Spatial and temporal assessment of atmospheric organic carbon and black carbon concentrations at South African DEBITS sites

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Petra

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Abstract

The baseline of uncertainty in aerosol radiative forcing is large and depends on aerosol characteristics (e.g. size and composition), which can vary significantly on a regional scale. Sources (natural and anthropogenic) can be directly linked to the aerosol characteristics of a region, making monitoring campaigns to determine aerosol composition in different regions very important.

Limited data currently exists for atmospheric aerosol black carbon (BC) and organic carbon (OC) in South Africa. In this study, BC and OC concentrations were explored in terms of spatial and temporal patterns, mass fractions of BC and OC of the overall aerosol mass, as well as possible sources.

Primary pollutants, of which BC is an example, are emitted directly from the source. Certain primary pollutants can react with other pollutants to form secondary pollutants. OC can either be a primary or secondary pollutant, e.g. formed by gas-to-particle conversion of volatile organic compounds (VOCs) in the atmosphere (nucleation and condensation of gaseous precursors).

Greenhouse gases (GHG) and BC absorb terrestrial long wave radiation causing an increase of atmospheric temperature. In contrast, OC generally reflects incoming radiation, cooling the atmosphere. GHGs have a long residence time in the atmosphere (10 to 100 years), while the residence time of aerosols is usually only a week or more. The climatic effects of aerosols are therefore particularly important from a regional perspective. Aerosols are also important from an air quality perspective, especially since ultrafine particles (diameter smaller than 100nm) are small enough to go through the membranes of the respiratory tract and into the blood stream. They can then be transported to the brain.

Up to 2005, DEBITS (Deposition of Biogeochemical Import Trace Species) activities in South Africa did not include aerosol measurements. In order to initiate aerosol monitoring, campaigns were launched during the 2005 to 2007 period. Additionally, OC and BC measurements for the PM_{10} and $PM_{2.5}$ (particulate matter smaller than or equal to 10 and 2.5 µm, respectively) fractions were started in 2009. PM_{10} and $PM_{2.5}$ samples were collected at five sampling sites in South Africa operated within the

DEBITS network, i.e. Louis Trichardt, Skukuza, Vaal Triangle, Amersfoort and Botsalano, with MiniVol samplers. The selected sites are mostly located in rural areas, but with the surrounding atmosphere influenced by industries, transportation, biomass burning, etc. Winters are characterised by an increase in biomass burning (fires) and combustion for domestic use (cooking and space heating). Samples were analysed with a Thermal/Optical Carbon analyser (Desert Research Institute).

OC and BC results showed that the total carbonaceous content decreased during the summer due to less biomass burning (fires). BC was the highest at the industrially influenced sites, while OC was highest at regional background sites. OC was higher than BC concentrations at all sites in both size fractions. Most OC and BC occurred in the $PM_{2.5}$ fraction. OC/BC ratios reflected the setting of the different DEBITS sites, with sites in or close to anthropogenic source regions having the lowest OC/BC ratios, while background sites had the highest OC/BC ratios.

The OC mass fraction percentage of the total aerosol weight varied up to 24% and the BC up to 12%. The highest OC mass fraction was found at Skukuza, which was attributed to both natural (lies within the savannah biome) and anthropogenic (dominant path of air mass movement from the anthropogenic industrial hub of South Africa) reasons. The highest mass fraction of BC was found in the Vaal Triangle, since it is situated within a well-known anthropogenic source region. Household combustion for space heating and cooking also seemed to make a significant contribution to BC at this site in the cold winter months.

A relatively well-defined seasonal pattern was observed, with higher OC and BC concentrations measured from May to October, which coincides with the dry season in the interior of South Africa. Positive correlations between OC and BC concentrations with the distance back trajectories passed fires were observed, indicating that fires contribute significantly to both atmospheric OC and BC during the burning season.

Keywords: Organic carbon (OC), Black carbon (BC), Spatial, Temporal, DEBITS, IDAF

Preface

Introduction

This MSc dissertation was submitted in an article format for evaluation, as allowed and described by the A-rules of the North-West University (NWU). This entails that the article is added into the dissertation as prepared for submission to an accredited journal. The conventional experimental, as well as results and discussions chapters were excluded, since the relevant information is summarised and presented in the article. A separate background and motivation chapter (Chapter 1), a literature chapter (Chapter 2) and a project evaluation chapter (Chapter 4) were included in the dissertation, even though certain information presented in these chapters was summarised in the article. This will result in some repetition of ideas or similar text in some of the chapters and in the article. The numbering of Chapter 3 (article) is also not consistent with the rest of the dissertation, since it was added in the exact format of the journal that it was prepared for.

Rationale in submitting dissertation in article format

Currently, it is a pre-requisite at the NWU that an MSc dissertation is handed in with a draft article prepared. In practice, many of these draft papers are never submitted for peer-reviewed publication. However, in this study, the candidate decided to submit this MSc dissertation in article format, since it required the candidate to prepare an article that is suitable for submission to an ISI-accredited journal. Therefore, the pre-requisites of the NWU were exceeded.

Co-authors for the above-mentioned article (Chapter 3)

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Contributions to the article

The contributions of the various co-authors were as follows. The work was conducted by me, Petra Maritz, with conceptual ideas, recommendations and guidance during the project by J.P. Beukes (supervisor) and P.G. van Zyl (supervisor). E.H. Conradie assisted especially during the initial phases of the project with logistical arrangements. J.J. Pienaar initiated the measurements of OC and BC within the South African DEBITS network and made conceptual contributions. C. Liousse and C. Galy-Lacaux contributed conceptually and assisted with the experimental work. A. Ramandh and G. Mkhatshwa provided financial and conceptual contributions to the study. A.D. Venter assisted with data processing.

Formatting and current status of article

The article was formatted in accordance with the specifications of *Atmospheric Environment*, which is an Elsevier Journal. The guide to the authors that was followed in preparation of the article is available at: http://www.elsevier.com/journals/atmospheric-environment/1352-2310/guide-for-authors (Date of access: 29 October 2013). A final decision to which journal this article will be submitted has not yet been made and it might therefore be submitted to a journal other than *Atmospheric Environment*.

Declaration by co-authors

All the co-authors of the article had the opportunity to comment on the draft article as included in Chapter 3 and gave consent that it may be included in this MSc dissertation.

Chapter 1

Introduction

1.1. Background and motivation

In atmospheric chemistry, the concentrations, properties and reactions of chemical species in the atmosphere, as well as their impacts on the environment, are investigated. It is also important to determine the major sources and sinks of atmospheric chemical species. Inorganic and organic chemical species are present in the atmosphere, which can occur either in the gas phase or particulate matter. Atmospheric chemical species have impacts on general air quality and climate change depending on their properties and concentrations in ambient air (Pőschl, 2005:44; Godish, 2004). Poor air quality is usually associated with harmful impacts on human health, vegetation, animals and natural ecosystems. Chemical species in the atmosphere also have an influence on the radiative balance of the earth, which can lead to either warming or cooling of the atmosphere of the earth (IPCC, 2013; Andreae, 2007:365).

According to Pőschl (2005:44) and Slanina and Zhang (2004:76), atmospheric aerosols are solid or liquid particulate matter (PM) suspended in the atmosphere with diameters ranging from 10^{-9} to 10^{-4} m. These species have atmospheric lifetimes of up to approximately one week (Pőschl, 2005:44; Kneip & Lioy, 1980). The impacts of atmospheric aerosols on the environment are determined by their physical (size, mass, structure, concentration and optical density) and chemical properties. Atmospheric aerosols typically comprise black carbon (BC), organic compounds (OC), sulphate, nitrate, ammonium and trace metal species. These chemical species influence the physical properties of atmospheric aerosols and determine whether airborne aerosols have a cooling or a warming effect on the atmosphere. BC, for instance, absorbs radiative energy, which leads to the heating of the atmosphere, while white or grey particles such as sulphate and most organic compounds scatter sunlight, which has a cooling effect on the earth's atmosphere. It is therefore important to chemically characterise atmospheric PM species (IPCC, 2013; Andreae, 2007:365)

In addition to the impacts of atmospheric aerosols on climate change, there are also other environmental-related problems associated with these species. They have impacts on general air quality, which could include detrimental human health (e.g. cardiopulmonary diseases and respiratory diseases) effects, stratospheric ozone loss, acid deposition (especially through ammonium, nitrate and sulphate) and eutrophication (deposition of large quantities of nutrients, especially nitrate that causes damage to the ecosystem). Particulate matter, i.e. $PM_{2.5}$ (particulate matter with a diameter smaller than 2.5µm), is especially associated with severe health effects, which include cardiovascular-, respiratory- and allergic diseases. Fine particles, i.e. PM_1 (diameter smaller than 1µm), are small enough to penetrate through the membranes of the respiratory tract into the bloodstream and can be transported to the brain. There is still uncertainty whether physical or chemical properties of PM are the most important factors that determine the impacts of these species on human health. Airborne particles also spread biological organisms, reproductive materials and pathogens such as pollen, viruses and bacteria. These pathogens can also cause or enhance cardiopulmonary- and allergic diseases (Pőschl, 2005:44; Gauderman *et al*., 2004:351; Ring *et al*., 2001:13).

Aerosols have an impact on local, regional and global air quality and climate. The main impacts of aerosols on these different scales are listed below (Slanina & Zhang, 2004:76):

- Local scale: Aerosols affect human health and reduce visibility.
- Regional scale: Aerosols contribute to acid deposition and eutrophication, as well as affecting photochemistry and ozone production.
- Global scale: Aerosols reflect or absorb sunlight and are therefore responsible for climate change. Aerosols increase stratospheric ozone loss (Antarctic ozone hole).

Atmospheric aerosols are emitted from natural and anthropogenic sources. Natural sources include biomass burning fires, volcanic eruptions, soil, dust and sea salt, as well as different biological materials such as plant fragments, pollen and micro-organisms. Major anthropogenic sources include industrial activities, incomplete combustion of fossil fuels, biomass burning (fires and household combustion) and traffic emissions. Aerosols can be emitted directly from these sources as primary pollutants, or are secondary pollutants that are formed through atmospheric chemical reactions such as gas-to-particle conversion of volatile organic compounds (VOCs) in the atmosphere. Gas-to-particle conversion may occur through different pathways (Andreae & Rosenfeld, 2008:89; Pőschl, 2005:44), which include:

1. New particle formation: Gas-phase reactions from semi-volatile organic compounds (SVOCs). SVOCs participate in the nucleation and growth of new aerosol particles (Pőschl, 2005:44).
2. Gas-particle partitioning: SVOCs that are formed by gas-phase reactions and are adsorbed by pre-existing aerosols or cloud particles (Pőschl, 2005:44).
3. Heterogeneous (or multiphase) reactions: Chemical reaction of VOCs or SVOCs at the surface or large quantities of aerosols or cloud particles form lower volatility organic compounds (LVOCs) or non-volatile organic compounds (NVOCs) (Pőschl, 2005:44).

BC is mainly directly emitted into the atmosphere, while OC could consist of primary and secondary aerosols (Pőschl, 2005:44; Putaud *et al*., 2004:38). Atmospheric aerosols are removed from the atmosphere through dry and wet deposition. Larger particles are usually deposited in areas close to their sources, while small particles can be deposited in areas further from their sources (Zhang & Vet, 2006:4).

Although Africa is regarded as the largest source region of anthropogenic primary OC aerosols and atmospheric BC (Kanakidou *et al*., 2005:5), it is one of the least studied continents. Within Africa, southern Africa is an important source region. Biomass burning events (fires) are endemic across the southern African savannah region, especially during the dry season when almost no precipitation occurs (Vakkari *et al.*, 2013:13). South Africa is also the economic and industrial hub in southern Africa with large anthropogenic point sources (Beukes *et al*., 2013:12). It is therefore important to conduct atmospheric measurements for this region.

The Deposition of Biogeochemical Important Trace Species (DEBITS) project is an international project that was established as a long-term initiative to measure atmospheric pollutants. In South Africa, atmospheric gaseous and aerosol species are collected at five regionally representative background sites. Atmospheric measurements at these sites are currently the most comprehensive long-term measurement dataset available for the deposition of chemical atmospheric species in southern Africa. (Martins, 2009)

Limited data exists for atmospheric OC and BC in South Africa. Martins (2009) determined BC and OC concentrations at two South African DEBITS sites. These measurements were, however, restricted to three two-week winter campaigns and one two-week summer campaign. Considering the lack of OC and BC data for South Africa, the general objective of this study was to present a spatial and temporal assessment of BC and OC concentrations at the South African DEBITS sites.

1.2. Objectives

In order to achieve the general objective of this study presented in the previous section, the specific objectives of this study were:

- to collect $PM_{2.5}$ and PM_{10} atmospheric aerosol samples at the South African DEBITS sites;
- to analyse the collected $PM_{2.5}$ and PM_{10} samples to determine the OC and BC concentrations;
- to assess the current *status quo* of OC and BC aerosol concentration trends at the regionally representative South African DEBITS sites; and
- to link the OC and BC concentrations measured to possible sources.

Chapter 2

Literature survey

2.1. Introduction to air pollution

The atmosphere of the earth is divided into various different vertical layers. These layers, starting with the layer closest to the earth's surface, include the troposphere, stratosphere, mesosphere, thermosphere and exosphere. The atmospheric layer closest to the surface of the earth and the troposphere is separated by a boundary layer that is approximately 1 km from the surface. Chemical and physical processes that occur in the troposphere and stratosphere have the largest influence on the surface of the earth and are usually studied in atmospheric sciences. The stratosphere is more stable than the troposphere with not that many atmospheric chemical compounds present compared to the troposphere.

According to Brasseur *et al*. (1999), between 85 and 90% of the atmospheric chemical species in the atmosphere are present in the troposphere, with the exception of ozone, of which 90% is found in the stratosphere. The predominant chemical compounds present in the troposphere and stratosphere include gaseous species, i.e. nitrogen and oxygen, and noble gases, e.g. helium, neon, argon and krypton. Smaller amounts of water vapour, carbon dioxide (CO_2) and ozone (O_3) are also present in the troposphere. Particulate matter (PM) or aerosols, i.e. solid or liquid species suspended in the atmosphere, is also present in the troposphere and stratosphere.

Air pollution is usually associated with the addition of chemical compounds into atmosphere in a sufficient concentration to have a measurable effect on humans, animals, vegetation and different atmospheric processes. Harrison (1999) stated that atmospheric pollutants, especially in the boundary layer and troposphere, have an impact on air quality and human health, as well as climate and weather. Pollutant species in the atmosphere are emitted from natural and anthropogenic sources. Natural sources include fires, volcanic eruptions, mineral dust and biological materials, while anthropogenic sources comprise largely incomplete combustion of fossil fuels, industrial emissions, traffic, household combustion and biomass burningfires (Assamoi & Liousse, 2010:44; Andreae & Rosenfeld, 2008:89; Laakso *et al.*, 2008:8; Pőschl, 2005:44;).

2.2. Impacts of air pollution

The impacts of atmospheric pollutant species on the environment are usually described in terms of their impacts on general air quality and their influence on climate change, which will be discussed in the subsequent sections.

2.2.1. Air quality

The atmosphere surrounding the environment of the earth is not completely uncontaminated. The monitoring of air quality is important for the present and for the future in order to establish its effects on human health and the environment, as well as to apply the appropriate mitigation procedures through proper air quality management (Pőschl, 2005:44; Bond & Sun, 2005:39). Various pollutant gaseous and PM species are released into the atmosphere, which has negative impacts on human health and the environment. Pollutants also affect visibility and contribute to the staining of monuments (Van Dingenen *et al*., 2004:38). According to Godish (2004), the chemical and physical properties of the pollutants determine their impacts on air quality. The impacts of air pollution on air quality can be classified according to the types of pollution, viz.:

Type I air pollution: Primary pollutants, i.e. sulphur dioxide (SO_2), large particles and dust fall that are emitted from outdoor sources. This type of pollution occurs all over the world and is associated with negative health effects, i.e. upper respiratory tract inflammation and infection.

Type II air pollution: Primary and secondary pollutants are emitted from outdoor as well as indoor sources. According to Behrendt *et al*. (1995) and Ring *et al*. (2001:13), it is common in the highly populated Western world, industrial regions and in rich urban areas. Allergic sensitisation and diseases are associated with this type of pollution.

Krämer *et al*. (1999:28) and Franze *et al*. (2005:39) stated that an increase occurred during the last decade concerning allergic diseases associated with atmospheric pollution. Allergies in West German children were reported to occur more frequently when they are exposed to vehicular exhaust emissions (Ring *et al*., 2001:13). Franze *et al*. (2005:39) also reported that allergic diseases are linked to traffic emissions, as well as the combination of ozone concentrations and high nitrogen oxide levels. Various studies have indicated that fine particulates and gaseous species related to traffic emissions enhance mortality, cardiopulmonary diseases, respiratory tract inflammation, infection and allergic diseases (Gauderman *et al*., 2004:351; Ring *et al*., 2001:13).

2.2.2. Climate change

Climate change involves the decrease or increase of the atmospheric temperatures of the earth. The physical and chemical properties of atmospheric pollutants determine whether species will have either a warming or a cooling effect on the atmosphere. The impacts of species on climate change are generally described in terms of their influence on radiative forcing (RF), which indicates whether infrared radiation from the surface of the earth is mainly absorbed or whether incoming solar radiation is predominantly reflected by species. Atmospheric species with a negative RF lead to the cooling of the atmosphere, while species with a positive RF cause the warming of the atmosphere. Greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and water vapour, as well as particulate black carbon (BC) have a warming influence on the earth's atmosphere, while light aerosols such as sulphates (SO_4^{2-}) have a cooling effect (IPCC, 2013; Andreae & Gelencsér, 2006:6; Bond & Sun, 2005:39). Figure 1 below indicates the impacts of atmospheric gaseous species and aerosols on RF (IPCC, 2007). The net radiative forcing is a total of 1.6 $W.m^{-2}$ and it is due to anthropogenic sources.

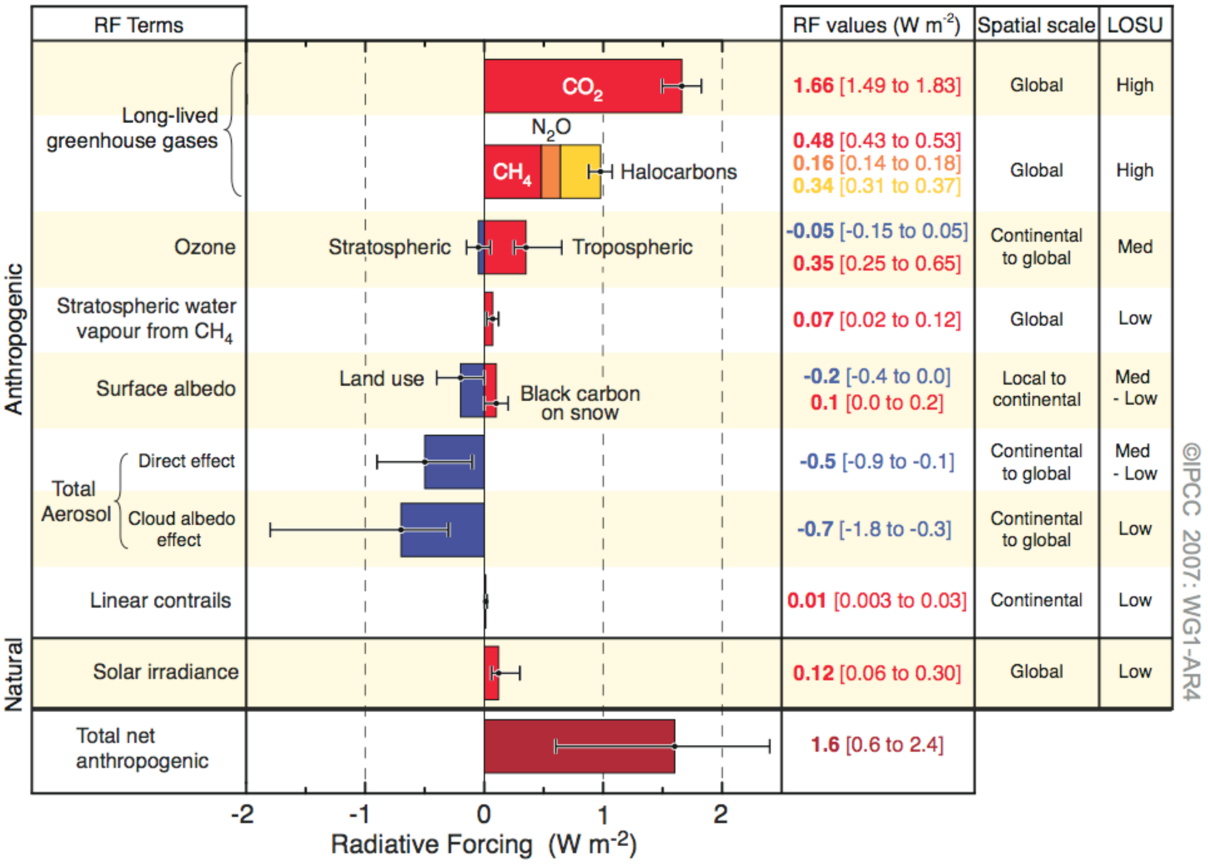

Figure 1: Average global RF in 2005 (IPCC, 2007)

According to Tyson and Preston-Whyte (2000), the atmospheric temperature rose slightly each year since 1970 in the entire southern hemisphere. The South African atmospheric temperatures rose by approximately 0.37°C due to global warming (Tyson and Preston-Whyte, 2000). According to the fourth assessment of the International Panel on Climate Change Report (IPPC, 2007), climate change observed during the past fifty years can be predominantly attributed to human activities. The impacts of climate change include changes in weather patterns, e.g. longer and more intense droughts, more frequent heat waves, heavy rain, intensity of tropical cyclones (Evan *et al*., 2011:479), changes in precipitation amounts, wind patterns and less frequent cold events (IPCC, 2013; Tyson and Preston-Whyte, 2000). These changes in weather pattern also lead to increases in ocean temperature, higher sea-levels due to the melting of ice and changes in oceanic salinity. Large volcanic eruptions can reduce the earth's temperature with about half a degree, which can last for months or years (IPCC, 2013; Pőschl, 2005:44; National Research Council, 1996).

2.3. Types of pollutants

As mentioned previously, large numbers of different chemical species are present in the atmosphere. These species have different sources, chemical compositions, transformations and impacts on the environment and its inhabitants. However, atmospheric chemical species share certain similarities and can be divided into two main types of pollutants, i.e. gaseous species and aerosols.

2.3.1. Gaseous species

The main gaseous atmospheric species include CO_2, CH_4, N_2O, ozone (O_3), water vapour, nitrogen oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), carbon monoxide (CO) and volatile organic compounds (VOCs). The atmospheric lifetime of these species ranges between a few seconds up to several hundreds of years. The atmospheric concentrations of these gases depend on the rates at which these species are emitted into the atmosphere and removed from or chemically transformed in the atmosphere. Major anthropogenic sources of gaseous species include fossil fuel combustion, as well as industrial- and vehicular emissions, while the main natural sources include fires, biogenic material and volcanic eruptions. Primary gaseous species emitted directly into the atmosphere can also be transformed through different chemical reactions to form secondary gaseous species (IPCC, 2013; Pőschl, 2011:101; Formenti *et al.*, 2003:108). Atmospheric gaseous species are removed through various processes such as atmosphere-ocean gas transfer, chemical- and biological (photosynthesis) processes and by reaction with solar radiation.

2.3.2. Aerosols

As previously mentioned, aerosols are a suspension of liquid or solid particles in the atmosphere. Typical examples of aerosols are cloud condensed nuclei (CCN), dust and smoke (IPCC, 2013; Franze *et al.,* 2005:39). Aerosols are emitted directly into the atmosphere as primary aerosols or are formed as secondary particulates through chemical reactions and gas-to-particle conversions. A detailed discussion on aerosols is presented in the subsequent section, since an assessment of organic carbon (OC) and BC in aerosols was the main aim of this study.

2.4. Atmospheric aerosols

Aerosols consist of a large number of species that include SO_4^{2-}, nitrates (NO_3^-), ammonium (NH_4^+), trace metals, OC and BC. Aerosol particles generally have shorter lifetimes than gaseous species and can be present in the atmosphere for a few days (coarse particles) or up to one week (fine particles) (Lazaridis *et al*., 2002:285). Aerosols emitted from volcanic eruptions can, however, have lifetimes up to approximately two years. These aerosols are emitted into the mesosphere and can have an extended influence on the climate IPCC (2013).

Atmospheric aerosols have particle diameters that range typically between 10^{-9}-10^{-4} m (Pőschl, 2005:44; Slanina & Zhang, 2004:76). Aerosols are defined according to their aerodynamic diameters. In this study, aerosols with an aerodynamic diameter ≤ 2.5 µm ($PM_{2.5}$) and ≤ 1 µm (PM_1) were considered to be the fine fraction, while the coarse fraction was aerosols ≤ 10 µm (PM_{10}). Aerosols can also be divided into smaller size fractions consisting of particles ≤ 0.1 µm ($PM_{0.1}$) (Pőschl, 2005:44: Slanina & Zhang, 2004:76). These smaller size fractions are generally referred to as the ultrafine particulates.

2.4.1. Sources and sinks

Natural sources of aerosols include mineral dust, soil, sea salt aerosols, volcanic dust, fires and biogenic sources (plant fragments, pollen and micro-organisms)

(IPCC, 2013; Franze *et al.,* 2005:39). Major anthropogenic sources are industrial activities, incomplete combustion of fossil fuels, biomass burning (household combustion for spatial heating and cooking) and traffic emissions (Venter *et al.*, 2012; Laakso *et al.*, 2008:8; Pőschl, 2005:44). Aerosols are emitted primarily into the atmosphere from sources or they are formed in the atmosphere as secondary pollutants. Secondary aerosols are formed in the atmosphere through gas-to-particle conversion, which can occur through new particle formation, gas-particle partitioning and heterogeneous (or multiphase) chemical reactions (Andreae & Rosenfeld, 2008:89; Pőschl, 2005:44; Balasubramanian *et al., 2003:108*).

Particles that originated from vehicle emissions and coal-fired power plants typically range from 0.003 to 1 μm in size. The size of pollen and soil dust is mostly bigger than 2 μm, while ash from coal combustion can range from 0.1 up to 50 μm (Seinfeld and Pandis, 2006).

Kneip and Lioy (1980) stated that sink processes generally include volume and area sinks. Cloud formation is considered to be a volume sink, while the removal of aerosols through wet- and dry deposition from the atmosphere is known as an area sink. The transport of aerosols to other layers in the atmosphere is also considered to be a sink process (Pőschl, 2005:44; Kneip & Lioy, 1980). The rate of dry deposition depends on particle size, as well as wind and other meteorological factors. Wet deposition occurs when rain, snow or fog collects aerosols in the atmosphere and transport them onto the ground (Zhao *et al.*, 2012:12; Pőschl, 2005:44).

2.4.2. Impacts

Atmospheric aerosol studies were commenced to mainly investigate their impacts on climate, sensitive ecosystems and human health (Pőschl, 2005:44; Lazaridis *et al*., 2002:285). It is important that the sources and composition of aerosols are identified in order to assist in the understanding of the impacts of PM on radiative forcing and health.

Aerosols can lead to warming or cooling of the atmosphere, since PM can either absorb infrared radiation or scatter solar radiation. Cloud aerosols, for instance, can have a cooling or a warming effect on the atmosphere. Clouds reflect incoming solar radiation, but also radiate long-wave energy back the Earth's surface (IPCC, 2013; Andreae & Gelencsér, 2006:6; Bond & Sun, 2005:39; Chow *et al.,* 2002:49). BC absorbs infrared radiation, which leads to the warming of the atmosphere. Aerosols can also act as cloud condensation nuclei (CCN) and ice nuclei (IN) (Lohmann and Feichter, 2005:5), which contribute to the formation of clouds, which leads to the scattering of solar radiation (Laakso *et al.*, 2013:13; Pőschl, 2011:101; Pőschl, 2005:44). The absorption and scattering of radiation by aerosols could also reduce visibility (Lazaridis *et al*., 2002:285; Hegg *et al*., 1993:98; Trijonis *et al*., 1991).

Some of the impacts of aerosols on the environment are acidification and eutrophication due to the wet and dry deposition of especially SO_4^{2-} and NO_3^- aerosols (Lazaridis *et al*., 2002:285). These particles can also stain painted surfaces, artworks and historic monuments (Ligocki *et al*., 1993:27A; Baedecker *et al*., 1992:26B). Rohr and Wyzga (2012:62) presented a summary of the health impacts associated with different particulate size ranges ($PM_{2.5}$, PM_{10}) and species (OC, BC, trace metals). Health effects typically associated with atmospheric particulates smaller than $PM_{2.5}$, included respiratory and cardiovascular problems, inflammatory, oxidative stress, heart rate variability, asthma, congestive heart failure, diabetes, strokes and an increase in premature deaths (Gauderman *et al*., 2004:351).

Fine aerosols (smaller than $PM_{0.1}$) can penetrate through membranes of the lungs in the human respiratory tract and can then be carried by the bloodstream to the brain and other nerves. It is still not clear what chemical properties of fine particulates are responsible for the negative health effects in humans (Oberdőrster *et al*., 2004:16). Primary fine particles emitted from traffic sources are considered to be the most harmful to human health (Donaldson *et al*., 2003:34). Norbert *et al.* (2008) stated that diesel soot is carcinogenic to humans. There is also a correlation between cancer and the continuous exposure to high levels of PM_{10} (Franze *et al*., 2005:39; Donaldson *et al*., 2003:34; Krämer *et al*., 1999:28; Beeson *et al*., 1998:106). According to Wilson and Spengler (1996), if atmospheric PM_{10} mass concentrations increased by 10 μg.m^{-3}, premature mortality increased by 0.5 to 1.5% in the event of short-term exposure and 5% for long-term exposure. Research conducted by Wyzga (2002) indicated that PM_{10} is mainly associated with respiratory responses, while $PM_{2.5}$ is predominantly linked to cardiovascular diseases. It is still uncertain whether the physical or chemical characteristics are responsible for the mortality associated with PM.

It is evident from the discussions presented in this section that the regulation and monitoring of ambient aerosol concentrations and emissions from sources are important for the environment and humans.

2.4.3. Composition

As previously mentioned, aerosols consist of a large number of chemical species such as sea salt, SO_4^{2-}, NO_3^-, NH_4^+, trace metals, OC and BC. These chemical species have an influence on the physical properties of atmospheric aerosols, which will determine, for instance, whether atmospheric aerosols will have a cooling or a warming effect on the atmosphere of the earth (IPCC, 2013; Andreae, 2007:365). Chemical compounds in the $PM_{2.5}$ fraction are usually associated with anthropogenic processes such as combustion of fossil fuels, biomass burning, pyrometallurgical industries and traffic emissions, while chemical species in the $PM_{10\text{-}2.5}$ fraction are usually considered to originate from natural sources such as wind-blown dust and sea salt (Putaud *et al*., 2004:38).

2.5. OC and BC

A large fraction of atmospheric aerosols consists of different kinds of carbon (e.g. soot, brown carbon, light-absorbing carbon (LAC), elemental carbon (EC), OC and BC), with the concentrations of these species depending on the source regions. Soot is black or brown particles that are formed by combustion. Brown carbon is defined as a light-absorbing organic matter in aerosols in the atmosphere from different sources, e.g. soil humus, humic like substances (HULIS), bioaerosols and tarry matter from combustion. LAC includes soot and brown carbon. EC is a part of BC and is mostly referred to as the oxidised carbon from combustion (Andreae & Gelencsér, 2006:6).

It is usually expected that OC levels will be higher in rural areas that are not directly impacted by anthropogenic activities. Aged air masses passing over these areas would largely comprise secondary OC. Regions that are frequently impacted by biomass burning (fires and household combustion) would also have higher atmospheric OC and BC concentrations (Nam *et al*., 2008:156).

2.5.1. Sources and sinks

Large numbers of natural and anthropogenic sources exist for atmospheric OC and BC. Volcanic eruptions, fires and biological materials (e.g. plant fragments) are typical natural sources of these species. Anthropogenic sources include industrial activities, traffic emissions, biomass burning (fires and household combustion) and the combustion of fossil fuels (Assamoi & Liousse, 2010:44; Andreae & Rosenfeld, 2008:89; Laakso *et al.*, 2008:8; Pőschl, 2005:44). BC is mainly emitted from combustion processes and is present in the atmosphere as primary particulates. OC can be emitted into the atmosphere from anthropogenic and biogenic sources or can be formed in the atmosphere through chemical transformations as secondary aerosols (Putaud *et al*., 2004:38).

OC and BC are removed from the atmosphere through similar processes as discussed in section 2.4.1. The atmospheric lifetime of OC and BC can be from a few seconds up to a couple of weeks depending on their physical and chemical properties (IPCC, 2013; Pőschl, 2011:101; Pőschl, 2005:44). Kneip and Lioy (1980) stated that OC and BC particulates suspended above the stratosphere can have atmospheric lifetimes up to a few years before they are removed from the atmosphere (Pőschl, 2005:44).

2.5.2. Impacts

Atmospheric OC and BC have different impacts on the environment and climate, depending on their physical and chemical properties. BC absorbs terrestrial long-wave radiation and thereby contributes to the warming of the atmosphere. According to the draft fifth assessment of the IPCC (IPCC, 2013), atmospheric BC is currently considered to be the second most important atmospheric greenhouse species after CO_2 (Bond & Sun, 2005:39). Therefore, the measurement of BC in the atmosphere is considered to be one of the most important subject matters in the atmospheric sciences. Although it is considered that OC mainly has a cooling effect on the atmosphere, OC can absorb (warming of atmosphere) or reflect (cooling of atmosphere) solar radiation depending on its chemical properties (IPCC, 2013; Andreae, 2007:365).

OC and BC can also have influences on weather patterns. Aerosols shade the earth's surface, which reduces evaporation and this leads to reduced rainfall (IPCC, 2013; Andreae, 2007:365). Evan *et al*. (2011:479) also indicated an increase in cyclones over the Arabian Sea from 1979 to 2010 due to increased aerosol load in general, as well as increased BC and SO_4^{2-} emissions from anthropogenic sources. The health effects of OC and BC are similar to the impacts discussed for aerosols in general in section 2.4.2, which include mainly cardiopulmonary diseases, infections and allergies.

2.6. OC and BC: An African perspective

OC and BC assessments have been performed extensively in a large number of first world countries in the United Kingdom, Europe and the United States of America. Although Africa is considered to be one of the largest sources of atmospheric OC and BC, it is one of the least studied continents with limited OC and BC data (Kanakidou *et al*., 2005:5). Assamoi and Liousse (2010:44) measured OC and BC in fourteen different cities in West Africa (Benin, Burkina Faso, Gambia, Ghana, Guinea, Guinea Bissau, Ivory Coast, Liberia, Mali, Niger, Nigeria, Senegal, Sierra Leone and Togo) and two central African countries (Cameroon and Chad). The major sources of atmospheric OC and BC were considered to be two-stroke engines of two-wheel vehicles. The atmospheric OC and BC concentrations were much higher compared to OC and BC levels typically measured in first world countries. Arku *et al*. (2008:402) measured aerosol concentrations for three weeks at four sites in Accra, Ghana, which is located in the Gulf of Guinea. Atmospheric aerosols measured were mainly attributed to household biomass combustion for cooking and heating. $PM_{2.5}$ concentrations ranged between 22.3 and 40.2 µg/m^3, while PM_{10} levels were between 57.9 and 93.6 µg/m^3, which are considered to be very high. Ten to 11% of the $PM_{2.5}$ mass consisted of BC, while approximately 50% of the mass consisted of OC. No OC and BC mass percentage was given for PM_{10} in Arku *et al*. (2008:402). These values are the average shown for the three-week measurement period.

South Africa is an important source region of atmospheric pollutants, especially during the dry season when almost no precipitation takes place and a large number of fires occur (Laakso *et al*., 2012:12). Furthermore, South Africa is the economic and industrial hub of southern Africa with many large anthropogenic point sources (Beukes *et al*., 2013:12), e.g. coal-fired power plants, petrochemical industries and pyrometallurgical smelters. South Africa has a well-developed infrastructure with associated high traffic emissions.

BC was measured with a multi-angle absorption photometer (MAAP) at Elandsfontein in the Mpumalanga Province from 2008 to 2010 during the EUCAARI campaign. The site is considered to be a regional site influenced by the large number of industrial activities in the Mpumalanga Highveld. Aerosol samples were also collected on filters. The results of these measurements are currently not published in peer-reviewed literature. It is, however, foreseen that the results would be published in 2014. In another study conducted at Elandsfontein, Collett *et al*. (2010:106) presented a single diurnal plot for BC measured. Venter *et al*. (2012:108) presented limited BC data collected at a mobile monitoring site at Marikana in the North West Province. The site was situated in the centre of the highly industrialised western Bushveld Complex. In the air quality paper of Venter *et al*. (2012:108), BC data was used to explain CO and PM_{10} concentrations measured. It concluded that all these species were mainly attributed to household combustion for space heating and cooking. Hyvärinen *et al*. (2013:6) used BC data collected with a MAAP at Elandsfontein and Welgegund to explain the use of a newly-developed method to correct BC values that were measured with a MAAP. Welgegund is a regional atmospheric measurement station in the North West Province that is impacted by the major sources in the interior of South Africa.

2.7. South African DEBITS measurements

The Deposition of Biogeochemical Important Trace Species (DEBITS) project is an international project and was established in the 1990s as a long-term initiative to measure atmospheric pollutants. It is a joint initiative of the International Global Atmospheric Chemistry (IGAC) programme and the World Meteorological Organisation (WMO). The main objectives of this project are to monitor the removal rates (e.g. dry and wet deposition processes) of biogeochemically important trace species and to determine which factors (e.g. physical or chemical) control deposition fluxes. Protocols and guidelines were designed for the quality control of the experiments and analyses for all the DEBITS stations (Galy-Lacaux *et al.,*2003:27).

In South Africa, atmospheric gaseous and aerosol species are collected at five regionally representative background sites. Atmospheric measurements at these sites are currently the most comprehensive long-term measurement dataset available for the wet and dry deposition of chemical atmospheric species in southern Africa (Martins, 2009). However, the collection of 24-hour aerosol samples once a month at these sites only commenced in 2009. In this investigation, the spatial and temporal assessment of OC and BC concentrations measured at these sites will be presented.

Martins (2009) determined OC and BC concentrations at two of the South African DEBITS sites. However, this data was not published in the in peer-reviewed public domain. Furthermore, these measurements were restricted to three winter campaigns and one summer campaign, with each campaign consisting of two weeks.

2.8. South African meteorology

Recently, Laakso *et al*. (2012:12), with references therein, presented an overview of the meteorology over the South African Highveld (where most of the DEBITS sites are situated), as well as the interaction between meteorological patterns and pollutant levels. Atmospheric circulation over the southern African Highveld occurs mainly through an anti-cyclonic recirculation pattern througout the year (Tyson & Preston-Whyte, 2000), which is attributed to a continental high pressure cell that dominates the interior of South Africa. This anti-cyclonic recirculation leads to the build-up of pollutant species. This is especially pronounced during the cold dry winter (June to August) and early spring months (September to middle October), when strong inversion layers trap pollutants at several different heights, thereby inhibiting vertical mixing.

The interior of South Africa is characterised by two distinct wet and dry seasons. Almost all the precipitation occurs during the wet season from middle October to May, while nearly no precipitation takes place during the dry season from May to middle October. The absence of precipitation during the dry season leads to an increase in pollutant levels due to a decrease in the wet removal of pollutant species and the increase in the frequency of large-scale fires. During the cooler autumn and cold winter months (May to August), household combustion for cooking and space heating is also a regular occurrence in semi-formal and informal settlements (Venter *et al*., 2012:108).

The weather and the seasons of southern Africa are greatly influenced by different elements like the temperature features (e.g. perturbations in the westerly winds) of the overall circulation and elements that originates in tropical (e.g. the easterly winds) and subtropical areas (e.g. the South Indian Anticyclone and the South Atlantic Anticyclone) (Tyson & Preston-Whyte, 2000). These elements are responsible for the changes in clouds, rainstorms, droughts and temperature rise and falls and are discussed and explained in greater detail in Tyson and Preston-Whyte (2000).

2.9. Gaps in literature

From the relevant literature that was obtained on atmospheric OC and BC, it was evident that very little atmospheric OC and BC data exists for South Africa in peer-reviewed literature. Therefore, in this study, the results obtained for 24-hour OC and BC aerosol samples that were collected for two years and one month at the five South African DEBITS sites are presented. According to the knowledge of the author, this is currently the most comprehensive OC and BC dataset presented for South Africa.

Chapter 3

Article

Spatial and temporal assessment of organic and black carbon at DEBITS-IDAF sites in South Africa

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Abstract

Limited data currently exist for atmospheric black carbon (BC) and organic carbon (OC) in South Africa. In this paper BC and OC concentrations were explored in terms of spatial and temporal patterns, mass fractions of BC and OC of the overall aerosol mass, as well as possible sources. PM_{10} and $PM_{2.5}$ samples were collected at five sampling sites in

South Africa operated within the Deposition of Biogeochemical Important Trace Species-IGBP DEBITS in Africa (DEBITS-IDAF) network, i.e. Louis Trichardt, Skukuza, Vaal Triangle, Amersfoort and Botsalano, with MiniVol samplers. Samples were analysed with a Thermal/Optical Carbon analyser. OC were higher than BC concentrations at all sites in both size fractions. Most OC and BC occurred in the $PM_{2.5}$ fraction. OC/BC ratios reflected the setting of the different IDAF sites, as well as possible sources impacting these sites. The OC mass fraction percentage of overall aerosol mass varied up to 24% and the BC up to 12%. A relatively well define seasonal pattern was observed, with higher OC and BC concentrations measured from May to October, which coincide with the dry season in the interior of South Africa. An inverse seasonal pattern was observed for the fractional mass contributions of OC and BC. This indicated that although OC and BC concentrations are higher in the dry season, their fraction mass contributions were lower due substantially higher aerosol load during this time of the year. Correlations between OC and BC concentrations with the distance back trajectories passed biomass burning fires and large point sources proved that biomass burning fires contribute significantly to regional OC and BC concentrations during the burning season, while large point sources did not contribute as significantly to regional OC and BC concentrations. From the VT site data it was also proved that household combustion for space heating contributed to at least local OC and BC concentrations.

Keywords: Organic carbon (OC), Black carbon (BC), Spatial, Temporal, DEBITS, IDAF

1. Introduction

Atmospheric aerosols have impacts on climate change and general air quality, which are determined by their physical (size, mass, structure, concentration and optical density) and chemical properties (Seinfeld and Pandis, 2006). Typical chemical species present in atmospheric aerosols include wind-blown dust particles (e.g. pollen, bacteria, smoke, ash, sea salt), black carbon (BC), organic carbon (OC), sulphates (SO_4^{2-}), nitrates (NO_3^-), ammonium (NH_4^+) and trace metal species. Aerosols are generally classified according to their size, e.g. PM_{10} (aerodynamic diameter ≤ 10 µm), $PM_{2.5}$ (aerodynamic diameter ≤ 2.5 µm), PM_1 (aerodynamic diameter ≤ 1 µm) and $PM_{0.1}$ (aerodynamic diameter ≤ 0.1 µm) particulates (Pöschl, 2005; Slanina & Zhang, 2004). The baseline of uncertainty in aerosol radiative forcing is large and depends on the afore-mentioned aerosol characteristics, which can vary significantly on a regional and global scale (IPCC, 2013; Slanina & Zhang, 2004). General detrimental effects of atmospheric aerosol pollution on human health include increased cardiopulmonary and respiratory diseases (Gauderman et al., 2004), while $PM_{0.1}$ can even diffuse through the membranes of the respiratory track into the blood stream (Pöschl, 2005; Oberdőrster et al., 2004). Environmental impacts of atmospheric aerosol pollution include acid deposition and eutrophication (Pöschl, 2005; Lazaridis et al., 2002).

Atmospheric BC is emitted as a primary species, while OC can consist of primary and secondary aerosols (Pöschl, 2005; Putaud et al., 2004). Major sources of BC and OC include incomplete combustion of fossil fuels, biomass burning and traffic emissions. OC is also emitted from biogenic sources and can be formed through the oxidation of volatile organic compounds (VOCs). BC absorbs terrestrial long-wave radiation that has a warming effect on the atmosphere, while OC, depending on the chemical properties, could absorb or reflect incoming solar radiation. In general it is accepted that OC has a net cooling effect. After CO_2, BC is considered to be the second most important contributor to global warming (IPCC, 2013; Bond & Sun, 2005). The impacts of BC are especially significant on local and regional scale, since BC has a relatively short atmospheric lifetime (e.g. days to weeks). Greenhouse gases (GHG) spend much longer periods in the atmosphere, i.e. between 10 to 100 years (de Richter & Caillol, 2011).

Although Africa is regarded as the largest source region of anthropogenic primary OC and atmospheric BC (Kanakidou et al., 2005; Liousse et al., 1996), it is one of the least studied continents. Within Africa, southern Africa is an important source region. Biomass burning fires are endemic across this region especially during the dry season when almost no precipitation occurs (Laakso et al., 2012; Tummon et al., 2010; Formenti et al., 2003). Biomass burning fire plumes from southern Africa are known to impact Australia and South America (Swap et al., 2004). In addition, South Africa is the economic and industrial hub of southern Africa with large anthropogenic point sources (e.g. Lourens et al., 2011). However, the relative importance of OC and BC contributions from these anthropogenic sources are still largely unknown, although some papers have been published that considered sources in west African capitals (Val et al., 2013; Doumbia et al., 2012). Venter et al. (2012) used BC data that were collected at Marikana in the North West province (South Africa) to prove that the origin of CO and PM_{10} was related to BC, while Collett et al. (2010) only presented a single diurnal plot for BC measured at Elandsfontein in the Mpumalanga Highveld. Hyvärinen et al. (2013) used BC data collected at Welgegund in the North West province to illustrate how to use a newly developed method to correct BC values measured with a multi-angle absorption photometer (MAAP), but did not go into further detail of the BC data.

In the framework of the DEBITS-IDAF (The Deposition of Biogeochemical Important Trace Species-IGBP DEBITS in Africa) project (Martins et al., 2007; Galy-Lacaux et al., 2003), atmospheric gaseous and aerosol measurements have been performed continuously since 1994, at 7 sites in central and western Africa, as well as 3 sites in South Africa.

Regarding carbonaceous aerosol, Martins (2009) determined BC and OC concentrations at two of the South African IDAF sites. However, these measurements were restricted to three two-week winter campaigns and one two-week summer campaign. This data have also not yet been published in the peer reviewed scientific domain.

In order to address the current knowledge gap, i.e. very limited BC and OC data for South Africa the main objectives of this paper were to present spatial and temporal assessments of BC and OC concentrations at the South African IDAF sites, determine mass fractions of BC and OC of the overall aerosol mass, as well as to investigate possible sources.

2. Experimental

2.1 Sampling sites

Aerosol samples were collected at five sampling sites in South Africa operated within the IDAF network, i.e. Louis Trichardt (LT), Skukuza (SK), Vaal Triangle (VT), Amersfoort (AF) and Botsalano (BS). The locations of these sites within a regional context are presented in Fig. 1. The South African IDAF sites are located in the north eastern part of the interior of South Africa. Mphepya et al. (2006) and Martins et al. (2007) have previously introduced LT and SK, but not the other sites. In order to contextualise all the sites a short description of each site is given in Table 1. LT, SK and BT are considered to be background sites. In contrast AF lies southeast of the internationally well-known NO_2 hotspot that is clearly visible from satellite observations over the Mpumalanga Highveld of South Africa (Lourens et al., 2012), while VT lies within an area that has been proclaimed as a national air pollution hotspot in terms of the South African National Environmental Management Act: Air Quality (Government Gazette Republic of South Africa, 2005). Although not specified in Table 1, all the South African IDAF sites are likely to be impacted by local, as well as regional biomass burning fire emissions.

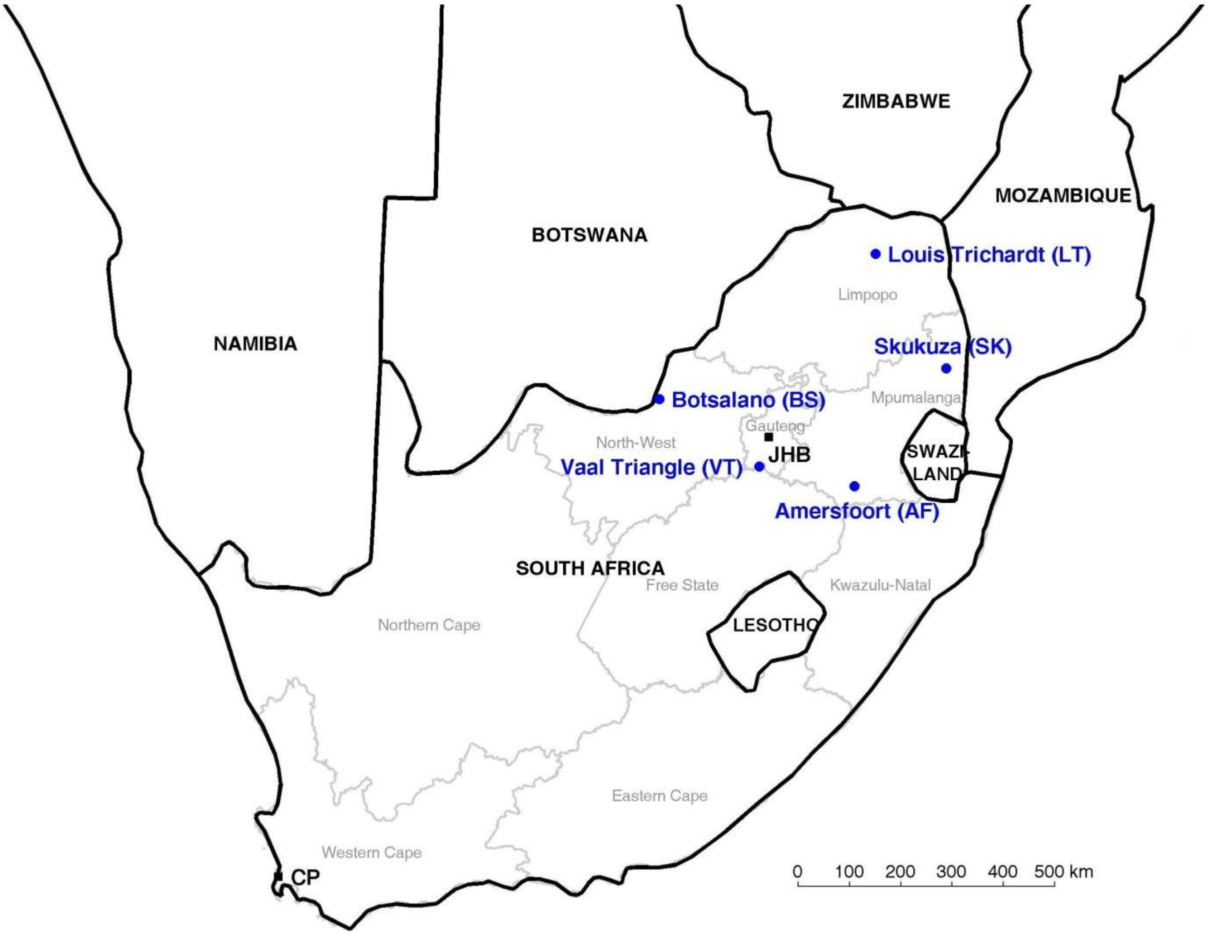


Fig.2. The location (blue dots) of the South African IDAF sampling sites where OC and BC measurements were conducted are indicated on a southern African map. Provincial boarders with the provincial names within South Africa, as well as Johannesburg (JHB) and Cape Town (CP) are also included for reference.

Table 1 Geographic coordinates and short descriptions of South African IDAF sampling sites where OC and BC measurements were conducted.

Site	Location	Description
Amersfoort (AF)	27˚04'13"S 29˚52'02"E, 1628 m amsl	Semi-arid, within grassland biome, impacted by anthropogenic activities on the Mpumalanga Highveld
Louis	22˚59'10"S 30˚01'21"E,	Semi-arid, within savannah biome, rural site

Trichardt (LT)	1300 m amsl	predominantly used for agricultural purposes
Skukuza (SK)	24˚59'35"S 31˚35'02"E, 267 m amsl	Semi-arid, within savannah biome, regional background site in a protected area (Kruger National Park)
Vaal Triangle (VT)	26°43'29"S 27°53'05"E, 1320 m amsl	Semi-arid, within grassland biome, situated in the highly industrialized Vaal Triangle area, impacted by emissions from various industries, traffic and household combustion
Botsalano (BS)	25 32'28"S, 25 45'16"E 1424 m amsl	Semi-arid, within savannah biome, regional background site in a protected area (Botsalano Game Reserve)

2.2 Regional meteorology

Recently Laakso et al. (2012) and references therein gave an overview of the meteorology over the South African Highveld, as well as the interaction between meteorological patterns and pollutant levels. Therefore only a synopsis is given here. Atmospheric circulation over the South African Highveld is dominated by an anti-cyclonic recirculation pattern throughout the year (Tyson & Preston-Whyte, 2000), due to the dominance of a continental high pressure cell over the interior. This recirculation contributes significantly to the build-up of pollutants. This is especially significant during the cold dry winter (June – August) and early spring months (September – middle October) when strong inversion layers trap pollutants at several different heights inhibiting vertical mixing. This frequently causes an increase in atmospheric pollutant concentrations near the surface. In addition, the interior of South Africa is also characterised by a distinct wet and dry season. Almost all the precipitation occurs during the wet season from middle October to April, while nearly no precipitation takes place during the dry season from May to middle October. The lack of precipitation during the dry season leads to a decrease in wet deposition of pollutants and indirectly to the increase in pollutant levels due to the more frequent occurrence of large scale biomass burning fires. During the cooler autumn and cold winter months (May to August) household combustion for space heating is also a common occurrence in especially semi-formal and informal settlements (Venter et al., 2012).

2.3 Sampling

24-hour $PM_{2.5}$ and PM_{10} aerosol samples were collected on quartz filters (with a deposit area of 12.56 cm^2) once a month from March 2009 to April 2011 at each site. A total of 258 samples were collected, i.e. 52 samples for each site, except for BS for which only 50 samples were collected. Since both size fractions were sampled each month at each site, therefore half of the samples were $PM_{2.5}$ and the other half PM_{10}. The quartz filters were prebaked at 900°C for 4 hours and cooled down in a desiccator, prior to sample collection. MiniVol samplers developed by the United States Environmental Protection Agency (US-EPA) and the Lane Regional Air Pollution Authority were used during sampling (Baldauf et al., 2001). These samplers have a pump that is controlled by a programmable timer, which allows for the collection of samples at a constant flow rate over a pre-determined time period. In this study, samples were collected at a flow rate of 5 L/min, which was verified by using a handheld flow meter that was supplied with the MiniVol samplers. Filters were handled with tweezers while wearing surgical gloves, as a precautionary measure to prevent possible contamination of the filters. All thermally pre-treated filters were also visually inspected to ensure that there were no weak spots or flaws. After inspection, acceptable filters were weighed and packed in airtight Petri dish holders until they were used for sampling. After sampling, the filters were again placed in Petri dish holders, sealed off, bagged and stored in a portable refrigerator for transport to the laboratory. At the laboratory the sealed filters were stored in a conventional refrigerator. 24 hours prior to analysis, samples were removed from the refrigerator and weighed just prior to analysis.

2.4 OC and BC Analysis

Several methods can be used to analyse OC and BC collected on filters (Chow et al., 2001). We decided to apply the IMPROVE thermal/optical (TOR) protocol (Guillaume et al., 2008; Environmental analysis facility, 2008; Chow et al. 2004; Chow et al., 1993) by using a Desert Research Institute (DRI) analyser. In this method, filters are submitted to volatilization at temperatures of 120, 250, 450 and 550°C in a pure Helium (He) atmosphere and thereafter to combustion at temperatures of 550, 700 and 800°C in a mixture of He (98%) and oxygen (O_2) (2%) atmosphere. The carbon compounds that are released are then converted to CO_2 in an oxidation furnace with a manganese dioxide (MnO_2) catalyst at 932°C. Then, the flow passes into a digester where the CO_2 is reduced to methane (CH_4) on a nickel-catalysed reaction surface. The amount of CH_4 formed is detected by a flame ionization detector (FID), which is converted to carbon mass using a calibration coefficient. The carbon mass peaks detected correspond to the different temperatures at which the seven separate carbon fractions, which include four OC and three BC fractions, were released. These fractions were depicted as different peaks on the thermogram, of which the surface areas were proportional to the amount of CH_4 detected.

The reflectance from the deposited sample is monitored throughout the afore-mentioned analysis. This reflectance usually decreases during the volatilization process due to the pyrolysis of OC. When oxygen is added, the reflectance is increased as the BC is burnt and removed. OC is defined as the fraction which evolves prior to re-attainment of the original reflectance (the non-absorbing light particles) and BC is defined as the fraction which evolved after the original reflectance has been attained (the light absorbing particles). The DRI instrument can detect OC and BC as low as 0.1 μg/cm^2.

2.5 Back trajectory analysis

Back trajectories of air masses were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, 2014) model (version 4.8), developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler & Hess, 2004). This model was run with meteorological data of the GDAS archive of the National Centre for Environmental Prediction (NCEP) of the United States National Weather Service and archived by the ARL (Air Resources Laboratory, 2014a). The HYSPLIT model computes air trajectories and more complicated dispersion and deposition simulations. This model uses the Lagrangian- and the Eulerian approach. The Lagrangian approach uses a moving frame as the air particles move from their original location. The Eulerian approach uses a fixed three-dimensional grid as frame. The Lagrangian framework follows the transport of the air particles, while the Eulerian approach calculates the pollutant concentrations on a fixed grid. The Hysplit model is mainly used for tracking and forecasting the release of different pollutants (e.g. radioactive material, volcanic ash, wildfire smoke) from stationary or mobile emission sources (Air Resources Laboratory, 2014b).

All back trajectories were calculated for 24 hours, arriving on the hour at a height of 100 m above ground level at each of the sites presented in Table 1. Although a number of uncertainties have to be taken into account when working with the HYSPLIT data (Air Resources Laboratory, 2014c), the most relevant here was the spatial complexity of the area. Therefore, an arrival height of 100 m was chosen, since the orography in HYSPLIT is not very well defined, which could results in increased error margins on individual trajectory calculations if lower arrival heights were used. For back trajectories calculated in this manner, maximum error margins of 15 to 30% of the trajectory distance travelled have been reported (Vakkari et al., 2011; Riddle et al., 2006; Stohl, 1998).

2.6 Correlation between back trajectory analysis and sources

In this study back trajectory analysis of air masses was employed to relate BC and OC concentrations measured at a specific sampling site with the closest distance between the trajectory calculated for a specific 24-hour sampling period and biomass burning fire events occurring during that time, as well as large point sources. Although a number of products can be used to obtain biomass combustion fire locations, e.g. EUMETSAT (EUMETSAT, 2014) fire locations used in this paper were obtained from the remote sensing observations of fires from the MODIS collection 5 burned area product (MODIS, 2014; Roy et al., 2008). Since MODIS burned area observations are obtained from a satellite passing over an area once a day, the 24-hour back trajectories were calculated to arrive at the middle of each 24-hour sampling period. Fig. 2 presents an illustration of the method applied for a specific sampling site to determine the shortest distance between a 24-hour back trajectory and burned areas identified within the period correlating closest to the sampling period. The distances between burned areas (indicated by the red areas) and a specific back trajectory were calculated for each of the hourly locations of the 24-hour back trajectory (indicated by the blue dots in Fig. 2). In the example presented here (Fig. 2), the symbol A indicates the shortest distance between hourly locations of this specific trajectory and burned areas. Similar calculations were made to determine the shortest distance that the afore-mentioned back trajectories had passed large point sources. In the graphical example presented here (Fig. 2), symbol B indicates the shortest distance between hourly locations of this specific trajectory and large point sources in the north-east of South Africa. Similar calculations were undertaken for each OC and BC sampling period, where after BC and OC levels were plotted against the shortest distances between back trajectory paths and fire events/large point sources for all days at all sites.

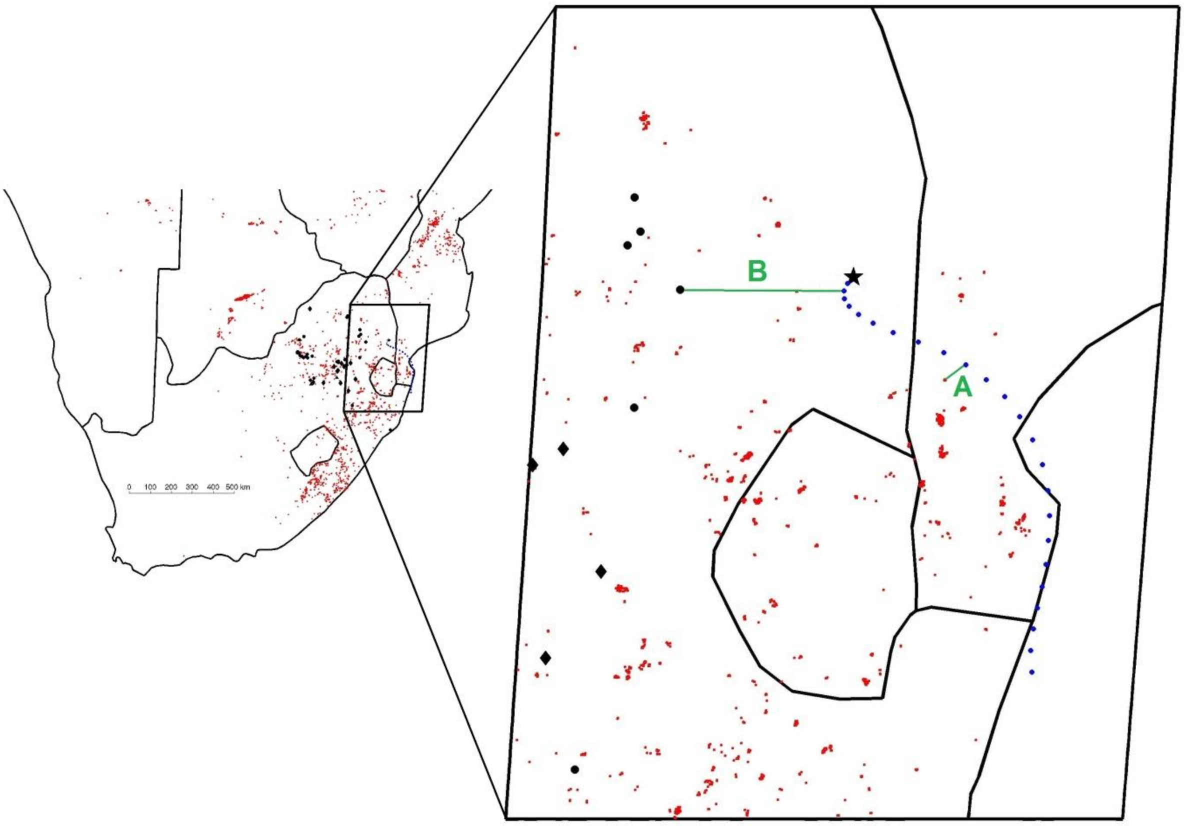
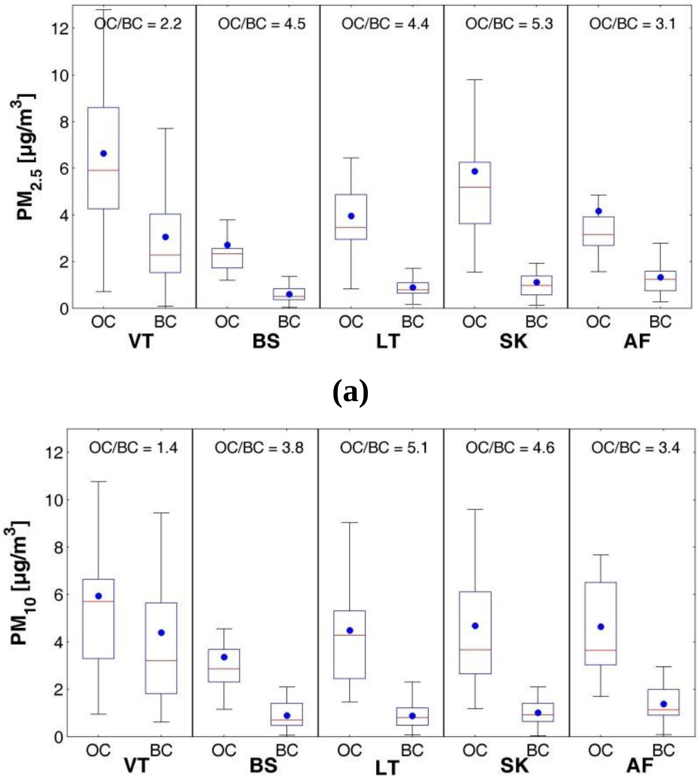


Fig.3. Example to illustrate the method applied to determine the shortest distance between 24-hour back trajectories and burned areas, as well as large point sources. The red areas indicate burned areas identified by the MODIS collection 5 burned area product on a specific overpass, the black markers large point sources (e.g. circles being pyro-metallurgical smelters and diamonds being coal-fired power stations and), while the blue dots represent the hourly locations of the example 24-hour back trajectory calculated for Skukuza (indicated by the black star). Symbol A indicates shortest distance between the trajectory and a burned area, while symbol B indicates the shortest distance that the back trajectory had passed a large point source.

3. Results and discussion

3.1. Spatial assessment

In Fig. 3 box and whisker plots of the concentrations of OC and BC measured, in the $PM_{2.5}$ (a) and PM_{10} (b) size fractions at each of the sites for the entire sampling period, is presented, with OC/BC ratios also indicated.



(a)

(b)

Fig. 3. Statistical distribution of $PM_{2.5}$ (a) and PM_{10} (b) OC and BC measured at the various DEBITS-IDAF sites. The red line of each box indicates the median, the blue dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ± 2.7 σ (99.3% coverage if the data has a normal distribution). The average OC/BC ratio for every site is also shown.

From Fig. 3 it is evident that OC concentrations were higher than BC levels at all the South African IDAF sites in the $PM_{2.5}$ (3a) and PM_{10} (3b) fractions. In general OC and BC concentrations in both size fractions were the highest at VT, with especially the BC levels being much higher compared to the other sampling sites. Therefore the OC/BC ratios of VT, i.e. 2.2 ($PM_{2.5}$) and 1.4 (PM_{10}), were also significantly lower than for the other sites. AF had the second lowest OC/BC ratio, i.e. 3.1 ($PM_{2.5}$) and 3.4 (PM_{10}), whereas it varied between 3.8 and 5.3 for the remaining sties. The reason, for the higher OC and BC levels and the lower OC/BC ratio for the VT, is likely due to its setting being so different to the other sites. The VT is situated in an area where most of the South African petrochemical and related chemical industries are located, together with other large point sources that include two coal-fired power stations and numerous metallurgical smelters (Beukes et al., 2013). This area is also densely populated with large semi-formal and informal settlements. Venter et al. (2012) recently reported that the dominant source of PM_{10} measured at a site in a highly industrialised region in South Africa, with numerous semi- and informal settlements in close proximity, was household combustion. This indicates that household combustion for space heating and cooking in these settlements in the VT area could also be a significant source of OC and BC. Higher traffic volumes in this densely populated area will also contribute to OC and BC concentrations. Less dilution of BC and lower secondary formed OC due to the close proximity to the sources also contribute to the different behaviour of the VT site.

The OC concentrations at LT, SK and AF were in the same range in the PM_{10} fraction, while slightly higher OC levels were measured at SK in the $PM_{2.5}$ fraction compared to LT and AF. The lowest OC concentrations were measured at BS. The BC concentrations at BS, LT, SK and AF were in the same order in the PM_{10} and $PM_{2.5}$ fractions throughout the sampling period, although BC levels were slightly higher at the anthropogenically impacted AF (Table 1). LT, SK and BS are regarded as background sampling sites (Table 1).

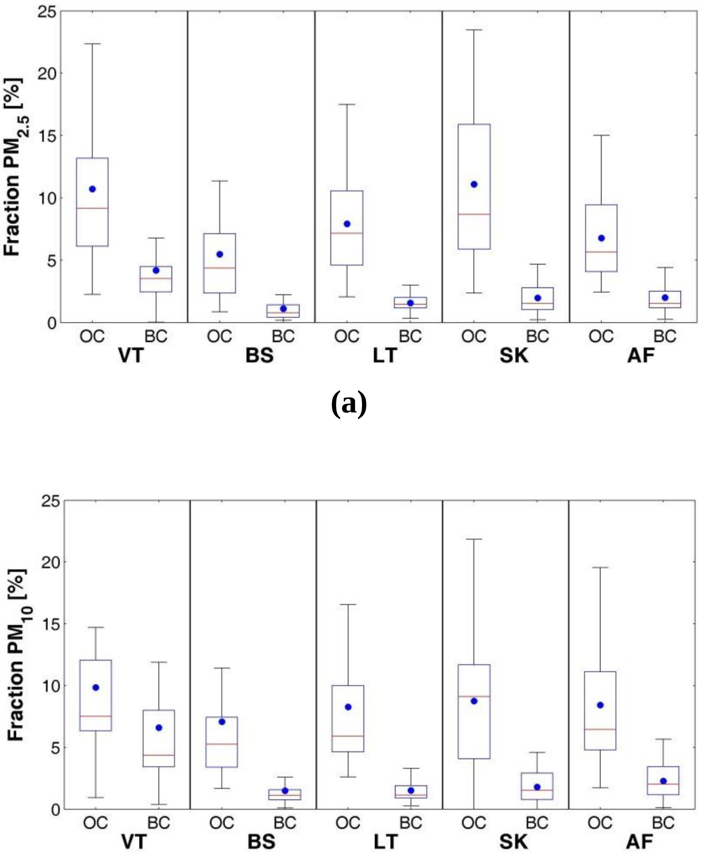
It is also evident from Fig. 3 that most of the OC and BC species measured were in the $PM_{2.5}$ fraction, since OC and BC concentrations in the $PM_{2.5}$ fraction did not differ significantly compared to OC and BC concentrations in the PM_{10} fraction that also included $PM_{2.5}$ particulates. This indicates that the major sources of OC and BC are anthropogenic activities (e.g. incomplete combustion of fossil fuels, household combustion) and biomass combustion fires (that can be natural and anthropogenic in South Africa – Vakkari et al., 2014). An anomaly in the data was that the OC levels measured at VT were higher in the $PM_{2.5}$ fraction than in the PM_{10} fraction, which is impossible. This can be attributed to an artefact in the sampling method utilised. As described in the experimental section, PM_{10} and $PM_{2.5}$ samples were collected for the same sampling period with two separate MiniVol samplers. Flows were check and prior and after sampling. Although no deviations were observed from the set point flow, it is possible that the sampling flow rate of 5 L/min was not maintained constantly in a single, or a small number of measurements, resulting in differences in sampling volumes. However, this anomaly was no present for any of the other sites. Additionally, the anomaly observed for the VT site does not detract from the conclusion made for all the sampling sites that the both OC and BC occurred mostly in the smaller size fraction, i.e. $PM_{2.5}$.

As previously mentioned the OC/BC ratios of VT was significantly different from the other sites. However, it can also be stated that the OC/BC ratio of AF, i.e. 3.1 ($PM_{2.5}$) and 3.4 (PM_{10}), is in-between that of the directly anthropogenic impacted VT and the background sites, i.e. BS, LT and SK. According to Junker and Liousse (2008) biomass burning fire emissions have a higher OC/BC ratio than fossil fuel sources. Additionally biofuels also have higher OC/BC emission ratios than fossil fuels. The calculated OC/BC ratios therefore indicate that VT is most significantly influenced by fossil fuel sources, while BS, LT and SK are more significantly influenced by biomass burning fire emissions. Mphepya et al. (2006)

have previously indicated that SK is significantly influenced by biomass burning fire emissions during the dry season. AF's in-between OC/BC ratio indicates influence by both biomass burning fire and fossil fuel combustion emissions. The OC/BC ratios therefore reflect the setting and possible sources impacting the different IDAF sites, as indicated in Table 1.

The OC/BC ratios at the South African IDAF sites compare well with other measurements. Cachier et al. (2005) reported OC and BC measurements at five sites in France, i.e. Martigues, Marseilles, Réaltor, Plan d'Aups and Dupail. OC/BC ratios determined at Martigues and Marseilles, which are considered to be impacted by anthropogenic activities, were 2.16 and 2.07, respectively, while Réaltor that is slightly removed from Martigues and Marseilles had an OC/BC ratio of 2.88. The OC/BC ratios for the two back ground sites, Plan d'Aups and Dupail, were 4.5 and 4.9, respectively. Chazette and Liousse (2001) determined an OC/BC ratio of 2.87 for Thessaloniki, which is the second biggest industrial city in Greece. If the OC/BC ratio source characteristics proposed by Junker and Liousse (2008) are considered, hard coal seems to be the dominant source type at VT, while wood fuel, charcoal and motor gasoline's typical OC/BC ratios correlated with that found at the other four sites. During SAFARI 2000, OC and BC samples were collected over the Atlantic Ocean, just off Namibia and Angola's shore. The smoke of biomass burning fires was widely distributed and between one and two days old. In these samples the OC/BC ratios varied between 5.9 and 10.0 (Formenti et al., 2003). The higher OC/BC ratios reported by Formenti et al., (2003) is most likely due the aging of the plumes and the absence of significant anthropogenic fossil fuels source contributions, as can be expected at the South African IDAF sites. Even the background site, i.e. BS, LT and SK are influenced by re-circulating anthropogenic emissions of the South African Highveld.

As far as the authors could assess, the mass fractions of OC and BC as a function of the overall aerosol mass have not yet been investigated for South Africa. Therefore, in Fig. 4 box and whisker plots of the mass fraction percentage OC and BC of the total aerosol measured, in the $PM_{2.5}$ (4a) and PM_{10} (4b) size fractions, at each of the sites for the entire sampling period, are presented.



(a)

(b)

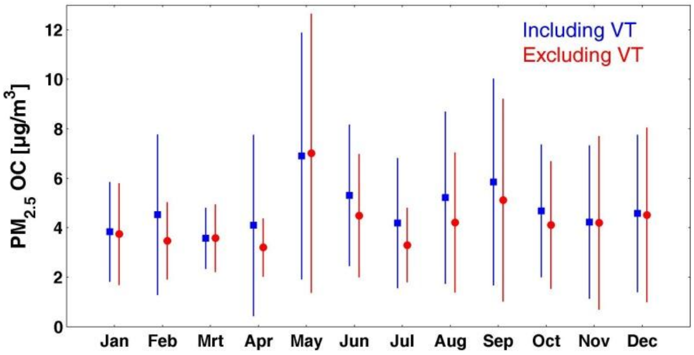
Fig. 4. OC and BC as a fraction percentage of the total aerosol mass in $PM_{2.5}$ (a) and PM_{10} (b). The red line of each box indicates the median, the blue dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ± 2.7 σ (99.3% coverage if the data has a normal distribution).

As expected the mass fraction OC is higher than the BC at all the sites for $PM_{2.5}$ and PM_{10}. The OC mass fraction percentage was up to 24% and the BC up to 12 % for all the sites and for both $PM_{2.5}$ and PM_{10}. Putaud et al. (2004) reported OC $PM_{2.5}$ mass fractions as 20-30% (rural sites) and 22-38% (near-city and kerbside sites), whereas PM_{10} mass fractions were 12-30% (rural sites) and 20-25% (near-city and kerbside sites) at 24 western European sites in winter. The BC contributions for $PM_{2.5}$ were reported as 5-11% (rural sites) and 5-23% (near-city and kerbside sites), while the BC contributions for PM_{10} were 2-8% (rural sites) and 4-15% (near-city and kerbside sites). Yin et al. (2005) reported the OC mass fraction in Ireland for $PM_{2.5}$ as 30-40% (non-urban sites) and 10-30% (urban sites), while the PM_{10} mass fractions were 15-45% (non-urban sites) and 4-20% (urban sites). The $PM_{2.5}$ BC mass fractions were 25-30% (non-urban sites) and 8-10% (urban sites), while PM_{10} fractions were 12-22% (non-urban sites) and 3-5% (urban sites). From the afore-mentioned references it seems that the OC and BC measured at the South African IDAF sites were in the same order of magnitude, or lower than the mass fractions measured in western Europe. However, the study of Putaud et al. (2004) was biased towards winter, while all seasons are represented in the South African IDAF results. Additionally, fractional contribution to the overall aerosol load of sulphate has substantially decreased in first world countries where deSOx technology has been applied (Zhang et al., 2007). However, in South Africa sulphate is still the dominant aerosol species (Tiitta et al., 2014; Martins et al., 2007) since substantial deSOx technology have not yet been applied.

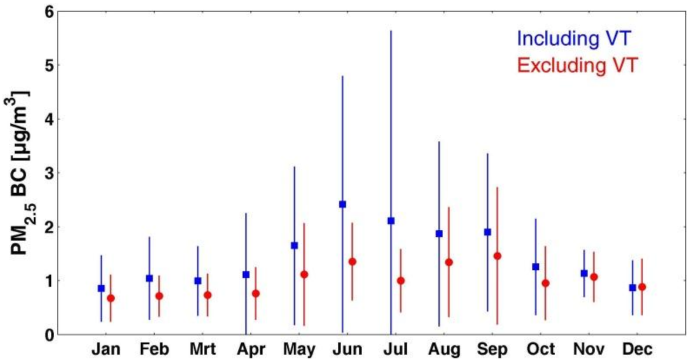
The mass fraction OC at SK and the mass fraction BC at VT were the highest for all the sites for both $PM_{2.5}$ and PM_{10}. The high OC mass fraction at SK can be attributed to both natural and anthropogenic reasons. Mphepya et al. (2006) previously indicated the substantial impact of biomass burning fire emissions, at SK. SK, LT and BS lies within the savannah biome (Mucina & Rutherford, 2006), which emits more natural biogenic volatile organic compounds (BVOCs) than the Dry Highveld Grassland Bioregion wherein VT and AF lie (Mucina & Rutherford, 2006). The atmospheric lifetime of BVOC are mostly in the order of minutes to hours (Atkinson and Arey, 2003), indicating that BVOC can be converted to lower volatile species that will be sampled as part of aerosols in the area where it is emitted. In contrast anthropogenic VOCs have much longer atmospheric lifetimes (Jaars et al., 2014 and references therein), implying that the lower volatility species are more likely to be formed further away from the source(s). SK lies on the dominant path of air mass movement from the anthropogenic industrial hub of South Africa, which implies that primary emitted anthropogenic VOC species have time to oxidise to form secondary species that are measured as part of the OC fraction at SK. The high mass fraction of BC at VT is due to this site being within a well-known anthropogenic source region as previously indicated and the nature of the sources occurring there.

3.2. Temporal assessment

As previously discussed, most of the OC and BC occurred in the $PM_{2.5}$ fraction, since there was not a significant difference between OC and BC concentrations in the $PM_{2.5}$ and PM_{10} fractions (Fig. 3). Therefore the temporal variation of only the $PM_{2.5}$ measurements is presented and discussed further. A statistically meaningful seasonal temporal assessment for OC and BC concentrations could not be performed for each individual sampling site, since only one 24-hour $PM_{2.5}$ sample was obtained for each month at each site – one day cannot be construed as being representative of an entire month. However, since all 5 the South African IDAF sites occurred in a region with similar meteorological conditions and seasonal patterns, the results obtained at all the sites for the 2 year and 1 month measurement period were combined and statistically evaluated. Such a monthly temporal presentation of data gives a regional, rather than a site specific temporal impression. In contrast to previous figures, a box and whisker plot was not deemed appropriate for this presentation, since there were too few data points per month, i.e. between 10 and 15. In Fig. 5 a scatter plot indicating averages and standard deviations of the monthly OC (5a) and BC (5b) concentrations measured in the $PM_{2.5}$ fractions for all the sites over the entire sampling period, are presented (indicated in blue). Additionally, the same data is also indicated in another colour (red) with the only difference being that the VT data was excluded from this dataset. This was done, since it was previously pointed out that the OC/BC ratio of the VT was substantially different to the other sites (Fig. 3), due to the close proximity and the nature of large point sources near the VT site.



(a)

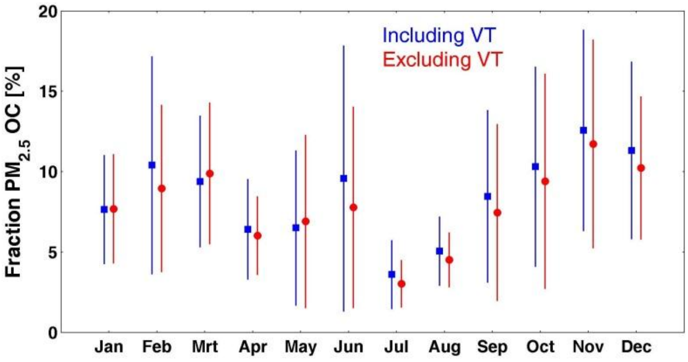


(b)

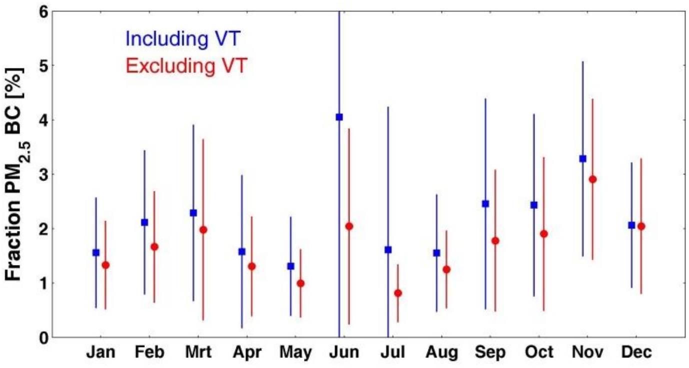
Fig. 5. Temporal variations of the average and standard deviation OC (a) and BC (b) concentrations in the $PM_{2.5}$ fraction at all the sampling sites (Including VT) and at all the sampling sites excluding VT (Excluding VT) for the entire sampling period, i.e. March 2009 to April 2011.

From the data (Fig. 5), a relatively distinct seasonal pattern is observed, with higher OC and BC concentrations generally occurring during the period from May to September with the only exception being the lower OC levels observed for July. The afore-mentioned seasonal trend was true, irrespective if VT was in or excluded from the data (indicated with different colours in Fig. 5). The period with generally higher OC and BC levels (May to September in Fig. 5) coincide with the onset of the dry season that is typically from May to early October in the interior of South Africa. During the wet season (middle October to April) aerosols are more frequently removed from the atmosphere through wet deposition. Furthermore, the peak frequency of biomass combustion fires occurs during the dry period in southern Africa. Fire burning frequency is especially high during late winter and early spring, i.e. August and September in southern Africa. This will be explored further, later in the paper. The period with generally higher OC and BC levels also coincide with the time of the year that persistent low-level inversion layers trap pollutants close to the surface (Laakso et al., 2012), which leads to an increase in atmospheric concentrations of pollutant species. The colder months (May to August) are additionally characterised by increased household combustion for space heating (Venter et al., 2012), which could lead to higher atmospheric OC and BC concentrations. The possible contributions of sources will be explored later.

In Fig. 6 temporal variations of the average and standard deviation OC (6a) and BC (6b) mass fractions of $PM_{2.5}$ for all the sites, in- and excluding VT, over the entire sampling period are presented. Apart from the OC and BC mass fraction of June, it can be seen that the OC and BC seasonal mass fraction distribution (Fig. 6) is an inverse of the seasonal OC and BC concentrations presented in Fig. 5. This indicates that although OC and BC concentrations are in general higher in the dry and cold period of May to August (Fig. 5), the atmospheric aerosol load during this period is also substantially higher, therefore resulting in a lower fractional representation of OC and BC (Fig. 6). Unfortunately complete mass closure with all possible species were not conducted during this study and it cannot be stated with certainty what other species are higher during the period of May to August. However, it is likely that wind-blown dust concentrations will be higher during this time of the year, since less rainfall will result in more wind-blown dust (Mphepya et al., 2004). Possible higher fractional sulphate content of aerosols in the dry season (Tiitta et al., 2014) could also contribute to the lower OC and BC mass fractions. Sulphate is the dominant species in South African aerosols (Tiitta et al., 2014; Martins et al., 2007).



(a)



(b)

Fig. 6. Temporal variations of the average and standard deviation OC (a) and BC (b) mass fraction percentage in the $PM_{2.5}$ fraction at all the sampling sites (Including VT) and at all the sampling sites excluding VT (Excluding VT) for the entire sampling period, i.e. March 2009 to April 2011.

3.2 Possible sources of OC and BC

Although it seem straight forward that biomass combustion fires contribute significantly to OC and BC concentrations, this was explored further. In Fig. 7 the frequency of biomass combustion fires (obtained from MODIS burned area measurements) from March 2009 to April 2011 (correlating to the sampling period in this study) are presented for southern Africa in the region between 15 – 35˚S and 10 – 41˚E. The numbers of fires within a 1000 km radius from the middle of the 5 IDAF sites are also indicated. From this data (Fig. 7) it is evident that the fires mainly occurred between June and October, which correlates with the seasonal pattern observed for OC and BC (Fig. 5). Additionally the highest frequency of fires occurred in August and September. The highest number of fire events recorded for southern Africa (15 – 35˚S and 10 – 41˚E) in a single month was approximately 1.2 million in September 2011. Roughly 550 000 of these biomass burning fire events took place within the 1000 km radius of the middle of the 5 IDAF sites.

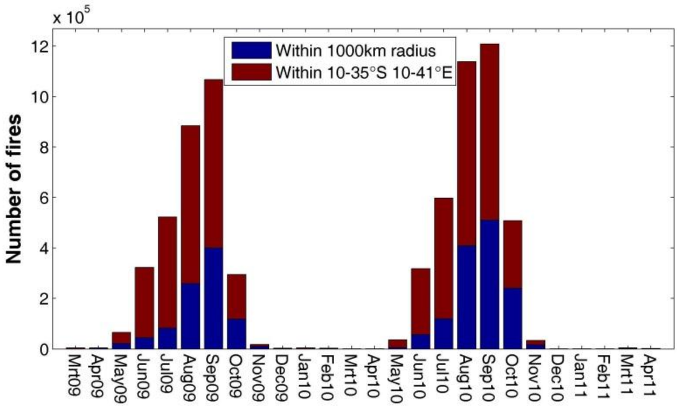
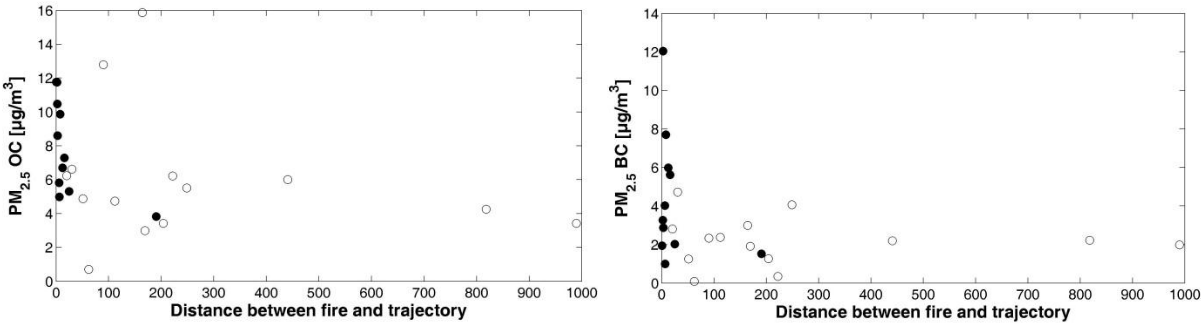
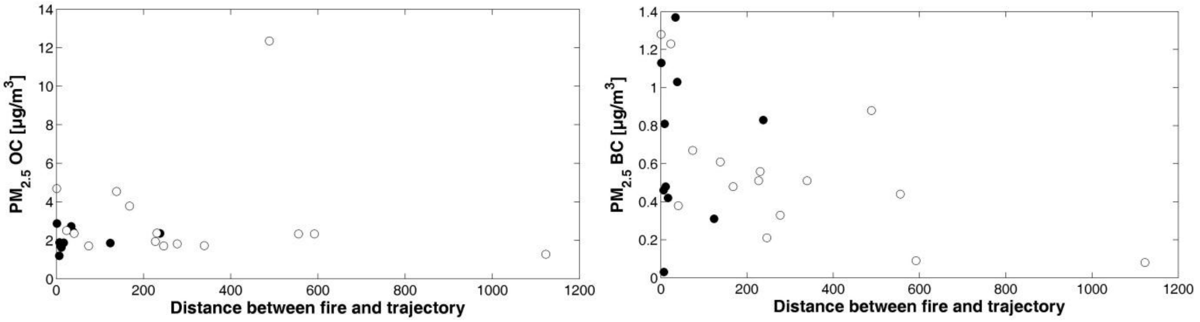


Fig. 7. The frequency of biomass burning fires (obtained from MODIS burned area measurements) from March 2009 to April 2011 in southern Africa (15 – 35˚S and 10 – 41˚E), as well as the number of fires within a 1000 km radius from the middle of the 5 IDAF sites.

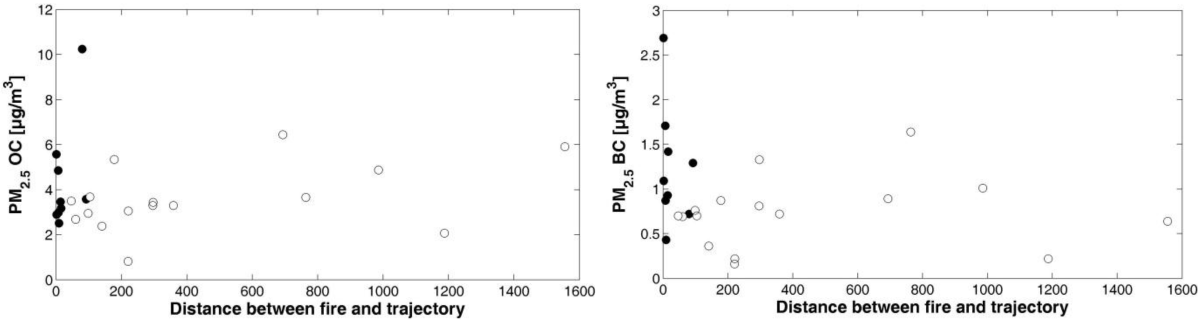
As previously described, the distances between back trajectories calculated for arrival in the middle of each sampling period and biomass burning fire events recorded from the previous 24 hours were compared to OC and BC concentrations measured. In Fig. 8 OC and BC concentrations measured for $PM_{2.5}$ are plotted against the shortest distances between the 24-hour back trajectories and fire events for each sample at VT (8a), BS (8b), LT (8c), SK (8d) and AF (8e). The black dots indicated OC and BC concentrations measured during months that most fires occurred, i.e. June to October, while the open circles represent months with no or very few fire events (according to Fig. 7).



(a) VT

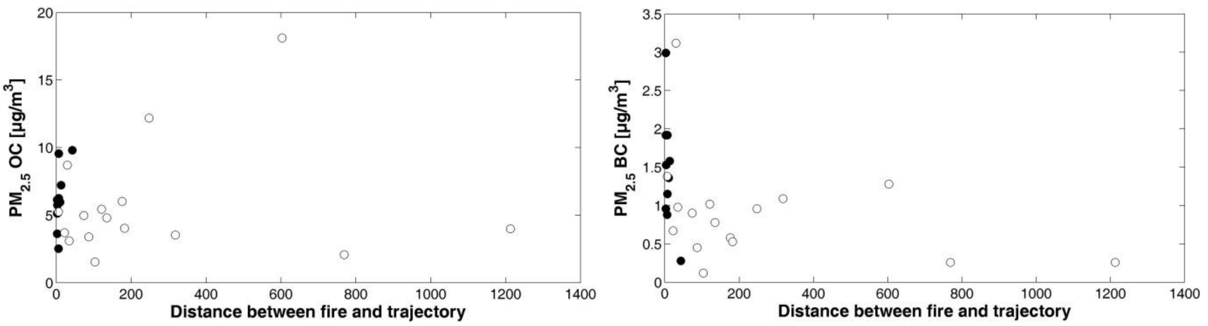


(b) BS

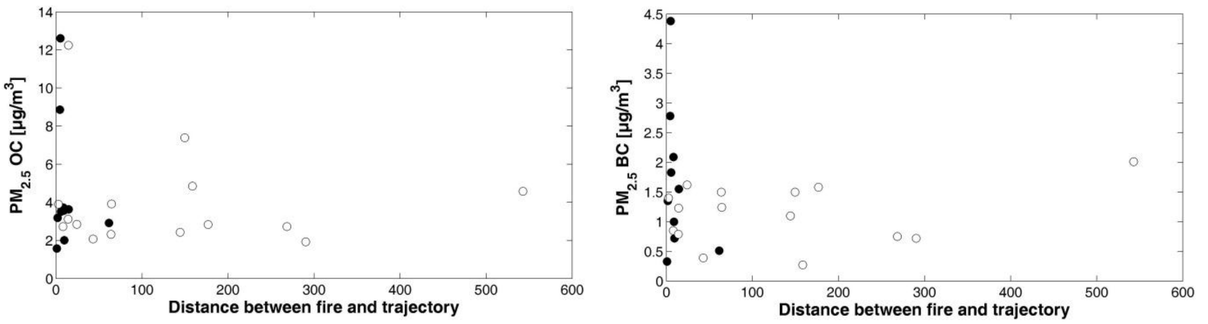


(c) LT

Fig. 8. PM$_{2.5}$ OC and BC concentrations plotted against the shortest distances between the back trajectories and the fire events, at VT (a), BS (b), LT (c), SK (d) and AF (e). The black dots represent the months during which most fires occurred (June to November), while the open circles represent months with fewer fire events (December to May).



(d) SK

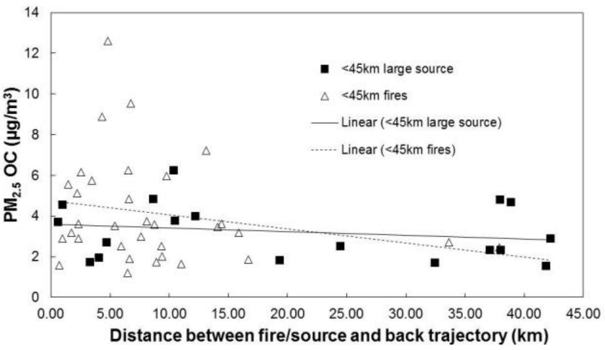


(e) AF

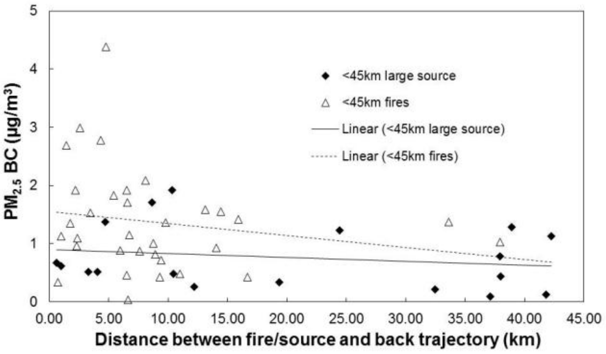
Fig. 8. continued. PM$_{2.5}$ OC and BC concentrations plotted against the shortest distances between the back trajectories and the fire events, at VT (a), BS (b), LT (c), SK (d) and AF (e). The black dots represent the months during which most fires occurred (June to November), while the open circles represent months with fewer fire events (December to May).

From Fig. 8 it seems that higher OC and BC concentrations were measured when trajectories passed closer to fires during the months when most fires occurred (June to October). In contrast, during the months with fewer fires, OC and BC concentrations did not seem to be influenced by the distances between the trajectories and fires. This indicates that fires are a major source of OC and BC during the months with high fire frequencies, while OC and BC measured during other months were mainly emitted from other sources in this region. The afore-mentioned trend, i.e. higher OC and BC contribution from biomass combustion fires in months with more fires, are somewhat obscured due to all the averaging periods in the data, i.e. 24-hour sampling, calculation of a single trajectory in the middle of the sampling period and 24-hour clustering of fire events by MODIS burned area measurements.

In an effort to further explore the regional contribution of biomass combustion fires to OC and BC, the data presented in Fig. 8 for individual sites were combined into a two figures, i.e. Figs. 9a for OC and 9b for BC. These two figures therefore again give a regional, rather than a site specific perspective, of OC and BC concentrations as a function of distance to the closest fire for each calculated back trajectory. Since the VT sampling site was within an industrialised and residential region that could lead to bias in the data presentation, OC and BC measured at this sampling site were excluded from Fig. 9. Additionally the data points where the distance to the fire for a specific back trajectory was > 45 km were not included in this analysis (Fig. 9).



(a)



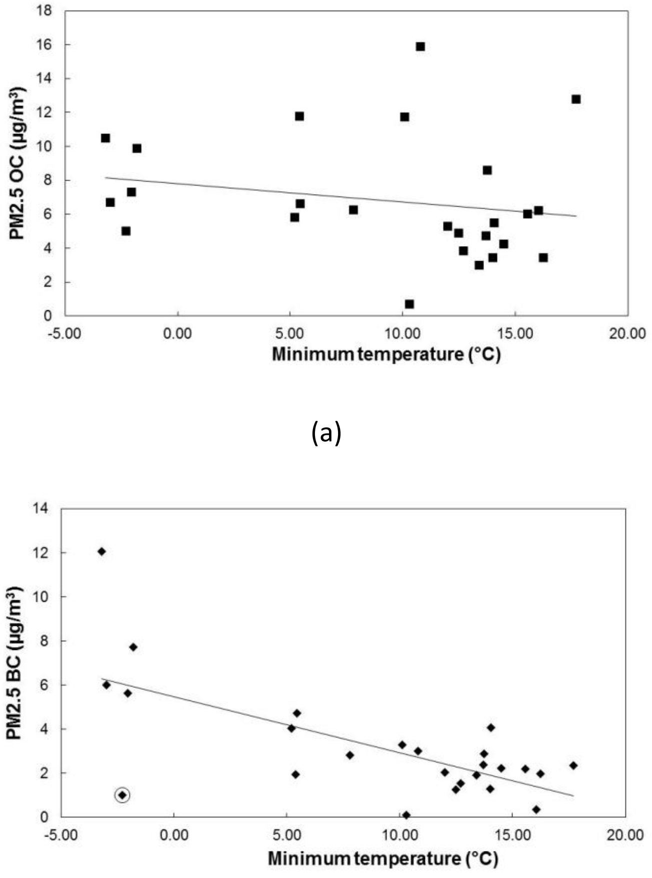
(b)

Fig. 9. PM$_{2.5}$ OC (a) and BC (b) concentrations of June to October (months with higher fire frequency, according to Fig. 7) at all the sampling sites as a function of shortest distance between back trajectories and fires, excluding VT data and data where the shortest distances >45 km. Additionally, PM$_{2.5}$ OC (a) and BC (b) concentrations of SK, LT and BS as a function of shortest distance between back trajectories and large point source, excluding data where the shortest distances >45 km, are presented for the entire sampling period.

Although not well defined, there seems to be a general trend between the OC and BC concentrations and the distance a back trajectory had passed a biomass burning fire, as presented in Fig. 9. As previously mentioned, the reason for the scattered nature of the data in Fig. 9 is due to multiple averaging periods that had to be applied, i.e. 24-hour sampling, calculation of a single trajectory in the middle of the sampling period and 24-hour grouping of fire events by MODIS burned area measurements. Notwithstanding these data limitations, it is evident that OC and BC are higher if a biomass combustion fire event(s) had impacted on a back trajectory air mass. Therefore, fires seem to contribute significantly to both OC and BC concentrations during the period when biomass burning fires frequently occur, i.e. June to October.

Similar to the data presented in Fig. 8, $PM_{2.5}$ OC and BC concentrations were plotted against the shortest distance a back trajectory for every sampling period had passed large point sources in the north-east of South Africa, for each sampling site. Thereafter, these individual datasets of SK, LT and BS were combined to again give a regional, rather than a site specific perspective. The AF data was excluded since it had a large point source close to it, while VT was also excluded since it was within a source region with many large sources nearby. For the combined dataset of SK, LT and BS data points where the distance between back trajectories and large point sources were > 45 km were also not included in this analysis. The afore-mentioned combined dataset for SK, LT and BS is presented as a second data series in Fig. 9. From this data it is evident that $PM_{2.5}$ OC and BC concentrations were not influenced by the distances back trajectories had passed the large point sources. This indicates that these large point sources do not contribute as significantly to OC and BC concentrations as the biomass combustion fires. The observations that large point sources do not contribute significantly to regional BC concentrations is feasible, since emissions regulations in South Africa have historically regulated particulate emissions (of which BC is part) much more stringently than gaseous emissions.

The last possible source of OC and BC that has already been mentioned, but not yet evaluated is household combustion. Venter et al. (2012) previously suggested that household combustion in informal and semi-formal settlements in South Africa could be a significant source of BC, at least on a local scale. Household combustion can serve two needs, i.e. cooking or space heating. In order to verify if household combustion for space heating contributed to OC and BC concentrations, the $PM_{2.5}$ OC and BC concentrations of VT were plotted against the minimum temperature measured during the actual sampling periods (Fig. 10). The VT site was specifically chosen for this analysis, since many informal and semi-formal settlements occur in the immediate area surrounding the measurement site, while this is not the case for AF, SK, LT and BS.



(a)

(b)

Fig. 10. $PM_{2.5}$ OC (a) and BC (b) concentrations of VT plotted as a function of actual minimum temperature when the samples were taken.

As is evident from Fig. 10, both $PM_{2.5}$ OC and BC concentrations were inverse related to the average monthly minimum temperature. This implies that lower temperatures resulted in more household combustion for space heating, which resulted in higher OC and BC emissions. However, the correlation of $PM_{2.5}$ OC and minimum temperature was weaker than the correlation found for $PM_{2.5}$ BC and minimum temperature. This is understandable, since measured OC do not only consist of primary emitted particles, but also of secondary formed particles. In contrast BC are emitted as primary particles, hence the better correlation with the occurrence of household combustion for space heating that was implicated by minimum temperatures. The R^2 value for the correlation between $PM_{2.5}$ BC and minimum temperature was found to be significant, i.e. 0.45. This correlation is even more significant, i.e. 0.63, if the single circled value in Fig. 10b is excluded.

4. Conclusions

The OC and BC dataset presented in this paper is the most comprehensive presented to date in the peer reviewed public domain. OC were higher than BC concentrations at all the South African IDAF sites in the PM_{10} and $PM_{2.5}$ fractions. Most OC and BC occurred in the smaller size fraction, i.e. $PM_{2.5}$. OC and BC concentrations, as well as OC/BC ratios reflected the setting of the different IDAF sites, as well as the type of sources impacting the different sites. VT, which is situated in an industrial and urban setting, had the highest OC and BC concentrations with the lowest OC/BC ratio. Of the sites investigated, it was mostly likely also most significantly impacted by fossil fuel combustion. AF, which is influenced by an industrial source region, had the second lowest OC/BC ratio, while the background sites (BS, LT and SK) had the highest OC/BC ratios. The background sites were also likely to be impacted by non-fossil fuel sources such as biomass burning fires. The OC mass fraction percentage varied up to 24% and the BC up to 12 % for all the sites and for both $PM_{2.5}$ and PM_{10}.

A relatively well define seasonal pattern was observed, with higher OC and BC concentrations measured from May to October, which coincide with the dry season and biomass burning in the interior of South Africa. Seasonal OC and BC mass fractions for all the sites over the entire sampling were found to be the inverse of the seasonal OC and BC concentrations. This indicates that although OC and BC concentrations are in general higher in the dry and cold period, the atmospheric aerosol load during this period is also substantially higher, likely due to wind-blown dust.

Positive correlations between OC and BC concentrations with the distance back trajectories passed biomass combustion fires were observed, while no such correlations were observed for the distance back trajectories had passed large point sources. This seems to prove that biomass combustion fires contribute significantly to both OC and BC concentrations on a regional scale, while this is not true for large point sources. Correlation of OC and BC concentrations with the minimum temperatures during the sampling periods at the VT site proved that household combustion for space heating in semi- and informal settlements contributed to OC and BC levels, at least on a local scale.

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Chapter 4

Project evaluation and future perspective

4.1. Project evaluation

The general aim of this study was to determine the spatial and temporal distribution of black carbon (BC) and organic carbon (OC) at South African DEBITS sites. In Chapter 1, specific objectives were listed in order to achieve the main objective of the study. These objectives are critically evaluated in this section in view of the successes and shortcomings of the study.

Objective 1

Collect $PM_{2.5}$ and PM_{10} atmospheric aerosol samples at the South African DEBITS sites.

$PM_{2.5}$ and PM_{10} atmospheric aerosol samples were successfully collected at five South African DEBITS sites, i.e. Vaal Triangle (VT), Amersfoort (AF), Botsalano (BS), Louis Trichardt (LT) and Skukuza (SK). Duplicate 24-hour samples were collected with MiniVol samplers once a month for a period of two years from March 2009 to April 2011 at each of the sites. Successful atmospheric aerosol sampling over these periods at the different South African DEBITS sites was very important to conduct a spatial and temporal assessment of BC and OC. Only approximately two samples collected at each site could not be analysed, since these samplers were wet due to rain events or problems that were experienced with the MiniVol^{TM} samplers.

A deficiency experienced with the sampling of atmospheric aerosols with MiniVol^{TM} samplers was that there were minor instances where $PM_{2.5}$ concentrations were higher than the PM_{10} levels, which is not possible. This was attributed to small differences in the flow rates of the two MiniVol^{TM} samplers used to collect $PM_{2.5}$ and PM_{10}. The flow rate of the MiniVol^{TM} samplers is manually adjusted to 5 L/min. Therefore, human error could cause small differences in the flow rates of the two

MiniVol^{TM} samplers used to collect $PM_{2.5}$ and PM_{10} samples concurrently at each of the sites. A flow rate of 5 L/min was used in the calculation of all the BC and OC concentrations. Therefore, small differences in the actual flow rate during the 24-hour sampling period could have an influence on the calculated concentrations. This phenomenon was also observed in previous studies where MiniVol^{TM} samplers were used (Van Wyngaardt, 2011; Kleynhans, 2008).

Objective 2

Analyse the collected $PM_{2.5}$ and PM_{10} samples to determine the OC and BC concentrations.

The samples were analysed with a Thermal/Optical carbon analyser (Desert Research Institute) in Toulouse (France) at the Laboratoire d’ Aérologie during a one-month research visit. OC and BC analysis is a relatively complicated analytical technique that requires a certain level of experience and skill. Therefore, the successful OC and BC analysis of a large number of $PM_{2.5}$ and PM_{10} samples, during one month, by the candidate with the Thermal/Optical carbon analyser can be considered a very good accomplishment. The OC and BC concentrations obtained from the analytical instrument (µg C/m^2) could be converted to atmospheric concentrations of these species (µg.m^{-3}). All the results obtained from the analysis of the aerosol samples could be used for the assessment of OC and BC concentrations.

Objective 3

Assess the current *status quo* of OC and BC aerosol concentration trends at the regionally representative South African DEBITS sites.

The current situation of OC and BC concentrations at the South African DEBITS sites could be assessed in terms of temporal and spatial variations of these species. The results indicated that OC levels were higher than BC concentrations at all the South African DEBITS sites in both size fractions measured. OC and BC concentrations, as well as OC/BC ratios, were characteristic of the location of the different DEBITS sites. VT that is situated in an industrial and urban area had the highest OC and BC concentrations with the lowest OC/BC ratio. AF, which is influenced by an industrial source region, had the second lowest OC/BC ratio. The background sites (BS, LT and SK) had the highest OC/BC ratios. The OC mass fraction percentage varied up to 24% and the BC up to 12% for all the sites and for both $PM_{2.5}$ and PM_{10}.

A relatively distinct seasonal pattern was observed with higher OC and BC concentrations measured from May to October, which coincides with the dry and cold season in the interior of South Africa. Seasonal OC and BC mass fractions for all the sites over the entire sampling period were found to be the inverse of the seasonal OC and BC concentrations. This indicates that although OC and BC concentrations are in general higher in the dry and cold period, the atmospheric aerosol load during this period is also substantially higher.

<u>Objective 4</u>

Link the OC and BC concentrations measured to possible sources.

The OC and BC measured at South African DEBITS sites could partially be linked to sources of these species. The mass fraction OC at SK and the mass fraction BC at VT were the highest for all the sites for both $PM_{2.5}$ and PM_{10}. The high OC mass fraction at SK can be attributed to both natural (lies within the savannah biome) and anthropogenic (dominant path of air mass movement from the anthropogenic industrial hub of South Africa) reasons. The high mass fraction of BC at VT is due to this site being within a well-known anthropogenic source region, which includes the incomplete combustion of fossil fuels, industrial activities, household combustion and traffic emissions. The mass fractions calculated for OC and BC also indicated an increased load of wind-blown dust during the dry period.

Positive correlations between OC and BC concentrations with the distance that back trajectories passed over fires were observed. Although there is an uncertainty associated with these correlations due the uncertainty between the exact time when a fire occurred within a 24-hour period and the 24-hour sample period, it seems evident that wild fires contribute significantly to both atmospheric OC and BC during the burning season.

A shortcoming with regard to Objectives 3 and 4 was that aerosol samples collected to determine OC and BC concentrations were only collected once a month for 24 hours at each of the sites. However, due to logistical reasons, this is the highest frequency of aerosol samples that could be collected at the South African DEBITS sites at present. These sites cannot be visited more frequently for collection of aerosol samples with MiniVol^{TM} samplers due to the remote nature of these sites and the availability of onsite personnel. A more comprehensive dataset of OC and BC concentrations at the South African DEBITS sites would allow for a more accurate temporal and spatial assessment, as well as linkage to sources of these species. However, the OC and BC concentrations reported in this study are at present the most comprehensive OC and BC dataset reported on for South Africa.

4.2. Future perspectives

The deficiency associated with the use of MiniVol^{TM} samplers for the collection of $PM_{2.5}$ and PM_{10} samples indicated previously could be overcome by the use of high-volume samplers with one inlet equipped with impactors that separate PM in different size fractions. It was considered to use Dekati impactors for future sampling of aerosol samples at the South African DEBITS sites. However, these impactors collect aerosols on the filters in a manner that is not suitable for analysis with the Thermal/Optical carbon analyser. Other size segregated aerosol sampling methods should be explored. In addition, aerosol sampling instruments that measure PM_1 should also be considered. The measurement of OC and BC concentrations in smaller particulates is especially important to establish the health impacts associated with atmospheric aerosols.

In future, it is also important to possibly improve the frequency of aerosol sampling at the South African DEBITS sites. A higher sampling resolution would lead to an improved assessment of temporal and spatial variations. However, due to the remote location of the South African DEBITS sites, it will be difficult to improve the sampling frequency with the sampling methods currently employed. A possible solution may be to use automated samplers at the sites for aerosol collection. However, these samplers are expensive and will require a relatively large capital investment.

The OC and BC concentrations must also be related to other measurements conducted at the South African DEBITS sites, which will further assist in explaining the temporal and spatial variation observed.

It is important that the measurements of OC and BC concentrations at the South African DEBITS sites continue in the future, even at the current frequency of sampling. Long-term measurements of these species for a region, for which very little data exists, is critical in order to determine annual variations and assist in the implementation of the appropriate mitigation procedures.

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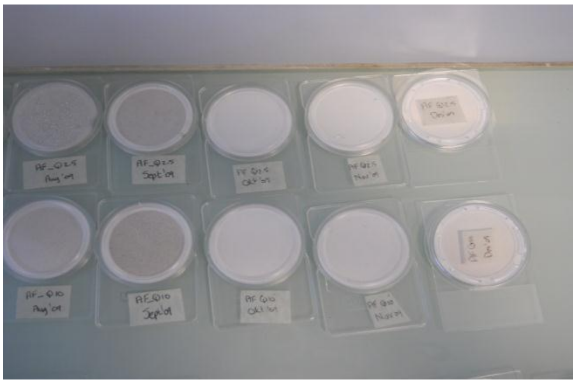
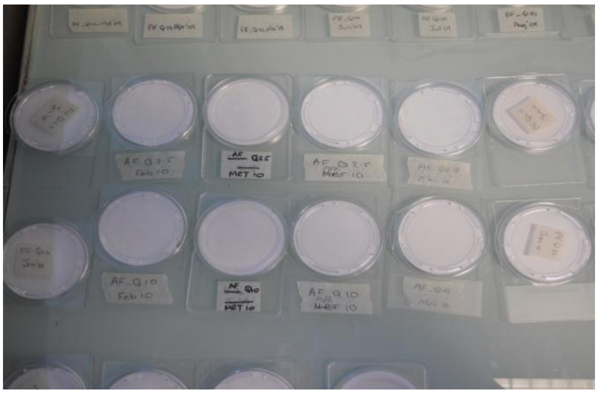
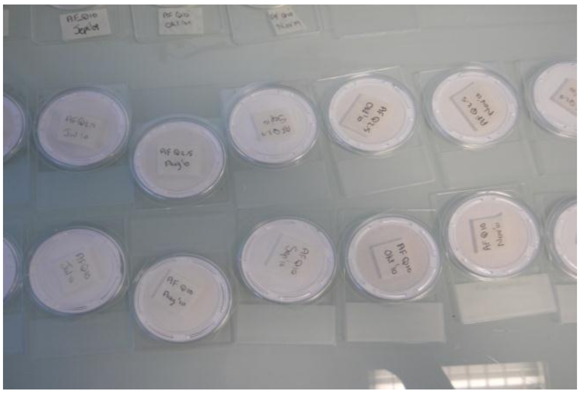
Appendix A

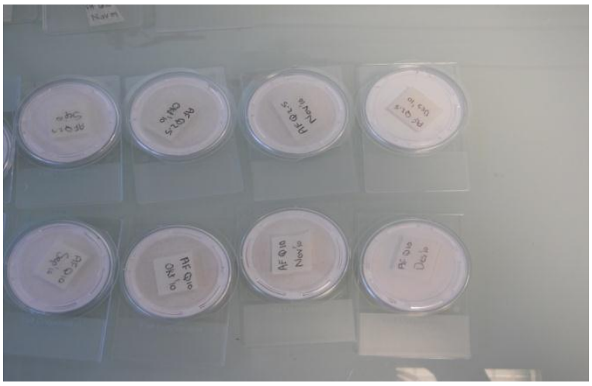
Images of samples collected at all the sites

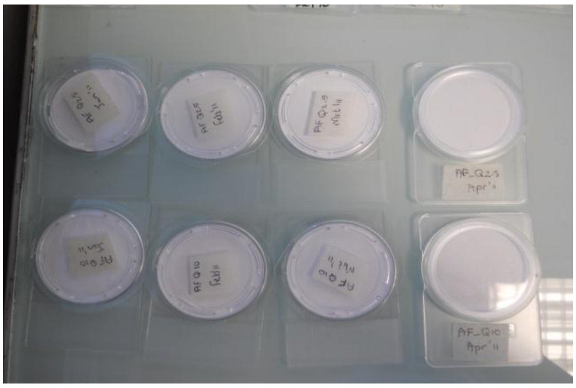
Amersfoort





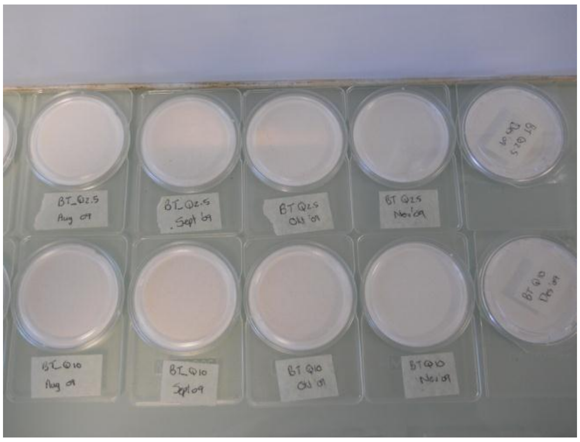


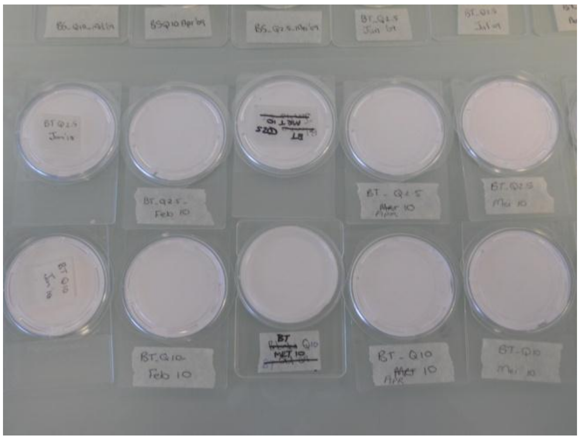


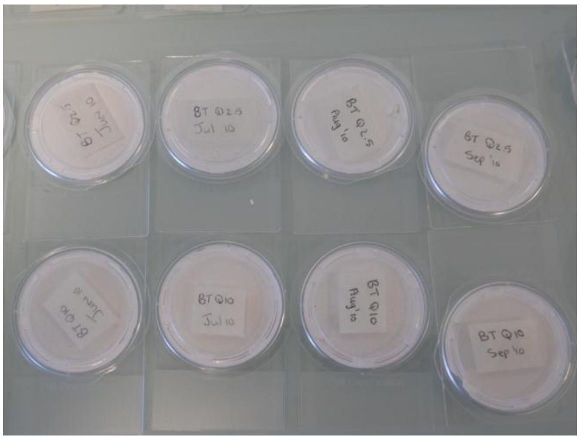


Botsalano


BS_Q2.5_Mar'09
BS Q2.5 Apr'09
BS_Q10_Mei'09
BT_Q10 Jun'09
BT_Q10 Jul'09
BS_Q10_Mar'09
BS Q10 Apr'09
BS_Q2.5_Mei'09
BT_Q2.5 Jun'09
BT_Q2.5 Jul'09


BT_Q2.5 Aug 09
BT_Q2.5 Sept'09
BT Q2.5 Okt'09
BT Q2.5 Nov'09
BT Q2.5 Des'09
BT_Q10 Aug 09
BT_Q10 Sept'09
BT Q10 Okt'09
BT Q10 Nov'09
BT Q10 Des'09


BS_Q10_Mar'09
BS Q10 Apr'09
BS_Q2.5_Mei'09
BT_Q2.5 Jun'09
BT_Q2.5 Jul'09
BT Q2.5 Jan'10
BT_Q2.5 Feb 10
BT Q2.5 ~~MET 10~~
BT - Q2.5 ~~Mer~~ 10 Apr
BT_Q2.5 Mei 10
BT Q10 Jan 10
BT_Q10 Feb 10
BT Q10 MET 10
BT - Q10 ~~Mer~~ 10 Apr
BT-Q10 Mei 10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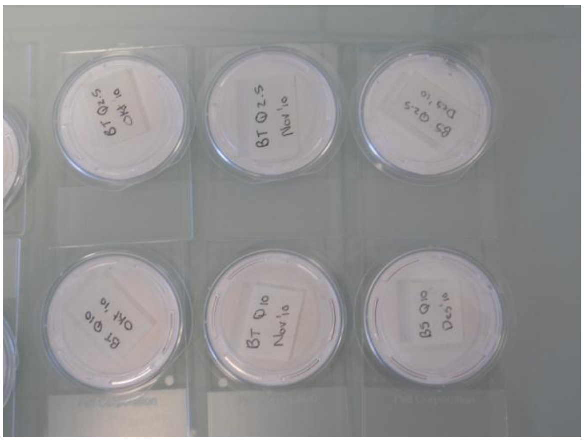
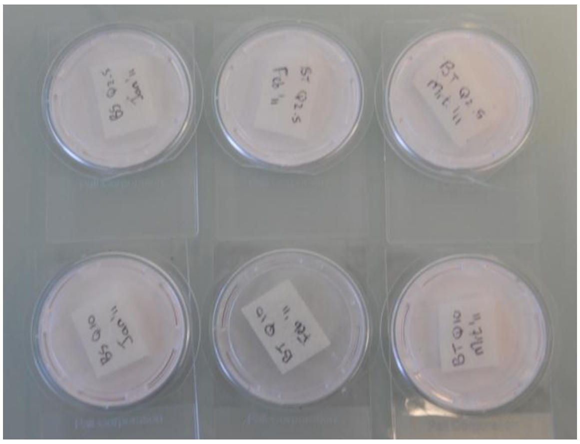
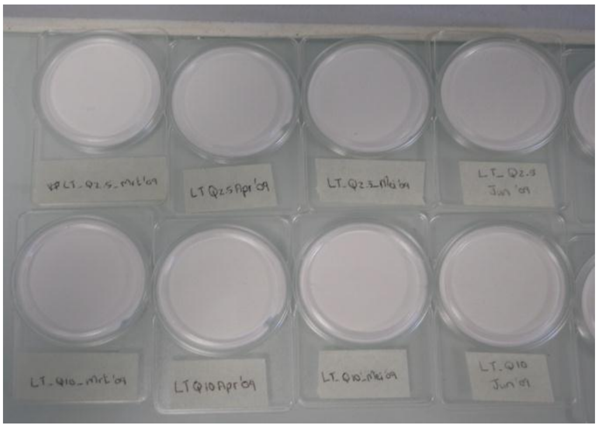
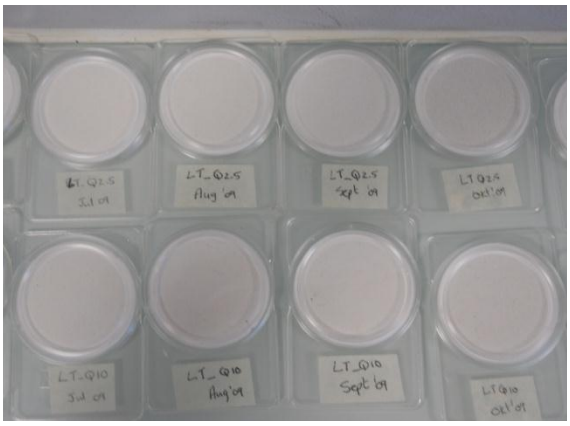
BT Q2.5 Jul 10
BT Q2.5 Aug'10
BT Q2.5 Sep'10
BT Q10 Jun 10
BT Q10 Jul 10
BT Q10 Aug'10
BT Q10 Sep'10

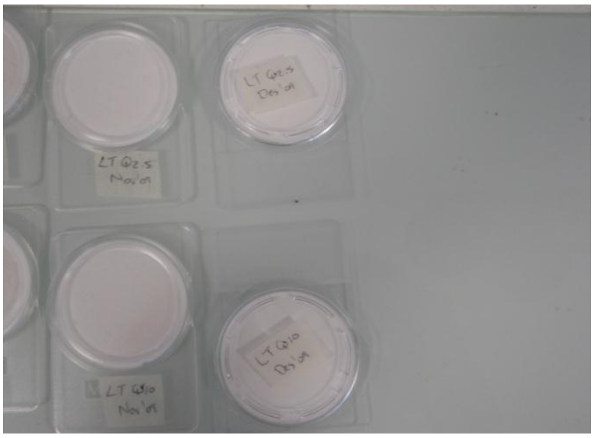

BT Q2.5 Okt'10
BT Q2.5 Nov'10
BS Q2.5 Des'10
BT Q10 Okt'10
BT Q10 Nov'10
BS Q10 Des'10

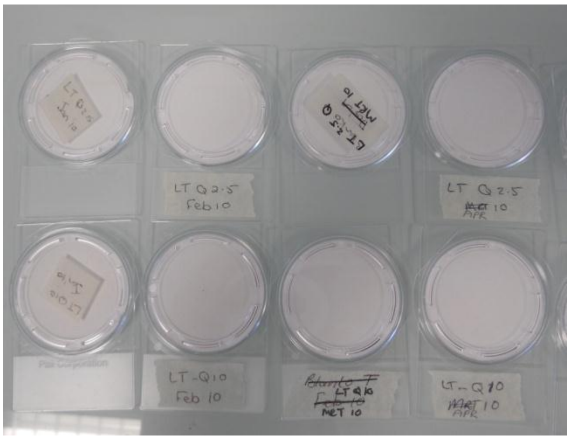

BS Q2.5 Jan'11
BT Q2.5 Feb'11
BT Q2.5 Mrt'11
BS Q10 Jan'11
BT Q10 Feb'11
BT Q10 Mrt'11

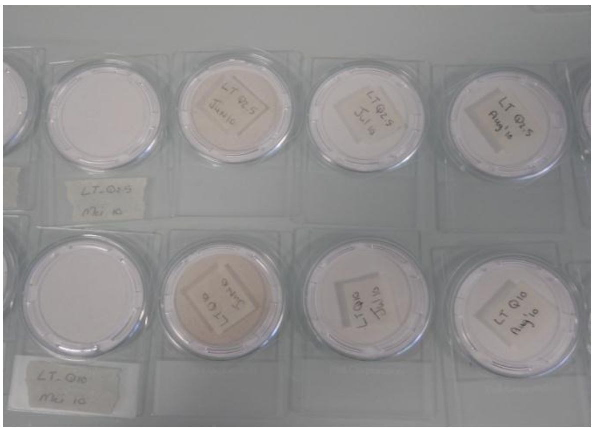
Louis Trichardt

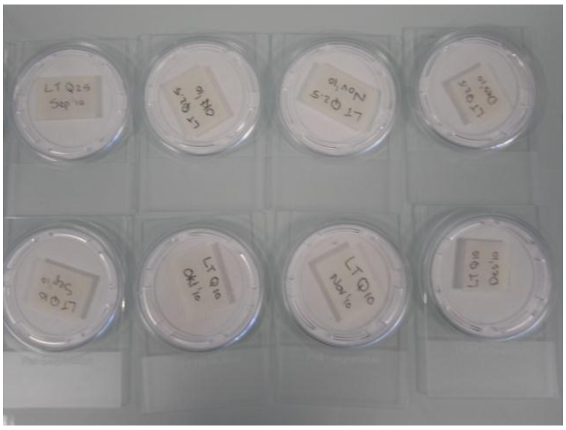


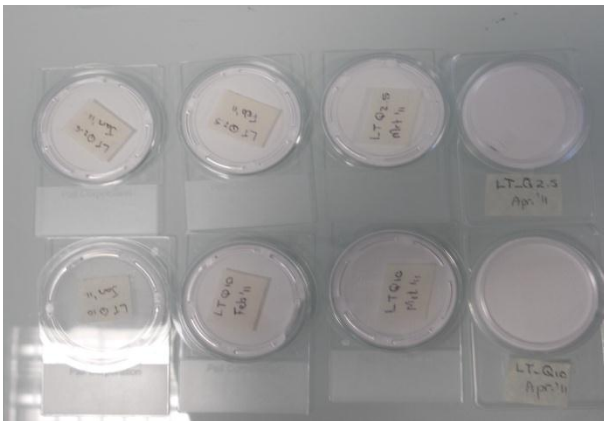




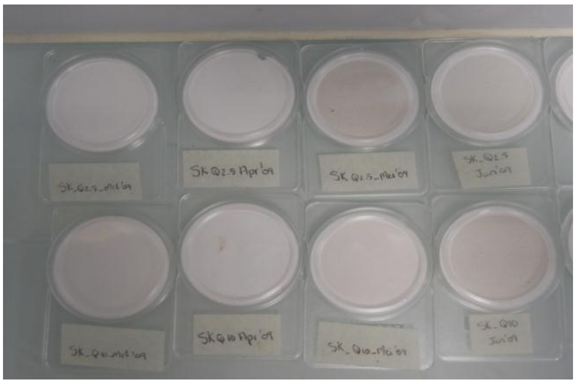




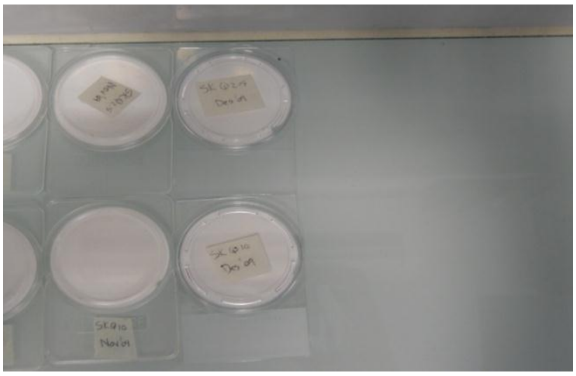


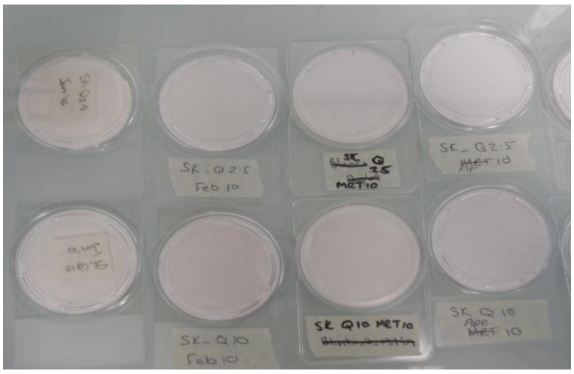


Skukuza


SK_Q2.5_Mrt'09
SK Q2.5 Apr'09
SK_Q2.5_Mei'09
SK_Q2.5 Jun'09
SK_Q10_Mrt'09
SK Q10 Apr'09
SK_Q10_Mei'09
SK_Q10 Jun'09


SK_Q2.5 Jul 09
SK_Q2.5 Aug'09
SK_Q2.5 Sept'09
SK Q2.5 Okt'09
SK Q10 Jul 09
SK_Q10 Aug'09
SK_Q10 Sept'09
SK Q10 Okt 09


SK Q2.5 Des'09
SK Q10 Des'09
SK Q10 Nov'09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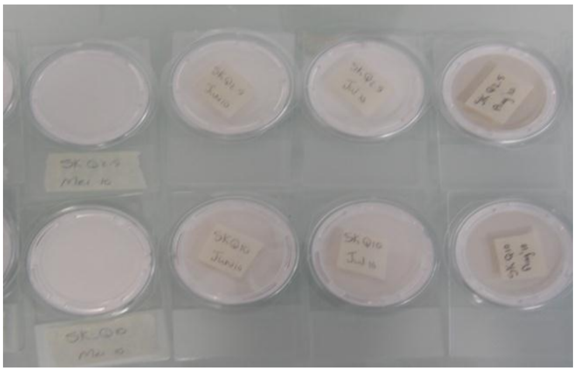
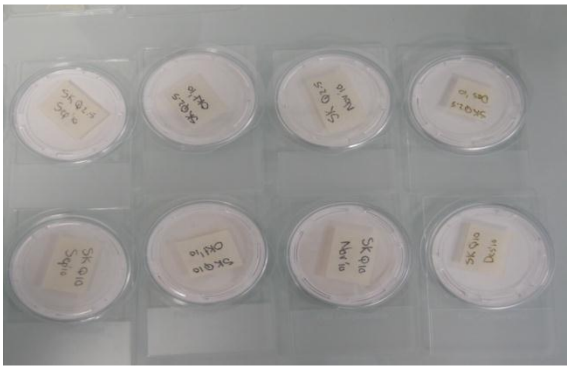
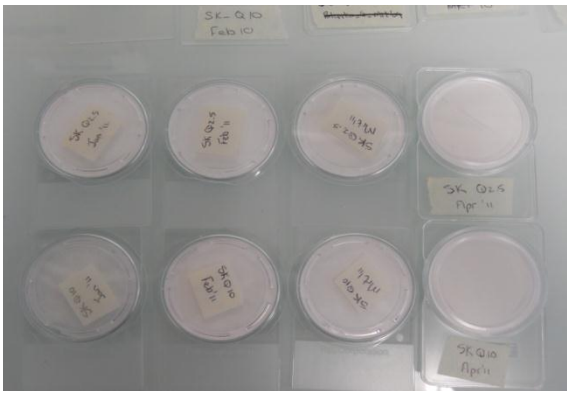
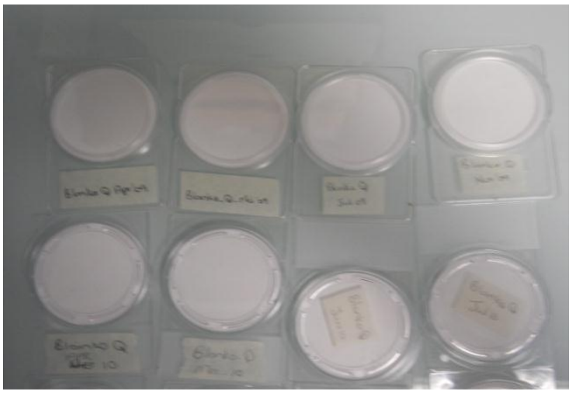
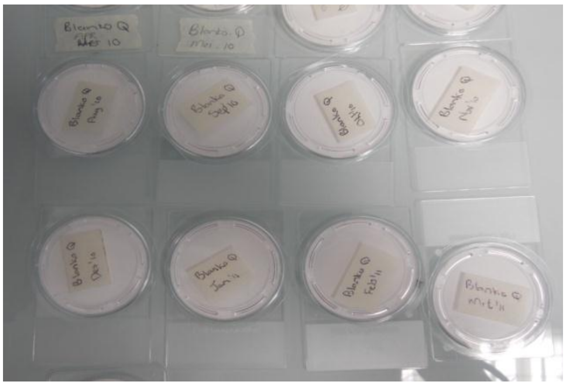
SK Q 2.5 MRT10
SK_Q2.5 MRT 10
SK Q10 MRT10
SK Q 10 APR 10
SK_Q10 Feb 10


SK Q2.5 Mei 10
SK Q10 Mei 10
SK Q10 Jun 10
SK Q10 Jul 10


SK Q10 Nov 10
SK Q10 Des 10

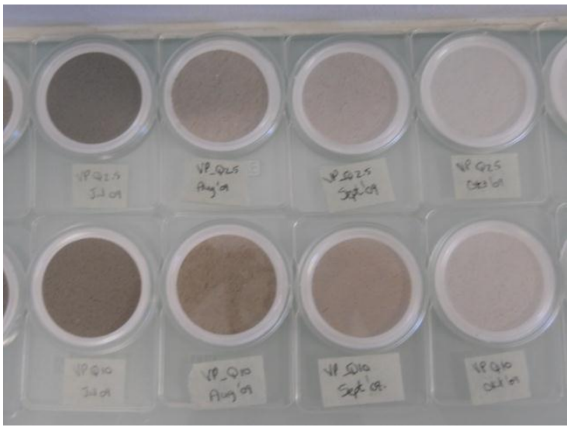

SK_Q10 Feb 10
SK Q2.5 Apr '11
SK Q10 Feb '11
SK Q10 Apr'11

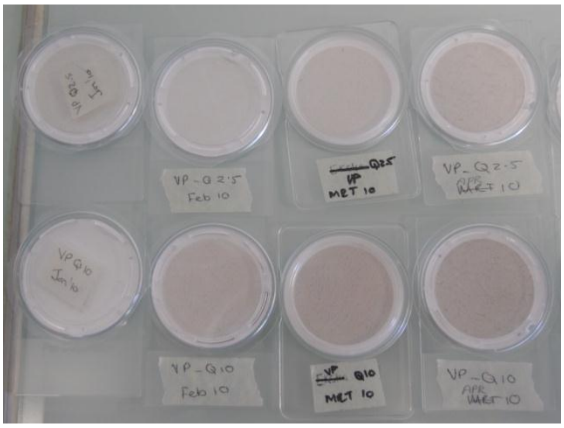


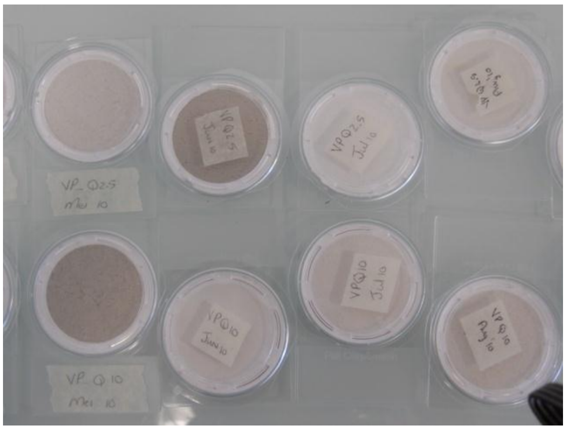

Blanko Q
Apr 10
Blanko Q
Mei 10
Blanko Q
Aug '10
Blanko Q
Sept '10
Blanko Q
Okt '10
Blanko Q
Nov '10
Blanko Q
Dec '10
Blanko Q
Jan '11
Blanko Q
Feb '11
Blanko Q
Mrt '11

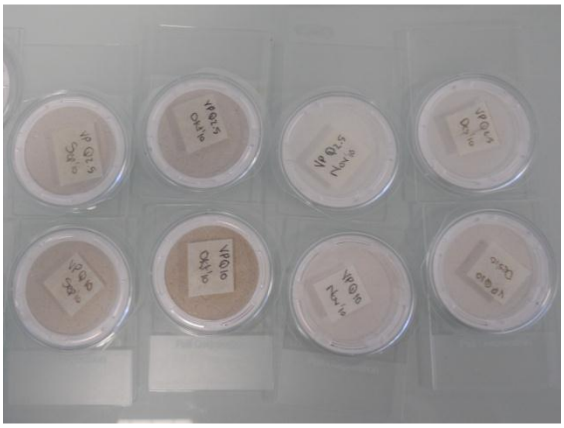

Blanko Q
Apr '11

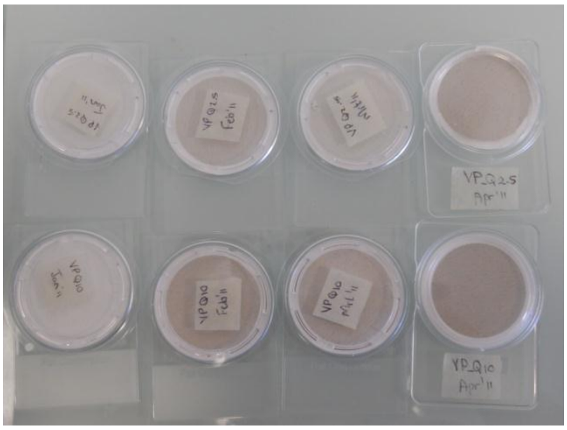
Vaal Triangle





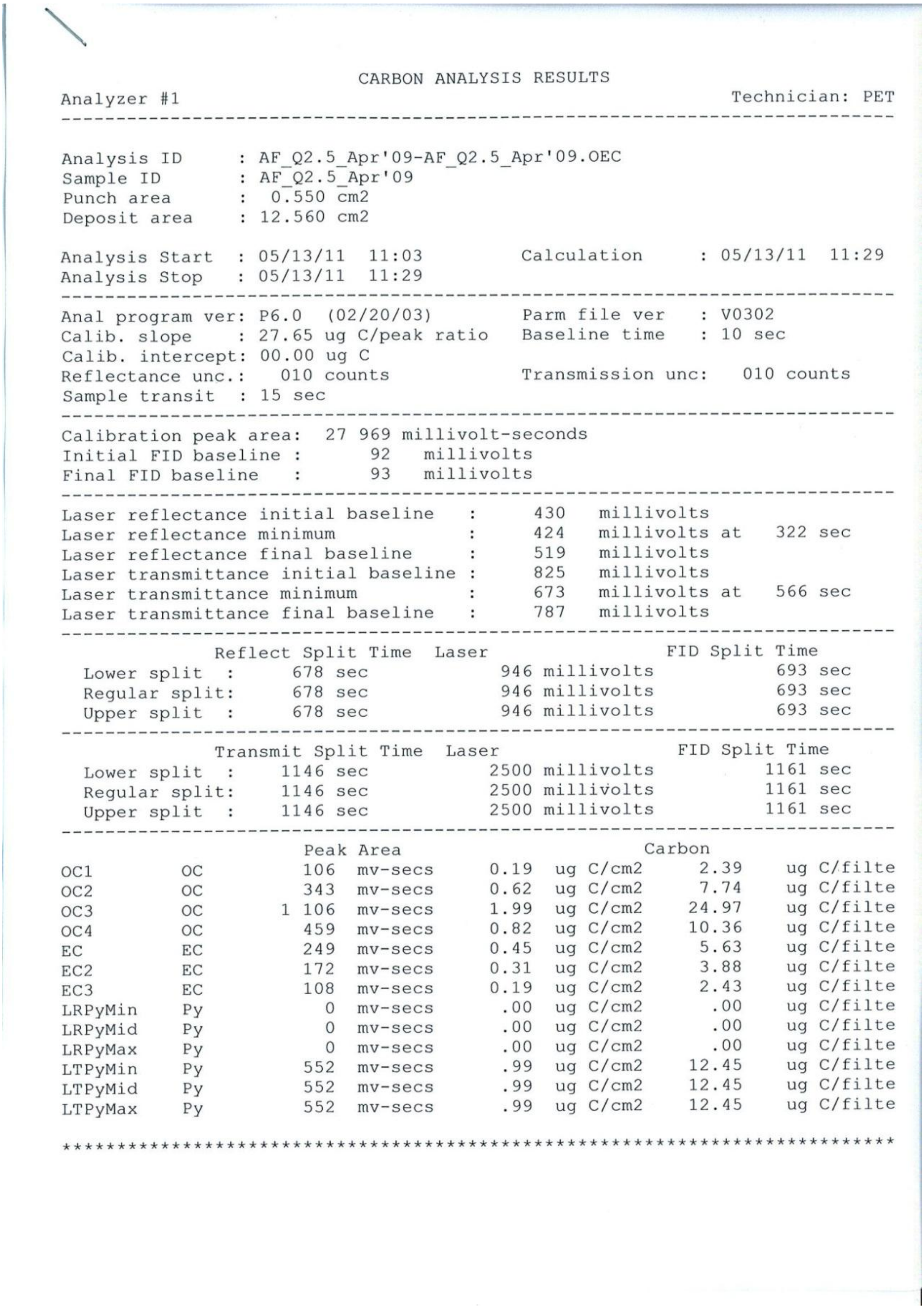




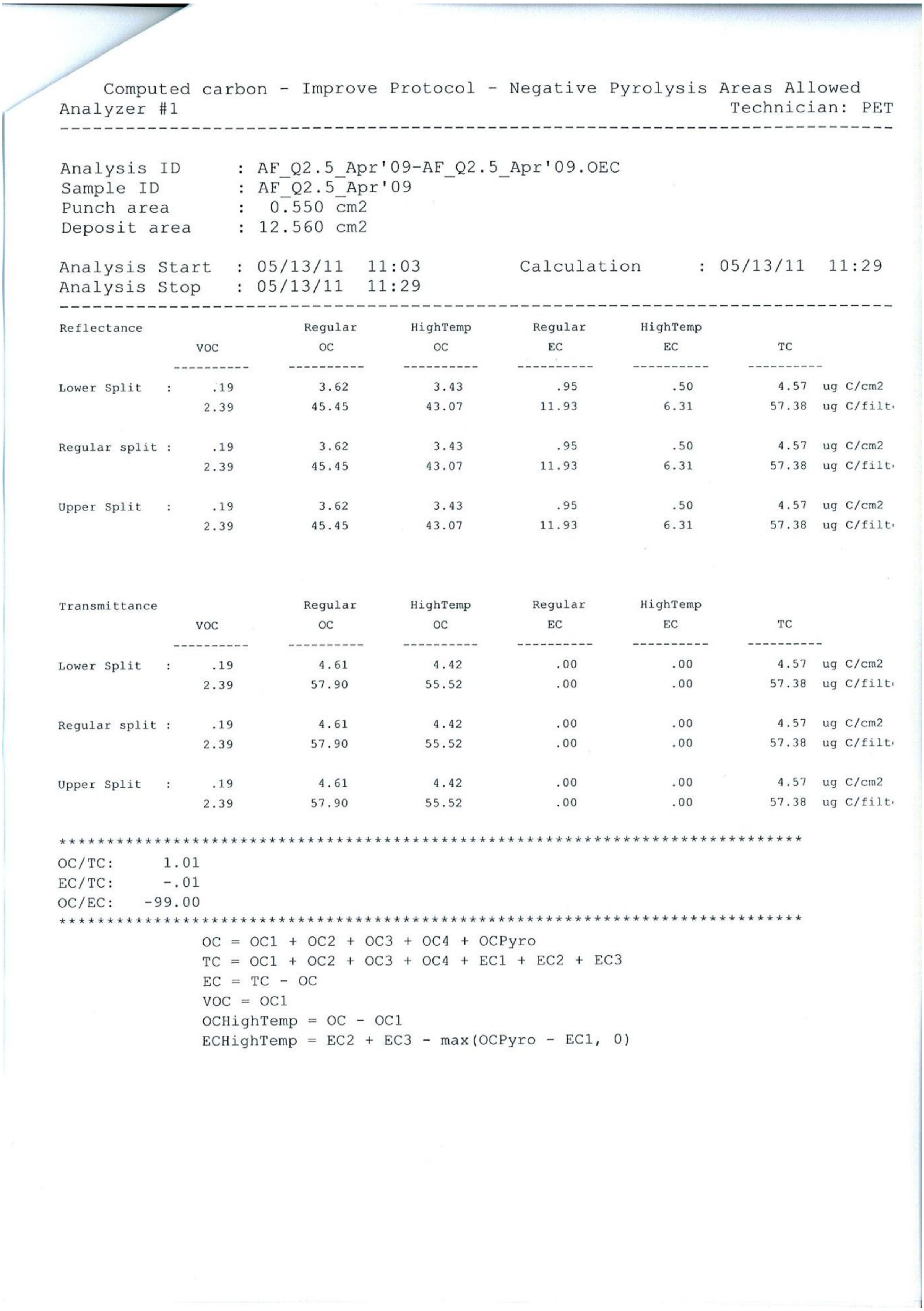


Appendix B

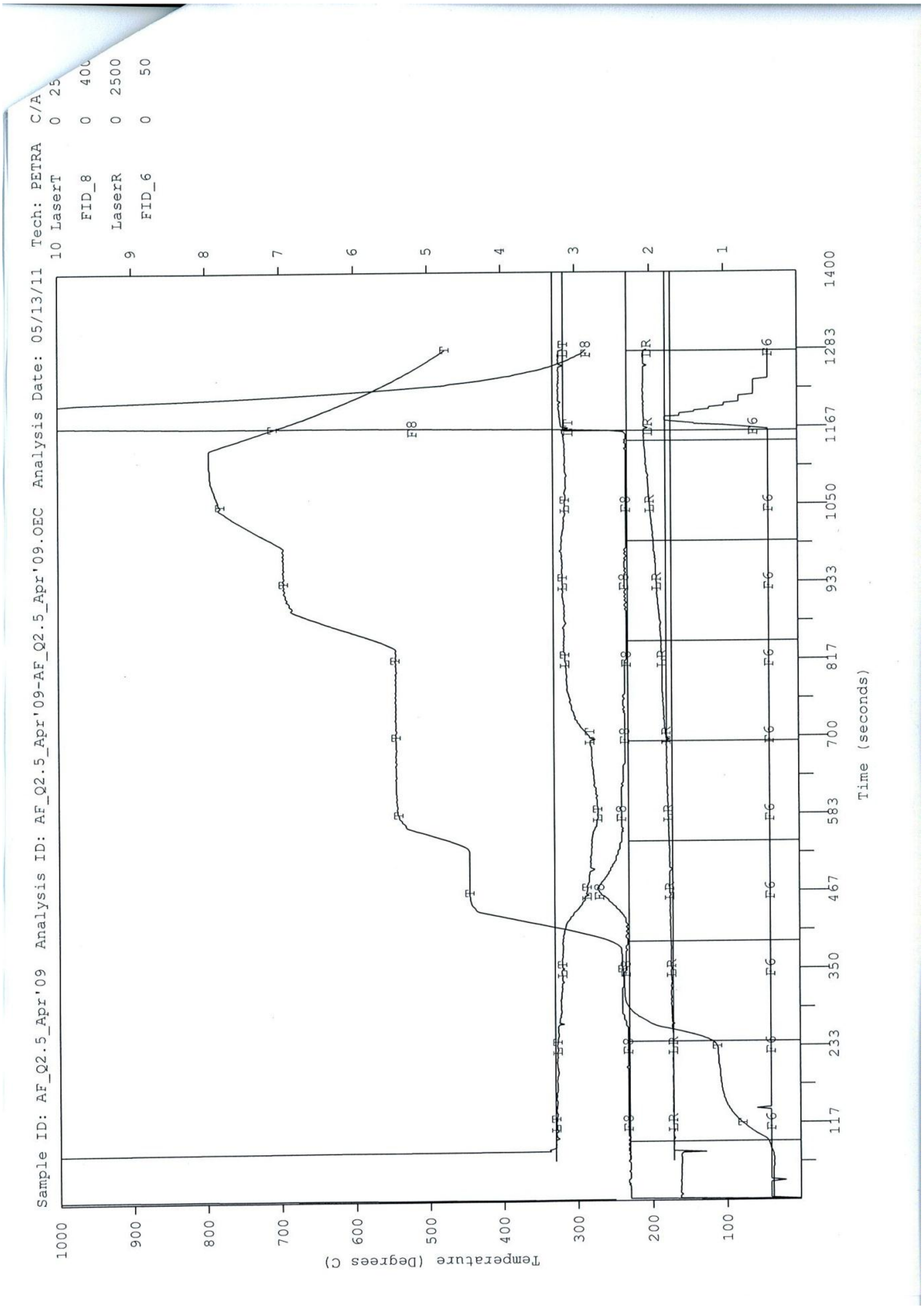
Example of raw data for one of the samples



```
                            CARBON ANALYSIS RESULTS
Analyzer #1                                                 Technician: PET
-----------------------------------------------------------------------------

Analysis ID       : AF_Q2.5_Apr'09-AF_Q2.5_Apr'09.OEC
Sample ID         : AF_Q2.5_Apr'09
Punch area        :  0.550 cm2
Deposit area      : 12.560 cm2

Analysis Start    : 05/13/11  11:03        Calculation      : 05/13/11  11:29
Analysis Stop     : 05/13/11  11:29
-----------------------------------------------------------------------------
Anal program ver: P6.0  (02/20/03)         Parm file ver    : V0302
Calib. slope     : 27.65 ug C/peak ratio   Baseline time    : 10 sec
Calib. intercept: 00.00 ug C
Reflectance unc.:   010 counts             Transmission unc:   010 counts
Sample transit   : 15 sec
-----------------------------------------------------------------------------
Calibration peak area:  27 969 millivolt-seconds
Initial FID baseline :      92   millivolts
Final FID baseline   :      93   millivolts
-----------------------------------------------------------------------------
Laser reflectance initial baseline    :     430   millivolts
Laser reflectance minimum             :     424   millivolts at   322 sec
Laser reflectance final baseline      :     519   millivolts
Laser transmittance initial baseline :     825   millivolts
Laser transmittance minimum           :     673   millivolts at   566 sec
Laser transmittance final baseline    :     787   millivolts
-----------------------------------------------------------------------------
              Reflect Split Time  Laser                 FID Split Time
  Lower split  :      678 sec           946 millivolts            693 sec
  Regular split:      678 sec           946 millivolts            693 sec
  Upper split  :      678 sec           946 millivolts            693 sec
-----------------------------------------------------------------------------
              Transmit Split Time  Laser                 FID Split Time
  Lower split  :     1146 sec          2500 millivolts           1161 sec
  Regular split:     1146 sec          2500 millivolts           1161 sec
  Upper split  :     1146 sec          2500 millivolts           1161 sec
-----------------------------------------------------------------------------
                        Peak Area                     Carbon
OC1         OC          106  mv-secs      0.19  ug C/cm2      2.39     ug C/filte
OC2         OC          343  mv-secs      0.62  ug C/cm2      7.74     ug C/filte
OC3         OC        1 106  mv-secs      1.99  ug C/cm2     24.97     ug C/filte
OC4         OC          459  mv-secs      0.82  ug C/cm2     10.36     ug C/filte
EC          EC          249  mv-secs      0.45  ug C/cm2      5.63     ug C/filte
EC2         EC          172  mv-secs      0.31  ug C/cm2      3.88     ug C/filte
EC3         EC          108  mv-secs      0.19  ug C/cm2      2.43     ug C/filte
LRPyMin     Py            0  mv-secs       .00  ug C/cm2       .00     ug C/filte
LRPyMid     Py            0  mv-secs       .00  ug C/cm2       .00     ug C/filte
LRPyMax     Py            0  mv-secs       .00  ug C/cm2       .00     ug C/filte
LTPyMin     Py          552  mv-secs       .99  ug C/cm2     12.45     ug C/filte
LTPyMid     Py          552  mv-secs       .99  ug C/cm2     12.45     ug C/filte
LTPyMax     Py          552  mv-secs       .99  ug C/cm2     12.45     ug C/filte

*****************************************************************************
```



```
    Computed carbon - Improve Protocol - Negative Pyrolysis Areas Allowed
Analyzer #1                                                 Technician: PET
---------------------------------------------------------------------------

Analysis ID      : AF_Q2.5_Apr'09-AF_Q2.5_Apr'09.OEC
Sample ID        : AF_Q2.5_Apr'09
Punch area       :  0.550 cm2
Deposit area     : 12.560 cm2

Analysis Start   : 05/13/11  11:03        Calculation      : 05/13/11  11:29
Analysis Stop    : 05/13/11  11:29
---------------------------------------------------------------------------
Reflectance                         Regular      HighTemp       Regular      HighTemp
                  VOC                 OC            OC             EC           EC            TC
               ----------         ----------    ----------     ----------   ----------    ----------

Lower Split   :    .19               3.62          3.43           .95          .50           4.57  ug C/cm2
                  2.39              45.45         43.07          11.93         6.31          57.38  ug C/filt

Regular split :    .19               3.62          3.43           .95          .50           4.57  ug C/cm2
                  2.39              45.45         43.07          11.93         6.31          57.38  ug C/filt

Upper Split   :    .19               3.62          3.43           .95          .50           4.57  ug C/cm2
                  2.39              45.45         43.07          11.93         6.31          57.38  ug C/filt


Transmittance                       Regular      HighTemp       Regular      HighTemp
                  VOC                 OC            OC             EC           EC            TC
               ----------         ----------    ----------     ----------   ----------    ----------

Lower Split   :    .19               4.61          4.42           .00          .00           4.57  ug C/cm2
                  2.39              57.90         55.52           .00          .00          57.38  ug C/filt

Regular split :    .19               4.61          4.42           .00          .00           4.57  ug C/cm2
                  2.39              57.90         55.52           .00          .00          57.38  ug C/filt

Upper Split   :    .19               4.61          4.42           .00          .00           4.57  ug C/cm2
                  2.39              57.90         55.52           .00          .00          57.38  ug C/filt

******************************************************************************
OC/TC:     1.01
EC/TC:     -.01
OC/EC:   -99.00
******************************************************************************
               OC = OC1 + OC2 + OC3 + OC4 + OCPyro
               TC = OC1 + OC2 + OC3 + OC4 + EC1 + EC2 + EC3
               EC = TC - OC
               VOC = OC1
               OCHighTemp = OC - OC1
               ECHighTemp = EC2 + EC3 - max(OCPyro - EC1, 0)
```


Sample ID: AF_Q2.5_Apr'09 Analysis ID: AF_Q2.5_Apr'09-AF_Q2.5_Apr'09.OEC Analysis Date: 05/13/11 Tech: PETRA C/A
10 LaserT 0 25
FID_8 0 400
LaserR 0 2500
FID_6 0 50
Temperature (Degrees C)
1000
900
800
700
600
500
400
300
200
100
Time (seconds)
117
233
350
467
583
700
817
933
1050
1167
1283
1400
1
2
3
4
5
6
7
8
9
T
LT
F8
LR
F6