta*, *Elionurus muticus* and *Eragrostis lehmanniana*, and the moist Rand Highveld Grassland in the south-east by *Ctenium concinnum*, *Digitaria monodactyla*, *Monocymbium ceresiforme*, *Panicum natalense* and *Trachypogon spicatus*. The north-eastern parts of the study area on dolomite are dominated by *Brachiaria serrata*, *Digitaria tricholaenoides*, *Eragrostis racemosa* and *Loudetia simplex*.

3.2 MEASUREMENT TECHNIQUES

In Figure 3-6, the Welgegund atmospheric research station is presented. Some of the measurements conducted are also indicated. The atmospheric measurement station, which was commissioned in May 2010, is operated in collaboration between the North-West University (NWU), the University of Helsinki (UH) and the Finnish Metrological Institute (FMI). A more detailed description of the station, measurement instruments, operation procedures, data analysis, as well as calibration and maintenance procedures has been presented by Beukes et al. (2015) and Tiitta et al. (2014).

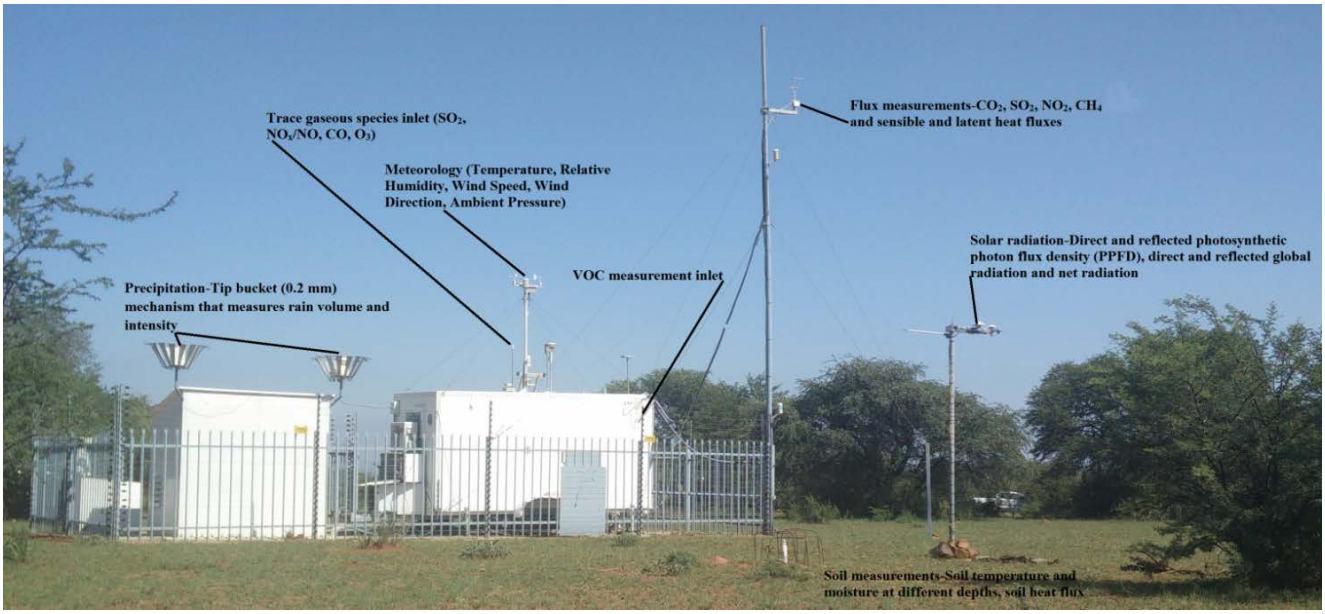

Figure 3-6: Welgegund atmospheric research station indicating some of the measurements conducted

3.2.1 VOC measurements and analysis

VOC measurements were conducted for a period of more than two years through a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays. Several previous studies have demonstrated that the maximum emissions of isoprene and monoterpenes from vegetation occur around midday (Kuhn et al., 2002, Fuentes et al., 2000). Obviously, this repetitive sampling schedule, i.e. same days each week and same hours of the day, was prone to some bias. Large point sources in South Africa, i.e. industrial stack emissions, are regulated on an availability basis. This implies that off-gas cleaning equipment must be operational for a certain percentage of the overall operating time (typically 97-99 %) and not on a time basis, e.g. specific days or hours when emissions are allowed. It was therefore impossible to set a sampling schedule to capture possible large releases of VOCs by such point sources. Traffic emissions, which can be considered as a point or area source, depending on how far the emissions are from the measurement site, are another example of a potential time-bound VOC source that had to be considered. At the Welgegund site, only a small gravel road, used by a few farmers, is nearby. Local traffic emissions are therefore almost negligible. Large traffic volumes in especially the Johannesburg-Pretoria megacity could be a significant area source of VOCs for Welgegund. However, since Welgegund is ~ 100 km west of Johannesburg, it was difficult to set a sampling schedule to capture such time-bound emissions that are transported at different rates on different

days with different meteorological conditions. Considering the distance of the sampling site from the nearest town and logistical limitations during the sampling campaigns, the sampling schedule applied was the most feasible option that enabled the collection of more than two years data.

VOCs were sampled at a height of 2m above ground level, with a 1.75m long inlet. The first 1.25m of the inlet was made of stainless steel and the second 0.5m of Teflon. The first 1.2m of the stainless steel section of the inlet was heated to 120 ^{o}C using heating cables and thermostats (Thermionic), thereby removing O_3 from the sample stream, which could possibly lead to sample degradation (Hellén et al., 2012a). The last 0.5 m of the stainless steel section and the entire Teflon section were housed within the measurement container, wherein the temperature was regulated at 24 ^{o}C. The O_3 removal efficiency was checked with an O_3 monitor at regular intervals, which revealed that O_3 concentrations decreased from median values ~30 to <2 ppb (Beukes et al., 2013).

Prior to sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 min at 350 ^{o}C at a flow of 40 mL min^{-1}. After treatment, the tubes were sealed with Swagelok® brass 0.25 inch caps and stored in a fridge at temperatures below 18 ^{o}C before they were transported to the field for sampling. VOC samples were collected on Tenax-TA and Carbopack-B adsorbent tubes (6.3mm ED×90 mm, 5.5mm ID) by using a constant-flow-type automated programmable sampler. A needle valve attached to the pump was used to keep the flow constant, while magnetic valves were used to direct flow to a specific sample tube. After a specific tube was sampled, the tube was automatically sealed off and the next tube selected for sampling. The flow of the pump was calibrated each week. A sampling flow between 100 and 110 mL min^{-1} was used throughout the study. (Hellén et al., 2002) reported no breakthrough for Tenax-TA and Carbopack-B tubes when sampling for 4 h at a flow rate of 100 mL min^{-1}. Once a week, the tubes were removed from the automated sampler and closed with Swagelok® caps. Each tube was separately wrapped in aluminium foil and stored in a container for transport to the laboratory. Tubes were stored in the laboratory in a freezer within a clean environment to minimise pre-analysis elution and breakdown of the sampled compounds. For each month, a field blank was analysed to compensate for the possibility of contamination from sample handling and storage.

The analyses and preparation of the adsorbent tubes were done at the FMI. In Figure 3-7, the instrumental setup is presented, which were a thermal desorption instrument (TD) (Perkin-Elmer TurboMatrix™ 650, Waltham, USA) connected to a gas chromatograph (GC) (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 µm) column and a mass selective detector (MSD) (Perkin-Elmer® Clarus® 600T, Waltham, USA). The sample tubes were desorbed at 300 ^{o}C for 5 min and cryofocused in a Tenax cold trap (−30 ^{o}C) prior to injection of the sample into the column by rapidly heating the cold trap (40 ^{o}C min^{-1}) to 300 ^{o}C. A three-point calibration curve was obtained by using liquid standards dissolved in methanol. Standard solutions were injected into

adsorbent tubes and were flushed with nitrogen (100mL min^{-1}) for 10 min in order to evaporate the methanol. The tubes containing the standards were desorbed and analysed with the same method used for the sampled tubes.

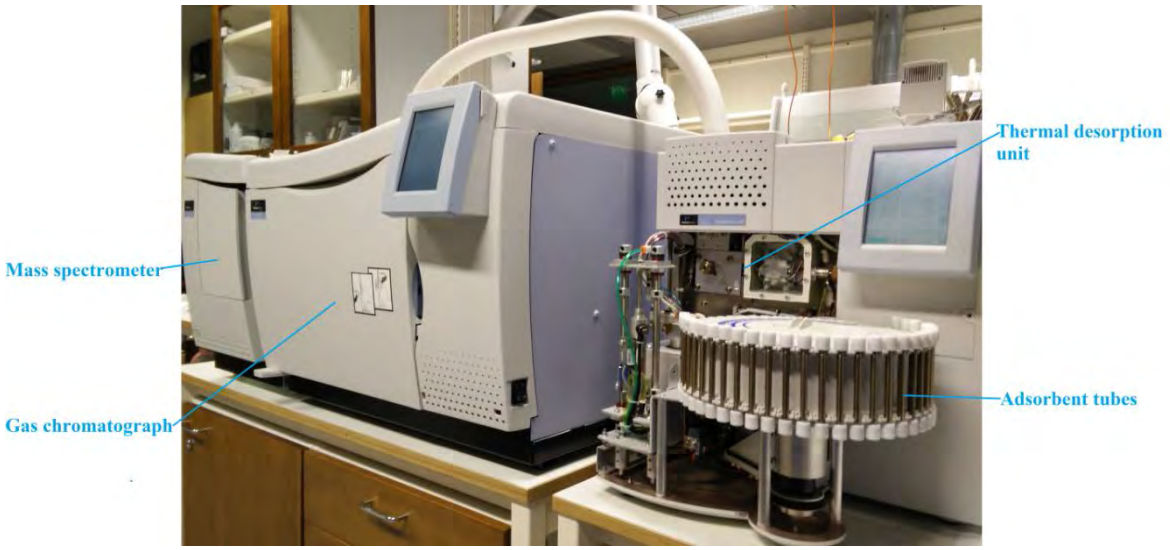

Figure 3-7: Thermal desorption instrument connected to a gas chromatograph and a mass selective detector

3.2.2 Ancillary measurements

Ancillary measurements continuously performed at the Welgegund measurement station were used to assist in the interpretation of the measured VOC concentrations. General meteorological parameters, i.e. temperature (T), relative humidity (RH), wind speed and direction, and precipitation were measured. Soil temperature and moisture at different depths (5 and 20 cm) were measured with a PT-100 and Theta probe ML2x (Delta-T), respectively. Additional soil moisture information was obtained with a 100 cm PR2 soil moisture profile probe (Delta-T). Direct photosynthetic photon flux density (PPFD) between 400 and 700 nm was measured with a Kipp & Zonen pyranometer (The CMP 3 pyranometer (ISO 9060:1990 Second Class)).

Trace gas measurements were performed by utilising a Thermo-Electron 43S sulphur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU nitrogen oxide (NOx) analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 carbon monoxide (CO) analyser (Horiba, Kyoto, Japan). The net ecosystem exchange (NEE) of carbon dioxide (CO_2) was measured with the eddy covariance method with a Licor 7000 closed path infrared gas analyser (IRGA) and a three-dimensional Metek sonic anemometer at a height of 9 m, which is well above

the average tree height of 2.5 m. A more detailed description of additional parameters monitored at Welgegund is given by Beukes et al. (2015).

3.3 DATA ANALYSIS

3.3.1 Positive matrix factorisation analysis

PMF analysis of the VOCs and trace gases was performed with the EPA PMF 5.0 program. The PMF method is described in literature (Paatero, 1997, Paatero and Tapper, 1994) and the principle of the model is explained here briefly. PMF is, in essence, a factor analysis tool that decomposes a data matrix into two matrices, i.e. factor contributions and factor profiles. The objective of PMF analysis is to identify a user-specified number of factors, which are regarded as pollution sources. The equation to be solved by PMF analysis is:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \ , \qquad (3.1)$$

where x_{ij} is the j^{th} species concentration in the i^{th} sample; g_{ik} is the particulate mass concentration from the k^{th} source contributing to the i^{th} sample; f_{kj} is the mass fraction of the j^{th} species from the k^{th} source; e_{ij} is the residual associated with the j^{th} species concentration, measured in the i^{th} sample; p is the total number of independent factors. The results are constrained to ensure that there are no negative source contributions.

Each data point is individually weighted by utilising the estimated uncertainty for each species. In this study, the uncertainties for each sample were calculated by using measurement uncertainties (MU%) and minimum detection limits (MDL) in an equation-based uncertainty procedure described by Polissar et al. (1998). The conditional probability function (CPF) (Kim et al., 2003) was applied to the daily PMF dataset in order to estimate the impacts of sources from different directions. The CPF was calculated for each factor using relative source contributions and average wind directions for each sample – data collected on days with low wind speeds (<1 m/s) were removed from the dataset. CPF was calculated as follows:

$$CPF_{\theta} = \frac{m_{\theta}}{n_{\theta}} \ , \qquad (3.2)$$

where m_{θ} is the number of average wind vectors (days) that fall in the wind sector θ that exceed the threshold criteria (80^{th} percentile), while n_{θ} is the total number of vectors occurring in the same wind sector. The largest peak contributions in the time series were then selected for each factor for further analysis. If several factors were peaking at the same time, the largest peak was selected. In many cases, the CPFs of the factors showed quite mixed wind direction contributions, which were in particular the case for biogenic factors, where the source is located in close proximity to the station and the source direction is not evident.

3.3.2 Reactivity of VOCs

The destruction rates between O_3 and VOCs were calculated as per Eq. (3.3):

$$\text{destruction rates} = k_{X,O3}[X][O_3], \quad (3.3)$$

where $k_{X,O3}$ is the reaction rate constant between X and O_3, [X] is the VOC concentration and [O_3] is the ozone concentration. The OH reactivities (s^{-1}) of the various compounds were calculated using Eq. (3.4):

$$\text{OH reactivity} = k_{X,OH}[X], \quad (3.4)$$

where $k_{X,OH}$ is the reaction rate constant between X and OH, [X] is the VOC concentration. The O_3 formation potential of VOCs was calculated by multiplying the average concentration of a specific VOC with the maximum incremental reactivity (MIR) coefficient of each compound, i.e. OFP = VOC×MIR (Carter, 2009).

3.3.3 Risk assessment

The Risk Assessment Guidance for Superfund (RAGS) Volume I: Human Health Evaluation Manual part F, Supplemental Guidance for Inhalation Risk Assessment (USEPA, 2009) was used as a guideline to estimate the nature and the possibility of adverse health effects of each VOC in plumes that have passed over the source regions identified by in Article one or reported in other studies. Risk probability values, i.e. inhalation reference concentration (RfC) and unit risk (UR) were obtained through the risk model calculator established by the University of Tennessee ((RAIS, 2016) and reference therein), by giving priority to the most recent available data and are listed in Table 3-1. The impacts of VOCs on human health were assessed by estimating the non-carcinogenic and carcinogenic risks. The hazard ratio (HR) of each compound was calculated by Eqs. (3.5) and (3.6) in order to estimate the non-carcinogenic influence as follows:

$$HR = \frac{EC}{RfC}, \quad (3.5)$$

$$EC = \frac{CA \times ET \times EF \times ED}{ED \times 365\left(^{days}/_{year}\right) \times 24\left(^{hours}/_{day}\right)}, \quad (3.6)$$

where EC is the exposure concentration (μg m^{-3}); RfC (μg m^{-3}) corresponding to a specific compound (Table 3-1); CA is the concentrations (μg m^{-3}) of each VOC in plumes that have passed over the source regions identified or reported in other studies; ET is the exposure time (hours day^{-1}); EF is the exposure frequency (days $year^{-1}$); and ED is the exposure duration (years).

Table 3-1: Non-cancer reference concentrations, cancer unit risks of the VOCs found during the campaigns and their carcinogenic classifications in the IARC at Welgegund. Risk probability values (inhalation reference concentration and unit risk) were obtained through the risk model calculator, established by the University of Tennessee ((RAIS, 2016) and reference therein), by giving priority to the most recent available data

	Non-cancer			Cancer	
	RfC (µg m^{-3})	Source	MW (g mol^{-1})	UR (µg m^{-3})$^{-1}$	Source
Benzene	9.6	ATSDR	78.11	6.00E-06	WHO
Toluene	3770	ATSDR	92.14	-	-
Ethylbenzene	1300	ATSDR	106.17	2.50E-06	CALEPA
(m,p)-xylene	217	ATSDR	106.17	-	-
Styrene	850	ATSDR	104.15	-	-
o-xylene	217	ATSDR	106.17	-	-
Propylbenzene	100	PPRTV	120.1916	-	-
3-ET	n.a.	-	120.1916	-	-
4- ET	n.a.	-	120.1916	-	-
1,3,5-TMB	6	PPRTV	120.1916	-	-
2- ET	n.a.	-	120.1916	-	-
1,2,4-TMB	7	PPRTV	120.1916	-	-
1,2,3-TMB	5	PPRTV	120.1916	-	-
2,2,4-trimethylpentane	n.a.	-	114.23	-	-
heptane	n.a.	-	100.21	-	-
hexane	700	IRIS	86.175	-	-
2-methylpentane	n.a.	-	86.175	-	-
octane	n.a.	-	114.229	-	-
nonane	20	PPRTV	128.26	-	-

Agency for Toxic Substances and Disease Registry (ATSDR); Integrated Risk Information System (IRIS); Provisional Peer Reviewed Toxicity Values (PPRTV); California Environmental Protection Agency (CALEPA) Office of Environmental Health Hazard Assessment (OEHHA); World Health Organization (WHO).

The lifetime cancer risk (LCR) was calculated in order to determine the number of individuals likely to acquire cancer due to their exposure to the VOCs of concern from inhalation intake as follows:

$$LCR = UR \times \frac{CA \times ET \times EF \times ED}{LT \times 365\left({}^{days}/_{year}\right) \times 24\left({}^{hours}/_{day}\right)}, \quad (3.7)$$

where UR is the estimated unit risk value (µg^{-1} m^3) (Table 1) and LT is the lifetime expectancy (years).

The assumptions made by Paralovo et al. (2016) were used as a reference in calculating the LCR and HR values: ED of 25 years (assuming that a resident lives 25 years at the same place on

average); the average LT of South Africans is 60 years; EF of 350 days in a year (if we assume that a person spends on average 15 days a year outside the area that they live); and ET of 15 h per day.

3.3.4 Air mass back trajectory analysis

Individual hourly back trajectories were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model version 4.8, developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess, 2004). This model was run with meteorological data from the GDAS archive of the US National Weather Service's National Center for Environmental Prediction (NCEP) and archived by the ARL (Air Resources Laboratory, 2012). Each hourly arriving back trajectory was calculated for 96 h (4 days) backwards. An arrival height of 100 m was chosen since VOCs are mainly emitted within the lowermost layer of the troposphere. Furthermore, the orography in HYSPLIT is not very well defined, and therefore lower arrival heights could result in larger error margins on individual trajectory calculations. Back trajectories were calculated for the start, middle and end of each measurement period, i.e. three-hourly arriving back trajectories calculated for each 2 h sample.

CHAPTER 4

AMBIENT AROMATIC HYDROCARBON MEASUREMENTS AT WELGEGUND, SOUTH AFRICA

4.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT

K. Jaars[1], J. P. Beukes[1], P. G. van Zyl[1], A. D. Venter[1], M. Josipovic[1], J. J. Pienaar[1], V. Vakkari[2,3], H. Aaltonen[2], H. Laakso[3], M. Kulmala[3], P. Tiitta[1,4] , A. Guenther[5], H. Hellén[2], L. Laakso[1,2], and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa

[2]Finnish Meteorological Institute, PL 503, 00101 Helsinki, Finland

[3]Department of Physics, University of Helsinki, Finland

[4]Department of Applied Physics, University of Eastern Finland, Kuopio, Finland

[5]Pacific Northwest National Laboratory, Richland WA, USA

Contributions of the various co-authors were as follows. The bulk of the work was done by the author **K Jaars**, i.e. sample analysis, data processing, research and writing of the scientific paper; PG van Zyl and JP Beukes were the promoters of this study who assisted in the interpretation of data, writing the article and also made conceptual contributions. The author, with assistance from AD Venter, M Josipovic and P Tiitta, measured the VOCs from February 2011 to February 2012, while H Hellén, H Aaltonen and H Hakola assisted with specialised analyses, preparation and expert opinions on the adsorbent tubes at the FMI with a TD-GC-MS. H Laakso built the automated VOC sampler, while V Vakkari and L Laakso assisted in creating the infrastructure at Welgegund and made conceptual contributions. JJ Pienaar, M Kulmala and A Guenther made conceptual contributions.

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

4.2 FORMATTING AND CURRENT STATUS OF ARTICLE

The article is presented as published in *Atmospheric Chemistry and Physics*, a European Geosciences Union journal. The journal detail can be found at http://www.atmospheric-chemistry-and-physics.net (Date of access: 11 June 2016). The article was ***received***: 25 October 2013, ***published*** in *Atmos. Chem. Phys. Discuss*.: 17 February 2014, ***revised***: 16 May 2014, ***accepted***: 5 June 2014 and ***published***: 11 July 2014. (*Atmospheric Chemistry and Physics,* 14, 7075-7089, **2014** www.atmos-chem-phys.net/14/7075/2014/ doi:10.5194/acp-14-7075-2014).

Atmos. Chem. Phys., 14, 7075–7089, 2014
www.atmos-chem-phys.net/14/7075/2014/
doi:10.5194/acp-14-7075-2014

Atmospheric Chemistry and Physics Open Access

Ambient aromatic hydrocarbon measurements at Welgegund, South Africa

K. Jaars[1], J. P. Beukes[1], P. G. van Zyl[1], A. D. Venter[1], M. Josipovic[1], J. J. Pienaar[1], V. Vakkari[2,3], H. Aaltonen[2], H. Laakso[3], M. Kulmala[3], P. Tiitta[1,4], A. Guenther[5], H. Hellén[2], L. Laakso[1,2], and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa
[2]Finnish Meteorological Institute, PL 503, 00101 Helsinki, Finland
[3]Department of Physics, University of Helsinki, Helsinki, Finland
[4]Fine Particle and Aerosol Technology Laboratory Department of Environmental Science, University of Eastern Finland
[5]Pacific Northwest National Laboratory, Richland, WA, USA

Correspondence to: P. G. van Zyl (pieter.vanzyl@nwu.ac.za)

Received: 25 October 2013 – Published in Atmos. Chem. Phys. Discuss.: 17 February 2014
Revised: 16 May 2014 – Accepted: 5 June 2014 – Published: 11 July 2014

Abstract. Aromatic hydrocarbons are associated with direct adverse human health effects and can have negative impacts on ecosystems due to their toxicity, as well as indirect negative effects through the formation of tropospheric ozone and secondary organic aerosol, which affect human health, crop production and regional climate. Measurements of aromatic hydrocarbons were conducted at the Welgegund measurement station (South Africa), which is considered to be a regionally representative background site. However, the site is occasionally impacted by plumes from major anthropogenic source regions in the interior of South Africa, which include the western Bushveld Igneous Complex (e.g. platinum, base metal and ferrochrome smelters), the eastern Bushveld Igneous Complex (platinum and ferrochrome smelters), the Johannesburg–Pretoria metropolitan conurbation (> 10 million people), the Vaal Triangle (e.g. petrochemical and pyrometallurgical industries), the Mpumalanga Highveld (e.g. coal-fired power plants and petrochemical industry) and also a region of anticyclonic recirculation of air mass over the interior of South Africa. The aromatic hydrocarbon measurements were conducted with an automated sampler on Tenax-TA and Carbopack-B adsorbent tubes with heated inlet for 1 year. Samples were collected twice a week for 2 h during daytime and 2 h during night-time. A thermal desorption unit, connected to a gas chromatograph and a mass selective detector was used for sample preparation and analysis. Results indicated that the monthly median (mean) total aromatic hydrocarbon concentrations ranged between 0.01 (0.011) and 3.1 (3.2) ppb. Benzene levels did not exceed the local air quality standard limit, i.e. annual mean of 1.6 ppb. Toluene was the most abundant compound, with an annual median (mean) concentration of 0.63 (0.89) ppb. No statistically significant differences in the concentrations measured during daytime and night-time were found, and no distinct seasonal patterns were observed. Air mass back trajectory analysis indicated that the lack of seasonal cycles could be attributed to patterns determining the origin of the air masses sampled. Aromatic hydrocarbon concentrations were in general significantly higher in air masses that passed over anthropogenically impacted regions. Inter-compound correlations and ratios gave some indications of the possible sources of the different aromatic hydrocarbons in the source regions defined in the paper. The highest contribution of aromatic hydrocarbon concentrations to ozone formation potential was also observed in plumes passing over anthropogenically impacted regions.

1 Introduction

Atmospheric measurements – which include, but are not limited to, speciated volatile organic compounds and other trace gasses, as well as size-resolved aerosols – are well established in developed countries. However, less emphasis is placed on such environmental issues in developing countries, since resources are mostly utilised for economic growth. For

Published by Copernicus Publications on behalf of the European Geosciences Union.

this reason, Africa is one of the least studied regions with respect to air quality (Laakso et al., 2006). South Africa has the largest industrialised economy in Africa and is known for its diverse anthropogenic pollutant sources, which include agriculture, metallurgical and mining operations, coal-fired power generation, petrochemical operations, coal dumps and transportation (Lourens et al., 2011). Unique meteorological conditions are prevalent in South Africa, which include relatively high atmospheric temperatures and solar radiation, which increases photochemical activity in the atmosphere, and dominant anticyclonic climatology and the presence of low-level inversion layers in winter cause trapping of pollutants (Tyson et al., 1996).

Atmospheric volatile organic compounds (VOCs) are emitted from both natural and anthropogenic sources (Bates et al., 2000; Brasseur et al., 1999; Hewitt, 1999). Anthropogenic VOC emissions result from petrochemical industries, combustion processes (e.g. fossil fuel, power plants), vehicular emissions, storage and transport of fuel, usage and production of solvents, hazardous waste facilities and landfills (Srivastava et al., 2005; Derwent et al., 2000; Kourtidis et al., 1999; Jose et al., 1998). Biomass burning (veld fires) can also be an important source of VOCs, especially in southern Africa, where large-scale biomass combustion occurs every year in the dry season (e.g. Crutzen and Andreae, 1990; Crutzen et al, 1979). However, these emissions are difficult to evaluate, as they are highly dependent on fuel type, humidity and burn rate (Lobert et al., 1990).

A large fraction of anthropogenic VOCs consists of aromatic hydrocarbons, of which benzene; toluene; ethylbenzene; and *o*-, *m*- and *p*-xylene (BTEX) are the most commonly measured compounds. Aromatic hydrocarbons participate in complex chemical reactions in the atmosphere to form secondary pollutants. Although reactions of aromatic hydrocarbons do not directly produce ozone (O_3), they play a role in O_3 formation when they are oxidised by the hydroxyl radical ($^{\bullet}OH$) in the troposphere, producing peroxy radicals ($RO_2^{\bullet}$) and hydroperoxy radicals ($HO_2^{\bullet}$), which then oxidise nitric oxide (NO), which removes a sink for O_3 (Atkinson, 2000). Aromatic hydrocarbons can also react with nitrate radicals ($NO_3^{\bullet}$) (Atkinson, 1994; Penkett et al., 1993) and halogen radicals (Finnlayson-Pitts et al., 1986). Various researchers have investigated gas-phase photooxidation of aromatic hydrocarbons (e.g. Birdsall et al., 2010; Arey et al., 2009; Coeur-Tourneur et al., 2006; Johnson et al., 2004, 2005; Takekawa et al., 2003; Calvert et al., 2002, and references therein; Olariu et al., 2002; Volkamer et al., 2002).

VOCs are also associated with adverse human health effects (Mukund et al., 1996; Kostiainen, 1995; Sweet and Vermette, 1992; Edgerton et al., 1989; Duce et al., 1983) and can also be harmful to ecosystems (Atkinson, 2000; Dewulf and Van Langenhove, 1997; Kuran and Sojak, 1996; Derwent, 1995). Benzene, for instance, is known as a genotoxic carcinogen (Hellén et al., 2002; WHO, 2000) and is closely linked to the induction of leukaemia. Studies have also indicated that VOCs can have detrimental impacts on crop production, which is important for global food security (Zunckel et al., 2006).

Limited research has been conducted to determine the emission rates of biogenic VOCs in southern Africa (Harley et al., 2003; Otter et al., 2002a, 2002b; Swap et al., 2002a, 2002b; Greenberg et al., 2002; Greenberg et al., 1999; Guenther et al., 1996). Even fewer data are available to characterise aromatic VOC levels in South Africa. Benzene is the only aromatic hydrocarbon that has a standard included in the National Ambient Air Quality Standards (NAAQS) (Government Gazette, 2009). According to the knowledge of the authors, only Lourens et al. (2011) has conducted a study in this region on BTEX concentrations that was published in the peer-reviewed public domain. This study was limited to measurements in the industrialised Mpumalanga Highveld and Vaal Triangle for 1 year. Additionally, some postgraduate studies focusing on BTEX have been conducted (van der Walt, 2008; Burger, 2006; Chiloane, 2005), but these were not published in the peer-reviewed public domain. Various industries also perform VOC measurements in South Africa to comply with legislation, but these results are in most instances not peer-reviewed and not available in the public domain.

To at least partially address the above-mentioned knowledge gap, i.e. very limited data on atmospheric aromatic hydrocarbons in South Africa, measurements were conducted for 1 year at the Welgegund measurement station. This station was strategically positioned to enable measurements of air masses that have passed over the regional background, as well as all the major anthropogenic source regions in South Africa (Beukes et al., 2014).

2 Measurement location and methods

2.1 Site description

The Welgegund measurement station (www.welgegund.org) is situated approximately 100 km west of Johannesburg (Fig. 1) on the property of a commercial farmer. The station is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity. The entire western sector (from north to south-east) contains no major point sources and can therefore be considered as representative of a relatively clean regional background. The site is, however, impacted by plumes from 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 (> 10 million people), the Vaal Triangle, the Mpumalanga Highveld and also a region of anticyclonic recirculation of air mass over the interior of South Africa. The impacts of regional biomass combustion occurring mainly in

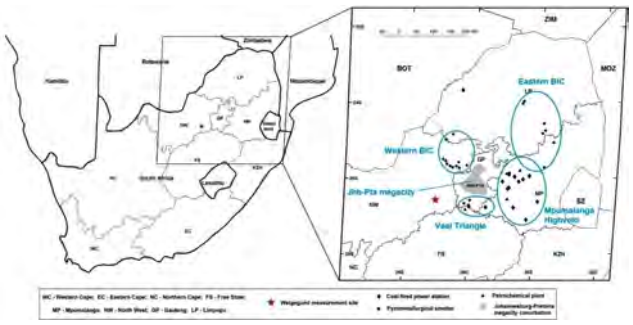

Figure 1. Map of southern Africa indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and anthropogenic source regions impacting Welgegund.

the dry winter and spring are also observed at Welgegund. A detailed description of the Welgegund measurement station and related source regions was recently presented by Beukes et al. (2014). In Fig. 1, the location of Welgegund is indicated (latitude 26°34′10″ S, longitude 26°56′21″ E; 1480 m a.s.l.) within a regional perspective, which also indicates the large point sources and source regions.

2.2 Measurement methods

The measurement instruments were placed inside a Eurowagon 4500u (length 4.5 m, width 2.1 m, height 2.3 m) measurement container. A detailed description of the measurement instruments, operation procedures and data analysis, as well as calibration and maintenance procedures has been presented by Beukes et al. (2014), Tiitta et al., 2014, Petäjä et al. (2013), Hirsikko et al. (2012), Venter et al. (2012), Vakkari et al. (2011) and Laakso et al. (2008).

2.2.1 Aromatic hydrocarbon measurements

The VOC measurement campaign was conducted for 1 year (9 February 2011 to 4 February 2012) to observe seasonal variability. Samples were collected twice a week for 2 h during daytime (11:00 to 13:00 local time, LT) and 2 h during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays. Obviously this repetitive sampling schedule, i.e. same days each week and same hours of the day, was prone to some bias. Large point sources, i.e. industrial stack emissions, in South Africa are regulated on an availability basis. This implies that off-gas cleaning equipment must be operational for a certain percentage of the overall operating time (typically 97–99 %) and not on a time basis, e.g. specific days or hours when emissions are allowed. It was therefore impossible to set a sampling schedule to capture possible large releases of VOCs by such point sources. Traffic emissions, which can be considered as a point or area source, depending on how far the emissions are from the measurement site, are another example of a potential time-bound VOC source that had to be considered. At the Welgegund site only a small gravel road, used by a few farmers, is nearby. Local traffic emissions are therefore almost negligible. Large traffic volumes in especially the Johannesburg–Pretoria megacity could be a significant area source of VOCs for Welgegund. However, since Welgegund is ~ 100 km west of Johannesburg, it was difficult to set a sampling schedule to capture such time-bound emissions that are transported at different rates on different days with different meteorological conditions. Considering the remote nature of the sampling site and logistical limitations during the sampling campaign, the sampling schedule applied was the most feasible option that enabled the collection of a full year of data. VOCs were sampled at a height of 2 m above ground level, with a 1.75 m long inlet. The first 1.25 m of the inlet was made of stainless steel and the second 0.5 m of Teflon. The first 1.2 m of the stainless steel section of the inlet was heated to 120 °C using heating cables and thermostats (Thermionic) to remove O_3, which could possibly lead to sample degradation (Hellén et al., 2012). The last 0.05 m of the stainless steel section and the entire Teflon section was housed within the measurement container, wherein the temperature was regulated at 24 °C. The O_3 removal efficiency was checked with an O_3 monitor at regular intervals, which revealed that O_3 concentrations decreased from median values ≥ 30 ppb (Beukes et al., 2014) to < 2 ppb.

Prior to sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 min at 350 °C at a flow of 40 mL min^{-1}. After treatment, the tubes were sealed with Swagelok® brass 0.25 in. caps and stored in a fridge at temperatures below 18 °C before they were transported to the field for sampling. VOC samples were collected on Tenax-TA and Carbopack-B adsorbent tubes (6.3 mm ED $\times$ 90 mm, 5.5 mm ID) by using a constant-flow-type automated programmable sampler. A needle valve attached to the pump was used to keep the flow constant, while magnetic valves were used to direct flow to a specific sample tube. After a specific tube was sampled, the tube was automatically sealed off and the next tube selected for sampling. The flow of the pump was calibrated each week. A sampling flow between 100 and 110 mL min^{-1} was used throughout the study. Hellén et al. (2002) reported no breakthrough for Tenax-TA and Carbopack-B tubes when sampling for 4 h at a flow rate of 100 mL min^{-1}. Once a week, the tubes were removed from the automated sampler and closed with Swagelok® caps. Each tube was separately wrapped in aluminium foil and stored in a container for transport to the laboratory. Tubes were stored in the laboratory in a freezer within a clean environment to minimise pre-analysis elution and breakdown of the sampled compounds. For each month, a field blank was analysed to compensate for the possibility of contamination from sample handling and storage. The total concentration of aromatic hydrocarbons in all field blanks was found to be < 0.076 ppb. Actual concentrations of all compounds reported in this paper were significantly higher than blank

values and also well above the detection limits. Blank values were subtracted from exposed samples.

The analyses and preparation of the adsorbent tubes were done by the Finnish Meteorological Institute. The instrumental setup was a thermal desorption instrument (Perkin-Elmer TurboMatrix™ 650, Waltham, USA) connected to a gas chromatograph (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 µm) column and a mass selective detector (Perkin-Elmer® Clarus® 600T, Waltham, USA). The sample tubes were desorbed at 300 °C for 5 min and cryofocused in a Tenax cold trap (−30 °C) prior to injection of the sample into the column by rapidly heating the cold trap (40 °C min^{-1}) to 300 °C. A three-point calibration curve was obtained by using liquid standards dissolved in methanol. Standard solutions were injected into adsorbent tubes and were flushed with nitrogen (100 mL min^{-1}) for 10 min in order to evaporate the methanol. The tubes containing the standards were desorbed and analysed with the same method used for the sampled tubes. Thirteen aromatic hydrocarbons were detected and quantified during this study.

2.2.2 Ancillary measurements

Trace gas measurements continuously conducted at Welgegund were used to assist in the interpretation of aromatic hydrocarbon results obtained. These were measured by utilising a Thermo-Electron 43S sulfur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU NO_x analyser (Advanced Pollution Instrumentation Inc., San Diego, CA, USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 CO analyser (Horiba, Kyoto, Japan). A more detailed description of additional parameters monitored at Welgegund is given by Beukes et al. (2014) and Petäjä et al. (2013).

2.2.3 Air mass back trajectory analysis

Individual hourly back trajectories were calculated with the Hybrid Single-Particle Lagrangian Intergrated Trajectory (HYSPLIT) model version 4.8, developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess, 2004). This model was run with meteorological data of the GDAS archive of the US National Weather Service's National Center for Environmental Prediction (NCEP) and archived by the ARL (Air Resources Laboratory, 2012). Each hourly arriving back trajectory was calculated for 96 h (4 days) backwards. An arrival height of 100 m was chosen, since aromatic hydrocarbons are mainly emitted within the lowermost layer of the troposphere. Furthermore, the orography in HYSPLIT is not very well defined, and therefore lower arrival heights could result in larger error margins on individual trajectory calculations. Back trajectories were calculated for the start, middle and end of each measurement period, i.e. 3-hourly arriving back trajectories calculated for each 2 h sample.

3 Results and discussion

3.1 Contextualising aromatic hydrocarbon concentrations measured at Welgegund

The monthly mean (median) aromatic hydrocarbon concentrations determined in this study ranged between 0.011 (0.01) and 3.2 (3.1) ppb). As previously mentioned, benzene is currently the only VOC listed as a criteria pollutant in the NAAQS (Lourens et al., 2011; Government Gazette, 2009), with an annual average limit of 1.6 ppb (2015 standard). The Welgegund annual mean (median) benzene concentration was 0.29 (0.13) ppb, which is well below the South African standard. The highest benzene concentration measured was 8.7 ppb, which indicates that the site is occasionally significantly impacted by pollution sources. Liu et al. (2000), who conducted a study in a relatively non-polluted area in the northeast of China, reported an average benzene concentration of 9.4 µg m^{-3} (2.94 ppb). Lourens et al. (2011) reported an annual median of 0.91 ppb in the Mpumalanga Highveld and the Vaal Triangle, which is higher than the annual median value measured at Welgegund. This can be attributed to the measurement sites in the Mpumalanga Highveld and the Vaal Triangle being closer to the large point sources than Welgegund. In another investigation, van der Walt (2008) measured benzene levels in a South African metropolitan area and reported an annual mean of 1.8 ppb. A comparison of the benzene concentrations measured at Welgegund with these studies indicates that Welgegund can be considered as a regional background site that is on occasion impacted by major plumes from different sources.

Toluene was the most abundant aromatic hydrocarbon, with an annual mean (median) concentration of 0.89 (0.63) ppb – nearly 5 times higher than the benzene annual median concentration. Lourens et al. (2011) also reported ambient toluene concentrations to be substantially higher than that of benzene over the interior of South Africa. Considering that toluene also has negative effects on human health, as well as that it is a precursor for O_3 and secondary organic aerosol formation, it should be considered to be included in future South African air quality legislation.

The second and third most abundant aromatic hydrocarbons measured were styrene and (m,p)-xylene with annual mean (median) concentrations of 0.83 (0.66) and 0.77 (0.50) ppb, respectively. o-Xylene and ethyl benzene had annual mean (median) concentrations of 0.30 (0.20) and 0.34 (0.25) ppb, respectively. The other aromatic hydrocarbons measured had annual median concentrations that were significantly lower. This does not necessarily mean that their emission sources were lower, since the ambient concentrations are

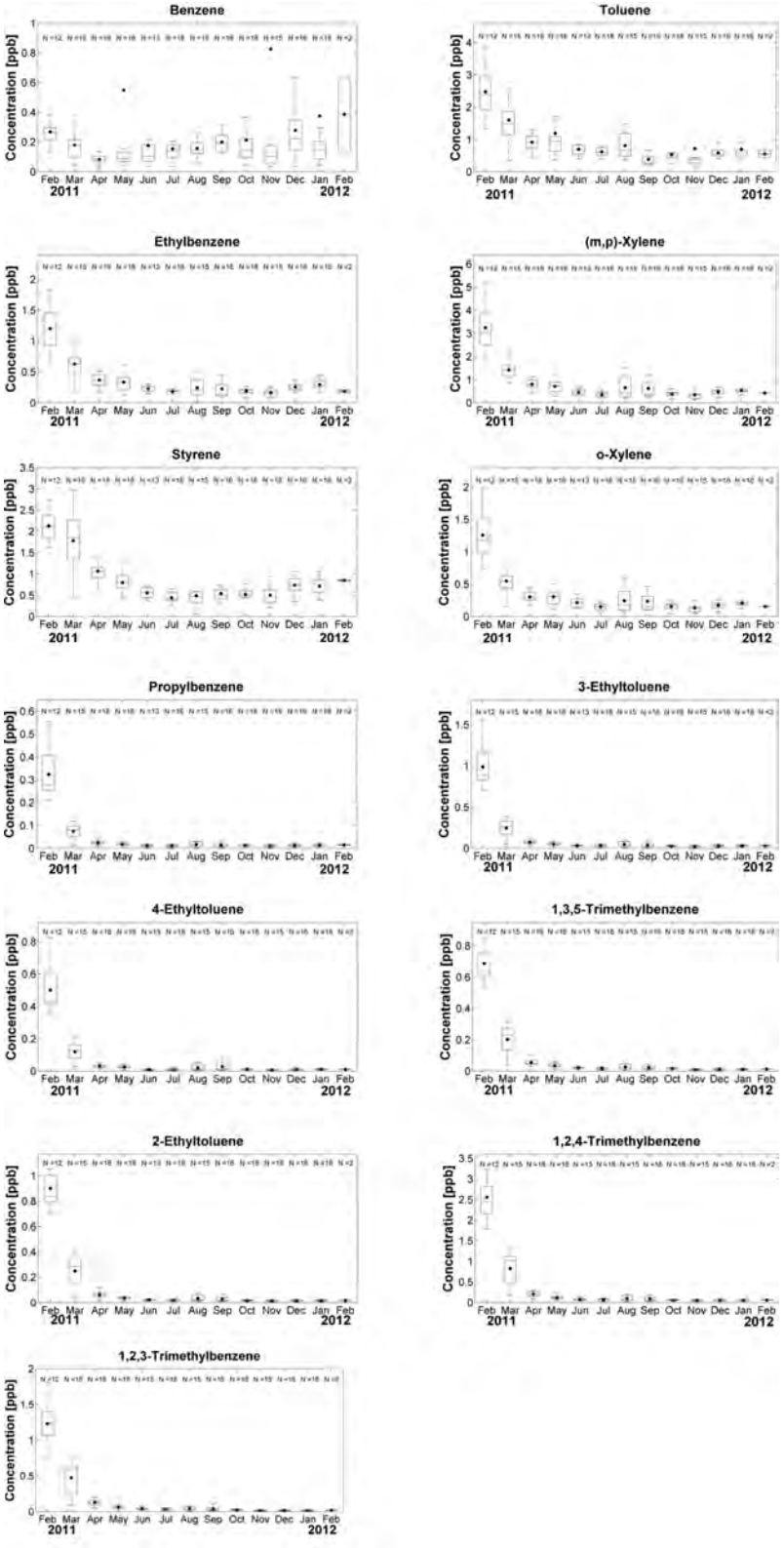

Figure 2. Monthly annual variation in aromatic hydrocarbon concentrations measured during the 1-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles, and the whiskers $\pm 2.7\sigma$ or 99.3 % coverage if the data have a normal distribution (MATLAB, 2010). The values displayed near the top of the graphs indicate the number of samples (N) analysed for each month.

determined by the emission rate and their atmospheric lifetimes (Parra et al., 2006).

3.2 Temporal variations

Although samples were collected during daytime and night-time in order to identify possible diurnal influences, results indicated no statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time. Also, no statistically significant differences were observed between Tuesdays and Saturdays. This indicates that there are no major local sources such as traffic that would result in a distinct diurnal pattern. Therefore, no distinction in the results was made in subsequent sections based on daytime and night-time, or day of the week.

The monthly temporal variations of the measured aromatic hydrocarbons are presented in Fig. 2. These figures indicate the median, mean and 25th and 75th percentiles, as well as ±2.7 of the quartiles for each compound (Matlab, 2010). The number of samples collected per month (N) is also provided. In general, no distinct seasonal pattern is observed for any of the compounds measured. The results indicate relatively high values during February 2011 and March 2011 for all the aromatic hydrocarbons, with the exception of benzene. If these higher values coincided with a seasonal cycle, it would have been expected that similar higher values had been observed in the corresponding months in the next year, which was not the case. The reason for these higher levels of aromatic hydrocarbons observed during these 2 months will be explored in Sect. 3.3. No seasonal patterns for BTEX were observed in a previous investigation conducted in the Mpumalanga Highveld and Vaal Triangle (Lourens et al., 2011).

3.3 Influence of source regions

Since no distinct seasonal cycles could be identified for the measured aromatic hydrocarbons (Fig. 2), the possible influence of air masses passing over different source regions on the concentration of these compounds was explored. Since VOCs were collected for only four 2 h sampling periods per week, the allocation of hourly back trajectories to air masses passing over all of the source regions defined by Beukes et al. (2014) was statistically not significant. Therefore, it was decided to group the Johannesburg–Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld source regions together, since these source regions were identified by Beukes et al. (2014) as the regions with the highest anthropogenic impacts. In this paper, this combined source regions will be referred to as area I. The WBIC, the EBIC and the anticyclonic source regions that lie on the anticyclonic recirculation path of air masses moving towards Welgegund (Beukes et al., 2014) were grouped together and are referred to as area II. Lastly, the "regional background" source region was kept as defined by Beukes et al. (2014). In Fig. 3, the different source regions considered in this study are presented.

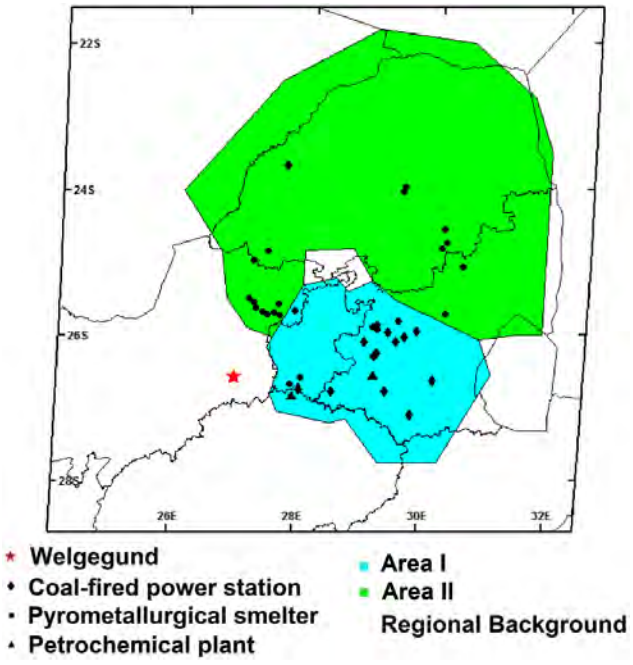

Figure 3. Map of the north-eastern part of South Africa indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and the source regions defined in this study.

For the entire VOC measurement period, 582 back trajectories were generated. Back trajectory sets, i.e. three trajectories per sampling period, were classified as passing over the different source regions defined in Fig. 3. For the two anthropogenically influenced source regions, i.e. areas I and II, only back trajectory sets that had passed over one of these source regions were considered. Therefore, back trajectory sets that had passed over both these source regions were not considered in further discussions on the influence of source regions. Back trajectory sets were considered as passing over the regional background if such trajectories did not pass over either area I or II, or both area I and II. Taking this into consideration, 86 % of all back trajectory sets could be classified as passing over just one of the three source regions defined.

In Fig. 4, the back trajectories of air masses passing over the different source region are presented. In total, 39 % of the VOC samples were collected during periods when air mass back trajectory sets had passed over area II, while 33 and 14 % of VOC samples were collected when air mass back trajectory sets passed over the regional background and area I, respectively. The reason for the lower percentage of air masses passing over area I can be attributed to the persistence of the anticyclonic circulation pattern over the interior of South Africa, which favours the arrival of air masses at Welgegund from the north to north-eastern sector.

In Fig. 5, the monthly fractional distribution of VOC samples collected during periods when air mass back trajectory

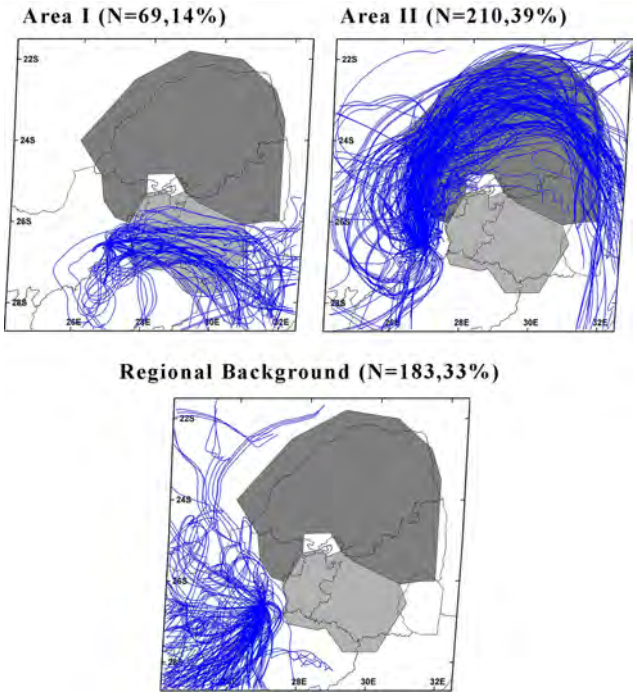

Figure 4. Graphical representations of back trajectories considered as passing over the defined source regions. The percentage of the trajectories considered as passing over a specific source region and the number of trajectories it represents are provided in brackets.

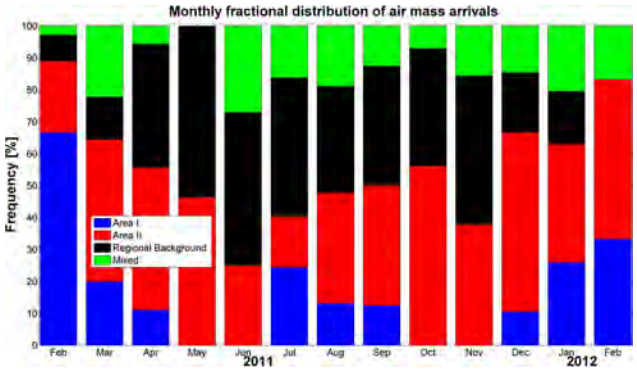

Figure 5. Monthly fractional distribution of VOC samples allocated according to air mass back trajectory sets after passing over the defined source regions.

sets had passed over the different source regions is presented. In this figure, air masses that had passed over multiple source regions were defined as mixed. The monthly fractional distribution (Fig. 5) can possibly be used to explain the lack of seasonal pattern observed for the aromatic hydrocarbons (Fig. 2). During February 2011, more than 60 % of the air masses that arrived at Welgegund passed over area I, which consists of the Johannesburg–Pretoria metropolitan conurbation, the Vaal Triangle and the Mpumalanga Highveld. According to Lourens et al. (2012), 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, 2007; Government Gazette, 2005). Considering the high frequency of air masses arriving at Welgegund after passing over area I during the initial period of the study (Fig. 5), the relatively high aromatic hydrocarbon levels measured in February 2011 and March 2011 (Fig. 2) can be related to the relatively polluted air masses arriving during this period. Conversely, during the rest of the study, most of the air masses that arrived at Welgegund passed only over area II and the regional background, which corresponds to lower concentrations measured (Fig. 2). It is therefore postulated that the monthly seasonal cycles presented for the aromatic hydrocarbons (Fig. 2) are not directly related to seasonal patterns in emissions, but rather depend on the origin of the air masses sampled. Any monthly differences are likely to be a result of month-to-month differences in air mass trajectories. The aforementioned postulation is strengthened by a slight concentration increase in most of the aromatic hydrocarbons observed during August and September 2011 (Fig. 2), which correlated with an increase in frequency of the arrival of air masses that had passed over area I (Fig. 5).

The aromatic hydrocarbon concentrations measured for air masses passing over the three source regions are presented in Fig. 6. As expected, aromatic hydrocarbon concentrations were in general significantly higher for air masses that passed over area I, which are considered to be more polluted. Air masses that passed over area II and the regional background had much lower aromatic hydrocarbon levels and were of the same order. The large point sources in area II are mainly pyrometallurgical smelters (Fig. 2) that produce metals from ores by means of reducing processes (e.g. ferrochromium, as indicated by Beukes et al., 2010, 2012). Aromatic hydrocarbon emissions are not usually associated with these activities and so the relatively low values are expected. In addition, the large point sources in area II are on average further away from Welgegund than the large point sources in area I. This longer travelling time can result in the increased oxidation of the aromatic hydrocarbons. Aromatic hydrocarbons measured in air masses from the regional background can possibly be attributed to smaller cities and agricultural activities in this region, but may also be associated with natural emissions (e.g. Heiden et al., 1999).

3.4 Inter-compound correlations: an indication of sources

Several authors (Hoque et al., 2008, and references therein) have performed correlation analyses to determine the possible source(s) for aromatic hydrocarbons. In this section, Pearson's correlation analyses were applied to correlate the concentrations of the different aromatic hydrocarbons

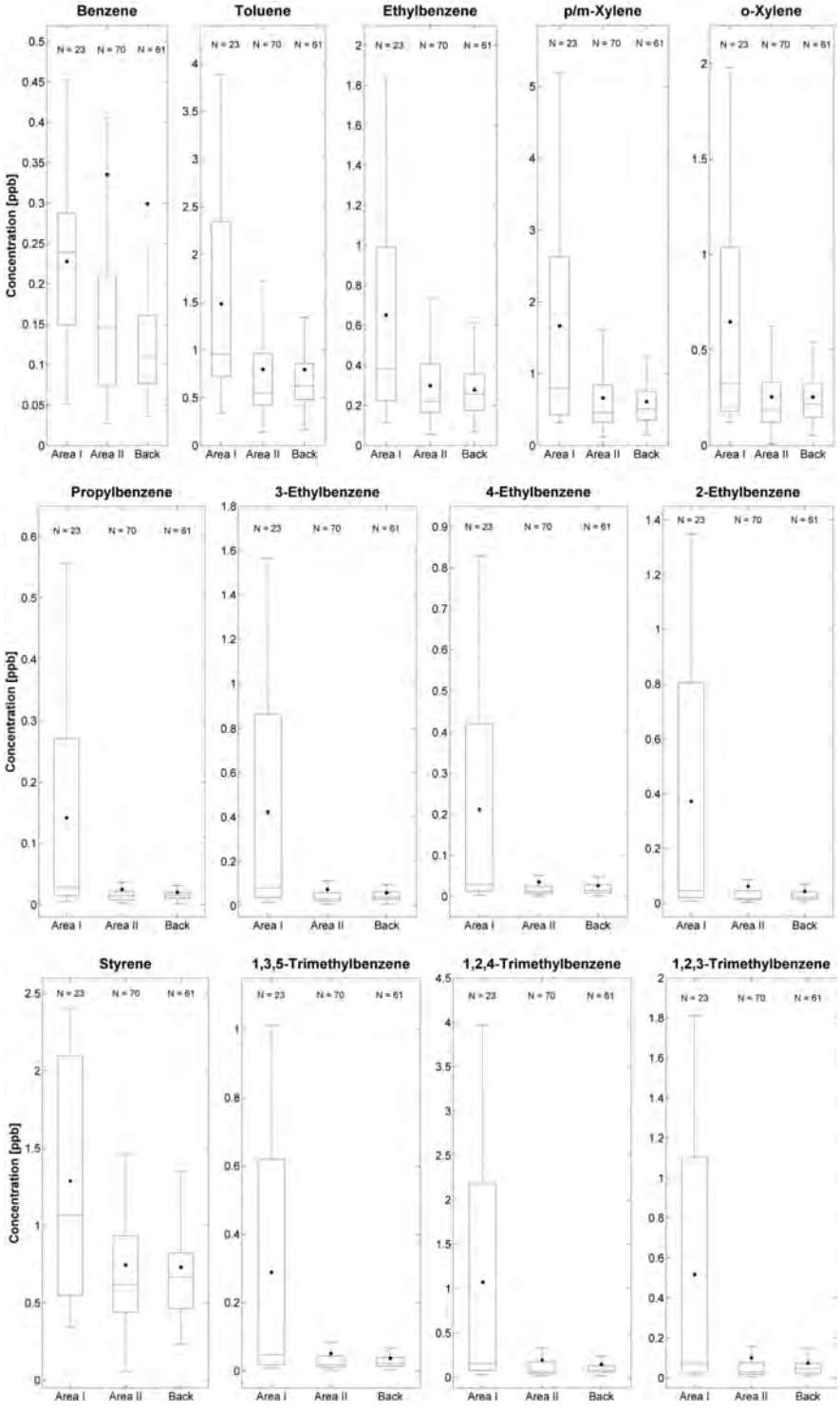

Figure 6. BTEX concentrations measured in air masses arriving at Welgegund, after they had passed over the defined source regions. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles, and the whiskers $\pm 2.7\sigma$ or 99.3 % coverage if the data have a normal distribution (MATLAB, 2010). The values displayed near the top of the graphs indicate the number of samples (N) analysed for each source area.

measured to one another, as well as to trace gas concentrations for air masses passing over each of the three source regions defined. These correlations are graphically presented in Fig. 7.

For air masses that had passed over area I, relatively good correlations ($r > 0.8$) between the aromatic hydrocarbons were observed, except for benzene. The correlations of benzene with the other aromatic hydrocarbons were less significant, i.e. $r > 0.6$. This indicates that all the aromatic hydrocarbons, except possibly benzene, could be from similar sources. Karl et al. (2009) used aircraft flux measurements to show that toluene to benzene ratios can vary greatly (< factor of 3 to > factor of 15) on a spatial scale of tens of kilometres, indicating differences associated with various sources within a region, indicating that a high correlation between benzene and toluene will not always be the case. Large coal-fired power stations and petrochemical operations in source area I, together with vehicle emissions, are expected to be the dominant sources of aromatic hydrocarbons in this source region. Venter et al. (2012) recently indicated that household combustion, which is a very common occurrence in semi- and informal settlements in particular, could also contribute significantly. None of the aromatic hydrocarbons correlated with any of the inorganic gaseous compounds, except benzene, which had a correlation coefficient of 0.612 with CO. Benzene also showed a negative correlation with O_3. Both the correlation with CO and the negative correlation with O_3 indicate that benzene was mainly present in fresher plumes arriving at Welgegund. The partial correlation of benzene with CO indicates that incomplete combustion sources such as vehicle emissions, household combustion and biomass combustion may be the dominant benzene emissions sources in area I.

With the exception of benzene and toluene, the other aromatic hydrocarbons in air masses that had passed over area II correlated relatively well ($r > 0.73$) with one another. Although benzene and toluene did not correlate with the other aromatic hydrocarbons, they correlated relatively well (r =0.74) with one another. Therefore, it seems that benzene and toluene had a similar source(s), while the other aromatic hydrocarbons had a different source(s). However, neither benzene nor toluene correlated with CO, as was the case for benzene in air masses that had passed over area I. Incomplete combustion sources were therefore unlikely to be the main sources of these two compounds. The nature of large point sources in area II is dramatically different to that of area I. Virtually no large combustion point sources occur in area II, since pyrometallurgical operations mainly focussing on reductive smelting are dominant.

For air masses that had passed over the regional background, benzene correlated well ($r = 0.92$) with toluene. However, in contrast to air masses that had passed over areas I and II, not all of the remaining aromatic hydrocarbons correlated with one another. Only a few significant correlations existed, e.g. ethylbenzene, styrene, (m,p)-xylene and

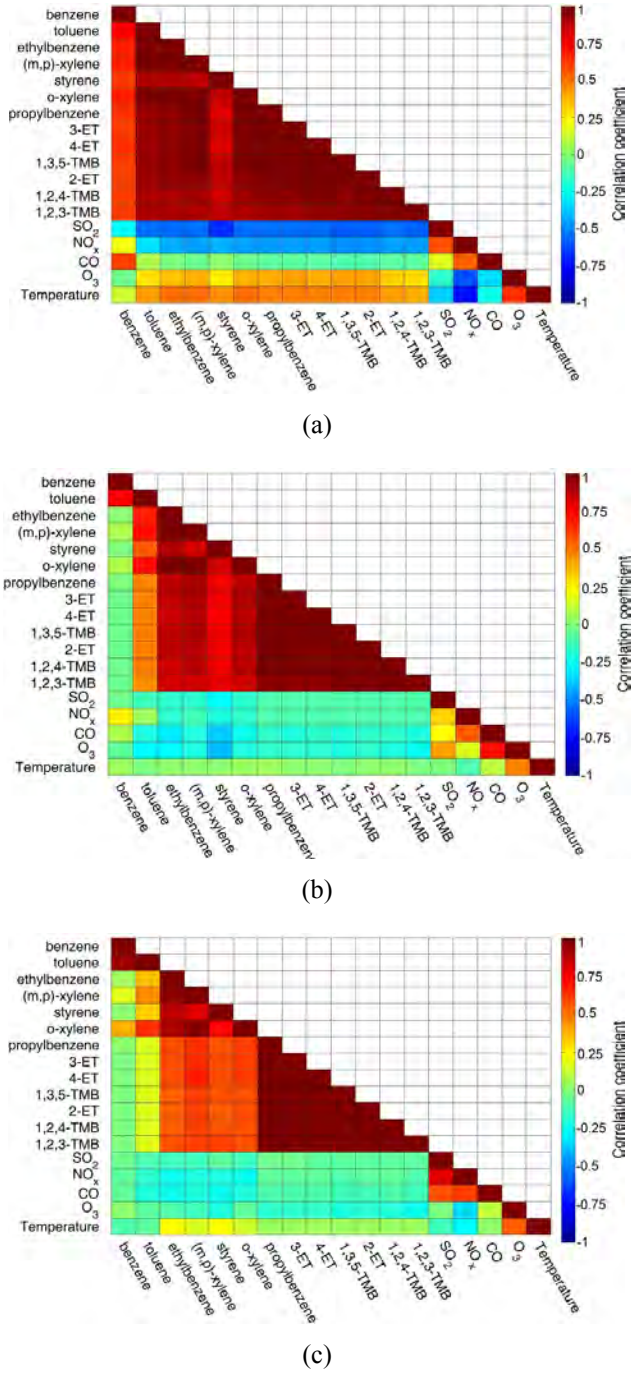

Figure 7. Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gases in samples that were collected when back trajectory sets had passed over area I **(a)**, area II **(b)** and the regional background **(c)**.

o-xylene correlated well ($r > 0.8$) with each other. This indicates that the sources of benzene and toluene were again linked but that the sources of the other aromatic hydrocarbons were not necessarily linked. The lower concentrations measured in air masses that had passed over the regional

Table 1. The aromatic hydrocarbon ratios for the specific source regions.

	Area I	Area II	Regional background	Automotive exhaust
toluene / benzene	6.51	2.38	2.66	2.7[a]
(m,p)-xylene / benzene	7.31	1.97	2.05	1.8[b]
o-xylene / benzene	2.84	0.76	0.85	0.9[c]
ethylbenzene / benzene	2.87	0.89	0.93	
1,3,5-TMB / benzene	1.27	0.15	0.13	
styrene / benzene	5.66	2.23	2.44	
propylbenzene / benzene	0.62	0.07	0.07	
(m,p)-xylene / ethylbenzene	2.55	2.20	2.19	
o-xylene / ethylbenzene	0.99	0.85	0.91	

[a] Brocco et al. (1997), Guicherit (1997), [b] Stevenson et al. (1997), [c] Guicherit (1997).

background also resulted in more uncertainty, which could lead to lower correlations. Additionally, the natural emissions of aromatic hydrocarbons were also explored. Heiden et al. (1999) proved that some plant species release toluene. Of the species evaluated by Heiden et al. (1999), only sunflower is relevant to the situation at Welgegund – sunflower is the second most common crop species in the area. Heiden et al. (1999) stated that significant diurnal variation in toluene emissions from sunflowers occur, with daytime emissions being a factor of 2 higher than night-time emissions. This was attributed to either differences in photo active radiation (PAR) and/or temperature (T) between daytime and night-time. As is evident from Fig. 7c, toluene did not correlate or anti-correlate with T for the regional background. Therefore, although it is not impossible that vegetation contributes to toluene concentrations measured, it does not seem to be the dominant source.

3.5 Inter-compound ratios: an indication of sources and aging

In addition to inter-compound correlations, inter-compound ratios can also be used as an indicative method to determine possible sources for aromatic hydrocarbon and the age of air masses (Hoque et al., 2008, and references therein). The inter-compound ratios of the average atmospheric concentrations of aromatic hydrocarbons with benzene are presented in Table 1. Since most of the aromatic hydrocarbons are more reactive than benzene, the toluene / benzene (T / B), (m,p)-xylene / benzene ((m,p)-X / B), o-xylene / benzene (o-X / B) and (m,p)-xylene / ethylbenzene ((m,p)-X / EB) ratios can provide information on the distance from emission sources and the estimated photochemical age of the air mass (Monod et al., 2001; Derwent et al., 2000). The atmospheric T / B ratio, for instance, is usually high close to anthropogenic emissions and will decrease with an increase in distance from the sources (Lee et al., 2002). Globally a T / B ratio below 3 was found to be characteristic of fresh emissions originating from traffic, while a T / B ratio > 4.3 is typical for solvent sources (Lan et al., 2013, and references therein).

As indicated in Table 1, the highest aromatic hydrocarbon ratios were observed for plumes passing over area I, whereas lower ratios were detected in plumes passing over area II and the regional background. The ratios (calculated from the average concentrations) for plumes passing over area I were 6.51, 7.31, 2.84, 2.55 and 2.87 for (T / B), ((m,p)-X / B), (o-X / B) ((m,p)-X / EB) and (EB / B), respectively. These ratios indicate the influence of anthropogenic activities in this area, as well as the closer proximity of especially the Johannesburg–Pretoria megacity, which is part of area I, to the Welgegund monitoring station.

The ratios for plumes passing over area II were 2.38, 1.97, 0.76, 2.20 and 0.89 for (T / B), ((m,p)-X / B), (o-X / B) ((m,p)-X / EB) and (EB / B), respectively. As mentioned previously, although anthropogenic activities are also present in this source area, the major industrial activities in this area are not usually associated with high emissions of VOCs. Additionally, sources in area II are also further away from the measurement site compared to sources in area I. The ratios therefore also indicate aged air masses, which might be transported by the dominant anticyclonic circulation pattern of air masses from the industrial hub of South Africa. Therefore, it is likely that most of the aromatic hydrocarbons in air masses that had passed over area II had undergone photochemical degradation.

For air masses passing over the regional background, the aromatic hydrocarbon inter-compound ratios were 2.66, 2.05, 0.85, 2.19 and 0.93 for (T / B), ((m,p)-X / B), (o-X / B) ((m,p)-X / EB) and (EB / B), respectively. These ratios compared well with the ratios calculated for area II, which also indicate no local sources of atmospheric aromatic hydrocarbons.

According to the literature, the use of solvents (e.g. in paint) is thought to be a major non-traffic source of aromatic hydrocarbons. Brocco et al. (1997) stated that toluene, ethylbenzene and o,m,p-xylene (TEX) make up the largest portions of solvents. In Fig. 8, the concentration ratios of TEX / total aromatics for air masses that had passed over the three sources regions are illustrated. The ratios show a

Table 2. Ozone formation potential of the aromatic hydrocarbon concentrations of air masses passing over the three source regions.

	Area I			Area II		Regional background	
	Mean	MIR coefficient	O_3 formation potential	Mean	O_3 formation potential	Mean	O_3 formation potential
benzene	0.228	0.42	0.096	0.335	0.141	0.299	0.125
toluene	1.482	2.70	4.001	0.796	2.148	0.796	2.148
ethylbenzene	0.653	2.70	1.762	0.300	0.809	0.279	0.753
(*m*,*p*)-xylene	1.665	8.20	13.653	0.661	5.418	0.612	5.014
styrene	1.288	2.20	2.834	0.746	1.641	0.730	1.607
o-xylene	0.647	6.50	4.208	0.254	1.651	0.253	1.645
propylbenzene	0.142	2.10	0.298	0.025	0.053	0.021	0.043
1,3,5-TMB	0.289	10.10	2.916	0.051	0.512	0.038	0.381
1,2,4-TMB	1.073	8.80	9.444	0.196	1.728	0.146	1.289
1,2,3-TMB	0.518	8.90	4.608	0.101	0.900	0.076	0.674

Note: TMB stands for trimethylbenzene.

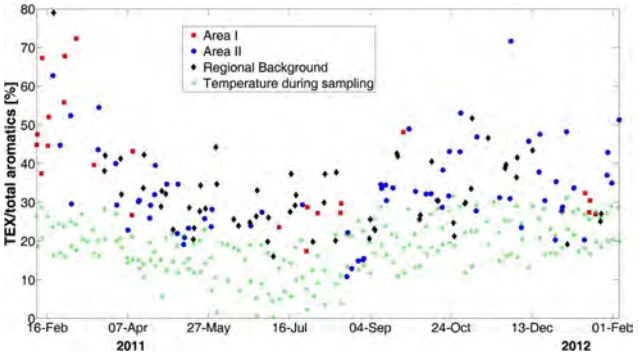

Figure 8. Temporal variation in the concentration ratios of the sum of toluene, ethylbenzene and xylenes (TEX) to total aromatics from air masses arriving at Welgegund after passing over the three source regions.

seasonal pattern with the maximum values in summer and minimum in winter. This is similar to the observation made by Rappenglück and Fabian (1999) who reported that the evaporation of solvents makes a greater contribution to atmospheric VOCs during summer. The average temperatures measured during the sampling periods, as presented in Fig. 8, also indicate a similar pattern than the TEX concentration ratios. This further supports the hypothesis that TEX concentrations are strongly influence by the effect of temperature on evaporation rates. Although not tested in this paper, it is, however, also possible that the differences in aromatic hydrocarbon lifetimes between the different season could result in the aforementioned temporal pattern. It is therefore clear that aromatic hydrocarbons originating from solvents make a contribution to aromatic hydrocarbons in air masses that had passed over all three source regions, including the regional background. However, the magnitude of this contribution was not determined from these data.

3.6 O_3 formation potential of aromatic hydrocarbons

While the evaluation of aromatic hydrocarbons on a concentration (ppb) basis is of interest in order to assess human exposure to toxic compounds such as benzene, it is also of interest to examine the relative importance of these pollutants pertaining to their role in the production of O_3 (Carter, 1994). Beukes et al. (2014), Laakso et al. (2013) and Venter et al. (2012) indicated that O_3 is currently the most problematic pollutant in South Africa. Tropospheric O_3 impacts air quality, food security (Zunckel et al., 2006) and regional climate change (Fry et al., 2013). Therefore, the relative contributions of aromatic hydrocarbons to photochemical O_3 formation in air masses that had passed over the three source regions were examined. Several reactivity scales can be used to estimate O_3 formation for specific hydrocarbons. One method that determines the ability of aromatic hydrocarbons to produce O_3 entails calculating the product of the average concentration and the maximum incremental reactivity coefficient (MIR) of each compound, i.e. O_3 formation potential = VOC × MIR (Carter, 1994). The MIR scale has been used to assess O_3 formation potential for aromatic hydrocarbon in numerous previous studies (Hoque et al., 2008; Na et al., 2005; Grosjean et al., 1998).

The ranking of the aromatic hydrocarbons according to air mass origin for O_3 formation potential is provided in Table 2. As indicated (Table 2), the highest contributions of aromatic hydrocarbon concentrations to O_3 formation potential were observed for plumes passing over area I. The O_3 formation potential for air masses that had passed over area II and the regional background was of the same order of magnitude. Based on the O_3 formation potential values, xylenes ((*m*,*p*)-xylene plus *o*-xylene) are the dominant contributor to O_3 formation for air masses that have passed over area I, with 1,2,4-trimethylbenzene the second largest contributor. The O_3 formation potential of benzene was the lowest, even though it is considered to be the most hazardous compound of the atmospheric aromatic hydrocarbons. As previously stated, the use

of solvents (e.g. in paint) is thought to be a major non-traffic source of aromatic hydrocarbons, with toluene, ethylbenzene and *o*,*m*,*p*-xylene (TEX) making up the largest portion of solvents (Brocco et al., 1997). It was also shown that the ratio of TEX / total aromatic hydrocarbons followed a typical seasonal pattern, demonstrating the contribution from solvents (Fig. 8) in all three source regions. From Table 2 it is evident that TEX contributes significantly to O_3 formation relative to the other compounds considered in this paper. The contribution of the evaporation of solvents to O_3 formation as a fraction of the overall aromatic hydrocarbons O_3 formation potential therefore seems to be significant.

4 Conclusions

Benzene is the only VOC listed as a criteria pollutant in the NAAQS, and had an annual average (median) of 0.29 (0.13) ppb, which was well below the South African standard limit of 1.6 ppb. Toluene was the most abundant aromatic hydrocarbon, with an annual average (median) concentration of 0.89 (0.63) ppb. Lourens et al. (2011) also previously reported ambient toluene concentrations in the interior of South Africa as being significantly higher than that of benzene. It is therefore recommended that a national air quality threshold for toluene be considered in future. Since the concentrations of ethylbenzene, (*m*,*p*)-xylene, *o*-xylene and styrene were also of the same order as that of toluene, these compounds could also be considered for inclusion in such legislation.

No statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time, or during Tuesdays and Saturdays, were found. This indicates the lack of local sources. However, it should be regarded as an important future perspective to set sampling schedules that would eliminate all possible time-bound biases. This could be achieved with continuous online analysis, which would also enable proper assessment of diurnal cycles and specific case studies. Additionally, no distinct seasonal patterns were observed for any of the compounds measured, which could be attributed to the origin of the air masses sampled. Aromatic hydrocarbon concentrations were in general significantly higher in air masses that had passed over anthropogenically influenced source regions.

Inter-compound correlations indicated that all the aromatic hydrocarbons, except benzene, originated from the same source(s) in area I, where benzene most likely originated from incomplete combustion. For area II and the regional background, benzene and toluene were found to originate from the same source(s), while all the other aromatic hydrocarbons were emitted by a different source(s). Inter-compound ratios indicated the influence of anthropogenic activities, especially in area I, and also the closer proximity of the Johannesburg–Pretoria megacity in area I to the Welgegund monitoring station, i.e. less aged plumes. The concentration ratios of TEX / total aromatics for air masses that had passed over the three sources regions indicated a seasonal dependence, i.e. higher temperatures resulting in higher evaporation rates that contribute to higher ambient concentrations.

The highest contributions of aromatic hydrocarbon concentrations to O_3 formation potential were observed for plumes passing over area I. Xylenes ((*m*,*p*)-xylene plus *o*-xylene) were the dominant contributor to O_3 formation, with 1,2,4-trimethylbenzene being the second largest contributor. The O_3 formation potential of benzene was the lowest.

Acknowledgements. The authors would like to express their appreciation for financial support from the Finnish Academy (project no. 132640), the University of Helsinki, the Finnish Meteorological Institute and the North-West University. The authors also thank Diederik and Jackie Hattingh and their family who are the owners of the commercial farm on which the Welgegund measurement station is situated.

Edited by: J. Rinne

References

Air Resources Laboratory, 2009. Gridded meteorological data archives, available at: http://www.arl.noaa.gov/archives.php (last access: 12 January 2012).

Arey, J., Obermeyer, G., Aschmann, S. M., Chattopadhyay, S., Cusick, R. D., and Atkinson, R.: Dicarbonyl products of the OH radical-initiated reaction of a series of aromatics hydrocarbons, Environ. Sci. Technol., 43, 683–689, 2009.

Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., 34, 2063–2101, 2000.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, Journal of Physical and Chemical Reference Data, Monograph, 2, 1–216, 1994.

Bates, M. S., Gonzalez-Flesca N., Sokhi, R. and Cocheo, V.: Atmospheric volatile organic compound monitoring. Ozone induced artefact formation, Environ. Monit. Assess., 65, 89–97, doi:10.1023/A:1006420412523, 2000.

Beukes, J. P., Vakkari, V., van Zyl, P. G., Venter, A. D., Josipovic, M., Jaars, K., Tiitta, P., Laakso, H., Kulmala, M., Worsnop, D., Pienaar, J. J., Järvinen, E., Chellapermal, R., Ignatius, K., Maalick, Z., Cesnulyte, V., Ripamonti, G., Laban, T. L., Skrabalova, L., du Toit, M., Virkkula, A., Siebert S. J., Laakso, L.: Source region plume characterisation of the interior of South Africa, as measured at Welgegund, as measured at Welgegund, in preparation, 2014.

Beukes, J. P., Van Zyl, P. G., and Ras, M.: Treatment of Cr(VI)-containing wastes in the South African ferrochrome industry – review of currently applied methods, S. African Inst. Min. M., 112, 413–418, 2012.

Beukes, J. P., Dawson, N. F., and Van Zyl, P. G.: Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry, S. Afr. Inst. Min. M., 110, 743–750, 2010.

Birdsall, A. W., Andreoni, J. F., and Elrod, M. J.: Investigation of the role of bicyclic peroxy radicals in the oxidation mechanism of toluene, J. Phys. Chem., 114, 10655–10663, 2010.

Bonn, B., Kulmala, M., Riipinen, I., Sihto, S.-L., and Ruuskanen, T.: How biogenic terpenes govern the correlation between sulphuric acid concentrations and new particle formation, J. Geophys. Res., 113, D12209, doi:10.1029/2007JD009327, 2008.

Brasseur, G, Orlando, J. and Tyndall, G.: Atmospheric chemistry and global change. New York, Oxford University Press, 1007 pp., 1999.

Brocco, D., Fratarcangelli, R., Lepore, L., Petricca, M., and Ventrone, I.: Determination of aromatic hydrocarbons in urban air of Rome, Atmos. Environ., 31, 557–566, 1997.

Burger, J. W.: Identification and comparison of the volatile organic compound concentrations in ambient air in the Cape Town metropolis and the Vaal Triangle, PhD-thesis, North-West University, Potchefstroom, Republic of South Africa, 2006.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: The mechanism of atmospheric oxidation of aromatics hydrocarbons, Oxford University Press, New York, USA, 566 pp., 2002.

Carter, W. P. L.: Development of ozone reactivity scales for volatile organic compounds, J Air Waste Manage, 44, 881-899, 1994

Chiloane, H. J.: Volatile organic compounds (VOCs) analysis from Cape Town haze ll study, MSc-thesis, University of Witwatersrand, Johannesburg, Republic of South Africa, 80 pp., 2005.

Coeur-Tourneur, C., Henry, F., Janquin, M.-A., and Brutier, L.: Gas-phase reaction of hydroxyl radicals with m-, o- and p-cresol, Int. J. Chem. Kin., 38, 553–562, 2006.

Crutzen, P. J. and Andreae, M. O.: Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, Science, 250, 1669-1678, 1990.

Crutzen, P. J., Heidt, L. E., Krasneck, J. P., Pollock, W. H., Seiler,W.: Biomass burning as a source of atmospheric trace gases: CO, H_2, N_2O, NO, CH_3Cl and COS, Nature, 282, 253–256, 1979.

Derwent, R. G.: Volatile organic compounds in atmosphere, Iss. Environ. Sci. Technol., 4, 1–15, 1995.

Derwent, R. G., Davies, T. J., Delaney, M., Dollard, G. J., Field, R. A., Dumitrean, P., Nason, P. D., Jones, B. M. R., and Pepler, S. A.: Analysis and interpretation of the continuous hourly monitoring data for 26 C_2-C_8 hydrocarbons at 12 United Kingdom sites during 1996, Atmos. Environ., 34, 297–312, 2000.

Dewulf, J. and Van Langenhove, H.: Analytical techniques for determination of measurement data of 7 chlorinated C1 and C2 hydrocarbons and 6 monocyclic aromatic hydrocarbons in remote air masses, Atmos. Environ., 31, 3291–3307, 1997.

Draxler, R. R. and Hess, G. D: Description of the HYSPLIT_4 modeling system. NOAA Tech. Memo. ERL ARL-224, NOAA Air Resources Laboratory, Silver Spring, Marlyland, USA, 24 pp., 1997.

Duce, R. A., Mohnen, V. A., Zimmerman, P. R., Grosjean, D., Cautreels, W. J., Chatfield, R., Jaenicke, R., Ogren, J. A., Pellizzari, E. D., and Wallace, G. T.: Organic material in global troposphere, Rev. Geophys. Space Phys., 21, 921–952, 1983.

Edgerton, S. A., Holdren, M. W., and Smith, D. L.: Inter-urban comparison of ambient volatile organic compound concentrations in US cities, J. Air Poll. Contr. Assoc., 39, 729–732, 1989.

Finlayson-Pitts, B. and Pitts Jr., J. N.: Atmospheric Chemistry: Fundamentals and Experimental Techniques, Wiley, New York, Chichester, Brisbane, 1–1098, 1986.

Fry, M. M., Schwarzkopf, M. D., Adelman, Z., and West, J. J.: Air quality and radiative forcing impacts of anthropogenic volatile organic compound emissions from ten world regions, Atmos. Chem. Phys., 13, 21125–21157, doi:10.5194/acpd-13-21125-2013, 2013.

Gelencser, A., Siszler, K., Hlavay, J.: Toluene-benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources, Environ. Sci. Technol., 31, 2869–2872, 1997.

Government Gazette Republic of South Africa, 14 October 2005 No. 28132, available at: http://www.info.gov.za/view/DownloadFileAction?id=73046 (last access: 16 October 13), 2007.

Government Gazette Republic of South Africa, 4 May 2007 No. 29864, available at: http://www.info.gov.za/view/DownloadFileAction?id=73046 (last access: 16 October 13), 2007.

Government Gazette Republic of South Africa, 2009. 24 December 2009, No. 32816, available at: http://faolex.fao.org/docs/pdf/saf122986.pdf (last access: 16 October 2013), 2009.

Greenberg, J. P., Guenther, A., Harley, P., Otter, L., Veenendaal, E. M. Hewitt, C. N. James, A. E., and Owen, S. M.: Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana, J. Geophys. Res., 108, 8466, doi:10.1029/2002JD002317, 2003.

Grosjean, E., Rasmussen, R. A., and Grosjean, D.: Ambient levels of gas phase pollution in Porto Alegre, Brazil. Atmos. Environ., 32, 3371–3379, 1998.

Guenther, A., Otter, L. B., Zimmerman, P., Greenberg, J., Scholes, R., Scholes, M. C.: Biogenic hydrocarbon emissions from southern Africa savannas, J. Geophys. Res., 101, 25859–25865, 1996.

Guicherit, R.: Traffic as a source of volatile hydrocarbons in ambient air, Science Total Environment, 205, 201–213, 1997.

Harley, P., Otter, L. B., Guenther, A., Greenberg, J.: Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna, J. Geophys. Res., 108, 8468, doi:10.1029/2002JD002592, 2003.

Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., Shao, M., and Wildt, J.: Toluene emissions from plants, Geophys. Res. Lett., 26, 1283–1286, 1999.

Hellén, H., Kuronen, P., and Hakola, H.: Heated stainless steel tube for ozone removal in the ambient air measurements of mono- and sesquiterpenes, Atmos. Environ., 57, 35–40, 2012.

Hellén, H., Hakola, H., Laurila, T., Hiltunen, V., and Koskentalo, T.: Aromatic hydrocarbon and methyl tert-butyl ether measurements in ambient air of Helsinki (Finland) using diffusive samplers, Sci. Total Environ., 298, 55–64, 2002.

Hewitt, C. N.: Reactive hydrocarbons in the atmosphere, San Diego, CA, Academic Press, 322 pp., 1999.

Hirsikko, A., Vakkari, V., Tiitta, P. Manninen, H. E., Gagné, S., Laakso, H., Kulmala, M., Mirme, A., Mirme, S., Mabaso, D., Beukes, J. P., and Laakso, L..: Characterisation of sub-micron particle number concentrations and formation events in the western Bushveld Igeneous Complex, South Africa, Atmos. Chem. Phys., 12, 3951–3967, doi:10.5194/acp-12-3951-2012, 2012.

Hoque, R. R., Khillare, P. S., Agarwal, T., Shridhar, V., and Balachandran, S.: Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India, Sci. Total Environ., 392, 30–40, 2008.

Johnson, D., Jenkin, M., Wirtz, K., and Martin-Reviejo, M.: Simulating the formation of secondary organic aerosol from the photooxidation of toluene, Environ. Chem., 1, 150–165, 2004.

Johnson, D., Jenkin, M. E., Wirtz, K., and Martin-Reviejo, M.: Simulating the formation of secondary organic aerosol from the photooxidation of aromatics hydrocarbons, Environ. Chem., 2, 35–48, 2005.

Jose, M. B., Rose, D., and Josep, C.: Applying receptor models to analyze urban/suburban VOCs air quality in Martorell (Spain), Environ. Sci. Technol., 32, 405–412, 1998.

Karl, T., Apel, E., Hodzic, A., Riemer, D. D., Blake, D. R., Wiedinmyer, C.: Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, Atmos. Chem. Phys., 9, 271–285, doi:10.5194/acp-9-271-2009, 2009.

Kostiainen, R.: Volatile organic compounds in the indoor air of normal and sick houses, Atmos. Environ., 29, 693–702, 1995.

Kourtidis, K. A., Ziomas, I. C., Rappenglueck, B., Proyou, A., and Balis, D.: Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens, Atmos. Environ., 33, 3831–3842, 1999.

Kuran, P. and Sojak, L.: Environmental analysis of volatile organic compounds in water and sediment by gas chromatography, J. Chrom. A, 733, 119–141, 1996.

Laakso, L., Koponen, I. K., Mönkkönen, P., Kulmala, M., Kerminen, V.-M., Wehner, B., Wiedensohler, A., Wu, Z., Hu, M.: Aerosol particles in the developing world; a comparison between New Delhi in India and Beijing in China,Water Air Soil Poll., 1–16, 5–20, doi:10.1007/s11270-005-9018-5, 2006.

Laakso, L., Laakso, H., Aalto, P. P., Keronen, P., Petäjä, T., Nieminen, T., Pohja, T., Siivola, E., Kulmala, M., Kgabi, N., Phalatse, D., Molefe, M., Mabaso, D., Pienaar, and J. J., and Kerminen, V.-M.: Basic characteristics of atmospheric particles, trace gases and meteorology in a relatively clean Southern African Savannah environment, Atmos. Chem. Phys., 8, 4823–4839, doi:10.5194/acp-8-4823-2008, 2008.

Laakso, L., Merikanto, J., Vakkari, V., Laakso, H., Kulmala, M., Molefe, M., Kgabi, N., Mabaso, D., Carslaw, K. S., Spracklen, D. V., Lee, L. A., Reddington, C. L., and Kerminen, V.-M.: Boundary layer nucleation as a source of new CCN in savannah environment, Atmos.Chem. Phys., 13, 1957–1972, doi:10.5194/acp-13-1957-2013, 2013.

Lan, T. T. N. and Minh, P. A.: BTEX pollution caused by motorcycles in the megacity of HoChiMinh, J. Environ, Sci., 25(2), 348-356, 2013.

Lee, S. C., Chiu, M. Y, Ho, K. F., Zou, S. C., and Wang, X.: Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong, Chemosphere, 48, 375–382, 2002.

Liu, C., Xu, Z., Du, Y., and Guo, H.: Analyses of volatile organic compounds concentrations and variation trends in the air of Changchun, the northeast of China, Atmos. Environ., 34, 4459–4466, 2000.

Liu, J., Mu, Y., Zhang, Y., Zhang, Z., Wang, X., and Liu, Y. : Atmospheric levels of BTEX compounds during the 2008 Olympic Games in the urban area of Beijing, Sci. Tot. Environ., 408, 109–116, 2009.

Lobert, J. M., Scharffe, D. H., Hao, W. M., and Crutzen, P. J.: Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases, Nature, 346, 552–554, 1990.

Lourens, A. S, Beukes, J. P, Van Zyl, P. G., Fourie, G. D., Burger, J. W, Pienaar, J. J., Read, C. E., and Jordaan, J. H.: Spatial and temporal assessment of gaseous pollutants in the Highveld of South Africa, S. Afr. J. Sci., 107, 8 pp., doi:10.4102/sajs.v107i1/2.269, 2011.

Lourens, A. S. M., Butler, T. M., Beukes, J. P., Van Zyl, P. G., Beirle, S., Wagner, T., Heue, K-P., Pienaar, J. J., Fourie, G. D., and Lawrence, M. G.: Re-evaluating the NO_2 hotspot over the South African Highveld, S. Afr. J. Sci., 108, 6 pp., doi:10.4102/sajs.v108i11/12.1146.1146, 2012.

MATLAB. Version 7.10.0 (R2010a). 24 Prime Park Way, Natick, MA, 01760-1500, USA, The MathWorks Inc., 2010.

Monod, A., Sive, B. C., Avino, P., Chen, T., Blake, D. R., Rowland, F. S.: Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene, Atmos. Environ., 35, 135–149, 2001.

Mukund, R., Kelly, T. J., and Spicer, C. W.: Source attribution of ambient air toxics and other VOCs in Colombus Ohio, Atmos. Environ., 30, 3457–3470, 1996.

Na, K., Moon, K.-C., and Kim, Y. P.: Source contribution to aromatic VOC concentration and ozone formation potential in the atmosphere of Seoul, Atmos. Environ., 39, 5517–5524, 2005.

Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H., and Mocanu, R.: FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmos. Environ., 36, 3685–3697, 2002.

Otter, L. B., Guenther, A., and Greenberg, J.: Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands, Atmos. Environ., 36, 4265–4275, 2002a.

Otter, L. B., Scholes, R. J., Dowty, P., Privette, J., Caylor, K., Ringrose, S., Mukelabai, M., Frost, P., Hanan, N., Totolo, O., and Veenendaal, E. M.: The Southern African Regional Science Initiative (SAFARI 2000): Wet season campaigns, S. Afr. J. Sci., 98, 131–137, 2002b.

Parra, M. A., Elustondo, D., and Garrigo, J.: Spatial and temporal trends of volatile organic compounds (VOC) in a rural area of northern Spain, Sci. Total Environ., 370, 157–167, 2006.

Penkett, S. A., Blake, N. J., Lightman, P., Marsh, A. R. W., and Anzwyl, P.: The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: possible evidence for extensive reaction of hydrocarbons with the nitrate radical, J. Geophys. Res., 98, 2865–2885, 1993.

Petäjä, T., Vakkari, V., Pohja, T., Nieminen, T., Laakso, H., Aalto, P. P., Keronen, P., Siivola, E., Kerminen, V.-M., Kulmala, M., and Laakso, L.: Transportable aerosol characterization trailer with trace gas chemistry: design, instruments and verification, Aerosol Air Qual. Res., 13, 421–435, 2013.

Simon, V., Baer, M., Torres, L., Olivier, S., Meybeck, M., and Della Massa, J. P.: The impact of reduction in the benzene limit value in gasoline on airborne benzene, toluene and xylenes levels, Sci. Total Environ., 334–335, 177–183, 2004.

Stevenson, K. J., Stacey, B., and Willis, P. G.: Air Quality at Heathrow Airport, Annual Report for 1996, AEA Technology, London, UK, 1997.

Rappenglück, B. and Fabian, P.: Non-methane hydrocarbons (NMHC) in the Greater Munich Area/Germany, Atmos. Environ., 33, 3843–3857, 1999.

Srivastava, A., Sengupta, B., and Dutta, S. A.: Source apportionment of ambient VOCs in Delhi city, Sci. Total Environ., 343, 207–220, 2005.

Swap, R. J., Annegarn, H. J., and Otter, L. B.: Southern African Regional Science Initiative (SAFARI 2000): Summary of science plan, S. Afr. J. Sci., 98, 119–124, 2002a.

Swap, R. J., Annegarn, H.J., Suttles, J. T., Haywood, J., Helmlinger, M. C., Hely, C., Hobbs, P. V., Holben, B. N., Ji, J., King, M. D., Landmann, T., Maenhaut, W., Otter, L., Pak, B., Piketh, S. J., Platnick, S., Privette, J., Roy, D., Thompson, A. M., Ward, D., Yokelson, R.: The Southern African Regional Science Initiative (SAFARI 2000): Overview of the dry season field campaign, S. Afr. J. Sci., 98, 125–130, 2002b.

Sweet, C.W. and Vermette, S. J.: Toxic volatile organic compounds in urban air in Illinois, Environ. Sci. Technol., 26, 165–173, doi:10.1021/es00025a020, 1992.

Takekawa, H., Minoura, H., and Yamazaki, S.: Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37, 3413–3424, 2003.

Tiitta, P., Vakkari, V., Josipovic, M., Croteau, P., Beukes, J. P., van Zyl, P. G., Venter, A. D., Jaars, K., Pienaar, J. J., Ng, N. L., Canagaratna, M. R., Jayne, J. T., Kerminen, V.-M., Kulmala, M., Laaksonen, A., Worsnop, D. R., and Laakso, L.: Chemical composition, main sources and temporal variability of PM1 aerosols in southern African grassland, Atmos. Chem. Phys., 14, 1909–1927, doi:10.5194/acp-14-1909-2014, 2014.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over Boreal forests, Science, 312, 261–263, 2006.

Tyson, P. D., Garstang, M., and Swap, R.: Large-scale recirculation of Air over Southern Africa, J. Appl. Meteorol., 35, 2218–2236, 1996.

Vakkari, V., Laakso, H., Kulmala, M., Laaksonen, A., Mabaso, D., Molefe, M., Kgabi, N., and Laakso, L.: New particle formation events in semi-clean South African savannah, Atmos. Chem. Phys., 11, 3333–3346, doi:10.5194/acp-11-3333-2011, 2011.

van der Walt, H.J.: The impact of hydrocarbons emissions on regional air quality in a South African metropolitan area, PhD-thesis, North-West University, Potchefstroom, Republic of South Africa, 2008.

Venter, A. D., Vakkari, V., Beukes, J. P., Van Zyl, P. G., Laakso, H., Mabaso, D., Tiitta, P., Josipovic, M., Kulmala, M., Pienaar, J. J., and Laakso, L.: An air quality assessment in the industrialised western Bushveld Igneous Complex, South Africa, S. Afr. J. Sci., 108, 1059, doi:10.4102/sajs.v108i9/10.1059, 2012.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., and Washida, N.: OH-initiated oxidation of benzene Part 1. Phenol formation under atmospheric conditions, Phys. Chem. Chem. Phys., 4, 1598–1610, 2002.

Welgegund, available at: http://www.welgegund.org/ (last access: 3 January 2012), 2012.

WHO: Air quality guidelines for Europe, 2nd edition. Copenhagen: WHO Regional Publications; European Series, No. 91, 2000.

Zunckel, M., Koosailee, A., Yarwood, G., Maure, G., Venjonoka, K., Van Tienhoven, A. M. and Otter, L.: Modelled surface ozone over southern Africa during the cross border air pollution impact assessment project, Environ. Modell. Softw., 21, 911–924, 2006.

CHAPTER 5

MEASUREMENTS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS AT A GRAZED SAVANNAH-GRASSLAND-AGRICULTURE LANDSCAPE IN SOUTH AFRICA

5.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT

K. Jaars[1], P. G. van Zyl[1], J. P. Beukes[1], H. Hellén[2], V. Vakkari[2], M. Josipovic[1], A. D. Venter[1], M. Räsänen[3], L. Knoetze[1], D. P. Cilliers[1], S. J. Siebert[1], M. Kulmala[3], J. Rinne[4], A. Guenther[5], L. Laakso[1,2] and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa

[2]Finnish Meteorological Institute, PL 503, 00101 Helsinki, Finland

[3]Department of Physics, University of Helsinki, Finland

[4]Department of Physical Geography and Ecosystem Science Lund University Sölvegatan 12

S-223 62 Lund, Sweden

[5]Department of Earth System Science, University of California, Irvine, USA

Contributions of the various co-authors were as follows. The bulk of the work was done by the author, **K Jaars**, i.e. sample analysis, data processing, research and writing of the scientific paper; PG van Zyl and JP Beukes were the promoters of this study, who assisted in interpretation of data, writing the article and also made conceptual contributions. The author, with assistance from AD Venter and M Josipovic measured the BVOCs from February 2011 to February 2011 and December 2013 to February 2015, while H Hellén and H Hakola assisted with specialised analyses, preparation and expert opinions of the adsorbent tubes at the FMI with a TD-GC-MS. L Knoetze, DP Cilliers and SJ Siebert conducted the vegetation survey. M Räsänen assisted with CO_2 flux analysis. V Vakkari and L Laakso helped create the infrastructure at Welgegund and made conceptual contributions. M Kulmala, J Rinne and A Guenther made conceptual contributions.

All the co-authors on the article 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 is presented as submitted to *Atmospheric Chemistry and Physics*, a European Geosciences Union journal. The similarity report generated by the journal when article was submitted is also included. The journal detail can be found at http://www.atmospheric-chemistry-and-physics.net (Date of access: 11 June 2016). The article was ***submitted***: 3 June 2016.

Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa

K. Jaars[1], P. G. van Zyl[1], J. P. Beukes[1], H. Hellén[2], V. Vakkari[2], M. Josipovic[1], A. D. Venter[1], M. Räsänen[3], L. Knoetze[1], D. P. Cilliers[1], S. J. Siebert[1], M. Kulmala[3], J. Rinne[4], A. Guenther[5], L. Laakso[1,2] and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa

[2]Finnish Meteorological Institute, PL 503, 00101 Helsinki, Finland

[3]Department of Physics, University of Helsinki, Finland

[4]Department of Physical Geography and Ecosystem Science Lund University Sölvegatan 12

S-223 62 Lund, Sweden

[5]Department of Earth System Science, University of California, Irvine, USA

Correspondence to: P.G. van Zyl (pieter.vanzyl@nwu.ac.za)

Abstract

Biogenic volatile organic compounds (BVOCs) are an important role player in the chemistry of the troposphere, especially in the formation of tropospheric ozone (O_3) and secondary organic aerosols (SAO). Ecosystems produce and emit a large number of BVOCs, and as a result it is estimated on a global scale that approximately 90 % of annual VOC emissions are BVOCs. In this study, measurements of BVOCs were conducted at the Welgegund measurement station (South Africa), which is considered to be a regionally representative background site situated in savannah grassland. Very few BVOC measurements exist for grassland savannah and results presented in this study are the most extensive for this type of landscape. Samples were collected twice a week for two hours during daytime and two hours during night-time through two long-term sampling campaigns from February 2011 to February 2012 and from December 2013 to February 2015. Individual BVOCs were identified and quantified using a thermal desorption instrument, connected to a gas chromatograph and a mass selective detector. The annual median concentrations of isoprene, 2-methyl-3-butene-2-ol (MBO), monoterpenes and sesquiterpenes (SQT) during the first campaign were 14, 7, 120 and 8 pptv and 14, 4, 83 and 4 pptv during the second campaign. The sum of the concentration of the monoterpenes were at

least an order of magnitude higher than the concentrations of other BVOC species during both sampling campaigns, with α-pinene being the most abundant species. The highest BVOC concentrations were observed during the wet season and elevated soil moisture was associated with increased BVOC concentrations. However, comparisons with measurements conducted at other landscapes in southern Africa and the rest of the world that have more woody vegetation indicated that BVOC concentrations were, in general, significantly lower. Furthermore, BVOC concentrations were an order of magnitude lower compared to total aromatic concentrations measured at Welgegund. An analysis of concentrations by wind direction indicated that isoprene concentrations were higher from the western direction, while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. Statistical analysis indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpenes and SQT concentrations, while temperature had the greatest influence on isoprene levels. The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured at Welgegund for all of the months during both sampling campaigns.

1 Introduction

Ecosystems produce and emit a large number of biogenic volatile organic compounds (BVOCs) that are involved in plant growth and reproduction, as well as acting as defensive compounds, e.g. enhancing tolerance to heat and oxidative stress (Sharkey and Yeh, 2001;Loreto and Schnitzler, 2010), preventing the colonisation of pathogens after wounding, and deterring insects or recruiting natural enemies of herbivores (Holopainen and Gershenzon, 2010). The BVOC production rate in an ecosystem depends on several physical (e.g. temperature, precipitation, moisture, solar radiation and CO_2 concentration) and biological parameters (e.g. plant species and the associated emission capacity, phenology, biotic and abiotic stresses, attraction of pollinators) (Blande et al., 2014;Fuentes et al., 2000;Kesselmeier and Staudt, 1999;Sharkey and Yeh, 2001), with typically 0.2 to 10 % of the carbon uptake in photosynthesis being converted to BVOCs (Kesselmeier et al., 2002). It is estimated that, on a global scale, approximately 90 % of annual VOC emissions are by vegetation (~1000 Tg C $year^{-1}$) (Guenther et al., 2012).

BVOCs can contribute significantly to the carbon balance in certain ecosystems (Kesselmeier et al., 2002;Malhi, 2002). BVOC concentrations in ambient air depend on several factors, which include emission rates from vegetation, atmospheric transport and mixing, and the chemical composition and oxidative state of the atmosphere, which determines the sink of these species. BVOCs are important in

the formation of tropospheric ozone (O_3) and secondary organic aerosol (SOA). BVOCs in the troposphere react with the major oxidants in the atmosphere, which include tropospheric O_3, hydroxyl radicals ($^{\bullet}OH$, referred to, from here on, as OH for simplicity) and nitrate radicals ($NO_3^{\bullet}$, referred to, from here on, as NO_3 for simplicity) (Atkinson and Arey, 2003a). These oxidants strongly affect the concentrations of atmospheric BVOCs (Lelieveld et al., 2008;Di Carlo et al., 2004). BVOCs are also crucial in the formation of the stabilised Criegee intermediate – a carbonyl oxide with two free-radical sites – or its derivative (Mauldin III et al., 2012;Welz et al., 2012), which also contributes to atmospheric oxidation. A complex range of reaction products are formed from atmospheric BVOCs, including less volatile oxygenated compounds that condense to form aerosol particles.

Various studies have indicated the link between BVOCs and the formation of SOA (Vakkari et al., 2015;Andreae and Crutzen, 1997;Ehn et al., 2014), while BVOCs also have an influence on the growth of newly formed aerosol particles (Kulmala et al., 2004;Tunved et al., 2006). However, there are many uncertainties associated with the exact chemical reactions and physical processes involved in SOA formation and aerosol particle growth, which largely depends on regional emissions and atmospheric processes (Kulmala et al., 2013;Ehn et al., 2014). Vakkari et al. (2015) indicated the importance of VOCs for new particle formation and growth in clean background air in South Africa. Therefore, it is essential to understand the sources, transport and transformations of these compounds for air quality management and climate change-related studies, as well as for the modelling of atmospheric chemistry at global, regional and local scales (Laothawornkitkul et al., 2009;Peñuelas and Staudt, 2010;Peñuelas and Llusià, 2003).

Long-term ambient BVOC measurements to establish seasonal cycles have been conducted extensively in several regions, which include boreal forest (Hakola et al., 2009;Hakola et al., 2000;Rinne et al., 2000;Rinne et al., 2005;Rantala et al., 2015;Räisänen et al., 2009;Eerdekens et al., 2009;Lappalainen et al., 2009), hemiboreal mixed forest (Noe et al., 2012), temperate (Spirig et al., 2005;Stroud et al., 2005;Fuentes et al., 2007;Mielke et al., 2010), Mediterranean (Davison et al., 2009;Harrison et al., 2001) and tropical (Rinne et al., 2002) ecosystems. Shorter campaigns have also been conducted in Western and Central Africa, which include several different studies in the framework of African Monsoon Multidisciplinary Analyses (AMMA) (Grant et al., 2008;Saxton et al., 2007) and EXPeriment for the REgional Sources and Sinks of Oxidants (EXPRESSO) (Serca et al., 2001)). Zunckel et al. (2007) and references therein indicated that limited research has been conducted on BVOC emissions in southern Africa, which consisted mainly of short campaigns measuring BVOC emission rates. Considering that BVOC emissions on a global scale are considered to be significantly higher (ca. 10 times) than the emission of anthropogenic VOCs, it is very important that longer-term BVOC measurements are conducted in southern Africa. Furthermore, a large part of the land cover in South

Africa consists of a grassland bioregion, as indicated in Fig. 1. Although it is considered that grasslands cover approximately one quarter of the Earth's land surface, relatively few studies have been conducted on BVOC emissions from grasslands, while there are no long-term BVOC studies reported for these landscapes (Bamberger et al., 2011;Ruuskanen et al., 2011;Wang et al., 2012). Therefore, the aim of this study was to quantify the ambient BVOC concentrations over different seasons at a regional background site in South Africa. In addition, it the aim was also to characterise their seasonal patterns, as well as to relate BVOC concentrations measured in southern Africa to levels in other regions in the world. According to the knowledge of the authors, this is the first record of ambient BVOC concentrations covering a full seasonal cycle in southern African and for a grassland bioregion anywhere in the world.

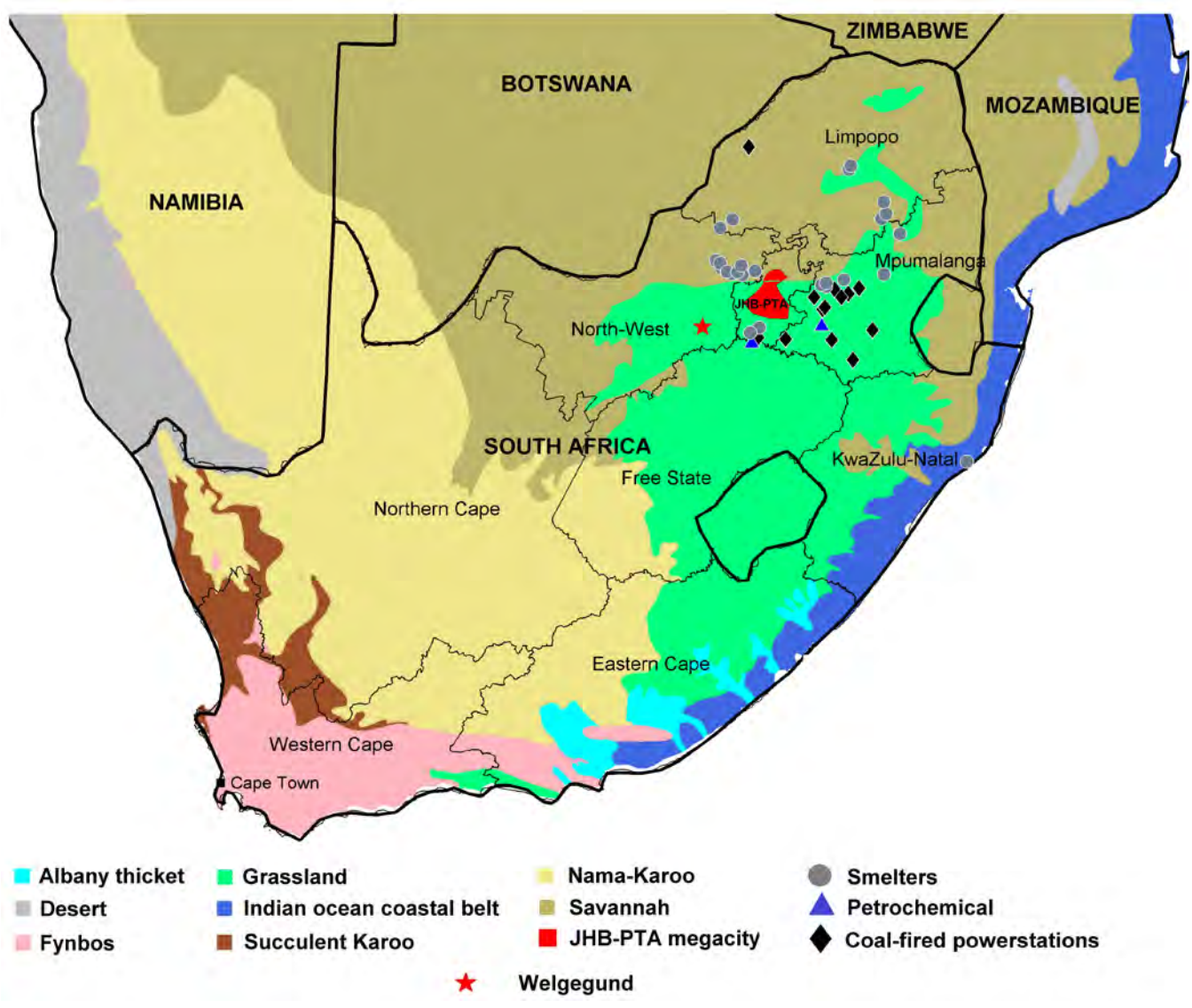

Fig. 1. Map of southern African indicating the location of the Welgegund measurement station within the context of bioregion and large point sources in the industrial hub of South Africa (Mucina and Rutherford, 2006).

2 Measurement location and methods

2.1 Site description

Measurements were conducted at the Welgegund measurement station (26.57°S, 26.94°E, 1480 m a.s.l.) (Welgegund measurement station, 2016), which is located on the property of a commercial maize and cattle farmer approximately 100 km west of Johannesburg, as indicated in Fig.1. Welgegund is a regional background station with no pollutant sources in close proximity. The distances to the nearest blacktop road and nearest town are approximately 10 and 30 km, respectively. Welgegund is, however, affected by the major anthropogenic source regions in the north-eastern interior of South Africa (as indicated by the major large point sources in Fig.1), which also include the Johannesburg-Pretoria conurbation. From Fig.1, it is also evident that the western sector contains no major point sources and can therefore be considered to be representative of a relatively clean regional background.

Welgegund is geographically located within the South African Highveld, which is characterised by two distinct seasonal periods, i.e. a dry season from May to September that predominantly coincides with winter (June to August), and a wet season during the warmer months from October to April. The dry period is characterised by low relative humidity, while the wet season is associated with higher relative humidity and frequent rains that predominantly occur in the form of thunderstorms. The mean annual precipitation is approximately 500 mm with approximately >80% of rain events occurring during the wet season. During the sampling period, the coldest temperature recorded in winter at Welgegund was -5.1 °C in June 2011, while the highest temperature recorded in summer was +35.6 °C in October 2011. The mean maximum temperature ranges between 16 and 32 ^{0}C, while the mean minimum temperature ranges between 0 and 15^{0}C. Winters are also characterised by frequent and severe frost days (26-37 per year) (Mucina and Rutherford, 2006).

2.2 Vegetation

The Welgegund measurement station is located in the Grassland Biome (Fig. 1), which covers 28% of South Africa's land surface (Mucina and Rutherford, 2006). This biome has been significantly transformed, primarily as a result of cultivation, plantation forestry, urbanisation and mining (Daemane et al., 2010) and references therein). It has also been severely degraded by erosion and agricultural development. The station is situated within Vaal-Vet Sandy Grassland with Andesite Mountain Bushveld of the Savannah Biome prominent on nearby ridges. At present, only 0.3 % of the Vaal-Vet Sandy Grassland is statutorily conserved, while the rest is mostly used for grazing and crop production. In Fig. 2, a land cover map within a 60 km radius from Welgegund is presented indicating the extent of cultivation in this region. The land cover survey was performed within a region that was estimated to

represent the BVOC footprint at Welgegund, which was calculated from typical atmospheric lifetimes (Table 1) of the species measured and the general wind speed(s) (Fig. 3) at Welgegund. The immediate area surrounding Welgegund is grazed by livestock, with the remaining area covered by crop fields (mostly maize and to a lesser degree sunflower). In the demarcated 60 km radius, a further three vegetation units of the Dry Highveld Grassland Bioregion (Grassland Biome) and another two of the Central Bushveld Bioregion (Savannah Biome) are also present. In addition, alluvial vegetation is found associated with major rivers and inland saline vegetation in scattered salt pans.

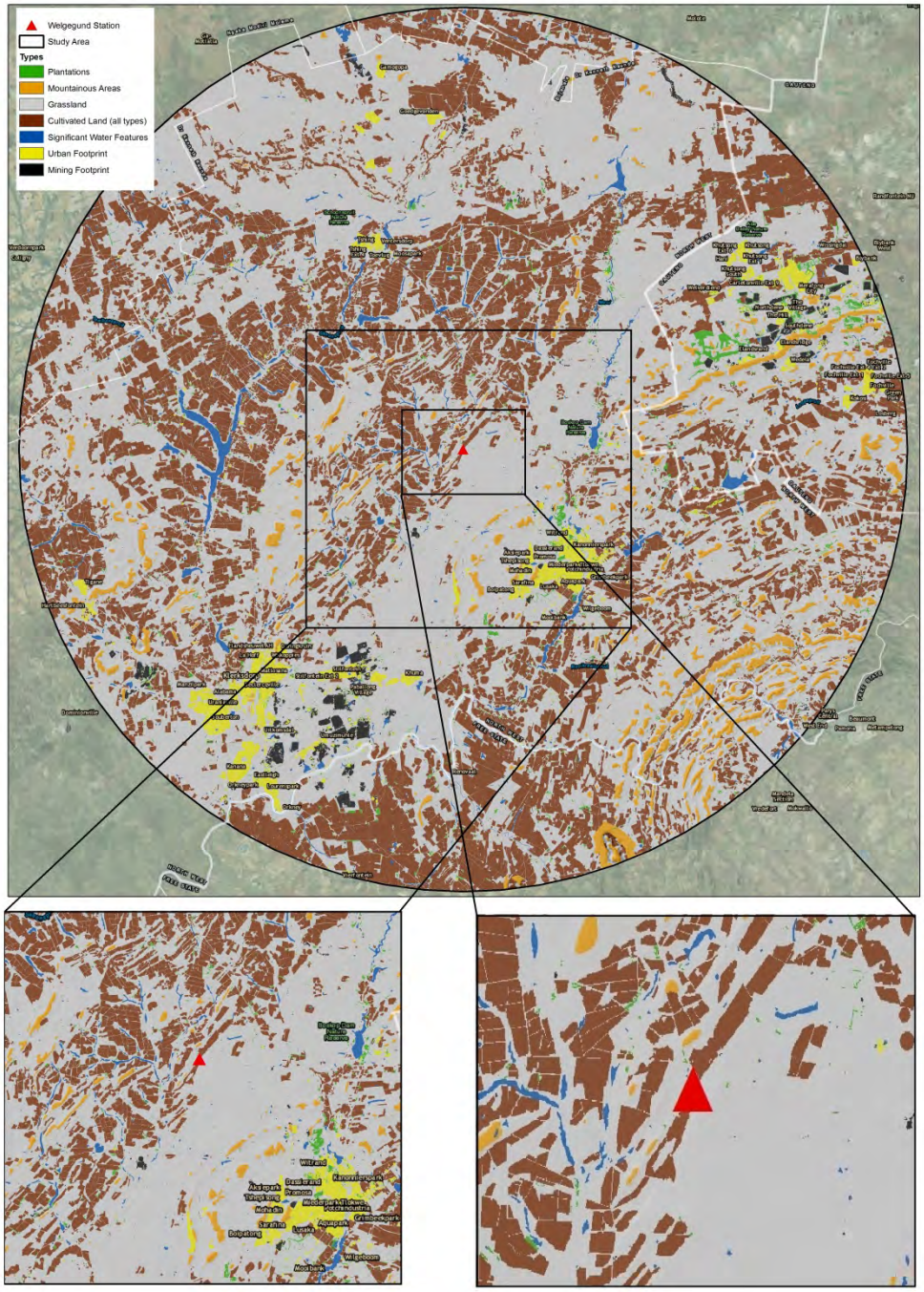

Fig. 2. General vegetation map for 60 km radius of Welgegund measurement station.

The study area comprises a highly variable landscape with scattered hills and sloping, slightly irregular, undulating plains, which are dissected by prominent rocky ridges. Soil in the catchment area is heterogeneous and rocky, varying from sandy to clayey depending on the underlying rock types, such as andesite, chert, dolomite, mudstone, quartzite, sandstone and shale.

Land use within the surrounding area is divided into six major land cover types, i.e. cultivated land, grasslands, mountainous areas, plantations, urban areas and water bodies, as indicated in Fig. 2. Mountainous areas, grassland and water bodies (riparian areas) comprised many different vegetation units. The other homogenous areas were anthropogenically altered and no longer representative of the surrounding natural vegetation. The study area is characterised by a grassland-woodland vegetation complex, dominated by various grass and woody species, and recognised by the presence of non-native species in altered environments.

The dominant woody species of the entire study area include the trees *Celtis africana*, *Searsia pyroides*, *Vachellia karroo* and *Ziziphus mucronata*, and the thorny shrub *Asparagus laricinus*. Tree diversity increases where there are patches of deep sand, characterised by *Gymnosporia buxifolia* and *Vachellia erioloba*, or in mountainous areas, where *Euclea undulata*, *Grewia flava* and *Senegallia caffra* become most prominent. Woody vegetation occurs sparsely in grasslands and when present is found on isolated ridges, including the small trees *Pavetta zeyheri*, *Vangueria infausta* and *Zanthoxylum capense*. In anthropogenically altered environments, native species decrease and introduced species dominate, such as *Eucalyptus camaldulensis*, *Pinus roxburghiana* and *Populus canescens* in plantations; *Gleditsia triacanthos*, *Pyracantha coccinea* and *Salix babylonica* along rivers and water bodies; and *Celtis sinensis*, *Melia azedarach* and *Robinia pseudoacacia* in the urban footprint.

The most dominant species of the grass sward in the entire study area include *Cynodon dactylon*, *Eragrostis chloromelas*, *Heteropogon contortus*, *Setaria sphacelata* and *Themeda triandra*. The dry, western grassland (Vaal-Vet Sandy Grassland specifically) is characterised by *Anthephora pubescens*, *Cymbopogon caesius*, *Digitaria argyrograpta*, *Elionurus muticus* and *Eragrostis lehmanniana*, and the moist Rand Highveld Grassland in the south-east by *Ctenium concinnum*, *Digitaria monodactyla*, *Monocymbium ceresiforme*, *Panicum natalense* and *Trachypogon spicatus*. The north-eastern parts of the study area on dolomite are dominated by *Brachiaria serrata*, *Digitaria tricholaenoides*, *Eragrostis racemosa* and *Loudetia simplex*.

2.3 Measurement methods

2.3.1 BVOC measurements and analysis

BVOC measurements were conducted for a period of more than two years through a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays. Several previous studies have demonstrated that the maximum emissions of isoprene and monoterpenes from vegetation occur around midday (Fuentes et al., 2000;Kuhn et al., 2002). Understandably, the chosen sampling schedule, i.e. same days each week and same hours of the day, was prone to some bias. As mentioned by Jaars et al. (2014), considering the distance of the sampling site from the nearest town and logistical limitations during the sampling campaigns, the sampling schedule applied was the most feasible option that enabled the collection of data for more than two years. VOCs were sampled at a height of 2 m above ground level, with a 1.75 m long inlet. The first 1.25 m of the inlet was a stainless steel tube (grade 304 or 316) and the second 0.5 m was Teflon. To prevent the degradation of BVOC by O_3, the stainless steel part of the inlet was heated to 120ºC using heating cables and thermostats (Thermonic), thereby removing ozone from the sample stream (Hellén et al., 2012a). At regular intervals, the efficiency of this O_3 removal was verified with an O_3 monitor.

VOCs were collected with stainless steel adsorbent tubes (6.3 mm ED x 90 mm, 5.5 mm ID) packed with Tenax-TA and Carbotrap-B by using a constant flow type automated programmable sampler. A detailed description of the sampling procedure is presented by Jaars et al. (2014). In short, the flow rate of the pump was set at between 100 and 110 ml min^{-1} throughout the campaigns and was calibrated each week. Prior to sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 minutes at 350 ºC at a flow of 40 ml min^{-1}.

Individual BVOCs were identified and quantified using a thermal desorption instrument (Perkin-Elmer TurboMatrixTM 650, Waltham, USA) connected to a gas chromatograph (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 μm) column and a mass selective detector (Perkin-Elmer® Clarus® 600T, Waltham, USA). Samples were analysed using the selected ion mode (SIM). A five-point calibration was performed by using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes that were flushed with helium at a flow of 100 ml min^{-1} for 10 min in order to remove methanol. BVOCs quantified for the two campaigns included isoprene with method detection limit (MDL) between 1.2 and 2.4 pptv and for 2-methyl-3-butene-2-ol (MBO) between 0.9 and 1.4 pptv. The monoterpenes (MT) (α-pinene, camphene, β-pinene, Δ^3-carene, p-cymene, limonene, 1,8-cineol, terpinolene, 4-acetyl-1-methylcyclohexene (AMCH), nopinone,

bornylacetate and 4-allylanisole) MDL was between 0.6 and 1.6 pptv. The sesquiterpenes (SQT) (longicyclene, iso-longifolene, aromadendrene, α-humulene and alloaromadendrene) MDL was ~0.6 pptv. Since the analytical system did not separate myrcene and β-pinene, β-pinene concentrations determined were the sum of these two species. VOC concentrations were field and lab blank corrected. When monthly median BVOC concentrations were calculated, sample concentrations below the method detection limit (MDL) were replaced with ½MDL.

2.3.2 Ancillary measurements

Ancillary measurements continuously performed at the Welgegund station were used to interpret the measured BVOC concentrations. General meteorological parameters, i.e. temperature (T), relative humidity (RH), wind speed and direction, and precipitation were measured. Soil temperature and moisture at different depths (5 and 20 cm) were measured with a PT-100 and Theta probe ML2x (Delta-T), respectively. Additional soil moisture information was obtained with a 100 cm PR2 soil moisture profile probe (Delta-T). Direct photosynthetic photon flux density (PPFD) between 400 and 700 nm was measured with a Kipp & Zonen pyranometer (CMP 3 pyranometer, ISO 9060:1990 Second Class).

Trace gas measurements were performed utilising a Thermo-Electron 43S sulphur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU nitrogen oxide (NO_x) analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 carbon monoxide (CO) analyser (Horiba, Kyoto, Japan). The net ecosystem exchange (NEE) of carbon dioxide (CO_2) was measured with the eddy covariance method with a Licor 7000 closed path infrared gas analyser (IRGA) and a three-dimensional Metek sonic anemometer at a height of 9 m, which is well above the average tree height of 2.5 m (Räsänen et al., 2016). A more detailed description of additional parameters monitored at Welgegund is given by Beukes et al. (2015).

2.3.3 Lifetime of BVOCs

In Table 1, the atmospheric lifetimes (τ) of BVOCs measured in this study calculated from OH- and O_3 reactivity are reported. BVOC lifetimes according to O_3 reactivity were calculated with Eq. (1):

$$\tau = \tau_{O3} = \frac{1}{k_{O3,[O_3]}} \quad (1)$$

where $[O_3]$ is the annual average O_3 concentration (ca. 36 ppbv) measured during the two campaigns at Welgegund and k_{O3} the reaction rate constant for the reaction between a specific BVOC and O_3. Since direct OH reactivity measurements were not available, the average concentration of OH radicals ([OH]) (ca. 0.04 pptv) reported by Ciccioli et al. (2014) was used in the calculations, using Eq. (2):

$$\tau = \tau_{OH} = \frac{1}{k_{OH,[OH]}} \quad (2)$$

where k_{OH} is the reaction rate constant for the reaction between a specific BVOC and OH.

Table 1. Lifetime (τ) of BVOCs calculated for the average concentration of OH radicals (ca. 0.04 pptv) as reported by Ciccioli et al. (2014) and the annual average O_3 (ca. 36 ppbv) concentration measured for the two campaigns at Welgegund.

		τ_{OH}	τ_{O3}
	Isoprene	2.8 hr	1 day
	MBO	10.3 hr	7.5 day
Monoterpenes	α-Pinene	5.3 hr	3.6 hr
	Camphene	5.3 hr	14.5 day
	β-Pinene	3.6 hr	20.9 hr
	Δ^3-Carene	3.2 hr	8.5 hr
	p-Cymene	18.8 hr	261.6 day
	1,8-Cineol	12.5 hr	-
	Limonene	1.7 hr	1.6 hr
	Terpinolene	12.6 hr	2.3 hr
	AMCH	2.9 hr	-
	Nopinene	1.4 day	-
	Bornylacetate	1.5 day	-
	4-Allylanisole	5.2 hr	1.1 day
Sesquiterpenes	Longicyclene	1.3 day	-
	iso-Longifolene	2.9 hr	1.1 day
	Aromadendrene	4.5 hr	1.1 day
	α-Humulene	1 hr	21.6 min

3 Results and discussion

3.1 Meteorological conditions during the measurement campaigns

Local meteorological influences on the measured BVOC concentrations are likely to be more significant than regional impacts of air masses due to the short lifetimes associated with atmospheric BVOCs (Table 1). Therefore, BVOC concentrations were only interpreted in terms of local meteorological patterns and no back trajectory analyses were employed. In Fig. 3, the monthly medians of the meteorological parameters – precipitation, T, RH, wind speed and -direction, and soil moisture depth (5 and 20 cm) – measured at Welgegund during each of the two sampling campaigns are presented. From Fig. 3a and b, the wet season (October to April) associated with warmer months and the dry season (May to September) associated with colder months as discussed in section 2.1 are evident. Rainfall in this region of South Africa is typically characterised by relatively large inter-annual variability

(Conradie et al., 2016). The monthly median temperatures for the periods during which samples were collected ranged between 8.8 and 13°C in winter and 19.7 and 24.9 °C in summer (Fig. 3b). During the warmer months, temperatures up to 30 °C and higher were reached frequently. During the wet season, the monthly median RH ranged between 30 (with the onset of the wet season) and 80% (at the end of the wet season), while the RH ranged between 20 and 50% during the dry season (Fig. 3c). The highest monthly median wind speeds occurred during the warmer months (Fig. 3d) when unstable meteorological conditions are prevalent in the interior of South Africa (Tyson et al., 1996). The seasonal variations of wind direction during the two sampling campaigns (Fig. 3e) indicated that the prevailing wind direction was from the northern to eastern sector, which agrees with the back trajectory analysis performed for the first sampling period at Welgegund by Jaars et al. (2014). Soil moisture measurements mimicked the seasonal precipitation pattern, i.e. higher soil moisture associated with the wet season (Fig. 3f and 3g). The soil moisture measurements conducted from January to August at a depth of 20 cm were significantly higher during the first sampling campaign. During December 2010 and January 2011, prior to the first sampling campaign, precipitation (Fig. 3a) was clearly higher than during the second campaign, i.e. December 2013 to January 2014. Subsequently, the soil moisture measured at 20 cm (Fig. 3g) was clearly higher during the first sampling campaign than during the second campaign from the beginning of the campaign until the middle of the dry season.

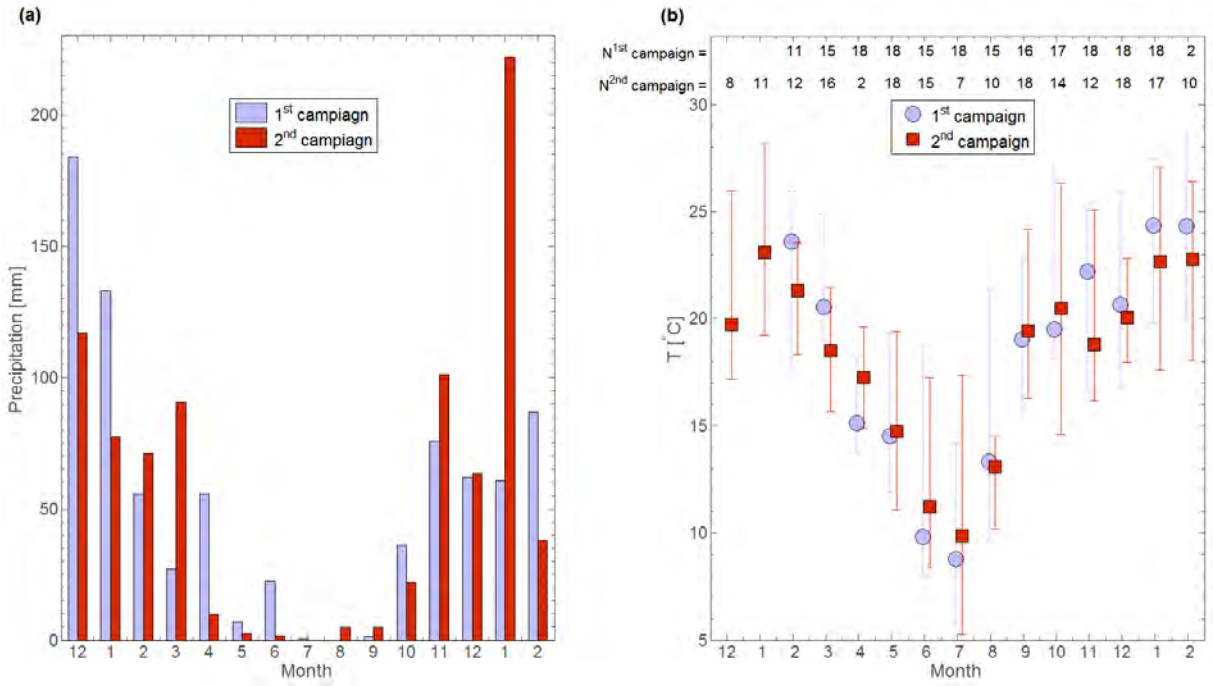

Fig. 3. Monthly variation of **(a)** accumulated precipitation, **(b)** temperature, **(c)** relative humidity, **(d)** wind speed, **(e)** wind direction, and **(f)** and **(g)** soil moisture at 5 and 20 cm depth, respectively. Error bars indicate upper and lower quartiles.

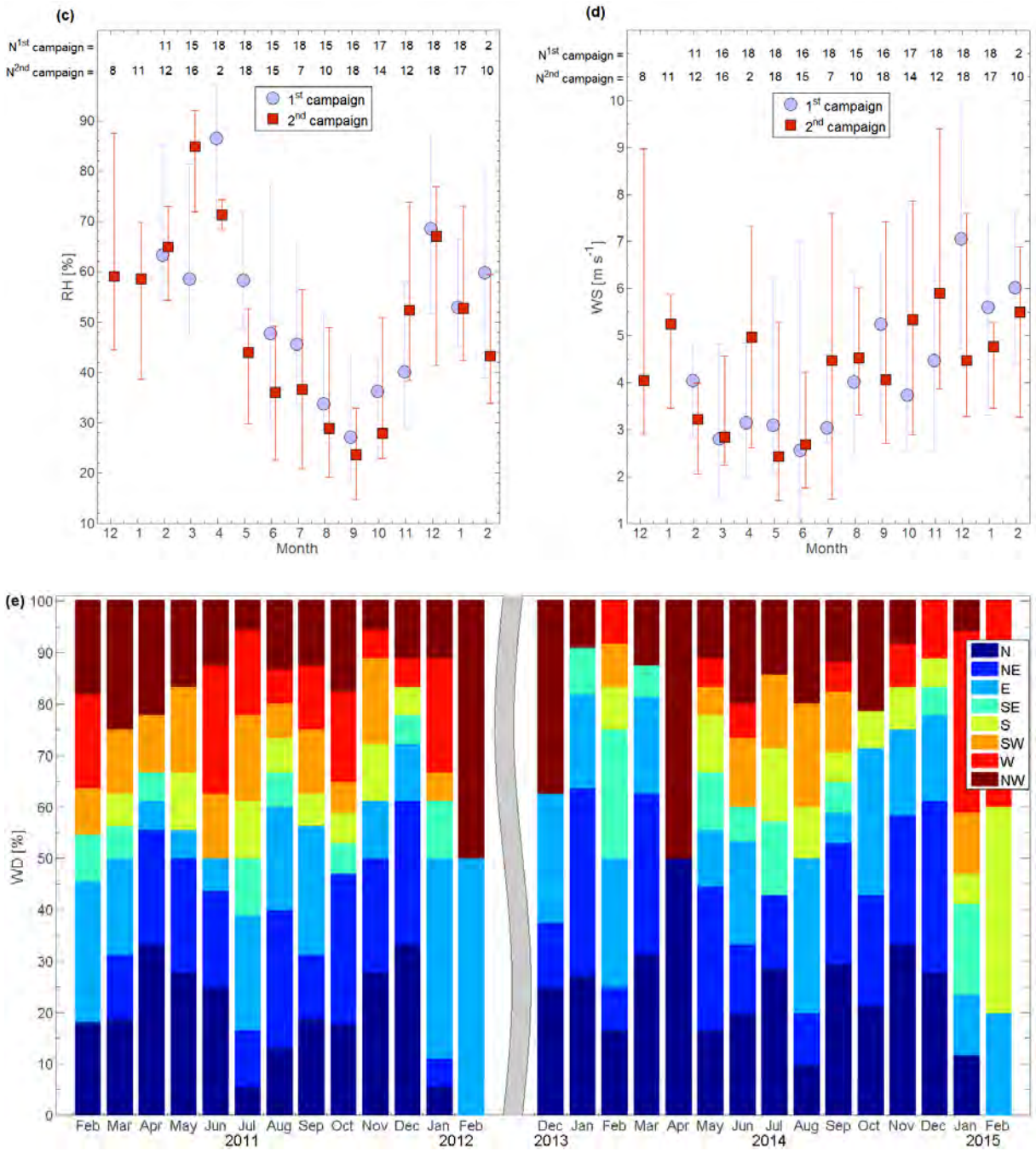

Fig. 3. Continued.

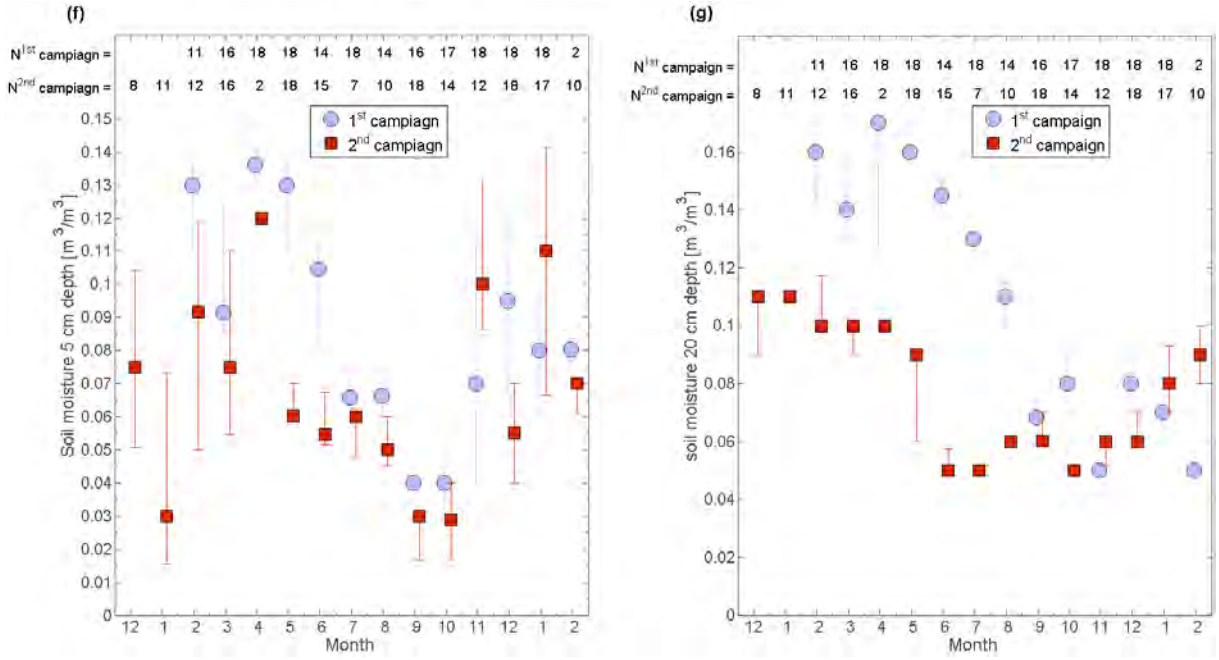

Fig. 3. Continued.

Fig. 4 presents micrometeorological CO_2 flux measurements at Welgegund, which indicate typical changes in the seasonal uptake of CO_2 by vegetation. Negative values (downward CO_2 flux) indicate the net uptake of CO_2 by vegetation, with the gross primary production (GPP) exceeding the total respiration. Positive values indicate the emission of CO_2 by the vegetation. A period of an approximately 0 (small positive) net CO_2 flux is observed in the winter months that extend until September, which can be attributed to decreased microbial activity associated with lower temperatures, low rainfall and most of the vegetation losing their leaves. The net ecosystem exchange (NEE) at full light (maximum downward flux) increases gradually until February in response to the increases of the photochemical efficiency of CO_2 assimilation in the vegetation surrounding the site and the solar elevation angle. The daily maximum NEE starts to decrease in March/April when the solar elevation angle declines and soil moisture drops.

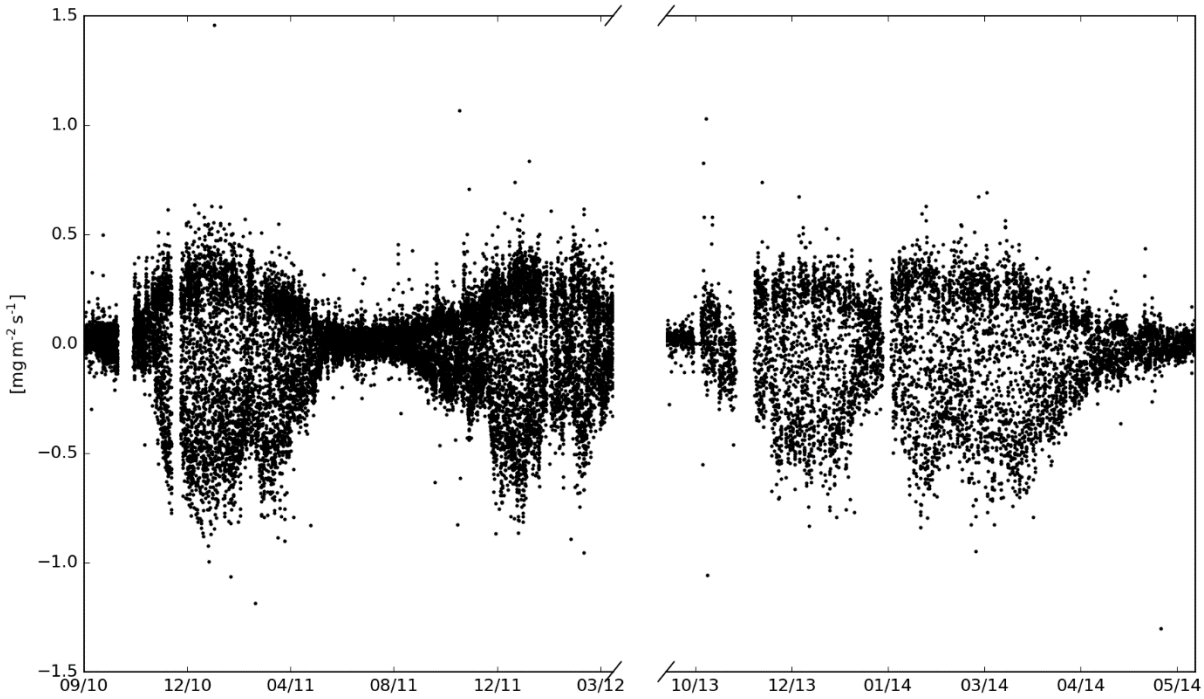

Fig. 4. Micrometeorological CO_2 flux measurements at Welgegund (Räsänen et al., 2016).

3.2 Contextualising BVOC concentrations measured at Welgegund

In Table 2, the median (mean) and inter-quartile range (IQR, 25th to 75th) concentrations of the BVOC species determined during the two sampling campaigns at Welgegund are presented. In Table 3, the concentrations of BVOC species measured during other campaigns in South Africa and the rest of the world are presented.

Table 2. The ambient BVOC concentration for the two campaigns measured at Welgegund.

	First campaign			Second campaign		
pptv	Median (Mean)	IQR (25th - 75th)	N	Median (Mean)	IQR (25th - 75th)	N
Isoprene	14 (28)	6-35	187	14 (23)	7-24	175
MBO	7 (12)	3-16	178	4 (8)	3-10	163
α-Pinene	37 (71)	28-83	197	15 (57)	9-23	191
Camphene	4 (8)	2-9	178	2 (4)	1-3	113
β-Pinene	9 (19)	5-48	195	3 (5)	2-6	171
Δ^3-Carene	3 (6)	2-5	156	2 (4)	1-4	58
p-Cymene	20 (48)	12-33	197	7 (15)	4-13	186
1,8-Cineol	3 (13)	1-7	162	1 (2)	1-2	75
Limonene	21 (30)	9-40	197	16 (54)	9-36	187
Terpinolene	4 (14)	3-11	141	22 (28)	16-34	25
AMCH	5 (7)	1-12	41	3 (4)	2-5	24
Nopinene	6 (7)	4-9	167	8 (11)	6-13	176
Bornylacetate	1 (2)	1-2	49	2 (3)	1-3	101
4-Allylanisole	8 (11)	5-13	118	1 (12)	1-3	70
Σ Monoterpenes	120 (235)	73-242		83 (198)	54-145	

Table 2. Continued

Longicyclene	2 (4)	1-4	152	1 (2)	1-3	34
iso-Longifolene	2 (3)	1-4	52	1 (1)	1	7
Aromadendrene	1 (1)	1	2	2 (2)	1-3	73
a-Humulene	1 (1)	1	3	1 (3)	1-5	4
Alloaromadendrene	2 (3)	1-4	31			
Σ Sesquiterpenes	8 (12)	5-14		4 (8)	3-11	

Table 3. Ambient BVOC concentrations (pptv) as reported by Noe et al. (2012) for various ecosystems and then modified. avg = mean value, med = median value, max = maximal value of the measurements reported.

Location	Isoprene	MBO	Monoterpenes	Date	References
Grassland					
Welgegund, SA	28 (avg), 202(max)	12 (avg), 61(max)	235(avg), 1744(max)	Febr. 2011-Febr. 2012	this study
	23(avg), 182(max)	7 (avg), 47(max)	198(avg), 3081(max)	Dec. 2013-Febr. 2015	this study
Savannah					
KNP, SA	390(avg),860(max)			Febr. 2001	Harley et al. (2003)
Benin, WA	>3000(max)		>5000(max)	7-13 Jun. 2006	Saxton et al. (2007)
Rural village, Senegal	300(avg)			Sept. 2006	Grant et al. (2008)
Boreal					
Hyytiälä			900(avg), 1800(max)	2000-2007	Hakola et al. (2009)
	40–110		100–700	Apr. 2005	Eerdekens et al. (2009)
	220(med), 360(max)		300(med), 600(max)	Summer 2006/2007	Lappalainen et al. (2009)
	70(med), 110(max)		200(med), 300(max)	Winter 2006/2007	
	110(avg), 430(max)		100(avg), 2700(max)	Jul. 2004	Rinne et al. (2005)
			40–450	37 m, Aug. 1998	Rinne et al. (2000)
			140–500	19.5 m, Aug. 1998	
			450–630	2 m, Aug. 1998	
Huhus, Finland			900(avg), 2160(max)	Jun.–Sept. 2003	Räisänen et al., (2009)
Pötsönvaara, Finland	320–1690		1700–3200	Apr.–Oct. 1997, 1998	Hakola et al. (2000)
Hemiboreal					
Järvselja, Estonia	360–2520		1800–7200	Spring and Summer 2010	Noe et al. (2012)
	120–200 (med)		400–1400 (med)	Oct. 2009–Sep. 2010	Noe et al. (2012)
Temperate					
Michigan, USA	2520(avg), 8160(max)		310(avg), 1100(max)	Summer 2008	Mielke et al. (2010)
Jülich, Germany	1980(avg), 10790(max)		250(avg), 1470(max)	Jul. 2003	Spirig et al. (2005)
Duke Forest, USA	1500–2200		310–790	Jul. 2003	Stroud et al. (2005)
Oak Ridge, USA	5000–15000		500–1600	Jul. 1999	Fuentes et al. (2007)
MEF, USA	70(avg)	1346(avg)	0.497(avg)	22-28 Aug. 2008	Nakashimaet al. (2014)
Mediterranean					
Castelpoziano, Italy	141–250		100–200	May–Jun. 2007	Davison et al. (2009)
AM, Greece	1500(avg), 7900(max)		900(avg), 5000(max)	Jul.–Aug. 1997	Harrison et al. (2001)
Tropical					
FNT, Brazil	2000(avg), 4000(max)		50(avg), 130(max)	Jul. 2000	Rinne et al. (2002)
NNNP, NC	1820±870			16–24 Mar. 1996	Serca et al. (2001)
	730±480			21 Nov.–11 Dec. 1996	

SA = South Africa, WA = West Africa, KNP = Kruger National Park, MEF = Manitou Experimental Forest, AM = Agrafa Mountains, FNT = Floresta Nacional do Tapajos, NNNP = Nouabale-Ndoki National Park, NC = Northern Congo

The most abundant species observed throughout the study was the monoterpene, α-pinene, and the total monoterpene concentration was at least an order of magnitude higher compared to the concentrations of other BVOC categories. The total annual median (IQR) monoterpene concentration was 120 (73-242)

pptv during the first campaign and 83 (54-145) pptv during the second campaign. As indicated in Table 2, α-pinene, p-cymene and limonene were the predominant compounds measured during the first campaign, constituting more than 63% of the ambient monoterpene concentrations, while during the second campaign, the dominant monoterpenes were α-pinene, limonene and terpinolene, constituting more than 70% of the ambient monoterpene concentrations. BVOC flux measurements conducted by Greenberg et al. (2003) during SAFARI 2000 at a mopane woodland in Botswana indicated that 60% of the monoterpene flux was attributed to α-pinene, while limonene and β-pinene contributed almost all of the rest of the monoterpenes. Various studies in other regions have also indicated that α-pinene is the dominant monoterpene in ambient air reflecting the ubiquitous nature of its emission (Hellén et al., 2012b;Hakola et al., 2012;Noe et al., 2012). During the AMMA experiment, Saxton et al. (2007) also detected several monoterpenes in ambient air at Djougou with concentrations generally higher than monoterpene concentrations recorded by Serca et al. (2001) (less than 20 pptv) during EXPRESSO at a forest in northern Congo. Monoterpene concentrations reported for boreal forest (Hakola et al., 2009;Hakola et al., 2000;Rinne et al., 2000;Rinne et al., 2005;Rantala et al., 2015;Räisänen et al., 2009;Eerdekens et al., 2009;Lappalainen et al., 2009), hemiboreal mixed forest (Noe et al., 2012), temperate (Spirig et al., 2005;Stroud et al., 2005;Fuentes et al., 2007;Mielke et al., 2010), Mediterranean (Davison et al., 2009;Harrison et al., 2001) and tropical (Rinne et al., 2002) ecosystems ranged between 40 and 7 200 pptv (Table 3). Therefore, there is a large variation in the monoterpene concentrations measured in different ecosystems, with concentrations measured at Welgegund being in the low to mid-range. Unlike isoprene that is approximately 10 times lower than isoprene levels at other ecosystems in the world, the mean monoterpene concentration at Welgegund is comparable to the previous studies at other ecosystems summarised in Table 3.

The annual median (IQR) isoprene concentration measured during the first campaign was 14 (6-35) pptv, while the annual median (IQR) isoprene concentration measured during the second sampling campaign was 14 (7-24) pptv. The highest isoprene concentration, i.e. 202 pptv, was recorded in summer (wet season). Harley et al. (2003) reported that the maximum isoprene concentration measured during an eight-day campaign in the wet season at a *Combretum-Acacia* savannah in southern Africa was 860 pptv with a mean midday concentration of 390 pptv, which is considerably higher than isoprene levels measured at Welgegund. Ambient BVOC measurements conducted by Saxton et al. (2007) at a rural site near Djougou, Benin in June 2006 during the AMMA project indicated isoprene concentrations >3 000 pptv. Grant et al. (2008) conducted VOC measurements at a small rural Senegalese village during September 2006 that was also a sampling location for the AMMA project and reported that isoprene, which had a mean concentration of 300±100 pptv, was the only biogenic hydrocarbon present in all air samples. Serca et al. (2001) reported ambient the mean isoprene

concentration for a tropical forest of Northern Congo during the EXPRESSO study to be 1820±870 pptv at the beginning of the wet season and 730±480 pptv at the end of the wet season. Nakashima et al. (2014) reported that the mean isoprene concentration at the Manitou Experimental Forest (MEF) was 68 ± 69 pptv. In general, mean isoprene concentrations measured at Welgegund were at least an order of magnitude smaller compared to other isoprene measurements in South Africa, Africa and most other parts of the world.

The annual median (IQR) MBO concentrations measured during the first and second campaign were 7 (3-16) and 4 (3-10) pptv, respectively. MBO and isoprene are both produced from dimethylallyl diphosphate (DMADP) (Gray et al., 2011). Guenther (2013) indicated that MBO is emitted from most isoprene emitting vegetation at an emission rate of ~1% of that of isoprene. However, MBO measured at Welgegund was approximately 30% of the isoprene concentrations, which indicated that the main source of MBO at Welgegund is not from isoprene emitters, but from other MBO emitters. MBO concentration measurements at Manitou Experimental Forest, USA were 1 346 ± 777 pptv (Nakashima et al., 2014), which is three orders of magnitude higher compared to the MBO levels measured at Welgegund. According to the knowledge of the authors, there are no previous ambient MBO concentrations measured for Africa.

Most SQTs are highly reactive species and are difficult to detect in ambient air samples, which resulted in concentrations of these species being frequently below the detection limit of the analytical procedure. This is also reflected in the concentrations of these species being an order of magnitude lower compared to the other BVOC species measured in this study. The total annual median (IQR) SQT concentration measured during the first sampling campaign was 8 (5-14) pptv and 4 (3-11) pptv during the second sampling campaign. The most abundant SQT during the first sampling campaign was longicyclene with an annual mean concentration of 4 (1-4) pptv. During the second sampling campaign, α-humulene was the most abundant SQT with an annual mean concentration of 3 (1-5) pptv.

The lower BVOC concentrations measured at Welgegund compared to other regions can mainly be attributed to the much lower isoprene concentrations measured. However, monoterpenes that are important for SOA formation are similar to levels thereof in other environments. In an effort to explain the BVOC concentrations measured at Welgegund, a comprehensive vegetation study was conducted, as described in section 2.2. The influence of the type of vegetation in the region surrounding Welgegund on ambient BVOC concentrations will be further explored.

Jaars et al. (2014) presented concentrations of aromatic VOCs measured at Welgegund during the same two sampling campaigns discussed in this paper. The total BVOC concentrations measured were at least an order of magnitude lower compared to concentrations of aromatic VOCs measured at Welgegund. The most abundant aromatic compound, toluene, had a median value of 630 pptv, while the most

abundant BVOC measured, α-pinene, had a median value of 37 pptv. In addition, the median of the concentrations of the all the monoterpene species (120 and 83 pptv) was approximately six times lower compared to toluene concentrations (Jaars et al., 2014).

3.3 Seasonal variations

In Fig. 5, the panels on the left show monthly median concentrations of (a) isoprene, (b) MBO, (c) monoterpenes and (d) SQT measured for the two campaigns, while the panels on the right present the wet (October to April) and dry (May to September) season concentrations of the respective compounds measured for the two campaigns. Seasonal variations in BVOC concentrations are expected due to the response of emissions to changes in environmental conditions, e.g. temperature and rainfall, as discussed in section 3.1, and the associated biogenic activity. In addition, BVOC emission is expected to be lower during the winter months (June to August), since foliar densities rapidly decrease due to deciduous trees dropping their leaves in winter (Otter et al., 2002). As expected, it is evident that the concentrations of all the BVOC species, with the exception of the isoprene (Fig. 5a), and SQT values (Fig. 5d) measured during the second sampling campaign, were higher in the wet season. The wet season also had more occurrences of BVOC concentrations that were higher than the range of the box and whisker plot (whiskers indicating ±2.7σ or 99.3% coverage if the data have a normal distribution). In an isoprene and monoterpene emissions modelling study for southern Africa conducted by Otter et al. (2003), it was estimated that BVOC emissions will decrease by as much as 85% in the dry winter season for grassland and savannah regions. BVOC concentrations measured in this study indicated much lower decreases from summer (December to February) to winter (June to August), with isoprene and monoterpene decreasing by only 37 and 29%, respectively during the first sampling campaign, while isoprene and monoterpene decreased by only 42 and 23%, respectively during the second sampling campaign. This can partially be attributed to the significant transformation of this biome, as discussed in section 2.2, with large areas transformed to cultivated land, as indicated in Fig. 2. In addition, the study by Otter et al. (2003) was conducted for the entire southern African region.

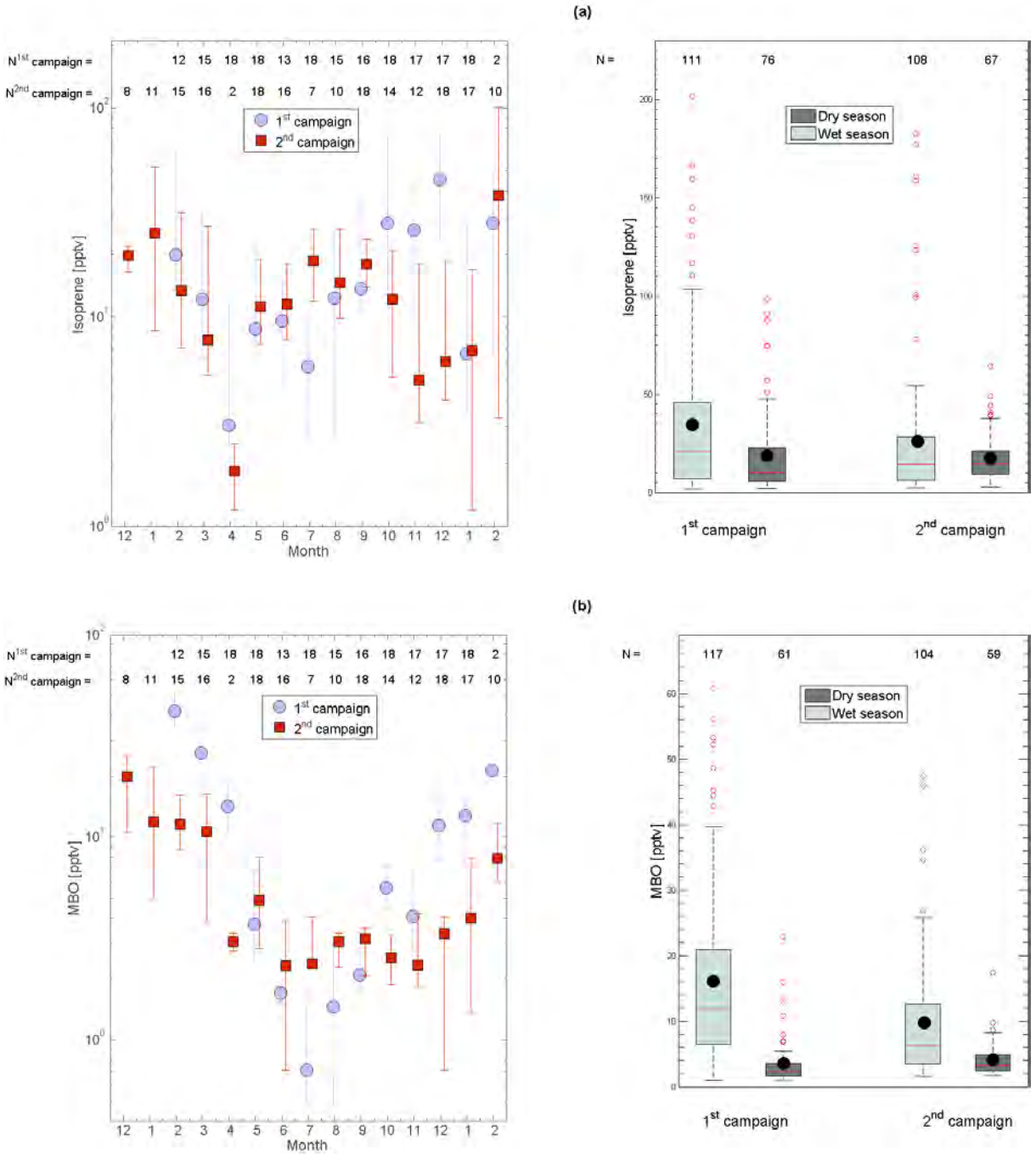

Fig. 5. The panels on the left show monthly median concentrations of (a) isoprene, (b) MBO, (c) monoterpenes and (d) SQT measured for the two campaigns. Error bars indicate upper and lower quartiles. The values displayed near the top of the graphs indicate the number of samples (N^{1st} and N^{2nd} campaign) analysed for each month. The panels on the right show the wet and dry season concentrations of the respective compounds measured for the two campaigns. The red line of each box indicates the median (50^{th} percentile), the black dot the mean, the top and bottom edges of the box the 25^{th} and 75^{th} percentiles, the whiskers ±2.7σ or 99.3% coverage if the data have a normal distribution and the red circles outliers of the range of the box and whisker plot. The values displayed near the top of the graphs indicate the number of samples (N) analysed for the wet and dry season.

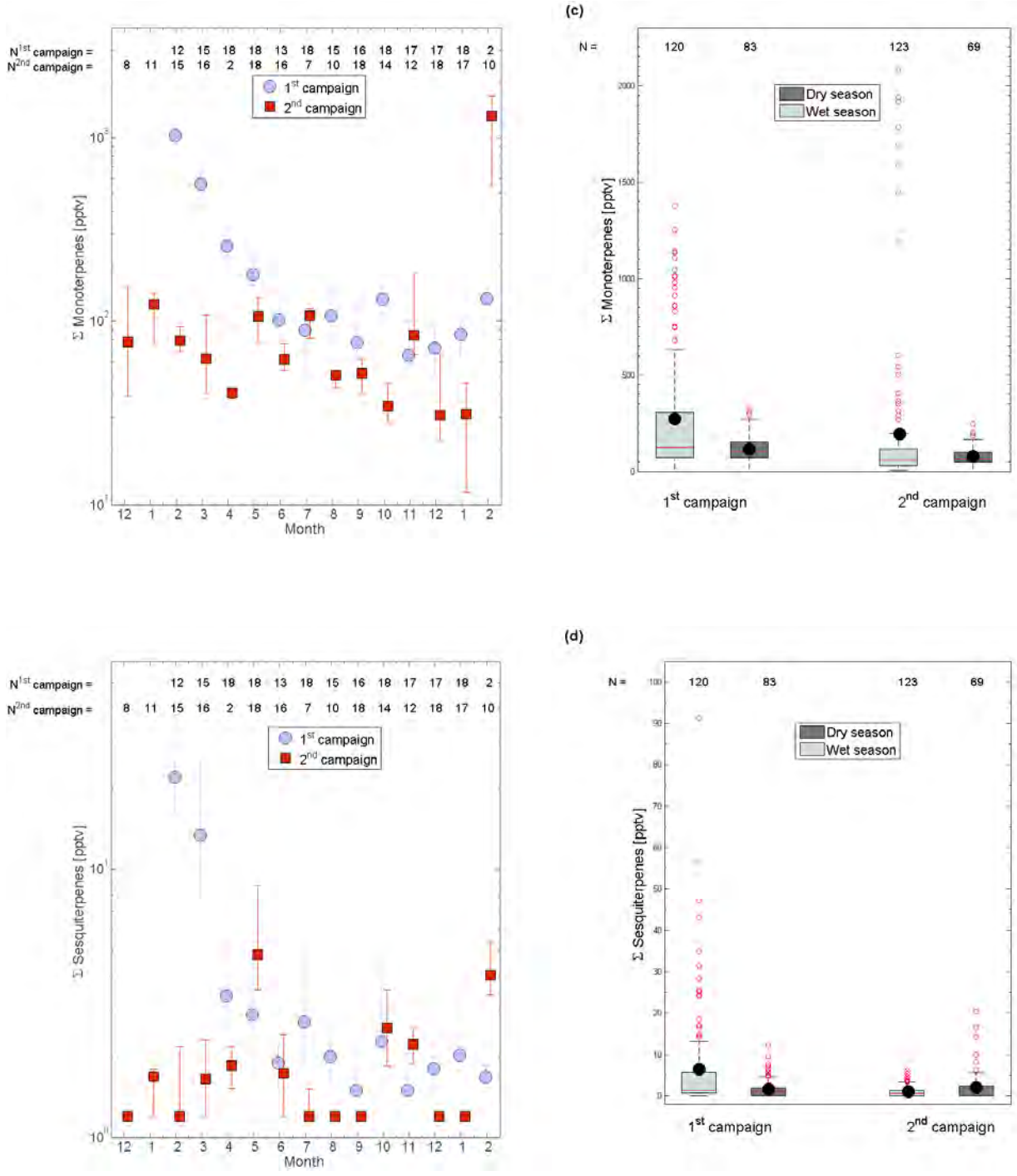

Fig. 5. Continued.

The monthly median isoprene concentrations (Fig. 5a) measured during the first sampling campaign indicated the expected seasonal pattern with higher isoprene concentrations coinciding with the wet and warmer months, with the exception of April that had lower isoprene concentrations. Surprisingly, during the second sampling campaign, there was no distinct seasonal pattern observed. However, higher isoprene concentrations seem to coincide with higher wind speeds (Fig. 3d), which are observed for both sampling campaigns. This indicates that the major sources of isoprene measured at Welgegund can be considered not to be within close proximity. However, since oxidation products of isoprene (e.g.

methyl vinyl ketone, methacrolein) were not measured in this study, more distant sources of isoprene could not be verified. It is evident from Fig. 2 that the region in close proximity of Welgegund in the south-western to north-eastern sector largely comprises cultivated land, while in the north-eastern to south-western sector the predominant land coverage is grassland and natural vegetation. It is expected that isoprene emissions from the cultivated land will be lower compared to savannah grassland (Otter et al., 2003). Therefore, if Welgegund is more frequently affected by winds from the south-western to north-eastern sector, higher wind speeds will coincide with higher isoprene levels, since the savannah grassland fetch region is distant from Welgegund and related to the approximately three-hour atmospheric lifetime of isoprene due to OH radicals.

In Fig. 6, the wind roses for the BVOCs species measured in this study are presented. It is evident that the highest isoprene concentrations for the first sampling period were associated with winds originating from the south to south-western sector, i.e. predominantly from the grassland region in close proximity during the first sampling campaign resulting in a relatively more distinct seasonal pattern for isoprene levels. During the second sampling campaign, higher isoprene concentrations were associated with winds originating from the south-western to the northern sector, i.e. from the cultivated land area. Therefore, isoprene concentrations measured during the second sampling period coincided predominantly with stronger wind speeds from more distant fetch regions.

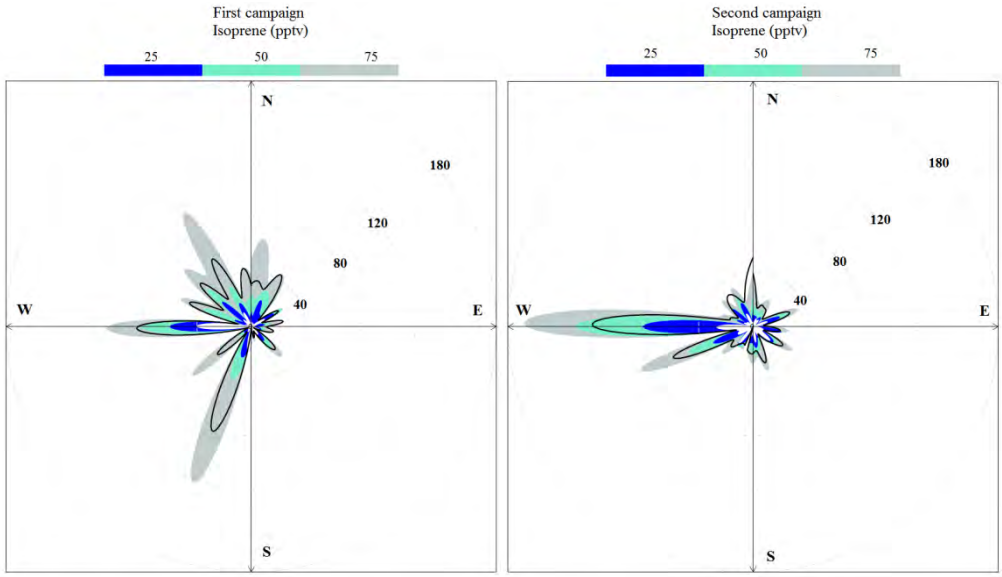

Fig. 6. BVOC concentration rose at Welgegund for the two sampling campaigns. Different colours represent percentiles: blue 25%, aquamarine 50%, azure75% and the black solid line the average.

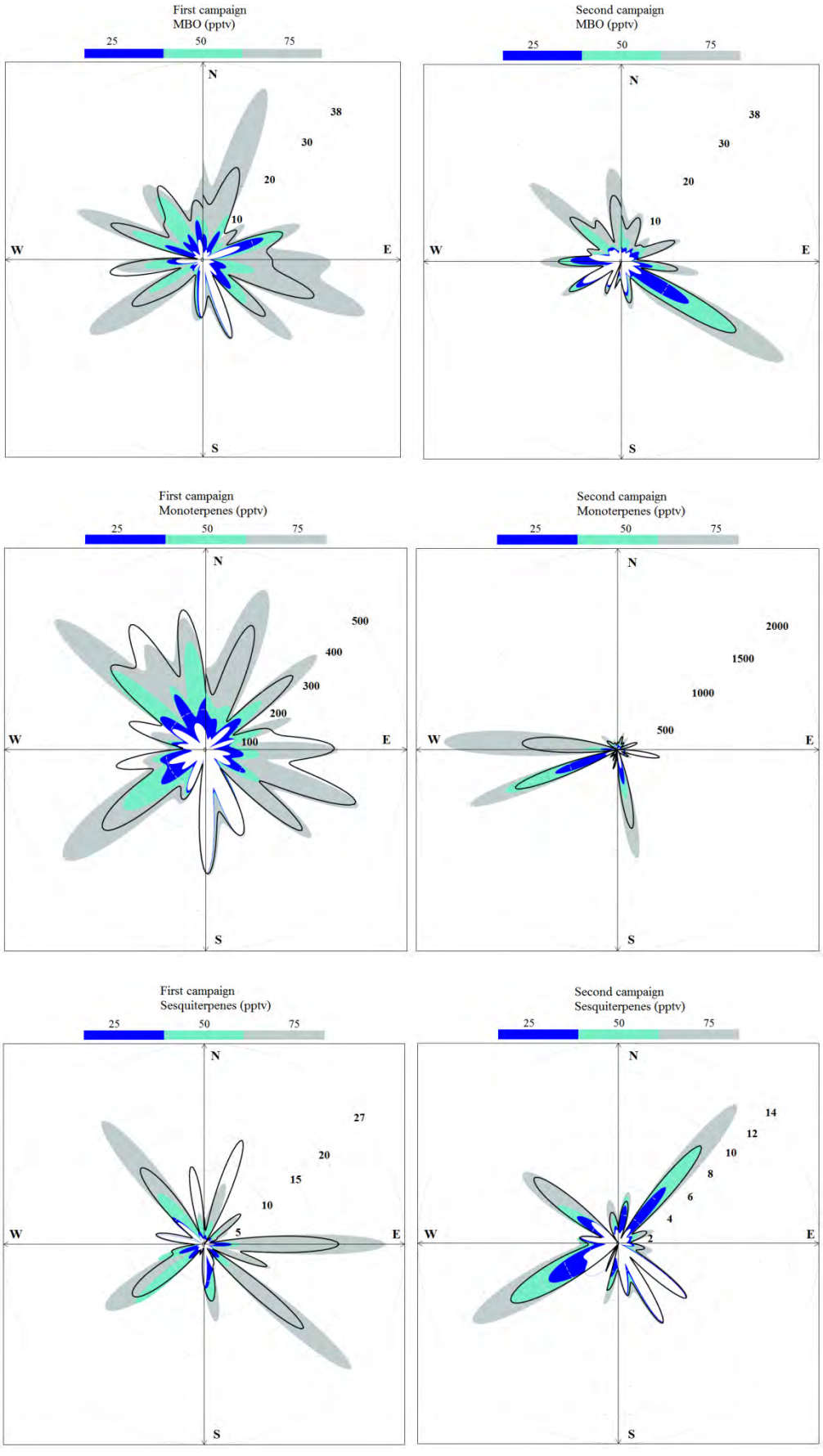

Fig. 6. Continued.

Distinct seasonal patterns are observed for MBO (Fig. 5b) concentrations during both sampling campaigns, i.e. higher MBO concentrations coinciding with wet warm months and lower levels corresponding with dry cold months (Fig. 3). The MBO concentrations also corresponded to the seasonal CO_2 uptake (Fig. 4). It is also evident from Fig. 5b that MBO concentrations during the wet season in the first sampling campaign were higher compared to the second sampling campaign, especially from February to April 2011. As mentioned in section 3.1, the soil moisture measured at a depth of 20 cm (Fig. 3g) during the first sampling campaign was significantly higher from February to August compared to the second sampling campaign. Therefore, these increased MBO levels measured during the first sampling campaign can be attributed to increased emissions from deep-rooted plants, e.g. shrubs and trees. In addition to decreased biogenic activity in the dry winter, the conversion of MBO to isoprene in the atmosphere could also lead to decreased MBO levels during this period. Jaoui et al. (2012) reported that MBO conversion to isoprene increased by an order of magnitude during dry conditions compared to humid conditions. This can also contribute to elevated isoprene concentrations measured during the dry months at Welgegund (Fig. 5a).

No distinct seasonal pattern is observed for monoterpene and SQT concentrations, with the exception of significantly higher levels measured from February to April 2011 during the first sampling campaign. These increased monoterpene and SQT concentrations can also be attributed to the significantly higher soil moisture measured at a depth of 20 cm during the first sampling campaign (Fig. 3g), as observed for the MBO. The monoterpene and SQT concentrations measured during the first sampling campaign were generally higher compared to the second sampling campaign. Otter et al. (2002) also reported a more pronounced seasonal pattern for isoprene compared to monoterpene emissions at the Nylsvley Nature Reserve, which is approximately 200 km north-west from Welgegund.

3.4 BVOC emissions from surrounding vegetation

As discussed in section 2.2 and indicated in Fig.2, Welgegund is situated in a region that has been significantly transformed through cultivation. Cultivated land within the demarcated 60 km radius (Fig. 2) consists mainly of maize and, to a lesser degree, sunflower production. These cultivated lands are also typically characterised by eucalyptus trees, which have a very high BVOC emission potential (Kesselmeier and Staudt, 1999), planted on their peripheries as is evident in Fig. 2. The grassland region in close proximity of Welgegund (south-western to north-eastern sector) has a high diversity of grass and woody species, as mentioned in section 2.2. In general, it can be considered that the woody species in the grasslands are major sources of all the BVOCs measured in this study. Otter et al. (2003) also considered woody vegetation to be the most important in terms of BVOC emissions in southern Africa. It is generally considered that crops and grass have very low isoprene-emitting capacities

(Kesselmeier and Staudt, 1999;Guenther, 2013). However, Schuh et al. (1997) indicate that sunflowers emit isoprene; the monoterpenes α-pinene, β-pinene, sabinene, 3-carene and limonene; and the sesquiterpene β-caryophyllene predominantly. In addition, Chang et al. (2014) (with references therein) also indicated that isoprene has anthropogenic sources in urban areas, which indicates that the surrounding towns can also contribute to the isoprene concentrations.

In an effort to determine possible sources of BVOC species concentrations, roses were compiled, as presented in Fig. 6. In general, the concentration roses indicated that isoprene concentrations were higher from the western direction (indicated by the average and highest concentrations), while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. On occasion, higher MBO, monoterpene and SQT concentrations were observed from the south-eastern region, which may be attributed to a large eucalyptus plantation approximately 15 km south-east from Welgegund, indicated in Fig. 2. However, high isoprene emissions are also usually associated with eucalyptus trees, which are not observed in the isoprene concentration roses. Therefore, other sources of MBO, monoterpene and SQT in these regions are most likely to be the main sources, which can possibly include the urban footprint indicated in this region.

The similar concentration roses determined for monoterpenes and SQT during the first sampling campaign can be attributed to similar sources of these species. However, most SQTs have short atmospheric lifetimes (< 4 min) (Atkinson and Arey, 2003a), which indicated similar sources within close proximity (~1 – 2 km radius) of Welgegund. Gouinguené and Turlings (2002) indicated the emissions of several SQT from young maize plants by testing the effects of soil humidity, air humidity, temperature, light and fertilisation rate on the emission of BVOCs from these plants. Therefore, maize production may be a source of monoterpenes and SQT. The higher SQT concentrations in the south-west and north-west can most likely be attributed to smaller eucalyptus plantations within a 1 to 2 km radius, as indicated in Fig. 2. The high monoterpene concentrations determined during the second sampling campaign may be associated with specific monoterpene emitting plants in the region.

Although a comprehensive vegetation survey has been conducted within a 60 km radius of Welgegund, vegetation types have been identified only generally at this stage, as indicated in section 2.2. Therefore, the predominant woody species in each of the regions surrounding Welgegund associated with specific BVOC emissions have not yet been characterised.

3.5 Statistical correlations

Spearman's correlation analyses were applied to correlate the measured concentrations of isoprene, MBO, monoterpenes and SQT measured to each other in order to substantiate sources of these species. These correlations for the two sampling campaigns are presented in Table 4, with correlations in the wet

seasons listed in the lower bottom (highlighted light blue) and correlations in the dry season presented in the top right (highlighted light grey). It is evident that MBO had good correlations with monoterpenes and SQT in the wet season, as well as with monoterpenes in the dry season during the first sampling campaign. Although not as distinct as during the first sampling campaign, MBO did also correlate with monoterpenes during the wet and dry season, as well as with SQT in the dry season during the second sampling campaign. During the first sampling campaign, monoterpenes had a strong correlation with SQT in the wet season and moderate correlation during the dry season, while strong correlations between monoterpene and SQT were determined in the dry season and a moderate correlation during the wet season during the second sampling campaign. As indicated previously, concentration roses did indicate similar sources of MT and SQT, especially during the first sampling campaign, which is signified by these correlations.

Table 3. Spearman's correlation coefficients between the BVOCs during the wet and dry season of the first campaign (a) and second campaign (b).

(a)

		Dry season			
		Isoprene	MBO	MT	SQT
Wet season	Isoprene	**1.00**	**0.52**	0.03	-0.10
	MBO	0.09	**1.00**	**0.57**	-0.10
	MT	-0.20	**0.68**	**1.00**	0.27
	SQT	-0.04	**0.56**	**0.80**	**1.00**

(b)

		Dry season			
		Isoprene	MBO	MT	SQT
Wet season	Isoprene	**1.00**	0.39	-0.11	0.09
	MBO	**0.50**	**1.00**	0.39	**0.48**
	MT	0.27	0.38	**1.00**	**0.60**
	SQT	0.20	0.01	0.26	**1.00**

Spearman correlations between BVOCs and other paramaters measured at Welgegund did not show significant correlations. However, in certain instances, good correlations were observed between soil moisture and MBO, monoterpenes and SQT concentrations. This is expected, since the monthly average concentrations of these species indicated increased levels thereof that were associated with increased soil moisture from February to April 2011. Therefore, in an effort to further statistically explore the dataset, explorative multilinear regression was performed by using all ancillary measurements as input

data in order to indicate parameter interdependencies on the BVOC concentrations measured. In Fig. 7, the root mean square error (RMSE) difference between the calculated and measured BVOC concentrations, as a function of the number of independent variables included in the optimum MLR solution, is presented. It is evident that interdependence between temperature, soil temperatures and PAR yielded the largest decrease in RMSE for isoprene concentrations measured. However, for MBO, monoterpenes and SQT, a much more significant contribution from soil moisture is observed to decrease the RMSE differences between calculated and measured BVOC levels. It is also evident that the interdependence between soil moisture and soil temperature at 20 cm is important to estimate MBO, monoterpene and SQT concentrations. Therefore, explorative MLR indicated that temperature had the largest influence on isoprene concentrations, while soil moisture was the most significant for MBO, monoterpenes and SQT levels.

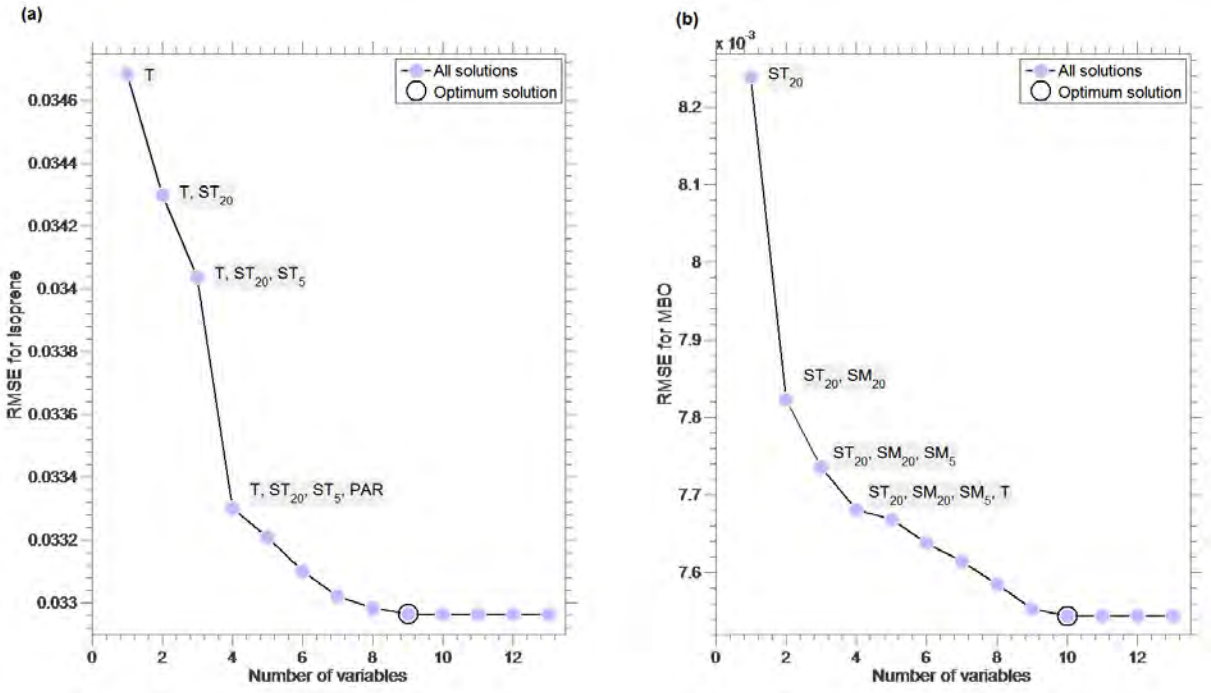

Fig. 7. The optimum combination of independent variables to include in a MLR equation to calculate the dependant variable, i.e. BVOC concentrations. The root mean square error (RMSE) difference between the calculated and measured concentrations indicated that the inclusion of (a) 9 parameters for isoprene, (b) 10 parameters for MBO, (c) 7 parameters for MT, and (d) 12 parameters for SQT in the MLR solution was the optimum.

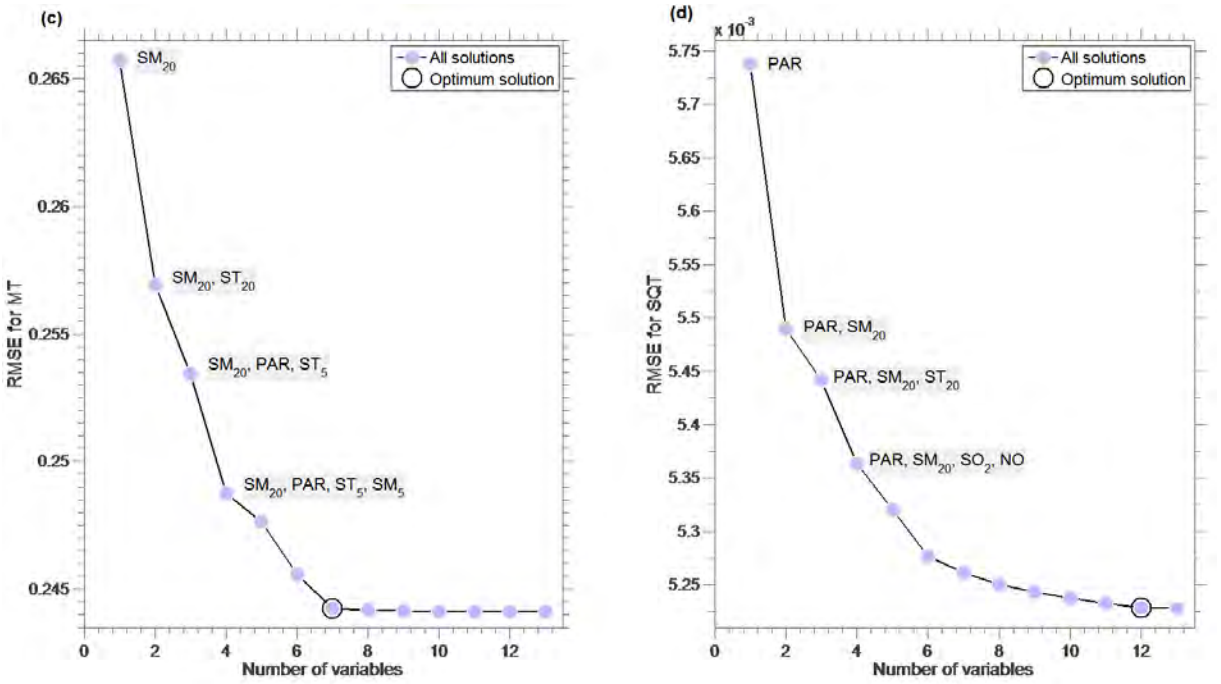

Fig. 7. Continued.

3.6 Reactivity of BVOCs

It is important to evaluate the significance of BVOCs on their atmospheric reactivity, since these species are important precursor species in the photochemical formation of tropospheric O_3 and SOA. This is particularly relevant for South Africa, with various recent studies indicating that O_3 is currently the most problematic pollutant in South Africa (Laakso et al., 2013;Venter et al., 2012;Beukes et al., 2013). In addition, Vakkari et al. (2015) also indicated the importance of VOCs for new particle formation and growth. Therefore, the O_3 formation potential (OFP), reaction rates with O_3 and OH reactivities of the BVOCs measured in this study were evaluated.

The OFP of BVOCs was determined by calculating the product of the average concentration and the maximum incremental reactivity (MIR) coefficient of each compound, i.e. OFP = VOC×MIR (Carter, 2009). The MIR scale has been used to assess OFP for aromatic hydrocarbons in numerous previous studies (Hoque et al., 2008;Jaars et al., 2014;Na et al., 2005). The reaction rates for reactions between O_3 and BVOCs were calculated with Eq. (3):

$$\text{reaction rates} = k_{\text{X,O3}}[\text{X}][\text{O}_3], \quad (3)$$

where [X] is the BVOC concentration, [O_3] the ozone concentration and $k_{X,O3}$ the reaction rate constant for the reaction between X and O_3. Since direct OH reactivity measurements were not available, the OH reactivities (s^{-1}) of the BVOCs were calculated, using Eq. (4):

$$\text{OH reactivity} = k_{\text{X,OH}}[\text{X}] \quad (4)$$

where [X] is the BVOC concentration and $k_{X,OH}$ the reaction rate constant of the reaction between X and OH. In Table 5, the OFP calculated for each of the BVOCs measured in this study, as well as the reaction rate constants for the reactions of these species with O_3 and OH, are listed.

Table 5. Photochemical properties of measured BVOCs during the first and second campaign at Welgegund.

			First period		Second period		[cm^3 molecule^{-1} s^{-1}]	
		MIR[a]	Average	OFP	Average	OFP	$k_{OH} \times 10^{12}$	$k_{O3} \times 10^{18}$
	Isoprene	10.28	28	289	23	234	101.0	13.0
	MBO	4.73	12	56	7.7	37	27.5	1.8
Monoterpenes	α-Pinene	4.38	71	313	57	251	53.7	86.6
	Camphene		7.9		3.8		53.0	0.9
	β-Pinene	3.38	19	64	4.6	16	78.9	15.0
	Δ^3-Carene	3.13	6.1	19	4.1	13	88.0	37.0
	p-Cymene	4.32	48	206	15	66	15.0	0.05
	1,8-Cineol		13		1.9		22.6	
	Limonene	4.4	30	131	54	236	171.0	200.0
	Terpinolene	6.16	14	84	28	170	22.5	138.0
	AMCH		6.7		4.2		98.6	430.0
	Nopinene		7.3		11		8.6	
	Bornylacetate		1.7		3.1		7.7	
	4-Allylanisole		11		12		54.3	12.0
Sesquiterpenes	Longicyclene		4.2		1.7		9.4	
	iso-Longifolene		3.0		0.9		96.2	11.4
	Aromadendrene		1.0		2.4		62.5	12.0
	α-Humulene		0.9		2.7		290.0	870.0
	Alloaromadendrene		3.2					

[a]MIR denotes maximum incremental reactivity (g O_3/g VOCs) (Carter, 2009). The rate constants are from Atkinson (2000) and Atkinson and Arey (2003b) except those for α-humulene and longifolene OH reaction rates, which are from Shu and Atkinson (1995). Other sesquiterpene data is from CSID:1406720, http://www.chemspider.com/Chemical-Structure.1406720.html (last access: 2 May 2016). Predicted data is generated using the US Environmental Protection Agency's EPI Suite.

Table 5 indicates that, according to the OFP calculated with MIR coefficients, α-pinene, isoprene and p-cymene had the highest OFP in descending order during the first sampling campaign. During the second sampling campaign, α-pinene also had the highest OFP, while limonene and isoprene had the second and third highest OFPs, respectively. A comparison of the OFP calculated in this study to the OFP calculated by Jaars et al. (2014) for anthropogenic aromatic hydrocarbons measured at Welgegund (with MIR coefficients) indicates that the OFP of BVOCs is an order of magnitude smaller than the OFP of aromatic hydrocarbons at Welgegund. The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively.

In Fig. 8 (a), the monthly mean reaction rates for the reactions between O_3 and BVOCs measured in this study are presented. Higher reaction rates between BVOCs and O_3 contribute to increased atmospheric O_3 depletion. Significantly higher reaction rates were calculated for February 2015. It is evident from Fig. 8(a) that α-pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions the O_3 depletion. The other BVOCs also had relatively low reaction rates for their reactions with O_3. In Fig. 8(b), the relative monthly contributions of each of the BVOCs to the total OH-reactivity of BVOCs are presented. It is evident that largest contributions to the OH-reactivity of BVOCs measured at Welgegund are from limonene, α-pinene and terpinolene for all of the months during both sampling campaigns. This is expected, since monoterpenes had the highest atmospheric concentrations compared to the other BVOCs measured in this study. It is also evident, especially during the first sampling campaign, that isoprene levels increased with the onset of spring in September.

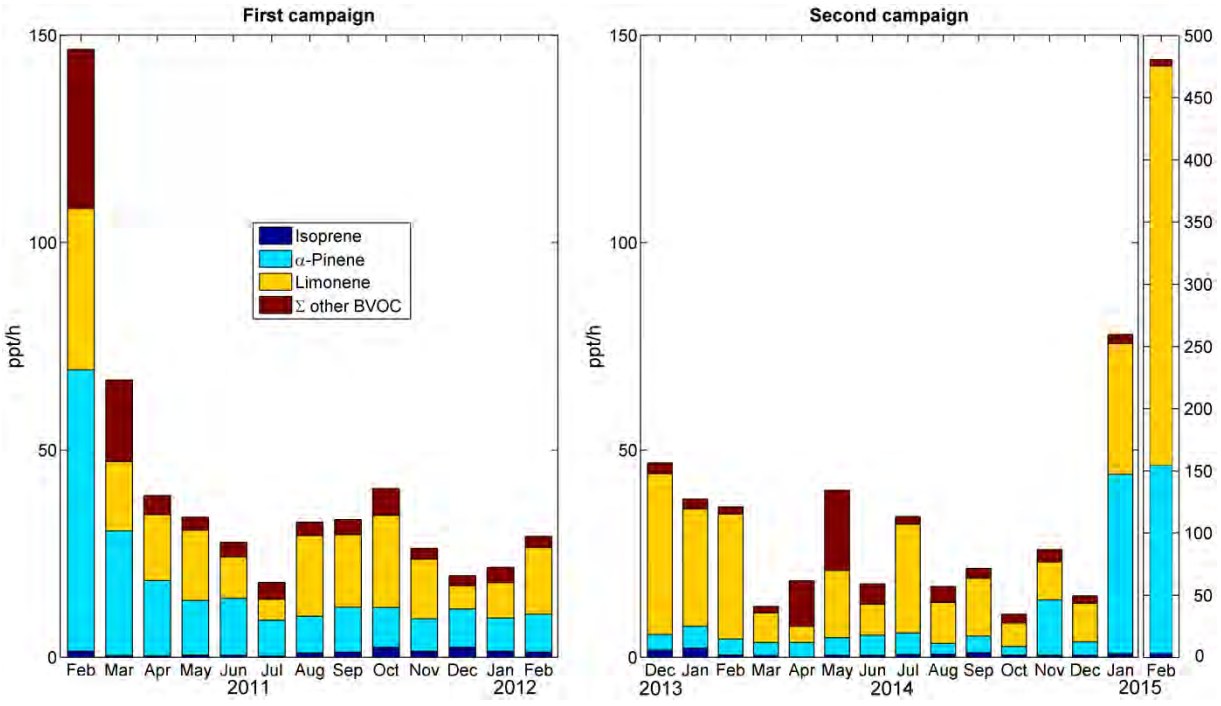

Fig. 8a. Monthly means of reaction rates calculated for reactions between O_3 and BVOCs at Welgegund. A secondary axis is introduced for reaction rates calculated for February 2015 due to much higher reaction rates caluclated for this month.

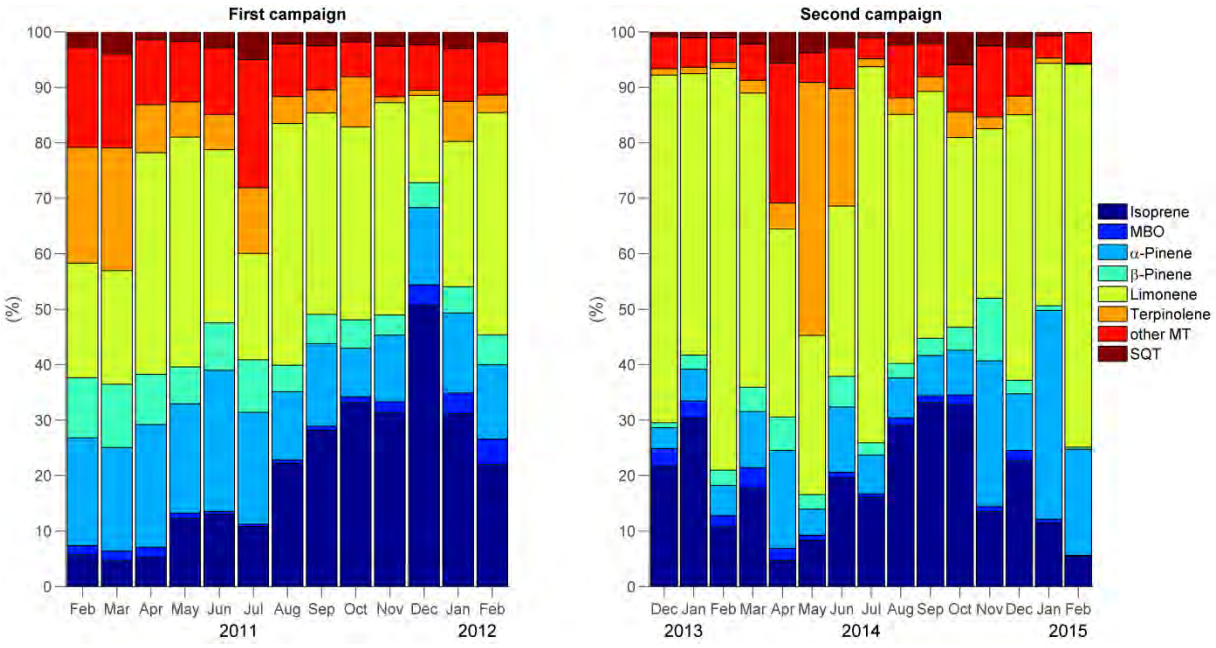

Fig. 8b. The relative monthly contribution of different BVOCs to the OH-reactivity at Welgegund.

4 Conclusions

The annual median concentrations of isoprene, MBO, monoterpenes and SQT during the first campaign were 14, 7, 120 and 8 pptv and 14, 4, 83 and 4 pptv during the second campaign. The concentrations of BVOCs measured during the second campaign were generally lower compared to levels during the first campaign, which can be attributed to significantly higher rainfall during the wet season preceding the first campaign. The sum of the concentration of the monoterpenes was an order of magnitude higher than the concentrations of other BVOC species during both sampling campaigns, with α-pinene being the most abundant species. Very low isoprene concentrations at Welgegund led to a significantly lower total BVOC concentration compared to levels measured at other regions in the world as well as during the SAFARI 2000 campaign in a South African national park. However, monoterpene concentrations were similar to levels reported in most previous studies. In addition, total BVOC concentrations were an order of magnitude lower compared to the total aromatic VOC concentrations measured by Jaars et al. (2014) at Welgegund.

The monthly median MBO levels measured during both campaigns, as well as, although less pronounced, the monthly median isoprene concentrations measured during the first campaign indicated a distinct seasonal pattern with higher isoprene concentrations coinciding with the wet and warmer months. During the second campaign, higher isoprene concentrations were associated with higher wind speeds, which were attributed to a larger fetch and a distant source region. No distinct seasonal pattern was observed for monoterpene and SQT concentrations, with the exception of significantly higher levels measured from February to April 2011 during the first campaign. In addition, MBO concentrations measured during these months were also significantly higher. These increased MBO,

monoterpene and SQT concentrations were attributed to the significantly higher soil moisture measured at a depth of 20 cm resulting from the wet season preceding the first campaign, which is indicative of biogenic emissions from deep-rooted plants.

Concentration roses indicated that isoprene concentrations were higher from the western direction, while wind direction did not indicate any significant differences in the concentrations of other BVOC species. Woody species in the grassland region were considered to be the main sources of BVOCs measured, while sunflower and maize crops were also considered to be potential sources for BVOCs in this region.

Multilinear regression analysis utilising all the ancillary measurements at Welgegund indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpenes and SQT concentrations, while temperature had the greatest influence on isoprene levels. MLR was not performed to indicate how the plant physiological mechanisms are involved in the emission of the BVOCs, since the plant physiological mechanisms were not measured during this study.

The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively, with isoprene and the monoterpenes: α-pinene, isoprene, p-cymene, limonene and terpinolene, having the largest contribution to O_3 formation potential. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured at Welgegund for all of the months during both sampling campaigns.

A comprehensive study on BVOC emissions from important plant species must also be performed in order to relate the emission capacities of vegetation types in the area surrounding Welgegund to the measured atmospheric BVOCs. It is also recommended that oxidation products of BVOC species are measured in future studies in order to verify distant source regions.

Acknowledgements

The authors would like to acknowledge the Finnish Academy (project #132640), the University of Helsinki, the Finnish Meteorological Institute, the North-West University and the National Research Foundation (NRF) for financial support. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the NRF. Assistance with MATLAB from Ms Rosa Gierens is also acknowledged.

References

Andreae, M. O., and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058, 1997.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmospheric environment, 34, 2063-2101, 2000.

Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmospheric Environment, 37, 197-219, 10.1016/s1352-2310(03)00391-1, 2003a.

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chemical reviews, 103, 4605-4638, 2003b.

Bamberger, I., Hörtnagl, L., Ruuskanen, T., Schnitzhofer, R., Müller, M., Graus, M., Karl, T., Wohlfahrt, G., and Hansel, A.: Deposition fluxes of terpenes over grassland, Journal of Geophysical Research: Atmospheres, 116, 2011.

Beukes, J. P., Vakkari, V., Van Zyl, P. G., Venter, A. D., Josipovic, M., Jaars, K., Tiitta, P., Kulmala, M., Worsnop, D., and Pienaar, J. J.: Source region plume characterization of the interior of South Africa, as observed at Welgegund, National Association for Clean Air, The Clean Air Journal, 23, 7-10, 2013.

Beukes, J. P., Venter, A. D., Josipovic, M., Van Zyl, P. G., Vakkari, V., Jaars, K., Dunn, M., and Laakso, L.: Automated Continuous Air Monitoring, Comprehensive Analytical Chemistry, 70, 183-208, 2015.

Blande, J. D., Holopainen, J. K., and Niinemets, Ü.: Plant volatiles in polluted atmospheres: stress responses and signal degradation, Plant, cell & environment, 37, 1892-1904, 2014.

Carter, W. P.: Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications, California Air Resources Board Contract, 07-339, 2009.

Chang, C.-C., Wang, J.-L., Candice Lung, S.-C., Chang, C.-Y., Lee, P.-J., Chew, C., Liao, W.-C., Chen, W.-N., and Ou-Yang, C.-F.: Seasonal characteristics of biogenic and anthropogenic isoprene in tropical–subtropical urban environments, Atmospheric Environment, 99, 298-308, 10.1016/j.atmosenv.2014.09.019, 2014.

Ciccioli, P., Centritto, M., and Loreto, F.: Biogenic volatile organic compound emissions from vegetation fires, Plant, cell & environment, 37, 1810-1825, 2014.

Conradie, E. H., van Zyl, P. G., Pienaar, J. J., Beukes, J. P., Galy-Lacaux, C., Venter, A. D., and Mkhatshwa, G. V.: Assessment of precipitation chemistry and wet deposition in the interior of South Africa, Submitted to Atmospheric Environment,, 2016.

Daemane, M. E., Cilliers, S. S., and Bezuidenhout, H.: An ecological study of the plant communities in the proposed Highveld National Park, in the peri-urban area of Potchefstroom, South Africa, Koedoe, 52, 10.4102/koedoe.v52i1.708, 2010.

Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J., Rinne, J., and Hewitt, C.: Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy, Biogeosciences, 6, 1655-1670, 2009.

Di Carlo, P., Brune, W. H., Martinez, M., Harder, H., Lesher, R., Ren, X., Thornberry, T., Carroll, M. A., Young, V., and Shepson, P. B.: Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs, Science, 304, 722-725, 2004.

Eerdekens, G., Yassaa, N., Sinha, V., Aalto, P., Aufmhoff, H., Arnold, F., Fiedler, V., Kulmala, M., and Williams, J.: VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events, Atmos. Chem. Phys, 9, 8331-8350, 2009.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., and Lee, B.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476-479, 2014.

Fuentes, J. D., Gu, L., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J., Ciccioli, P., Lamb, B., Geron, C., and Guenther, A.: Biogenic hydrocarbons in the atmospheric boundary layer: a review, Bulletin of the American Meteorological Society, 81, 2000.

Fuentes, J. D., Wang, D., Bowling, D. R., Potosnak, M., Monson, R. K., Goliff, W. S., and Stockwell, W. R.: Biogenic hydrocarbon chemistry within and above a mixed deciduous forest, Journal of atmospheric chemistry, 56, 165-185, 2007.

Gouinguené, S. P., and Turlings, T. C.: The effects of abiotic factors on induced volatile emissions in corn plants, Plant Physiology, 129, 1296-1307, 2002.

Grant, D. D., Fuentes, J. D., Chan, S., Stockwell, W. R., Wang, D., and Ndiaye, S. A.: Volatile organic compounds at a rural site in western Senegal, Journal of atmospheric chemistry, 60, 19-35, 2008.

Gray, D. W., Breneman, S. R., Topper, L. A., and Sharkey, T. D.: Biochemical characterization and homology modeling of methylbutenol synthase and implications for understanding hemiterpene synthase evolution in plants, J Biol Chem, 286, 20582-20590, 10.1074/jbc.M111.237438, 2011.

Greenberg, J., Guenther, A., Harley, P., Otter, L., Veenendaal, E., Hewitt, C., James, A., and Owen, S.: Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana, Journal of Geophysical Research: Atmospheres, 108, 2003.

Guenther, A., Jiang, X., Heald, C., Sakulyanontvittaya, T., Duhl, T., Emmons, L., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions, 2012.

Guenther, A.: Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere, ISRN Atmospheric Sciences, 2013, 1-27, 10.1155/2013/786290, 2013.

Hakola, H., Laurila, T., Rinne, J., and Puhto, K.: The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site, Atmospheric Environment, 34, 4971-4982, 2000.

Hakola, H., Hellén, H., Tarvainen, V., Bäck, J., Patokoski, J., and Rinne, J.: Annual variations of atmospheric VOC concentrations in a boreal forest, Boreal Environ. Res, 14, 722-730, 2009.

Hakola, H., Hellén, H., Hemmilä, M., Rinne, J., and Kulmala, M.: In situ measurements of volatile organic compounds in a boreal forest, Atmos. Chem. Phys., 12, 11665-11678, 10.5194/acp-12-11665-2012, 2012.

Harley, P., Otter, L., Guenther, A., and Greenberg, J.: Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna, Journal of Geophysical Research: Atmospheres, 108, 2003.

Harrison, D., Hunter, M., Lewis, A., Seakins, P., Bonsang, B., Gros, V., Kanakidou, M., Touaty, M., Kavouras, I., and Mihalopoulos, N.: Ambient isoprene and monoterpene concentrations in a Greek fir (Abies Borisii-regis) forest. Reconciliation with emissions measurements and effects on measured OH concentrations, Atmospheric Environment, 35, 4699-4711, 2001.

Hellén, H., Kuronen, P., and Hakola, H.: Heated stainless steel tube for ozone removal in the ambient air measurements of mono- and sesquiterpenes, Atmospheric Environment, 57, 35-40, 10.1016/j.atmosenv.2012.04.019, 2012a.

Hellén, H., Tykkä, T., and Hakola, H.: Importance of monoterpenes and isoprene in urban air in northern Europe, Atmospheric environment, 59, 59-66, 2012b.

Holopainen, J. K., and Gershenzon, J.: Multiple stress factors and the emission of plant VOCs, Trends in plant science, 15, 176-184, 2010.

Hoque, R. R., Khillare, P. S., Agarwal, T., Shridhar, V., and Balachandran, S.: Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India, Science of the Total Environment, 392, 30-40, 10.1016/j.scitotenv.2007.08.036, 2008.

Jaars, K., Beukes, J. P., van Zyl, P. G., Venter, A. D., Josipovic, M., Pienaar, J. J., Vakkari, V., Aaltonen, H., Laakso, H., Kulmala, M., Tiitta, P., Guenther, A., Hellén, H., Laakso, L., and Hakola, H.: Ambient aromatic hydrocarbon measurements at Welgegund, South Africa, Atmospheric Chemistry and Physics, 14, 7075-7089, 10.5194/acp-14-7075-2014, 2014.

Jaoui, M., Kleindienst, T., Offenberg, J., Lewandowski, M., and Lonneman, W.: SOA formation from the atmospheric oxidation of 2-methyl-3-buten-2-ol and its implications for PM 2.5, Atmospheric Chemistry and Physics, 12, 2173-2188, 2012.

Kesselmeier, J., and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, Journal of Atmospheric Chemistry, 33, 23-88, 10.1023/a:1006127516791, 1999.

Kesselmeier, J., Ciccioli, P., Kuhn, U., Stefani, P., Biesenthal, T., Rottenberger, S., Wolf, A., Vitullo, M., Valentini, R., and Nobre, A.: Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget, Global Biogeochemical Cycles, 16, 2002.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T., and Kesselmeier, J.: Isoprene and monoterpene emissions of Amazonian tree species during the wet season: Direct and indirect investigations on controlling environmental functions, Journal of Geophysical Research: Atmospheres, 107, 2002.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, Journal of Aerosol Science, 35, 143-176, 2004.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., and Rantala, P.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943-946, 2013.

Laakso, L., Merikanto, J., Vakkari, V., Laakso, H., Kulmala, M., Molefe, M., Kgabi, N., Mabaso, D., Carslaw, K., and Spracklen, D.: Boundary layer nucleation as a source of new CCN in savannah environment, Atmospheric Chemistry and Physics, 13, 1957-1972, 2013.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytol, 183, 27-51, 10.1111/j.1469-8137.2009.02859.x, 2009.

Lappalainen, H., Sevanto, S., Bäck, J., Ruuskanen, T., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmospheric Chemistry and Physics, 9, 5447-5459, 2009.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740, 10.1038/nature06870, 2008.

Loreto, F., and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends in plant science, 15, 154-166, 2010.

Malhi, Y.: Carbon in the atmosphere and terrestrial biosphere in the 21st century, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 360, 2925-2945, 2002.

Mauldin III, R., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurten, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur dioxide, Nature, 488, 193-196, 2012.

Mielke, L. H., Pratt, K. A., Shepson, P. B., McLuckey, S. A., Wisthaler, A., and Hansel, A.: Quantitative Determination of Biogenic Volatile Organic Compounds in the Atmosphere Using Proton-Transfer Reaction Linear Ion Trap Mass Spectrometry†, Analytical chemistry, 82, 7952-7957, 2010.

Mucina, L., and Rutherford, M. C.: The Vegetation of South Africa, Lesotho and Swaziland, South African National Biodiversity Institute, 2006.

Na, K., Moon, K.-C., and Kim, Y. P.: Source contribution to aromatic VOC concentration and ozone formation potential in the atmosphere of Seoul, Atmospheric environment, 39, 5517-5524, 2005.

Nakashima, Y., Kato, S., Greenberg, J., Harley, P., Karl, T., Turnipseed, A., Apel, E., Guenther, A., Smith, J., and Kajii, Y.: Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign, Atmospheric Environment, 85, 1-8, 2014.

Noe, S., Hüve, K., Niinemets, Ü., and Copolovici, L.: Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest, Atmospheric Chemistry and Physics, 12, 3909-3926, 2012.

Otter, L., Guenther, A., and Greenberg, J.: Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands, Atmospheric Environment, 36, 4265-4275, 2002.

Otter, L., Guenther, A., Wiedinmyer, C., Fleming, G., Harley, P., and Greenberg, J.: Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator, Journal of Geophysical Research: Atmospheres, 108, 2003.

Peñuelas, J., and Llusià, J.: BVOCs: plant defense against climate warming?, Trends in plant science, 8, 105-109, 2003.

Peñuelas, J., and Staudt, M.: BVOCs and global change, Trends in plant science, 15, 133-144, 2010.

Räisänen, T., Ryyppö, A., and Kellomäki, S.: Monoterpene emission of a boreal Scots pine (Pinus sylvestris L.) forest, Agricultural and forest meteorology, 149, 808-819, 2009.

Rantala, P., Aalto, J., Taipale, R., Ruuskanen, T., and Rinne, J.: Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere, Biogeosciences, 12, 5753-5770, 2015.

Räsänen, M., Aurela, M., Vakkari, V., Beukes, J. P., van Zyl, P. G., Josipovic, M., Venter, A. D., Jaars, K., Siebert, S. J., Laurela, T., Tuovinen, J.-P., Rinne, J., and Laakso, L.: Carbon balance of a grazed savanna grassland ecosystem in South Africa, In preparation for submission to Biogeosciences,, 2016.

Rinne, H., Guenther, A., Greenberg, J., and Harley, P.: Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, Atmospheric Environment, 36, 2421-2426, 2002.

Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü.: Canopy scale monoterpene emissions of Pinus sylvestris dominated forests, Atmospheric Environment, 34, 1099-1107, 2000.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal environment research, 10, 425-436, 2005.

Ruuskanen, T., Müller, M., Schnitzhofer, R., Karl, T., Graus, M., Bamberger, I., Hörtnagl, L., Brilli, F., Wohlfahrt, G., and Hansel, A.: Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, Atmospheric Chemistry and Physics, 11, 611-625, 2011.

Saxton, J., Lewis, A., Kettlewell, J., Ozel, M., Gogus, F., Boni, Y., Korogone, S., and Serça, D.: Isoprene and monoterpene measurements in a secondary forest in northern Benin, Atmospheric Chemistry and Physics, 7, 4095-4106, 2007.

Schuh, G., Heiden, A., Hoffmann, T., Kahl, J., Rockel, P., Rudolph, J., and Wildt, J.: Emissions of volatile organic compounds from sunflower and beech: dependence on temperature and light intensity, Journal of Atmospheric Chemistry, 27, 291-318, 1997.

Serca, D., Guenther, A., Klinger, L., Vierling, L., Harley, P., Druilhet, A., Greenberg, J., Baker, B., Baugh, W., and BOUKA-BIONA, C.: EXPRESSO flux measurements at upland and lowland Congo tropical forest site, Tellus B, 53, 220-234, 2001.

Sharkey, T. D., and Yeh, S.: Isoprene emission from plants, Annual review of plant biology, 52, 407-436, 2001.

Shu, Y., and Atkinson, R.: Atmospheric lifetimes and fates of a series of sesquiterpenes, Journal of Geophysical Research: Atmospheres, 100, 7275-7281, 1995.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmospheric Chemistry and Physics, 5, 465-481, 2005.

Stroud, C., Makar, P., Karl, T., Guenther, A., Geron, C., Turnipseed, A., Nemitz, E., Baker, B., Potosnak, M., and Fuentes, J. D.: Role of canopy-scale photochemistry in modifying biogenic-atmosphere exchange of reactive terpene species: Results from the CELTIC field study, Journal of Geophysical Research: Atmospheres, 110, 2005.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 261-263, 2006.

Tyson, P., Garstang, M., and Swap, R.: Large-scale recirculation of air over southern Africa, Journal of applied meteorology, 35, 2218-2236, 1996.

Vakkari, V., Tiitta, P., Jaars, K., Croteau, P., Beukes, J. P., Josipovic, M., Kerminen, V. M., Kulmala, M., Venter, A. D., and Zyl, P. G.: Reevaluating the contribution of sulfuric acid and the origin of organic compounds in atmospheric nanoparticle growth, Geophysical Research Letters, 42, 2015.

Venter, A. D., Vakkari, V., Beukes, J. P., Van Zyl, P. G., Laakso, H., Mabaso, D., Tiitta, P., Josipovic, M., Kulmala, M., and Pienaar, J. J.: An air quality assessment in the industrialised western Bushveld Igneous Complex, South Africa, South African Journal of Science, 108, 1-10, 2012.

Wang, H., Xia, J., Mu, Y., Nie, L., Han, X., and Wan, S.: BVOCs emission in a semi-arid grassland under climate warming and nitrogen deposition, Atmospheric Chemistry and Physics, 12, 3809-3819, 2012.

Welgegund measurement station: http://www.welgegund.org/, access: 27 May, 2016.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct kinetic measurements of Criegee intermediate (CH2OO) formed by reaction of CH2I with O2, Science, 335, 204-207, 2012.

Zunckel, M., Chiloane, K., Sowden, M., and Otter, L.: Biogenic volatile organic compounds: The state of knowledge in southern Africa and the challenges for air quality management, South African Journal of Science, 103, 2007.

CHAPTER 6

RECEPTOR MODELLING AND RISK ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS MEASURED AT WELGEGUND, SOUTH AFRICA

6.1 AUTHOR LIST, CONTRIBUTIONS AND CONSENT

K. Jaars[1], M. Vestenius[2], P. G. van Zyl[1], J. P. Beukes[1], H. Hellén[2], V. Vakkari[2], M. Venter[1] and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa

[2]Finnish Meteorological Institute, PL 503, 00101 Helsinki, Finland

Contributions of the various co-authors were as follows. The bulk of the work was done by the author, **K Jaars**, i.e. sample analysis, data processing, research and writing of the scientific paper; PG van Zyl and JP Beukes were the promoters of this study who assisted in interpretation of data, writing the article and also made conceptual contributions. The author, with assistance from M Venter measured the VOCs, while H Hellén and H Hakola assisted with specialised analyses, preparation and expert opinions of the adsorbent tubes at the FMI with a TD-GC-MS. M Vestenius assisted with the PMF analysis of the data. V Vakkari helped create the infrastructure at Welgegund and made conceptual contributions.

All the co-authors on the article 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. *Atmospheric Chemistry and Physics*, a European Geosciences Union journal. The figures and tables of this article are also added at the end of the text, as prescribed by the journal. The author's guide that was followed in preparation of the article is available at http://www.atmospheric-chemistry-and-physics.net/for_authors/submit_your_manuscript.html (Date of access: 11 June 2016). 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.

Receptor modelling and risk assessment of volatile organic compounds measured at Welgegund, South Africa

K. Jaars[1], M. Vestenius[2], P. G. van Zyl[1], J. P. Beukes[1], H. Hellén[2], V. Vakkari[2], M. Venter[1] and H. Hakola[2]

[1]Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa
[2]Finnish Meteorological Institute, Atmospheric Composition Unit, P.O. Box 503, 00101 Helsinki, Finland

Correspondence to: P. G. van Zyl (Pieter.VanZyl@nwu.ac.za)

Abstract

Volatile organic compounds (VOCs) can have significant impacts on climate and human health. Certain VOCs are proven to be carcinogenic and toxic, which can affect human health directly and indirectly. In order to develop climate change reduction strategies and to assess the impacts of VOCs on human health, it is crucial to determine the sources of VOCs, which can be emitted from biogenic and anthropogenic sources. The aim of this study was to perform positive matrix factorisation (PMF) analysis on VOC data collected at a regional background atmospheric monitoring station affected by the major sources in the interior of South Africa in order to conduct a source apportionment study. In addition, a risk assessment study was also performed in view of the major source regions affecting Welgegund in order to quantify the impacts of anthropogenic VOCs measured at Welgegund on human health. Measurements were conducted at the Welgegund measurement station located on a commercial farm approximately 100 km west of Johannesburg for a period of more than two years. PMF analysis revealed ten meaningful factor solutions, of which five factors were associated with biogenic emissions and five with anthropogenic sources. Three of the biogenic factors were characterised by a specific biogenic species, i.e. isoprene, limonene and 2-methyl-3-buten-2-ol (MBO), while the other two biogenic factors comprised mixtures of biogenic species with different tracer species. The temporal factor contribution for the isoprene, limonene and MBO factors correlated relatively well with the seasonal wet pattern. Wind roses indicated that Welgegund was affected by biogenic species from all wind directions in the surrounding environment. Two anthropogenic factors were associated with emissions from a densely populated anthropogenic source region to the east of Welgegund with a large

number of industrial activities. An anthropogenic factor was also identified that reflected the influence of solvents on atmospheric VOC concentrations, while two anthropogenic factors were determined that indicated the influence of farming activities in close proximity to Welgegund. A non-cancer- (hazard ratios) and cancer-risk (lifetime cancer risks) assessment study conducted for VOCs measured at Welgegund in relation to three source regions identified indicated that the non-cancerous influence of VOCs measured in the source regions is significantly lower compared to the cancerous influence of these species on human health, which poses a significant cancer risk. An assessment of the OH reactivity of anthropogenic VOCs indicated that OH reactivity was higher for VOCs in air masses passing over a highly industrialised source region; while the highest OH reactivity was determined for species for which high ozone formation potential was determined in previous studies.

1 Introduction

Volatile organic compounds (VOCs) can have significant impacts on the oxidising capacity and radiative balance of the atmosphere through their role in tropospheric ozone and secondary organic aerosol (SOA) formation, as well as their effect on stratospheric ozone depletion and the enhancement of the global greenhouse effect (Seinfeld and Pandis, 2012;Kulmala et al., 2004;Tunved et al., 2006;Sillman, 1999). In addition to their climatic impacts, VOCs also have significant effects on human health. It has been proven that certain VOCs and their reaction products are carcinogenic and toxic, which can affect human health directly and indirectly (Delfino et al., 2003;Kim et al., 2002;Otto et al., 1992;Payne-Sturges et al., 2004;Wichmann et al., 2009). Benzene, for instance, is classified by the International Agency for Research on Cancer (IARC) and the United States Agency for Toxic Substances and Disease Registry (ATSDR) as being a carcinogen and toxic (IARC, 2012;ATSDR, 2015). It has been estimated that a lifetime exposure to atmospheric benzene levels of 0.31 ppbv leads to approximately six cases of leukaemia per million inhabitants (World Health Organization, 2000). Therefore, an annual ambient limit for benzene of 1.6 ppbv has been set by South Africa (Government Gazette Republic of South Africa, 2009), the European Union (European Union, 2008), India and South Korea (The Gazette of India, 2009;Korean Ministry of Environment, 2011), while an Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10 000) of 4 ppbv was established by ATSDR (ATSDR, 2016).

It is crucial to determine the sources of VOCs to develop efficient ozone and particulate pollution control, as well as for the development of climate change reduction strategies. VOCs can be emitted from various anthropogenic and biogenic sources. Globally, the major anthropogenic sources of atmospheric VOCs are considered to be fossil fuel combustion, petrochemical industries, vehicular emissions, storage and transport of fuel, usage and production of solvents, hazardous waste facilities and landfills (Shi et al., 2015). Biomass burning (veld fires) can also be an important source of VOC, especially in southern Africa, where large-scale biomass combustion occurs every year in the dry season (Vakkari et al., 2015). Shi et al. (2015) state that a lack of information exists for VOC emissions specifically from coal-fired sources, while a number of studies have been performed on VOC emissions from vehicles, biomass burning, solvents, petrochemical industries and refineries. In addition to

anthropogenic sources, biogenic VOCs (BVOCs) from ecosystems are also important and it is estimated on a global scale that ~90 % of annual VOC emissions are from vegetation (~1000 Tg C $year^{-1}$) (Guenther et al., 2012).

Notwithstanding the importance of atmospheric VOCs on climate, the environment and human health, very few papers have been published in the peer-reviewed literature on atmospheric VOCs in South Africa, while, especially, limited research has been conducted on BVOC emissions in southern Africa (Otter et al., 2003;Scholes and Andreae, 2000;Jaars et al., 2016). Continuous VOC measurements are mainly limited to compliance monitoring by industries, while certain provincial governments and local municipalities perform atmospheric VOC measurements. According to Forbes and Rohwer (2008), VOCs (specifically benzene, toluene, ethylbenzene and xylenes, collectively referred to as BTEX) are monitored at nine sites across three provinces by local municipalities in South Africa. Brunke et al. (2001) reported interesting results for non-methane hydrocarbons monitored at Cape Point within the context of biomass burning episodes. Burger (2006) reported measurements of BTEX in the Vaal Triangle and Cape Town, whereas Van der Walt (2008) measured hydrocarbons in a metropolitan area in the Vaal Triangle. Lourens et al. (2011) measured BTEX in the Mpumalanga Highveld and the Vaal Triangle with passive samplers for one year. VOCs have also been studied within the context of emissions from spontaneous combustion of coal (Pone et al., 2007) and the Cape Town brown haze (Burger et al., 2004;Chiloane, 2006).

Jaars et al. (2014) and Jaars et al. (2016) presented concentrations of aromatic hydrocarbons and BVOCs, respectively obtained from active VOC measurements conducted at the regionally representative Welgegund background site in South Africa. In these papers, the concentrations of aromatic carbons and BVOCs measured at Welgegund were contextualised, while the seasonal patterns of these species were also presented. The impacts of source regions according to back trajectory analysis (aromatic hydrocarbons) and meteorological patterns (BVOCs) on concentrations of these species were also discussed, while calculations (e.g. inter-compound ratios) and explorative statistical analysis were also performed in order to indicate possible sources of these species. In addition, the ozone formation potential of aromatic hydrocarbons and BVOCs, as well as the atmospheric reactivity of BVOCs, was also estimated.

Receptor modelling is an effective technique applied in source appointment studies ((Zhang et al., 2014;Yuan et al., 2009) and references therein) with positive matrix factorisation (PMF) analysis commonly employed. PMF is a very effective statistical method for environmental source apportionment analysis, which can apportion ambient concentration data to sources by identifying the intrinsic characteristics of the data, while limiting all the elements in the factor profiles and the factor loading matrix to positive values (Yuan et al., 2009). Therefore, the aim of this paper was to perform PMF analysis on all the VOC data collected at the Welgegund atmospheric monitoring station for more than two years in order to conduct a source apportionment study, which could substantiate sources identified with back trajectory and meteorological pattern analysis, and explorative statistical methods employed by Jaars et al. (2014) and Jaars et al. (2016). In addition, an exposure and risk assessment study was also performed in view of the major source regions affecting Welgegund in order to quantify the impacts of anthropogenic VOCs measured at Welgegund on human health. According to the knowledge of the authors, this is the first study in South Africa where PMF analysis is applied to long-term VOC measurements and the impacts of VOCs on health is assessed.

2 Experimental

2.1 Site description and measurement methods

Measurements were conducted at the Welgegund measurement station (26.57°S, 26.94°E, 1480 m a.s.l.) (Welgegund measurement station, 2016), which is located on a commercial maize and cattle farm approximately 100 km west of Johannesburg, as indicated in Fig.1. Welgegund is a regional background site with no sources in close proximity. It is, however, affected by the major pollutant source regions in the interior of South Africa, as well as a relatively clean western sector with no large point sources. It is also frequently affected by regional savannah and grassland fires (Vakkari et al., 2015). Detailed descriptions of the Welgegund atmospheric measurement station in view of geographical and bioregion location, meteorology and the major source regions affecting Welgegund were presented by Jaars et al. (2014) and Jaars et al. (2016), as well as in a number of papers published on atmospheric measurements conducted at Welgegund (Vakkari et al., 2015;Tiitta et al., 2014;Beukes et al., 2015;Räsänen et al.,

2016;Booyens et al., 2015;Kuik et al., 2015). In addition, Jaars et al. (2016) also presented a detailed land cover map indicating the typical vegetation surrounding the Welgegund station.

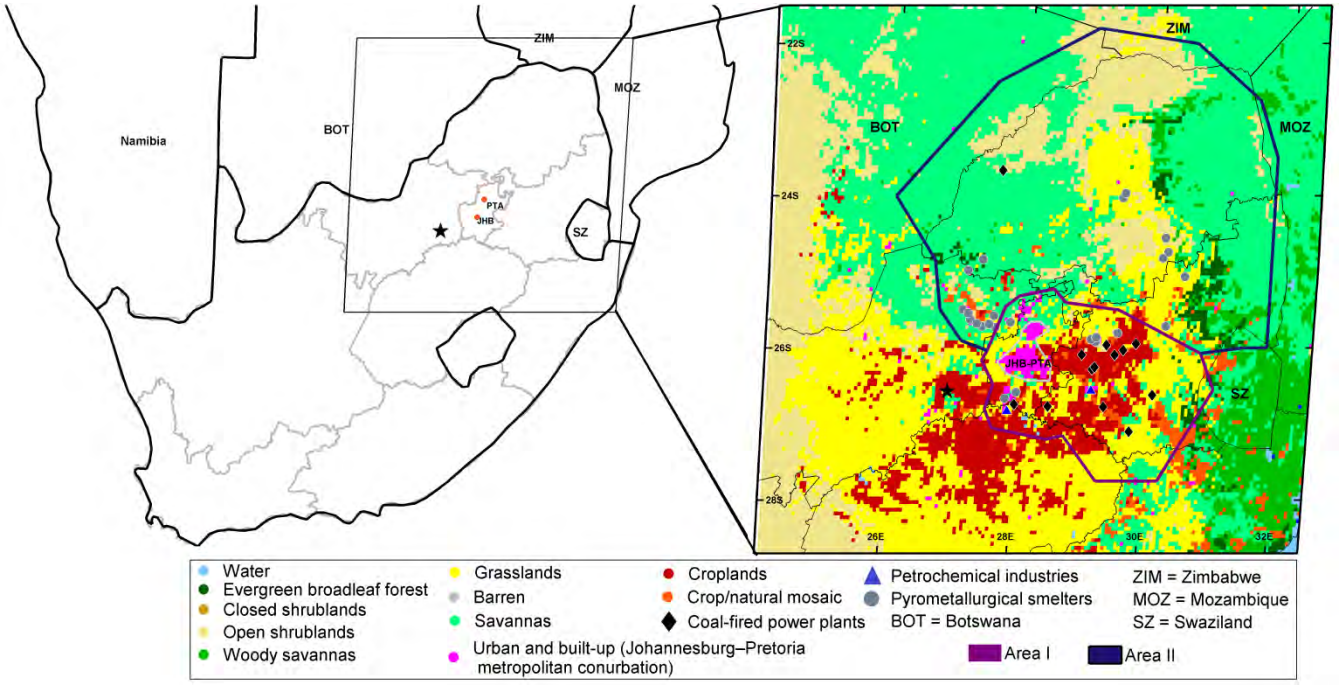

Fig. 1. On the left, a geographical map of southern Africa indicating the location of the Welgegund measurement station, as well as the JHB-PTA megacity. On the right is a map of the north-eastern part of South Africa indicating the International Geosphere-Biosphere Programme (IGBP) vegetation classification for southern Africa for 2010 based on MODIS collection 5 land cover type product (Friedl et al., 2002;Friedl et al., 2010;Scepan, 1999;Belward et al., 1999). Also on the left, the large point sources in the industrial hub of South Africa and the source regions defined are indicated.

Jaars et al. (2014) and Jaars et al. (2016) presented a detailed description on the VOC measurements. In short, VOC samples were collected at a height of 2 m above ground level, with a 1.75 m long inlet on Tenax-TA and Carbopack-B adsorbent tubes with an automated programmable sampler for a period of more than two years, i.e. a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. O_3 was also removed from the sample stream to prevent degradation of VOCs by heating the inlet. Samples were collected on Tuesdays and Saturdays each week for two hours during daytime (11:00 to 13:00 local time, LT) and

two hours during night-time (23:00 to 1:00 LT). The bias associated with the sampling schedule was realised. However, Jaars et al. (2014) indicated that considering the distance of the sampling site from the nearest town and logistical limitations during the sampling campaigns, the sampling schedule applied was the most feasible option. A total of ~395 samples were collected during the two sampling campaigns. Analysis of the collected VOC samples was performed with a thermal desorption instrument (Perkin-Elmer TurboMatrixTM 650, Waltham, USA) connected to a gas chromatograph (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 µm) column and a mass selective detector (Perkin-Elmer® Clarus® 600T, Waltham, USA).

Trace gas measurements were included in the PMF analysis in order to support the source apportionment of VOCs. Trace gas measurements were performed utilising a Thermo-Electron 43S sulphur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU nitrogen oxide (NO_x) analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 carbon monoxide (CO) analyser (Horiba, Kyoto, Japan).

2.2 Data analysis

2.2.1 Positive matrix factorisation (PMF) analysis

PMF analysis of the VOCs and trace gases was performed with the EPA PMF 5.0 program. The PMF method is described in literature (Paatero, 1997;Paatero and Tapper, 1994) and the principle of the model is explained here briefly. PMF is, in essence, a factor analysis tool that decomposes a data matrix into two matrices, i.e. factor contributions and factor profiles. The objective of PMF analysis is to identify a user-specified number of factors, which are regarded as pollution sources. The equation to be solved by PMF analysis is:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} , \quad (1)$$

where x_{ij} is the j^{th} species concentration in the i^{th} sample; g_{ik} is the particulate mass concentration from the k^{th} source contributing to the i^{th} sample; f_{kj} is the mass fraction of the j^{th} species from the k^{th} source; e_{ij} is the residual associated with the j^{th} species concentration, measured in the i^{th} sample; p is the total

number of independent factors. The results are constrained to ensure that there are no negative source contributions.

Each data point is individually weighted by utilising the estimated uncertainty for each species. In this study, the uncertainties for each sample were calculated by using measurement uncertainties (MU%) and minimum detection limits (MDL) in an equation-based uncertainty procedure described by Polissar et al. (1998). The conditional probability function (CPF) (Kim et al., 2003) was applied to the daily PMF dataset in order to estimate the impacts of sources from different directions. The CPF was calculated for each factor using relative source contributions and average wind directions for each sample – data collected on days with low wind speeds (<1 m/s) were removed from the dataset. CPF was calculated as follows:

$$CPF_{\theta} = \frac{m_{\theta}}{n_{\theta}}, \quad (2)$$

where m_{θ} is the number of average wind vectors (days) that fall in the wind sector θ that exceed the threshold criteria (80^{th} percentile), while n_{θ} is the total number of vectors occurring in the same wind sector. The largest peak contributions in the time series were then selected for each factor for further analysis. If several factors were peaking at the same time, the largest peak was selected. In many cases, the CPFs of the factors showed quite mixed wind direction contributions, which were in particular the case for biogenic factors, where the source is located in close proximity to the station and the source direction is not evident.

2.2.2 Risk assessment

The Risk Assessment Guidance for Superfund (RAGS) Volume I: Human Health Evaluation Manual part F, Supplemental Guidance for Inhalation Risk Assessment (USEPA, 2009) was used as a guideline to estimate the nature and the possibility of adverse health effects of each VOC in plumes that have passed over the source regions identified by Jaars et al. (2014) (Fig. 1) or reported in other studies. Risk probability values, i.e. inhalation reference concentration (RfC) and unit risk (UR) were obtained through the risk model calculator established by the University of Tennessee ((RAIS, 2016) and reference therein), by giving priority to the most recent available data and are listed in Table 1. The

impacts of VOCs on human health were assessed by estimating the non-carcinogenic and carcinogenic risks. The hazard ratio (HR) of each compound was calculated by Eqs. (3) and (4) in order to estimate the non-carcinogenic influence as follows:

$$HR = \frac{EC}{RfC}, \quad (3)$$

$$EC = \frac{CA \times ET \times EF \times ED}{ED \times 365\left(^{days}/_{year}\right) \times 24\left(^{hours}/_{day}\right)}, \quad (4)$$

where EC is the exposure concentration (μg m^{-3}); RfC (μg m^{-3}) corresponding to a specific compound (Table 1); CA is the concentrations (μg m^{-3}) of each VOC in plumes that have passed over the source regions identified or reported in other studies; ET is the exposure time (hours day^{-1}); EF is the exposure frequency (days $year^{-1}$); and ED is the exposure duration (years).

Table 1. Non-cancer reference concentrations, cancer unit risks of the VOCs found during the campaigns and their carcinogenic classifications in the IARC at Welgegund. Risk probability values (inhalation reference concentration and unit risk) were obtained through the risk model calculator, established by the University of Tennessee ((RAIS, 2016) and reference therein), by giving priority to the most recent available data.

	Non-cancer			Cancer		
	RfC (μg m^{-3})	Source	MW (g mol^{-1})	Group IARC	UR (μg m^{-3})$^{-1}$	Source
Benzene	9.6	ATSDR	78.11	1	6.00E-06	WHO
Toluene	3770	ATSDR	92.14	3	-	-
Ethylbenzene	1300	ATSDR	106.17	2B	2.50E-06	CALEPA
(m,p)-xylene	217	ATSDR	106.17	3	-	-
Styrene	850	ATSDR	104.15	2B	-	-
o-xylene	217	ATSDR	106.17	3	-	-
Propylbenzene	100	PPRTV	120.1916	-	-	-
3-ET	n.a.	-	120.1916	-	-	-
4- ET	n.a.	-	120.1916	-	-	-

Table 2. Continued.

1,3,5-TMB	6	PPRTV	120.1916	-	-	-
2- ET	n.a.	-	120.1916	-	-	-
1,2,4-TMB	7	PPRTV	120.1916	-	-	-
1,2,3-TMB	5	PPRTV	120.1916	-	-	-
2,2,4-TMP	n.a.	-	114.23	-	-	-
heptane	n.a.	-	100.21	-	-	-
hexane	700	IRIS	86.175	-	-	-
2-MP	n.a.	-	86.175	-	-	-
octane	n.a.	-	114.229	-	-	-
nonane	20	PPRTV	128.26	-	-	-

Agency for Toxic Substances and Disease Registry (ATSDR); Integrated Risk Information System (IRIS); Provisional Peer Reviewed Toxicity Values (PPRTV); California Environmental Protection Agency (CALEPA) Office of Environmental Health Hazard Assessment (OEHHA); World Health Organization (WHO). TMP = trimethylpentane, MP = methylpentane

The lifetime cancer risk (LCR) was calculated in order to determine the number of individuals likely to acquire cancer due to their exposure to the VOCs of concern from inhalation intake as follows:

$$LCR = UR \times \frac{CA \times ET \times EF \times ED}{LT \times 365\left(^{days}/_{year}\right) \times 24\left(^{hours}/_{day}\right)}, \quad (5)$$

where UR is the estimated unit risk value (μg^{-1} m^3) (Table 1) and LT is the lifetime expectancy (years).

The assumptions made by Paralovo et al. (2016) were used as a reference in calculating the LCR and HR values: ED of 25 years (assuming that a resident lives 25 years at the same place on average); the average LT of South Africans is 60 years; EF of 350 days in a year (if we assume that a person spends on average 15 days a year outside the area that they live); and ET of 15 h per day.

3 Results and discussion

3.1 General characteristics of VOC concentrations

In Table 2, the median (mean) and inter-quartile range (IQR, 25^{th} to 75^{th}) concentrations of all the VOCs determined during the two campaigns at Welgegund are summarised that were used for PMF and risk assessment analysis in this paper. The aromatic hydrocarbon concentrations measured during the

first campaign and the BVOC concentrations measured during both campaigns have been presented and discussed in detail by Jaars et al. (2014) and Jaars et al. (2016), respectively. It is evident that during the first campaign the most abundant VOCs were toluene, styrene and (*m,p*)-xylene with an annual median (IQR) concentration of 0.63 (0.46-1.07), 0.66 (0.46-1.00) and 0.50 (0.36-0.85) ppbv, respectively. During the second campaign, the most abundant compounds were toluene and (*m,p*)-xylene with annual median (IQR) concentration of 5.43 (3.53-7.83) and 1.25 (0.91-1.79) ppbv, respectively. The total median (mean) concentrations of VOCs measured during the first campaign were 3.23 (5.17) ppbv of which aromatics accounted for 82%, alkanes for 14% and biogenics for 4%, while the total median (mean) concentrations of VOCs concentration during the second campaign were 9.13 (22.18) ppbv of which 88%, 11% and 1% were aromatics, alkanes and biogenics, respectively. It is evident that the contributions of aromatic species to the total VOC levels were significantly higher compared to the other compounds measured at Welgegund. It is also noticeable that total VOC concentrations measured during the second campaign were higher than the first campaign, which can be mainly attributed to the higher concentrations of toluene, ethylbenzene and *(m,p)*-xylene measured during the second campaign. Higher concentrations of these species can be ascribed to more air masses moving over the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld source regions (Fig. 1 and 2). Heptane and decane were the most abundant alkane species during the first campaign, with concentrations similar to that of benzene. During the second campaign, hexane was the most abundant alkane. The total alkane concentrations were approximately five times lower than the levels of aromatic compounds, while BVOC concentrations were an order of magnitude lower compared to aromatic species concentrations (Jaars et al., 2016).

Table 2. Summary of VOC concentrations measured at Welgegund.

	First campaign		Second campaign	
	Median (Mean)	IQR (25th - 75th)	Median (Mean)	IQR (25th - 75th)
Aromatics (ppbv)				
Benzene	0.13 (0.29)	0.9-0.22	0.1 (0.11)	0.03-0.16
Toluene	0.63 (0.89)	0.46-1.07	5.43 (8.59)	3.53-7.83
Ethylbenzene	0.25 (0.34)	0.18-0.40	0.78 (2.04)	0.56-1.16
(*m*,*p*)-xylene	0.50 (0.77)	0.36-0.85	1.25 (5.80)	0.91-1.79
styrene	0.66 (0.83)	0.46-1.00	0.60 (0.72)	0.43-0.84
o-xylene	0.20 (0.30)	0.14-0.35	0.40 (1.82)	0.30-0.57
Propylbenzene	0.01 (0.04)	0.01-0.02	0.02 (0.06)	0.01-0.03
3-ET	0.03 (0.11)	0.03-0.07	0.11 (0.15)	0.08-0.17
4-ET	0.01 (0.05)	0.01-0.03	0.008 (0.02)	0.004-0.02
1,3,5-TMB	0.02 (0.08)	0.01-0.04	0.006 (0.027)	0.003-0.01
2- ET	0.02 (0.10)	0.01-0.05	0.008 (0.024)	0.004-0.02
1,2,4-TMB	0.07 (0.30)	0.05-0.17	0.029 (0.096)	0.02-0.05
1,2,3-TMB	0.03 (0.15)	0.02-0.08	0.008 (0.026)	0.004-0.02
Alkanes (ppbv)				
2,2,4-Trimethylpentane	0.01 (0.01)	0.003-0.01		
Heptane	0.21 (0.23)	0.13-0.29	0.08 (0.17)	0.05-0.11
Hexane	0.05 (0.08)	0.03-0.08	0.05 (1.83)	0.05-1.02
2-Methylpentane	0.02 (0.03)	0.02-0.04		
Octane	0.07 (0.08)	0.05-0.09	0.06 (0.16)	0.04-0.09
Nonane	0.04 (0.04)	0.02-0.02	0.05 (0.19)	0.02-0.11
Decane	0.13 (0.20)	0.08-0.26	0.07 (0.16)	0.03-0.11
Biogenics (pptv)				
Isoprene	14 (28)	6-35	14 (23)	7-24
2-Methyl-3-buten-2-ol	7 (12)	3-16	4 (8)	3-10
α-Pinene	37 (71)	28-83	15 (57)	9-23
Camphene	4 (8)	2-9	2 (4)	1-3
β-Pinene	9 (19)	5-48	3 (5)	2-6
Limonene	21 (30)	9-40	16 (54)	9-36
Terpinolene	4 (14)	3-11	22 (28)	16-34
ΣMonoterpenes	119 (215)	74-217	62 (152)	39-110
ΣSesquiterpenes	2 (6)	1-6	2 (3)	1-3

Table 2. Continued.

ΣAromatics (ppbv), (%)	2.57 (82)	1.83-4.43	8.75 (88)	5.89-12.66
ΣAlkanes (ppbv), (%)	0.52 (14)	0.32-0.81	0.29 (11)	0.19-1.44
ΣBiogenics (ppbv), (%)	0.14 (4)	0.08-0.27	0.08 (1)	0.05-0.15
Total VOCs, unit (%)	3.23 (5.17)	2.24-5.43	9.13 (22.18)	6.13-14.25

3.2 Positive matrix factorisation (PMF) analysis

In addition to the VOC data, continuous trace gas measurements, i.e. SO_2, NO_x, CO and O_3 were also included for the receptor modelling. The datasets collected during the first (February 2011 to February 2012) and second (December 2013 to February 2015) campaign were labelled (A) and (B), respectively. A critical first step in PMF source apportionment methods is to determine the number of meaningful factor solutions. In this study, five to 12 factor solutions were tested for both datasets in order to obtain meaningful solutions by taking into consideration the known environmental surroundings with regard to biogenic and anthropogenic sources affecting Welgegund (Jaars et al., 2014; Jaars et al., 2016). Certain species, which included mainly sesquiterpenes, were excluded or down-weighted, mainly because of the low reliability and noise in the data attributed to low concentrations of these species. Outliers were also examined and down-weighted according to the model residual analysis. Ten meaningful factor solutions providing a good fit to the data were obtained for both datasets, which are listed in Table 3 together with the main tracer species corresponding to each factor. Five factors, i.e. isoprene (F1), limonene (F2), biogenic emission 1 (F4) and 2 (F5), and 2-methyl-3-buten-2-ol (MBO) (F6) were associated with biogenic emissions, while five factors corresponded to anthropogenic sources, i.e. traffic/savannah fires/long-range transport (LRT) (F3), TEX (toluene, ethylbenzene, xylenes) (F7), aromatics (F8), diesel sources (F9) and coal combustion (F10). In Fig. 2, the relative factor loadings, the factor contributions and the main wind directions associated with each factor are presented.

Table 3. Identified factors and the corresponding tracer species identified with PMF.

	Factor	Name of the factor	Main tracers
First campaign Dataset A	F1A	Isoprene	Isoprene
	F2A	Limonene	Limonene
	F3A	Traffic/savannah fires/LRT	O_3,NO, NO_2, NO_x , CO, 2,2,4-Trimethyl pentane and Benzene
	F4A	Biogenic emission 1	α-Pinene, β-Pinene, Δ^3-Carene
	F5A	Biogenic emission 2	Terpinolene, β-Pinene, Δ^3-carene and 1,8-cineol
	F6A	MBO	MBO
	F7A	TEX	Toluene, Ethylbenzene, (*m,p)*-Xylene and *o*-Xylene
	F8A	Aromatics	Propylbenzene, 3-ET, 4-ET, 1,3,5-TMB, 2-ET, 1,2,4-TMB, 1,2,3-TMB
	F9A	Diesel source	Nonane and Decane
	F10A	Coal combustion	SO_2 and NO_x
Second campaign Dataset B	F1B	Isoprene	Isoprene
	F2B	Limonene	Limonene
	F3B	Traffic/savannah fires/LRT	NO_2, NO_x , NO, CO, O_3, 2,2,4-Trimethylpentane,Benzene and 1,8-Cineol
	F4B	Biogenic emission 1	α-Pinene, Camphene and p-Cymene
	F5B	Biogenic emission 2	Terpinolene, β -Pinene, Δ^3-Carene, 1,8-Cineol, Heptane
	F6B	MBO	MBO
	F7B	TEX	Toluene, Ethylbenzene, (*m,p)*-Xylene and *o*-Xylene
	F8B	Aromatics	3-ET, 4-ET, 1,3,5-TMB, 2-ET, 1,2,4-TMB, 1,2,3-TMB
	F9B	Diesel source	Nonane and decane
	F10B	Coal combustion	SO_2 and NO_x

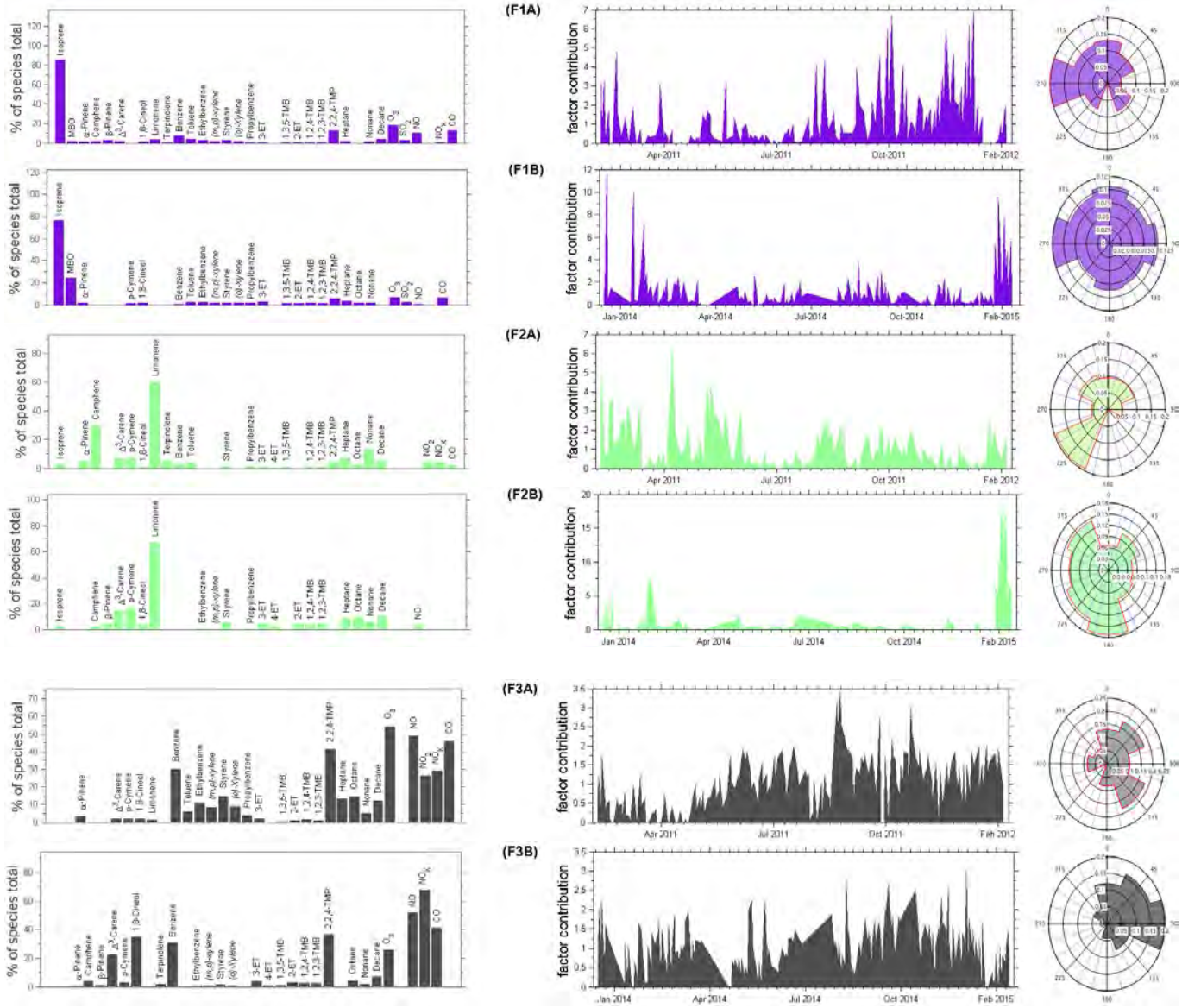

Fig. 2. The factor loadings determined for the first (F1A-F10A) and second campaign (F1B-F10B) (left), the relative factor contributions (centre), and wind roses for each factor (right).

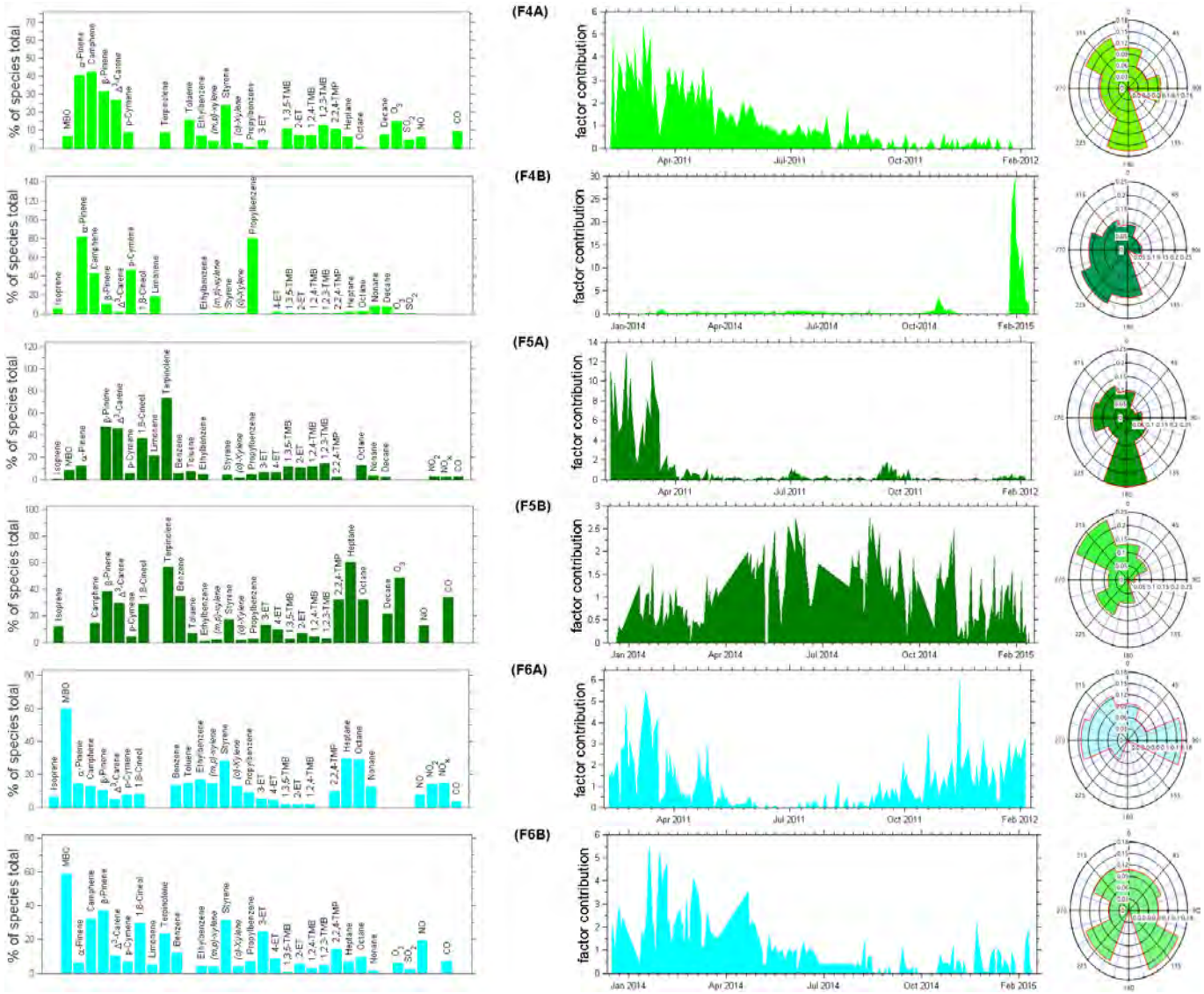

Fig. 2. Continued.

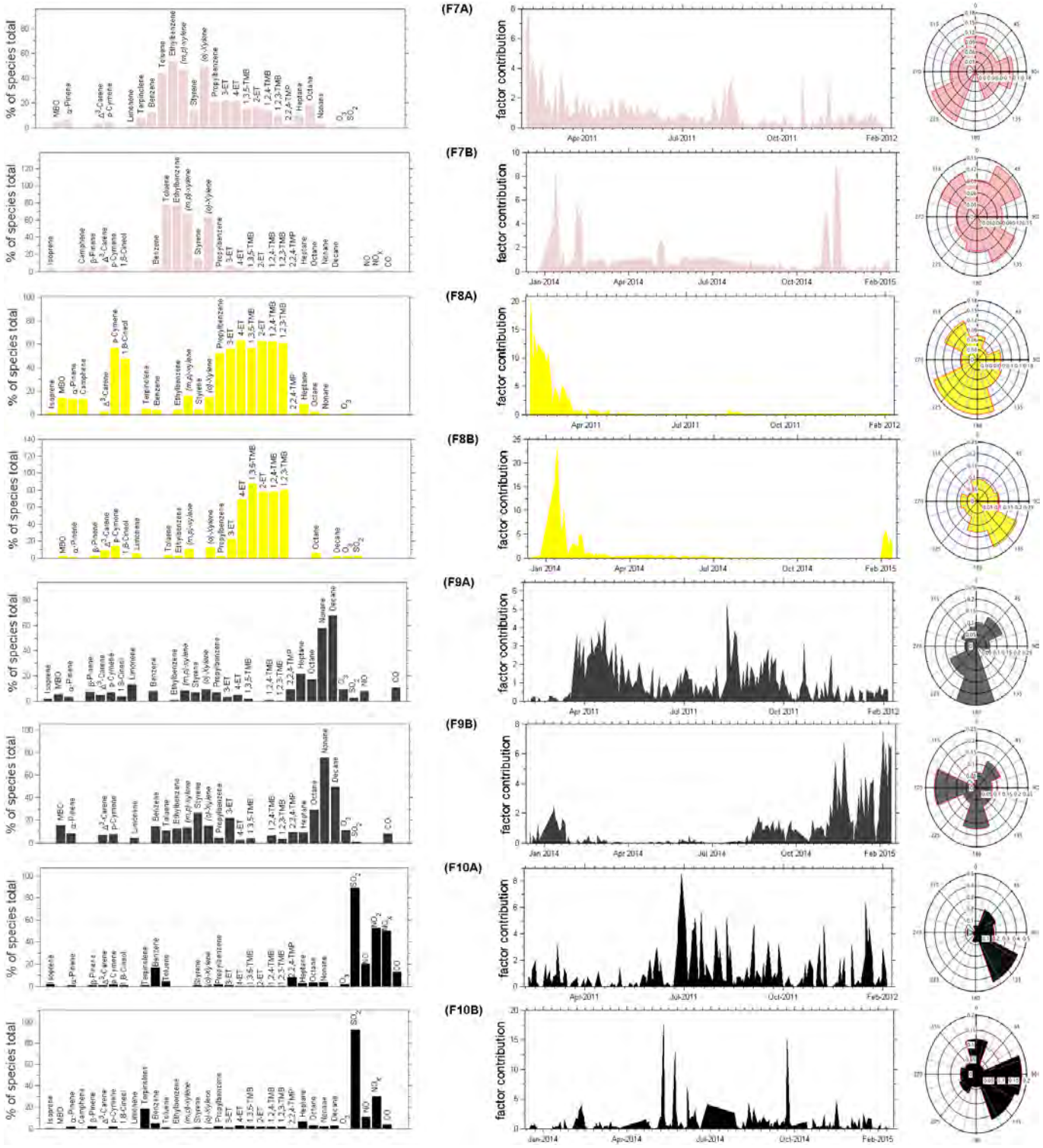

Fig. 2. Continued.

Three factors were identified that were dominated by one specific biogenic species, i.e. isoprene, limonene and MBO, which were therefore considered to represent each of these species. In factor F1, isoprene accounted for 86 and 77% of the variations in F1A and F1B, respectively. Limonene was the predominant species in factor F2, with loadings of 60 and 67% calculated for campaigns (A) and (B), respectively. MBO accounted for 60 and 59% of the loadings in factors F6A and F6B. Relatively notable contributions were made by MBO to F1B (isoprene), while camphene also contributed to factor F2B (limonene). In the MBO factor, relatively significant contributions were also made from a few other VOCs. From the wind roses determined for these three factors, it seems that isoprene was higher from the western direction, while limonene was higher from the south-western sector. In addition, wind roses compiled for the MBO factor F6A indicated more sources of species associated with this factor from an easterly direction that also correlated with higher concentrations of VOCs associated with anthropogenic activities in this region (Fig. 1). However, in general, wind direction did not indicate significant differences in the contributions of these three factors from different directions. The factor contributions of these three factors did correlate relatively well with the wet season (Jaars et al., 2016), with, especially, the MBO factor indicating a relatively strong seasonal pattern as was indicated by the temporal variation presented by Jaars et al. (2016), i.e. higher BVOC concentrations associated with the wet season.

Factors F4 and F5 comprised a mixture of loadings of biogenic species with α-pinene, β-pinene, Δ^3-carene and p-cymene the main tracer species in F4, while terpinolene, β-pinene, Δ^3-carene and 1,8-cineol were the main tracer species in F5. In Factor 4A, α-pinene, β-pinene and Δ^3-carene accounted for 42, 40 and 32% of the variations, respectively, while α-pinene contributed to 81% of the factor load in F4B. Terpinolene, β-pinene, Δ^3-carene and 1,8-cineol accounted for 73, 47, 46% and 37 % variations in factor F5A, while in factor F5B terpinolene, β-pinene and 1,8-cineol contributed to 57, 38 and 29% of the factor load, respectively. These two biogenic factors were also characterised by high loadings of species associated with anthropogenic activities, i.e. styrene and propylbenzene in factor F4, and heptane, benzene, octane and 2,2,4-trimethylpentane (isooctane) in factor F5. The association with these anthropogenic VOCs indicates that these biogenic emissions coincided with anthropogenic activities.

As mentioned previously, Welgegund is situated on a commercial maize and cattle farm. Therefore, everyday farming activities in close proximity of Welgegund will contribute to anthropogenic impacts. The anthropogenic VOCs in factor F5 are usually associated with vehicular emissions. The factor contributions for these two factors did not indicate a clear seasonal pattern. The wind roses for factors F4 and F5 indicate that these factors originate predominately from the southern to north-western sector, with a very small contribution of these factors from the northern to south-eastern sector where the predominant anthropogenic source regions are situated (Fig. 1). This also signifies that anthropogenic VOCs present in these factors are predominantly associated with local farming activities. In general, the biogenic factors determined with PMF indicate that Welgegund is affected by biogenic emissions from all directions, as indicated by Jaars et al. (2016).

Factor F3 was considered to be characterised by species typically associated with traffic emissions, with high loadings of NO_x, CO, 2,2,4-trimethyl pentane (isooctane) and benzene. In addition, factor F3 was also considered to represent wild fires as reflected by the NO_x and CO loadings, as well as the long-range transport (LRT) of polluted air masses as indicated by the high O_3 loading, especially during the first campaign. O_3 is a secondary pollutant that is usually indicative of aged air masses. The wind roses compiled for factor F3 indicated that these factor loadings originate predominantly from the north-eastern to south-eastern sector, wherein the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld source regions are located, which was categorised as the Area I source region by Jaars et al. (2014) (Fig. 1). Therefore, increased impacts of traffic emissions are expected for winds originating from this densely populated region. In this source region, household combustion could also be an additional source of species in factor F3. Jaars et al. (2014) also attributed incomplete combustion sources (e.g. vehicular emissions, wild fires and household combustion) in Area I as dominant sources of benzene.

Relatively high loadings of NO_x, NO_2 and NO, typically associated with traffic emissions and wild fires, were also observed for factor F10. However, the SO_2 load, which was not present in Factor F3, accounted for approximately 90% of the variation in this factor. In addition, significantly lower loadings of CO and O_3 were determined in factor F10. Therefore, this factor was considered to represent coal combustion. The wind roses compiled for factor F10 also indicate a predominant influence from the

source region Area I where nine coal-fired power stations and a petrochemical plant are situated (Fig. 1). Wind roses compiled for the second campaign (F10B) also indicate this factor originating from the northern sector, which was classified as Area II by Jaars et al. (2014). This area holds a large number of pyrometallurgical smelters (Fig. 1). Area II also holds the anti-cyclonic source regions that lie on the anti-cyclonic recirculation path of air masses moving towards Welgegund. Wind roses compiled for factor F3 also indicated some impacts from the north, which are therefore also reflected by the O_3 factor loading. No distinct seasonal pattern is observed from the factor contributions of these factors.

Factors F7 and F8 comprised a mixture of loadings of the aromatic VOCs. Factors F7A and F7B contained predominantly factor loadings from toluene (44 and 77%), ethylbenzene (53 and 76%) and xylenes (*(m,p)*-xylene: 47 and 66%; *o*-xylene: 49 and 63%)(TEX), while the main tracer species in F8A and F8B were 3-ethyltoluene (56 and 22%), 4-ethyl toluene (63 and 69%), 1,3,5-trimethylbenzene (57 and 88%), 2-ethyltoluene (63 and 78%), 1,2,4-trimethylbenzene (62 and 68%), 1,2,3-trimethylbenzene (61 and 80%). Relatively higher factor loadings are also observed from propylbenzene (52%), as well as the biogenic species p-cymene (57%) and 1,8-cineol (47%) in F8A. It is generally deliberated that TEX species are the primary constituents of organic paints, and are regarded as chemical tracers of solvent utilisation (Choi et al., 2011;Watson et al., 2001;Guo et al., 2004). Therefore, factor F7 was considered to represent VOC emissions from solvent utilisation. The factor contributions for factor F7 indicate the highest contributions of these species during the warm summer months. Jaars et al. (2014) also indicated that the TEX/total aromatic concentrations had maximum values in summer, while the average temperatures measured during the sampling period also followed a similar pattern than the TEX concentration ratios. Therefore, the factor contribution for factor F7 also signifies that higher TEX concentrations are associated with higher contributions of solvents during the summer. The wind roses compiled for factor F7 did not indicate that this factor originated predominantly from specific regions with factor F7 occurring in all wind directions. Jaars et al. (2014) also indicated that the TEX compounds originated from air masses that had passed over all three source regions, including the regional background (Fig. 1). The concentrations of the aromatic VOCs characterising factor F8 were significantly lower compared to the concentrations of the other aromatic VOC species, i.e. the BTEX compounds (Table 2). The wind roses compiled for factor F8 indicate this factor originating

predominantly from the south-eastern to north-western sectors, i.e. the regional background classified by Jaars et al. (2014) (Fig. 1). Therefore, local sources, such as general farming activities and local vehicular emissions could be considered the major sources of factor F8. The factor contribution from this factor was relatively high during February 2011 to March 2011 and December 2013 to February 2014.

The main tracer species in Factor F9 were nonane and decane, with relatively higher loadings also from heptane (F9A) and octane (F9B). In factor F9A, decane and nonane accounted for 68 and 58% of the variations, respectively, while in factor F9B, decane and nonane contributed to 50 and 75% of the factor load, respectively. Nonane and decane are typically good tracers for diesel exhaust emissions (Watson et al., 2001;Song et al., 2007;Liu et al., 2008), and therefore this factor was considered to represent diesel emissions. Wind roses reveal that this factor originated predominantly from the south-south-eastern to the west-north-western sector, which is part the regional background (Fig. 1). The main diesel sources in this region can be considered to be local and regional farming activities, which include pick-up trucks, tractors, electricity generators and other diesel engines typically used on farms. Although the wind roses also indicate factor F9 originating from the major anthropogenic source regions from the north-east, it can be assumed that these diesel emissions can also be attributed to local and regional farming activities. Although very low factor contributions are observed for factor F9B form March 2014 to August 2014, the temporal factor contributions did not indicate any significant seasonal pattern for diesel emissions. This period of low diesel emissions affecting Welgegund could be related to periods of decreased farming activity or less frequent impacts by winds blowing from areas where diesel sources are operated.

3.3 Risk assessment

3.3.1 Air masses passing over source regions

The risk assessment study was performed in relation to the source regions identified by Jaars et al. (2014), i.e. Area I, Area II and regional background as indicated in Fig. 1. Back trajectory analyses were performed in order to determine air masses passing over the different source regions during the two campaigns, which are presented in Fig. 3. Jaars et al. (2014) showed that for the first campaign, 39% of

the VOC samples were collected during periods when air mass back trajectory sets had passed over Area II, while 33 and 14% of VOC samples were collected when air mass back trajectory sets passed over the regional background and Area I, respectively. Back trajectory analysis performed for the second campaign indicated that 51, 23 and 8% of VOC samples were collected when air masses passed over Area II, the regional background and Area I, respectively. Jaars et al. (2014) attributed the lower percentage of air masses passing over Area I to the persistence of the anticyclonic circulation pattern over the interior of South Africa, which favours the arrival of air masses at Welgegund from the north to north-eastern sector.

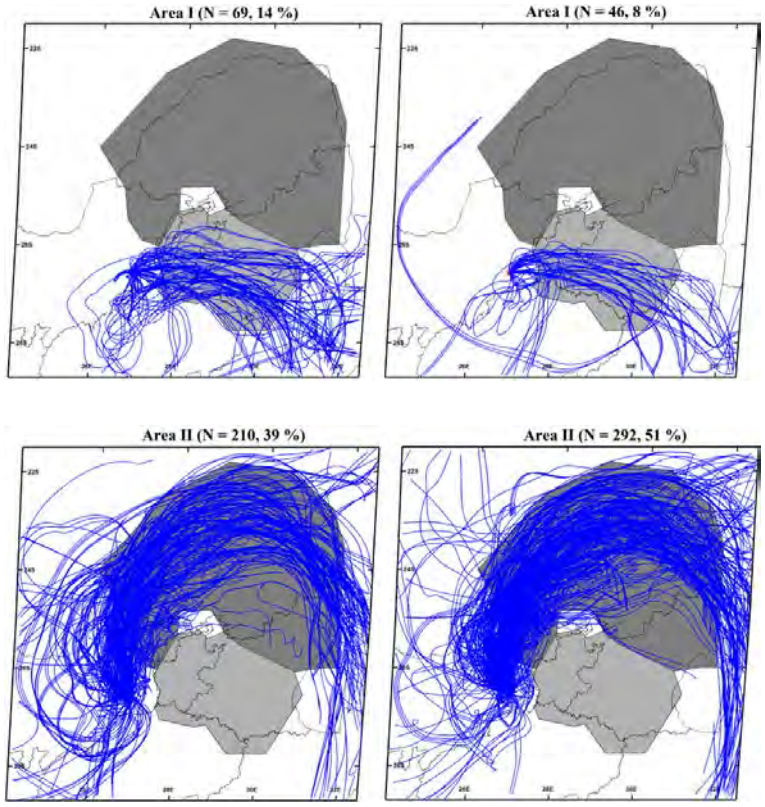

Fig. 3. Graphical representations of back trajectories allocated as passing over the defined source regions during the first (left) and second (right) campaign. The percentage of the trajectories allocated as passing over a specific source region and the number of trajectories it represents are provided in brackets..

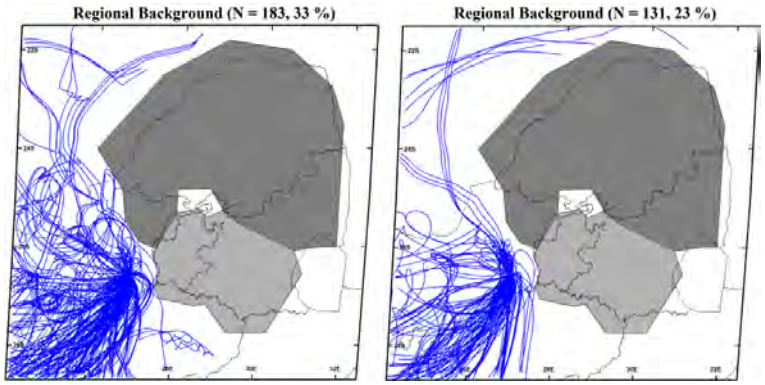

Fig. 3. Continued.

3.3.2 Non-cancer risk assessment

Twelve of the 20 anthropogenic VOCs quantified in this study had RfC values that could be obtained from literature (Table 1) that could be used to calculate HRs from which non-cancer effects could be estimated. In Fig. 4, box and whisker plots of the HRs associated with the concentrations of each of the VOCs (with RfC values) in air masses that passed over the different source regions during both campaigns are presented. The red line of each box indicates the median, the black squares the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ (99.3% coverage if the data have a normal distribution) and the red circles HR values not included in the range of the box and whisker plot. The green lines in Fig. 4 (a) and (b) indicate the level of concern threshold HR value, i.e. 1.

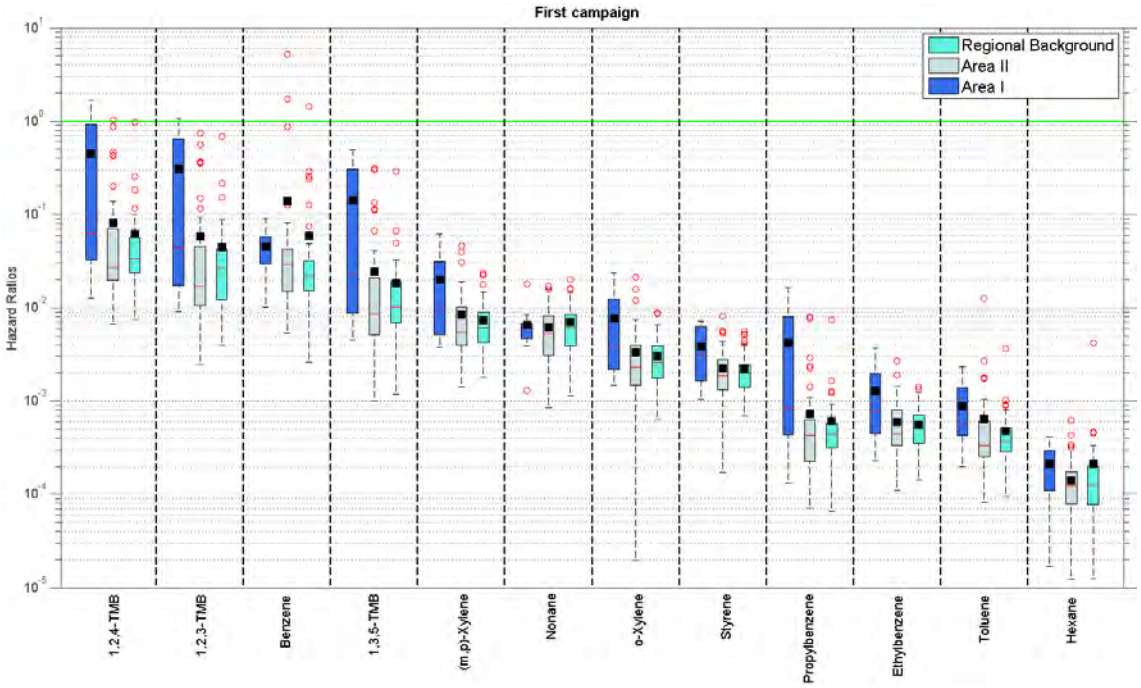

Fig. 4. Box and whisker plots of HR values calculated for concentrations of each of the VOC levels in air masses passing over the three source regions identified during the first and second campaign. The red line of each box indicates the median, the black squares the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ (99.3% coverage if the data have a normal distribution) and the red circles HR values not included in the range of the box and whisker plot.

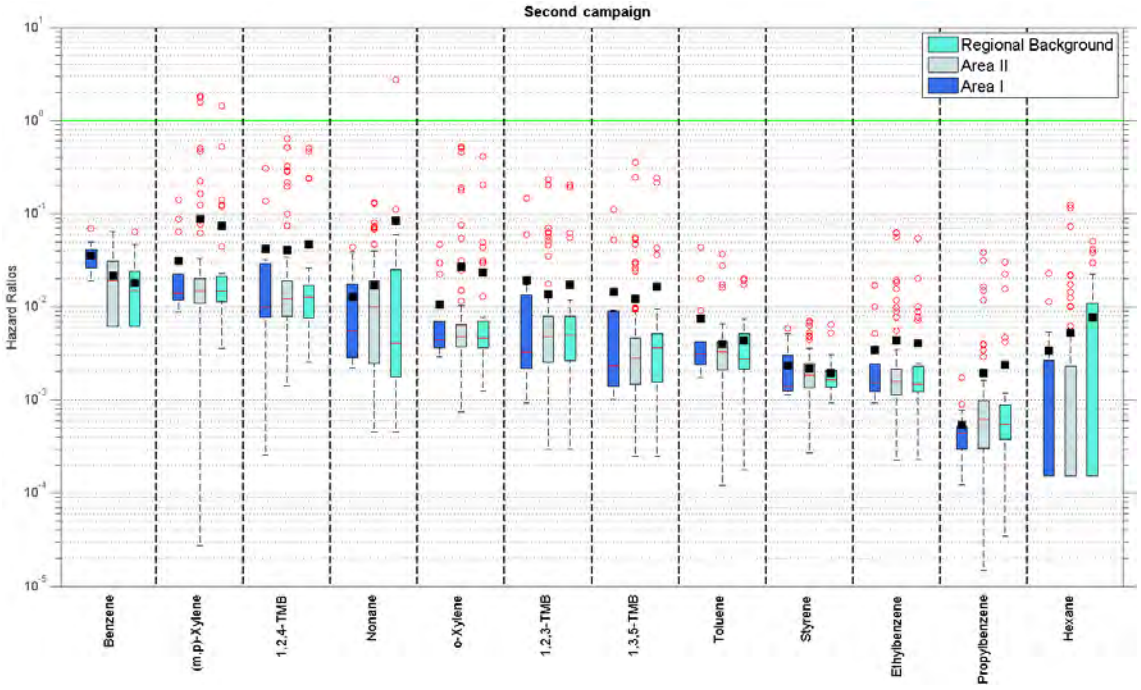

Fig. 4. Continued.

It is evident from Fig. 4 that during both sampling campaigns the calculated HRs for all VOCs occurring in air masses passing over all three source regions was well below the level of concern threshold, with the exception of a few occurrences. The median and average HR values calculated for the VOCs in air masses passing over all three source regions were in general significantly lower than the threshold value of 1. During the first campaign, the whiskers of the box and whisker plot of the HRs calculated for 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene exceeded the threshold value in air masses passing over Area I, while there was one occurrence of the HR of 1,2,4-trimethylbenzene in air masses passing over Area II exceeding the value of 1. Benzene HR values exceeded the level of concern threshold once and twice in air masses passing over the regional background and Area II, respectively. During the second campaign, HRs of *(m,p)*-xylene exceeded the threshold value three times and once in air masses passing over Area II and the regional background, respectively, while nonane exceeded that level of concern threshold values once in air masses passing over the regional background. The highest HR values were calculated for 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene during the first campaign, with average HR values higher than 0.1, while the average HR of benzene calculated for air masses passing

over Area II were also higher than 0.1. These relatively high average HR values calculated for these species could be indicative of a potential future concern (McCarthy et al., 2009). Furthermore, 1,2,3- and 1,2,4-trimethylbenzene are currently not included as hazardous organic pollutants in the WHO Air Quality Guidelines (WHO, 2000) or the USEPA list of Hazardous Air Pollutants (USEPA, 1994). This study indicates that in future research more attention could be given to these two compounds.

In Table 4, the HR values calculated for the average VOC concentrations determined in other studies conducted in the Highveld, JHB-PTA megacity and the Vaal Triangle in South Africa are presented. From the average HRs values listed in Table 4, it is evident that HRs of toluene, ethylbenzene and xylenes were also significantly lower than the level of concern threshold, with average HR values similar to average HRs determined in this study. The average HR values of benzene were 0.18, 0.4 and 0.36 in the Highveld, JHB-PTA megacity and the Vaal Triangle, respectively. Although these values are well below the threshold value, these HRs can also be indicative of potential future concern, especially the HRs calculated for the polluted JHB-PTA megacity and the Vaal Triangle. The average benzene HR in the Highveld is similar to the benzene average HR determined for benzene in air masses passing over Area II.

Table 4. The HR and LCR values calculated for other VOC studies conducted in South Africa.

	Lourens et al. (2011) (Highveld)			Lourens (2012) (Jhb-Pta megacity)			van der Walt (2008)		
	Average (µg m-3)	HR	LCR	Average (µg m-3)	HR	LCR	Average (µg m-3)	HR	LCR
Benzene	2.8	1.8E-01	4.2E-06	6.5	4.0E-01	9.7E-06	5.7	3.6E-01	8.6E-06
Toluene	3.9	6.3E-04		12.1	1.9E-03				
Ethylbenzene	0.8	3.8E-04	5.1E-07	2.0	9.0E-04	1.2E-06			
(m,p)-xylene	1.1	3.1E-03		9.0	2.5E-02				
o-xylene	0.7	1.8E-03							

3.3.3 Cancer risk assessment

Only benzene and ethylbenzene had UR values in literature (Table 1) that could be used to calculate LCRs from which cancer effects could be estimated. In Fig. 5, box and whisker plots of the LCRs associated with the concentrations of benzene and ethylbenzene in air masses that passed over the different source regions during both campaigns are presented. The red line of each box indicates the median, the black squares the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ (99.3% coverage if the data have a normal distribution) and the red circles LCR values not included in the range of the box and whisker plot. The green line indicates the acceptable LCR threshold value of 1×10^{-6}, i.e. one person in a million, recommended for adults by USEPA (USEPA, 2009b; Robson and Toscano, 2007).

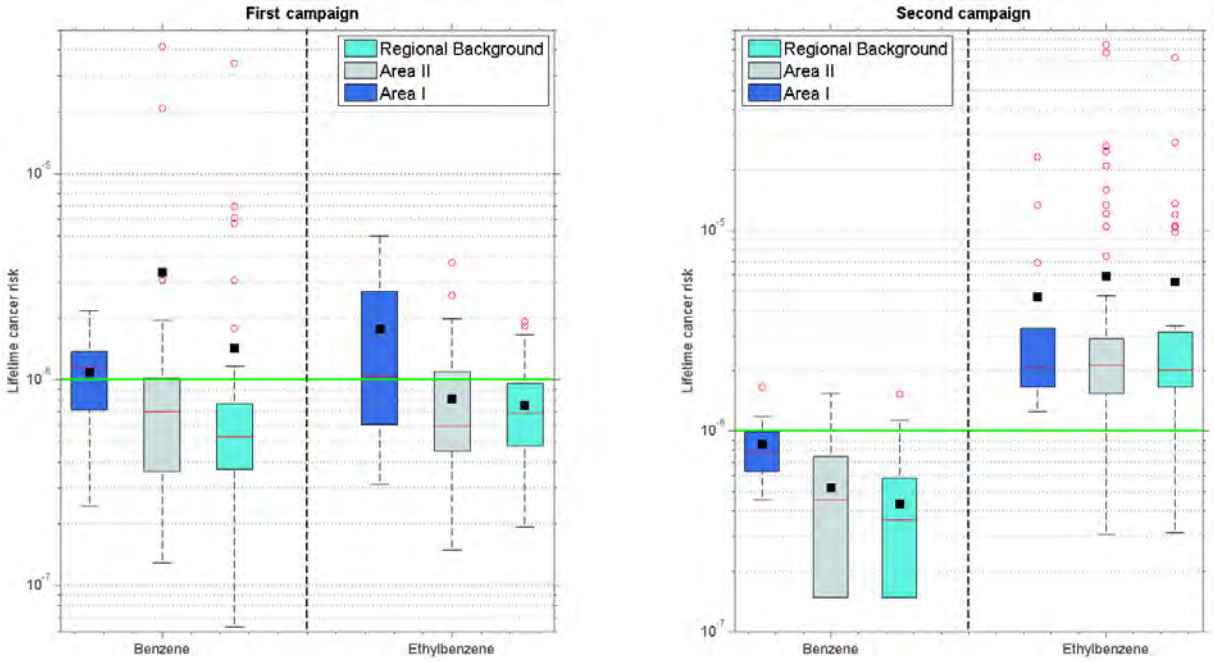

Fig. 5. Box and whisker plots of LCR values calculated for concentrations of benzene and ethylbenzene in air masses passing over the three source regions identified during the first and second campaign. The red line of each box indicates the median, the black squares the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ (99.3% coverage if the data have a normal distribution) and the red circles LCR values not included in the range of the box and whisker plot.

During the first campaign, the median and average LCR values calculated for benzene and ethylbenzene in air masses passing over Area I exceeded the LCR threshold value, while the 75th percentiles of LCR values of these compounds in air masses passing over Area II

exceeded this threshold. The average LCR value of benzene in air masses passing over Area II and the regional background also exceed the threshold value. For the regional background, the whiskers of the box and whisker plot of LCR values of benzene and ethylbenzene were higher than 1×10^{-6} during the first campaign. During the second campaign, the 75th percentile of LCR values calculated for benzene in air masses passing over Area I, as well as the whiskers of the box and whisker plot of LCR values determined for benzene in air masses passing over Area II and the regional background exceeded the acceptable threshold value. Almost all the LCR values calculated for ethylbenzene during the second campaign in air masses passing over all three source region exceeded the threshold, with the average and mean LCR values significantly higher than 1×10^{-6}. The cumulative cancer risks associated with benzene and ethylbenzene in air masses passing over the different source regions were determined by totalling the average LCR values of these compounds. From these calculations, the cumulative cancer risks during the first campaign were estimated to induce cancer development in 2.9, 4.1 and 2.2 people in one million during a lifetime in Area I, Area II and the regional background, respectively. The cumulative cancer risks determined during the second campaign estimated the inducement of cancer development in 5.5, 6.4 and 6 people in one million during a lifetime in Area I, Area II and the regional background, respectively. According to the Guidance on Risk Assessment for Air Contaminant Emission, a cancer development risk lower or equal to one person in a million (1×10^{-6}) can be considered negligible, while cancer development risks higher than one person in ten thousand (1×10^{-4}) are considered unacceptable (NJDEP, 2009). It is evident from the LCR calculated for benzene and ethylbenzene in this study for air masses that passed over the different source regions exceeded the threshold LCR frequently, which poses a significant cancer risk (Dutta et al., 2009). Measurements conducted by Lourens et al. (2011) in the South African Highveld, Lourens (2012) in the JHB-PTA megacity and Van der Walt (2008) in a South African metropolitan area also exceeded the cancer development risk limit as presented in Table 4. Based on LCR values determined in this study and in studies in other parts of South Africa, it is important that that the potential cancer risks associated with ambient VOC exposure should be considered a health concern in the source region in South Africa.

As mentioned previously, benzene is currently the only VOC listed as a criteria pollutant in the National Ambient Air Quality Standards (NAAQS) with an annual average limit of 1.6 ppb (5 μg m^{-3}) (Government Gazette Republic of South Africa, 2009). Jaars et al. (2014) indicated that the mean benzene concentration did not exceed the annual average limit.

However, during both campaigns, benzene levels higher than the Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10,000) of 4 ppbv established by the United States Environmental Protection Agency (USEPA, 2009a) were determined in six samples collected at Welgegund, i.e. four plumes passing over Area II and two plumes passing over the regional background.

3.4 OH reactivity of anthropogenic VOCs

Although it is important to evaluate the significance of VOCs with regard to human health through risk assessments related to atmospheric concentrations of VOCs and exposure to the species, it is also important to examine the role of these pollutants in the production of O_3 (Carter, 1994) and secondary organic aerosols (SOA). Various studies (Laakso et al., 2013;Venter et al., 2012;Beukes et al., 2013) have indicated that O_3 is currently considered to be the most problematic pollutant in South Africa, while Vakkari et al. (2015) also indicated the relevance of VOCs in the formation of SOAs. Jaars et al. (2014) presented the O_3 formation potential (OFP) for aromatic VOCs measured during the first campaign by calculating the product of the average concentration and the maximum incremental reactivity coefficient (MIR) of each compound. In addition, Jaars et al. (2016) evaluated the OFP, reaction rates with O_3 and OH reactivities of all the BVOCs measured during both campaigns. Therefore, in this study, the OH reactivity of all the anthropogenic VOCs measured during both campaigns was determined.

The assessment of the reactivity of VOCs with the OH radical is frequently used to determine the initial peroxy radical (RO_2) formation rate, which might be the rate-limiting step in O_3 formation in polluted air (Carter, 1994). While this approach does not account for the total atmospheric chemistry of the compounds considered, it does provide a simple approach to evaluate the relative contribution of individual VOCs to photochemistry (Goldan et al., 2004). The OH reactivities (s^{-1}) of the anthropogenic VOCs were calculated, using Eq. (7):

$$\text{OH reactivity} = k_{\text{X,OH}}[\text{X}] , \quad (7)$$

where [X] is the VOC concentration and $k_{\text{X,OH}}$ is the reaction rate constant of the reaction between X and OH. $k_{\text{X,OH}}$ values published by Atkinson and Arey (2003) were used to calculate rate coefficients (Atkinson and Arey, 2003).

In Fig. 6, the OH reactivities of the aromatics and alkanes measured in air masses passing over the three source regions during both campaigns are compared. The OH reactivity was

significantly higher for VOCs in air masses passing over the heavily polluted Area I during the first sampling campaign, especially with regard to aromatic species, while the OH reactivity was similar for air masses passing over all three source regions during the second sampling campaign. Toluene, ethylbenzene, xylenes and styrene had the highest OH reactivity of all the anthropogenic VOCs during both campaigns, while relatively high OH reactivity was determined for hexane during the second campaign. In addition, relatively high OH reactivity was also determined for 3-ethyltoluene, and 1,3,5-, 1,2,4- and 1,2,3-trimethylbenzene in air masses passing over Area I during the first campaign. Jaars et al. (2014) also indicated that the highest OFP for aromatic VOCs was associated with xylenes, toluene, ethylbenzene and 1,2,4-trimethylbenzene.

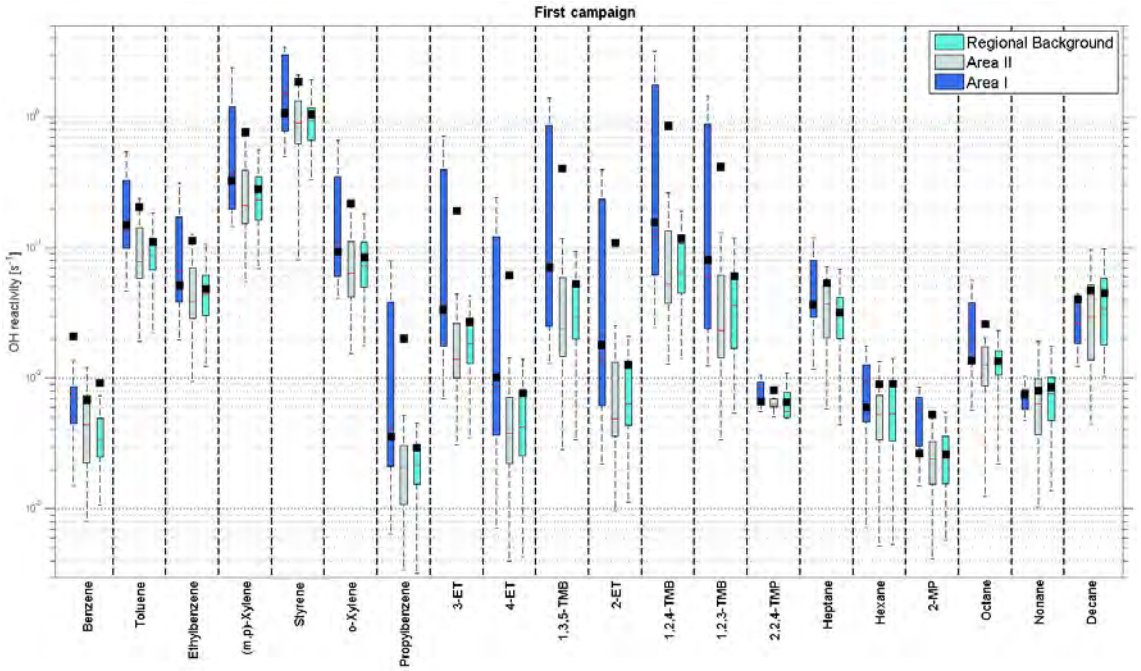

Fig. 6. The OH reactivity of measured aromatics and alkanes when air masses had passed over the source regions during first and second campaign.

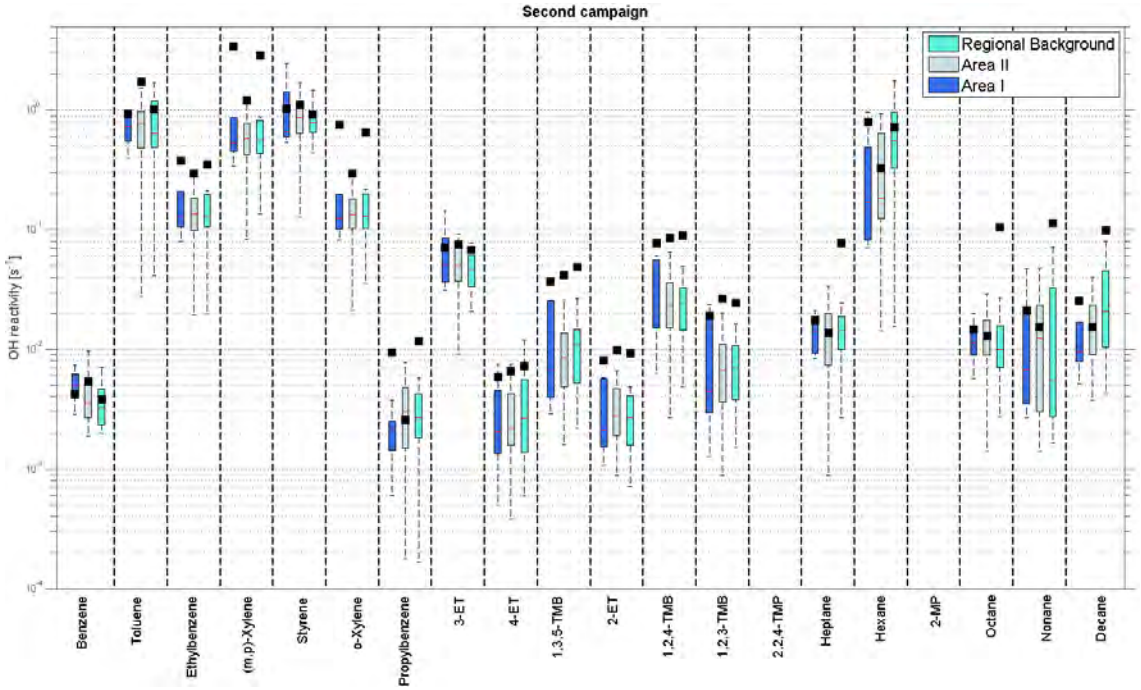

Fig. 6. Continued.

4 Conclusions

In this study, VOC concentrations determined for samples collected during two campaigns at Welgegund were subjected to PMF analysis in order to establish sources of the species, as well as to substantiate sources of aromatics and BVOCs determined with other methods in previous studies. Ten meaningful factor solutions were obtained for both datasets, of which five factors were associated with biogenic emissions and five with anthropogenic sources. Three of the biogenic factors were dominated by one specific biogenic species, i.e. isoprene, limonene and MBO. The other two biogenic factors comprised mixtures of biogenic species with different tracer species, while each of these factors was also associated with anthropogenic VOCs. The temporal factor contributions of the isoprene, limonene and MBO factors correlate relatively well with the wet seasons. Wind roses compiled for all the biogenic factors did not, in general, indicate any specific source region of these species. Isoprene, however, seemed to be higher from the western direction, which was also indicated by Jaars et al. (2016). Two of the anthropogenic factors were associated with emissions from a densely populated anthropogenic source region with a large number industrial activities to the east of Welgegund, i.e. the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld. An anthropogenic factor was also identified that reflected the influence of solvents on atmospheric VOC concentrations. Two anthropogenic factors were

also determined that indicated the influence of farming activities in close proximity to Welgegund, i.e. a diesel source factor and a factor comprising aromatic species with low concentrations that are not associated with solvents.

The impact on human health was assessed by preforming a non-cancer (HR) and cancer risk (LCR) assessment study for VOCs measured at Welgegund in relation to three source regions identified. The HR values determined for 12 VOCs measured at Welgegund passing over the three source regions indicated that these values were well below the level of concern threshold of 1. Relatively higher median and average HR values, i.e. 0.1, were determined for 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene, and benzene, with these species also exceeding the threshold on few instances during the sampling periods, which is indicative of potential future concern. LCR values could only be calculated for benzene and ethylbenzene, which indicated frequent exceedances of the acceptable threshold LCR value of 1×10^{-6}. Although the cumulative cancer risk associated with benzene and ethylbenzene exceeded the threshold, which does raises concern, LCR values were within an acceptable range. Therefore, from the risk assessment studies, it is evident that the non-cancerous influence of VOCs measured in the source regions is significantly lower compared to the cancerous influence of these species on human health, which poses a significant cancer risk.

Acknowledgements

The authors would like to acknowledge the Finnish Academy (project #132640), the University of Helsinki, the Finnish Meteorological Institute, the North-West University and the National Research Foundation (NRF) for financial support. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the NRF. Assistance with MATLAB from Ms Rosa Gierens is also acknowledged.

References

Agency for Toxic Substances and Disease Registry: http://www.atsdr.cdc.gov/substances/indexAZ.asp#B, access: 24 May, 2015.

Agency for Toxic Substances and Disease Registry, Minimal Risk Levels (MRLs) for Hazardous Substances: http://www.atsdr.cdc.gov/mrls/mrllist.asp#14tag, access: 24 May, 2016.

Belward, A. S., Estes, J. E., and Kline, K. D.: The IGBP-DIS global 1-km land-cover data set DISCover: A project overview, Photogrammetric Engineering and Remote Sensing, 65, 1013-1020, 1999.

Beukes, J. P., Vakkari, V., Van Zyl, P. G., Venter, A. D., Josipovic, M., Jaars, K., Tiitta, P., Kulmala, M., Worsnop, D., and Pienaar, J. J.: Source region plume characterization of the interior of South Africa, as observed at Welgegund, National Association for Clean Air, The Clean Air Journal, 23, 7-10, 2013.

Beukes, J. P., Venter, A. D., Josipovic, M., Van Zyl, P. G., Vakkari, V., Jaars, K., Dunn, M., and Laakso, L.: Automated Continuous Air Monitoring, Comprehensive Analytical Chemistry, 70, 183-208, 2015.

Booyens, W., Van Zyl, P. G., Beukes, J. P., Ruiz-Jimenez, J., Kopperi, M., Riekkola, M.-L., Josipovic, M., Venter, A. D., Jaars, K., Laakso, L., Vakkari, V., Kulmala, M., and Pienaar, J. J.: Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa, Journal of Atmospheric Chemistry, 72, 43-64, 10.1007/s10874-015-9304-6, 2015.

Brunke, E.-G., Labuschagne, C., and Scheel, H.: Trace gas variations at Cape Point, South Africa, during May 1997 following a regional biomass burning episode, Atmospheric Environment, 35, 777-786, 2001.

Burger, J., Pienaar, J., Fourie, L., and Jordaan, J.: Identification and quantification of volatile organic compounds in the Cape Town brown haze, Advances in air pollution series, 631-640, 2004.

Burger, J. W.: Identification and comparison of the volatile organic compound concentrations in ambient air in the Cape Town metropolis and the Vaal Triangle, North-West University, 2006.

Chiloane, K. E.: Volatile organic compounds (VOC's) analysis from Cape Town haze ll study, 2006.

Choi, E., Choi, K., and Yi, S.-M.: Non-methane hydrocarbons in the atmosphere of a Metropolitan City and a background site in South Korea: Sources and health risk potentials, Atmospheric environment, 45, 7563-7573, 2011.

Delfino, R. J., Gong Jr, H., Linn, W. S., Pellizzari, E. D., and Hu, Y.: Asthma symptoms in Hispanic children and daily ambient exposures to toxic and criteria air pollutants, Environmental health perspectives, 111, 647, 2003.

Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe,: http://eur-lex.europa.eu/, access: 24 May, 2008.

Forbes, P., and Rohwer, E.: Monitoring of trace organic air pollutants–a developing country perspective, Air Pollution XVI, 116, 345-355, 2008.

Friedl, M. A., McIver, D. K., Hodges, J. C., Zhang, X., Muchoney, D., Strahler, A. H., Woodcock, C. E., Gopal, S., Schneider, A., and Cooper, A.: Global land cover mapping from MODIS: algorithms and early results, Remote Sensing of Environment, 83, 287-302, 2002.

Friedl, M. A., Sulla-Menashe, D., Tan, B., Schneider, A., Ramankutty, N., Sibley, A., and Huang, X.: MODIS Collection 5 global land cover: Algorithm refinements and characterization of new datasets, Remote Sensing of Environment, 114, 168-182, 2010.

National Ambient Air Quality Standards: http://faolex.fao.org/docs/pdf/saf122986.pdf, access: 24 May 2009.

Guenther, A., Jiang, X., Heald, C., Sakulyanontvittaya, T., Duhl, T., Emmons, L., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions, 2012.

Guo, H., Wang, T., and Louie, P.: Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model, Environmental Pollution, 129, 489-498, 2004.

IARC: Chemical agents and related occupations, IARC Monographs On The Evaluation Of Carcinogenic Risks To Humans / World Health Organization, International Agency For Research On Cancer, 100, 9-562, 2012.

Jaars, K., Beukes, J. P., van Zyl, P. G., Venter, A. D., Josipovic, M., Pienaar, J. J., Vakkari, V., Aaltonen, H., Laakso, H., Kulmala, M., Tiitta, P., Guenther, A., Hellén, H., Laakso, L., and Hakola, H.: Ambient aromatic hydrocarbon measurements at Welgegund, South Africa, Atmospheric Chemistry and Physics, 14, 7075-7089, 10.5194/acp-14-7075-2014, 2014.

Jaars, K., van Zyl, P. G., Beukes, J. P., Hellén, H., Vakkari, V., Josipovic, M., Venter, A. D., Räsänen, M., Knoetze, L., Cilliers, D. P., Siebert, S. J., Kulmala, M., Rinne, J., Guenther, A., Laakso, L., and Hakola, H.: Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa, Atmos. Chem. Phys. Discuss., 2016, 1-46, 10.5194/acp-2016-471, 2016.

Kim, E., Hopke, P. K., and Edgerton, E. S.: Source identification of Atlanta aerosol by positive matrix factorization, Journal of the Air & Waste Management Association, 53, 731-739, 2003.

Kim, Y. M., Harrad, S., and Harrison, R. M.: Levels and sources of personal inhalation exposure to volatile organic compounds, Environmental science & technology, 36, 5405-5410, 2002.

Air Quality Standards and Air Pollution Level,: http://eng.me.go.kr/eng/web/index.do?menuId=253&findDepth=1, access: 24 May, 2011.

Kuik, F., Lauer, A., Beukes, J. P., Van Zyl, P. G., Josipovic, M., Vakkari, V., Laakso, L., and Feig, G. T.: The anthropogenic contribution to atmospheric black carbon concentrations in southern Africa: a WRF-Chem modeling study, Atmos. Chem. Phys., 15, 8809-8830, 10.5194/acp-15-8809-2015, 2015.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, Journal of Aerosol Science, 35, 143-176, 2004.

Laakso, L., Merikanto, J., Vakkari, V., Laakso, H., Kulmala, M., Molefe, M., Kgabi, N., Mabaso, D., Carslaw, K., and Spracklen, D.: Boundary layer nucleation as a source of new CCN in savannah environment, Atmospheric Chemistry and Physics, 13, 1957-1972, 2013.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmospheric Environment, 42, 6247-6260, 2008.

Lourens, A. S., Beukes, J. P., Van Zyl, P. G., Fourie, G. D., Burger, J. W., Pienaar, J. J., Read, C. E., and Jordaan, J. H.: Spatial and temporal assessment of gaseous pollutants in the Highveld of South Africa, South African Journal of Science, 107, 1-8, 2011.

Lourens, A. S. M.: Air quality in the Johannesburg-Pretoria megacity: its regional influence and identification of parameters that could mitigate pollution/ASM Lourens, North-West University, 2012.

Otter, L., Guenther, A., Wiedinmyer, C., Fleming, G., Harley, P., and Greenberg, J.: Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator, Journal of Geophysical Research: Atmospheres, 108, 2003.

Otto, D. A., Hudnell, H. K., House, D. E., Mølhave, L., and Counts, W.: Exposure of humans to a volatile organic mixture. I. Behavioral assessment, Archives of Environmental Health: An International Journal, 47, 23-30, 1992.

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111-126, 1994.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemometrics and intelligent laboratory systems, 37, 23-35, 1997.

Paralovo, S. L., Borillo, G. C., Barbosa, C. G. G., Godoi, A. F. L., Yamamoto, C. I., de Souza, R. A. F., Andreoli, R. V., Costa, P. S., Almeida, G. P., Manzi, A. O., Pöhlker, C., Yáñez-Serrano, A. M., Kesselmeier, J., and Godoi, R. H. M.: Observations of atmospheric monoaromatic hydrocarbons at urban, semi-urban and forest environments in the Amazon region, Atmospheric Environment, 128, 175-184, 10.1016/j.atmosenv.2015.12.053, 2016.

Payne-Sturges, D. C., Burke, T. A., Breysse, P., Diener-West, M., and Buckley, T. J.: Personal exposure meets risk assessment: a comparison of measured and modeled exposures and risks in an urban community, Environmental Health Perspectives, 112, 589, 2004.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over Alaska: 2. Elemental composition and sources, Journal of Geophysical Research: Atmospheres, 103, 19045-19057, 1998.

Pone, J. D. N., Hein, K. A., Stracher, G. B., Annegarn, H. J., Finkleman, R. B., Blake, D. R., McCormack, J. K., and Schroeder, P.: The spontaneous combustion of coal and its by-

products in the Witbank and Sasolburg coalfields of South Africa, International Journal of Coal Geology, 72, 124-140, 2007.

The Risk Assessment Information System: https://rais.ornl.gov/tools/profile.php, access: 26 June, 2016.

Räsänen, M., Aurela, M., Vakkari, V., Beukes, J. P., van Zyl, P. G., Josipovic, M., Venter, A. D., Jaars, K., Siebert, S. J., Laurela, T., Tuovinen, J.-P., Rinne, J., and Laakso, L.: Carbon balance of a grazed savanna grassland ecosystem in South Africa, Submitted to Biogeosciences, 2016.

Scepan, J.: Thematic validation of high-resolution global land-cover data sets, Photogrammetric engineering and remote sensing, 65, 1051-1060, 1999.

Scholes, M., and Andreae, M. O.: Biogenic and pyrogenic emissions from Africa and their impact on the global atmosphere, AMBIO: A Journal of the Human Environment, 29, 23-29, 2000.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, 2012.

Shi, J., Deng, H., Bai, Z., Kong, S., Wang, X., Hao, J., Han, X., and Ning, P.: Emission and profile characteristic of volatile organic compounds emitted from coke production, iron smelt, heating station and power plant in Liaoning Province, China, Sci Total Environ, 515-516, 101-108, 10.1016/j.scitotenv.2015.02.034, 2015.

Sillman, S.: The relation between ozone, NO x and hydrocarbons in urban and polluted rural environments, Atmospheric Environment, 33, 1821-1845, 1999.

Song, Y., Shao, M., Liu, Y., Lu, S., Kuster, W., Goldan, P., and Xie, S.: Source apportionment of ambient volatile organic compounds in Beijing, Environmental science & technology, 41, 4348-4353, 2007.

National Ambient Air Quality Standards http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php, access: 24 May 2009.

Tiitta, P., Vakkari, V., Croteau, P., Beukes, J., Van Zyl, P., Josipovic, M., Venter, A., Jaars, K., Pienaar, J., and Ng, N.: Chemical composition, main sources and temporal variability of PM 1 aerosols in southern African grassland, Atmospheric Chemistry and Physics, 14, 1909-1927, 2014.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 261-263, 2006.

USEPA: Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). EPA-540-R-070-002, US Environmental Protection Agency, Washington, DC, USA, 2009.

Vakkari, V., Tiitta, P., Jaars, K., Croteau, P., Beukes, J. P., Josipovic, M., Kerminen, V. M., Kulmala, M., Venter, A. D., and Zyl, P. G.: Reevaluating the contribution of sulfuric acid and

the origin of organic compounds in atmospheric nanoparticle growth, Geophysical Research Letters, 42, 2015.

Van der Walt, H. J.: The impact of hydrocarbon emissions on regional air quality in a South African metropolitan area/Hermanus Johannes van der Walt, North-West University, 2008.

Venter, A. D., Vakkari, V., Beukes, J. P., Van Zyl, P. G., Laakso, H., Mabaso, D., Tiitta, P., Josipovic, M., Kulmala, M., and Pienaar, J. J.: An air quality assessment in the industrialised western Bushveld Igneous Complex, South Africa, South African Journal of Science, 108, 1-10, 2012.

Watson, J. G., Chow, J. C., and Fujita, E. M.: Review of volatile organic compound source apportionment by chemical mass balance, Atmospheric Environment, 35, 1567-1584, 2001.

Welgegund measurement station: http://www.welgegund.org/, access: 27 May, 2016.

Wichmann, F. A., Müller, A., Busi, L. E., Cianni, N., Massolo, L., Schlink, U., Porta, A., and Sly, P. D.: Increased asthma and respiratory symptoms in children exposed to petrochemical pollution, Journal of Allergy and Clinical Immunology, 123, 632-638, 2009.

World Health Organization: Air quality guidelines for Europe, 2 ed., World Health Organization Regional Publications, European Series, No. 91, 2000.

Yuan, Z., Lau, A. K. H., Shao, M., Louie, P. K., Liu, S. C., and Zhu, T.: Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing, Journal of Geophysical Research: Atmospheres, 114, 2009.

Zhang, J., Sun, Y., Wu, F., Sun, J., and Wang, Y.: The characteristics, seasonal variation and source apportionment of VOCs at Gongga Mountain, China, Atmospheric Environment, 88, 297-305, 10.1016/j.atmosenv.2013.03.036, 2014.

CHAPTER 7

PROJECT EVALUATION AND FUTURE PERSPECTIVES

7.1 PROJECT EVALUATION

In this chapter, the successes and shortcomings of the project are evaluated by considering each of the specific objectives of this investigation listed in Chapter 1. A critical evaluation of the outcome of this study will not only highlight the success of the study and the contribution it has made to the better understanding of VOCs in South Africa, but will also indicate possible key areas that need to be addressed in future research. Future recommendations are also suggested.

Objective I: Collection of ambient anthropogenic and biogenic VOCs with an appropriate sampling technique for at least a full seasonal cycle.

Anthropogenic and biogenic VOCs were successfully collected for a period of more than two years through a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays. VOCs were sampled at a height of 2 m above ground level, with a 1.75 m long inlet. The first 1.25 m of the inlet was a stainless steel tube (grade 304 or 316) and the second 0.5 m was Teflon. To prevent the degradation of VOC by O_3, the stainless steel part of the inlet was heated to 120ºC using heating cables and thermostats (Thermonic), thereby removing ozone from the sample stream. VOCs were collected with stainless steel adsorbent tubes (6.3 mm ED x 90 mm, 5.5 mm ID) packed with Tenax-TA and Carbotrap-B by using a constant flow type automated programmable sampler.

Objective II: Identification and quantification of atmospheric VOC species.

Approximately 40 VOCs were identified and quantified using a thermal desorption instrument connected to a gas chromatograph and a mass selective detector. These species included 20 anthropogenic VOCs, i.e. 13 aromatic hydrocarbons and seven alkanes, as well as 20 BVOCs. According to the author's knowledge, this is one of the most comprehensive datasets for ambient VOCs measured in South Africa. Previous VOC studies conducted in South Africa focused mainly on BTEX measurements or BVOC measurements in enclosures.

Objective III: Contextualise VOC concentrations measured at Welgegund to published VOC data from previous measurements conducted in South Africa and internationally.

The VOC concentrations determined in this study were to some extent lower than concentrations reported in other studies conducted in South Africa and other parts of the world. A comparison of the benzene concentrations measured at Welgegund with other studies in South Africa indicates that Welgegund can be considered to be a regional background site that is on occasion affected by major plumes from different source regions in the interior of South Africa. Benzene concentrations at Welgegund were lower compared to measurements of benzene in the Vaal Triangle and the Mpumalanga Highveld. Toluene was the most abundant aromatic hydrocarbon being nearly five times higher than the benzene levels, which is similar to the ratio of these compounds reported in other studies in South Africa and internationally. Benzene concentrations were also significantly lower than the South African air quality standard limit. There is a large variation in the monoterpene concentrations measured in different ecosystems. BVOC concentrations measured at Welgegund were generally in the low to mid-range levels measured in other ecosystems. Isoprene concentrations were significantly lower compared to other ecosystems, with levels being approximately 10 times lower. However, the sum of all the monoterpenes measured at Welgegund was similar to levels thereof in other parts of the world. According to the knowledge of the author, this is the first record of ambient BVOC concentrations covering a full seasonal cycle in southern Africa, as well as for a grassland bioregion anywhere in the world.

Objective IV: Determine the possible temporal trends for the atmospheric anthropogenic and biogenic VOCs species.

No statistically significant differences in the concentrations of aromatic hydrocarbons measured during day- and night-time were found, which indicates the absence of local sources. However, it should be regarded as an important future perspective to set sampling schedules that would eliminate all possible time-bound biases. This could be achieved with continuous online

analysis, which would also enable proper assessment of diurnal cycles and also allow for specific case studies. Additionally, no distinct seasonal patterns were observed for any of the compounds measured, which could be attributed to the origin of the air masses sampled.

BVOC species also did not indicate any diurnal patterns. The monthly median MBO levels measured during both campaigns and, although less pronounced, the monthly median isoprene concentrations measured during the first campaign indicated a distinct seasonal pattern with higher concentrations of these species coinciding with the wet and warmer months. During the second campaign, higher isoprene concentrations were associated with higher wind speeds, which were attributed to a larger fetch source region. No distinct seasonal pattern was observed for monoterpene and SQT concentrations, with the exception of significantly higher levels measured from February to April 2011, during the first campaign, with concentrations of MBO also significantly higher during this period. These increased MBO, monoterpene and SQT concentrations were attributed to significantly higher soil moisture measured at a depth of 20 cm that resulted from the wet season, with substantially higher rainfall preceding the first campaign, which could indicate biogenic emissions from deep-rooted plants.

Objective V: Determine the general transport patterns of VOCs.

Aromatic hydrocarbon concentrations were in general significantly higher in air masses that had passed over anthropogenically-influenced source regions. It could be determined that, in total, 39 and 51% of the VOC samples were collected during periods when air mass back trajectory sets had passed over Area II (western and eastern Bushveld Igneous Complex and an area over which the air masses typically followed an anti-cyclonic movement pattern), 14 and 8% over Area I (Mpumalanga Highveld, the Vaal Triangle and the Johannesburg-Pretoria conurbation), while 33 and 23% of VOC samples were collected when air mass back trajectory sets passed over the regional background during the first and second campaign, respectively. The lower percentage of air masses passing over Area I can be attributed to the persistence of the anticyclonic circulation pattern over the interior of South Africa, which favours the arrival of air masses at Welgegund from the north to north-eastern sector.

Concentration roses indicated that isoprene concentrations were higher from the western direction, while wind direction did not indicate any significant differences in the concentrations of other BVOC species. Woody species in the grassland region were considered to be the main sources of BVOCs measured, while sunflower and maize crops were also considered to be potential sources for BVOCs in this region.

Objective VI: Explain the observed trends by investigating the reactivity of VOCs, ozone formation potential, inter-compound correlations and ratios, as well as correlations with other high resolution ancillary data measured at Welgegund, e.g. meteorological data and trace gas concentrations.

The highest contributions of aromatic hydrocarbon concentrations to O_3 formation potential were observed for plumes passing over area I. Xylenes ((m,p)-xylene plus oxylene) were the dominant contributor to O_3 formation, with 1,2,4-trimethylbenzene being the second largest contributor. The O_3 formation potential of benzene was the lowest. During the first campaign, the most important aromatic hydrocarbon contributor to the OH reactivity was styrene, followed by *(m,p)*-xylene. The other aromatic hydrocarbons played a smaller role in OH reactivity due to their low concentrations. Xylenes, toluene and styrene played a predominant role in the reactivity of VOCs during the second campaign. Although trimethylbenzenes had larger rate coefficients, they made a minor contribution because of their low concentrations.

The combined O_3 formation potentials of all the BVOCs measured during the first and second campaign were significantly lower compared to the aromatic VOCs, with isoprene and the monoterpenes: α-pinene, isoprene, p-cymene, limonene and terpinolene, having the largest contribution to O_3 formation potential. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured at Welgegund for all of the months during both sampling campaigns.

Inter-compound correlations indicated that all the aromatic hydrocarbons, with the exception of benzene, originated from the same source(s) in Area I, where benzene most likely originated from incomplete combustion. For Area II and the regional background, benzene and toluene were found to originate from the same source(s), while all the other aromatic hydrocarbons were emitted by (a) different source(s). Inter-compound ratios indicated the influence of anthropogenic activities, especially in Area I, and also the closer proximity to the Johannesburg-Pretoria megacity in Area I to the Welgegund monitoring station, i.e. fewer aged plumes. The concentration ratios of TEX/total aromatics for air masses that had passed over the three source regions indicated a seasonal dependence, i.e. higher temperatures resulting in higher evaporation rates that contribute to higher ambient concentrations.

Spearman correlations between BVOCs and other parameters measured at Welgegund did not show significant correlations. However, in certain instances, good correlations were observed between soil moisture and MBO, monoterpenes and SQT concentrations. This is expected, since the monthly average concentrations of these species indicated increased levels thereof

that were associated with increased soil moisture from February to April 2011. Explorative multi-linear regression analysis utilising all the BVOC and ancillary measurements at Welgegund indicated that soil moisture had the most significant impact on concentrations of MBO, monoterpenes and SQT, while temperature had the greatest influence on isoprene levels.

Objective VII: Source apportionment of VOCs measured at Welgegund by using positive matrix factorisation.

Positive matrix factorisation (PMF) was successfully applied to perform receptor modelling in order to conduct a source apportionment study. Ten meaningful factor solutions were obtained for both datasets, of which five factors were associated with biogenic emissions and five with anthropogenic sources. Three of the biogenic factors were dominated by one specific biogenic species, i.e. isoprene, limonene and MBO. The other two biogenic factors comprised mixtures of biogenic species with different tracer species, while each of these factors was also associated with anthropogenic VOCs. The temporal factor contributions of the isoprene, limonene and MBO factors correlate relatively well with the wet seasons. Wind roses compiled for all the biogenic factors did not, in general, indicate any specific source region of these species. Isoprene, however, seemed to be higher from the western direction, which was also indicated by Jaars et al. (2016). Two of the anthropogenic factors were associated with emissions from a densely populated anthropogenic source region with a large number industrial activities to the east of Welgegund, i.e. the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld. An anthropogenic factor was also identified that reflected the influence of solvents on atmospheric VOC concentrations. Two anthropogenic factors were also determined that indicated the influence of farming activities in close proximity to Welgegund, i.e. a diesel source factor and a factor comprising aromatic species with low concentrations that are not associated with solvents.

Objective VIII: Evaluate the potential health risk when exposed to VOC in the plumes passing over the identified source regions.

The impact on human health could be assessed by preforming a non-cancer- (HR) and cancer-risk (LCR) assessment study for VOCs measured at Welgegund in relation to three source regions identified. The HR values determined for 12 VOCs measured at Welgegund passing over the three source regions indicated that these values were well below the level of concern threshold of 1. Relatively higher median and average HR values, i.e. 0.1, were determined for 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene, and benzene, with these species also exceeding the threshold on few instances during the sampling periods, which is indicative of potential future concern. LCR values could only be calculated for benzene and ethylbenzene, which indicated

frequent exceedances of the acceptable threshold LCR value of 1×10^{-6}. Although the cumulative cancer risk associated with benzene and ethylbenzene exceeded the threshold, which does raise concern, LCR values were within an acceptable range. The LCR values calculated for benzene and ethylbenzene measured in the Mpumalanga Highveld and Vaal Triangle also indicated levels higher than the threshold value. Therefore, from the risk assessment studies, it is evident that the non-cancerous influence of VOCs measured in the source regions is significantly lower compared to the cancerous influence of these species on human health, which poses a significant cancer risk.

In general, it can be concluded that this research project was successfully completed, according to the above evaluation of the objectives of this study. A few shortcomings were, however, identified that could be improved upon in future studies.

7.2 FUTURE PERSPECTIVES

In addition to future perspectives indicated by discussing the shortcomings of the study in the previous section, the following recommendations with regard to possible future studies are made:

1. Although measurements were conducted for more than two years in this study, it is recommended that a longer measurement campaign is conducted spanning over several years, which will provide additional insight into seasonal VOC patterns, as well as indicate inter-annual differences.
2. Although long-term continuous online measurements with instruments such as proton transfer reaction mass spectrometry are more expensive, these measurements will provide much better insight into diurnal variations of VOCs and will enable the reporting of peak concentrations. It will also assist in conducting case studies during which air masses passing over specific source regions could be isolated and investigated. A longer measurement campaign and continuous on-line sampling will also improve receptor modelling for VOC species.
3. Although an extensive vegetation survey of the area surrounding Welgegund was conducted in this study, a more detailed vegetation mapping of the region surrounding Welgegund must be performed in future to better characterise specific sources of biogenic species. In addition, it is also very important that biogenic emissions from specific plant species in close to proximity of Welgegund must be quantified in future studies.

4. Measure the total atmospheric OH reactivity and compare it to calculated OH reactivity to see whether all the OH sinks are measured. If the OH concentration in combination with NO_3, O_3 and photolysis is known for Welgegund, then the atmospheric lifetimes of the VOCs can be calculated for this specific site.

APPENDIX A

In this appendix, additional temporal patterns obtained from the concentrations of anthropogenic VOC species, i.e. the alkanes from both campaigns and the aromatic hydrocarbons from the second campaign, which were not published in any of the research papers included in this thesis, are presented for completeness of the dataset used in this PhD study. The first article (Jaars et al., 2014) included in this thesis reported the main deductions that could be made for the anthropogenic VOCs, i.e. contextualisation, temporal patterns, source group contribution determined from back trajectory analysis, correlations and ozone formation potential based on the first campaign's aromatic VOC measurements. At the time when this research paper (Jaars et al., 2014) was prepared and reviewed, the concentrations of the aromatic VOCs determined during the second campaign, as well as the alkanes determined for both campaigns, were not available. In addition, monthly contributions of aromatic VOCs to OH reactivity that were not included in the first paper are also presented as an appendix.

A.1 Temporal patterns of anthropogenic VOCs

In Figure A-1, the monthly median VOC concentrations determined for each of the two campaigns are presented, while the panels on the right present the VOC concentrations determined during the warm, wet (October to April) and cold, dry (May to September) months calculated from VOC concentrations measured during both campaigns. Jaars et al. (2014) concluded that no distinct seasonal cycles could be identified for the measured aromatic hydrocarbons, while Lourens et al. (2011) also observed no seasonal pattern for BTEX measurements conducted in the Mpumalanga Highveld and Vaal Triangle. The seasonal pattern presented for the second sampling campaign, as well as the seasonal patterns presented for alkanes, also did not reflect a clear seasonal pattern. Jaars et al. (2014) indicated that higher VOC concentrations were attributed to Welgegund being more frequently affected by air masses passing over source regions identified. It is also evident that toluene concentrations measured during the second sampling campaign were significantly higher compared to the first sampling campaign. In addition, higher VOC concentrations from solvent emissions were also associated with higher temperatures by Jaars et al. (2014) for the first campaign aromatic measurements. Therefore, the comparison of anthropogenic VOC concentrations measured during the warm, wet and cold, dry seasons determined from VOC measurements for both campaigns also indicates relatively higher VOC levels in the warmer, wet months for certain anthropogenic VOCs.

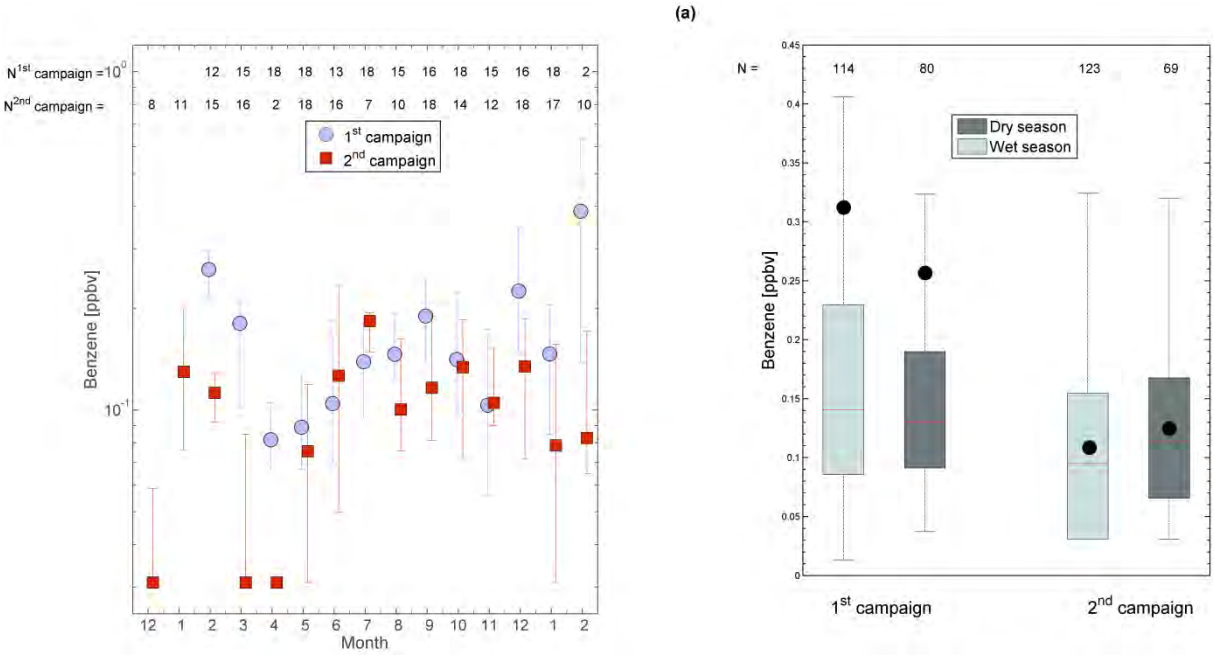

Figure A-1: The panels on the left show monthly median concentrations of (a) benzene, (b) toluene, (c) ethylbenzene, (d) m,p-xylene, (e) styrene (f), o-xylene, (g) propylbenzene, (h) 3-ethyltoluene, (i) 4-ethyltoluene, (j) 1,3,5-trimethylbenzene, (k) 2-ethyltoluene, (l) 1,2,4-trimethylbenzene, (m) 1,2,3-trimethylbenzene, (n) heptane, and (o) octane measured for the two campaigns. Error bars indicate upper and lower quartiles. The values displayed near the top of the graphs indicate the number of samples (N^{1st} and N^{2nd} campaign) analysed for each month. The panels on the right show the wet and dry season concentrations of the respective compounds measured for the two campaigns. The red line of each box indicates the median (50^{th} percentile), the black dot the mean, the top and bottom edges of the box the 25^{th} and 75^{th} percentiles, the whiskers ±2.7σ or 99.3% coverage if the data have a normal distribution and the red circles outliers of the range of the box and whisker plot. The values displayed near the top of the graphs indicate the number of samples (N) analysed for the wet and dry season

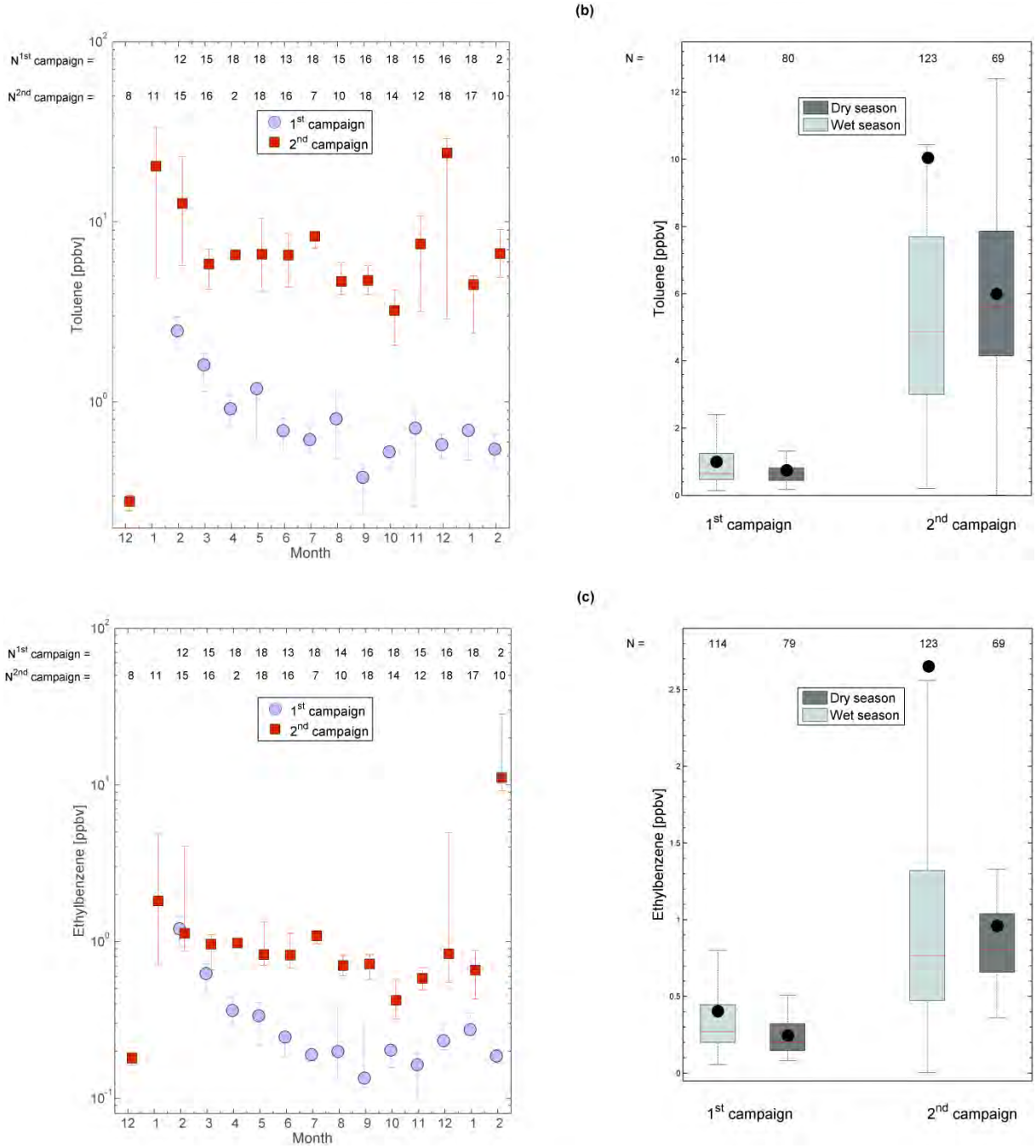

Figure A-1: *Continued from previous page*

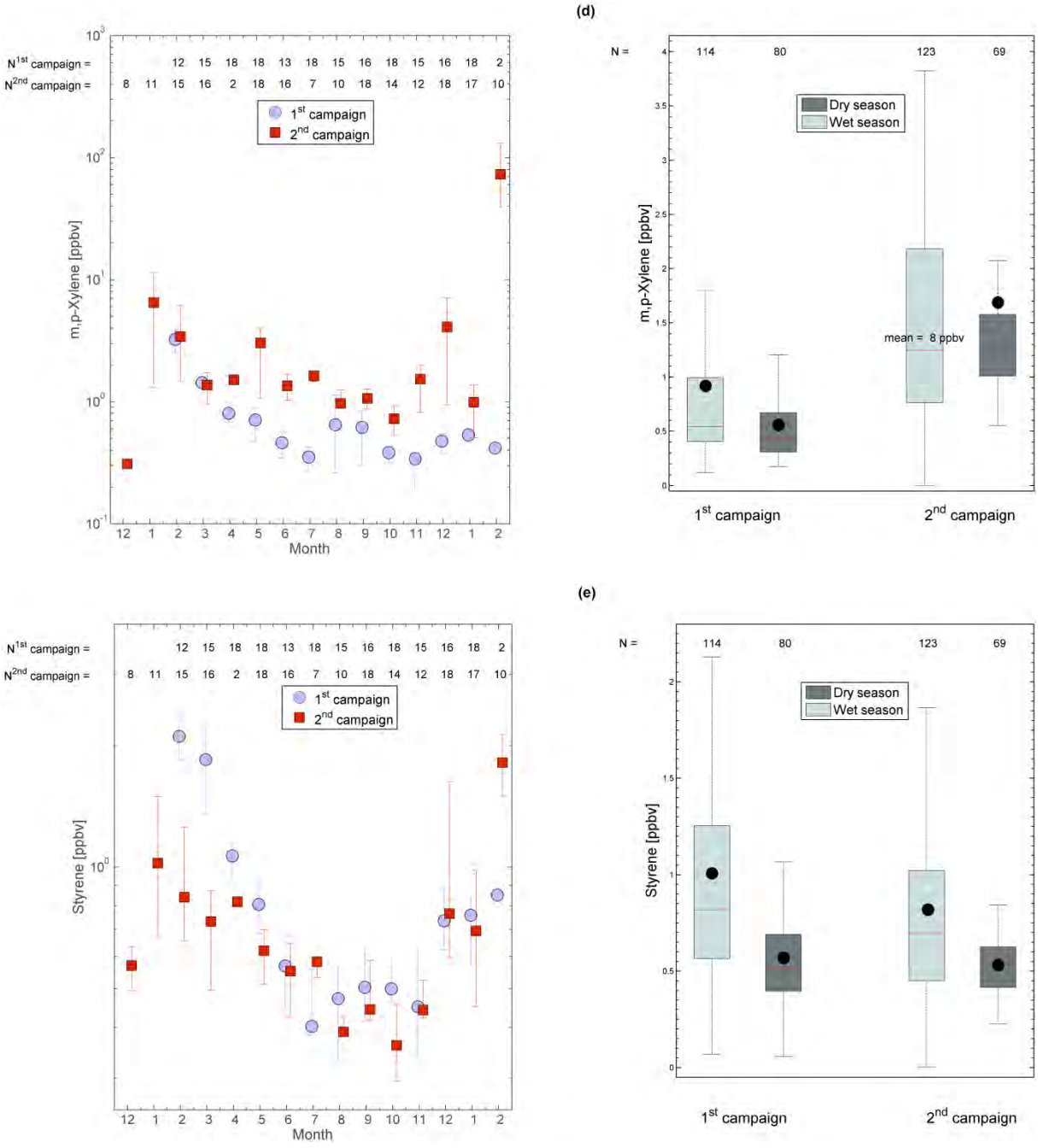

Figure A-1: *Continued from previous page*

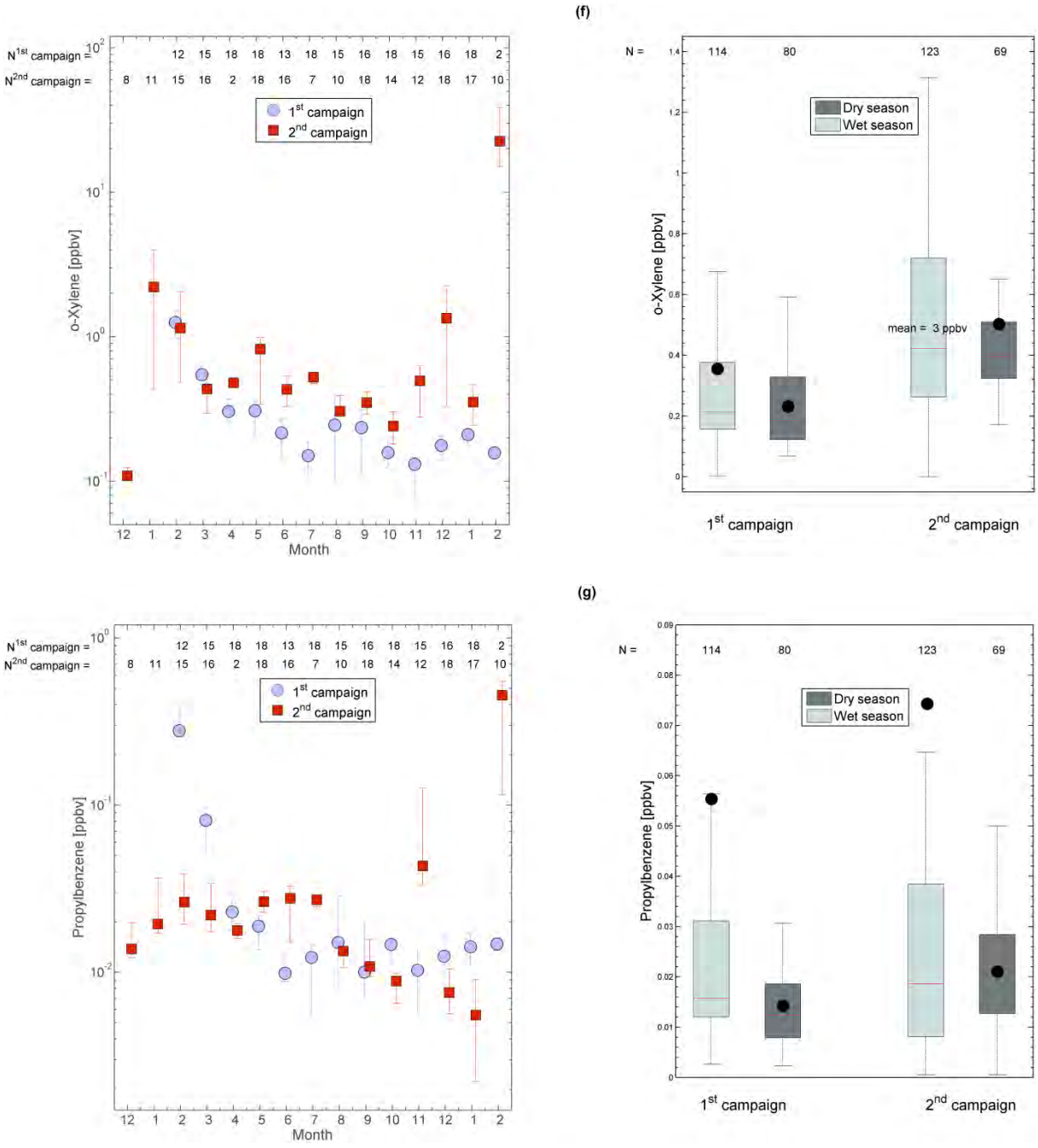

Figure A-1: *Continued from previous page*

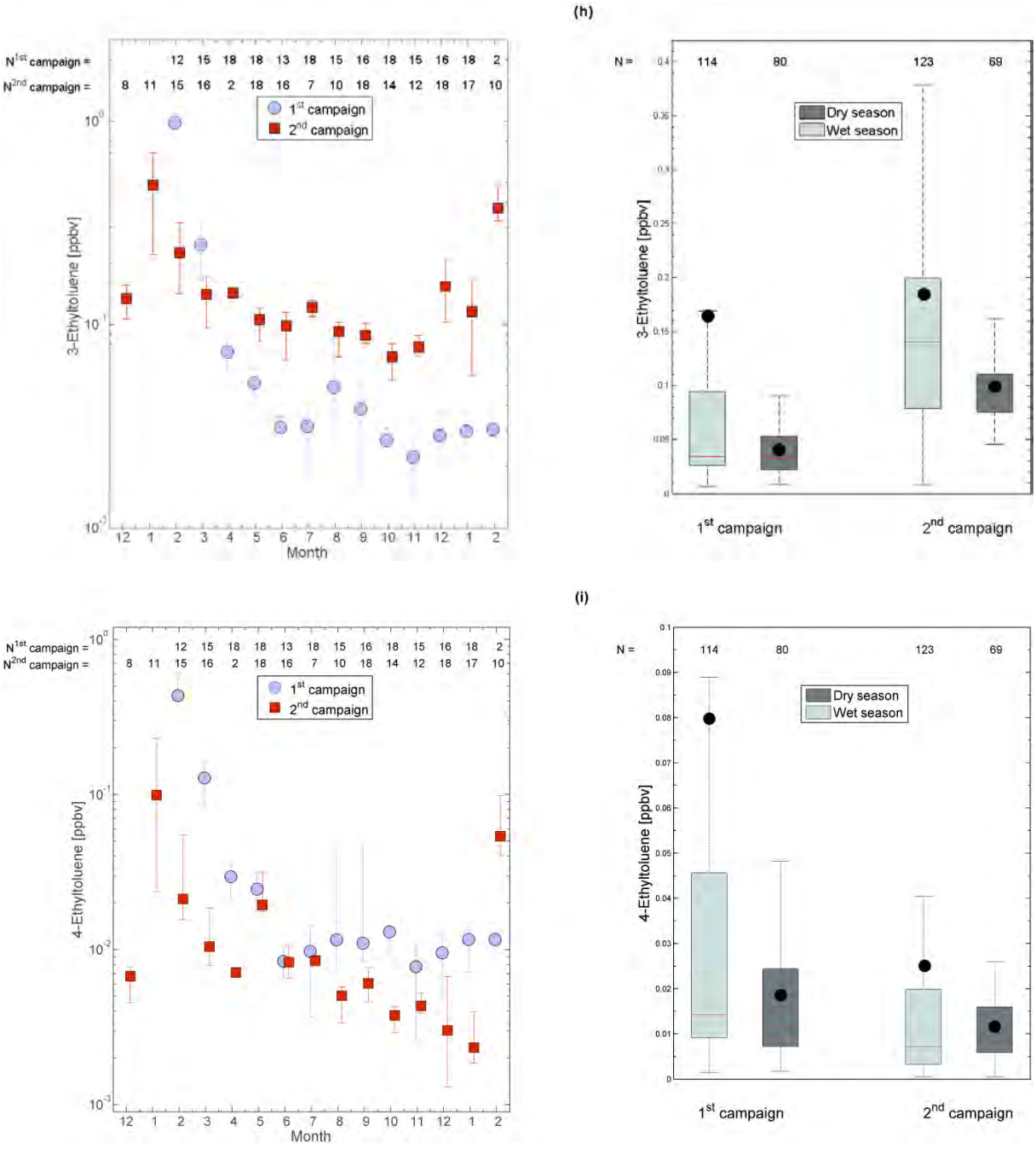

Figure A-1: *Continued from previous page*

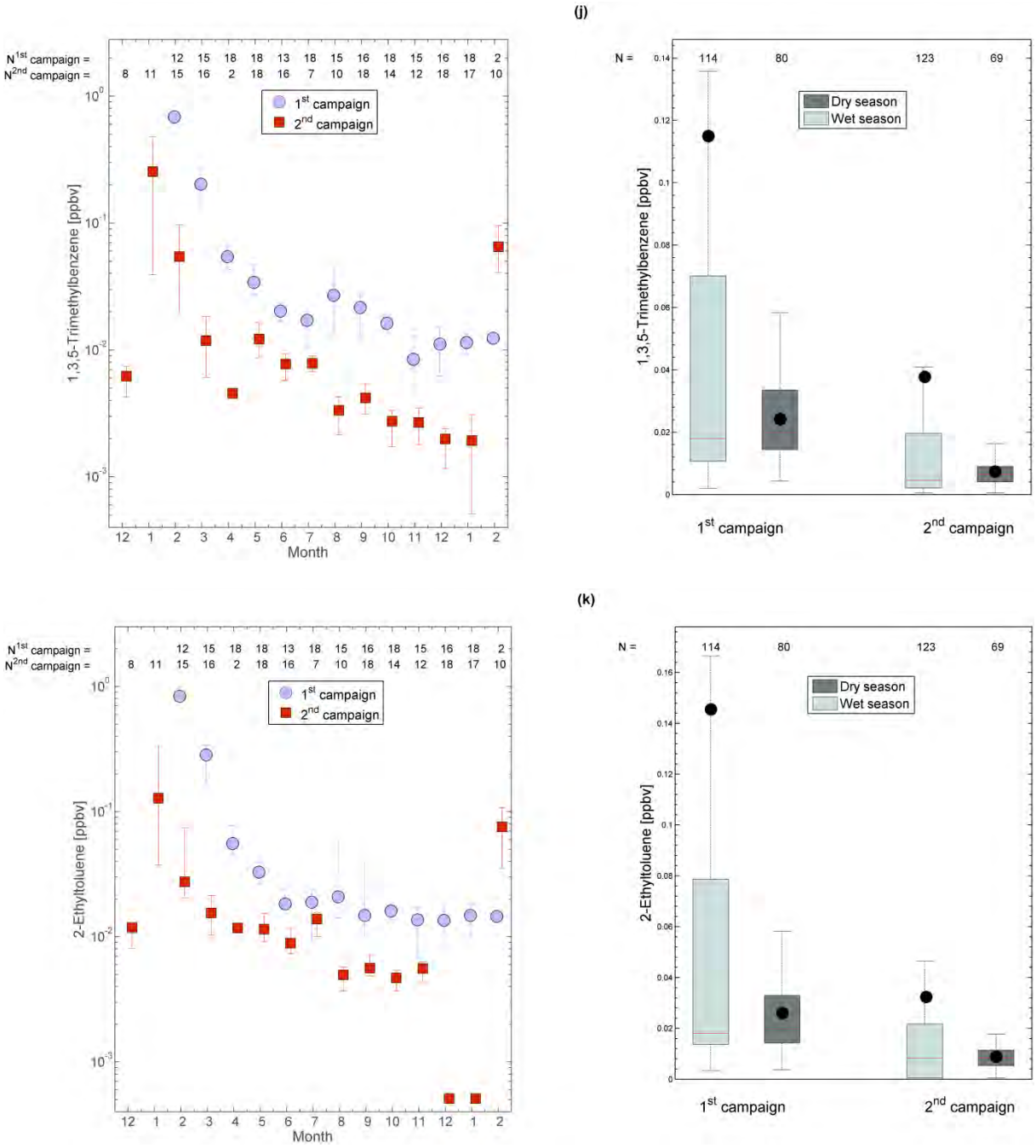

Figure A-1: *Continued from previous page*

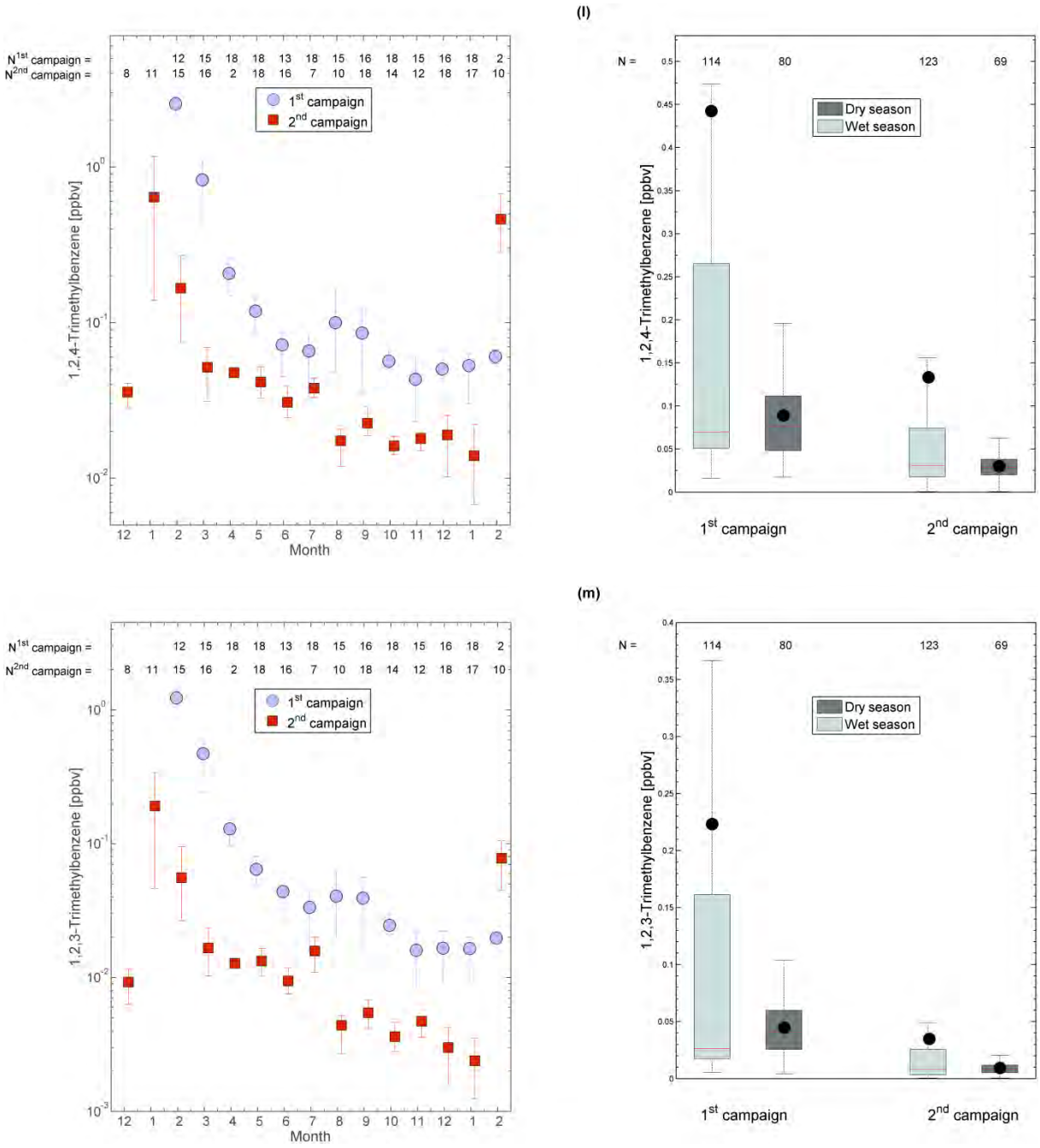

Figure A-1: *Continued from previous page*

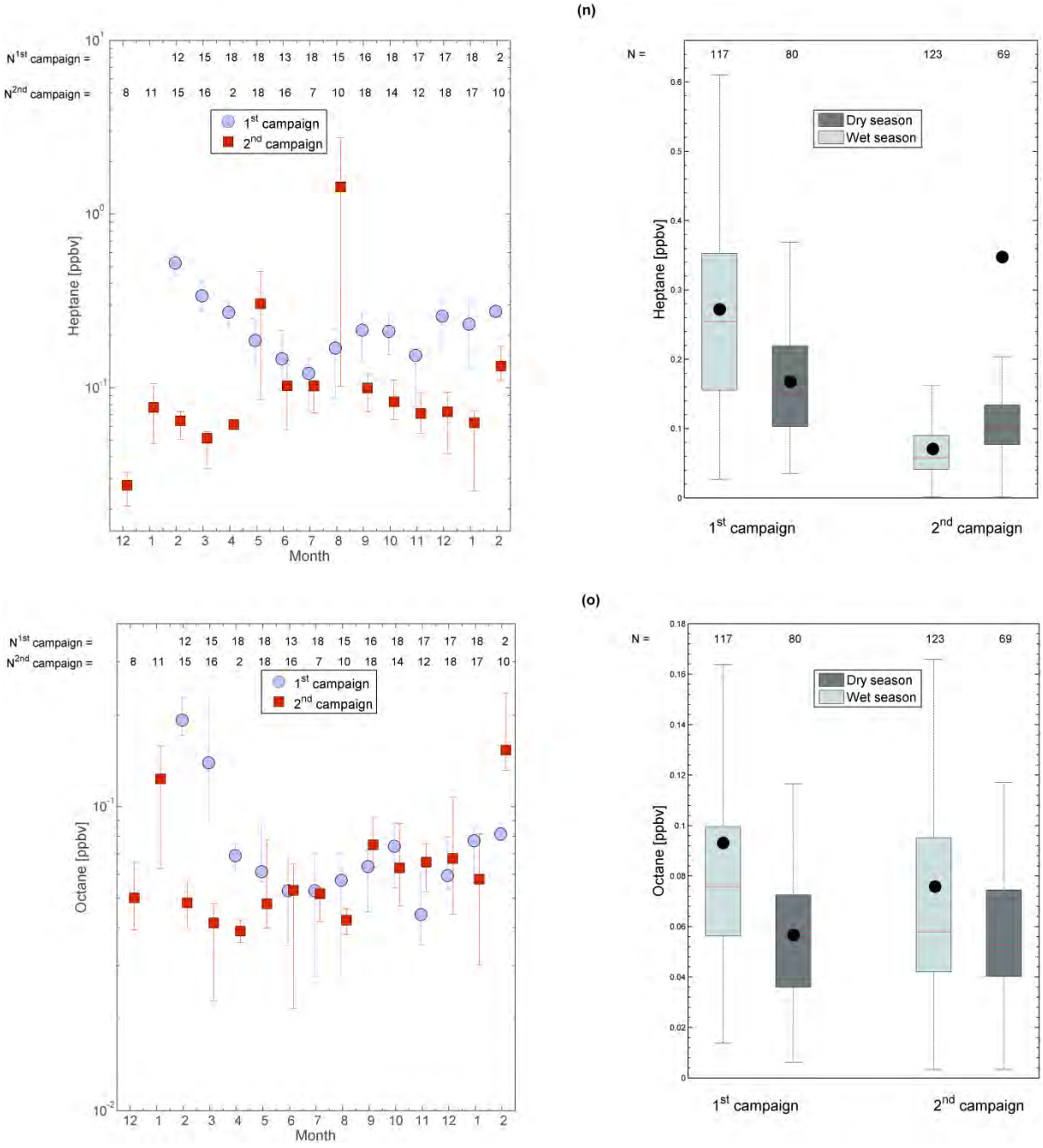

Figure A-1: *Continued from previous page*

A.2 Monthly contributions of aromatic VOCs to OH reactivity

In Figure A-2, the monthly contribution of aromatic hydrocarbons to the total OH reactivity is presented. For the first campaign, the most important contributor to the OH reactivity was styrene, followed by *(m,p)*-xylene. The other aromatic hydrocarbons played a smaller role in OH

reactivity due to their low concentrations. During the second campaign, xylenes, toluene and styrene played a predominant role in the reactivity of VOCs. Although trimethylbenzenes had larger rate coefficients, they made a minor contribution because of their low concentrations. As already shown in article 1, the highest concentrations of aromatic hydrocarbons were in the warm, wet season when the consumption rate of OH and the ozone formation potential were the highest. Usually, it is expected that VOC concentrations should be lower in summer due to increased OH reactivity, which was not the case in this study. This could possibly be attributed to the higher emission of VOC sources, associated with higher temperatures.

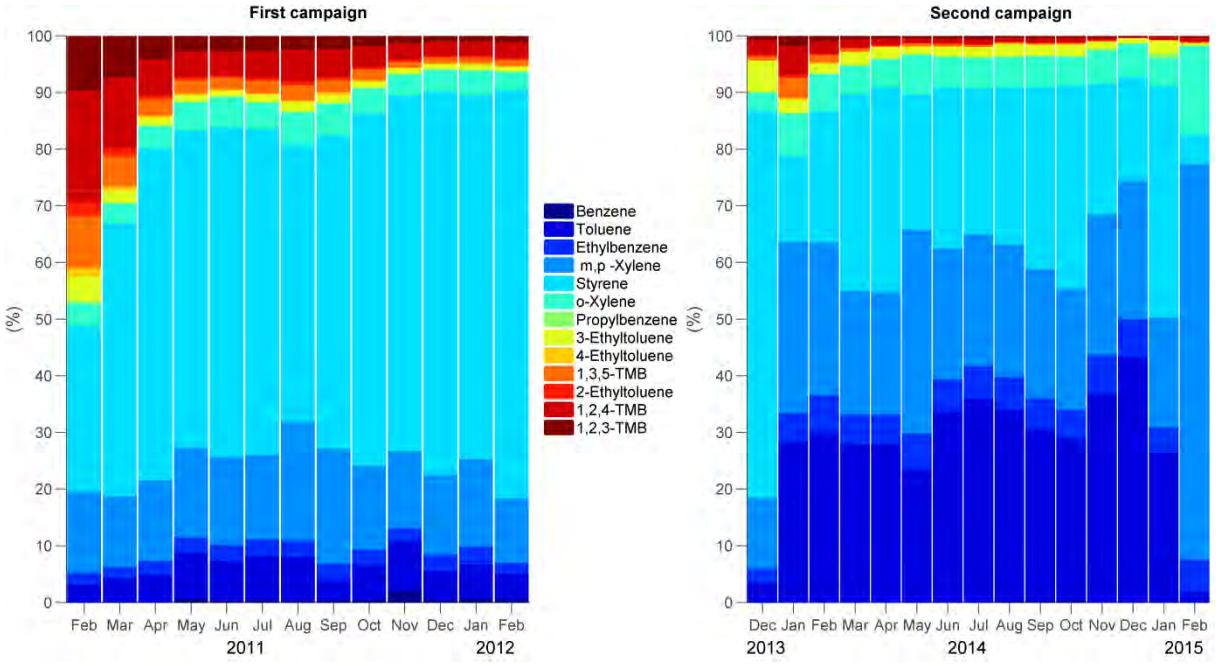

Figure A-2. Relative contribution of measured aromatics to OH loss rate at Welgegund, respectively

BIBLIOGRAPHY

AGUILERA, I., SUNYER, J., FERNÁNDEZ-PATIER, R., HOEK, G., AGUIRRE-ALFARO, A., MELIEFSTE, K., BOMBOI-MINGARRO, M. T., NIEUWENHUIJSEN, M. J., HERCE-GARRALETA, D. & BRUNEKREEF, B. 2007. Estimation of outdoor NO x, NO2, and BTEX exposure in a cohort of pregnant women using land use regression modeling. *Environmental science & technology,* 42**,** 815-821.

AIR RESOURCES LABORATORY. 2016. *Gridded Meteorological Data Archive,* [Online]. Available: http://www.arl.noaa.gov/ [Accessed 25 MAy 2016].

ANDREAE, M. O. & CRUTZEN, P. J. 1997. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science,* 276**,** 1052-1058.

ANDREAE, M. O. & MERLET, P. 2001. Emission of trace gases and aerosols from biomass burning. *Global biogeochemical cycles,* 15**,** 955-966.

ATKINSON, R. 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. *Journal of Physical and Chemical Reference Data,* 26**,** 215-290.

ATKINSON, R. 2000. Atmospheric chemistry of VOCs and NOx. *Atmospheric environment,* 34**,** 2063-2101.

ATKINSON, R. 2007. Gas-phase tropospheric chemistry of organic compounds: a review. *Atmospheric Environment,* 41**,** 200-240.

ATKINSON, R. & AREY, J. 2003a. Atmospheric degradation of volatile organic compounds. *Chemical reviews,* 103**,** 4605-4638.

ATKINSON, R. & AREY, J. 2003b. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmospheric Environment,* 37**,** 197-219.

ATSDR. 2015. *Agency for Toxic Substances and Disease Registry* [Online]. Available: http://www.atsdr.cdc.gov/substances/indexAZ.asp#B [Accessed 24 May 2016].

ATSDR. 2016. *Agency for Toxic Substances and Disease Registry, Minimal Risk Levels (MRLs) for Hazardous Substances* [Online]. 4770 Buford Hwy NE, Atlanta, GA 30341. Available: http://www.atsdr.cdc.gov/mrls/mrllist.asp#14tag [Accessed 24 May 2016].

BAMBERGER, I., HÖRTNAGL, L., RUUSKANEN, T., SCHNITZHOFER, R., MÜLLER, M., GRAUS, M., KARL, T., WOHLFAHRT, G. & HANSEL, A. 2011. Deposition fluxes of terpenes over grassland. *Journal of Geophysical Research: Atmospheres,* 116.

BERNDT, T., JOKINEN, T., SIPILÄ, M., MAULDIN, R. L., HERRMANN, H., STRATMANN, F., JUNNINEN, H. & KULMALA, M. 2014. H 2 SO 4 formation from the gas-phase reaction of stabilized Criegee Intermediates with SO 2: Influence of water vapour content and temperature. *Atmospheric Environment,* 89**,** 603-612.

BEUKES, J. P., VAKKARI, V., VAN ZYL, P. G., VENTER, A. D., JOSIPOVIC, M., JAARS, K., TIITTA, P., KULMALA, M., WORSNOP, D. & PIENAAR, J. J. 2013. Source region plume characterization of the interior of South Africa, as observed at Welgegund. *National Association for Clean Air, The Clean Air Journal,* 23**,** 7-10.

BEUKES, J. P., VENTER, A. D., JOSIPOVIC, M., VAN ZYL, P. G., VAKKARI, V., JAARS, K., DUNN, M. & LAAKSO, L. 2015. Automated Continuous Air Monitoring. *Comprehensive Analytical Chemistry,* 70**,** 183-208.

BOOYENS, W., VAN ZYL, P. G., BEUKES, J. P., RUIZ-JIMENEZ, J., KOPPERI, M., RIEKKOLA, M.-L., JOSIPOVIC, M., VENTER, A. D., JAARS, K., LAAKSO, L., VAKKARI, V., KULMALA, M. & PIENAAR, J. J. 2015. Size-resolved characterisation of organic compounds in atmospheric aerosols collected at Welgegund, South Africa. *Journal of Atmospheric Chemistry,* 72**,** 43-64.

BOY, M., MOGENSEN, D., SMOLANDER, S., ZHOU, L., NIEMINEN, T., PAASONEN, P., PLASS-DÜLMER, C., SIPILÄ, M., PETÄJÄ, T., MAULDIN, L., BERRESHEIM, H. & KULMALA, M. 2013. Oxidation of SO2 by stabilized Criegee intermediate (sCI) radicals as a crucial source for atmospheric sulfuric acid concentrations. *Atmos. Chem. Phys.,* 13**,** 3865-3879.

BRIMBLECOMBE, P. 2008. Air pollution history. *In:* SOKHI, R. S. (ed.) *World atlas of atmospheric pollution.* London, United Kingdom: Anthem Press.

BRUNKE, E.-G., LABUSCHAGNE, C. & SCHEEL, H. 2001. Trace gas variations at Cape Point, South Africa, during May 1997 following a regional biomass burning episode. *Atmospheric Environment,* 35**,** 777-786.

BURGER, J., PIENAAR, J., FOURIE, L. & JORDAAN, J. 2004. Identification and quantification of volatile organic compounds in the Cape Town brown haze. *Advances in air pollution series***,** 631-640.

BURGER, J. W. 2006. *Identification and comparison of the volatile organic compound concentrations in ambient air in the Cape Town metropolis and the Vaal Triangle.* North-West University.

CALVERT, J. G., ATKINSON, R., BECKER, K. H., KAMENS, R. M., SEINFELD, J. H., WALLINGTON, T. J. & YARWOOD, G. 2002. *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*, Oxford University Press New York.

CALVERT, J. G., ATKINSON, R., KERR, J., MADRONICH, S., MOORTGAT, G., WALLINGTON, T. J. & YARWOOD, G. 2000. *The mechanisms of atmospheric oxidation of the alkenes,* New York, Oxford University Press

CARTER, W. P. 2009. Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. *California Air Resources Board Contract***,** 07-339.

CASTRO, T., MADRONICH, S., RIVALE, S., MUHLIA, A. & MAR, B. 2001. The influence of aerosols on photochemical smog in Mexico City. *Atmospheric Environment,* 35**,** 1765-1772.

CHAMEIDES, W., FEHSENFELD, F., RODGERS, M., CARDELINO, C., MARTINEZ, J., PARRISH, D., LONNEMAN, W., LAWSON, D., RASMUSSEN, R. & ZIMMERMAN, P. 1992. Ozone precursor relationships in the ambient atmosphere. *Journal of Geophysical Research: Atmospheres,* 97**,** 6037-6055.

CHILOANE, K. E. 2006. *Volatile organic compounds (VOC's) analysis from Cape Town haze II study.*

CHUTEL, L. 2016. *South Africa just lost its spot as Africa's second largest economy* [Online]. Quartz Africa. Available: http://qz.com/682877/south-africa-loses-its-spot-as-africas-second-largest-economy-to-egypt/ [Accessed 24 May 2016].

CLAEYS, M., GRAHAM, B., VAS, G., WANG, W., VERMEYLEN, R., PASHYNSKA, V., CAFMEYER, J., GUYON, P., ANDREAE, M. O. & ARTAXO, P. 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science,* 303**,** 1173-1176.

DAEMANE, M. E., CILLIERS, S. S. & BEZUIDENHOUT, H. 2010. An ecological study of the plant communities in the proposed Highveld National Park, in the peri-urban area of Potchefstroom, South Africa. *Koedoe,* 52.

DAVISON, B., TAIPALE, R., LANGFORD, B., MISZTAL, P., FARES, S., MATTEUCCI, G., LORETO, F., CAPE, J., RINNE, J. & HEWITT, C. 2009. Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy. *Biogeosciences,* 6**,** 1655-1670.

DELFINO, R. J., GONG JR, H., LINN, W. S., PELLIZZARI, E. D. & HU, Y. 2003. Asthma symptoms in Hispanic children and daily ambient exposures to toxic and criteria air pollutants. *Environmental health perspectives,* 111**,** 647.

DEPARTMENT OF ENVIRONMENTAL AFFAIRS. 2005. *Government Notice, Department of Environmental Affairs and Tourism, Notice of intentention to declare the Vaal Triangle air-shed priority area in terms of section 18(1) of the National Environmental Management: Air Quality Act 2004, (Act no. 39 of 2004),* [Online]. Available: https://www.environment.gov.za/sites/default/files/gazetted_notices/nemaqa_vaalair_priorityarea_g28132gon1007.pdf [Accessed 7 July 2016].

DEPARTMENT OF ENVIRONMENTAL AFFAIRS. 2007. *Government Notice, Department of Environmental Affairs and Tourism, National Environmental Management: Air Quality Act, 2004 (Act no. 39 of 2004), Declaration of the Highveld as priority area in terms of Section 18(1) of The National Environmental Management: Air Quality Act, 2004 (Act no. 39 of 2004),* [Online]. Available: https://www.environment.gov.za/sites/default/files/gazetted_notices/nema_highvelddeclaration_g30518gon1123.pdf [Accessed 7 July 2016].

DEPARTMENT OF ENVIRONMENTAL AFFAIRS. 2012. *Government Gazette, Notice 495 of 2012, Department of Environmental Affairs, National Environmental Management: Air Quality Act, 2004 (Act no. 39 of 2004), Declaration of the Waterberg National Prioriy Area,* [Online]. Available: https://www.environment.gov.za/sites/default/files/gazetted_notices/nemaqa_waterberg_declaration_g35435gen495.pdf [Accessed 7 July 2016].

DIAB, R., THOMPSON, A., MARI, K., RAMSAY, L. & COETZEE, G. 2004. Tropospheric ozone climatology over Irene, South Africa, from 1990 to 1994 and 1998 to 2002. *Journal of Geophysical Research: Atmospheres,* 109.

DRAXLER, R. & HESS, G. 2004. Description of the HYSPLIT 4 modeling system,. *NOAA Technical Memorandum ERL ARL–224,*.

DUDAREVA, N., NEGRE, F., NAGEGOWDA, D. A. & ORLOVA, I. 2006. Plant volatiles: recent advances and future perspectives. *Critical reviews in plant sciences,* 25**,** 417-440.

DURMUSOGLU, E., TASPINAR, F. & KARADEMIR, A. 2010. Health risk assessment of BTEX emissions in the landfill environment. *Journal of hazardous materials,* 176**,** 870-877.

EERDEKENS, G., YASSAA, N., SINHA, V., AALTO, P., AUFMHOFF, H., ARNOLD, F., FIEDLER, V., KULMALA, M. & WILLIAMS, J. 2009. VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events. *Atmos. Chem. Phys,* 9**,** 8331-8350.

EHN, M., THORNTON, J. A., KLEIST, E., SIPILÄ, M., JUNNINEN, H., PULLINEN, I., SPRINGER, M., RUBACH, F., TILLMANN, R. & LEE, B. 2014. A large source of low-volatility secondary organic aerosol. *Nature,* 506**,** 476-479.

EUROPEAN UNION. 2008. *Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe,* [Online]. Available: http://eur-lex.europa.eu/ [Accessed 24 May 2016].

FLEMING, G. & VAN DER MERWE, M. 2002. *Spatial disaggregation of greenhouse gas emissions inventory data for Africa south of the equator* [Online]. Available: http://gis.esri.com/library/userconf/proc00/professional/papers/PAP896/p896.htm [Accessed 25 May 2016 2016].

FORBES, P. & ROHWER, E. 2008. Monitoring of trace organic air pollutants–a developing country perspective. *Air Pollution XVI,* 116**,** 345-355.

FUENTES, J. D., GU, L., LERDAU, M., ATKINSON, R., BALDOCCHI, D., BOTTENHEIM, J., CICCIOLI, P., LAMB, B., GERON, C. & GUENTHER, A. 2000. Biogenic hydrocarbons in the atmospheric boundary layer: a review. *Bulletin of the American Meteorological Society,* 81.

FUENTES, J. D., WANG, D., BOWLING, D. R., POTOSNAK, M., MONSON, R. K., GOLIFF, W. S. & STOCKWELL, W. R. 2007. Biogenic hydrocarbon chemistry within and above a mixed deciduous forest. *Journal of atmospheric chemistry,* 56**,** 165-185.

GARSTANG, M., TYSON, P., SWAP, R., EDWARDS, M., KÅLLBERG, P. & LINDESAY, J. 1996. Horizontal and vertical transport of air over southern Africa. *Journal of Geophysical Research: Atmospheres,* 101**,** 23721-23736.

GEORGE, M., SHARMA, A., MISHRA, S. & KAUR, J. 2013. Delhi smog 2012: cause and concerns. *Journal of Pollution Effects & Control,* 2013.

GOVERNMENT GAZETTE REPUBLIC OF SOUTH AFRICA. 2009. *National Ambient Air Quality Standards* [Online]. Pretoria. Available: http://faolex.fao.org/docs/pdf/saf122986.pdf [Accessed 24 May 2016].

GRANT, D. D., FUENTES, J. D., CHAN, S., STOCKWELL, W. R., WANG, D. & NDIAYE, S. A. 2008. Volatile organic compounds at a rural site in western Senegal. *Journal of atmospheric chemistry,* 60**,** 19-35.

GREENBERG, J., GUENTHER, A., HARLEY, P., OTTER, L., VEENENDAAL, E., HEWITT, C., JAMES, A. & OWEN, S. 2003. Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana. *Journal of Geophysical Research: Atmospheres,* 108.

GUENTHER, A. 2002. The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems. *Chemosphere,* 49**,** 837-844.

GUENTHER, A., JIANG, X., HEALD, C., SAKULYANONTVITTAYA, T., DUHL, T., EMMONS, L. & WANG, X. 2012. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions.

GUENTHER, A., OTTER, L., ZIMMERMAN, P., GREENBERG, J., SCHOLES, R. & SCHOLES, M. 1996. Biogenic hydrocarbon emissions from southern African savannas. *Journal of Geophysical Research: Atmospheres,* 101**,** 25859-25865.

GUO, H., SO, K., SIMPSON, I., BARLETTA, B., MEINARDI, S. & BLAKE, D. 2007. C 1–C 8 volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment. *Atmospheric Environment,* 41**,** 1456-1472.

GWAZE, P., HELAS, G., ANNEGARN, H. J., HUTH, J. & PIKETH, S. J. 2007. Physical, chemical and optical properties of aerosol particles collected over Cape Town during winter haze episodes. *South African journal of science,* 103**,** 35-43.

HAAGEN-SMIT, A. J. 1952. Chemistry and physiology of Los Angeles smog. *Industrial & Engineering Chemistry,* 44**,** 1342-1346.

HAKOLA, H., HELLÉN, H., TARVAINEN, V., BÄCK, J., PATOKOSKI, J. & RINNE, J. 2009. Annual variations of atmospheric VOC concentrations in a boreal forest. *Boreal Environ. Res,* 14**,** 722-730.

HAKOLA, H., LAURILA, T., RINNE, J. & PUHTO, K. 2000. The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site. *Atmospheric Environment,* 34**,** 4971-4982.

HAKOLA, H., TARVAINEN, V., LAURILA, T., HILTUNEN, V., HELLÉN, H. & KERONEN, P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmospheric Environment,* 37**,** 1623-1634.

HALLQUIST, M., WENGER, J. C., BALTENSPERGER, U., RUDICH, Y., SIMPSON, D., CLAEYS, M., DOMMEN, J., DONAHUE, N. M., GEORGE, C., GOLDSTEIN, A. H., HAMILTON, J. F., HERRMANN, H., HOFFMANN, T., IINUMA, Y., JANG, M., JENKIN, M. E., JIMENEZ, J. L., KIENDLER-SCHARR, A., MAENHAUT, W., MCFIGGANS, G., MENTEL, T. F., MONOD, A., PRÉVÔT, A. S. H., SEINFELD, J. H., SURRATT, J. D., SZMIGIELSKI, R. & WILDT, J. 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.,* 9**,** 5155-5236.

HAO, L., ROMAKKANIEMI, S., YLI-PIRILÄ, P., JOUTSENSAARI, J., KORTELAINEN, A., KROLL, J., MIETTINEN, P., VAATTOVAARA, P., TIITTA, P. & JAATINEN, A. 2011. Mass yields of secondary organic aerosols from the oxidation of α-pinene and real plant emissions. *Atmospheric Chemistry and Physics,* 11**,** 1367-1378.

HARLEY, P., OTTER, L., GUENTHER, A. & GREENBERG, J. 2003. Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna. *Journal of Geophysical Research: Atmospheres,* 108.

HARRISON, D., HUNTER, M., LEWIS, A., SEAKINS, P., BONSANG, B., GROS, V., KANAKIDOU, M., TOUATY, M., KAVOURAS, I. & MIHALOPOULOS, N. 2001. Ambient isoprene and monoterpene concentrations in a Greek fir (Abies Borisii-regis) forest. Reconciliation with emissions measurements and effects on measured OH concentrations. *Atmospheric Environment,* 35**,** 4699-4711.

HELLÉN, H., HAKOLA, H., LAURILA, T., HILTUNEN, V. & KOSKENTALO, T. 2002. Aromatic hydrocarbon and methyl tert-butyl ether measurements in ambient air of Helsinki (Finland) using diffusive samplers. *Science of the total environment,* 298**,** 55-64.

HELLÉN, H., KURONEN, P. & HAKOLA, H. 2012a. Heated stainless steel tube for ozone removal in the ambient air measurements of mono- and sesquiterpenes. *Atmospheric Environment,* 57**,** 35-40.

HELLÉN, H., TYKKÄ, T. & HAKOLA, H. 2012b. Importance of monoterpenes and isoprene in urban air in northern Europe. *Atmospheric Environment,* 59**,** 59-66.

HEO, J., DE FOY, B., OLSON, M. R., PAKBIN, P., SIOUTAS, C. & SCHAUER, J. J. 2015. Impact of regional transport on the anthropogenic and biogenic secondary organic aerosols in the Los Angeles Basin. *Atmospheric Environment,* 103**,** 171-179.

HERNÁNDEZ, E. J. A., KRÜEGER, A., CÁRDENAS, C. I. R., STREMME, W., FRIEDRICH, M. M., BEZANILLA, A. & GRUTTER, M. 2016. The MAX-DOAS network in Mexico City to measure atmospheric pollutants. *Atmósfera,* 29**,** 157-167.

HOLZINGER, R., KLEISS, B., DONOSO, L. & SANHUEZA, E. 2001. Aromatic hydrocarbons at urban, sub-urban, rural (8 52′ N; 67 19′ W) and remote sites in Venezuela. *Atmospheric Environment,* 35**,** 4917-4927.

HOQUE, R. R., KHILLARE, P. S., AGARWAL, T., SHRIDHAR, V. & BALACHANDRAN, S. 2008. Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India. *Science of the Total Environment,* 392**,** 30-40.

IARC 2012. Chemical agents and related occupations. *IARC Monographs On The Evaluation Of Carcinogenic Risks To Humans / World Health Organization, International Agency For Research On Cancer,* 100**,** 9-562.

IPCC 2013. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change,* Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.

JAIMES-PALOMERA, M., RETAMA, A., ELIAS-CASTRO, G., NERIA-HERNÁNDEZ, A., RIVERA-HERNÁNDEZ, O. & VELASCO, E. 2016. Non-methane hydrocarbons in the atmosphere of Mexico City: Results of the 2012 ozone-season campaign. *Atmospheric Environment,* 132**,** 258-275.

JENKIN, M. E., SAUNDERS, S. M., WAGNER, V. & PILLING, M. J. 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. *Atmos. Chem. Phys.,* 3**,** 181-193.

JOSIPOVIC, M., ANNEGARN, H. J., KNEEN, M. A., PIENAAR, J. J. & PIKETH, S. J. 2010. Concentrations, distributions and critical level exceedance assessment of SO2, NO2 and O3 in South Africa. *Environmental monitoring and assessment,* 171**,** 181-196.

KERBACHI, R., BOUGHEDAOUI, M., BOUNOUA, L. & KEDDAM, M. 2006. Ambient air pollution by aromatic hydrocarbons in Algiers. *Atmospheric Environment,* 40**,** 3995-4003.

KESSELMEIER, J., CICCIOLI, P., KUHN, U., STEFANI, P., BIESENTHAL, T., ROTTENBERGER, S., WOLF, A., VITULLO, M., VALENTINI, R. & NOBRE, A. 2002. Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget. *Global Biogeochemical Cycles,* 16.

KESSELMEIER, J. & STAUDT, M. 1999. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry,* 33**,** 23-88.

KHODER, M. I. 2007. Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo. *Atmospheric Environment,* 41**,** 554-566.

KIENDLER-SCHARR, A., WILDT, J., DAL MASO, M., HOHAUS, T., KLEIST, E., MENTEL, T. F., TILLMANN, R., UERLINGS, R., SCHURR, U. & WAHNER, A. 2009. New particle formation in forests inhibited by isoprene emissions. *Nature,* 461**,** 381-384.

KIM, E., HOPKE, P. K. & EDGERTON, E. S. 2003. Source identification of Atlanta aerosol by positive matrix factorization. *Journal of the Air & Waste Management Association,* 53**,** 731-739.

KIM, Y. M., HARRAD, S. & HARRISON, R. M. 2002. Levels and sources of personal inhalation exposure to volatile organic compounds. *Environmental science & technology,* 36**,** 5405-5410.

KIRKBY, J., CURTIUS, J., ALMEIDA, J., DUNNE, E., DUPLISSY, J., EHRHART, S., FRANCHIN, A., GAGNÉ, S., ICKES, L. & KÜRTEN, A. 2011. Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature,* 476**,** 429-433.

KOPPMANN, R. 2007. Volatile Organic Compounds in the Atmosphere: An Overview. *In:* KOPPMANN, R. (ed.) *Volatile organic compounds in the atmosphere.* Blackwell Publishing Ltd.

KOPPMANN, R. 2008. *Volatile organic compounds in the atmosphere*, John Wiley & Sons.

KOREAN MINISTRY OF ENVIRONMENT. 2011. *Air Quality Standards and Air Pollution Level,* [Online]. Available: http://eng.me.go.kr/eng/web/index.do?menuId=253&findDepth=1 [Accessed 24 May 2016].

KUHN, U., ROTTENBERGER, S., BIESENTHAL, T., WOLF, A., SCHEBESKE, G., CICCIOLI, P., BRANCALEONI, E., FRATTONI, M., TAVARES, T. & KESSELMEIER, J. 2002. Isoprene and monoterpene emissions of Amazonian tree species during the wet season: Direct and indirect investigations on controlling environmental functions. *Journal of Geophysical Research: Atmospheres,* 107.

KULMALA, M., KONTKANEN, J., JUNNINEN, H., LEHTIPALO, K., MANNINEN, H. E., NIEMINEN, T., PETÄJÄ, T., SIPILÄ, M., SCHOBESBERGER, S. & RANTALA, P. 2013. Direct observations of atmospheric aerosol nucleation. *Science,* 339**,** 943-946.

KULMALA, M., PETÄJÄ, T., EHN, M., THORNTON, J., SIPILÄ, M., WORSNOP, D. & KERMINEN, V.-M. 2014. Chemistry of atmospheric nucleation: on the recent advances on precursor characterization and atmospheric cluster composition in connection with atmospheric new particle formation. *Annual review of physical chemistry,* 65**,** 21-37.

KULMALA, M., PIRJOLA, L. & MÄKELÄ, J. M. 2000. Stable sulphate clusters as a source of new atmospheric particles. *Nature,* 404**,** 66-69.

KULMALA, M., VEHKAMÄKI, H., PETÄJÄ, T., DAL MASO, M., LAURI, A., KERMINEN, V.-M., BIRMILI, W. & MCMURRY, P. H. 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *Journal of Aerosol Science,* 35**,** 143-176.

LAAKSO, L., LAAKSO, H., AALTO, P., KERONEN, P., PETÄJÄ, T., NIEMINEN, T., POHJA, T., SIIVOLA, E., KULMALA, M. & KGABI, N. 2008. Basic characteristics of atmospheric particles, trace gases and meteorology in a relatively clean Southern African Savannah environment. *Atmospheric Chemistry and Physics Discussions,* 8**,** 6313-6353.

LAAKSO, L., VAKKARI, V., VIRKKULA, A., LAAKSO, H., BACKMAN, J., KULMALA, M., BEUKES, J., VAN ZYL, P., TIITTA, P. & JOSIPOVIC, M. 2012. South African EUCAARI measurements: seasonal variation of trace gases and aerosol optical properties. *Atmospheric Chemistry and Physics,* 12**,** 1847-1864.

LABAN, T. L., BEUKES, J. P. & VAN ZYL, P. G. 2015. Measurement of surface ozone in South Africa with reference to impacts on human health: commentary. *Clean Air Journal= Tydskrif vir Skoon Lug,* 25**,** 9-12.

LAMARQUE, J.-F., BOND, T. C., EYRING, V., GRANIER, C., HEIL, A., KLIMONT, Z., LEE, D., LIOUSSE, C., MIEVILLE, A. & OWEN, B. 2010. Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application. *Atmospheric Chemistry and Physics,* 10**,** 7017-7039.

LAPPALAINEN, H., SEVANTO, S., BÄCK, J., RUUSKANEN, T., KOLARI, P., TAIPALE, R., RINNE, J., KULMALA, M. & HARI, P. 2009. Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors. *Atmospheric Chemistry and Physics,* 9**,** 5447-5459.

LAUROS, J., SOGACHEV, A., SMOLANDER, S., VUOLLEKOSKI, H., SIHTO, S.-L., MAMMARELLA, I., LAAKSO, L., RANNIK, Ü. & BOY, M. 2011. Particle concentration and flux dynamics in the atmospheric boundary layer as the indicator of formation mechanism. *Atmospheric Chemistry and Physics,* 11**,** 5591-5601.

LELIEVELD, J., BUTLER, T. M., CROWLEY, J. N., DILLON, T. J., FISCHER, H., GANZEVELD, L., HARDER, H., LAWRENCE, M. G., MARTINEZ, M., TARABORRELLI, D. & WILLIAMS, J. 2008. Atmospheric oxidation capacity sustained by a tropical forest. *Nature,* 452**,** 737-40.

LOURENS, A. S., BEUKES, J. P., VAN ZYL, P. G., FOURIE, G. D., BURGER, J. W., PIENAAR, J. J., READ, C. E. & JORDAAN, J. H. 2011. Spatial and temporal assessment of gaseous pollutants in the Highveld of South Africa. *South African Journal of Science,* 107**,** 1-8.

LOURENS, A. S., BUTLER, T. M., BEUKES, J. P., VAN ZYL, P. G., BEIRLE, S., WAGNER, T. K., HEUE, K.-P., PIENAAR, J. J., FOURIE, G. D. & LAWRENCE, M. G. 2012. Re-evaluating the NO2 hotspot over the South African Highveld. *South African Journal of Science,* 108**,** 83-91.

MAKKONEN, R., ASMI, A., KERMINEN, V.-M., BOY, M., ARNETH, A., GUENTHER, A. & KULMALA, M. 2012. BVOC-aerosol-climate interactions in the global aerosol-climate model ECHAM5. 5-HAM2. *Atmospheric Chemistry and Physics,* 12**,** 10077-10096.

MARTINS, J., DHAMMAPALA, R., LACHMANN, G., GALY-LACAUX, C. & PIENAAR, J. 2007. Long-term measurements of sulphur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in southern Africa using passive samplers. *South African journal of science,* 103**,** 336-342.

MAULDIN III, R., BERNDT, T., SIPILÄ, M., PAASONEN, P., PETÄJÄ, T., KIM, S., KURTEN, T., STRATMANN, F., KERMINEN, V.-M. & KULMALA, M. 2012. A new atmospherically relevant oxidant of sulphur dioxide. *Nature,* 488**,** 193-196.

MELLOUKI, A., LE BRAS, G. & SIDEBOTTOM, H. 2003. Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase. *Chemical reviews,* 103**,** 5077-5096.

MIELKE, L. H., PRATT, K. A., SHEPSON, P. B., MCLUCKEY, S. A., WISTHALER, A. & HANSEL, A. 2010. Quantitative Determination of Biogenic Volatile Organic Compounds in the Atmosphere Using Proton-Transfer Reaction Linear Ion Trap Mass Spectrometry†. *Analytical chemistry,* 82**,** 7952-7957.

MOGENSEN, D. 2015. Insights into atmospheric oxidation.

MUCINA, L. & RUTHERFORD, M. C. 2006. *The Vegetation of South Africa, Lesotho and Swaziland*, South African National Biodiversity Institute.

NAKASHIMA, Y., KATO, S., GREENBERG, J., HARLEY, P., KARL, T., TURNIPSEED, A., APEL, E., GUENTHER, A., SMITH, J. & KAJII, Y. 2014. Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign. *Atmospheric Environment,* 85**,** 1-8.

NOE, S. M., HÜVE, K., NIINEMETS, Ü. & COPOLOVICI, L. 2012. Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest. *Atmospheric Chemistry and Physics,* 12**,** 3909-3926.

OTTER, L., GUENTHER, A. & GREENBERG, J. 2002. Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands. *Atmospheric Environment,* 36**,** 4265-4275.

OTTER, L., GUENTHER, A., WIEDINMYER, C., FLEMING, G., HARLEY, P. & GREENBERG, J. 2003. Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator. *Journal of Geophysical Research: Atmospheres,* 108.

OTTO, D. A., HUDNELL, H. K., HOUSE, D. E., MØLHAVE, L. & COUNTS, W. 1992. Exposure of humans to a volatile organic mixture. I. Behavioral assessment. *Archives of Environmental Health: An International Journal,* 47**,** 23-30.

PAASONEN, P., NIEMINEN, T., ASMI, E., MANNINEN, H., PETÄJÄ, T., PLASS-DÜLMER, C., FLENTJE, H., BIRMILI, W., WIEDENSOHLER, A. & HORRAK, U. 2010. On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation. *Atmospheric Chemistry and Physics,* 10**,** 11223-11242.
PAATERO, P. 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and intelligent laboratory systems,* 37**,** 23-35.
PAATERO, P. & TAPPER, U. 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics,* 5**,** 111-126.
PANEL, A. P. 2015. Africa Progress Report "Power People Planet: seizing Africa's energy and climate opportunities". *Africa Progress Panel*.
PARALOVO, S. L., BORILLO, G. C., BARBOSA, C. G. G., GODOI, A. F. L., YAMAMOTO, C. I., DE SOUZA, R. A. F., ANDREOLI, R. V., COSTA, P. S., ALMEIDA, G. P., MANZI, A. O., PÖHLKER, C., YÁÑEZ-SERRANO, A. M., KESSELMEIER, J. & GODOI, R. H. M. 2016. Observations of atmospheric monoaromatic hydrocarbons at urban, semi-urban and forest environments in the Amazon region. *Atmospheric Environment,* 128**,** 175-184.
PAYNE-STURGES, D. C., BURKE, T. A., BREYSSE, P., DIENER-WEST, M. & BUCKLEY, T. J. 2004. Personal exposure meets risk assessment: a comparison of measured and modeled exposures and risks in an urban community. *Environmental Health Perspectives,* 112**,** 589.
PIKETH, S., ANNEGARN, H. & TYSON, P. 1999. Lower tropospheric aerosol loadings over South Africa: The relative contribution of aeolian dust, industrial emissions, and biomass burning. *Journal of Geophysical Research: Atmospheres,* 104**,** 1597-1607.
PINHO, P., PIO, C. & JENKIN, M. 2005. Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data. *Atmospheric Environment,* 39**,** 1303-1322.
POLISSAR, A. V., HOPKE, P. K., PAATERO, P., MALM, W. C. & SISLER, J. F. 1998. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. *Journal of Geophysical Research: Atmospheres,* 103**,** 19045-19057.
POLLACK, I. B., RYERSON, T. B., TRAINER, M., NEUMAN, J., ROBERTS, J. M. & PARRISH, D. D. 2013. Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010. *Journal of Geophysical Research: Atmospheres,* 118**,** 5893-5911.
PONE, J. D. N., HEIN, K. A., STRACHER, G. B., ANNEGARN, H. J., FINKLEMAN, R. B., BLAKE, D. R., MCCORMACK, J. K. & SCHROEDER, P. 2007. The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. *International Journal of Coal Geology,* 72**,** 124-140.
RAIS. 2016. *The Risk Assessment Information System* [Online]. The University of Tennessee. Available: https://rais.ornl.gov/tools/profile.php [Accessed 26 June 2016].
RÄISÄNEN, T., RYYPPÖ, A. & KELLOMÄKI, S. 2009. Monoterpene emission of a boreal Scots pine (Pinus sylvestris L.) forest. *Agricultural and forest meteorology,* 149**,** 808-819.
RANTALA, P., AALTO, J., TAIPALE, R., RUUSKANEN, T. & RINNE, J. 2015. Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere. *Biogeosciences,* 12**,** 5753-5770.
REIMANN, S. & LEWIS, A. C. 2007. Anthropogenic VOCs. *Volatile organic compounds in the atmosphere***,** 33-70.
RINNE, H., GUENTHER, A., GREENBERG, J. & HARLEY, P. 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmospheric Environment,* 36**,** 2421-2426.
RINNE, J., HAKOLA, H., LAURILA, T. & RANNIK, Ü. 2000. Canopy scale monoterpene emissions of Pinus sylvestris dominated forests. *Atmospheric Environment,* 34**,** 1099-1107.
RINNE, J., RUUSKANEN, T. M., REISSELL, A., TAIPALE, R., HAKOLA, H. & KULMALA, M. 2005. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem. *Boreal environment research,* 10**,** 425-436.

ROHRER, F. & BERRESHEIM, H. 2006. Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. *Nature,* 442**,** 184-187.
RUUSKANEN, T., MÜLLER, M., SCHNITZHOFER, R., KARL, T., GRAUS, M., BAMBERGER, I., HÖRTNAGL, L., BRILLI, F., WOHLFAHRT, G. & HANSEL, A. 2011. Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF. *Atmospheric Chemistry and Physics,* 11**,** 611-625.
SAXTON, J., LEWIS, A., KETTLEWELL, J., OZEL, M., GOGUS, F., BONI, Y., KOROGONE, S. & SERÇA, D. 2007. Isoprene and monoterpene measurements in a secondary forest in northern Benin. *Atmospheric Chemistry and Physics,* 7**,** 4095-4106.
SEINFELD, J. H. & PANDIS, S. N. 2006. Atmospheric chemistry and physics. Hoboken. NJ: Wiley.
SERCA, D., GUENTHER, A., KLINGER, L., VIERLING, L., HARLEY, P., DRUILHET, A., GREENBERG, J., BAKER, B., BAUGH, W. & BOUKA-BIONA, C. 2001. EXPRESSO flux measurements at upland and lowland Congo tropical forest site. *Tellus B,* 53**,** 220-234.
SIPILÄ, M., BERNDT, T., PETÄJÄ, T., BRUS, D., VANHANEN, J., STRATMANN, F., PATOKOSKI, J., MAULDIN, R. L., HYVÄRINEN, A.-P. & LIHAVAINEN, H. 2010. The role of sulfuric acid in atmospheric nucleation. *Science,* 327**,** 1243-1246.
SIPILÄ, M., JOKINEN, T., BERNDT, T., RICHTERS, S., MAKKONEN, R., DONAHUE, N., MAULDIN III, R., KURTÉN, T., PAASONEN, P. & SARNELA, N. 2014. Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO 2 and organic acids. *Atmospheric Chemistry and Physics,* 14**,** 12143-12153.
SMOLANDER, S., HE, Q., MOGENSEN, D., ZHOU, L., BÄCK, J., RUUSKANEN, T., NOE, S., GUENTHER, A., AALTONEN, H. & KULMALA, M. 2014. Comparing three vegetation monoterpene emission models to measured gas concentrations with a model of meteorology, air chemistry and chemical transport. *Biogeosciences,* 11.
SPIRIG, C., NEFTEL, A., AMMANN, C., DOMMEN, J., GRABMER, W., THIELMANN, A., SCHAUB, A., BEAUCHAMP, J., WISTHALER, A. & HANSEL, A. 2005. Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry. *Atmospheric Chemistry and Physics,* 5**,** 465-481.
STEIN, D. C., SWAP, R. J., GRECO, S., PIKETH, S. J., MACKO, S. A., DODDRIDGE, B. G., ELIAS, T. & BRUINTJES, R. T. 2003. Haze layer characterization and associated meteorological controls along the eastern coastal region of southern Africa. *Journal of Geophysical Research: Atmospheres,* 108.
STEINER, A. H. & GOLDSTEIN, A. L. 2007. Biogenic VOCs. *In:* KOPPMANN, R. (ed.) *Volatile Organic Compounds in the Atmosphere.* Oxford: Blackwell Publishing Ltd.
STROUD, C., MAKAR, P., KARL, T., GUENTHER, A., GERON, C., TURNIPSEED, A., NEMITZ, E., BAKER, B., POTOSNAK, M. & FUENTES, J. D. 2005. Role of canopy-scale photochemistry in modifying biogenic-atmosphere exchange of reactive terpene species: Results from the CELTIC field study. *Journal of Geophysical Research: Atmospheres,* 110.
SUN, Y., ZHUANG, G., TANG, A., WANG, Y. & AN, Z. 2006. Chemical characteristics of PM2. 5 and PM10 in haze-fog episodes in Beijing. *Environmental science & technology,* 40**,** 3148-3155.
TAATJES, C. A., MELONI, G., SELBY, T. M., TREVITT, A. J., OSBORN, D. L., PERCIVAL, C. J. & SHALLCROSS, D. E. 2008. Direct observation of the gas-phase Criegee intermediate (CH2OO). *Journal of the American Chemical Society,* 130**,** 11883-11885.
THE GAZETTE OF INDIA. 2009. *National Ambient Air Quality Standards* [Online]. New Delhi. Available: http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php [Accessed 24 May 2016].
TIITTA, P., VAKKARI, V., CROTEAU, P., BEUKES, J., VAN ZYL, P., JOSIPOVIC, M., VENTER, A., JAARS, K., PIENAAR, J. & NG, N. 2014. Chemical composition, main sources and temporal variability of PM 1 aerosols in southern African grassland. *Atmospheric Chemistry and Physics,* 14**,** 1909-1927.

TIWARI, S., DAHIYA, A. & KUMAR, N. 2015. Investigation into relationships among NO, NO 2, NO x, O 3, and CO at an urban background site in Delhi, India. *Atmospheric Research,* 157**,** 119-126.
TOWNSEND, A. R., HOWARTH, R. W., BAZZAZ, F. A., BOOTH, M. S., CLEVELAND, C. C., COLLINGE, S. K., DOBSON, A. P., EPSTEIN, P. R., HOLLAND, E. A. & KEENEY, D. R. 2003. Human health effects of a changing global nitrogen cycle. *Frontiers in Ecology and the Environment,* 1**,** 240-246.
TUNVED, P., HANSSON, H.-C., KERMINEN, V.-M., STRÖM, J., DAL MASO, M., LIHAVAINEN, H., VIISANEN, Y., AALTO, P., KOMPPULA, M. & KULMALA, M. 2006. High natural aerosol loading over boreal forests. *Science,* 312**,** 261-263.
TYSON, P., GARSTANG, M. & SWAP, R. 1996. Large-scale recirculation of air over southern Africa. *Journal of applied meteorology,* 35**,** 2218-2236.
TYSON, P. D. & PRESTON-WHYTE, R. A. 2000. *weather and climate of southern Africa*, Oxford University Press.
USEPA 2009. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation

Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). EPA-540-R-070-002. *In:* OFFICE OF SUPERFUND REMEDIATION AND TECHNOLOGY INNOVATION (ed.). Washington, DC, USA: US Environmental Protection Agency.
VAKKARI, V. 2013. On the sources of submicron aerosol particles in savannah: implications for climate and air quality.
VAKKARI, V., LAAKSO, H., KULMALA, M., LAAKSONEN, A., MABASO, D., MOLEFE, M., KGABI, N. & LAAKSO, L. 2011. New particle formation events in semi-clean South African savannah. *Atmos. Chem. Phys.,* 11**,** 3333-3346.
VAKKARI, V., TIITTA, P., JAARS, K., CROTEAU, P., BEUKES, J. P., JOSIPOVIC, M., KERMINEN, V. M., KULMALA, M., VENTER, A. D. & ZYL, P. G. 2015. Reevaluating the contribution of sulfuric acid and the origin of organic compounds in atmospheric nanoparticle growth. *Geophysical Research Letters,* 42.
VAN DER WALT, H. J. 2008. *The impact of hydrocarbon emissions on regional air quality in a South African metropolitan area/Hermanus Johannes van der Walt.* North-West University.
VANREKEN, T., GREENBERG, J., HARLEY, P., GUENTHER, A. & SMITH, J. 2006. Direct measurement of particle formation and growth from the oxidation of biogenic emissions. *Atmospheric Chemistry and Physics,* 6**,** 4403-4413.
VOGEL, B., FIEDLER, F. & VOGEL, H. 1995. Influence of topography and biogenic volatile organic compounds emission in the state of Baden-Württemberg on ozone concentrations during episodes of high air temperatures. *Journal of Geophysical Research: Atmospheres,* 100**,** 22907-22928.
WAGNER, P. & KUTTLER, W. 2014. Biogenic and anthropogenic isoprene in the near-surface urban atmosphere—a case study in Essen, Germany. *Science of the Total Environment,* 475**,** 104-115.
WANG, J.-F., HU, M.-G., XU, C.-D., CHRISTAKOS, G. & ZHAO, Y. 2013. Estimation of citywide air pollution in Beijing. *PloS one,* 8**,** e53400.
WELZ, O., SAVEE, J. D., OSBORN, D. L., VASU, S. S., PERCIVAL, C. J., SHALLCROSS, D. E. & TAATJES, C. A. 2012. Direct kinetic measurements of Criegee intermediate (CH2OO) formed by reaction of CH2I with O2. *Science,* 335**,** 204-207.
WENT, F. W. 1960. Blue hazes in the atmosphere. *Nature,* 187**,** 641-643.
WICHMANN, F. A., MÜLLER, A., BUSI, L. E., CIANNI, N., MASSOLO, L., SCHLINK, U., PORTA, A. & SLY, P. D. 2009. Increased asthma and respiratory symptoms in children exposed to petrochemical pollution. *Journal of Allergy and Clinical Immunology,* 123**,** 632-638.
WICKING-BAIRD, M. C., DE VILLIERS, M. & DUTKIEWICZ, R. K. 1997. *Cape Town brown haze study*, Energy Research Institute, University of Cape Town Cape Town.
WORLD HEALTH ORGANIZATION 2000. *Air quality guidelines for Europe*.

WORLD HEALTH ORGANIZATION 2006. *Regional Office for Europe, World Health Organization, Air quality guidelines: global update 2005: particulate matter, ozone, nitrogen dioxide, and sulfur dioxide*, World Health Organization.

ZHANG, A., QI, Q., JIANG, L., ZHOU, F. & WANG, J. 2013. Population exposure to PM 2.5 in the urban area of Beijing. *PloS one,* 8**,** e63486.

ZHAO, J., EISELE, F. L., TITCOMBE, M., KUANG, C. & MCMURRY, P. H. 2010. Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS. *Journal of Geophysical Research: Atmospheres,* 115.

ZUNCKEL, M., CHILOANE, K., SOWDEN, M. & OTTER, L. 2007. Biogenic volatile organic compounds: The state of knowledge in southern Africa and the challenges for air quality management. *South African Journal of Science,* 103.

ZUNCKEL, M., KOOSAILEE, A., YARWOOD, G., MAURE, G., VENJONOKA, K., VAN TIENHOVEN, A. & OTTER, L. 2006. Modelled surface ozone over southern Africa during the cross border air pollution impact assessment project. *Environmental Modelling & Software,* 21**,** 911-924.

ZUNCKEL, M., VENJONOKA, K., PIENAAR, J. J., BRUNKE, E. G., PRETORIUS, O., KOOSIALEE, A., RAGHUNANDAN, A. & VAN TIENHOVEN, A. M. 2004. Surface ozone over southern Africa: synthesis of monitoring results during the Cross border Air Pollution Impact Assessment project. *Atmospheric Environment,* 38**,** 6139-6147.