# Size-resolved characteristics of inorganic ionic species in atmospheric aerosols at a regional background site on the South African Highveld

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**Abstract**

Aerosols consist of organic and inorganic species, and the composition and concentration of these species depends on their sources, chemical transformation and sinks. In this study an assessment of major inorganic ions determined in three aerosol particle size ranges collected for one year at Welgegund in South Africa was conducted. $SO_4^{2-}$ and ammonium ($NH_4^+$) dominated the $PM_1$ size fraction, while $SO_4^{2-}$ and nitrate ($NO_3$) dominated the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions. $SO_4^{2-}$ had the highest contribution in the two smaller size fractions, while $NO_3^-$ had the highest contribution in the $PM_{2.5-10}$ size fraction. $SO_4^{2-}$ and $NO_3^-$ levels were attributed to the impacts of aged air masses passing over major anthropogenic source regions. Comparison of inorganic ion concentrations to levels thereof within a source region influencing Welgegund, indicated higher levels of most species within the source region. However, the comparative ratio of $SO_4^{2-}$ was significantly lower due to $SO_4^{2-}$ being formed distant from $SO_2$ emissions and submicron $SO_4^{2-}$ having longer atmospheric residencies. The PM at Welgegund was determined to be acidic, mainly due to high concentrations of $SO_4^{2-}$. $PM_1$ and $PM_{1-2.5}$ fractions revealed a seasonal pattern, with higher inorganic ion concentrations measured from May to September. Higher concentrations were attributed to decreased wet removal, more pronounced inversion layers trapping pollutants, and increases in

household combustion and wild fires during winter. Back trajectory analysis also revealed higher concentrations of inorganic ionic species corresponding to air mass movements over anthropogenic source regions.

**Keywords:** particulate matter; sulphate; nitrate; aerosol acidity; Welgegund

## 1 Introduction

Atmospheric aerosols or particulate matter (PM) are important components of the atmosphere with high temporal and spatial variability, which can have significant impacts on air quality and climate change (Boucher et al., 2013). Detailed physical and chemical characterisation are crucial in establishing the impacts of atmospheric aerosols (e.g. Andreae and Rosenfeld, 2008; Brunekreef and Holgate, 2002; Pope and Dockery, 2006; Pöschl, 2005). PM is usually classified according to their size as coarse ($PM_{10}$ – aerodynamic diameter < 10 μm), fine ($PM_{2.5}$ – aerodynamic diameter < 2.5 μm), submicron ($PM_1$ – aerodynamic diameter < 1 μm) and ultrafine ($PM_{0.1}$ – aerodynamic diameter < 0.1 μm) particulates. PM consists of a large number of chemical species (e.g. Booyens et al., 2015; Jimenez et al., 2009; Tiitta et al., 2014) of which the major inorganic ionic species usually considered include sulphate ($SO_4^{2-}$), nitrate ($NO_3^-$) and ammonium ($NH_4^+$), sodium ($Na^+$), potassium ($K^+$), chloride ($Cl^-$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$) and fluoride ($F^-$).

South Africa is a well-known source region of atmospheric pollutants as indicated by ground measurements and satellite retrievals over this region (e.g. Ghudea et al., 2009; Lourens et al., 2012; Sinha et al., 2004). South Africa has the largest industrialised economy in Africa, with significant industrial, mining and agricultural activities. Electricity is predominantly generated with coal-fired power plants that are centralised in the interior of South Africa. In addition, seasonal biomass burning (wild fires) also has a large impact on this region (e.g. Vakkari et al., 2013; 2014; Wai et al., 2014). In the interior of South Africa, the Welgegund measurement station (Beukes et al., 2013) located 100 km west of Johannesburg enables representative sampling of aerosols from both industrial source regions and regional background (Jaars et al., 2014; Tiitta et al., 2014), as well as studies on aerosol source processes such as biomass burning and new particle formation (Vakkari et al., 2014, 2015).

In this study, an assessment of major inorganic ions determined in three aerosol size ranges ($PM_1$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$) collected for one year at Welgegund is presented. The measurement of inorganic ions is especially important in South Africa, since the coal-fired power stations and most of the industries do not apply de-SOx and de-NOx technologies, which leads to elevated emissions of sulphur dioxide ($SO_2$) and nitrogen dioxide ($NO_2$), and the consequent formation of $SO_4^{2-}$ and $NO_3^-$. This paper is an extension of work presented in two previous papers wherein trace metals (Venter *et al.*, 2015) and organic compounds (Booyens *et al.*, 2014) determined in different size ranges for atmospheric aerosols collected at Welgegund were presented. In addition, this work supplements the work conducted by Tiitta *et al.* (2014), where $PM_1$ aerosols were chemically characterised with an aerosol chemical specification monitor (ACSM) (Ng *et al.*, 2011) during which organic aerosol (OA), $SO_4^{2-}$, $NH_4^+$, $NO_3^-$ and $Cl^-$ concentrations were determined on-line with 30-minute time resolution. Furthermore, inorganic ion

concentrations determined at Welgegund (a regional background site) are compared with levels of these species within a declared air quality priority area (indicating a source region with significantly high pollutant concentrations), which is also one of the major anthropogenic source regions impacting on Welgegund. These latter measurements were conducted at Marikana that is situated within the Bushveld Igneous Complex that forms part of the Waterberg Priority Area (Government Gazette, 2012).

## 2 Experimental

### 2.1 Site description

#### 2.1.1 Welgegund

Aerosol sampling was performed at the Welgegund atmospheric measurement station (www.welgegund.org, 26.569786 S and 26.939289 E, 1 480 m a.s.l.). Welgegund is situated on a commercially owned farm with no large pollution sources within proximity (~100 km). The site is situated in the interior of South Africa so that it is frequently impacted by air masses moving over the most important source regions in the interior of South Africa (e.g. the western Bushveld Igneous Complex, Vaal Triangle, Mpumalanga Highveld and the Johannesburg-Pretoria conurbation), as well as a relatively clean background region with no large point sources. In Beukes et al. (2013), Jaars et al. (2014) and Tiitta et al. (2014), maps indicating the location of Welgegund and a detailed description of site, which include site selection, prevailing biomes and major source regions are presented. Of the auxiliary measurements at Welgegund (Petäjä et al., 2013) only precipitation (by a Vaisala QMR102 tipping bucket) are utilised in this study.

#### 2.1.2 Marikana

Marikana (25.69845 S, 27.48056 E, 1170 m a.s.l.) is a village situated approximately 35 km east of Rustenburg, 110km north of Welgegund. Maps indicating the location of Marikana were presented by Hirsikko et al. (2012), Van Zyl et al. (2014) and Venter et al. (2012). Marikana is located within the western Bushveld Igneous Complex, which is well known for comprehensive mining and metallurgical activities (Beukes et al., 2013; Van Zyl et al., 2014; Venter et al., 2012). The site was situated in a residential area on the property of the Marikana municipal clinic. A detailed description of the measurement site and possible sources of pollutants are presented in Venter et al. (2012).

## 2.2 Sampling and analysis

PM samples were collected at Welgegund from 24 November 2010 until 28 December 2011. A Dekati (Dekati Ltd., Finland) $PM_{10}$ cascade impactor (ISO23210) equipped with Teflon filters was used to collect different particulate size ranges, i.e. $PM_{2.5-10}$, $PM_{1-2.5}$ and $PM_1$. The pump flow rate was set at 30 L/min. Samples were collected continuously for one week, after which filters were changed. A total of 54 samples were collected for each of the three size ranges.

An Airmetrics MiniVol™ portable air sampler was used for aerosol sample collection at Marikana for one year from November 2008 until October 2009. Two MiniVol samplers were used simultaneously to collect $PM_{10}$ and $PM_{2.5}$ samples (Airmetrics, 2011). A programmable timer controlled the pump in order to achieve sample collection of 12 hours per day for six days, beginning either at 06:00 for daytime data, or at 18:00 for night time data. Each sample contained PM collected for 72 hours. The actual sampling time and flow rate (5 L/min) were taken into consideration to determine the atmospheric concentrations of the species. All filter samples collected at Welgegund and Marikana were sealed-off in containers, which were stored in a freezer prior to analyses.

The filters were divided into two equal parts by a specially designed punching system, to be able to analyse both trace metals (Venter et al., 2015) and inorganic ions using a single set of samples. The inorganic ions in the aerosols collected on the Teflon filters were extracted with 5 mL deionised water (18.2 MΩ) in an ultrasonic bath for 30 minutes. Extracted aqueous samples were subsequently analysed with a Dionex ICS 3000 ion chromatograph (IC), with an IonPac AG18 (2 mm x 50 mm) guard and IonPac AS18 (2 mm x 50 mm) analytical column. The inorganic ionic species determined (with their detection limits indicated in brackets) included $SO_4^{2-}$ (9.4 ppb), $NH_4^+$ (4.0 ppb), $NO_3^-$ (6.0 ppb), $Na^+$ (5.8 ppb), $K^+$ (4.4 ppb), $Cl^-$ (4.8 ppb), $Ca^{2+}$ (14.2 ppb), $Mg^{2+}$ (20.5 ppb) and $F^-$ (10.4 ppb) ($F^-$ were not determined for samples collected at Marikana due to limitations of the analytical technique at the time when these samples were analysed).

## 2.3 Air mass history analysis

Individual 96-hour back trajectories arriving hourly with an arrival height of 100 m were calculated with HYSPLIT 4.820.19 (Draxler & Hess, 2004; Lourens et al., 2011; Venter et al., 2012) for the entire sampling period. An arrival height of 100 m was chosen since the orography in HYSPLIT is not very well defined with lower arrival heights resulting in increased error margins on individual trajectory calculations, which are estimated as 10-30 % of the distance travelled (Stohl et al., 2002).

## 3 Results

### 3.1 Size resolved inorganic ion concentrations

In Fig. 1, the concentrations of each of the inorganic ionic species determined in the three size ranges for Welgegund samples are presented. $SO_4^{2-}$, $NH_4^+$, $K^+$ and $F^-$ concentrations were significantly higher in the $PM_1$ size fraction, with concentrations of these species in the $PM_1$ size fraction approximately an order of magnitude higher compared to the levels of these species in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions. Slightly higher levels of $NO_3^-$, $Cl^-$ and $Mg^{2+}$ were measured in the $PM_{2.5-10}$ size fraction in relation to levels of these species in the other two size fractions, while $Na^+$ and $Ca^{2+}$ concentrations were evenly distributed in all three size ranges. $SO_4^{2-}$ levels in $PM_1$ were approximately three times higher than $NH_4^+$ in the $PM_1$ size fraction, while being an order magnitude higher compared to the concentrations of $NO_3^-$, $Na^+$, $K^+$ and $Ca^{2+}$ in all three size ranges, as well as to the concentrations of $SO_4^{2-}$and $NH_4^+$ in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions. $SO_4^{2-}$ concentrations in the $PM_1$ size fraction were two orders of magnitude higher compared to $Cl^-$, $Mg^{2+}$ and $F^-$ levels in all three size ranges. The median $SO_4^{2-}$, $NH_4^+$, $K^+$ and $F^-$ concentrations in the $PM_1$ fraction were 1.35 μg/m$^3$, 0.440 μg/m$^3$, 0.032 μg/m$^3$ and 0.015 μg/m$^3$, respectively. The median levels of $NO_3^-$, $Cl^-$ and $Mg^{2+}$ in the $PM_{2.5-10}$ size fraction were 0.057 μg/m$^3$, 0.007 μg/m$^3$ and 0.006 μg/m$^3$, respectively. The highest median concentrations for $Na^+$ were 0.021 μg/m$^3$ in the $PM_{1-2.5}$ size fraction, while $Ca^{2+}$ had the highest median of 0.014 μg/m$^3$ in the $PM_{2.5-10}$ size fraction.

**Insert Fig. 1**

The normalised contribution percentages of each of the inorganic ionic species in terms of their ionic concentrations observed at Welgegund are presented in Fig. 2 for the three size fractions. It is evident that the $PM_1$ size fraction is dominated by $SO_4^{2-}$ and $NH_4^+$, while the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions are dominated by $SO_4^{2-}$ and $NO_3^-$. However, $SO_4^{2-}$ was the most dominant species in both the smaller size fractions, while $NO_3^-$ had the highest concentration in $PM_{2.5-10}$. In South Africa $SO_4^{2-}$ in the smaller size fractions (especially $PM_1$) can be considered to be predominantly a secondary pollutant resulting from the oxidation of $SO_2$ in aged air masses (Tiitta et al., 2014; Vakkari et al., 2015). Most industries in South Africa utilise particulate filters to filter out particulates in off-gas. Therefore, primary emissions of $SO_4^{2-}$ are unlikely. However, as mentioned previously, most industries in South Africa do not employ de-SOx and de-NOx technologies (e.g. Collett et al., 2010; Lourens et al., 2011), which leads to higher $SO_2$ and $NO_2$ emissions. Furthermore, the highly industrialised interior of South Africa is characterised by anti-cyclonic recirculation of air masses wherein the aging of pollutant species occurs (Lourens

et al., 2012). Recently Vakkari et al. (2015) also indicated significant $SO_4^{2-}$ formation in connection to new particle formation in South Africa. Particulate $NH_4^+$ is almost exclusively a secondary formed aerosol (Seinfeld & Pandis 2006) and thus most of the inorganic ions in the $PM_1$ fraction at Welgegund can be considered to be of secondary origin. As mentioned previously, Tiitta et al. (2014) chemically characterised $PM_1$ aerosols with an ACSM at Welgegund, which also indicated higher contributions of $SO_4^{2-}$ and $NH_4^+$ to the chemical content in $PM_1$ aerosols.

**Insert Fig. 2**

Atmospheric $NO_3^-$ can mainly be attributed to the oxidation of $NO_2$ gaseous emissions associated predominantly with fossil fuel combustion (e.g. coal-fired power stations) and industries not employing de-$NO_x$ technologies as mentioned above. Vehicular emissions also contribute to increased $NO_2$ emissions on the South African Highveld (Lourens et al., 2016), while the significant contribution of household combustion for space heating and cooking on $NO_2$ levels has also been indicated (e.g. Venter et al., 2012). The much lower $NO_3^-$ concentrations in the $PM_1$ fraction can be ascribed to the high $SO_4^{2-}$ levels substituting $NO_3^-$ in $NH_4NO_3$ (Seinfeld & Pandis, 2006). In addition, the higher $NO_3^-$ contribution in the $PM_{2.5-10}$ size fraction are indicative of the influence of aged marine air masses, where hydrogen chloride has been displaced from NaCl by $HNO_3$ vapour to form $NaNO_3$ (Turner & Colbeck, 2008). This is also signified by the higher percentage contribution of $Na^+$ in the $PM_{2.5-10}$ size fractions. It is also important to note that since the primary sources of $SO_2$ and $NO_2$ in the northern interior of South Africa are coal-fired power stations, $SO_2$ emissions are directly proportional to the amount of coal combusted whereas $NO_2$ emissions vary depending on the burner technology implemented by each power station (Pretorius et al., 2015). Therefore the relative $SO_4^{2-}$ and $NO_3^-$ concentrations could also be related to the differences in emissions of $SO_2$ and $NO_2$ from coal-fired power plants.

Furthermore, the $PM_{2.5-10}$ size fraction also has higher percentage contributions from $Cl^-$, $Mg^{2+}$, $Ca^{2+}$ and $Na^+$ compared to the other two size fractions, which can be attributed to larger particles originating from marine (e.g. $Na^+$ and $Cl^-$) and terrigenous sources (e.g. $Ca^{2+}$ from wind-blown dust). Although Fig. 1 indicated that the concentrations of $Na^+$ and $Ca^+$ species were evenly distributed in all three size fractions, much lower contributions from $SO_4^{2-}$ and $NH_4^+$ in the $PM_{2.5-10}$ size fraction lead to an increase in the relative contribution of these species to the total inorganic ionic content. In addition, the $NO_3^-$, $Cl^-$ and $Mg^{2+}$ concentrations are higher in the $PM_{2.5-10}$ size fraction (Fig. 1). The marine influence on the PM composition was also estimated by comparing the ratios of $SO_4^{2-}$, $Cl^-$, $Mg^{2+}$, $K^+$ and $Ca^{2+}$ to $Na^+$ (assuming $Na^+$ is only of marine origin) with reference ratios of these species with

regard to $Na^+$ as presented by Keene et al. (1986), which are presented in Table 1. The significantly higher ratios of $SO_4^{2-}/Na^+$, $K^+/Na^+$ and $Ca^{2+}/Na^+$ compared to reference ratios indicate a very small contribution from marine sources on levels of these species measured at Welgegund. However, the $Mg^{2+}/Na^+$ ratio in all three size fractions were close to the sea water ratio, especially in the $PM_1$ size fraction, indicating a strong marine influence on $Mg^{2+}$ concentrations. The lower $Cl^-/Na^+$ ratio determined can be attributed to $Cl^-$ depletion in marine air masses (Feng et al., 2017) and the influence of non-marine species in the PM collected (Mouli et al., 2003).

**Insert Table 1**

### 3.2 Acidity

The acidity of atmospheric aerosols has an influence on their hygroscopicity, as well as their ability to produce heterogeneous sulphate and secondary organic aerosols (Jang et al., 2002; Pathak et al., 2011). As discussed by Tiitta et al. (2014), it is possible to estimate the acidity of PM by comparing the measured $NH_4^+$ mass concentration to the amount of $NH_4^+$ needed to completely neutralise the anions that were calculated using Eq. (1):

$$NH_{4\,cal}^{+} = 18 \times \left(2 \times \frac{SO_4^{2-}}{96} + \frac{NO_3^-}{62} + \frac{Cl^-}{35.5}\right) \quad (1)$$

Here, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ are the mass concentrations of the ions ($\mu g/m^3$) and the denominators correspond to their molecular weights, with 18 being the molecular weight of $NH_4^+$. If the measured $NH_4^+$ concentration is lower than the calculated values, particles are considered to be 'more acidic' or, if the two values are equal, they are considered 'bulk neutralised'. This approach assumes a minimal influence of metal ions, organic acids and bases on $NH_4$ concentration (Zhang et al., 2007). Only $PM_1$ was considered due to its significance in secondary aerosol formation, while $SO_4^{2-}$ and $NH_4^+$ were predominantly in the $PM_1$ size fraction as indicated in Fig. 2. The calculated $NH_4^+$ concentrations plotted against the measured values for $PM_1$ are presented in Fig. 3. In this figure, the 1:1 line corresponds to the bulk neutralised state, the dry months comprise the three driest months during the sampling period, i.e. July 2011 to September 2011, and the wet months include the months with the highest rainfall, i.e. December 2010 to February 2011 and November 2011 to December 2011. It is evident from the results that the submicron aerosols are closer to the neutralised state in the dry months than in the wet months. However, during wet and dry months, the $PM_1$ aerosols are essentially acidic in nature, implying that the atmospheric $NH_4$

concentration was insufficient to neutralise all $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ anions. From the results presented in Fig. 1 and 2, it could be deduced that $SO_4^{2-}$ was the dominating acidic ion, which indicates that a fraction of $NO_3^-$ and $Cl^-$ anions must be associated with cations other than $NH_4^+$. These results agree with previous observations by Tiitta et al. (2014) obtained from $PM_1$ measurements with an ACMS. In addition, Conradie et al. (2016) also indicated that rain samples collected at four sites in the interior of South Africa were in most instances acidic, with $SO_4^{2-}$ also the main acidic ion. In Fig. 3, the circled points indicate values that did not lie close to the linear fitted lines of the dry and wet season data. Although these data points were considered in the afore-mentioned linear fits, they clearly indicate somewhat different behaviour. Obviously, these 'outliers' could be as a result of sampling artefacts or the assumptions made in this approach, i.e. minimal influence of metal ions, as well as organic acids and bases on $NH_4$ concentrations (Zhang et al., 2007). However, these data points could also indicate that the aerosol acidities might be extremely acidic or basic on certain occasions, especially, aerosols in the wet season. $SO_4^{2-}$ levels in the wet season could also by possibly increased during cloud processing, which is considered to be efficient in secondary $SO_4^{2-}$ formation (Husain et al., 1991). Back trajectory analysis performed for these weeks during which these outlier values were determined did not reveal any particular sources/source regions. It is recommended that future studies utilise high-volume samplers to collect aerosol samples over shorter periods (e.g. 24 hours) to better quantify the influence of specific sources/source regions on the acidity of aerosols.

**Insert Fig. 3**

### 3.3 Comparison with inorganic ion concentrations measured within a source region

In order to contextualise the inorganic ion concentrations measured at Welgegund, the results were compared to levels determined for inorganic ionic species at Marikana. As mentioned previously, Marikana is situated within the industrialised Bushveld Igneous Complex, which is one of the major source regions influencing air masses measured at Welgegund (Beukes et al., 2013; Jaars et al., 2014; Tiitta et al., 2014). Venter et al. (2012) reported high $PM_{10}$ concentrations measured at Marikana, with $PM_{10}$ levels exceeding South African legislative standard limits.

In Fig. 4, the concentrations of each of the inorganic ionic species determined in two size ranges, i.e. $PM_{2.5}$ and $PM_{2.5-10}$ at Marikana are presented. As mentioned, MiniVol samplers were used to collect total $PM_{10}$ and $PM_{2.5}$ at Marikana. Therefore, $PM_{2.5-10}$ concentrations were calculated by subtracting $PM_{2.5}$ from the $PM_{10}$ measurements. Similar to measurements at Welgegund, $SO_4^{2-}$ and $NH_4^+$ occurred predominantly in the smaller size fraction

($PM_{2.5}$) with median concentrations of 1.83 μg/m$^3$ and 0.55 μg/m$^3$, respectively. $K^+$ concentrations were also higher in the $PM_{2.5}$ size fraction with a median concentration of 0.09 μg/m$^3$, while slightly higher median concentrations, i.e. 0.09 μg/m$^3$ and 0.07 μg/m$^3$ were measured for $Na^+$ and $Cl^-$, respectively, in the $PM_{2.5}$ size fraction compared to the $PM_{2.5-10}$ size fraction. Comparison of the concentrations of $K^+$ in the different size fractions indicate a larger concentration of $K^+$ in the $PM_{2.5-10}$ size fraction in relation to the $PM_{2.5}$ size fraction at Marikana compared to significantly lower concentrations measured at Welgegund in the $PM_{2.5-10}$ size fraction with respect to the $PM_1$ and $PM_{1-2.5}$ size fractions. $Na^+$ and $Cl^-$ concentrations in the $PM_{2.5-10}$ size fraction relative to the smaller size fractions at Welgegund were also higher compared to $PM_{2.5-10}$ levels in relation to $PM_{2.5}$ concentrations measured at Marikana. However, this can be attributed to the $PM_{2.5}$ size fraction containing both the $PM_1$ and $PM_{1-2.5}$ size fractions. $Ca^+$ and $Mg^+$ concentrations were higher in the $PM_{2.5-10}$ size fraction with median concentrations of 0.16 μg/m$^3$ and 0.05 μg/m$^3$, respectively, while the median $NO_3^-$ concentration was marginally higher in the $PM_{2.5-10}$ size fraction, i.e. 0.28 μg/m$^3$. The higher $Ca^+$, $Mg^+$ and $NO_3^-$ concentrations determined in the $PM_{2.5-10}$ size fraction in relation to the $PM_{2.5}$ size fractions are similar to the measurements at Welgegund where levels of these species were also higher in the $PM_{2.5-10}$ size fraction with respect to the smaller size fractions. At Marikana $SO_4^{2-}$ levels were approximately three and six times higher than $NH_4^+$ and $NO_3^-$ levels, respectively, while being an order magnitude higher compared to the concentrations of $Na^+$, $K^+$, $Ca^{2+}$, $Cl^-$ and $Mg^{2+}$ in both size ranges.

**Insert Fig. 4**

In Fig. 5, the normalised distribution percentages of the median concentrations of each inorganic ionic species in the $PM_{2.5}$ and $PM_{2.5-10}$ size-fractions measured at Marikana are presented. It is evident that the $PM_{2.5}$ size fraction is dominated by $SO_4^{2-}$, with $NH_4^+$ being the second most abundant species, which is similar to Welgegund where $SO_4^{2-}$ and $NH_4^+$ dominated the $PM_1$ and $PM_{1-2.5}$ size fractions. The high $SO_4^{2-}$ contributions in the $PM_{2.5}$ size fraction can be attributed to the strong influence of pyrometallurgical activities on the aerosols sampled in this region. It is well known that the platinum group metals (PGM) industries in the western Bushveld Igneous Complex are associated with high $SO_2$ emissions associated with sulphidic ores, without the concomitant formation of $NO_2$ associated with coal-fired power plant emissions (Xiao and Laplante, 2004). Van Zyl et al. (2014) also indicated the high elemental sulphur content in PM sampled in this region (as indicated with scanning electron microscopy-energy dispersive spectrometry). In addition, the highest contribution of $NO_3^-$ in the $PM_{2.5-10}$

size fractions at Marikana is similar to Welgegund where $NO_3^-$ also had the highest concentration in the $PM_{2.5-10}$ size fraction. The contribution of $Ca^{2+}$ in the $PM_{2.5-10}$ size fraction at Marikana, which is the second most abundant species in this size fraction at Marikana, is also similar to the contribution of $Ca^{2+}$ at Welgegund. However, a larger contribution of $Na^+$ in the $PM_{2.5-10}$ size fraction is observed at Welgegund compared to Marikana.

**Insert Fig. 5**

In general, the concentrations of all the inorganic species were higher at Marikana compared to Welgegund, with the exception of $NH_4^+$ that had similar concentrations in the $PM_1$ and $PM_{2.5}$ size fractions at Welgegund and Marikana, respectively. $SO_4^{2-}$ levels in the smaller size fractions ($PM_1$ and $PM_{2.5}$ size fractions at Welgegund and Marikana, respectively) were approximately 1.5 times higher at Marikana, while concentrations of $NO_3^-$, $Cl^-$, $Mg^{2+}$ $Na^+$ and $Ca^{2+}$ were an order of magnitude higher compared to levels thereof at Welgegund in the $PM_1$, $PM_{2.5}$ and $PM_{2.5-10}$ size fractions. $K^+$ levels in the $PM_{2.5}$ size fraction at Marikana (the smallest size fraction measured at Marikana that also contains $PM_1$ aerosols) were approximately 3 times higher than $K^+$ concentrations at Welgegund in the $PM_1$ size fraction (the size fraction that contained the highest $K^+$ concentration). Higher levels of inorganic species are expected, since Marikana is situated within a source region with a large number of industrial and mining activities, as well as a dense population that contributes to emissions from household combustion for space heating and cooking. However, it is of significance to note that, although $SO_4^{2-}$ levels were higher at Marikana compared to the regional background Welgegund site, the ratio (approximately 1.5) was substantially lower compared to the comparative ratios of other inorganic species measured at Marikana and Welgegund. This observation signifies the regional, and not only local, impact of $SO_2$ emissions from pyrometallurgical industries in the western Bushveld Igneous Complex. As mentioned previously, $SO_4^{2-}$ is predominantly a secondary pollutant in South Africa, which can be formed distant from $SO_2$ sources. Therefore, $SO_4^{2-}$ levels can also be relatively high at sites considered to be regional background or remote sites. $SO_4^{2-}$ levels at the industrialised Marikana site can also be additionally influenced by the regional impact of $SO_2$ emissions from coal-fired power stations. In addition, $SO_4^{2-}$ occurs predominantly in submicron particles that have longer atmospheric lifetimes and are transported over longer distances, compared to e.g. $NO_3^-$ in larger particles that are deposited faster from the atmosphere and closer to the source. This is also substantiated by similar concentrations determined for $NH_4^+$ at Marikana and Welgegund. Conradie et al. (2016) also indicated that $SO_4^{2-}$ were the dominant inorganic ion in rain samples collected, not only within proximity of anthropogenic sources, but also at

remote and/or background sites in the north-eastern interior of South Africa. The regional impacts of $SO_4^{2-}$ have also been indicated for other areas in the world (e.g. Yeh et al., 2015). Laban et al. (2018) also showed that concentrations of the secondary pollutant, $O_3$, were high at sites in the north-eastern interior of South Africa considered to be background sites due the regional impacts of precursor species.

As mentioned previously, day- and night-time samples were collected at Marikana. Comparisons between the concentrations of the inorganic ions measured during day- and night-time in the $PM_{10}$ and $PM_{2.5}$ size fractions did not reveal significant differences in concentrations of the ionic species, with the exception of $NO_3^-$ and $Cl^-$ concentrations in the $PM_{2.5}$ size fraction that were higher during night time, as indicated in Fig. 6. Venter et al. (2012) indicated increased $NO_2$ concentrations during night-time associated with household combustion at Marikana, which can be related to increased night-time $NO_3^-$. $Cl^-$ can be associated with fresh biomass burning emissions (Aurela et al., 2016) and therefore higher night-time $Cl^-$ can also be attributed to the influence of household combustion.

**Insert Fig. 6**

### 3.4 Temporal and spatial variability

In Fig. 7, the total monthly concentrations of the inorganic ionic species in $PM_{2.5-10}$ (a), $PM_{1-2.5}$ (b) and $PM_1$ (c) measured at Welgegund are presented, with the contributing concentrations of each of the inorganic ions indicated. No distinct seasonal pattern is observed for the $PM_{2.5-10}$ size fraction. However, the $PM_{1-2.5}$ and $PM_1$ size fractions indicated higher inorganic ion concentrations from May to September and May to August, respectively. These periods with elevated inorganic ion levels can at least partially be ascribed to seasonal variations in meteorological parameters. The months with higher inorganic ion concentrations in the $PM_{1-2.5}$ and $PM_1$ size fractions coincide with the cold and dry winter months experienced in this part of South Africa. Winter in South Africa occurs typically between June and August, which is associated with increased air mass recirculation, as well as more pronounced lower inversion layers that inhibit vertical mixing in the atmosphere and trap pollutant species near the surface (Grstang, 1996). Winter is also related to additional combustion of coal and wood for domestic heating, which results in elevated aerosol particle concentrations (Vakkari et al., 2013; Venter et al., 2012). Furthermore, this part of South Africa is characterised by distinct wet and dry seasons, with the dry season occurring typically between mid-May and mid-October (Tiitta et al., 2014). In Fig. 8, the monthly precipitation measured during the entire sampling period at Welgegund is presented, which clearly indicates a period with low

rainfall, i.e. May to September. Therefore, the removal rate of atmospheric PM is also reduced during these dry months. The influence of wet deposition on atmospheric inorganic ion concentrations is also illustrated by the difference in the concentrations measured for December 2010 and December 2011 (Fig. 7). Precipitation was higher in December 2010 compared to December 2011, which resulted in increased wet deposition of inorganic ionic species in December 2010. In addition, the periods with elevated levels of inorganic ions in the $PM_{1\text{-}2.5}$ and $PM_1$ size fractions coincide with increased occurrences of biomass burning (wild fires) from July to September (e.g. Vakkari et al., 2013 and 2014). Furthermore, although no clear seasonal pattern is observed for $PM_{2.5\text{-}10}$, the influence of weather (winter and precipitation) is to a certain extent reflected in higher inorganic ion concentrations measured in July and September in this size fraction, as well as much lower inorganic ion concentrations measured in December 2010 and January 2011, i.e. months associated with higher rainfall. (Fig. 8).

**Insert Fig. 7**

**Insert Fig. 8**

ACSM measurements conducted by Tiitta et al. (2014) indicated that $SO_4^{2-}$, $NH_4^+$, $NO_3^-$ and $Cl^-$ concentrations in $PM_1$ depended strongly on air mass history. Therefore, back trajectory analysis were performed for each of the sampling months, which are presented in Fig. 9 in order to establish the influence of air mass history on monthly inorganic ion concentrations. In Fig. 9, the typical source areas are represented by polygons. The blue polygon indicates the combined Vaal Triangle Airshed Priority Area, Highveld Priority Area and Gauteng (i.e. Johannesburg-Pretoria megacity conurbation). The red polygon incorporates the Waterberg Priority Area and the typical anti-cyclonic recirculation pathway of air masses sampled at Welgegund. From Fig. 9, it is evident that the frequency of air masses arriving at Welgegund passing over the two source regions and the background regions is different for certain months.

**Insert Fig. 9**

Similar air mass movements are observed for December 2010, April 2011, May 2011, August 2011, October 2011, November 2011 and December 2011 indicating frequent influences from the anti-cyclonic recirculation pathway passing over the Bushveld Igneous Complex (part of the Waterberg Priority Area) (Government Gazette, 2012). The difference in inorganic ion concentrations measured in December 2010 and

December 2011 can be ascribed to the influence of wet deposition on atmospheric PM, as discussed previously (Fig. 8). The inorganic ion levels determined in April 2011, October 2011, November 2011 and December 2011 were similar in all three size fractions, with the exception of inorganic ion concentrations in $PM_{1-2.5}$ in October. These months also had similar levels of rainfall, as indicted in Fig. 8. Higher inorganic ion concentrations were determined in May 2011 and August 2011 (especially in May 2011) in the $PM_1$ and $PM_{1-2.5}$, which can be attributed to these months being dry leading to a decrease in wet removal thereof. During June 2011, much lower inorganic ion concentrations were determined in the $PM_1$ and $PM_{1-2.5}$ size fractions compared to the higher inorganic ion concentrations measured in these two size fraction during the other colder and dryer months (May to September). Back trajectory analysis (Fig. 9) reveals that during June 2011, Welgegund was much more frequently impacted by air masses passing over the background region, leading to lower concentrations of inorganic ions. It is also evident from Fig. 9 that Welgegund was more frequently influenced by air masses passing over the Johannesburg-Pretoria conurbation in July 2011, with associated higher inorganic ion concentrations in all three size fractions, especially in the $PM_{2.5-10}$ size fractions. January 2011 and February 2011 back trajectories indicated more frequent influences from marine air masses at Welgegund, which are reflected in the higher $NO_3^-$ and $Na^+$ concentrations measured in the $PM_{2.5-10}$ size fraction in February 2011. As mentioned previously, the lower inorganic ion concentrations in January 2011 can be attributed to high precipitation and the associated wet deposition (Fig. 8).

The monthly concentrations of each of the inorganic ions in the three size fractions reflect the normalised contributing concentrations for the entire sampling period at Welgegund presented in Fig. 2, i.e. the smaller size fractions are dominated by $SO_4^{2-}$, while $NO_3^-$ concentrations were the highest in the $PM_{2.5-10}$ size fractions. The relatively large contribution from $NH_4^+$ in the $PM_1$ size fraction is also evident for each of the months, while the influence of the marine and crustal species on the $PM_{2.5-10}$ size fraction is also reflected in the monthly concentrations. A distinct seasonal pattern is observed for $NO_3^-$ in the $PM_1$ size fraction, with $NO_3^-$ concentrations only evident from June to October with elevated concentrations thereof from July to September. These higher $NO_3^-$ levels coincide with the peak biomass burning season from July to September. Vakkari et al. (2014) indicated that aerosols in fresh biomass burning (wild fires) plumes measured at Welgegund consisted of 7 to 10% $NO_3^-$. In aged biomass burning plumes, lower $NO_3^-$ concentrations are expected, since $SO_4^{2-}$ would have reacted with $NH_4NO_3$, which effectively removes $NO_3^-$ from that particulate phase. Therefore, fresh biomass burning plumes can be considered a source of $NO_3^-$ in the $PM_1$ size fraction. Higher $NO_3^-$ concentrations are also evident in August and September in the $PM_{1-2.5}$ size fractions, which can also be attributed to biomass burning emissions. A similar seasonal pattern is observed for $Cl^-$ in the $PM_{1-2.5}$ size fraction with relatively higher $Cl^-$ levels from July to

September, which can be attributed to primary biomass burning emissions (Vakkari et al., 2014). Tiitta et al. (2014) indicated a strong influence of biomass burning on organic aerosol and total $PM_1$ concentrations. In addition, Aurela et al. (2016) indicated that KCl was likely to occur in fresh smoke of burning savannah grass. However, a less significant impact of biomass burning is observed on the inorganic ionic species concentrations.

## 4 Conclusions

This paper presents the concentrations of inorganic ion species determined in aerosol samples collected in three size ranges, i.e. $PM_1$, $PM_{1-2.5}$ and $PM_{2.5-10}$ collected at Welgegund. $SO_4^{2-}$ concentrations in the $PM_1$ size fraction were significantly higher compared to the other species in all three size fractions, as well as levels thereof in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size ranges. $NH_4^+$ in the $PM_1$ size fraction and $NO_3^-$ in the $PM_{2.5-10}$ size fraction were the second and third most abundant species, respectively. Normalised contribution percentages indicated that $SO_4^{2-}$ and $NH_4^+$ dominated the $PM_1$ size fraction, while $SO_4^{2-}$ and $NO_3^-$ were the predominant species in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions. $SO_4^{2-}$ had the highest contribution in the two smaller size fractions, while $NO_3^-$ had the highest contribution in the $PM_{2.5-10}$ size fraction. $SO_4^{2-}$ and $NO_3^-$ levels were attributed to the impacts of aged air masses passing over source regions with high $SO_2$ and $NO_2$ emissions, while marine air masses were also considered a source of $NO_3^-$.

In general it is concluded that the anthropogenic $SO_4^{2-}$ dominates the inorganic ion budget at Welgegund and causes the aerosol to be acidic, which may have adverse implications for the environment (Jang et al., 2002; Pathak et al., 2011).

Comparison of the inorganic ion concentrations measured at Welgegund to measurements of these species at Marikana, which is situated within one of the major anthropogenic/industrial source regions influencing Welgegund, indicated that the concentrations of almost all the inorganic ion species were higher at Marikana. $SO_4^{2-}$ concentrations were also the highest at Marikana, which were approximately 1.5 times higher compared to levels thereof Welgegund. The concentrations of most of the other species were an order of magnitude higher. The smaller size fraction at Marikana was also dominated by $SO_4^{2-}$ and $NH_4$, while the larger size fraction was also dominated by $NO_3^-$. The comparative ratio of $SO_4^{2-}$ at Marikana and Welgegund was significantly lower in relation to the comparative ratios of most of the other inorganic ions at the two sites, which was attributed to the $SO_4^{2-}$ being a secondary aerosol that can be formed distant from the sources of $SO_2$, as well as $SO_4^{2-}$ occurring predominantly in submicron particulates that can be transported over longer distances in the atmosphere and influence background/remote sites.

The $PM_1$ and $PM_{1-2.5}$ fractions indicated higher inorganic ion concentrations from May to September. These months coincide with the colder and dryer months in this part of South Africa. Therefore, higher concentrations were mainly attributed to increases in pollutant concentrations associated with recirculation of air masses, more pronounced inversion layers trapping pollutants near the surface and increased emissions, in conjunction with a decrease in the wet removal of these species. In addition, air mass history of each of the sampling months revealed higher concentrations of inorganic ionic species corresponding to air mass movements over source regions, which also emphasises the significance of anthropogenic sources at Welgegund. Furthermore, biomass burning, which significantly affects OA (Tiitta et al., 2014), has only a minor effect (~10%) on inorganic ion concentrations by being a source of $NO_3$, Cl (and possibly K in $PM_1$) as indicated by increases in these species during the biomass burning season.

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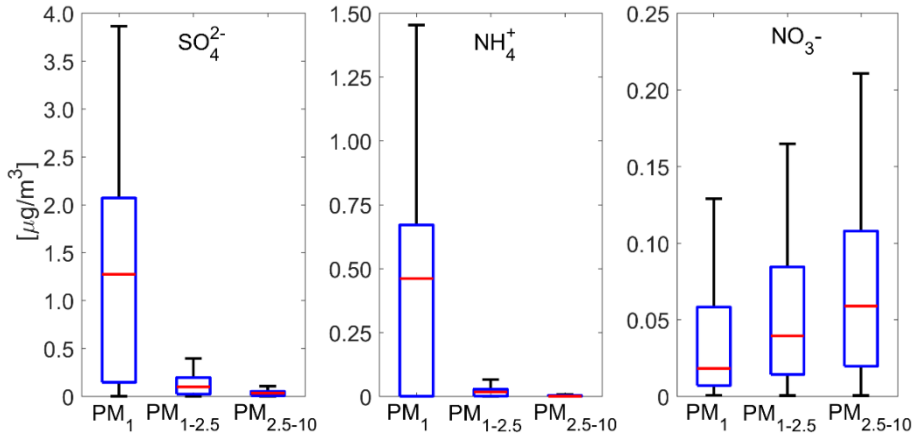


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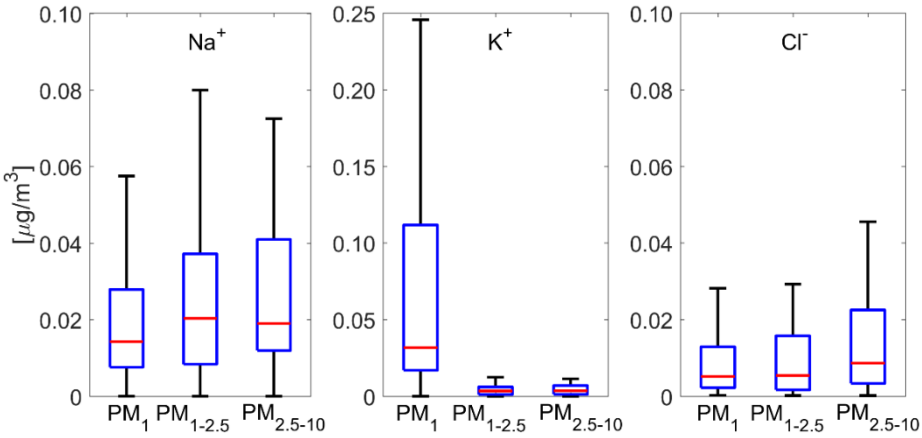


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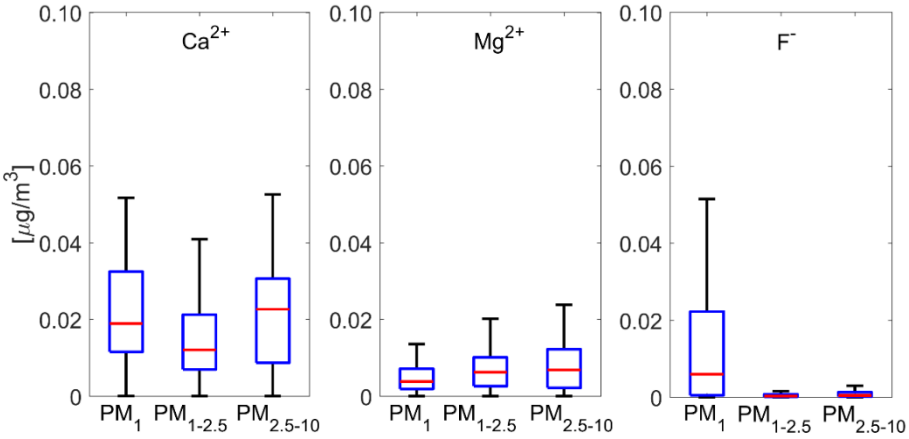



3

4 **Fig. 1** Boxplots of the concentrations of inorganic ionic species for $PM_1$, $PM_{1\text{-}2.5}$ and $PM_{2.5\text{-}10}$ measured at
5 Welgegund. The median (red line), 25$^{th}$ and 75$^{th}$ percentiles (blue box) and ± 2.7 times the standard deviation
6 (whiskers) are indicated

7

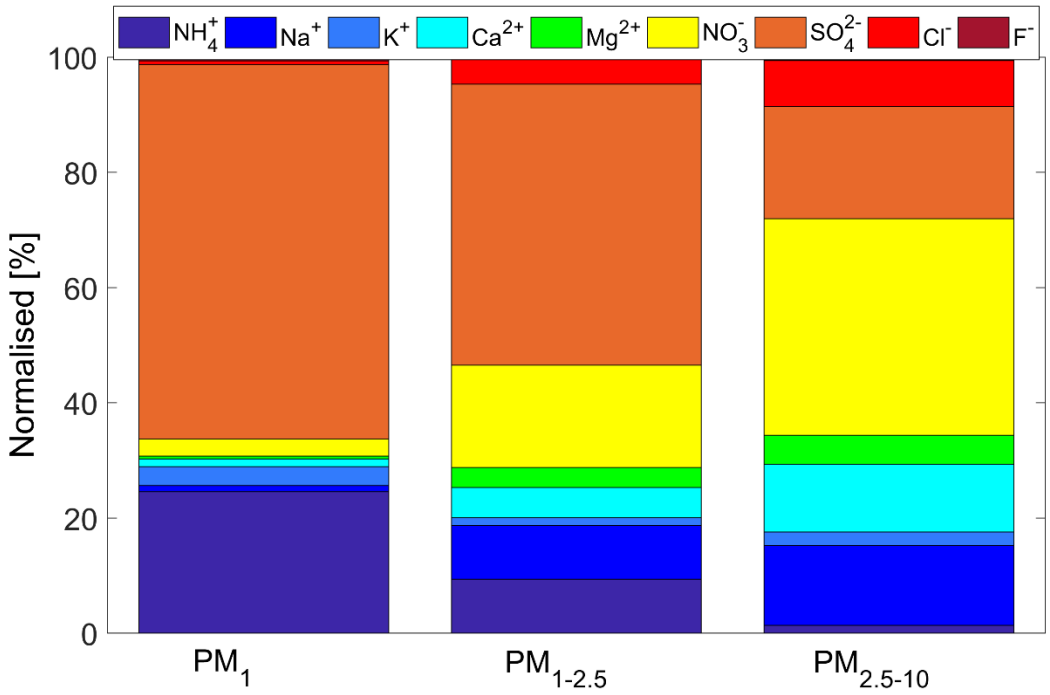
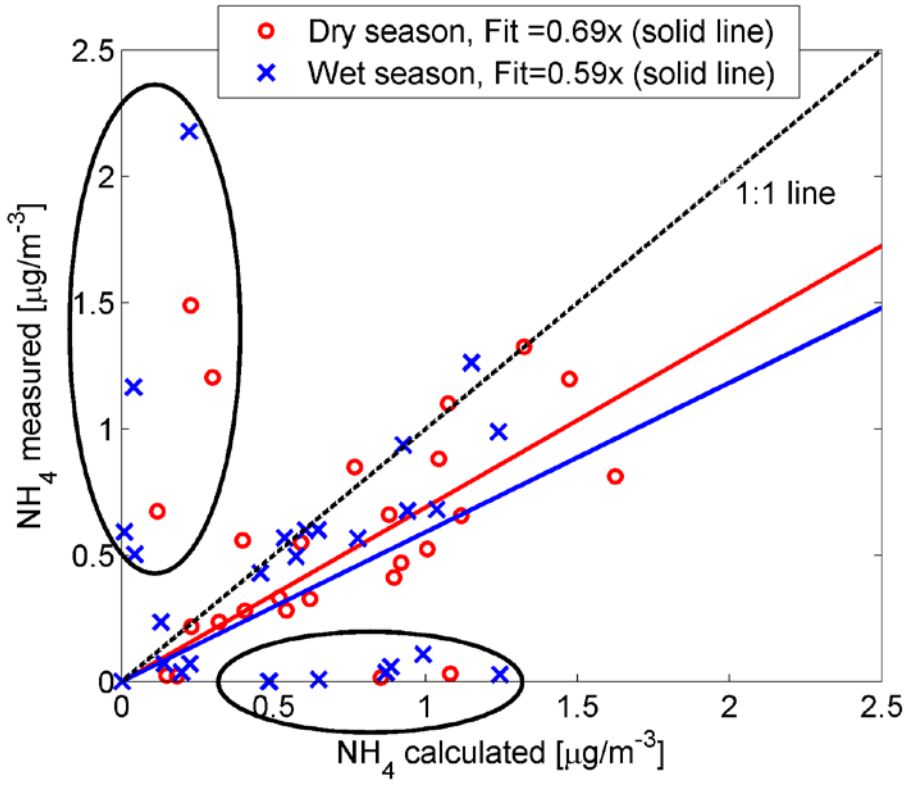



**Fig. 2** Normalised concentration distribution of the inorganic ionic species measured at Welgegund

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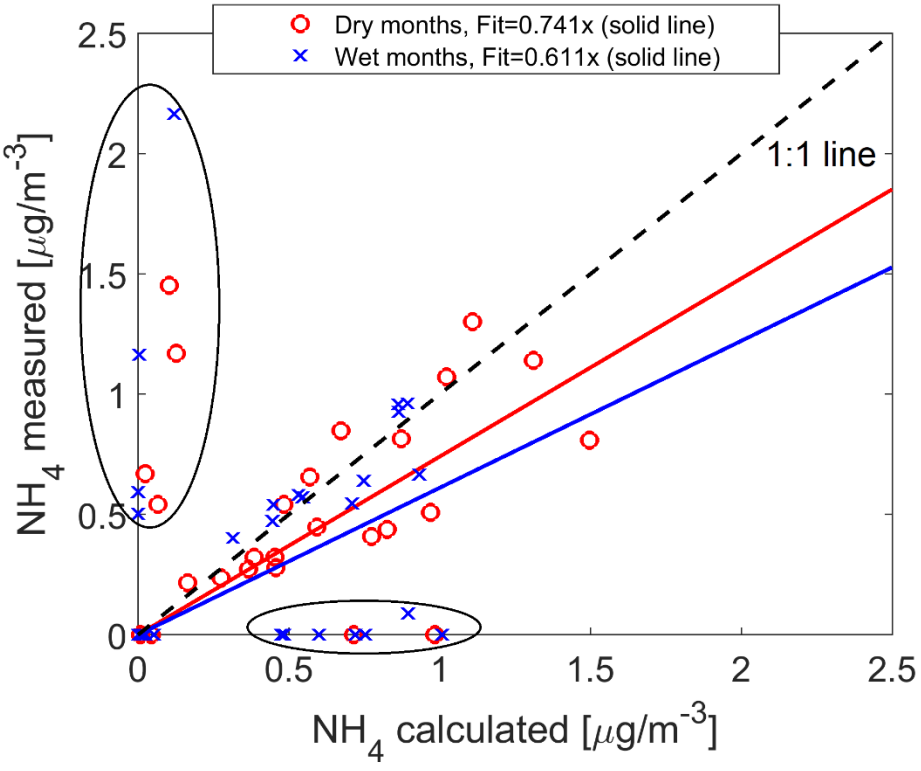



2

3 **Fig. 3** The measured $NH_4$ concentrations are plotted in relation to the calculated $NH_4$ values for $PM_1$. The red
4 circle and red trend line represent the dry months, while the blue crosses and blue trend line are for the wet months

5

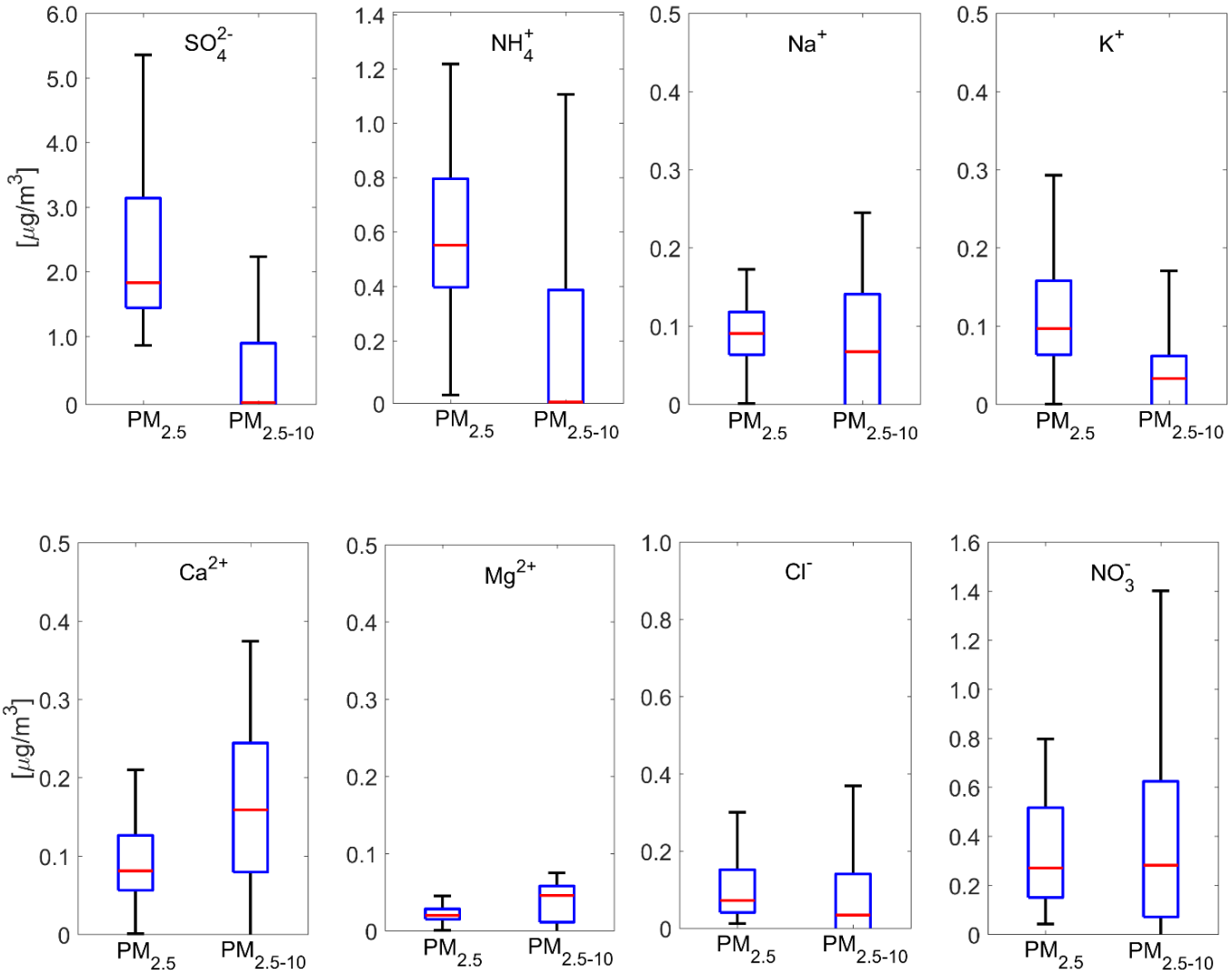



**Fig. 4** Boxplots of the concentrations of inorganic ionic species for $PM_{2.5}$, and $PM_{2.5-10}$ measured at Marikana. The median (red line), 25th and 75th percentiles (blue box) and ± 2.7 times the standard deviation (whiskers) are indicated

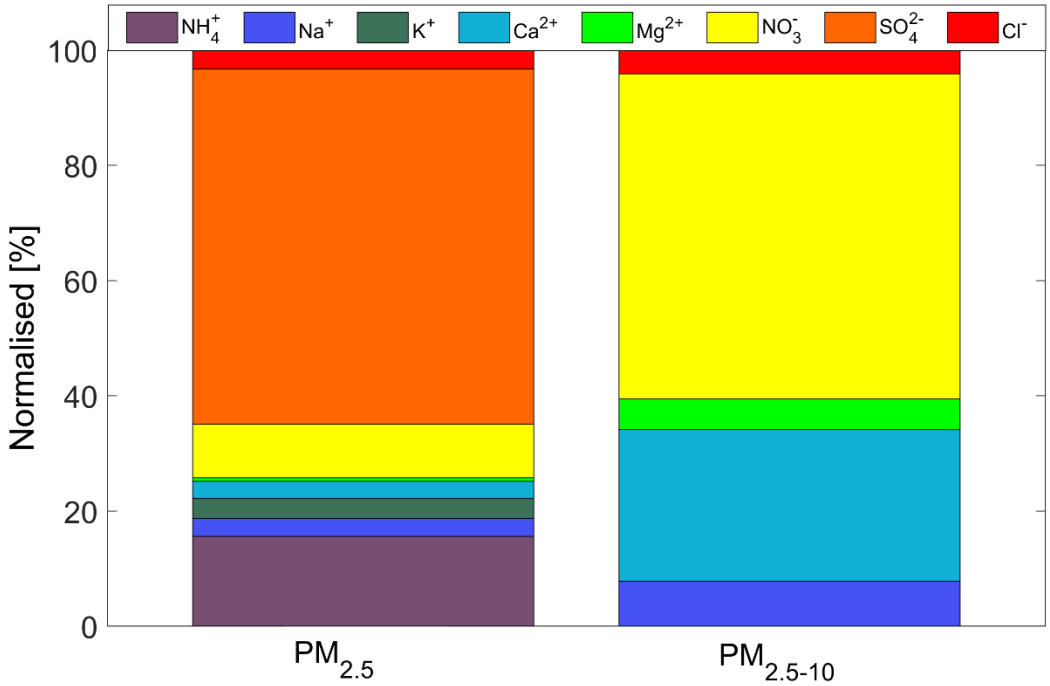



**Fig. 5** Normalised concentration distribution of inorganic ionic species measured at Marikana

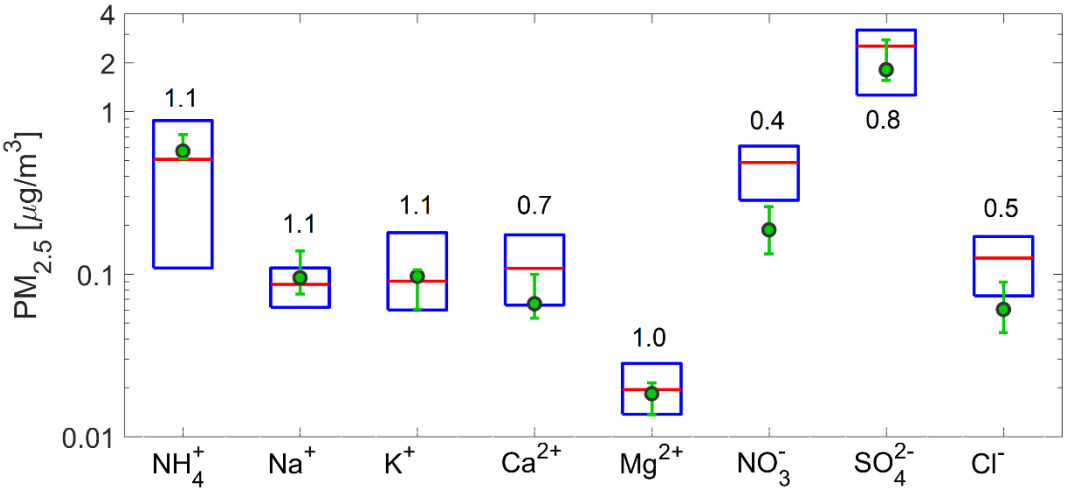
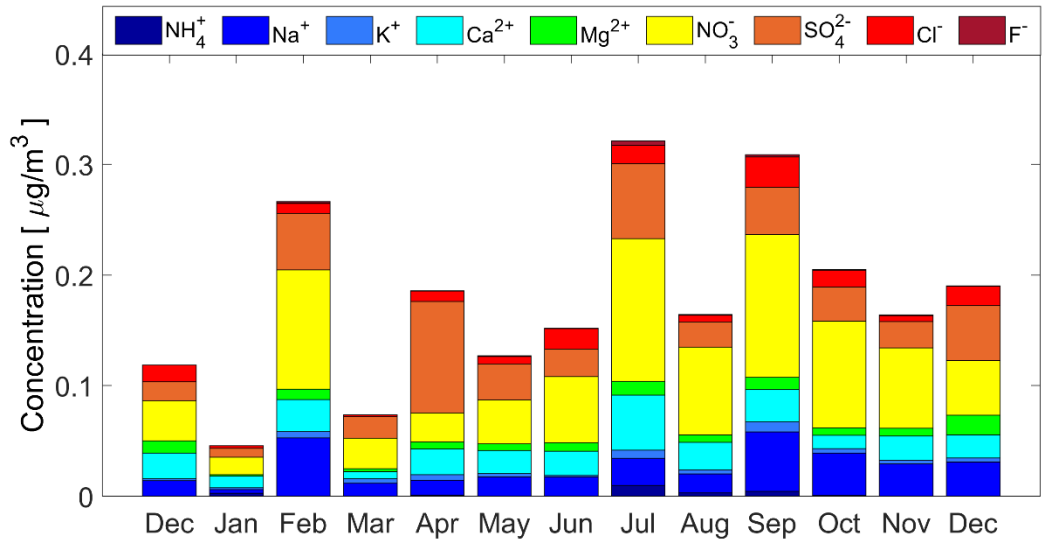
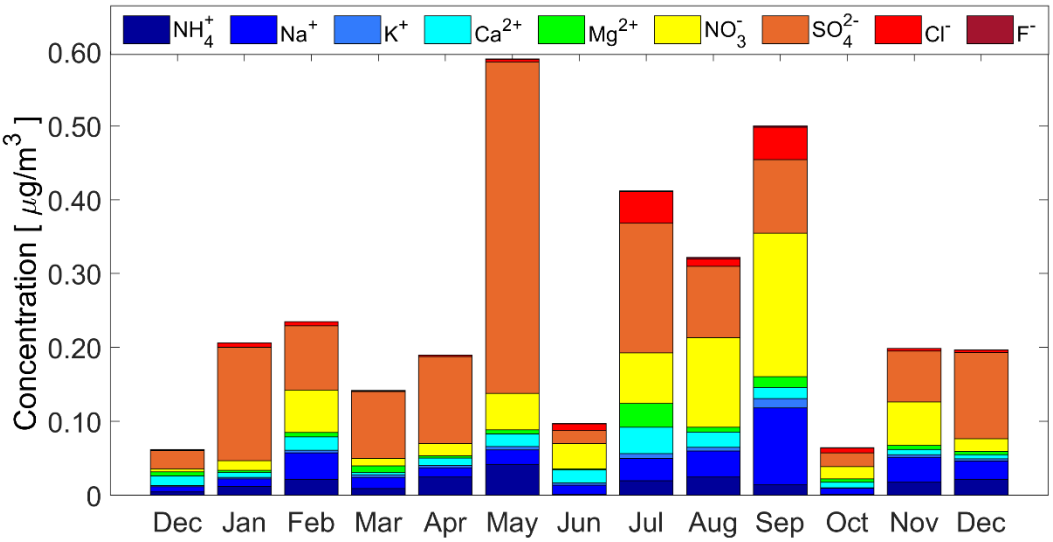


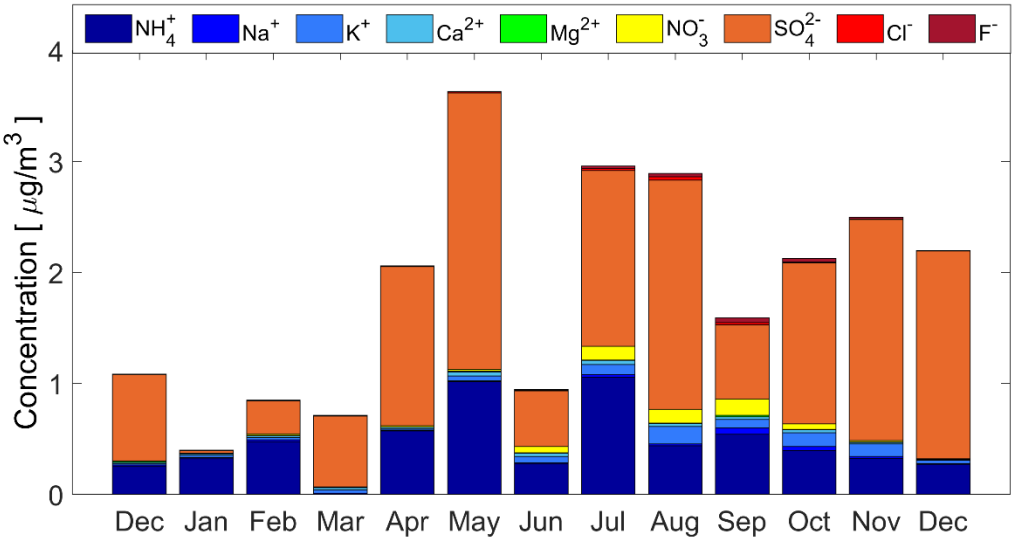

**Fig. 6** Concentrations of inorganic ionic species measured at Marikana during the daytime (circle) and night time (box plots). For daytime measurements the green circle represent the median values and the green whiskers the 25$^{th}$ and 75$^{th}$ percentiles, while for night-time measurements the red line represent the median and the blue box the 25$^{th}$ and 75$^{th}$ percentiles


NH4+
Na+
K+
Ca2+
Mg2+
NO3-
SO4 2-
Cl-
F-
Concentration [ μg/m3 ]
0
0.1
0.2
0.3
0.4
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

(a)


NH4+
Na+
K+
Ca2+
Mg2+
NO3-
SO4 2-
Cl-
F-
Concentration [ μg/m3 ]
0
0.10
0.20
0.30
0.40
0.50
0.60
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

(b)




(c)

**Fig. 7** Welgegund monthly median inorganic ion concentrations for (a) $PM_{2.5-10}$, (b), $PM_{1-2.5}$ and (c), $PM_1$

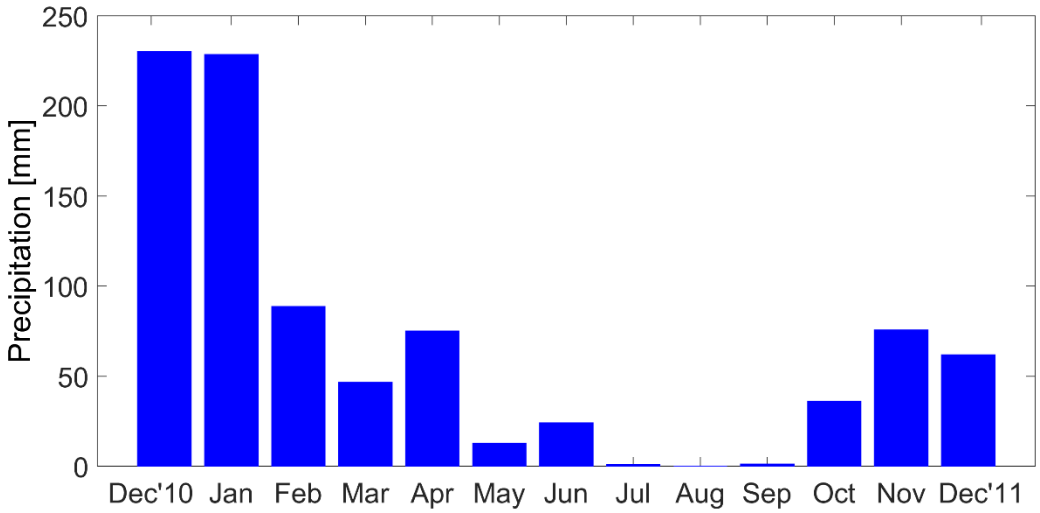



**Fig. 8** Monthly accumulated rainfall measured at Welgegund for the sampling duration

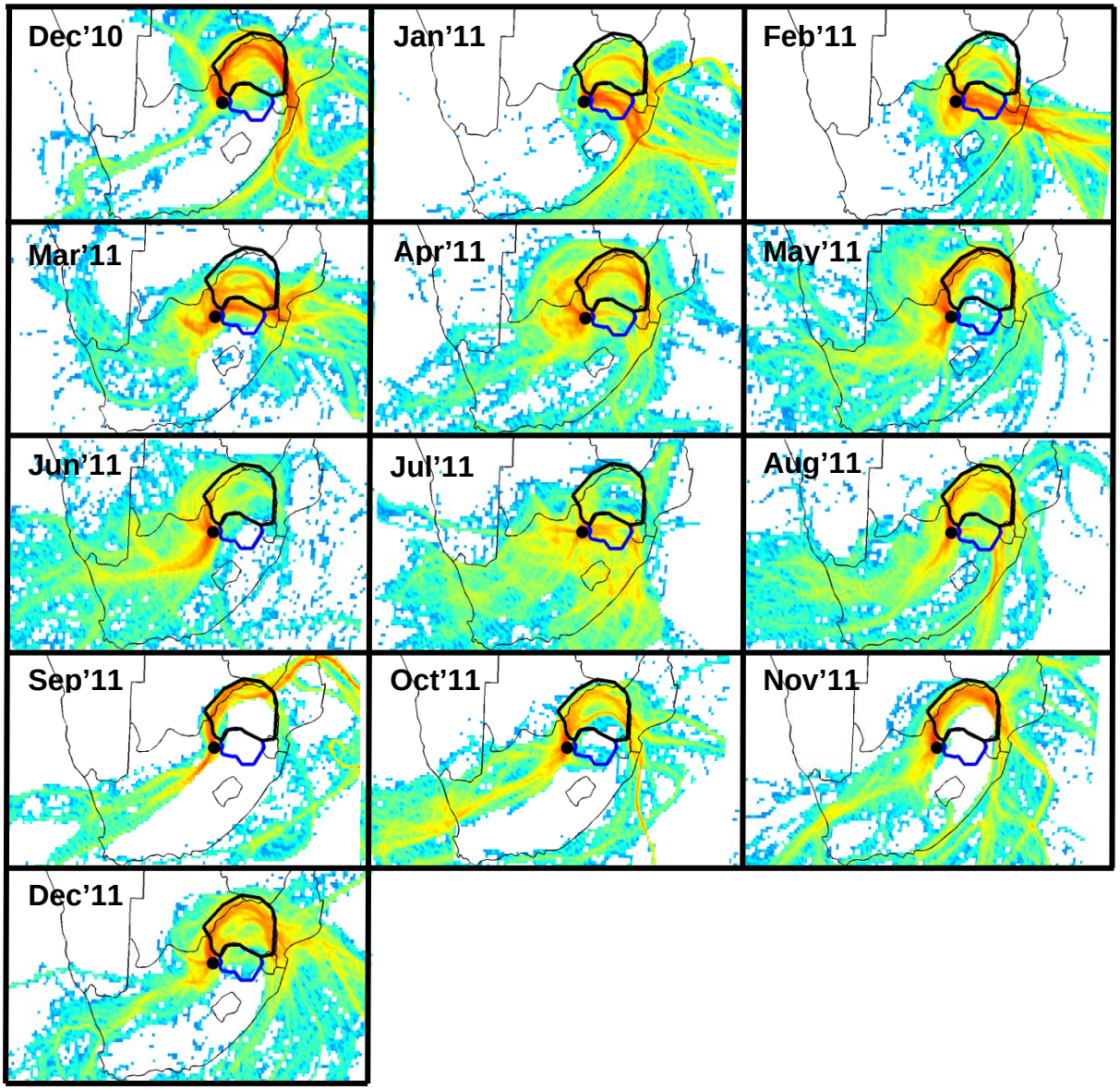



**Fig. 9** Monthly air-mass back trajectories as measured at Welgegund (black dot) during the sampling period. The colour scale indicates the percentage of trajectories passing over 0.2° x 0.2° grid cells, with blue to yellow to red indicating the lowest to highest frequency of air mass movement. The black polygon in the northern parts of South Africa indicates the typical anticyclonic recirculation area while the blue polygon contains the location of the majority of South African industries

**Table 1** Ratios of species to $Na^+$ in PM and reference seawater ratios (Keene et al., 1986)

| | $SO_4^{2-}/Na^+$ | $Cl^-/Na^+$ | $K^+/Na^+$ | $Mg^{2+}/Na^+$ | $Ca^{2+}/Na^+$ |
|---|---|---|---|---|---|
| Sea water | 0.121 | 1.161 | 0.022 | 0.227 | 0.044 |
| $PM_1$ | 67.02 | 0.48 | 2.46 | 0.24 | 1.38 |
| $PM_{1\text{-}2.5}$ | 3.51 | 0.34 | 0.17 | 0.27 | 0.72 |
| $PM_{2.5\text{-}10}$ | 1.28 | 0.57 | 0.16 | 0.29 | 0.92 |