

# The composition of ambient and fresh biomass burning aerosols at a savannah site, South Africa

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Atmospheric aerosols play a key role in climate change, and have adverse effects on human health. Given South Africa's status as a rapidly-developing country with increasing urbanisation and industrial growth, information on the quality of ambient air is important. In this study, the chemical composition of ambient particles and the particles in fresh biomass burning plumes were studied at a savannah environment in Botsalano, South Africa. The results showed that Botsalano was regularly affected by air masses that had passed over several large point sources. Air masses that had passed over the coal-fired Matimba power station in the Waterberg, or over the platinum group metal smelters in the western Bushveld Igneous Complex, contained high sulfate concentrations in the submicron ranges. These concentrations were 14 to 37 times higher compared with air masses that had passed only over rural areas. Because of the limited nature of this type of data in literature for the interior regions of southern Africa, our report serves as a valuable reference for future studies. In addition, our biomass burning study showed that potassium in the fresh smoke of burning savannah grass was likely to take the form of KCl. Clear differences were found in the ratios for potassium and levoglucosan in the smouldering and flaming phases. Our findings highlight the need for more comprehensive chamber experiments on various fuel types used in southern Africa, to confirm the ratio of important biomass burning tracer species that can be used in source apportionment studies in the future.

## Introduction

With regard to air quality, Africa is one of the least studied continents in the world. However, extensive aerosol measurements have been carried out in southern Africa within the framework of the SAFARI 92, SAFARI 2000 and EUCAARI campaigns.<sup>1,2</sup> The first two campaigns focused mainly on the emissions of biomass burning and regional transport in the atmosphere. The EUCAARI campaign focused on understanding the interactions between climate and air pollution around the world. Several other air pollution measurement studies in South Africa have focused on nucleation events, trace gases and optical properties of aerosols.<sup>3-8</sup> The chemistry of particles has been studied to a lesser extent.<sup>3-8</sup>

A few studies on the chemical characterisation or source apportionment of ambient aerosols have been conducted in Tanzania during the wet and dry seasons, and in various environments in Kenya.<sup>9-13</sup> However, apart from the SAFARI 2000 campaign (which included multiple studies in southern Africa), few reports have been published that focus on the chemical characterisation of aerosols in South Africa.<sup>1,14</sup> The most recent long-term measurements of aerosol chemical composition were conducted relatively close (approximately 100 km) to the Johannesburg–Pretoria megacity conurbation. In that study, different source regions were determined and the chemical characteristics of organics were investigated.<sup>15,16</sup>

The main objective of this paper is to contribute knowledge on the chemical composition of particles at a regional background location in North-West, a province of South Africa for which only sparse information on air quality is available. The chosen location is downwind of the Waterberg area on the dominant anti-cyclonic circulation route of air mass movement in this part of South Africa. The construction of a large new coal-fired power station, Medupi Power Station, in addition to the currently operational coal-fired power station in the Waterberg area, Matimba Power Station, highlights the need for such measurements to serve as a reference for future studies. Data on background aerosol chemical composition are also important because South Africa is a developing country with increasing urbanisation and industrial growth.

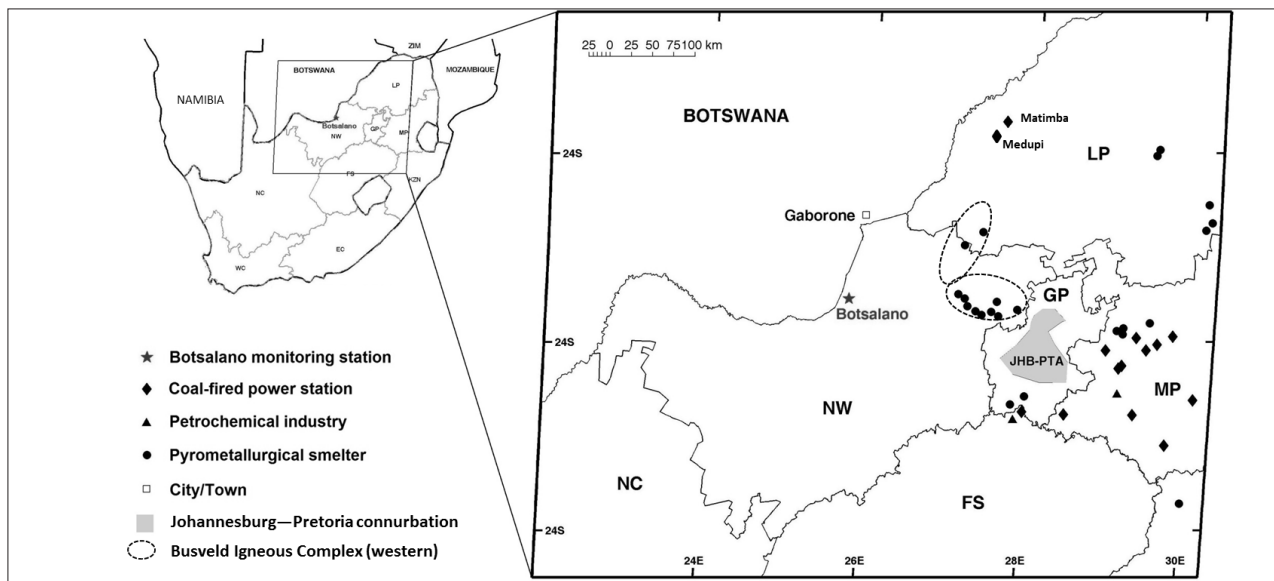
The sample site was chosen to represent a relatively clean background area with very little local pollution. The site gave us an opportunity to investigate how the chemical composition of aerosols changed depending on the origin of air masses. As far as we could assess, no other aerosol chemical composition studies have been published for this important area. Earlier studies have focused on the physical properties of aerosols at the site.<sup>17-19</sup> In this study we concentrated mainly on submicron particles, because particles that originate from anthropogenic and natural wildfire combustion sources are typically smaller than 1  $\mu\text{m}$  in aerodynamic size.

In addition to analysing the aerosol chemical composition of regional air masses, a biomass burning experiment was conducted onsite. This enabled us to investigate the chemical composition of aerosols originating from a fresh biomass burning plume.

## Methodology

### Site description and measurement periods

A mobile station for atmospheric measurement was deployed in the Botsalano game reserve in North-West Province, South Africa (25.541S, 25.754E, 1424 m AMSL).<sup>17,19</sup> This setting can be considered a dry savannah regional background site, with no major local anthropogenic sources. Figure 1 shows the main large sources around the measurement site. Briefly, the sector from north to south, in an easterly direction, contains several large sources. Possibly, one of the largest regional pollution source areas might be the mining and pyro-metallurgical smelting activities in the western limb of the Bushveld Igneous Complex (BIC).<sup>20-22</sup>



Key to provinces: LP, Limpopo; GP, Gauteng; MP, Mpumalanga; FS, Free State; NC, Northern Cape; NW, North West

**Figure 1:** Geographical map of southern Africa, indicating the location of the Botsalano measurement site (25.541S, 25.754E) and nearby large air pollution point sources.

The ambient measurements reported in this paper were carried out in two short campaigns during 9–15 October 2007 (spring) and 30 January–5 February 2008 (summer). In total, 11 sets of impactor samples with a typical 24-hour sampling time were collected. The meteorological conditions of Botsalano during the campaigns are presented in Figure 2. The beginning of the spring campaign was slightly colder than the summer campaign; otherwise the seasons had similar temporal variation in temperatures. The relative humidity and temperature were on average 19% and 22% higher, respectively, during the summer campaign compared with the spring campaign. The summer and spring campaign represented typical seasons, according to the study by Laakso et al. (2008) at the same site in 2006–2007.<sup>17</sup>

In addition to the ambient samples, a small-scale biomass burning measurement experiment was performed. During the biomass burning experiment, organic materials consisting mainly of dry grass and branches collected upwind of the site were burned. The distance between the sampling equipment and the fire was approximately 50 m. Two samples were collected. The first sample was taken from the main

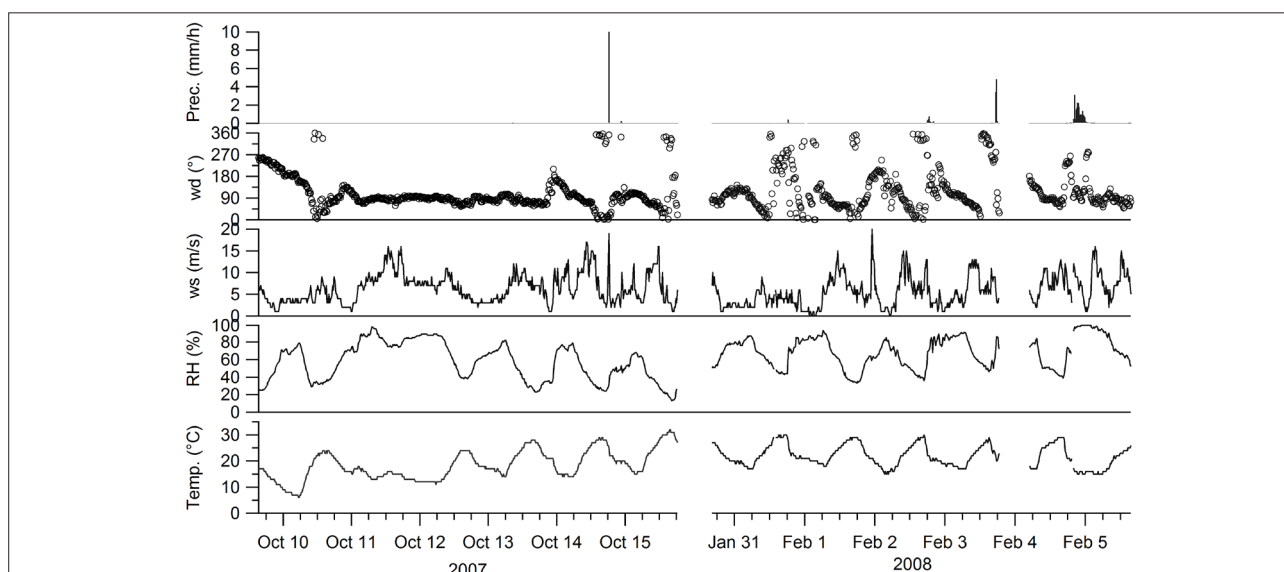
plume, which was sampled for 44 min, and the second sample was taken over 124 min during the period when the fire intensity and fuel amount were lower.

### Measurements

The samples were collected with a three-stage cascade impactor with aerodynamic cut-off diameters of 10  $\mu\text{m}$ , 2.5  $\mu\text{m}$  and 1  $\mu\text{m}$ , followed by a backup filter (Dekati®PM10). The PM10 inlet was used for cutting off particles greater than 10  $\mu\text{m}$ . The collection substrates were pre-heated quartz fibre filters (Tissuquartz, PALL). The sampling flow rate was 30 L/min and the sampling duration was approximately 24 h, except during the biomass burning experiment, when shorter sampling periods were utilised.

### Chemical analysis

Organic carbon (OC) and elemental carbon (EC) were analysed from a 1  $\text{cm}^2$  sample punched out of the quartz fibre filters, using a thermal optical carbon analyser (TOA; Sunset Laboratory Inc. Tigard, OR, USA).



**Figure 2:** Meteorological parameters (temperature, relative humidity, wind speed, wind direction, precipitation) during the campaigns.

The instrument uses a two-phase thermal method to separate OC and EC (EUSAAR\_1 and EUSAAR\_2).<sup>23</sup> Optical correction was performed to separate pyrolysed organic carbon from elemental carbon.

The sampled submicron particles ( $PM_{10}$ ) showed uniform deposition on the filters, but the larger fractions (particles  $> 1 \mu m$ ) were not uniformly spread. A previous study had shown that unevenly-spread samples yielded acceptable results when applying optical correction for impactor samples.<sup>24</sup> Therefore, we analysed all the samples. The amount of gaseous OC collected on the filters was not measured and hence was not subtracted from the concentrations of OC. The overall uncertainty of the TOA method was estimated to be 10% for OC and 20% for EC in concentrations above the quantification limit.

The field blank concentrations of OC for the backup filters ( $PM_{10}$ ), calculated for a one-day sampling period, were just above the detection limit during both the spring (measured amount was  $0.07 \mu g/m^3$ ) and summer (measured amount was  $0.10 \mu g/m^3$ ) campaigns. For the impactor stages, the combined corresponding blank concentrations were  $0.08 \mu g/m^3$  and  $0.09 \mu g/m^3$  during the spring and summer campaigns respectively. The blank concentration of EC was below the detection limit for the impactor stages ( $0.02 \mu g/m^3$ ) and for the backup filters ( $0.07 \mu g/m^3$ ). The measured OC concentrations were multiplied by a factor of 1.6 to obtain an estimate for total particulate organic matter (POM) mass concentration.<sup>25</sup>

The remaining portions of the quartz filters were analysed with ion chromatography (IC) to determine selected ions, namely chloride ( $Cl^-$ ), nitrate ( $NO_3^-$ ), sulfate ( $SO_4^{2-}$ ), oxalate, sodium ( $Na^+$ ), ammonium ( $NH_4^+$ ), potassium ( $K^+$ ), magnesium ( $Mg^{2+}$ ) and calcium ( $Ca^{2+}$ ). The uncertainty of the IC analysis was estimated according to the analysis of standards as 5% to 10%, depending on the ion analysed. The field blank concentration of each ion in the backup and impactor-stage filters was  $0.018 \mu g/m^3$  and  $0.008 \mu g/m^3$  respectively, during both campaigns. The determination limit was below  $0.002 \mu g/m^3$  for all the ions.

Concentrations of monosaccharide anhydrides (levoglucosan, galactosan and mannosan) collected on backup ( $PM_{10}$ ) filters were measured using an IC coupled to a quadrupole mass spectrometer.<sup>26</sup> The blank concentration of monosaccharide anhydrides was below the determination limit ( $1 \mu g/L$  to  $5 \mu g/L$ ), which corresponded to  $0.001 \mu g/m^3$  to  $0.005 \mu g/m^3$  for a 24-hour sample.

### Auxiliary data

Earlier publications<sup>17,19</sup> presented detailed descriptions of measurements obtained at Botsalano using a Differential Mobility Particle Sizer (DMPS), consisting of a Vienna-type Differential Mobility Analyser and TSI model 3010 Condensation Particle Counter. The measures included meteorological parameters (temperature, pressure, relative humidity, precipitation, wind speed and wind direction), trace gas concentrations ( $SO_2$ ,  $NO/NO_x$ , CO and  $O_3$ ) and submicron aerosol particle size distribution.

Total mass concentration of  $PM_{10}$  was not measured directly but was estimated from the DMPS size distribution, for the range 10 nm to 840 nm. For particles smaller than 840 nm, the particle number concentration of each DMPS size channel was converted to volume concentration (assuming spherical particles), multiplied by the estimated particle density, and summed to obtain the total mass concentration. The particle density value was calculated from the analysed chemical composition for each sample using an approach suggested by Saarnio et al.,<sup>27</sup> and it varied from 1.38 to  $1.75 g/cm^3$ .

### Air mass history

Air mass backward trajectories were calculated using the NOAA HYSPLIT backward trajectory model.<sup>28</sup> The 96-hour backward air mass trajectories were calculated to arrive at every hour of sampling, with an arrival height of 100 m above the ground.

## Results and discussion

### Overall ambient air results

An overview of the meteorological pattern in Botsalano showed that the north-easterly wind direction had the highest frequency.<sup>19</sup> This can be expected, as the meteorological pattern over the interior of South Africa

is dominated by an anticyclonic circulation pattern.<sup>29</sup> In addition, although Botsalano is a background site without significant local air pollution point sources, it is regularly affected by air masses that have passed over several large point sources. The Matimba coal-fired power station at Lephalale in the Waterberg, the silicon and platinum group metal (PGM) smelters near Polokwane, the PGM smelters in the Northam and Thabazimbi area, and the city of Gaborone are all situated on the dominant anticyclonic circulation path for air masses arriving at Botsalano. The mining and metallurgical activities in the western region, lying on the axis between the towns of Brits and Rustenburg (Bushveld Igneous Complex, BIC), are also likely to affect the site regularly.

The  $PM_{10}$  mass concentrations calculated from the DMPS results varied between  $1.4 \mu g/m^3$  and  $21.5 \mu g/m^3$  (mean  $11.3 \mu g/m^3 \pm 5.3 \mu g/m^3$ ). The total concentrations of all analysed components varied between  $2.9 \mu g/m^3$  and  $14.5 \mu g/m^3$  (mean  $9.0 \mu g/m^3 \pm 3.2 \mu g/m^3$ ). The lowest concentrations showed the greatest difference between mass concentration (estimated from DMPS) and the sum of analysed components, as shown in Figure 3. The mean ratio between these two measures was 0.84 and they were strongly correlated (Pearson  $r = 0.93$ ). Hence the analysed chemical components accounted for almost the entire total mass of the  $PM_{10}$  fraction. The lower mass concentration derived from DMPS was likely the result of a lower cut-off for particle size, compared with the PM sampler ( $840 nm$  vs  $1 \mu m$ ).

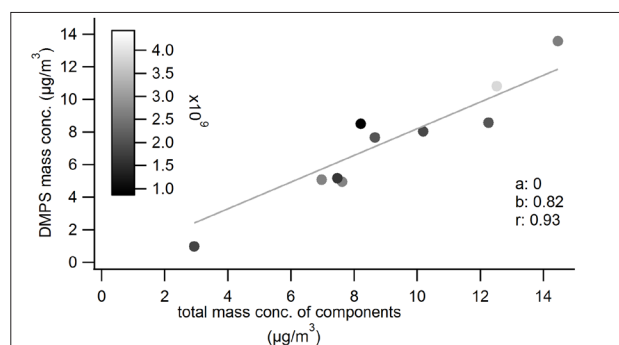


Figure 3: Mass concentrations of particles estimated from DMPS and the sum of the analysed components, greyscale-coded by total particle number concentration ( $\#/m^3$ ).

Figure 4 shows the  $PM_{10}$  fractional concentrations of the analysed components for the combined as well as the individual spring and summer campaigns. The mean values are shown in Table 1. For the combined results (spring and summer), sulfate had the highest individual component concentration at 44% ( $3.9 \mu g/m^3 \pm 2.3 \mu g/m^3$ ). POM was the second highest component at 39% ( $3.5 \pm 0.6 \mu g/m^3$ ). Two main cations, ammonium and potassium, contributed 11% and 2% respectively. The rest of the components together contributed approximately 4%.

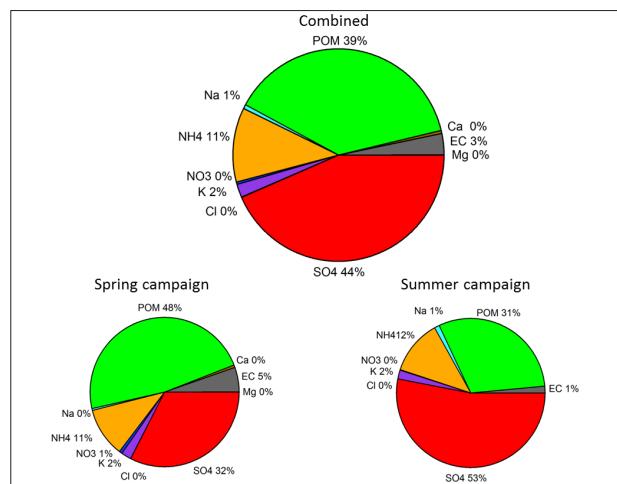


Figure 4:  $PM_{10}$  fractional component composition for ambient samples: summer, spring, and combined campaigns.

**Table 1:** Concentrations of particles ( $\mu\text{g}/\text{m}^3$ ) and gases (ppb) for spring, summer, all, and for the ambient case studies

	Spring	Summer	All	Case study 1	Case study 2	Case study 3
POM	3.63	3.25	3.46	2.21	3.28	3.47
SO <sub>4</sub> <sup>2-</sup>	2.48	5.65	3.92	0.20	2.82	7.48
NH <sub>4</sub> <sup>+</sup>	0.81	1.27	1.02	0.04	0.86	1.76
EC	0.40	0.16	0.29	0.28	0.34	0.20
NO <sub>3</sub> <sup>-</sup>	0.05	0.01	0.03	0.04	0.04	0.01
K <sup>+</sup>	0.17	0.20	0.18	0.03	0.16	0.36
Oxalate <sup>†</sup>	0.10	0.13	0.11	0.02	0.10	0.14
Ca <sup>2+</sup>	0.04	N/A		0.09	0.03	N/A
Na <sup>+</sup>	0.03	0.12	0.05	0.02	0.02	0.08
Mg <sup>2+</sup>	0.003	N/A		0.011	0.001	N/A
Cl <sup>-</sup>	0.004	BDL		0.005	0.003	BDL
Total <sup>#</sup> :	7.62	10.66	8.97	2.93	7.56	13.36
SO <sub>2</sub> (g)	1.16	0.64	0.93	0.05	1.36	0.52
NO <sub>x</sub> (g)	2.70	1.94	2.37	2.11	2.66	1.62
CO (g)	144	94	123	93	146	92
O <sub>3</sub> (g)	36	36	36	29	35	30

Case Study 1, regional background; Case Study 2, Waterberg overpass; Case Study 3, Western BIC overpass. Biomass burning experiments were excluded.

<sup>†</sup>Oxalate is also included in POM analysis

<sup>#</sup>Total particles, excluding oxalate

N/A, not analysed; BDL, below determination limit; g, gaseous compounds

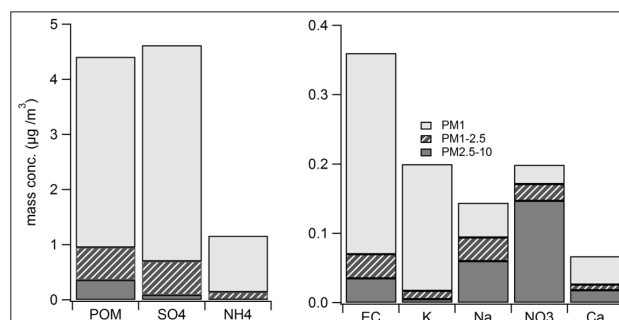
The equivalent ratio of sulfate to main cations for PM<sub>1</sub> indicated that sulfuric acid was not neutralised totally. The average contribution of sulfate in Botsalano was higher than the amounts measured in similar campaigns lasting approximately one year in various environments in Europe and China, and at Welgegund near Potchefstroom in South Africa.<sup>15,30,31</sup> However, at Welgegund a similar contribution has been noticed during the wet season, and similar findings have occurred in shorter campaigns at rural or remote sites in USA, Ireland and Japan.<sup>15,32</sup> According to aerosol mass spectrometer (AMS) studies, the overall average contribution of submicron sulfate and organic matter around the world are 32% (range 10% to 67%) and 45% (range 18% to 70%) respectively.<sup>32</sup>

A comparison of the results from the spring and summer campaigns showed that POM was the dominant component during spring, whereas sulfate dominated in summer. Sulfate concentrations were clearly higher during summer than spring, whereas the POM concentrations did not vary significantly between the two seasons (Table 1). It is well known that oxidation of SO<sub>2</sub> to sulfate occurs faster at higher relative humidity, as observed during summer, than in drier periods. The concentrations of SO<sub>2</sub> and the ratio of SO<sub>2</sub> to sulfate support this interpretation, with SO<sub>2</sub> clearly being lower during the summer campaign compared with spring. This finding indicates a faster removal of SO<sub>2</sub> in summer (Table 1).

Meteorological data for Botsalano, confirming the relative humidity levels, have previously been presented.<sup>17</sup> It has also been suggested that ozone (O<sub>3</sub>) concentrations might be positively correlated with the sulfur conversion rate.<sup>33</sup> However, in our study O<sub>3</sub> concentration did not show a substantial difference between summer (range 17 ppb to 63 ppb) and spring (range 11 ppb to 58 ppb), although solar radiation in summer was on average 28% higher than in spring.

The EC level during the spring campaign was substantially higher than during the summer campaign (Table 1), which confirms the influence of combustion during spring. Although the concentration of levoglucosan, a biomass burning marker,<sup>34</sup> remained relatively low throughout our study, it was substantially higher during spring than summer; the mean values were 0.010  $\mu\text{g}/\text{m}^3$  in spring and 0.006  $\mu\text{g}/\text{m}^3$  in summer. In addition, CO, which can be used as a gaseous tracer of combustion,<sup>35</sup> showed similar trends, with means of 145 ppb and 92 ppb during the spring and summer campaigns respectively.

As previously mentioned, we found that the total concentration of the components analysed was a good approximation for the total PM<sub>1</sub> mass, as calculated from DMPS data. Additionally, PM<sub>1</sub> particle depositions on the filters were uniform, whereas the larger-size fractions were not. Because mass closure could not be performed for the PM<sub>1-2.5</sub> and PM<sub>2.5-10</sub> size fractions, we do not discuss these fractions individually in detail but only in comparison with the PM<sub>1</sub> fraction. Figure 5 shows the analysed components for the various size fractions for the combined spring and summer ambient air sampling campaigns. From these data it is obvious that SO<sub>4</sub><sup>2-</sup>, POM, NH<sub>4</sub><sup>+</sup>, EC and K<sup>+</sup> were predominantly found in the PM<sub>1</sub> size fraction, whereas NO<sub>3</sub><sup>-</sup> occurred mostly in the coarser fractions. The size fraction analysis clearly indicates that the fine fraction (PM<sub>1</sub>) is dominated by water-soluble chemical compounds. Soil components, which were not analysed in this study, are likely to comprise the majority of the coarser fractions.



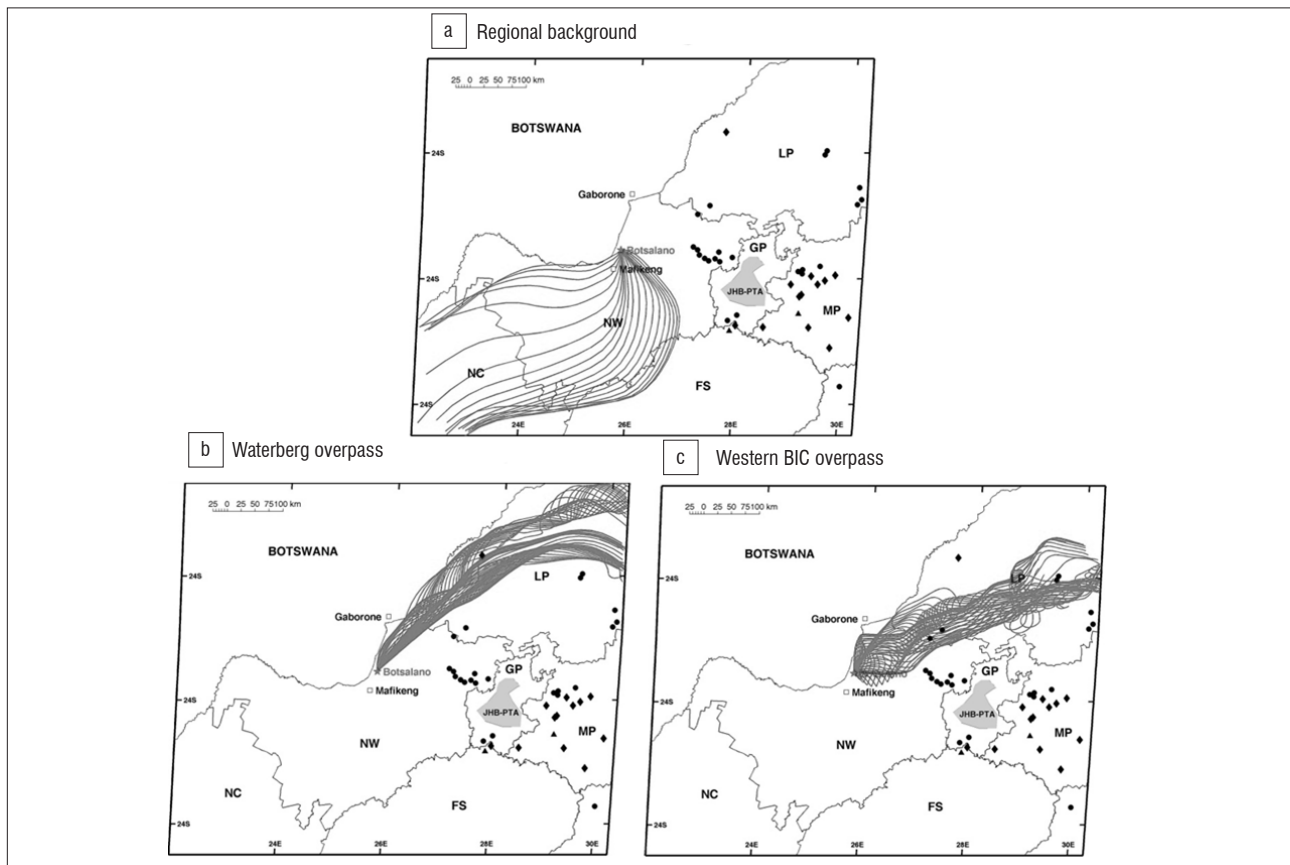
**Figure 5:** Comparison of PM<sub>1</sub>, PM<sub>1-2.5</sub> and PM<sub>2.5-10</sub> compositional analysis for the combined ambient campaigns.

### Ambient air case studies

In the previous paragraphs we established that the analysed chemical compounds were mainly found in the fine fraction (PM<sub>1</sub>). In addition, the mass balance could be calculated only for the PM<sub>1</sub> fraction. Therefore, the following case studies focus mainly on the PM<sub>1</sub> results.

**Case study 1:** Air masses that passed over the regional background  
According to backward air mass trajectory analysis, there was one sampling day (9–10 October 2007) when the air masses arrived at Botsalano from the south-west. In this direction there are no large air pollution point sources, apart from the town of Mafikeng (population approximately 260 000), as indicated in Figure 6a.

**Case study 2:** Air masses that passed over the Waterberg  
On three days during the sampling campaigns (11–12, 12–13 and 14–15 October 2007), air masses were likely to have been influenced by the coal-fired power station at Lephalale in the Waterberg, i.e. Matimba Power Station, without any influence from other large point sources (Figure 6b). The salience of this case study data is that at the time of writing, a second coal-fired power station – Medupi Power Station – had been commissioned for the Waterberg area. Matimba Power Station does not have equipment for removing sulfur and nitrogen gases from the emissions (de-SO<sub>x</sub> and de-NO<sub>x</sub>). By contrast, the newly-constructed Medupi Power Station will include such technology, although it is not yet clear if it will be implemented in the initial operations. The data in this case study could thus serve as a valuable reference for future studies in this region, to compare the concentrations of particles with and without NO<sub>x</sub> and SO<sub>x</sub> removal.



Key to provinces: LP, Limpopo; GP, Gauteng; MP, Mpumalanga; FS, Free State; NC, Northern Cape; NW, North West

**Figure 6:** Air mass history of identified ambient case studies: (a) regional background, (b) Waterberg overpass, (c) Western BIC overpass.

### Case study 3: Air masses that passed over the western BIC

On two days during the sampling campaign (30 January–1 February 2008), the air masses arriving at Botsalano had passed directly over the two closest PGM smelters in the western BIC, situated east of Rustenburg (Figure 6c). These air masses were also likely to have travelled over the PGM and silicon smelters near Polokwane, but not over any other large air pollution point sources. The large air pollution point sources in the western BIC are mainly ferrochrome and PGM smelters as well as base metal refineries.<sup>20</sup> The sampled air masses therefore do not represent all types of point sources that occur in the western BIC, but they do represent the PGM smelters occurring in this region.

### Comparison of case studies

In Table 1 the comparative results for the three case studies identified are listed. From these results it is clear that the background air masses we sampled were substantially cleaner than the anthropogenically-influenced air masses. This was despite a possible influence of pollution from Mafikeng on the background air masses sampled. The total concentrations of the components measured in the PM<sub>1</sub> fraction – which was also found to be a good approximation of the total PM<sub>1</sub> mass, as indicated earlier – were as follows: 2.9 µg/m<sup>3</sup> for the regional background, 7.6 µg/m<sup>3</sup> for the Waterberg overpass, and 13.4 µg/m<sup>3</sup> for the western BIC overpass.

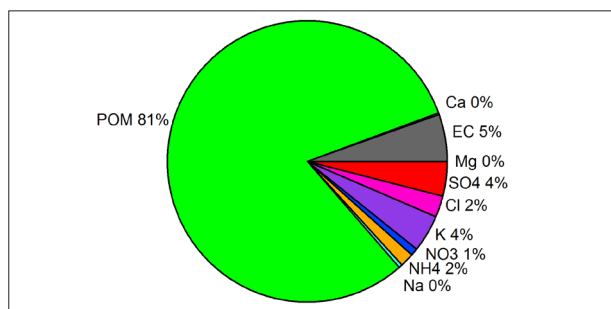
The anthropogenic influence of the large point sources on the chemical composition of the PM<sub>1</sub> fraction is especially apparent when sulfate compositions are considered. The regional background had a sulfate concentration of a mere 0.2 µg/m<sup>3</sup>, whereas air masses in the Waterberg overpass during spring and the Western BIC overpass during summer had levels of 2.8 µg/m<sup>3</sup> and 7.5 µg/m<sup>3</sup> respectively. During the Western BIC event, the sulfate-to-SO<sub>2</sub> ratio was higher than on average during the summer campaign, indicating faster oxidation of SO<sub>2</sub> or a longer transport time. The temperature and relative humidity during the event were similar to the averages, but the wind speed was lower than average. During the Waterberg event, the sulfate-to-SO<sub>2</sub> ratio was similar to the spring average.

### Samples from biomass burning experiments

During the ambient air sampling campaigns, no clear biomass burning plume could be identified, hence no ambient biomass burning plume case study is presented. The spring sampling season in mid-October was well past the peak activity of regional biomass burning, so we did not expect to find biomass-burning influences in the air masses. The highest levoglucosan concentration was 0.030 µg/m<sup>3</sup>, which was one order of magnitude lower than the background concentration (0.3 µg/m<sup>3</sup>) measured during the SAFARI 2000 campaign. The SAFARI 2000 campaign was conducted during a period of large-scale regional biomass combustion.<sup>35</sup>

Biomass burning is an important air pollution source in southern Africa, with implications for both air quality and climate change. To augment the ambient data already presented in this paper, data from the biomass burning experiment we conducted are presented in this section.

A fractional distribution graph of the time-weighted average for the various components analysed in the two biomass burning plume samples gives an overall indication of the relative importance of the components in fresh biomass burning plumes. These data are presented in Figure 7.



**Figure 7:** Time-weighted combined PM<sub>1</sub> fractional component composition of sampled biomass burning plumes.

The table shows that POM was much higher than the other components in the  $PM_{10}$  fraction. We realise that some of the detected OC might have been gaseous OC, as the amount of gaseous OC was not measured. Previous studies have shown the amount of gaseous OC in ambient measurement to be between 6% and 19%.<sup>9,27,37</sup> In our study, approximately a quarter of the analysed OC was vaporised during the first temperature step of the TOA analysis ( $T=75-200\text{ }^{\circ}\text{C}$ ), implying that these compounds were the most volatile. Some of these components might therefore have been gaseous OC absorbed or adsorbed into the filter substrate, or onto the particles collected on it. Despite this possibility, the dominance of POM in the  $PM_{10}$  fraction is evident.

The above finding is important, as it indicates that organic components released by biomass combustion during the dry season in southern Africa could play an important role during new particle formation and subsequent growth. This is in contrast to the wet season in southern Africa, when biogenic activities are mainly responsible for the release of organic components. The situation in southern Africa is therefore completely different from European and North American conditions, where biogenic activity is the main source of atmospheric organic compounds – at least in rural areas. The chemical and physical characteristics in the atmosphere are therefore likely to differ substantially across these continents.

The dominant contribution of POM to  $PM_{10}$  aerosol from biomass burning smoke supports the findings presented in a recent paper.<sup>38</sup> The relevant study had focused on the effect of biomass burning plumes on the formation and growth of ambient atmospheric aerosols in southern Africa, based on long-term data.<sup>38</sup> Apart from the high (81%) POM contribution to  $PM_{10}$  (Figure 7), further differences between biomass burning plume samples and other samples were the concentrations or the contributions of monosaccharide anhydrides, oxalate and potassium, which can be attributed as biomass burning tracers.<sup>36</sup> Their concentrations increased substantially during the biomass burning event, compared with the ambient samples. The concentration of submicron oxalate during the biomass burning event increased almost four-fold compared with the average of the ambient samples. However, the relative contribution of oxalate to POM (0.1%) was smaller than the oxalate contribution to all the ambient samples combined (2.7%). The contribution of  $K^+$  in  $PM_{10}$  during biomass burning (4% to 5%) was double that of the ambient samples (2%).

The ratios of monosaccharide anhydrides give information on the biomass burning material. The ratios of levoglucosan to mannosan and levoglucosan to galactosan in the first plume were 17.1 and 14.0 respectively; in the second plume, the ratios were 16.4 and 17.4 respectively. These ratios were quite similar to values measured in laboratory experiments in which savannah grass with acacia wood was burned (levoglucosan to mannosan ratio of 21.7, and levoglucosan to galactosan ratio of 15.2).<sup>39</sup> It has been reported that fresh smoke of savannah grass contains potassium chloride (KCl) particles, whereas aged smoke contains potassium sulfate ( $K_2SO_4$ ) and potassium nitrate ( $KNO_3$ ).<sup>36,40</sup> In our study,  $Cl^-$  was the most abundant anion (3%) in the first plume, followed by sulfate (2%) and nitrate (1%). These results indicate that most of the  $K^+$  was probably present as KCl. The calculation of equivalent ratios showed an excess of  $K^+$  compared with  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$ . However, if  $SO_4^{2-}$  was assumed to react first with  $NH_4^+$ , there was no excess sulfate left for  $K^+$ . The additional  $K^+$  might therefore be present as carbonaceous material such as  $K_2CO_3$ , which was detected in an earlier biomass burning study in southern Africa.<sup>41</sup>

Because components analysed in the coarse fractions ( $PM_{1-2.5}$  and  $PM_{2.5-10}$ ) are unlikely to approach mass closure, we present our results only in a comparative manner to the  $PM_{10}$  results (Figure 8). The dominance of the  $PM_{10}$  fraction in the overall  $PM_{10}$  chemical composition in fresh biomass burning plumes is evident from these results. More than 90% of the POM, EC,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $NH_4^+$  ammonium were in a  $PM_{10}$  fraction. The  $NO_3^-$ , Na<sup>+</sup> and oxalate were mainly in the  $PM_{10}$  fraction (62% to 83%), whereas at least 50% of  $Ca^{2+}$  was in the  $PM_{10}$  fraction.

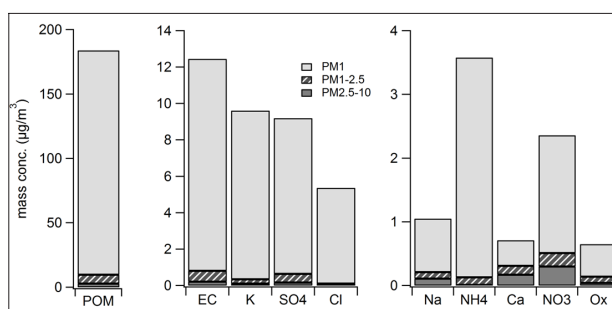


Figure 8: Comparison of  $PM_{10}$ ,  $PM_{1-2.5}$  and  $PM_{2.5-10}$  compositional analysis for the combined time-weighted average biomass burning plumes sampled.

## Conclusion

Size-segregated aerosol samples were collected using a three-stage impactor with backup filter at a relatively clean savannah environment at Botsalano Game Reserve in South Africa. The backup filter collected particles smaller than  $1\text{ }\mu\text{m}$ . Other size ranges were  $>10\text{ }\mu\text{m}$ ,  $2.5-10\text{ }\mu\text{m}$  and  $1-2.5\text{ }\mu\text{m}$ . Two campaigns were performed, one in spring (October 2007) and the other in summer (January–February 2008). In total throughout the entire study period, 11 sets of impactor samples were collected. In addition to these ambient measurements, a biomass burning experiment was performed to determine the chemical composition of fresh biomass burning fire plumes. Organic and elemental carbon, selected ions and monosaccharide anhydrides (e.g. levoglucosan) were analysed. These components essentially comprised the total mass of the  $PM_{10}$  fraction.

Results of the ambient air mass analyses indicated that sulfate, organic carbon, ammonium, elemental carbon and potassium were mostly associated with fine particles ( $PM_{10}$ ). Other components (sodium, chloride, nitrate and oxalate) were divided into fine and coarse fractions, but their concentrations were very small. POM was the dominant component during spring, whereas sulfate dominated in summer. Some indications of differing oxidation rates for  $SO_2$  were found between the seasons, explaining the higher sulfate concentrations during the summer campaign. Substantially higher elemental carbon concentrations in spring indicated the occurrence of more combusting processes compared with the summer campaign.

Although Botsalano is a background site, it is regularly affected by air masses that have passed over several large point sources. The anthropogenic influence of these large point sources on the chemical composition of the  $PM_{10}$  fraction was apparent, especially when the sulfate composition was considered. Air masses that passed over the coal-fired power station in Waterberg or the PMG smelter increased the sulfate concentration by 14 or 37 times compared with background air. Characterisation of air masses that had passed over the Waterberg area was especially important, because an additional large coal-fired power station was being commissioned at the time of writing (2015). The data presented here can be compared with the findings of similar studies, after the new coal-fired power station comes online. Comparisons can also be made between our data and those obtained after the de- $SO_x$  and de- $NO_x$  technologies of the new power station become operational. Such comparisons would help to assess the impact of large industrial developments in this region of South Africa.

The biomass burning study confirmed that potassium in fresh biomass plumes probably takes the form of KCl, for the most part, rather than  $K_2SO_4$  and  $KNO_3$ . Clear differences were also found in the ratios of potassium and levoglucosan in the smouldering and flaming phases. Our data highlight the need for more comprehensive chamber-type experiments on the major fuel types, to confirm the ratio of important biomass burning tracer species. Such information can, in future, be used to better quantify the contribution of biomass burning in source apportionment studies.

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## Authors' contributions

M.A. was the main investigator and wrote the primary manuscript; the study formed part of her PhD study, with S.S. as the degree supervisor. J.P.B. revised the manuscript, V.V. and L.L. maintained the research station and helped to generate the data, P.v.Z. made conceptual contributions, and K.T. assisted with chemical analysis. All authors reviewed and approved the final manuscript.

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