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ON THE SOURCES OF SUBMICRON AEROSOL PARTICLES IN  
SAVANNAH: IMPLICATIONS FOR CLIMATE AND AIR QUALITY

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Academic dissertation

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# **On the sources of submicron aerosol particles in savannah: implications for climate and air quality**

Ville Tapio Vakkari  
University of Helsinki, 2013

## **Abstract**

Aerosol is defined as solid or liquid particles suspended in a gas lighter than the particles, which means that the atmosphere we live in is an aerosol in itself. Although aerosol particles are only a trace component of the atmosphere they affect our lives in several ways. The aerosol particles can cause adverse health effects and deteriorate visibility, but they affect also the Earth's climate directly by scattering and absorbing solar radiation and indirectly by modulating the properties of the clouds. Anthropogenic aerosol particles have a net cooling effect on the climate, but the uncertainty in the amount of cooling is presently as large as the heating effect of carbon dioxide.

To reduce the uncertainty in the aerosol climate effects, spatially representative reference data of high quality are needed for the global climate models. To be able to capture the diurnal and seasonal variability the data have to be collected continuously over time periods that cover at least one full seasonal cycle. Until recently such data have been nearly non-existing for continental Africa and hence one aim of this work was to establish a permanent measurement station measuring the key aerosol particle properties in a continental location in southern Africa. In close collaboration with the North-West University in South Africa this aim has now been achieved at the Welgegund measurement station. The other aims of this work were to determine the aerosol particle concentrations including their seasonal and diurnal variation and to study the most important aerosol particle sources in continental southern Africa.

In this thesis the aerosol size distribution and its seasonal and diurnal variation is reported for different environments ranging from a clean rural background to an anthropogenically heavily influenced mining region in continental southern Africa. Atmospheric regional scale new particle formation has been observed at a world record high frequency and it dominates the diurnal variation except in the vicinity of low-income residential areas, where domestic heating and cooking are a stronger source. The concentration of aerosol particles in sizes that can act as cloud condensation nuclei was found to increase during the dry season because of reduced wet removal and increased aerosol production from incomplete combustion, which can be either domestic heating or savannah and grassland fires depending on location. During the wet season new particle formation was shown to be an important source of particles in the size range of cloud condensation nuclei.

Keywords: atmospheric aerosols, long-term measurements, size distribution, new particle formation

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## List of publications

This thesis consists of an introductory review, followed by seven research articles. In the introductory part, these papers are cited according to their roman numerals. Paper I is reproduced with permission from Aerosol and Air Quality Research and Papers II–VII under the Creative Commons Attribution 3.0 License.

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# 1. Introduction

The atmosphere we live in is an aerosol in itself, i.e. a mixture of solid or liquid particles suspended in a gas lighter than the particles (Seinfeld and Pandis, 2006), although the number of particles is highly variable. In remote arctic areas there may be only tens of particles per cubic centimetre (e.g. Koponen et al., 2003; Tunved et al., 2013) while in polluted megacities there may be several hundreds of thousands of particles within a cubic centimetre (e.g. Mönkkönen et al., 2005). Also the sizes of aerosol particles span a wide range from molecular clusters smaller than one nanometre (Eisele 1989a, 1989b; Kulmala et al., 2013) up to tens of micrometres (e.g. Betzer et al., 1988). Aerosol particles are a crucial component of the atmosphere because the water vapour supersaturation is never high enough for formation of cloud droplets without aerosol particles acting as seed particles or cloud condensation nuclei (CCN) (Andreae and Rosenfeld, 2008). In other words, without aerosol particles there would be no clouds or rain.

In the atmosphere aerosol particles affect the climate in two ways: by scattering and absorbing solar radiation, which is known as the aerosol direct climate effect and by modulating the properties of clouds, which is known as the indirect climate effect (e.g. Forster et al., 2007). How much aerosol particles scatter or absorb solar radiation depends not only on the total number of particles in an atmospheric column but also on their optical properties determined by their chemical composition and size (e.g. Seinfeld and Pandis, 2006). The aerosol direct effect is currently considered to be the second largest source of uncertainty in estimating the top of the atmosphere radiative forcing (Forster et al., 2007). The scattering of solar radiation from aerosol particles such as sulphate has a cooling effect on the atmosphere, whereas absorbing particles (e.g. soot) have a heating effect. The heating effect of soot particles has been proposed to be even the second-largest heating effect after carbon dioxide (CO<sub>2</sub>) emissions (Ramanathan and Carmichael, 2008). As a global average, however, the aerosol direct effect is estimated to result in a net cooling of the atmosphere (Forster et al., 2007; Kulmala et al., 2011).

The aerosol indirect climate effect is based on the number of CCN in a cloud: a higher number of CCN will lead to smaller cloud droplets, which in turn will increase the cloud brightness and lifetime (Andreae and Rosenfeld, 2008). In terms of Earth's radiative budget higher cloud cover and brighter clouds will lead to a larger fraction of incoming solar radiation being reflected back to space, i.e. in a net cooling effect (Forster et al., 2007; Seinfeld 2011).

Not all aerosol particles can act as CCN, though, but it depends on their chemical composition, size and the water vapour supersaturation during cloud formation (Andreae and Rosenfeld, 2008). Atmospheric processing, such as particle phase chemical reactions and secondary aerosol formation, leads to internally mixed aerosol that contains at least a fraction of water soluble constituents and therefore,

barring very fresh aerosol emissions, diameter is the most important aerosol property deciding whether a particle can act as a CCN or not (Dusek et al., 2006; Andreae and Rosenfeld, 2008). Typically particles larger than 50 to 100 nm in diameter will be able to act as CCN (Andreae and Rosenfeld, 2008; Kerminen et al., 2012). In the IPCC 2007 report the largest uncertainty in the top of the atmosphere radiative forcing is associated with the aerosol cloud albedo effect; for cloud lifetime effect no radiative forcing estimate is given (Forster et al., 2007). In total, the uncertainties in the direct and indirect aerosol climate effects are estimated to be close to the net heating effect of carbon dioxide and methane in the year 2100 climate projection (Forster et al., 2007).

In addition to climate effects the atmospheric aerosol particles have also other significant effects on our lives. One obvious consequence of their ability to scatter and absorb light is that they affect visibility (e.g. Charlson, 1969), of which the London smog of late 19<sup>th</sup> century is a classic example (e.g. Brimblecombe, 2008); a present-day example is the Beijing smog (e.g. Wang et al., 2013). On the other hand aerosol particles are also an efficient way of mass transport to human respiratory system. This can be used to deliver medicine (e.g. Dolovich and Dhand, 2011), but the payoff is that toxic compounds in ambient aerosol particles will also be effectively transported to respiratory system, which leads to adverse health effects (e.g. Pope and Dockery, 2006).

Studying the aerosol particle health effects mass concentration of particulate matter smaller than 10  $\mu\text{m}$  in diameter (PM<sub>10</sub>) is widely used (e.g. Pope and Dockery, 2006). Epidemiological studies have shown that daily mortality increases by roughly 0.5% per each 10  $\mu\text{g m}^{-3}$  of PM<sub>10</sub> in the air (Brunekreef and Holgate, 2002; Pope and Dockery, 2006). PM<sub>10</sub> is, though, not a perfect measure of air quality: particles smaller than 100 nm are probably more harmful for human health than the larger ones (e.g. Nel et al., 2006; Bräuner et al., 2007). On the other hand e.g. sea salt can contribute significantly to the PM<sub>10</sub> concentration without carrying toxic compounds (e.g. Seinfeld and Pandis, 2006). However, PM<sub>10</sub> is easier to measure than the concentration of particles smaller than 100 nm or the chemical composition of the aerosol and thus it still holds its ground as a robust measure of air quality. For this reason PM<sub>10</sub> is also the base of many air quality standards and legislation (e.g. Official Journal of the European Union, 2008).

Aerosol particles can be classified in two ways based on their origin. First of all they can be classified as natural or anthropogenic depending on whether they originate in natural or anthropogenic processes (Seinfeld and Pandis, 2006). On the other hand aerosol particles can be classified as primary or secondary based on whether they enter the atmosphere in particulate phase (primary aerosol) or are formed in the atmosphere from gaseous precursor compounds (secondary aerosol) (Seinfeld and Pandis, 2006). Considering aerosol mass the largest global sources are sea salt and mineral dust, which are both primary natural aerosol sources (Seinfeld and Pandis, 2006). In anthropogenic aerosol emissions, secondary aerosol is mass-



wise a prominent source. However, the largest anthropogenic aerosol mass sources are industrial dust and primary organic aerosol (Seinfeld and Pandis, 2006).

For climate, aerosol number concentration is often a more relevant parameter than aerosol mass concentration, but unfortunately the sources of aerosol particles in terms of the number of CCN are not as well known as the aerosol mass sources (Andreae and Rosenfeld, 2008; Seinfeld 2011). This also makes secondary aerosol formation an especially interesting source as it can increase both aerosol number and mass concentrations (e.g. Kerminen et al., 2012). Regional scale formation of new aerosol particles has been observed in nearly all environments where suitable measurements have been carried out (e.g. Kulmala et al., 2004; Kulmala and Kerminen, 2008).

Several aerosol sources have significant seasonality, for instance biomass burning in southern Africa or South America (e.g. Swap et al., 2003; Ito et al., 2007; Martin et al., 2010) or emissions of biogenic secondary aerosol precursor compounds (e.g. Guenther et al., 2006). Not only aerosol sources are seasonal, but seasonal changes in synoptic scale circulation may affect also the aerosol removal mechanisms. For instance in southern Africa there are very few rainy days during the dry season from May to August (e.g. Tyson and Preston-Whyte, 2000), and therefore also wet deposition is suppressed during this period. This underlines the need for long-term observations covering at least one full seasonal cycle to provide a reliable picture of the aerosol particle properties.

In the submicron size range aerosol particles are often classified into three modes: the accumulation mode from 100 nm to 1  $\mu\text{m}$ , the Aitken mode from 25 to 100 nm and the nucleation mode from 1 to 25 nm (Seinfeld and Pandis, 2006). Particles larger than 1  $\mu\text{m}$  form the coarse mode (Seinfeld and Pandis, 2006). In the lower troposphere aerosol particles in the accumulation mode can have residence times up to two to three weeks (Seinfeld and Pandis, 2006). Particles smaller than 100 nm have even shorter lifetimes, i.e. in the Aitken mode days and in the nucleation mode minutes to hours (Seinfeld and Pandis, 2006). Higher in the atmosphere aerosol particle lifetimes are longer because of the lack of wet and dry deposition and in the stratosphere particles may stay up to a year or even longer (Seinfeld and Pandis, 2006). However, compared to anthropogenic carbon dioxide emissions, which will keep atmospheric  $\text{CO}_2$  level elevated for hundreds of years (Archer et al., 2009), all aerosol particles are short-lived.

Because of their short atmospheric lifetime aerosol particles are not uniformly mixed over the globe, and consequently the aerosol particle optical and CCN properties depend significantly on local to regional scale sources (e.g. Seinfeld and Pandis, 2006; Seinfeld, 2011). This also implies that the global picture of the aerosol optical and CCN properties is only as good as the coverage of observations is. In the northern hemisphere there exists a number of continuous measurement stations and several campaigns covering at least one full seasonal cycle have been conducted (e.g. Spracklen et al., 2010; Asmi et al., 2011). However, for the southern

hemisphere such data, especially from continental locations are scarce (Laakso et al., 2006). In southern Africa aerosol observations have mainly been limited to intensive but short campaigns like the SAFARI-92 and SAFARI 2000 (Lindesay et al., 1996; Swap et al., 2003), or longer term measurements with limited instrumentation (e.g. Jayaratne and Verma, 2001; Martins et al., 2007; Josipovic et al., 2010; Queface et al., 2011). Although the long-term measurements at the Cape Point Global Atmospheric Watch station are comprehensive, they are not representative of continental southern Africa (e.g. Brunke et al., 2012).

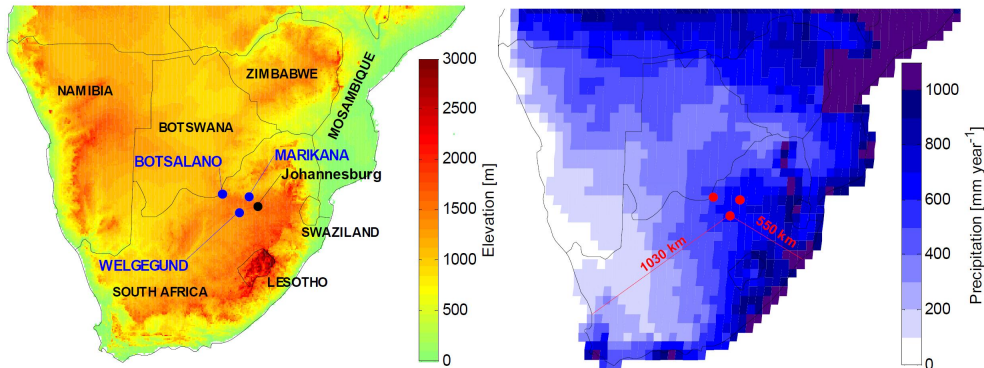
To fill this knowledge gap in the climatically most important aerosol particle properties over continental southern Africa, long term measurements were initiated in the North-West province of South Africa in July 2006 with a mobile measurement trailer (Laakso et al., 2008; Paper I) and, as a part of the EUCAARI campaign (Kulmala et al., 2009, 2011), a two-year intensive measurement campaign was carried out at the Elandsfontein measurement station (Laakso et al., 2012). Using the mobile measurement trailer (Paper I) the aims of this work have been

1. to establish a permanent measurement station in continental southern Africa (Papers I and II),
2. to determine the background concentrations and seasonal and diurnal cycles of submicron aerosol particles in continental southern Africa (Paper III) and
3. to study the most important sources of submicron aerosol particles in continental southern Africa (Papers IV, V and VI).

In addition to these primary goals the mobile measurement trailer (Paper I) was utilised also to carry out an air quality study in one of the three proclaimed air pollution hot spots in South Africa (Government Gazette Republic of South Africa, 2012; Paper VII).

## 2. Location

The measurements in this study were carried out at three locations as indicated in Figure 1. The first location was Botsalano game reserve close to the Botswana border (25.54 S, 25.75 E, 1420 m a.s.l.) from 20 July 2006 to 5 February 2008. After Botsalano the measurements were run at Marikana village (25.70 S, 27.48 E, 1170 m a.s.l.) from 8 February 2008 to 17 May 2010 and after that on 20 May 2010 the measurements were moved to a private farm at Welgegund (26.57 S, 26.94 E, 1480 m a.s.l.), which will remain as a permanent station. All three measurement sites are located on the Highveld, a plateau approximately 1500 metres above sea level in central southern Africa (Figure 1). The Marikana village is located in a 30 km by 60 km valley, which is bordered in the south by the Magaliesberg Mountains rising up to 1800 metres above sea level.

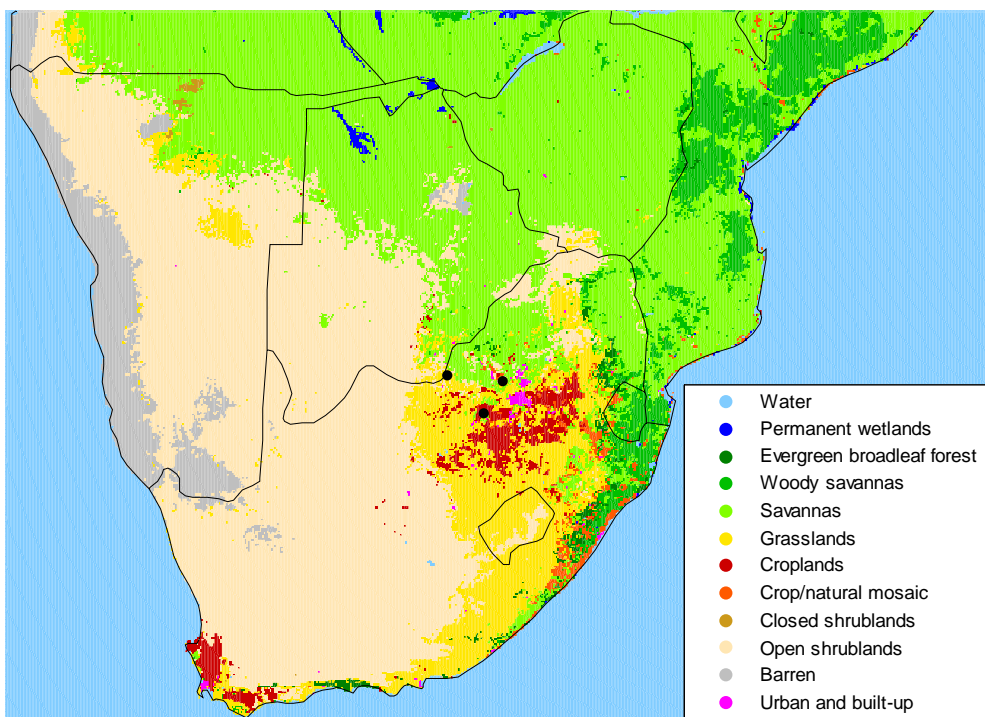


**Figure 1.** Topographic map of southern Africa (U.S. Department of Commerce, 2001) on the left and annual average precipitation (Rudolf and Schneider, 2005; Rudolf et al., 2010) on the right. Botsalano, Welgegund and Marikana are indicated on both maps. The map on the right also indicates the shortest distances between Welgegund and the coastline in the east and west. The distance between Botsalano and Welgegund is 165 km and between Marikana and Welgegund is 110 km.

The measurement sites are of continental nature, as the distance to the Indian Ocean in the east is at shortest more than 500 km and the distance to the Atlantic Ocean in the west is approximately 1000 km (cf. Figure 1). In the east the Drakensberg Mountains rise 3000 metres above sea level and form an escarpment at the edge of the Highveld, which air masses from the warm Indian Ocean have to cross before reaching the plateau.

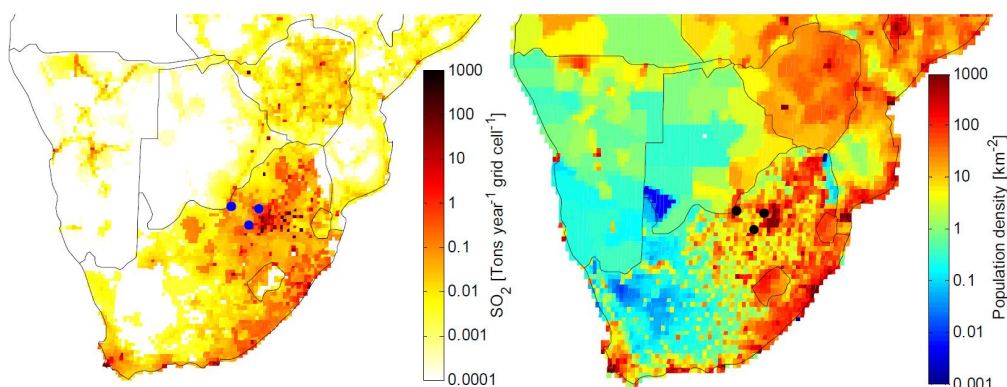
On the Highveld the annual rainfall has a clear gradient from east to west (Figure 1). All the three measurement sites are within the region that has annual rainfall of more than 500 mm, but the Botsalano and Welgegund sites are at the western edge of it and subsequently they are also at the western limit of the region of intensive

agricultural use (Figure 2), although the grassland biome extends another 200 km west of Welgegund. In the north-south direction the measurement sites are at the southern limit of the savannah biome (Figure 2). The location at the edge of the area of intensive agricultural use was one of the reasons to establish the long-term measurement station at Welgegund, because if future climate change leads to changes in rain patterns in southern Africa the effects will be first visible in the ecosystems on the borderline.



**Figure 2.** The International Geosphere-Biosphere Programme (IGBP) vegetation classification for southern Africa for the year 2010 based on MODIS collection 5 land cover type product (Belward et al., 1999; Scean, 1999; Friedl et al., 2002, 2010). Black dots indicate (from left to right) Botsalano, Welgegund and Marikana.

The differences in the anthropogenic activities between the three sites are more pronounced than the natural differences. In southern Africa industrial activities are concentrated at the Johannesburg megacity and surroundings as seen in the SO<sub>2</sub> emission inventory in Figure 3 (Fleming and van der Merwe, 2002). Botsalano is located 300 km west of Johannesburg with no local sources (Laakso et al., 2008) and is subsequently the cleanest location of the three measurements sites. However, even Botsalano cannot be considered as a remote location because the anthropogenic emissions from Johannesburg and surrounding industries keep e.g. annual median SO<sub>2</sub> concentration at 1 ppb and thus Botsalano is best characterised as a semi-clean location (Laakso et al., 2008; Papers III and IV).



**Figure 3.** SAFARI 2000  $\text{SO}_2$  emission inventory (Fleming and van der Merwe, 2002) on the left and population density in southern Africa (CIESIN, 2010) on the right. The measurement sites are indicated by dots on both maps: (from left to right) Botsalano, Welgegund and Marikana.

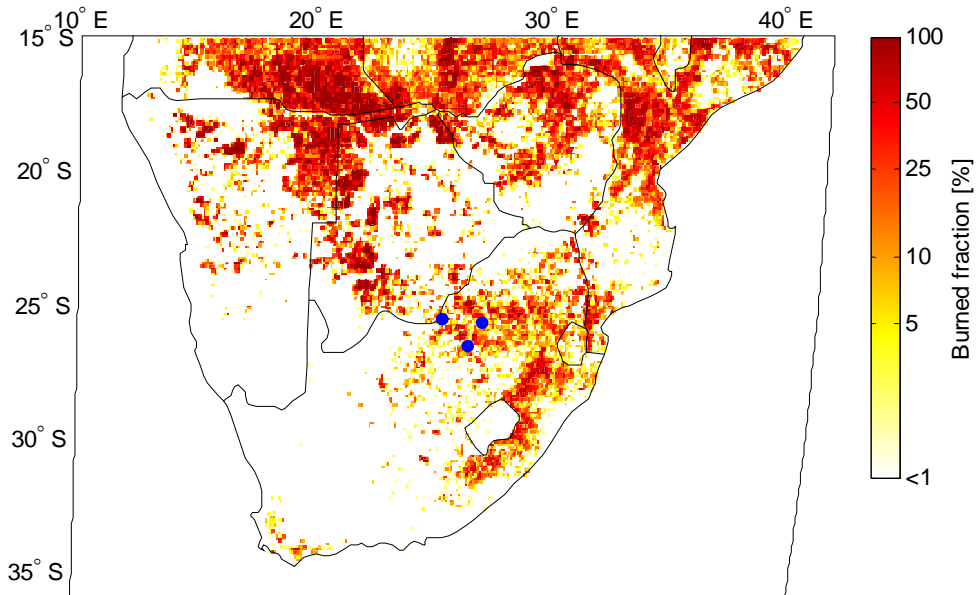
Marikana is the most polluted of the three sites because it is located in the middle of the western Bushveld Igneous Complex (Paper VII), where e.g. 80 % of world's platinum group metals are produced (Cramer et al., 2004; Xiao and Laplante, 2004). The refinery processes of chrome and platinum group metals are large sources of sulphur, and a large fraction of it is emitted into atmosphere as  $\text{SO}_2$  (Piketh et al., 2005). In addition to industrial sources Marikana is also heavily impacted by combustion in the surrounding low-income residential areas (Papers III, V and VII). At Marikana the effect of local point sources is amplified by the geography as the surrounding mountains trap the aerosol within the valley (Piketh et al., 2005).

Welgegund, like Botsalano, has no significant local sources. However, it is closer to the Johannesburg megacity with 10 million inhabitants (cf. the population density map in Figure 3) and surrounding industries and therefore the impacts of the megacity are stronger at Welgegund than at Botsalano. Several different source regions can be separated at Welgegund: the smelters in the western Bushveld Igneous Complex, the densely populated megacity itself, petrochemical industries at the southern perimeter of the megacity and the conglomeration of large coal fired power plants east of the megacity (Beukes et al., 2013). Even on a global scale the industrialized Highveld is recognised as one of the  $\text{NO}_2$  hotspots (Lourens et al., 2011, 2012).

To the west of Johannesburg both population density and anthropogenic  $\text{SO}_2$  emissions decrease quite rapidly, so that west of Botsalano and Welgegund anthropogenic sources are few. Therefore both sites have a wide clean sector to the west (Laakso et al., 2008; Beukes et al., 2013; Papers III and IV). However, the clean sector is not directly comparable to other directions because also the vegetation type changes from west to east (e.g. Friedl et al., 2002 and Figure 2). The

western sector has large areas where vegetation is sparse and hence also biogenic volatile organic compound (VOC) emissions are lower than in the northern and eastern sectors (Otter et al., 2003, 2004). This spatial covariance of biological and anthropogenic activity complicates separating the natural and anthropogenic components in the aerosol over the Highveld.

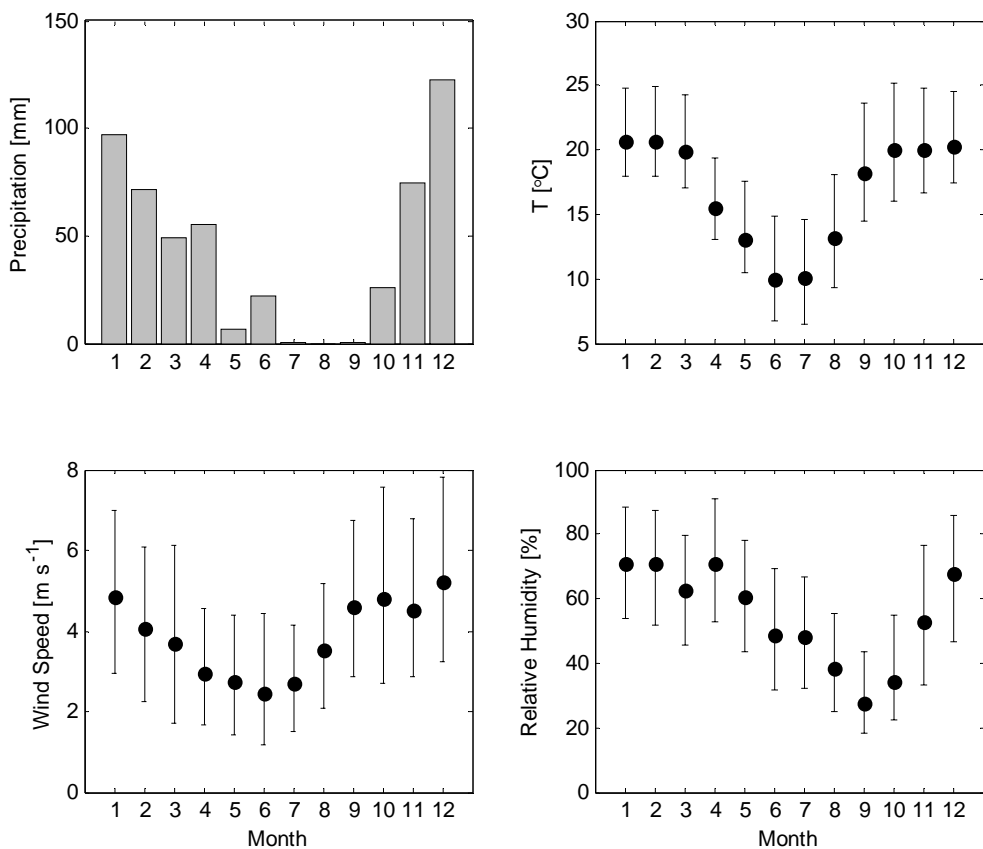
Another important aerosol source in southern Africa is open biomass burning, or veldt fires (e.g. Swap et al., 2003). The veldt fires in southern Africa are of both anthropogenic and natural origin, but majority of the fires are considered anthropogenic (Ito et al., 2007). The fires are generally more frequent north of 20° S, as seen in Figure 4, which displays the year 2011 fires based on the Moderate Resolution Imaging Spectroradiometer (MODIS) collection 5 burnt area product (Roy et al., 2002, 2005, 2008). The veldt fires have a strong seasonality in southern Africa (Ito et al., 2007) and most fires in the surroundings of the measurement locations in this study occur from July to October, i.e. the end of the dry season (Paper III). The intensity of the fires and the net amount of aerosol particles generated in the veldt fires depends on the amount of biomass available. A wet summer leads to more biomass during the dry season and will spawn more extensive fires and lead to higher aerosol load over the continent as seen e.g. during the SAFARI 2000 campaign (Swap et al., 2003).



**Figure 4.** Spatial distribution of veldt fires in 2011 from MODIS burnt area product (Roy et al., 2002, 2005, 2008). Blue dots indicate (from left to right) Botsalano, Welgegund and Marikana.

## 2.1 Meteorological aspects

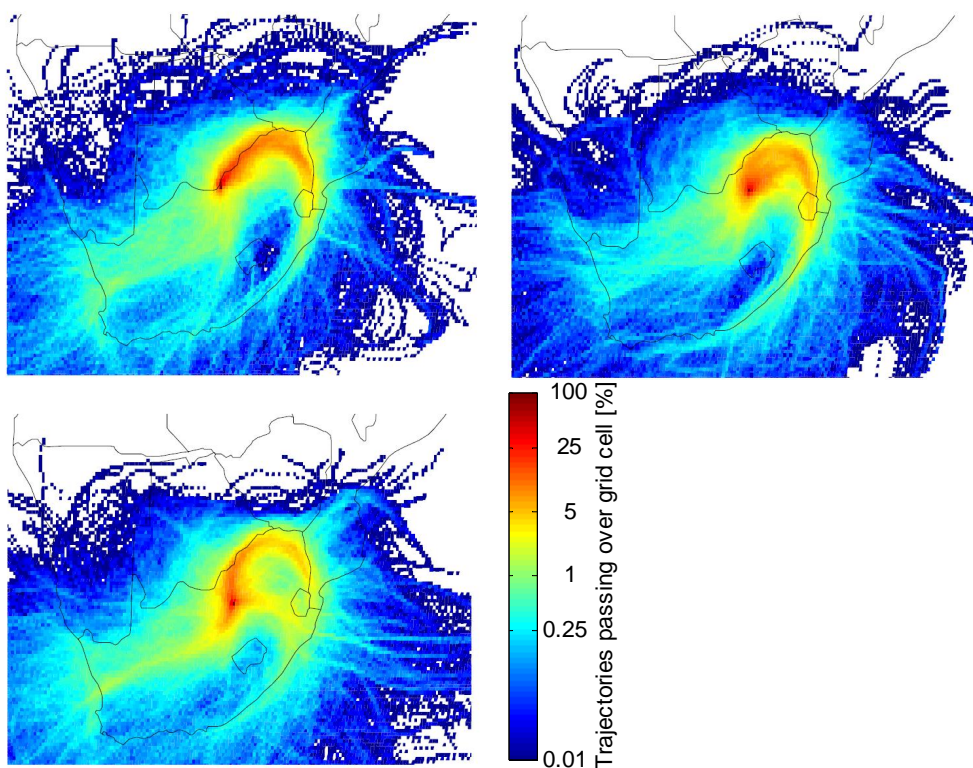
Seasons in southern Africa can be roughly divided into two: wet season, which typically begins in September–October and lasts until April or May, and dry season, which covers the rest of the year. This is typically the case also at Welgegund, although in June 2011 there was one rain event as seen in Figure 5. From 20 May 2010 to 15 April 2012 the average annual rainfall at Welgegund was 526 mm. The rains on the Highveld originate mostly from convective clouds and thunderstorms (Tyson and Preston-Whyte, 2000) and the rain intensities can be high. At Welgegund the highest observed 15 minute averaged rain intensity was  $67 \text{ mm h}^{-1}$ . Convective rain is an additional complication for global climate models because it occurs at a sub-grid scale, which may lead to underestimating the aerosol wet removal in global models (e.g. Paper VI).



**Figure 5.** Monthly mean precipitation and monthly median temperature, wind speed and relative humidity at Welgegund. The errorbars indicate the monthly upper and lower quartiles for temperature, wind speed and relative humidity. Precipitation is averaged from September 2010 to March 2012, with only full months included.



The seasonal cycle is also apparent in the temperature (Figure 5). If four seasons are defined in southern Africa, winter is usually from June to August, which is the coldest period of the year (Tyson and Preston-Whyte, 2000). Even during winter the daily maximum temperature reaches frequently +20 °C, although on the coldest nights temperature will drop below zero (Tyson and Preston-Whyte, 2000; Laakso et al., 2008). At Welgegund the coldest temperature of -5.1 °C was recorded in June and the highest temperature of +35.6 °C in October. Because of the high altitude, open landscape and clear-sky conditions the temperature difference between day and night is often large (Tyson and Preston-Whyte, 2000). The absence of rain, large diurnal temperature differences and warm days lead to very low relative humidity at the end of the dry season, when values even down to 10 % are not uncommon. At the end of the dry season wind speeds increase, which provides favourable conditions for development of both dust storms and wild fires (Tyson and Preston-Whyte, 2000).



**Figure 6.** Air mass history at Botsalano (top, left), Marikana (top, right) and Welgegund (bottom). Calculated from 96-hour back-trajectories for 100 m arrival height for the respective measurement periods.



The prevailing feature in horizontal air mass movement over southern Africa is anticyclonic circulation (Garstang et al., 1996), which is also seen in the back-trajectory overlay graphics for Botsalano, Marikana and Welgegund in Figure 6. The back-trajectories have been calculated for Botsalano from 20 July 2006 to 5 February 2008, for Marikana from 8 February 2008 to 17 May 2010 and for Welgegund from 20 May 2010 to 15 April 2012, i.e. the periods when measurements were carried out at each location. The trajectories have been calculated with the HYSPLIT 4.8 model (Draxler and Hess, 2004) using GDAS meteorological data (Air Resources Laboratory, 2012) for arrival height of 100 metres and length of 96 hours backwards. Back-trajectories were calculated for each hour, i.e. 24 trajectories per day.

In addition to the anticyclonic circulation, there are also two other frequently appearing transport patterns at the Highveld. One is westerly disturbance, which occurs quite regularly at 20–40 % frequency throughout the year, and the other is easterly disturbance, which is a common pattern during summer (30–50 % frequency), but occurs very seldom if at all during winter (Garstang et al., 1996). The anticyclonic circulation has a strong seasonality opposite to the easterly disturbances and is most frequent (up to 80 % of time) in winter, dropping down to 20–30 % frequency during summer (Garstang et al., 1996). During wintertime the anticyclonic circulation may keep the air masses recirculating over the continent up to 20 days at a time (Tyson et al, 1996).

The anticyclonic recirculation combined with strong temperature inversions during wintertime (Garstang et al., 1996; Tyson et al., 1996) can lead to layering of the atmosphere, where layers of clean air get trapped between polluted layers (Hobbs, 2003). The main transport out of the continent in wintertime appears to be to the Indian Ocean over south eastern South Africa (Garstang et al., 1996; Annegarn et al., 2002), which can originate in either anticyclonic circulation or westerly disturbances (Garstang et al., 1996). The other possible transport pattern is over northern Namibia and Angola to the Atlantic Ocean, which is connected mainly to easterly disturbances (Garstang et al., 1996).

A good example of the anticyclonic circulation can be seen in Figure 6 for Botsalano, where it also has important implications for aerosol properties. Because of the scarcity of direct transport from east to Botsalano (Figure 6), the air masses from anthropogenic sources have usually travelled a significantly longer path than the direct distance before reaching Botsalano and therefore there has been more time for removal processes and also more dilution before the polluted air reach Botsalano. In other words, because of the prevailing anticyclonic circulation Botsalano is a cleaner location than what the direct distance from the anthropogenic sources implies.

### 3. Measurements

The two most important questions when starting aerosol measurements are: “What is needed to measure and how can it be done?” If the target is set to monitor air quality, an easy starting point are the legislative requirements, most importantly the measurements of PM<sub>10</sub> and PM<sub>2.5</sub> (mass concentration of particulate matter smaller than 2.5 µm), but also the measurements of gas phase concentrations of nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>), ozone (O<sub>3</sub>) and carbon monoxide (CO) (e.g. Government Gazette Republic of South Africa 2005b; Official Journal of the European Union, 2008). In this case measurement stations or even complete measurement station networks can be purchased with turnkey delivery and the day to day maintenance required by the instruments is at its minimum. However, even the minimum maintenance does not mean that the devices could be left completely on their own as pointed out also by Scholes (2009). Aerosol inlets will need cleaning every week or two depending on the aerosol load and gas analyser inlet filters have to be replaced every two to four weeks, again depending on the total concentration of particulate matter. Therefore even if optimising for the minimum maintenance a trained technician is needed to visit the site once in one or two weeks (Paper I).

Another issue is the monitoring of data quality. If this is done during site visits only, the owner of the station must accept that the maximum time it takes to find a fault is the time interval between site visits. A better solution is to transfer the data daily or several times a day to a server and have someone check the data quality remotely (Paper I). This way malfunctions can be found sooner and the data coverage can be enhanced, but this requires internet access from the measurement site, i.e. more infrastructures. If the amount of (compressed) data per day is limited, even a GPRS modem operating in mobile telephone network is enough – and especially in developing countries the coverage of wireless network is better than landline network.

However, the smaller particles are potentially more harmful than the large ones (e.g. Nel et al., 2006; Bräuner et al., 2007) and therefore it would be desirable to extend the bare minimum legislative measurements towards e.g. submicron aerosol particle mass (PM<sub>1</sub>) or number concentration and chemical composition, but unfortunately the instrumentation will get more complicated. Even though there have been recent developments in the field of commercially available online aerosol mass spectrometers for long-term monitoring of submicron aerosol particle chemical composition, these devices still require specially trained personnel to start them up after a power break (e.g. Ng et al., 2011). One option is to do this with remote desktop programs (Ng et al., 2011), but then a faster network connection than GPRS is typically needed, which again implies more infrastructures.

On the other hand, for studying the climate effects of aerosol particles the most important parameters are aerosol particle size distribution, optical properties and chemical composition. Compared to the standard air quality instruments the complexity of the devices increases, and for instance extending the aerosol size distribution measurement to sizes below 3 nm has been achieved only very recently (Kulmala et al., 2007, 2013). Even with more conventional aerosol instrumentation the need for periodic flow and zero checks requires more skills from the technicians.

If the study on aerosol climate effects is extended to cover the sources of aerosol particles, the demand for measurements expands towards gas phase precursors of secondary aerosol such as sulphuric acid, hydroxyl radical and volatile organic compounds (e.g. Sipilä et al., 2010; Kirkby et al., 2011; Kulmala et al., 2013). While there are on-line devices for measuring these compounds (e.g. Eisele and Tanner, 1993; Mauldin et al., 1998; Jordan et al., 2009; Junninen et al., 2010), they tend to need attention by specially trained personnel to run continuously. For example, the sulphuric acid and hydroxyl radical data series from even the best infrastructures for ambient measurements very rarely cover even a full seasonal cycle (e.g. Birmili et al., 2003; Rohrer and Berresheim, 2006; Sihto et al., 2006; Petäjä et al., 2009; Berresheim et al., 2013; Kulmala et al., 2013). Therefore it is evident that compromises have to be made between completeness of the quantitative chemical and physical characterisation of the atmosphere and the spatial and temporal coverage of the measurements.

### **3.1 Instrumentation**

The starting point and first goal of the design of long-term measurements for southern Africa was to minimise the need of infrastructure and on-site maintenance (Paper I). Another aim in designing the measurements was gathering data from different environments, which makes it even more desirable to be able to operate the measurements with minimal supporting infrastructure and maintenance (Paper I). From these considerations the platform for the measurements was chosen as a 4.5 m long and 2.1 m wide trailer where the only infrastructure needed are 3-phase electricity, grounding (connection to a long enough metal fence at the minimum) and GSM-coverage for data transfer (Paper I). The instruments were selected so that they will start up automatically after a power failure and need on-site maintenance only every one to two weeks, which in practise means cleaning aerosol inlets, checking flows and aerosol device zero levels and replacing gas analyser filters when necessary (Paper I).

The aerosol, gas and meteorological measurements were chosen to facilitate studies on gas-to-particle conversion (Laakso et al., 2008; Paper I). With the above prerequisites in mind a Differential Mobility Particle Sizer (DMPS, Hoppel 1978;

Jokinen and Mäkelä, 1997) and an Air Ion Spectrometer (AIS, Mirme et al., 2007) were selected for aerosol particle size distribution measurements. The DMPS covers aerosol particle size range from 12 to 840 nm at 10 minute time resolution and the AIS ion size distribution from 0.7 to 42 nm at 5 minute time resolution. The DMPS measurements can be used to determine the aerosol particle formation and growth rates in regional new particle formation events with the modal fitting method (Dal Maso et al., 2005). From the AIS measurements the positive and negative ion growth rates can be determined with the maximum concentration method (Hirsikko et al., 2005). The ion formation rate is, though, more difficult to determine from the AIS measurements as it depends also on the neutral particle concentration at 2 nm (Kulmala et al., 2007, Paper IV).

The trace gas measurements at the trailer include CO, O<sub>3</sub>, NO, NO<sub>x</sub> and SO<sub>2</sub> measured with standard commercial instruments, which require only periodical flow checking and inlet filter replacement (Paper I). Calibration checks are performed on the gas analysers three to four times a year and the change in gas analyser response between calibration checks is taken into account in the final corrected concentration. This way there is no need to recalibrate the analysers at every calibration check if the response is close to the desired values, and also possible offset in the logging system is automatically accounted for.

The meteorological parameters measured at the trailer include solar radiation, wind speed and direction, pressure, temperature, relative humidity and temperature gradient (Paper I). One important aspect in planning the trailer measurements was to include such measurements that facilitate calculations of proxy estimates of compounds, which would require more complicated measurements (Paper I). For instance sulphuric acid concentration can be estimated from condensation sink, CS, which is obtained from DMPS measurements (Dal Maso et al., 2005), global radiation and SO<sub>2</sub> concentration (Petäjä et al., 2009; Mikkonen et al., 2011). On the other hand temperature and solar radiation are important parameters for estimating e.g. biogenic VOC emissions (e.g. Guenther et al., 2006).

The trailer aerosol particle measurements include also mass concentration with a Tapered Element Oscillating Microbalance (TEOM, Rupprecht & Patashnick Co. Inc.), which was connected to a custom-built inlet switcher for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> mass fractions (Paper I). However, because of low time resolution the inlet switcher was locked at PM<sub>10</sub> in October 2008 and in February 2009 the TEOM was replaced with a Thermo model 5030 SHARP mass monitor, which requires significantly less maintenance. However, the SHARP cannot be used together with the inlet switcher because the calibration of the SHARP is sensitive to the inlet pressure drop.

During the measurements in South Africa the aerosol instrumentation at the trailer has been updated to cover aerosol particle optical properties (Paper I). Aerosol absorption at 637 nm wavelength is measured with a Thermo model 5012 Multi-Angle Absorption Photometer (MAAP, Petzold and Schönlinner, 2004; Paper II)

since September 2009 and aerosol scattering at three wavelengths (425, 550 and 635 nm) with an Ecotech Aurora 3000 nephelometer with modified light source and inlet system (Müller et al., 2011) since January 2011.

The MAAP is used also to estimate the black carbon (BC) concentration assuming the built-in BC mass absorption coefficient  $6.6 \text{ m}^2 \text{ g}^{-1}$  (Paper II). However, using a constant mass absorption coefficient for converting measured aerosol absorption into BC concentration introduces a significant uncertainty in the BC reading because the mass absorption coefficient may vary significantly (e.g. Cheng et al., 2011). Organic coating over a BC core can act as a lens, and laboratory experiments indicate that this may increase the particle absorption by a factor of 2 compared to uncoated BC particles (Shiraiwa et al., 2010), which in the MAAP means directly a factor of 2 overestimation of BC concentration (Paper II). The magnitude of the error is still open to discussion, though, as recent observations from ambient aerosols show only minor (on average less than 20 %) enhancement of absorption because of BC particle coating (Cappa et al., 2012, 2013).

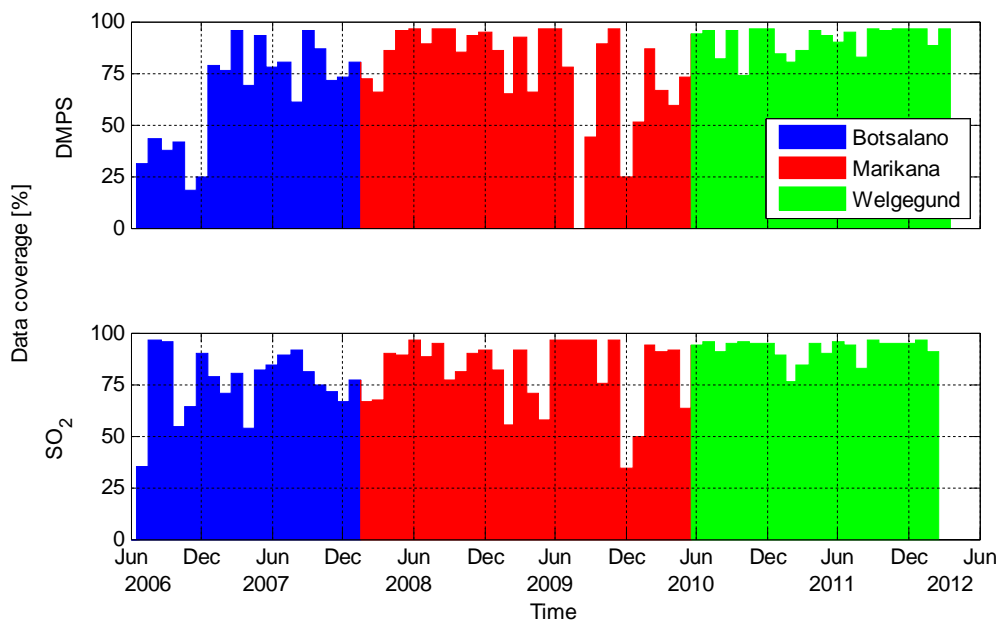
Late in 2009 a measurement artefact was detected in the MAAP during the EUCAARI campaign in India (Paper II) and it was soon observed also in the Marikana data. The artefact occurs only at filter change in high BC conditions, which are unfortunately frequent at Marikana (Paper VII). The artefact is apparently caused by erroneous dark counts from one of the photodetectors during filter change combined to the MAAP internal data inversion algorithm (Paper II). Paper II presents two ways to overcome this artefact. The first one is a correction algorithm based on the MAAP BC readings, if the times of filter change are known. The second correction algorithm is based on recalculating the BC concentration from the raw photodetector signals, which however are not included in standard print formats (Paper II). As the artefact depends on the rate of accumulation of BC on the filter, i.e. BC concentration times the flow rate (Paper II), also decreasing the flow rate will decrease the frequency of artefacts. At Welgegund the MAAP is currently operated at 6 litres per minute flow rate, which is low enough in this environment to avoid the artefact almost completely.

In August 2010, when the trailer was located permanently at the Welgegund site, the measurements were updated with  $\text{CO}_2$  and water vapour flux measurements with eddy-covariance technique (Baldocchi, 2003; Paper I). At the same time meteorological measurements were updated to include direct and reflected photosynthetically active radiation and global radiation, net radiation, soil heat flux, soil temperature profile and soil moisture profile (Paper I). At this point also the rain gauge was changed from the previous optical sensor (Thies 5.4103.20.041) to a Vaisala QMR102 sensor, which has a separate logger connected to an external battery. With the previous rain sensor data during power failures was lost, and therefore it could not be used to calculate the water balance. The latest addition in September 2012 in the continuous measurements at the trailer was a Vaisala ct25k ceilometer for aerosol vertical profile and mixing layer height.

## 4. Results and discussion

### 4.1 Data coverage

The data coverage of the measurements with the mobile measurement trailer (Paper I) has been at a good level after the first six months at Botsalano when e.g. the DMPS data coverage was below 50 % (Figure 7; Paper III). After the first six months period the most important improvements were better filtering of the incoming power and better temperature control including a temperature relay to switch off all measurements if indoor temperature exceeds 40 °C (Paper I). After solving the initial power and temperature issues the next major break in the data coverage was caused by a measurement PC virus infection in December 2009 that lasted until January 2010 (Papers I and III). Besides these issues most of the gaps in the measurements are due to instrument-specific problems: for instance the break in the DMPS measurements in August – September 2009 (Figure 7) was due to a CPC breakdown (Paper III). In order to minimise the breaks in measurements due to instrument wear and tear a supply of spare parts is kept at the trailer (Paper I).



**Figure 7.** Monthly data coverage of DMPS and SO<sub>2</sub> measurements at Botsalano, Marikana and Welgegund.

Providing continuous training for the students and technical personnel who have been responsible for the routine checks at the measurement trailer in South Africa

has also been an important factor in keeping the data coverage at a high level (Paper I). An essential part of the training has been development of detailed maintenance instructions and technical drawings of the solutions at the measurement trailer, which total 150 pages at the moment. The continuous development of the maintenance processes at the trailer has also led to increasing data coverage, as seen in Figure 7. For instance the DMPS data coverage has increased from 67 % at Botsalano (from July 2006 to January 2008) to 80 % at Marikana (from February 2008 to May 2010) and up to 94 % at Welgegund (from June 2010 to March 2012), which is comparable to even the best European research infrastructures (e.g. Asmi et al., 2011).

The increase in the data coverage from Marikana to Welgegund is partly due to a more reliable incoming power and a logistically better location at Welgegund. However, the most important factor in the success at Welgegund is having committed local partners who continuously monitor the data quality and can and will go to the site whenever required. One aim of this work has been establishing a permanent reference point for global climate models in continental southern Africa and with the excellent co-operation with North-West University in South Africa this goal has been achieved at Welgegund (Beukes et al., 2013).

## **4.2 Aerosol concentrations**

The total aerosol particle concentration from 12 to 840 nm, N<sub>12</sub>, is close to the high end of observations in comparable environments outside southern Africa at both Botsalano and Marikana (Jayaratne and Verma, 2001; Shen et al., 2011; Sheridan et al., 2001; Rissler et al., 2006; Asmi et al., 2011; Hyvärinen et al., 2011; Laakso et al., 2012; Paper III). At the semi-clean Botsalano the median total concentration was 1860 cm<sup>-3</sup> and at the polluted Marikana the total concentration was 7810 cm<sup>-3</sup> (Paper III). At Welgegund the median N<sub>12</sub> was 3950 cm<sup>-3</sup> (Beukes et al., 2013), which is between the total concentration at Botsalano and Marikana. This is reasonable considering that although there are no local sources at Welgegund it is closer than Botsalano to the anthropogenic sources in and around the megacity of Johannesburg. Furthermore, direct transport from the anthropogenic sources around Johannesburg is more frequent at Welgegund than at Botsalano. At Welgegund approximately 20 % of the 96-hour back-trajectories pass over the anthropogenic sources around Johannesburg (Figure 6), while at Botsalano less than 1 % of the 96-hour back-trajectories do so (Figure 6; Paper IV). This difference in the transport pattern is enough to offset the effect that in the recirculation path Welgegund is further from the anthropogenic sources than Botsalano (Figure 6) and thus Botsalano is indeed the cleanest of the three locations.

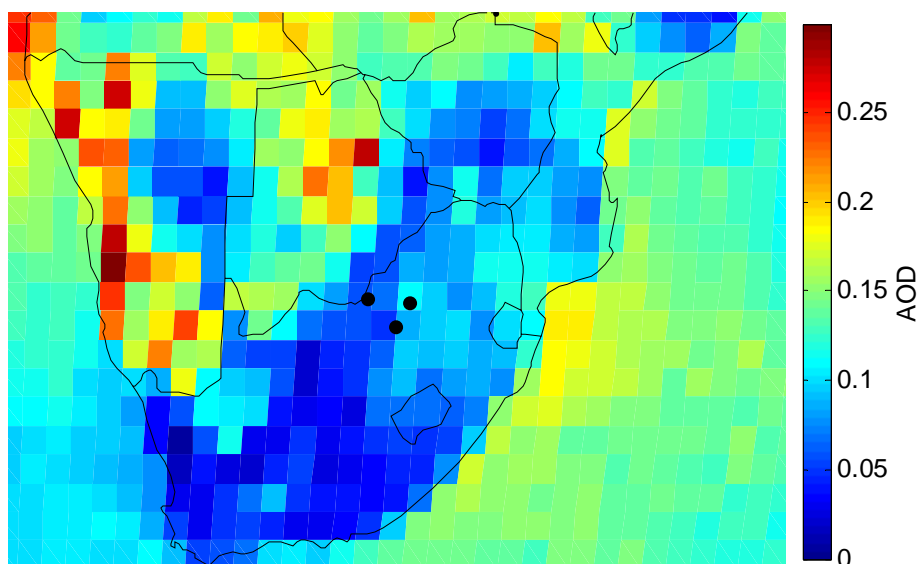
However, the concentrations of CCN-sized particles, i.e. particles in the size range of 50–840 nm (N<sub>50</sub>) and 100–840 nm (N<sub>100</sub>) are clearly lower at Botsalano and

Marikana than at other comparable environments (Jayaratne and Verma, 2001; Shen et al., 2011; Sheridan et al., 2001; Rissler et al., 2006; Asmi et al., 2011; Hyvärinen et al., 2011; Laakso et al., 2012; Paper III). At Botsalano for instance the mean N100 is  $880 \text{ cm}^{-3}$ , while at the semi-clean North China Plain the mean N100 is  $3470 \text{ cm}^{-3}$  (Shen et al., 2011) and at the semi-clean cropland in Hungary the mean N100 is  $1950 \text{ cm}^{-3}$  (Asmi et al., 2011). Also at Marikana the mean N100 is  $2190 \text{ cm}^{-3}$ , which is clearly less than e.g. at Gual Pahari, a semi-urban location in India, where the 75–800 nm particle concentration varies from 5150 to  $16\,970 \text{ cm}^{-3}$  (Hyvärinen et al., 2011) and even less than at an industrially polluted site in Italy, where the mean N100 is  $2890 \text{ cm}^{-3}$  (Asmi et al., 2011). The reason for high total concentration in southern Africa is high nucleation mode concentration (Laakso et al., 2008; Paper III).

The reason for the uncommonly high nucleation mode concentration compared to accumulation mode concentration lies in a combination of air pollution regulation and meteorological conditions. Historically the South African industries were required to have efficient particulate filtration, but cleaning of gaseous emissions was not always enforced (Paper III; Beukes et al., 2013). This is seen clearly at Marikana, where the ground-level  $\text{SO}_2$  concentration peaks after sunrise due to boundary layer development, but the N50 and N100 are not affected (Paper III), although they should increase if the particulate emissions were uncontrolled (e.g. Cantrell and Whitby, 1978). The combination of relatively low primary particle emission – and hence relatively low CS – and relatively high  $\text{SO}_2$  emission is ideal for formation of gas phase sulphuric acid and subsequent nucleation (e.g. Kulmala et al., 2005, 2013; Seinfeld and Pandis, 2006; Petäjä et al., 2009; Sipilä et al., 2010). Therefore it is no wonder that atmospheric new particle formation occurs in southern Africa nearly every sunny day, and as most of the days are sunny (e.g. Laakso et al., 2008) also the frequency of atmospheric new particle formation events is record high (Laakso et al., 2008; Papers III, IV and V).

The comparatively low N100 is reflected also in the MODIS collection 5 Aerosol Optical Depth (AOD, Remer et al., 2005) in Figure 8, which shows that the AOD is only marginally increased over the megacity and industrialised Highveld despite the high gaseous emissions (e.g. Lourens et al., 2011, 2012). The AOD seems to depend mostly on natural aerosol sources over southern Africa as the highest values over the continent originate in desert dust over the Kalahari and Namib deserts (e.g. Dentener et al., 2006). However, the ground level concentration of CCN-sized particles has significant spatial variation that does not follow the AOD pattern in southern Africa (Paper III), which also suggests that the AOD alone is probably not a very good indicator of CCN concentration over southern Africa.





**Figure 8.** Median MODIS 550 nm AOD over southern Africa from July 2006 to January 2008 (Remer et al., 2005). Black dots indicate (from left to right) Botsalano, Welgegund and Marikana.

At Botsalano the highest N100 concentrations are observed when air masses follow the route of anticyclonic recirculation or have passed over the industrialized Highveld (Paper III). Compared to the N100 concentration from the clean rural Karoo direction, the N100 from the anthropogenically affected direction is nearly four times as high – from the Karoo the median N100 is  $250 \text{ cm}^{-3}$  and from the recirculation path  $910 \text{ cm}^{-3}$  (Paper III). The closer to the anthropogenic sources the N100 is measured, the higher is the concentration: at Marikana the median N100 is  $1630 \text{ cm}^{-3}$  (Paper III).

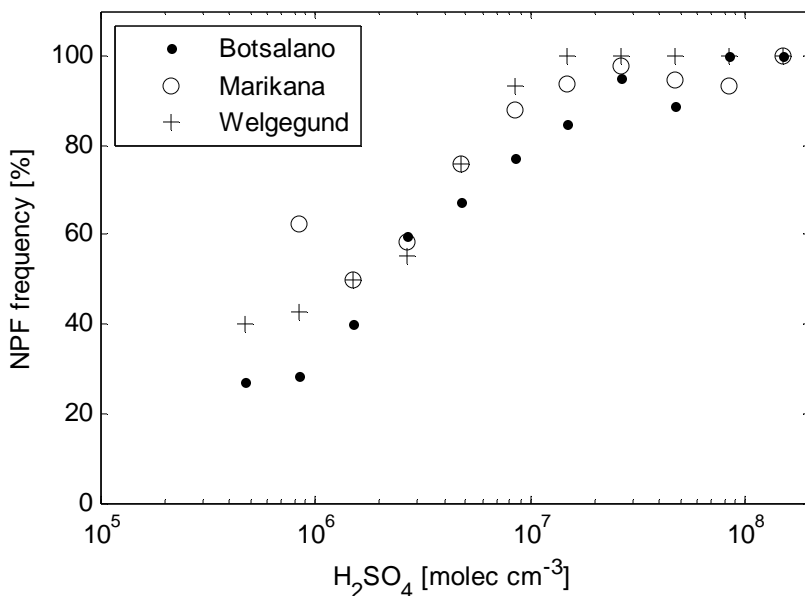
However, the clean sector at Botsalano is not uniform. The Karoo direction southwest of Botsalano is characterised by low accumulation mode and continuously present nucleation mode, but the Kalahari direction northeast of Botsalano has higher accumulation mode concentration (median N100 is  $430 \text{ cm}^{-3}$ ) though it lacks the nucleation mode almost completely (Paper III). The difference in the Karoo and Kalahari source regions lies in the meteorological patterns that lead to air mass transport from these source regions to Botsalano (Paper III). The Karoo source region is representative of fresh clean air mass and Kalahari of aged clean sector (Paper III). However, considering only the air mass history as in Paper III the differences in natural aerosol sources such as vegetation type changing from shrublands to savannah (Figure 2) cannot be separated from simultaneous changes in anthropogenic sources.

Diurnal variation of the aerosol particle size distribution is significant at both Botsalano and Marikana. The median diurnal variation at Botsalano has a factor of 1.5 difference between the lowest and highest N100 concentrations; for total concentration the difference is a factor of 2.2 (Paper III). At Botsalano both total concentration and N100 peak at noon and are the lowest in the early morning. At Marikana the daily difference between the lowest and highest N100 concentration is a factor of 1.9 and for the total concentration a factor of 2.7 (Paper III), the highest total concentration occurring just before noon. Regional new particle formation and growth is the main driver of diurnal variation at Botsalano and it is also the reason for the highest total concentrations at Marikana (Paper III). At Marikana, however, domestic heating and cooking are the largest source of variation for N50 and N100, which peak in the evening between 18 and 21 (Papers III and VII).

Seasonal variation is significant at Botsalano and Marikana. At Botsalano the difference in the highest and the lowest monthly median N100 is a factor of 2.1 and at Marikana a factor of 2.7 (Paper III). At both locations the aerosol concentration increases during the dry season and the seasonal variation is caused by a combination of increased source (i.e. incomplete combustion) and reduced removal processes (i.e. lack of wet removal, Paper III). However, the sources of incomplete combustion differ at the two sites. At Botsalano veldt fires, i.e. both anthropogenic and natural wild open biomass burning, is the most important source of aerosol particles during the dry season (Paper III). At Marikana, on the other hand, domestic heating and cooking in the nearby residential areas dominate over veldt fires (Paper III). Regional new particle formation is discussed in more detail in Chapter 4.3 and veldt fires and domestic heating and cooking in Chapter 4.4.

### ***4.3 New particle formation at a record high frequency***

Regional new particle formation (NPF) events and subsequent growth to CCN-sizes occur at a record high frequency in continental southern Africa. Clear regional NPF events – classes I and II in the classification scheme presented by Dal Maso et al. (2005) – were observed at Botsalano on 69 % of all days and at Marikana on 86 % of all days (Papers IV and V). At Welgegund, based on analysis of one year of size distribution measurements from 1 September 2010 to 31 August 2011 the frequency of new particle formation events was 75 %. In other environments the annual new particle formation frequency varies from less than 20 % to approximately 60 %, and thus the 86 % NPF frequency at Marikana is currently the world record (Kulmala et al., 2004; Kulmala and Kerminen, 2008; Manninen et al., 2010; Pryor et al., 2010; Hirsikko et al., 2011; Shen et al., 2011; Kanawade et al., 2012; Kim et al., 2013; Papers IV and V). The frequency of NPF events follows the logarithm of the estimated H<sub>2</sub>SO<sub>4</sub> concentration in all three measurement locations, as seen in Figure 9, which is in line with recent observations of the role of sulphuric acid in atmospheric new particle formation (Sipilä et al., 2010; Kulmala et al., 2013).



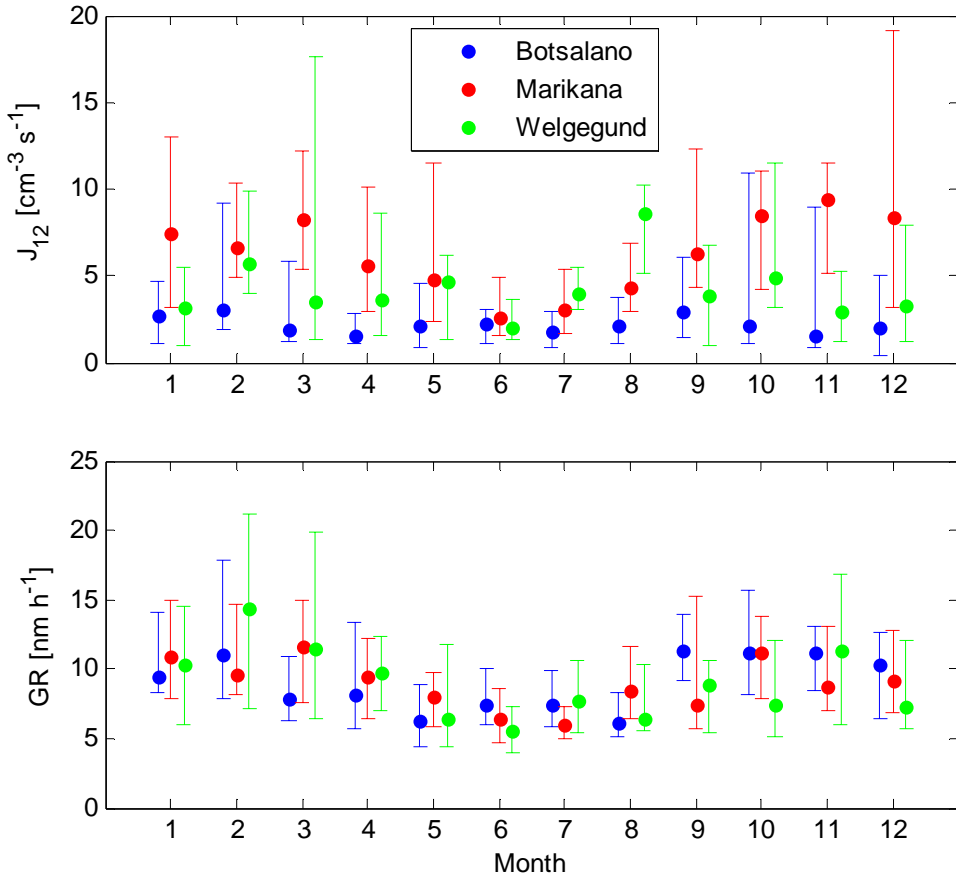
**Figure 9.** NPF frequency as a function of  $H_2SO_4$  concentration at the onset of the NPF event or at 9:30 (local time), if no NPF event was observed.

However, at Marikana and Welgegund the NPF frequency was higher than at Botsalano even at equal  $H_2SO_4$  levels, as seen in Figure 9. One possible explanation is that the differences in Figure 9 are coincidental, as after all the  $H_2SO_4$  concentration is estimated with a proxy developed for a very different environment (Petäjä et al., 2009) and without direct measurements the quality of the proxy cannot be estimated. On the other hand this may reflect differences in concentrations of ammonia or amines, which have been shown to increase the nucleation rate compared to binary nucleation of  $H_2O$  and  $H_2SO_4$  (Kurtén et al., 2008; Berndt et al., 2010; Kirkby et al., 2011; Kulmala et al., 2013); or even sulphuric acid formation through mechanisms that do not involve the OH radical (Mauldin et al., 2012). However, without state-of-the-art measurements these effects cannot be verified. In any case it is apparent that the heavier the anthropogenic influence at the site is, the higher is the frequency of new particle formation.

The air mass history studies at Botsalano show that new particle formation events are frequent for all other air mass origins except the Kalahari direction north-west of Botsalano, i.e. the aged clean sector (Papers III and IV). The lack of new particle formation for the Kalahari direction can be explained by the ratio of condensation sink and condensable vapour sources (cf. Kulmala et al., 2005). The CS from the Kalahari,  $3.4 \cdot 10^{-3} \text{ s}^{-1}$ , is nearly twice as high as the CS from the Karoo,  $1.8 \cdot 10^{-3} \text{ s}^{-1}$ , the fresh clean sector (Paper IV), while the biogenic and anthropogenic emissions of

condensable vapour precursors are close to equal for the Kalahari and Karoo (Fleming and van der Merwe, 2002; Otter et al., 2003, 2004).

The formation rate of 12–25 nm particles,  $J_{12}$  (Dal Maso et al., 2005), was higher closer to the anthropogenic sources. At Marikana the median  $J_{12}$  was  $5.9 \text{ cm}^{-3} \text{ s}^{-1}$ , at Botsalano the median  $J_{12}$  was  $2.2 \text{ cm}^{-3} \text{ s}^{-1}$  (Papers IV and V), and at Welgegund the median  $J_{12}$  was  $4.1 \text{ cm}^{-3} \text{ s}^{-1}$ . Furthermore, at Botsalano the median  $J_{12}$  from the clean Karoo direction was  $1.8 \text{ cm}^{-3} \text{ s}^{-1}$  and from the direction of the Highveld  $3.5 \text{ cm}^{-3} \text{ s}^{-1}$  (Paper IV). The median 2 nm ion formation rate (Kulmala et al., 2007) was  $0.8 \text{ cm}^{-3} \text{ s}^{-1}$  at Botsalano, which is clearly lower than the  $J_{12}$ . This is in accordance with recent observations from the northern hemisphere (e.g. Manninen et al., 2010; Hirsikko et al., 2011) and suggests that only a minor fraction of the nucleation is ion-induced, but the relatively large smallest diameter of the DMPS (12 nm) does not allow quantitative comparison on neutral and ion-induced nucleation (Paper IV).



**Figure 10.** Monthly median  $J_{12}$  and GR at Botsalano, Marikana and Welgegund. Errorbars indicate upper and lower quartiles.

At Botsalano the  $J_{12}$  peaked during spring and late summer and also at Marikana and Welgegund the  $J_{12}$  was higher during the wet season than during the dry season (Papers IV and V; Figure 10). At all sites the lowest formation rates occurred in June and July, i.e. mid-winter (Papers IV and V; Figure 10). The formation rate of 2 nm ions had no seasonality at all (Papers IV and V) and even the seasonality in  $J_{12}$  is more likely to originate in seasonality in aerosol particle growth rate than seasonality in the actual nucleation rate because the formation rate above 10 nm depends strongly on the growth rate below 10 nm (e.g. Kerminen and Kulmala, 2002; Pierce and Adams, 2007).

Contrary to the aerosol particle formation rate the growth rate of 12 to 30 nm particles (GR) was very close to each other at Botsalano, Marikana and Welgegund. The median GR was  $8.9 \text{ nm h}^{-1}$  at Botsalano,  $8.7 \text{ nm h}^{-1}$  at Marikana and  $8.5 \text{ nm h}^{-1}$  at Welgegund (Papers IV and V). At Botsalano the GR was clearly lower in air masses originating in the semi-arid Karoo direction compared to other directions, probably because of lower VOC emissions (Otter et al., 2003, 2004; Paper IV). From the Karoo direction the median GR was  $5.9 \text{ nm h}^{-1}$  and from the Highveld direction  $9.4 \text{ nm h}^{-1}$  (Paper IV). The highest growth rates at Botsalano were observed in air masses originating in north-eastern South Africa rather than in the industrial hub around Johannesburg, which suggests that for the GR biogenic precursors are more important than anthropogenic emissions (Paper IV).

Estimating the contribution of sulphuric acid to the aerosol growth (Nieminen et al., 2010; Paper IV) indicates that most of the growth and especially the seasonality of GR cannot be explained by sulphuric acid, but other compounds such as organics are needed (Paper IV). At all sites the lowest growth rates occur during winter, from June to August, and the highest during spring or late summer (Figure 10). Similar seasonality in GR has been observed also in the northern hemisphere, where it is commonly attributed to the seasonality of biogenic VOC emissions as precursors for condensable vapours in new particle formation events (e.g. Mäkelä et al., 1997; Kulmala et al., 2004; Dal Maso et al., 2005; Kulmala et al., 2013). Overall the observations that new particle formation frequency and sulphuric acid are closely connected and that organic precursor compounds are more important than sulphuric acid for aerosol particle growth in southern Africa (Papers IV and V) agree well with results from other environments (e.g. Sihto et al., 2006; Riipinen et al., 2007, 2011; Kuang et al., 2008; Paasonen et al., 2010, 2013; Kulmala et al., 2013).

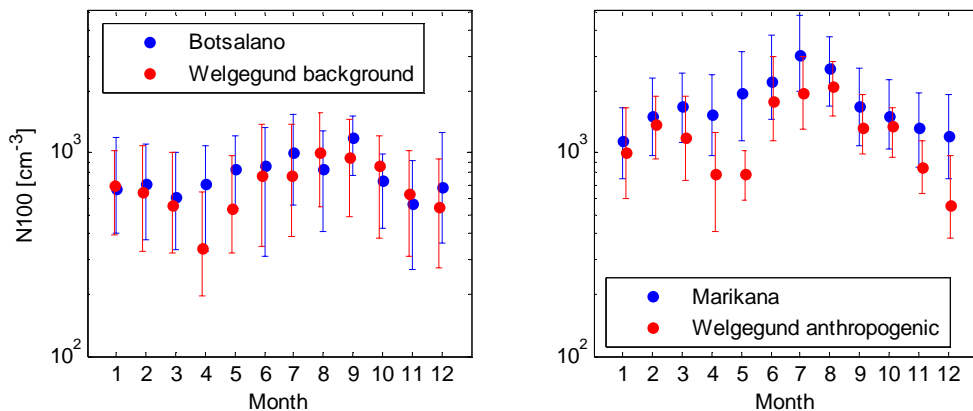
Regional new particle formation events are an important source of CCN-sized particles in southern Africa during the wet season, from October to April, as shown for Botsalano in Paper VI. During this period the new particle formation events lead to average 50 – 200 % increase in CCN-sized particle number concentration within 24 hours of the beginning of the new particle formation (Paper VI). On the other hand, during the dry season from May to September regional new particle formation events have a minimal effect on CCN-sized particle concentration and combustion sources are the dominating CCN-sized particle source (Tiitta et al., 2013; Papers III and VI).

The observed CCN production from new particle formation events at Botsalano was compared to a global climate model in Paper VI. However, although the model reproduces the frequent new particle formation well and the CCN number agrees with observations (cf. Merikanto et al., 2009, 2010; Spracklen et al., 2010), it cannot reproduce the CCN production from the new particle formation events during the wet season (Paper VI). In Paper VI this is attributed mainly to inaccuracy of available emission inventories used in the model, as the modelled CCN concentration was found to be most sensitive to anthropogenic sulphur emissions during the wet season and biomass burning emissions during the dry season. This discrepancy demonstrates that it is possible to model the correct CCN concentration from incorrect sources, as long as the model processes are correct – and therefore it would be essential to compare models and observations on process-level in addition to plain concentrations (Paper VI).

#### ***4.4 Challenges in quantifying aerosols from incomplete combustion***

Incomplete combustion, both veldt fires and domestic heating and cooking, is the most important submicron aerosol source in southern Africa during the dry season from May to October (e.g. Swap et al., 2003; Tiitta et al., 2013; Paper III). During the dry season N100 is highly correlated with CO – the monthly correlation coefficient stays above 0.7 at both Botsalano and Marikana (Paper III). Also the submicron chemical composition shows elevated organic aerosol and BC concentrations during the dry season. At Welgegund organic aerosol and BC were at least a factor of 3 higher during the dry season compared to the wet season (Tiitta et al., 2013). This is also the period when N100 is at its highest (Figure 11) and as a consequence also the CS is increased so much that together with lower aerosol growth rates it is enough to suppress CCN production from regional new particle formation events (Paper VI).

From a modelling point of view, biomass burning emissions are among the parameters that most influence the modelled CCN concentration, not only in southern Africa (Paper VI) but also globally (e.g. Spracklen et al., 2011). Modelling of biomass burning emissions is based on emissions factors of aerosol particles and gas phase compounds, which however have large variability depending on the type of burned biomass and the burning process (e.g. Akagi et al., 2011). Even within one vegetation type both aerosol number and mass emission factors can easily have  $\pm 50\%$  variation (e.g. Janhäll et al., 2010; Akagi et al., 2011). Global models typically use only average mass emission factors divided into a few different vegetation types (van der Werf et al., 2006, 2010; van Leeuwen and van der Werf, 2011; Akagi et al., 2011) and the mass emissions are then converted into number size distribution assuming constant density and log-normal size distribution parameters (e.g. Spracklen et al., 2011).



**Figure 11.** The monthly median of  $N_{100}$  and upper and lower quartiles at Botsalano, Marikana and Welgegund. Welgegund  $N_{100}$  is split into background and anthropogenic cases based on air mass history from back-trajectory calculations.

One of the main reasons for large variation of emissions between fires of similar vegetation is the ratio of flaming and smouldering combustion in the fire (e.g. Janhäll et al., 2010; Akagi et al., 2011). A higher fraction of smouldering combustion leads to higher emissions of particulate mass and gas phase compounds, such as CO and VOCs, while black carbon is produced almost exclusively in flaming combustion (e.g. Akagi et al., 2011). One way to measure the relative contribution of flaming and smouldering combustion is to determine the combustion efficiency in the fire, i.e. the ratio of carbon emitted as  $\text{CO}_2$  to all carbon in the fuel (e.g. Ward and Radke, 1993; Yokelson et al., 1996). However, as the combustion efficiency is difficult to measure a so called modified combustion efficiency, MCE, is often used instead (Akagi et al., 2011). MCE is defined as

$$MCE = \frac{\Delta\text{CO}_2}{\Delta\text{CO}_2 + \Delta\text{CO}}, \quad (1)$$

where  $\Delta$  denotes that the background concentration is subtracted from the plume concentration (e.g. Akagi et al., 2011). MCE is considered to be within a few percent of the actual combustion efficiency and it is routinely used instead of the combustion efficiency in emission factor calculations (e.g. Akagi et al., 2011).

Several studies report decreasing trends for both gas phase species and aerosol number and mass emissions with increasing MCE (e.g. Ward and Radke, 1993; Yokelson et al., 2003; 2009; Janhäll et al., 2010) and the change can be substantial.. For instance, the grassland  $\text{PM}_{2.5}$  mass emission factor decreases by a factor of 2.6 as MCE increases from 0.9 to 0.97, which covers most of the observations (Janhäll et al., 2010). On the other hand the emission dependency on MCE could be utilised

to calculate the emission factor for any known MCE (Akagi et al., 2011). However, there is significant scatter in the emission factor dependency on MCE and the linear fitting  $R^2$  statistics are often in the order of 0.5 or below, i.e. only half of the variance can be explained (e.g. Yokelson et al., 2009; Janhäll et al., 2010). Added uncertainty is that there is little information on the seasonal or spatial variability of the MCE (Akagi et al., 2011; van Leeuwen and van der Werf, 2011), and consequently MCE is not included in the widely used global biomass burning emission inventories Global Fire Emission Database GFED (van der Werf et al., 2006, 2010) and Fire Locating and Modeling of Burning Emissions FLAMBE (Reid et al., 2009).

At the moment most of the emission factors reported in ambient conditions are based on aircraft measurements using carbon mass balance method (Yokelson et al., 1996, 1999). The carbon mass balance method requires knowledge of the fuel carbon content, but as this ranges from 45 to 55 % for nearly all biomass burning fuels also the uncertainty remains less than 10 % even if the fuel carbon content is not known (e.g. Susott et al., 1996; Yokelson et al., 1997; McMeeking et al., 2009; Akagi et al., 2011). However, aircraft measurements are usually possible only in well-lofted plumes from comparatively large fires (Akagi et al., 2011) and therefore small fires and residual smouldering combustion (Christian et al., 2007; Akagi et al., 2013) are not fully included in the current emission factors. For this reason and also to cover the seasonality of the emissions more ground-based measurements would be needed (Akagi et al., 2011; van Leeuwen and van der Werf, 2011).

There are quite a few studies on the chemical characterisation of the biomass burning aerosol in ambient conditions (e.g. Akagi et al., 2011 and references therein). However, only a handful of studies report the aerosol particle number concentration or size distribution (Janhäll et al., 2010 and references therein), although especially for indirect aerosol climate effects the number of CCN-sized particles is more important than the mass concentration (Andreae and Rosenfeld, 2008). A further shortcoming is that the studies that do report aerosol number concentration in most cases lack the information on the aerosol size distribution below 100 nm (Janhäll et al., 2010) although in fresh veldt fire plumes the count mean diameter (CMD) can be as low as 50 nm (Vakkari et al., 2012). The lack of measurements below 100 nm leads to overestimation of the modal mean diameter in biomass burning emissions, which is one of the parameters that have the largest effect on CCN concentration in global models (Spracklen et al., 2011; Paper VI).

Characterising only the initial emissions has also another inherent complication. The processes in fresh biomass burning plume are rapid and significant changes occur in the plume aerosol in temporal and spatial scales below global climate model resolution (e.g. Ross et al., 2003; Yokelson et al., 2003, 2009, 2013; Akagi et al., 2012). Recent laboratory experiments suggest that during the first three to four hours new particle formation in the biomass burning plume may increase the CCN emission by a factor of two to three, something that current global climate models cannot reproduce (Hennigan et al., 2012). Therefore it appears that aging during the

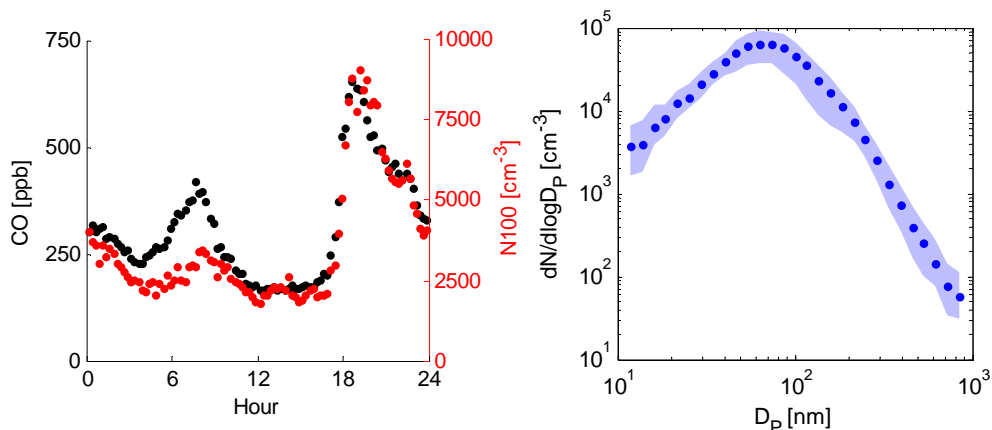


first few hours has as large an impact on the aerosol climate effects from a fire, as the combustion efficiency or the fuel type. However, very few studies in atmospheric plumes have quantified even the CCN-sized particle concentration changes during this time period (Ross et al., 2003; Vakkari et al., 2012).

The location of the Welgegund measurement station in an area of extensive biomass burning (Figure 4) enables studying several previously poorly quantified properties of biomass burning aerosol. The size distribution measurements can be extended below 100 nm for the first time in ambient conditions and also un-lofted plumes can be measured. As Welgegund is located in a mosaic of savannah, grassland and cropland environments (Figure 2), the effect of fuel type can be compared. Utilising ground-based measurements enables studying of previously nearly completely unmeasured night-time plumes (Akagi et al., 2011). Comparison to day-time plumes can be also used to study the effects of photochemical reactions in the plume aging, which is driven largely by secondary aerosol formation (Yokelson et al., 2009; Hennigan et al., 2012). On the other hand fixed point ground-based measurements have their limitations, most important of which are that the initial emissions can be measured only if the fire is very close and that the MCE cannot be defined accurately for all plumes because of the vegetation CO<sub>2</sub> exchange. However, the aging of the plume can be studied and it is one of the future objectives of research at Welgegund (Vakkari et al., 2012).

#### ***4.4.1 Domestic heating and cooking***

In southern Africa domestic heating is also an important aerosol source during the dry season and it can dominate over the regional veldt fire emissions close to informal and semi-formal residential areas as is seen at Marikana (Paper III). A typical July evening heating peak at Marikana is illustrated in Figure 12, which shows how N100 and CO increase concurrently after sunset and again in the morning. However, the size distribution of the evening peak is by no means limited to the accumulation mode, but all particle sizes down to 12 nm are present (Figure 12; Paper III). This is somewhat surprising, but during the evening peak the surface wind speed is very low and often below the lower threshold of the anemometer ( $0.1 \text{ m s}^{-1}$ ), which means that the aerosol is indeed from very nearby sources (Paper III). During winter nights the lowest inversion layers also form close to the surface, so that the evening burning peak at Marikana is really representative only of aerosol very close to the combustion sources (Paper III).



**Figure 12.** In the left panel are median diurnal variation of CO and N100 at Marikana in July 2009. In the right panel is the median size distribution at Marikana in July 2009 at 18:30 (local time). The upper and lower quartiles of the size distribution are indicated by the shaded area.

The aerosol particle seasonality at Marikana (Figure 11; Paper III) stays the same even if only daytime data is considered, which shows that domestic combustion dominates over regional veldt fires at least within the 60 km long and 30 km wide valley where Marikana is located (Paper III). However, the seasonality of accumulation mode particles at Welgegund (Figure 11) suggests that domestic heating at the megacity of Johannesburg may affect aerosol concentration even at a regional scale.

Figure 11 shows the seasonality of N100 at Botsalano, Marikana and Welgegund. The Welgegund data is split into two categories based on air mass history, i.e. trajectories originating in the direction of Johannesburg and surroundings are classified as anthropogenically influenced and trajectories from south and west are considered as background. Comparison to Botsalano and Marikana N100 in Figure 11 shows how the N100 seasonality and concentrations from the Johannesburg direction are close to what is observed at Marikana, but the background N100 is closer to Botsalano measurements. As the Marikana N100 seasonality is dominated by domestic heating and cooking, it seems probable that the likeness of Marikana and the Johannesburg direction seasonality at 100 km downwind of the city would be due to similar sources, i.e. domestic heating and cooking.

Papers III, V and VII show the first measurements of domestic heating and cooking emissions close to informal settlements in southern Africa. However, due to lack of CO<sub>2</sub> measurements, the combustion efficiency and subsequently emission factors cannot be defined at satisfactory accuracy. Furthermore, the fuel type is unknown and probably consists of biomass and fossil coal in variable ratios – although low

grade coal due to its cheap price is probably the most commonly used fuel (Piketh et al., 2005).

Nevertheless, the emission ratio of N100 to CO for the evening and morning peaks at Marikana can be calculated from the diurnal cycle. For the evening peak, the ratio of N100 increase to the ratio of CO increase (in standard temperature of 0°C and pressure of 101.325 kPa) from 16:30 to 19:00 is  $18 \text{ cm}^{-3} \text{ ppb}^{-1}$ . The morning peak emission ratio (from 4:30 to 08:00) is clearly lower than the evening peak,  $7.3 \text{ cm}^{-3} \text{ ppb}^{-1}$ , which implies significant differences between the evening and morning combustion. This is reasonable as the evening peak originates in both heating and cooking, but the morning peak consists of only cooking. The evening peak N100 emission ratio is comparable to the emission ratios observed for savannah and grassland fires, which range from 10 to  $30 \text{ cm}^{-3} \text{ ppb}^{-1}$  (Janhäll et al., 2010).

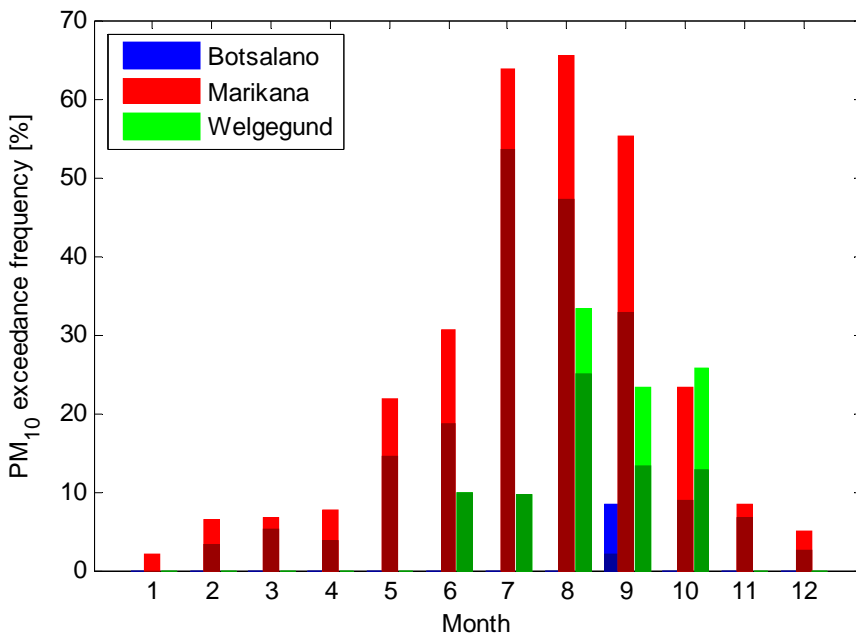
Despite the lack of CO<sub>2</sub> measurements at Marikana it is possible to make an order-of-magnitude estimate of the particle emission factor from the observed emission ratio using the carbon mass balance method (Yokelson et al., 1996, 1999) by estimating the combustion efficiency and fuel carbon content. Akagi et al. (2011) indicate combustion efficiency of 0.93 for open cooking, and low grade coal can be assumed to have carbon content of 75 %. With these assumptions the N100 emission factor for evening domestic heating and cooking at Marikana is  $2.3 \cdot 10^{15} \text{ kg}^{-1}$ . This is clearly higher than the N100 emission factors for savannah and grassland fires, which are  $0.67 \pm 0.21 \cdot 10^{15} \text{ kg}^{-1}$  and  $0.66 \pm 0.32 \cdot 10^{15} \text{ kg}^{-1}$ , respectively (Le Canut et al., 1996; Janhäll et al., 2010). However, considering the assumptions above the uncertainty in the Marikana emission factor is at least a factor of two. Notwithstanding this uncertainty, the data demonstrates that domestic heating and cooking emissions may be a significant aerosol source in southern Africa and definitely merit further study.

## ***4.5 Air quality and environmental effects***

The effect of industrial emissions on air quality is a current concern in South Africa (e.g. Piketh et al., 2005; Government Gazette Republic of South Africa, 2012; Paper VII) and at the moment three industrially affected areas have been declared as national air pollution priority areas (Government Gazette Republic of South Africa, 2005a, 2007, 2012), i.e. areas where air quality standards (Government Gazette Republic of South Africa, 2005b) are frequently exceeded or there is a strong risk of deteriorating air quality. The Waterberg priority area declared in 2012 (Government Gazette Republic of South Africa, 2012) encompasses also the Marikana measurement location, which was one of the reasons to carry out an air quality survey based on the measurements at Marikana (Paper VII).

Paper VII shows that PM<sub>10</sub> and O<sub>3</sub> frequently exceed both South African and European air quality standards at Marikana, but rather surprisingly the SO<sub>2</sub>, NO<sub>x</sub> and CO stay within limits although the site is surrounded by pyrometallurgical smelters. The SO<sub>2</sub> concentration exceeded the 10 minute and 1 hour standards on average 4 and 0.4 times a year, respectively, which is within the number of tolerable exceedances per year (Paper VII). The NO<sub>x</sub> and CO concentrations remained continuously within acceptable limits (Paper VII).

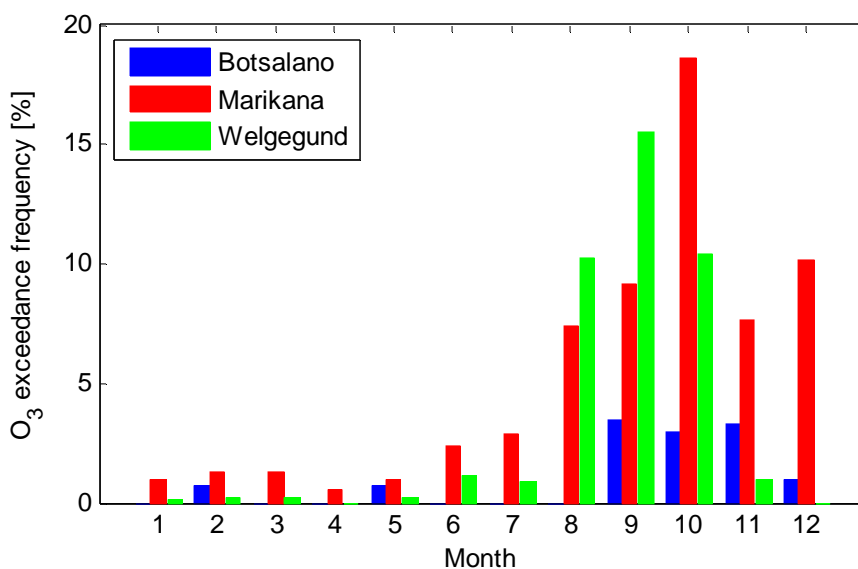
The PM<sub>10</sub> exceedances at Marikana are closely connected to domestic heating and cooking in the nearby informal and semi-formal residential areas as indicated by the seasonal and diurnal patterns of PM<sub>10</sub>, CO and black carbon (Paper VII). Furthermore, most PM<sub>10</sub> exceedances occur during winter (Figure 13, using EU standard of 50 µg m<sup>-3</sup> over 24 hour period), which is additional evidence of the significant role of domestic heating for PM<sub>10</sub> air quality at Marikana. A look at PM<sub>10</sub> levels at Welgegund (Figure 13) shows that also there a major fraction of the PM<sub>10</sub> air quality standard exceedances is closely connected with CO and black carbon and therefore incomplete combustion.



**Figure 13.** Monthly frequency of 24-hour mean PM<sub>10</sub> exceeding 50 µg m<sup>-3</sup> at Botsalano, Marikana and Welgegund. The shaded area of the bars indicates the fraction of exceedances associated with simultaneous CO and/or BC increase. At Botsalano four exceedances were observed over 18 months measurement period, which is below the limits of acceptable number of exceedances per year (Paper VII).

At Welgegund the PM10 exceedances occur later in the dry season than at Marikana, which suggests that the contribution of veldt fires to high PM10 may be more significant at Welgegund than at Marikana, Figure 13. At both locations PM10 correlates well with CO and BC (correlation coefficient above 0.75) on approximately two thirds of the days when 24h-average PM10 exceeds  $50 \mu\text{g m}^{-3}$ .

Ozone is a secondary pollutant and it is therefore more difficult to connect with any single source in the vicinity of Marikana (Paper VII). The seasonality of O<sub>3</sub> exceedances in Figure 14, however, is clearly different from the seasonality of PM10 exceedances at Marikana (Figure 13), which indicates that the sources responsible for the exceedances are different. Ozone is also the only air pollutant that frequently exceeds air quality standards even at the semi-clean Botsalano (Figure 14), which illustrates how O<sub>3</sub> precursors disperse over large areas in southern Africa.



**Figure 14.** Monthly frequency 8-hour running mean O<sub>3</sub> concentration exceeding 61 ppb at Botsalano, Marikana and Welgegund.

One demonstrated source of O<sub>3</sub> in southern Africa is veldt fires. In southern Africa O<sub>3</sub> formation up to 10 % of the CO produced in the fire has been observed during a few hours of plume transport (Jost et al., 2003; Yokelson et al., 2003). In North America even higher O<sub>3</sub> formation rates have been observed: Akagi et al. (2013) report O<sub>3</sub> formation up to 90 % of the CO emitted in a fire. However, looking at the measurements at Botsalano, Marikana and Welgegund it is apparent that O<sub>3</sub> exceeds the air quality standards more often the closer the measurements are to the megacity of Johannesburg and surrounding industrial sources (Figure 14). Furthermore, most of the O<sub>3</sub> exceedances occur during spring and early summer, which is one to two

months later than the peak of veldt fire intensity at these locations (Paper III). Therefore it seems unlikely that the high O<sub>3</sub> concentrations would originate only in the dry season biomass burning, but rather in a combination of anthropogenic precursors such as NO<sub>x</sub>, favourable meteorological conditions and possibly also biogenic VOC emissions in the spring time (Laakso et al, 2013). The seasonality of O<sub>3</sub> exceedances in Figure 14 is in fact similar to northern hemisphere, where O<sub>3</sub> concentrations are also the highest during spring (e.g. Monks 2000 and references therein).

Although the SO<sub>2</sub> and NO<sub>x</sub> concentrations do not exceed air quality standards at Marikana or the background locations of Botsalano and Welgegund, anthropogenic emissions of SO<sub>2</sub> and NO<sub>x</sub> have led to acidification of the rainwater even at remote areas in southern Africa (Mphepya et al., 2006). Fortunately the soils in southern Africa are not very sensitive to acidification (Kuylenstierna et al., 2001), although continuous acid deposition still poses a threat for the environment (Josipovic et al., 2011). On the other hand also the high spring-time O<sub>3</sub> concentrations pose a serious risk for agricultural production in southern Africa (e.g. van Tienhoven et al., 2006). Therefore, from air quality point of view, SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> should not be overlooked although PM<sub>10</sub> exceeds air quality standards more frequently at least in the vicinity of low-income residential areas.

## 5. Review of papers and author's contribution

I am solely responsible for the summary part of this thesis.

Paper I describes the instrumentation and technical solutions at the mobile measurement trailer, which is utilised in papers III–VII. Paper I also discusses the comparison measurements carried out at the SMEAR II station in Finland before the trailer was shipped to South Africa. I carried out most of the data analysis and wrote part of the text.

Paper II describes a measurement artefact at the Multi-Angle Absorption Photometer (MAAP), and describes correction algorithms for it. The measurement artefact appears only at high concentrations, but as biomass burning is widely spread in southern Africa, these algorithms are used to correct the black carbon concentration in papers IV–VII. I contributed to the field measurements and development of the correction algorithm in this paper.

Paper III describes seasonal and diurnal patterns in sub-micrometre aerosol size distribution in semi-clean and polluted savannah environments. It is shown that diurnal variation originates in regional new particle formation events and in the polluted savannah also in the domestic combustion for heating and cooking. The industrial emissions at the polluted savannah site were found to be mostly gaseous. The seasonal variation is attributed to a combination of combustion and lack of wet removal during the dry season. I contributed to the field measurements at the polluted savannah site, did all the data analysis, and wrote most of the text.

Paper IV describes new particle formation events at the semi-clean savannah site. The frequency of new particle formation events is found to follow the estimated sulphuric acid concentration, although the growth cannot be explained by sulphuric acid. The growth rate is found to have similar seasonality as in northern hemisphere, i.e. peaks during spring and late summer and a minimum during winter. The seasonality and air mass history suggests that the growth is connected to biogenic rather than anthropogenic precursors. I did all the data analysis and wrote most of the text.

Paper V describes new particle formation events at the polluted savannah site. The frequency of regional new particle formation events is reported to have a record high frequency, but the growth rate is observed to have still the same seasonality as at the semi-clean savannah. I contributed to the field measurements and data analysis, and to a minor extent to the text.

Paper VI discusses CCN production from regional new particle formation events at Botsalano and compares the observations to a global model. The CCN production from regional new particle formation events was found to exhibit a clear

seasonality, which the model cannot reproduce. I contributed to the field measurement data analysis and to a minor extent to the text.

Paper VII is an air quality assessment at the polluted savannah site. Exceedances of legislative thresholds for both gaseous and particulate pollutants are reported. PM10 mass concentration and O<sub>3</sub> concentration are identified as the source of quite frequent exceedances, but other pollutants stay within limits. I contributed to the field measurements and to the data analysis and to a minor extent to the text.



## 6. Conclusions

This study discusses submicron aerosol particle concentrations and sources in southern Africa, an environment with few previous observations covering a full seasonal cycle and extending to the ultrafine aerosol size range (Laakso et al., 2008). The results presented here are based on long-term measurements of aerosol particle and trace gas properties in three different environments: semi-clean savannah at Botsalano (Laakso et al., 2008; Papers III, IV and VI), polluted savannah at Marikana (Papers III, V and VII) and semi-clean grassland at Welgegund (Beukes et al., 2013). The first aim of this work was to establish a permanent measurement station in continental southern Africa as a reference point for global climate models. In co-operation with the North-West University in South Africa this has now been achieved at Welgegund.

Papers I and II describe the technical solutions used during the measurement campaigns. In addition having local partners committed to the measurements, frequent on site visits and detailed documentation of the measurement procedures in South Africa have been of critical importance in running the measurements at a high level. Even though the measurement setup has been designed to operate on minimal maintenance (Paper I), the weekly checks by the local partners have been a crucial element in the success of the campaign. On the other hand the measurement artefact in the Multi-Angle Absorption Photometer (MAAP) and the correction algorithms presented in Paper II are relevant for all MAAP measurements in high aerosol absorption conditions.

The second aim of this thesis was to study the concentrations, as well as diurnal and seasonal variations of submicron aerosol particles in continental southern Africa. The third aim was to study the most important sources of submicron aerosol particles in continental southern Africa. Paper III found the submicron aerosol particle concentrations at the semi-clean and polluted savannah sites to be at the high end of observations at comparable environments, but at the same time the CCN-sized particle concentrations were comparatively low. This is attributed to record high frequency of new particle formation in southern Africa combined with low primary aerosol emissions from industrial sources (Papers III, IV and V).

The seasonality of the CCN-sized particles at all study locations was found to depend on incomplete combustion together with lack of wet removal during the dry season (Paper III). At the cleaner environments, i.e. Botsalano and the clean sector at Welgegund, the seasonality is due to savannah and grassland fires (Paper III). In contrast at Marikana and also at Welgegund when air masses arrive from the direction of the megacity of Johannesburg, emissions from domestic heating dominate over the regional open biomass burning (Paper III). During the wet season new particle formation is a significant source of CCN-sized particles at least at Botsalano (Paper VI).

The regional new particle formation events at Botsalano and Marikana are studied in detail in Papers IV and V. The frequency of new particle formation is found to follow the estimated sulphuric acid concentration, which concurs with the central role of sulphuric acid in atmospheric nucleation in the northern hemisphere (e.g. Sipilä et al., 2010; Kulmala et al., 2013). However, the growth rates and especially the seasonality of the growth rate cannot be explained by the estimated sulphuric acid, but appear to be connected to biogenic volatile organic compound emissions (Papers IV and V). Also the aerosol particle formation rate at 12 nm was found to follow the seasonality of the growth rate (Papers IV and V).

From air quality point of view the aerosol emissions from domestic heating are a serious issue, at least close to low-income residential areas, and reducing these emissions would be very valuable for the communities (Paper VII). The other air pollutant that frequently exceeds air quality standards is O<sub>3</sub> (Paper VII), and the exceedances occur also at the cleanest studied environment. Savannah fires are a well-known source of O<sub>3</sub>. However, the seasonality and the increased frequency of high O<sub>3</sub> periods closer to the megacity of Johannesburg suggest that anthropogenic emissions may be a more important source of O<sub>3</sub>. Reducing industrial SO<sub>2</sub> emissions is also a topic of ongoing discussion in South Africa. In the light of this study, such reduced emissions may lead to a decrease in CCN-production during the wet season and therefore a decrease in the aerosol cooling effect – something that may happen also on global scale (e.g. Arneth et al., 2009).

In conclusion, four parameters have been identified as the most important for the concentrations of submicron aerosol particles and their climate effects in southern Africa. These are 1) SO<sub>2</sub>, which affects the frequency of regional new particle formation events (Paper IV), 2) biogenic VOC emissions, which affect the growth rate (Papers IV and V) and subsequently the survival probability of the newly formed particles up to CCN-sizes (e.g. Pierce and Adams, 2007), and 3) domestic heating and 4) open biomass burning (veldt fires), which are the most important sources during the dry season (Paper III). None of these parameters are likely to remain constant in the future. Air quality measures and socio-economic changes will most likely reduce the SO<sub>2</sub> emissions and emissions from the combustion sources. The predicted increase in temperature will also affect the biogenic VOC emissions (e.g. Guenther et al., 2006), even if the vegetation patterns remain unaffected. This highlights the need for process-level comparisons between observations and global climate models (e.g. Paper VI) to ensure that the models are able to predict the aerosol particle climate effects among changing anthropogenic and biogenic precursors in southern Africa.

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