

## Chemical composition, main sources and temporal variability of PM1 aerosols in southern African grassland

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### 1. Introduction

There are essentially no long-term high time resolution ambient aerosol chemical composition measurements available for Africa. Biomass burning processes generate significant amounts of PM1 aerosols over southern Africa during the dry season and also emit considerable amounts of combustion process trace gases. Biogenic secondary organic aerosols (BSOA) are expected to contribute a significant fraction of organic aerosols(OA) while anthropogenic aerosols formed from SO<sub>2</sub> and NO<sub>x</sub> emissions of fossil fuel combustions dominate inorganic submicron mass. This work provides an overview of the submicron chemical composition and oxidation levels in southern Africa and gives insights into the sources and atmospheric processing of organics aerosols at a site, Welgegund (North-West Province), well positioned to characterise influx of polluted industrial and urban source regions as well as cleaner background masses.

### 2. Location

The Welgegund measurement station (26°34'10"S, 26°56'21"E, 1480 m a.s.l.) is located approximately 100 km south-west of the Johannesburg-Pretoria conurbation with a population of over 10 million (Lourens *et al.*, 2012). There is no significant local pollution source close to the measurement site. However, it is frequently impacted by air masses from a number of country's major pollution source regions (the Johannesburg-Pretoria megacity, western and eastern "Bushveld Igneous" mining and metallurgical complexes, the petrochemical Vaal Triangle and mining, metallurgical and power-generation, industrial Mpumalanga Highveld). Importantly, air masses passing over the regional background from the west of Welgegund where no significant point sources exist regularly arrive at Welgegund (Beukes *et al.*, 2014).

### 3. Methods and instrumentation

#### 3.1 Instrumentation

The real-time measurements of non-refractory (evaporable at 600 C°) submicron aerosols (NR-PM1) were conducted with an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc.) from September 2010 to August 2011 at the Welgegund measurement station (<http://www.welgegund.org/>). The instrument is designed for continuous long-term measurements of the chemical composition of non-refractory submicron particulate matter and is based on the same technology as Aerodyne Aerosol Mass Spectrometers (AMS) (Ng *et al.*, 2011) (Figure 1).

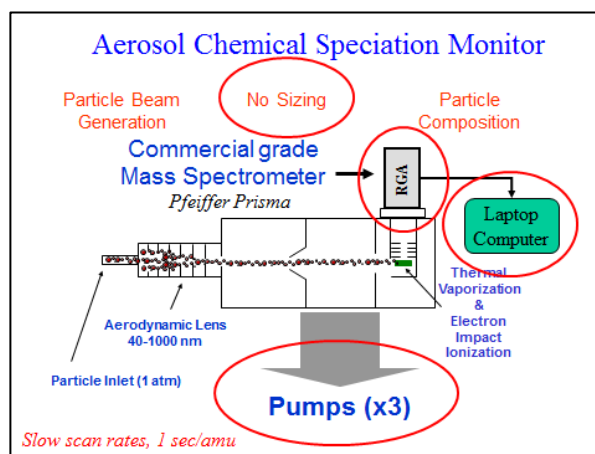


Figure 1: ACSM working diagram (source: Aerodyne Inc.)

Particle size distributions were measured with a differential mobility particle sizer (DMPS) system with a size range of 12–840 nm (Wiedensohler, 1998). Other ancillary data included trace gas concentrations and basic meteorological parameters. All instruments were checked and maintained at least once a week and data were

downloaded automatically to a server every day for daily quality control and quality assurance. All raw data were quality controlled and scientifically flagged before the data analyses, according to methods described by Laakso *et al.* (2008), and Vakkari *et al.* (2011).

### 3.2 Back Trajectories

The air mass history was investigated using back-trajectories calculated with the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) version 4.8 model. 96-h backtrajectories were obtained for every hour throughout the complete measurement period at an arrival height of 100 m (

Figure 2).

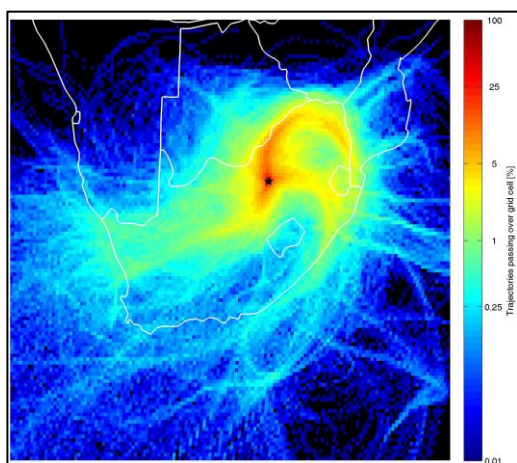


Figure 2: Hourly trajectories for Welgegund site (May 2010 - September 2011) (Beukes *et al.*, 2014)

### 3.3 Source regions identification

Based on air mass back-trajectories the source regions were recently defined for Welgegund by Beukes *et al.* (2014). They were classified into four source regions and were also applied in this study (Figure 3):

- the Industrial Highveld (**iHV**);
- the highly industrialised and relatively densely populated Vaal Triangle (**VT**);
- the anti-cyclonic recirculation of air masses over the South African interior with the Bushveld Igneous Complex (**ACBIC**);
- the regional background (**BG**), containing no large point sources, is located west from the Welgegund measurement site.

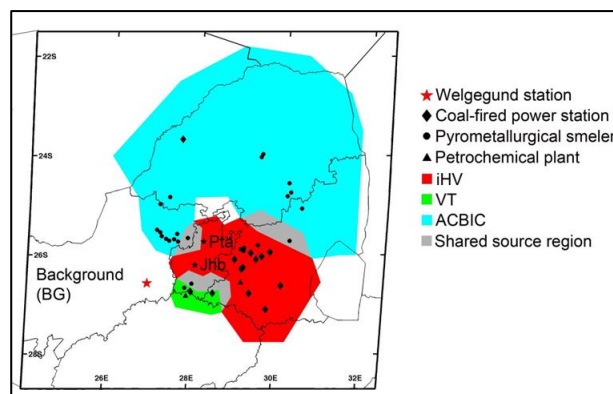


Figure 3: The measurement site and the air mass overpass regions (Beukes *et al.*, 2014).

### 3.4 Positive Matrix Factorisation (PMF)

The ACSM organic aerosol (OA) mass spectra were analysed through the use of PMF (Zhang *et al.*, 2005, 2011; Ulbrich *et al.*, 2009). We characterised the OA content and identified organic groups, their time-dependent concentrations and mass spectra (MS) from the OA dataset.

## 4. Results

The NR-PM<sub>1</sub> mass concentrations varied largely from less than 1  $\mu\text{g m}^{-3}$  to a maximum of 89  $\mu\text{g m}^{-3}$ . The aerosol composition was dominated by OA and sulphate compounds with the mean NR-PM<sub>1</sub> concentration of 7.5  $\mu\text{g m}^{-3}$  and total PM<sub>1</sub> of 9.1  $\mu\text{g m}^{-3}$ . Savanna fires occurring on a regional scale during the dry season increased both the primary combustion aerosols and the formation of secondary aerosols via combustion emitted precursor species. A significant fraction of the NR-PM<sub>1</sub> aerosols consisted of OA (63 % of total OA in the dry season and 37 % in the wet season). The composition OA differed and its concentration levels varied considerably between the seasons due to different sources and atmospheric conditions. For example, biomass burning organic aerosol (BBOA) represented 33 % of total OA in the dry season while no clear BBOA factor was identified in the wet season it was mixed with other factors. In general, OA was highly oxidised with average oxygen to carbon (O:C) ratios of 0.8 and 0.7 during the wet and dry season, respectively. The high oxidation levels and the differences between the seasons could be explained, at least partially, by the acidity of the aerosols. Highly oxidised organic aerosols were observed both during iHV and VT plumes (characterised by high  $\text{SO}_2^{-4}$  concentration) and anticyclonic circulation (characterised by long range transported aged aerosols) (Figure 4).

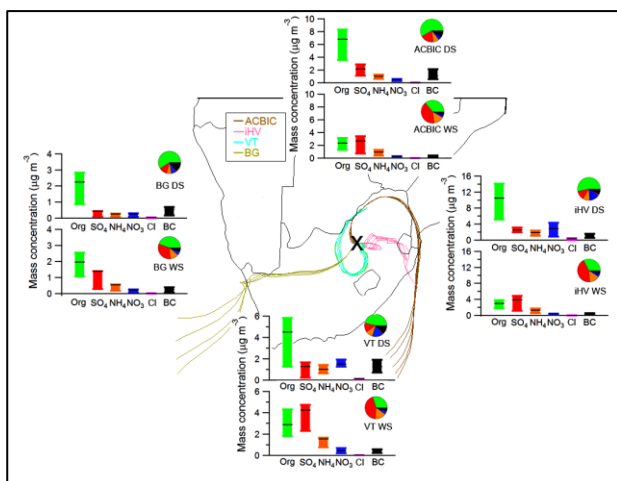


Figure 4: Summary of NR-PM1 & black carbon (BC) composition associated with each source region as well as representative 96 h backtrajectories marked in colours associated with the source regions. The box plots indicate the 25th and 75th percentiles and the line within the box marks the mean. Location of the Welgegend measuring site is marked as a black cross.

## 5. Conclusions

We measured non-refractory submicron aerosols (NR-PM1) and black carbon over a one year period in Welgegend, and investigated the seasonal and diurnal patterns of aerosol concentration levels, chemical composition, acidity and oxidation level. Based on air mass back trajectories, four distinct source regions were determined for NR-PM1. The dominant submicron aerosol constituent during the dry season was organic aerosol, reflecting high contribution from savannah fires and other combustion sources. Organic aerosol concentrations were lower during the wet season, presumably due to wet deposition as well as reduced emissions from combustion sources. Sulphate concentrations were usually high and exceeded organic aerosol concentrations when air-masses were transported over regions containing major point emission sources. Sulphate and nitrate concentrations peaked when air masses passed over the iHV area. In contrast, concentrations were much lower when air masses passed over the cleaner BG areas. Air masses associated with the ACBIC source region contained largely aged OA. PMF analysis of aerosol mass spectra was used to characterise the OA properties. The factors identified were oxidised organic aerosols (OOA) and BBOA in the dry season and low-volatile (LV-OOA) and semi-volatile (SV-OOA) organic aerosols in the wet season. The results highlight the importance of primary BBOA in the dry season, which represented 33% of the total OA. Aerosol

acidity and its potential impact on the evolution of OOA were highlighted as well.

## 6. Acknowledgments

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