Atmospheric trace metals measured at a regional background site (Welgegund) in South Africa

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Abstract

Atmospheric trace metals can cause a variety of health-related and environmental problems. Only a few studies on atmospheric trace metal concentrations have been conducted in South Africa. Therefore the aim of this study was to determine trace metals concentrations in aerosols collected at a regional background site, i.e. Welgegund, South Africa. PM_1, $PM_{1\text{-}2.5}$ and $PM_{2.5\text{-}10}$ samples were collected for 13 months and 31 atmospheric trace metal species were detected. Atmospheric iron (Fe) had the highest concentrations in all three size fractions, while calcium (Ca) was the second most abundant species. Chromium (Cr) and sodium (Na) concentrations were the third and fourth most abundant species, respectively. The concentrations of the trace metal species in all three size ranges were similar, with the exception of Fe that had higher concentrations in the PM_1 size fraction. With the exception of titanium (Ti), aluminium (Al) and manganese (Mg), 70% or more of the trace metal species detected were in the smaller size fractions, which indicated the influence of industrial activities. However, the large influence of wind-blown dust was reflected by 30% and more of trace metals being present in the $PM_{2.5\text{-}10}$ size fraction. Comparison of trace metals determined at Welgegund to those in the western Bushveld Igneous Complex indicated that at both locations similar species were observed with Fe being the most abundant. However, concentrations of these trace metal species were significantly higher in the western Bushveld Igneous Complex. Fe concentrations at the Vaal Triangle were similar to levels thereof at Welgegund, while concentrations of species associated pyrometallurgical smelting were lower. Annual average Ni was four times higher and annual average As was marginally higher than their respective European standard values, which could be attributed to regional influence of pyrometallurgical industries in the western Bushveld Igneous Complex. All three size fractions indicated elevated trace metal concentrations coinciding with the end of the dry season, which could partially be attributed to decreased wet removal and increases in wind generation of particulates. Principal component factor analysis (PCFA) revealed four meaningful factors in the PM_1 size fraction, i.e. crustal, pyrometallurgical-related and Au slimes dams. No meaningful factors were determined for the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions, which was attributed to the large influence of wind-blown dust on atmospheric trace metals determined at Welgegund. Pollution roses confirmed the influence of wind-blown dust on trace metal concentrations measured at Welgegund, while the impact of industrial activities was also substantiated.

1 Introduction

Atmospheric aerosols are either directly emitted into the atmosphere (primary aerosols) from natural and/or anthropogenic sources, or are formed through gaseous reactions and gas-to-particle conversions (secondary aerosols). Aerosols have high temporal and spatial variability, which increases the need and importance for detailed physical and chemical characterisation on a regional scale in order to assess the impacts of aerosols (Pöschl, 2005). Particulate matter (PM) is classified according to its aerodynamic diameter, as PM_{10}, $PM_{2.5}$, PM_1 and $PM_{0.1}$, which relates to aerodynamic diameters being smaller than 10, 2.5, 1 and 0.1 μm, respectively. Larger particulates have shorter lifetimes in the atmosphere compared to smaller particles, while the impacts of these species are also determined, to a large degree, by their size (Tiwari et al., 2012, Colbeck et al., 2011). The largest uncertainties in the estimation of direct and indirect radiative forcing from aerosols are related to the insufficient knowledge of the high spatial and temporal variability of aerosol concentrations, as well as their microphysical, chemical and radiative properties (IPCC, 2014). Aerosols consist of a large number of organic and inorganic compounds, of which typical inorganic species include ionic species and trace metals.

Natural sources of atmospheric trace metals include mineral dust, crustal species, oceans and biomass burning (wild fires), while major anthropogenic sources are pyrometallurgical processes, fossil fuel combustion and incineration (Pacyna and Pacyna, 2001). Larger aerosol particles (>2.5 μm) are usually associated with natural emissions through processes such as rock weathering and soil erosion (Nriagu et al., 1989). Trace metal species usually associated with natural emissions include sodium (Na), silicon (Si), magnesium (Mg), aluminium (Al), potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn) and iron (Fe) (Adgate et al., 2007). Arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), vanadium (V), molybdenum (Mo), mercury (Hg) and lead (Pb) are mostly related to anthropogenic activities (Pacyna (1998); Polidori et al., 2009). One of the most significant sources of anthropogenic trace metal emissions is the industrial smelting of metals. Industrial pyrometallurgical processes produce the largest emissions of As, Cd, Cu, Ni and Zn (Zahn et al., 2014). Cr, Ba, Mo, Zn, Pb and Cu are typically associated with motor-vehicle emissions and oil combustion, while Fe, Pb and Zn are emitted from municipal waste incinerators (Adgate et al., 2007). However, most of these atmospheric trace metals are emitted through a combination of different anthropogenic sources (Polidori et al., 2009).

Although trace heavy metals, i.e. metals > Ca, represent a relatively small fraction of atmospheric aerosols (with the exception of Fe that could contribute a few percent) (Colbeck, 2008), these species can cause a variety of health-related and environmental problems, which depends on the aerosol composition, extent and time of exposure (Pöschl, 2005). The potential hazard of several toxic species is well documented as discussed, for instance, by Polidori et al. (2009), indicating that trace metals such as As, Cd, Co, Cr, Ni, Pb and Se are considered human and animal carcinogens even in trace amounts (CDC, 2015). It has also been shown that Cu, Cr and V can generate reactive oxygenated species that can contribute to oxidative DNA damage (Nel, 2005). Furthermore, trace metals such as Cr, Fe and V have several oxidation states that can participate in many atmospheric redox reactions (Seigneur and Constantinou, 1995), which can catalyse the generation of reactive oxygenated species (ROS) that have been associated with direct molecular damage and with the induction of biochemical synthesis pathways (Rubasinghege et al., 2010). Guidelines for atmospheric levels of many trace metals are provided by the World Health Organization (WHO) (WHO, 2005). In addition, lighter metals such as Si, Al and K are the most abundant crustal elements (next to oxygen), which can typically constitute up to 50% of remote continental aerosols. These species are usually associated with the impacts of aerosols on respiratory diseases and climate.

South Africa has the largest industrialised economy in Africa, with significant mining and metallurgical activities. South Africa is a well-known source region of atmospheric pollutants, which is signified by three regions being classified through legislation as air pollution priority areas, i.e. Vaal Triangle Airshed Priority Area (DEAT, 2006), Highveld Priority Area (DEAT, 2007) and Waterberg-Bojanala Priority Area (DEA, 2012). Air quality outside these priority areas is often adversely affected due to regional transport and the general climatic conditions, such as low precipitation and poor atmospheric mixing in winter. Only a few studies on the concentrations of atmospheric trace metals in South Africa have been conducted (Van Zyl et al., 2014; Kgabi, 2006; Kleynhans, 2008). In addition, most of these studies were also conducted within these priority areas containing a significant number of large point sources, and regional impacts of atmospheric trace metals could therefore not be assessed.

In this study, trace metals were determined in three size ranges in aerosol samples collected for one year at the Welgegund atmospheric measurement station in South Africa. Welgegund is a comprehensively equipped regional background atmospheric measurement station that is ~100 km downwind of the most important source regions in the interior of South Africa (e.g. Tiitta et al., 2014). These source regions include the western Bushveld Igneous Complex (situated within the Waterberg-Bojanala Priority Area) where a large number of pyrometallurgical smelters are situated, which can be considered of global importance, e.g. as a supplier of platinum group metals (PGMs) utilised in automotive catalytic converters and as the dominant global chromium supplying region. In an effort to determine major sources of trace metals on a regional scale, source apportionment was also performed by applying principal component factor analysis (PCFA).

2 Experimental

2.1 Site description

Aerosol sampling was performed at Welgegund (www.welgegund.org, 26°34'11.23"S, 26°56'21.44"E, 1480 m a.s.l. (above sea level)) in South Africa, which is a regional background station with no large point sources in close proximity. As indicated in Figure 1 and the 96-hour overlay back trajectories presented in Figure S1, Welgegund is situated in the interior of South Africa and is frequently affected by air masses moving over the most important anthropogenic/industrial source regions in the interior (Beukes et al., 2013, Tiitta, et al., 2014, Jaars, et al., 2014, Vakkari et al., 2015; Booyens et al., 2015). Also indicated in Figure 1 are the major industrial point sources, i.e. coal-fired power plants, petrochemical industries and pyrometallurgical smelters. In Beukes et al. (2013) Tiitta, et al., 2014 and Jaars, et al., 2014, reasons for the site selection, prevailing biomes and pollution sectors are discussed in detail. In summary, air masses affecting the site from the west, between north- and south-west, are considered to be representative of the regional background, since they move over a sparsely populated region without any large point sources. In the sector between north and north-east from Welgegund lays the western limb of the Bushveld Igneous Complex, which holds eleven pyrometallurgical smelters (most commonly related to the production of Cr, Fe, V and Ni) within a ~55 km radius , in addition to other industrial, mining and residential sources. In the north-east to eastern sector, the Johannesburg-Pretoria (Jhb-Pta) conurbation is situated, which is inhabited by more than 10 million people, making it one of the forty largest metropolitan areas in the world. In the sector between east and south-east from Welgegund is the Vaal Triangle region, where most of the South African petrochemical and petrochemically-related industries are located, together with other large point sources, such as two coal-fired power stations (without desulphurisation (de-SOx) and denitrification (de-NOx)) and large pyrometallurgical smelters. Welgegund is also affected by the Mpumalanga Highveld in the eastern sector (indicated by MP in Figure 1). In this region, there are 11 coal-fired power stations (without de-SOx and de-NOx technologies) with a combined installed generation capacity of ca. 46 GW, as well as a very large petrochemical plant, several pyrometallurgical smelters and numerous coal mines, all within a ca. 60 km radius. Furthermore, Welgegund is also affected by air masses passing over the pyrometallurgical smelters in the eastern limb of the Bushveld Igneous Complex situated north-east from Welgegund in the Limpopo Province (indicated by LP in Figure 1).

Insert Figure 1

2.2 Sampling and analysis

Aerosol samples were collected for one year from 24 November 2010 until 28 December 2011. A Dekati (Dekati Ltd., Finland) PM_{10} cascade impactor (ISO23210) equipped with PTFE filters was used to collect different particulate size ranges, i.e. $PM_{2.5-10}$ (aerodynamic diameter ranging between 2.5 and 10 μm), $PM_{1-2.5}$ (aerodynamic diameter ranging between 1 and 2.5 μm) and PM_1 (aerodynamic diameter <1 μm). The pump flow rate was set at 30 L min^{-1}. Samples were collected continuously for one week, after which filters were changed. A total of 54 samples were collected for the 54-weeks sampling period for each of the three size ranges. The trace metals in the PM collected on the 216 PTFE filters were extracted by hot acid leaching (20 ml HNO_3 and 5 ml HCl) and diluted in deionised water (18.2 MΩ) up to 100 mL for subsequent analysis with an inductively coupled plasma mass spectrometer (ICP-MS). In total, 31 trace metals could be detected with ICP-MS analysis, which included Na, Mg, Al, K, Ca, Ti, Cr, Mg, Fe, As, Ba, Cd, Cu, Ni, Zn, V, Mo, Hg, Pb, manganese (Mn), cobalt (Co), platinum (Pt), beryllium (Be), boron (B), selenium (Se), palladium (Pd), barium (Ba), gold (Au), thallium (Tl), antimony (Sb) and uranium (U). Trace metal concentrations below the detection limit of the ICP-MS were considered to have concentrations half the detection limit of the species considered. This is a precautionary assumption that is frequently used in health-related environmental studies (e.g. Van Zyl et al., 2014).

2.3 Statistical analysis

In an attempt to identify possible sources of trace metals detected, PCFA with Varimax rotation (v. 13.0 SPSS Inc., Chicago, IL, USA) was performed on the dataset. PCFA has been used widely in receptor modelling to identify major source sectors. The technique operates on sample-to-sample fluctuations of the normalised concentrations. It does not directly yield concentrations of species from various sources, but identifies a minimum number of common factors for which the variance often accounts for most of the variance of species (e.g. Van Zyl et al., 2014 and references therein). The trace metal concentrations determined for the 32 species in all three size fractions were subjected to multivariate analysis of Box-Cox transformation and Varimax rotation, followed by subsequent PCFA. In addition, Spearman correlations were also performed in order to establish correlations between trace metals in order to substantiate results obtained with PCFA.

3 Results

3.1 Size-resolved concentrations and size distribution of trace metals

Although nitric digestion is commonly used to extract and dissolve metals for ICP-MS analysis, it is unable to dissolve and extract silicate minerals. Therefore Si could not be quantified in this study. In addition, this limitation of the nitric digestion could also result in determining lower concentrations of metals associated with the silicate component such as Al, K, Mg, Ca and Fe, especially, for samples that have high aeolian dust content. It is estimated that approximately only 7 % Si and 30 % Al is extracted by nitric acid leaching (Ahn et al., 2011). Therefore, since Si and Al are considered to be the most abundant crustal elements after oxygen, the trace metal concentrations presented in this paper should be related to the limitation of nitric digestion, i.e. Si-Al-K components missing from the digestions phase. Silicate minerals can be dissolved in a mixture of aqua regia and hydrofluoric acid. However, this is a very difficult procedure, which results in the formation of gaseous SiF_3 that is not determinable by ICP-MS.

In Figure 2, the combined trace metal concentrations in all three size fractions (Figure 2 (a)), as well as concentrations of the trace metals determined in each of the size fractions are presented (Figure 2 (b), (c) and (d)). Hg and Ag concentrations were below the detection limit of the analytical technique for the entire sampling period in all three size fractions and the concentrations of these species are therefore excluded from Figure 2.

Insert Figure 2

The highest median concentration was determined for atmospheric Fe, i.e. 1.4 μg m^{-3}, while Ca was the second most abundant species with a median concentration of 1.1 μg m^{-3}. Fe concentrations were significantly higher compared to the other trace metal species determined at Welgegund. Cr and Na concentrations were the third and fourth most abundant species, respectively. The median Cr concentration was 0.54 μg m^{-3}, while the median Na level was 0.39 μg m^{-3}. Relatively higher concentrations were also determined for Al, B, Mg, Ni and K with median concentrations of 0.20 μg m^{-3}, 0.30 μg m^{-3}, 0.18 μg m^{-3}, 0.02 μg m^{-3} and 0.18 μg

m^{-3}, respectively. The combined atmospheric concentrations of the other trace metals in all the size fractions were clearly lower.

A comparison of the trace metal concentrations in the three size fractions indicates that Fe and Ca were the most abundant species in all three size fractions. Fe had the highest median concentration in the PM_1 size fraction, i.e. 0.63 μg m^{-3}, while Ca had the highest median concentrations in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions, i.e. 0.39 μg m^{-3} and 0.29 μg m^{-3}, respectively. The median concentration of Fe in the PM_1 was significantly higher compared to the median concentrations thereof in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions. The third and fourth most abundant species in all three size fractions were Cr and Na, respectively. Relatively higher concentrations were also determined for Al, B, Mg, Ni and K in all three size fractions. With the exception of Fe concentrations in the PM_1 size fraction, the concentrations of each of the trace metal species were similar in all size fractions.

In Figure 3, the mean size distributions of each of the trace metal species identified above the detection limit in the three size fractions are presented. Ti had significantly higher contribution (80%) in the $PM_{2.5-10}$ size fraction, while Al and Mg also had relatively higher contributions (~50 and 45%, respectively) in the $PM_{2.5-10}$ size fraction. The $PM_{2.5-10}$ size fraction is usually associated with wind-blown dust. 70% or more of all the other trace metal species detected were in the two smaller size fractions, with approximately 35 to 60% occurring in the PM_1 size fraction. The presence of these trace metal species predominantly in the smaller size fractions, especially considering the relatively large contribution in the PM_1 size fractions, indicates the influence of industrial (high temperature) activities on air masses measured at Welgegund. Trace metal concentrations measured at Marikana, situated within the western Bushveld Igneous Complex, indicated that Cr, Mn, V, Zn and Ni occurred almost exclusively in the $PM_{2.5}$ size fraction, with no contribution by coarser particles (Van Zyl et al., 2014). The large influence of wind-blown dust on trace metal concentrations determined at Welgegund is also reflected with approximately 30% of most of these trace metals being present in the $PM_{2.5-10}$ size fraction.

Insert Figure 3

From Figure 2 and 3 it is evident that a major source of trace metal species in all three size fractions can be considered to be wind-blown dust typically comprising Fe, Ca, Mg, Al, K and Ti (Polidori et al., 2009). As mentioned, Welgegund is a regional background location affected by air masses passing over large pollutant source regions and a relatively clean background area (Figure 1). In Figure S1 96-hour overlay back trajectories arriving hourly at Welgegund for the entire sampling period (24 November 2010 until 28 December 2011) are presented. From Figure 1 and S1 it is evident that Welgegund is frequently impacted by long range transport of air masses passing over the relatively clean background region in the west (between north- and south-west). It is evident from Figure 1 that the arid Nama-Karoo biome is situated within this region west of Welgegund, which could be a potential regional source for wind-blown dust. In addition, Jaars et al., 2016 also indicated the extent of agricultural activities within a 60 km radius from Welgegund, which could be a significant local source of wind-blown dust. In addition, Figure S1 indicate that Welgegund is also frequently affected by air masses moving over the western Bushveld Igneous Complex, which is associated with a large number of pyrometallurgical smelters (e.g. ferrochrome, platinum and base metals) and mining activities (Venter et al, 2012, Tiitta et al., 2014; Jaars et al., 2014). This source region could therefore contribute to regional elevated levels of Fe, Cr, Ni, Zn, Mn and V measured at Welgegund. Venter at al., 2016 indicated that Cr(VI) concentrations were elevated in air masses that had passed over the western Bushveld Igneous Complex with the majority of Cr(VI) in the smaller $PM_{2.5}$ size fraction. The possible sources of trace metal species measured at Welgegund will be further explored in section 3.5.

3.2 Contextualisation of atmospheric trace metal concentrations

In Table 1, the annual average PM_{10} trace metal concentrations determined in this study are compared to trace metal concentrations determined in other studies. Although the aerosol sampling periods and frequencies for most of these previous trace metal studies were not similar to the aerosol sampling period and frequency in this investigation, these results could be utilised to contextualise the trace metal concentrations. As mentioned previously, Hg and Ag concentrations were below the detection limit of the analytical technique for the entire sampling period in all three size fractions. Therefore, concentrations presented for these species are most likely to be an over estimate due to the precautionary assumption.

Insert Table 1

The annual mean PM_{10} trace metal concentrations at Welgegund (Table 1) were typically lower than previous studies conducted in South Africa (Kgabi, 2006; Kleynhans, 2008; Van Zyl et al., 2014). This is expected, as Welgegund is a regional background location and the previous studies were conducted at sites within two priority areas, as mentioned previously. These sites were also located in two of the major source regions influencing air masses arriving at Welgegund. Marikana (Van Zyl et al., 2014) and Rustenburg (Kgabi, 2006) are situated approximately 100 km north-north-west from Welgegund within the western Bushveld Igneous Complex source region, while the site in the Vaal Triangle (Kleynhans, 2008) source region is situated approximately 90 km east from Welgegund.

Fe was also the most abundant species at Marikana and Rustenburg, with significantly higher concentrations compared to Welgegund. Mg was the second most abundant species at Marikana, while Mn and Cr concentrations were the second and third highest, respectively at Rustenburg. Cr levels at Rustenburg were approximately 2.5 times higher than levels thereof at Welgegund. However, Cr concentrations measured at Welgegund were approximately two times higher compared to Cr levels determined at Marikana, which could be attributed to the long range transport of Cr units (Figure 1 and S1). Venter et al., (2016) also indicated other combustion sources outside the western Bushveld Igneous Complex contributed to the atmospheric Cr(VI) concentrations at Welgegund. Ni and Zn concentrations at Welgegund were an order of magnitude lower compared to levels thereof at Marikana and Rustenburg, while Mn and V concentrations were significantly lower compared levels thereof measured at Rustenburg. Similar to Welgegund, Na, B and Al were also relatively abundant at Marikana with concentrations of these species an order of magnitude higher at Marikana. Fe concentrations were similar at Vaal Triangle than levels thereof at Welgegund, while the annual average Na concentration was seven times higher and the annual average K level was an order of magnitude higher at the Vaal Triangle. Cr, Ni and Zn, typically associated with pyrometallurgical industries, were significantly lower in the Vaal Triangle compared to levels thereof at Welgegund. However, Mn concentrations at the Vaal Triangle were higher compared to levels thereof at Welgegund and Marikana. This can be attributed to the presence of a ferromanganese (FeMn) smelter in the Vaal Triangle region, as indicated in Figure 1.

The atmospheric trace metal concentrations determined at Welgegund were also compared to measurements at regional background sites near Beijing, China (Duan et al., 2012), the west coast of Portugal (Pio et al., 1996) and Spain (Querol et al. 2007). Al concentrations near Beijing were significantly higher compared to other trace metal species, while Na was the second most abundant species. Elevated levels of K, Fe and Ca were also determined near Beijing. Al, Na and K concentrations were an order of magnitude higher compared to levels of these species determined at Welgegund, while Fe levels were twice as low near Beijing All the other trace metal species measured near Beijing (with the exception of Ca, Pb and Mn) were an order or two orders of magnitude lower compared to concentrations of these species at Welgegund. Annual average trace metal concentrations determined at the two European regional background sites were an order or two orders of magnitude lower compared to trace metal levels determined at Welgegund. The generally lower trace metal concentration determined at these sites in China and Europe compared to Welgegund can be attributed to the sites in China and Europe being more removed from a conglomeration of metal sources.

Also indicated in Table 1 are the existing ambient air quality guidelines and standard values for trace metal species prescribed by the WHO air quality guidelines for Europe (WHO, 2005), the European Commission Air Quality Standards (ECAQ, 2008) and the South African National Air Quality Standards of the South African Department of Environmental Affairs (DEA) (DEA, 2009). There are currently only guidelines and standards for seven trace metal species, of which each of the above-mentioned institutions only prescribe limit values for some of these trace metal species. Comparison of the annual average trace metal concentrations determined at Welgegund with the annual average standard values indicates that Ni and As exceeded standards set by the European Commission of Air Quality Standards. The annual average Ni concentration of 0.079 $\mu g\ m^{-3}$ were approximately four times higher than the European standard value of 0.02 $\mu g\ m^{-3}$, while the annual average As level of 0.0084 $\mu g\ m^{-3}$ marginally exceeded the annual standard of 0.006 $\mu g\ m^{-3}$. These exceedances can most probably be ascribed to the regional impacts of pyrometallurgical activities in the Bushveld Igneous Complex. Van Zyl et al. (2014) indicated that the exceedance of Ni at Marikana situated within the western Bushveld Igneous Complex could be attributed to base metal refining.

The WHO guideline of 2.5x10^{-5} µg m^{-3} listed for Cr is only for atmospheric concentrations of Cr(VI) with a lifetime risk of 1:1 000 000. The 0.50 µg m^{-3} annual average Cr concentration determined can therefore not be compared to the guideline, since this value represents the total atmospheric Cr concentrations in all the oxidation states. V only has a 24-hour standard value. Therefore, V concentrations determined in this study cannot directly be compared to this standard. However, the 24-hour average calculated from the highest weekly V concentration (0.084 µg m^{-3}) was 0.012 µg m^{-3}, which was two orders of magnitude lower than the 24-hour V standard of the European Commission Air Quality Standards.

Since Pb is the only trace metal for which a South African ambient air quality standard exists, it must also be noted that Pb concentrations did not exceed any standard. The annual average Pb concentrations determined at Welgegund (0.0078 µg m^{-3}) were an order of magnitude lower than levels thereof at Marikana and Vaal Triangle, and three orders of magnitude lower than Pb levels determined at Rustenburg. However, the annual average Pb concentrations at Vaal Triangle, Marikana and Rustenburg were below the standard value (Kleynhans, 2008; Van Zyl et al., 2014; Kgabi, 2006). These low Pb concentrations can be partially ascribed to de-leading of petrol in South Africa. Furthermore, Pb concentrations determined at Beijing were similar to levels thereof determined at Welgegund.

Since the measurement of the ambient Hg concentrations is receiving increasing attention in South Africa and it is foreseen that a standard value for Hg levels will be prescribed in the near future, it is also important to refer to the Hg concentrations that were below the detection limit of the analytical instrument for the entire sampling period. Van Zyl et al. (2014) also indicated that Hg was below the detection limit of the analytical technique for aerosol samples collected at Marikana. This can be expected, since particulate Hg only forms a small fraction of the total atmospheric Hg, with Hg being predominantly present in the atmosphere as gaseous elemental Hg (GEM) (Venter et al., 2015, Slemr et al., 2011).

3.3 Seasonal variability

The climate and weather of South Africa is characterised by its distinctive wet and dry seasons, which have an influence on concentrations of atmospheric species (Tyson and Preston-Whyte, 2000). Therefore, in Figure 4, the total concentrations of the trace metal species in the PM$_1$ (a),

$PM_{1-2.5}$ (b) and $PM_{2.5-10}$ (c) size fractions measured at Welgegund for each month are presented, with the contributing concentrations of each of the trace metals indicated. In the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions relatively higher total trace metal concentrations are observed from August to December. These periods coincided with the end of the dry season, which occurs in this part of South Africa typically from mid-May to mid-October (e.g. Tyson and Preston-Whyte, 2000). The end of the dry season is typically characterised by increases in wind speed in August (e.g. Tyson and Preston-Whyte, 2000). Therefore, these elevated trace metal concentrations determined in the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions can partially be attributed to decreased wet removal in conjunction with increases in wind generation thereof. The PM_1 size fractions also had relatively higher during the end of dry season period, especially during September and October. However, slightly higher trace metal concentrations are also observed in the PM_1 size fraction in the austral winter months from June to August. This can be ascribed to the presence of more pronounced inversion layers during this time of the year (e.g. Tyson and Preston-Whyte, 2000) that trap pollutants near the surface, which signifies the contribution of industrial sources to PM_1 species.

Insert Figure 4

The monthly concentrations of each of the trace metal species determined in the PM_1 and $PM_{1-2.5}$ size fractions reveal the highest contributions from Fe and Ca in both these size fractions for each of the months. The concentrations of Na and Cr that were the third and fourth most abundant species, respectively, as well as the elevated levels of Al, B, Mg, Ni and K are also reflected in the monthly distributions in the PM_1 and $PM_{1-2.5}$ size fractions. However, although Fe and Ca were slightly higher in the $PM_{2.5-10}$ size fraction, a more even contribution from the concentrations of Fe, Ca, Na, Cr, Al, B, Mg, Ni and K is observed (with the exception of November as mentioned previously). This can be attributed to species in this larger size fraction consisting predominantly of wind-blown dust (Adgate et al., 2007) with no additional industrial sources of these species.

3.4 Source apportionment

As a first approach in the source apportionment investigation, Spearman correlation diagrams were prepared for each size fraction. In Figure 5, Spearman correlations of the PM_1, $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions are presented, i.e. Figures 5a, 5b and 5c, respectively. From Figure 5 relatively good correlations is observed between trace metals associated with pyrometallurgical activities, i.e. Fe, Cr, Zn, Mn and V in all three size fractions. Na, Mg and Ca also correlate with each other in all three size fractions, indicating the crustal (earth) influence. Relatively good correlations are also observed between Ti and crustal species in the $PM_{2.5-10}$ size fraction. In addition, these crustal species (Na, Mg, and Ca) also correlate with species associated with pyrometallurgical activities (Fe, Cr, Zn, Mn and V). As mentioned in Sections 3.1 and 3.2, although the influence of the pyrometallurgical smelters in the western Bushveld Complex is evident, the large influence of wind-blown dust on trace metal concentrations determined at Welgegund is also reflected with approximately 30% of most of the trace metals being present in the $PM_{2.5-10}$ size fraction.

Insert Figure 5

In an effort to determine sources of trace metals, PCFA was applied as an exploratory tool, since much larger datasets are required for definitive source apportionment with PCFA. Therefore, only the most apparent groupings of metal species relating to expected sources in the region were identified. PCFA of the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions did not reveal any meaningful factors. This was attributed to the large influence of wind-blown dust on trace metals measured at Welgegund with all the factors obtained for the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions containing mostly crustal species loadings. In Figure 6, the factor loadings obtained for the PM_1 size fraction are presented indicating four statistically significant factors with eigenvalues equal to or greater than one (Pollisar et al., 1998). These four factors obtained explained 88% of the variance.

Insert Figure 6

Factor 1 explained 59.6 % of the total system variance and was mainly loaded with trace metal species that are typically associated with wind-blown dust, i.e. Ca, Fe, Na, Mg and Al (Adgate et al., 2007). Therefore, this factor was identified as the crustal factor. The contribution of small metal ore units from wind-blown dust is also reflected in this factor with a relatively high loadings of species such as V, Mn, Zn and Cr. Mn is present in most of the ores from which metals are produced in the western Bushveld Igneous Complex. The smaller contribution from Mn compared to Fe in this factor is also indicative of wind-blown dust, since Mn is more volatile than Fe (Kemink, 2000). Therefore, a higher contribution is expected from Mn compared to Fe from pyrometallurgical sources.

Factor 2 and 3 explained 16.5 and 4.3 % of the variance in the data, which was identified as pyrometallurgical-related factors. Factor 2 revealed higher loadings of Cr, Fe Mn, Ni and Cu, while Factor 3 was predominantly loaded with Cr, Fe and V. Fe and Cr are associated with the large number of ferrochromium smelters in the Bushveld Igneous Complex, while Ni related to base metal smelters that refine base metals extracted from the PGM production processes. In addition, Al present in Factor 2 is may be associated with fly ash formed during high temperature processes, which include coal combustion. It must be noted that coal fly ash has a composition, which is rather similar to that of crustal material (Mouli, et al., 2006). Mn has a substantially lower vapour pressure than most of the heavy metals produced in this region. Therefore, the coincidental influence of the pyrometallurgical industries is reflected by the high loadings of Mn and Ni in Factor 2.

Factor 4 was considered to be indicative of trace metal species associated with slimes dams from Au mining and recovery in the region, which is especially signified by the U and Au loadings in this factor. In addition, this factor is mostly loaded with the metal species for which significantly lower concentrations were measured. This factor explained 7.6 % of the total system variance.

Pollution roses of each of the trace metal species detected were also compiled in an effort to substantiate the sources identified with PCFA for the PM_1 size fraction, as well as to verify the influence of wind-blown dust that contributed to obtaining no meaningful factors for $PM_{1-2.5}$ and $PM_{10-2.5}$. In Figure 7, these pollution roses are presented, which indicate higher trace metal concentrations associated with wind directions from the north to western sector from Welgegund for all the trace metal species. As mentioned previously, the north to south-western sector from Welgegund is considered to be a relatively clean region without any large pollutant sources. Therefore, the most significant source of atmospheric trace metal species originating from this sector can be considered to be wind-blown dust (e.g. from the Karoo and Kalahari). This is also indicated by the higher atmospheric concentrations of specifically Ca, Fe, Na, Mg, Al and Ti associated with the north-western sector. Furthermore, the concentrations of trace metal species originating from the north can also be associated with pyrometallurgical industries in the western Bushveld Igneous Complex. The influence of these activities is reflected by the relatively higher concentrations of Cr, Ni, Mn, V and As associated with winds originating in the north. It is also evident form these pollution roses that atmospheric Fe concentrations have contributions from wind-blown dust from the north-western sector, as well as from pyrometallurgical activities in the north.

Insert Figure 7

4 Conclusions

Of the elements analysed in the aerosol samples, atmospheric Fe had the highest concentrations in all three size fractions, while Ca was the second most abundant species. Cr and Na concentrations were the third and fourth most abundant species, respectively, while relatively higher concentrations were also determined for Al, B, Mg, Ni and K. With the exception of Fe that had higher concentrations in the PM_1 size fraction, the concentrations of the trace metal species in all three size ranges were similar. With the exception of Ti, Al and Mg, 70% or more of the trace metal species detected were in the two smaller size fractions, which indicated the influence of industrial activities on trace metals measured at Welgegund. However, the large influence of wind-blown dust on trace metal concentrations determined at Welgegund is reflected by 30% and more of trace metals being present in the $PM_{2.5-10}$ size fraction

A comparison of trace metal concentrations determined at Welgegund with trace metal measurements conducted in the western Bushveld Igneous Complex (Kgabi, 2006; van Zyl et al., 2014) indicated that Fe was also the most abundant species, while other trace metals determined at Welgegund were also measured in the western Bushveld Igneous Complex. However, concentrations of these trace metal species were significantly higher in the western Bushveld Igneous Complex. Trace metal concentrations were also compared to levels thereof in the Vaal Triangle (Kleynhans, 2008) where. Fe concentrations were similar to levels thereof at Welgegund, while concentrations of species associated with pyrometallurgical smelting were lower. Comparison to atmospheric trace metal species measured at international background sites indicated that trace metal concentrations at Welgegund were generally lower, with the exception of Al, Na and K concentrations measured at Beijing, China (Duan et al., 2012) that were an order of magnitude higher. Annual average Ni (0.079 µg m^{-3}) were four times higher than the European Commission Air Quality Standards limit value, which could possibly be attributed to the influence of base metal refining in the western Bushveld Igneous Complex. As marginally exceeded the European Commission Air Quality Standards limit value, which also reflects the regional impacts of pyrometallurgical industries.

Al three size fractions indicated elevated trace metal concentrations coinciding with the end of the dry season. This could partially be attributed to decreased wet removal and increases in wind generation of particulates.

PCFA analysis revealed four statistically significant factors in the PM_1 size fraction, i.e. crustal, pyrometallurgical-related and Au slimes dams. No meaningful factors were determined for the $PM_{1-2.5}$ and $PM_{2.5-10}$ size fractions, which were attributed to the large influence of wind-blown dust on atmospheric trace metals determined at Welgegund. Pollution roses confirmed this influence of wind-blown dust on trace metal concentrations, while the impact of industrial activities was also substantiated.

There are limitations associated with nitric digestion for ICP-MS analysis employed in this study, which could lead to the underestimation of aluminosilicates and metal species associated with it. X-ray fluorescence (XRF), for instance, is an alternative analytical method that can be used to assess the chemical composition of PM collected on filters. The use of this technique has many advantages, e.g. non-destructive technique, little sample preparation required, relatively low cost per sample. In order to compare XRF with ICP-MS (digestion using ultrasonication in an HF-HNO_3 acid mixture) aerosol filter based analyses, Niu et al. (2010) analysed co-located duplicate samples collected in indoor and outdoor environments. Very good correlations for elements present at concentrations above the detection limits of both the ICP-MS and energy dispersive-XRF methods were found. However, much more elements analysed by the ICP-MS technique passed the quality criteria proposed by the afore-mentioned authors, including elements typical for alumina silicates and other wind blow dust compounds that were likely under estimated in the results presented in this paper. Therefore, although the digestion method used in this study is well established, it is recommended that future work should perform digestion using ultrasonication in an HF-HNO_3 acid mixture and, if possible, conduct both XRF and ICP-MS analyses since the results would supplement one another, e.g. elements below the detection limits of the XRF would be detected by the ICP-MS method.

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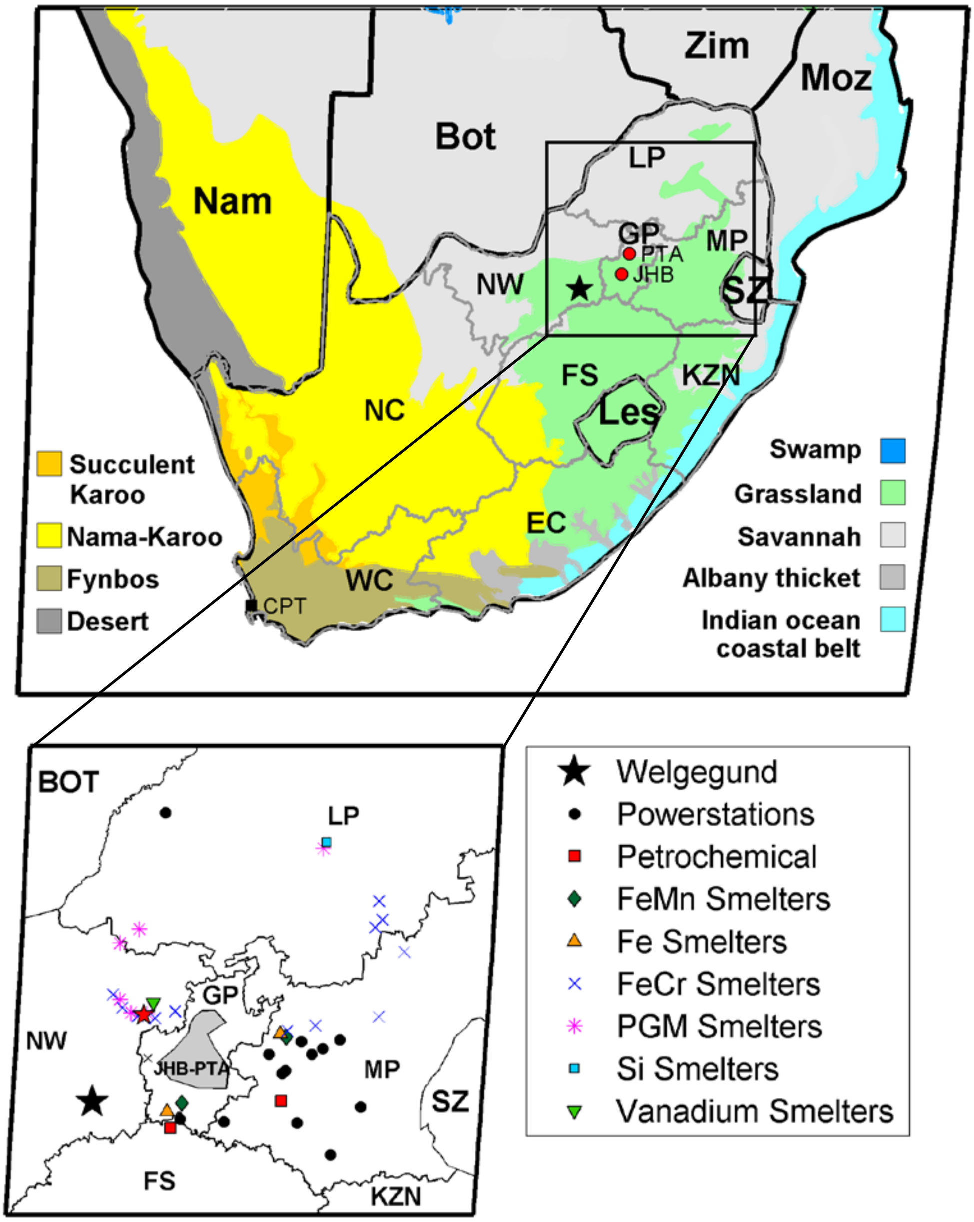
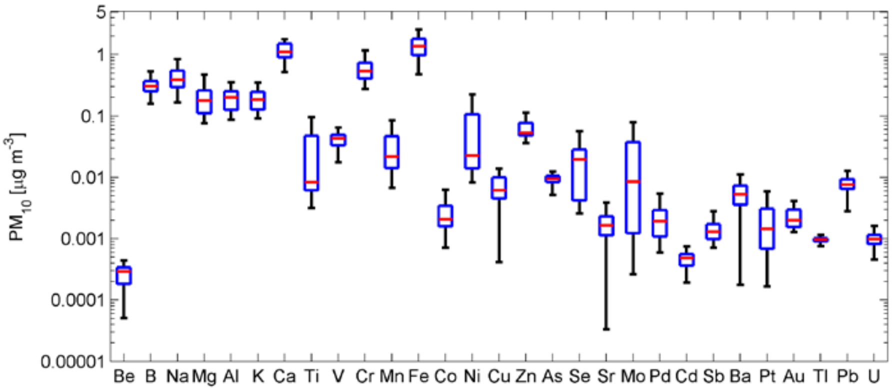
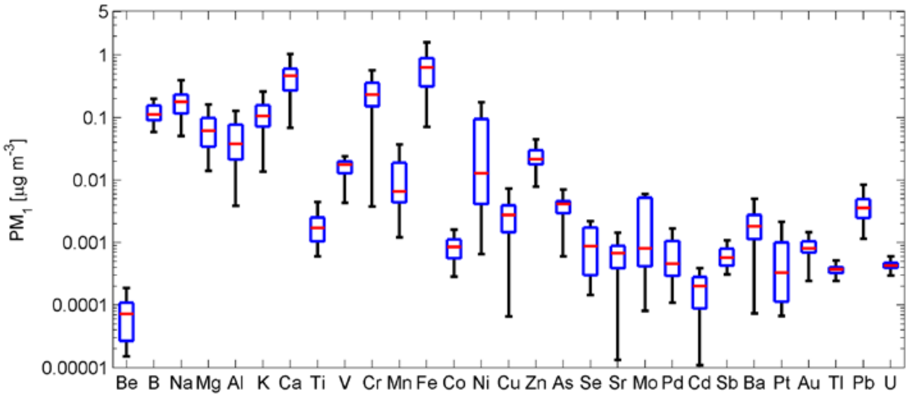


Figure 1: A bio-geographical map indicating Welgegund (black star), as well as the major point sources and the Johannesburg-Pretoria (JHB-PTA) conurbation. Neighbouring countries to South Africa (Nam = Namibia, Bot = Botswana, Zim = Zimbabwe, Mos = Mozambique, SZ = Swaziland, Les = Lesotho) as well as South African provinces (LP = Limpopo , NW = North-West, FS = Free State, KZN = Kwa-Zulu Natal, MP = Mpumalanga, NC = Northern Cape, EC = Eastern Cape and WC = Western Cape) are also indicated.



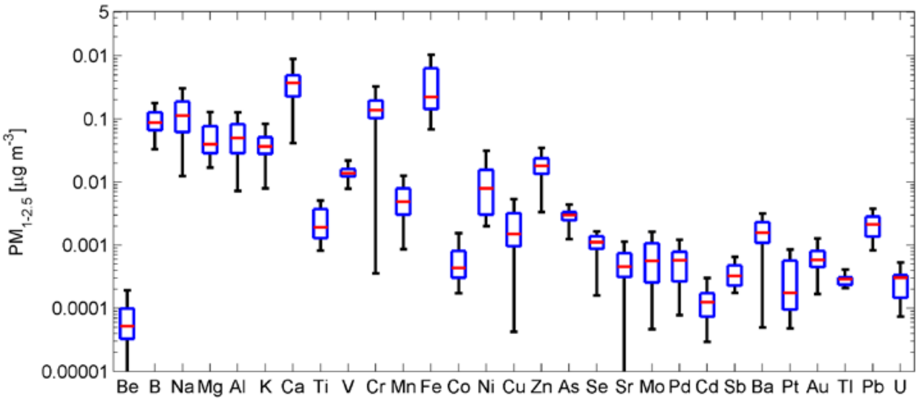
PM$_{10}$ [μg m^{-3}]
5
1
0.1
0.01
0.001
0.0001
0.00001
Be B Na Mg Al K Ca Ti V Cr Mn Fe Co Ni Cu Zn As Se Sr Mo Pd Cd Sb Ba Pt Au Tl Pb U

(a)



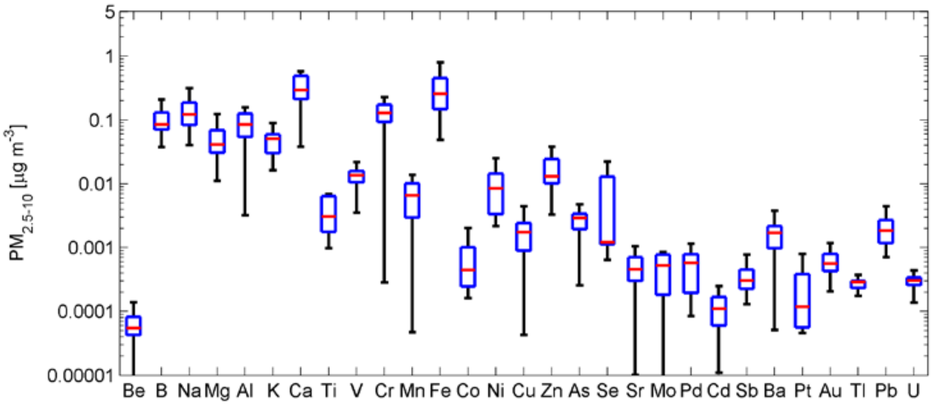
PM$_{1}$ [μg m^{-3}]
5
1
0.1
0.01
0.001
0.0001
0.00001
Be B Na Mg Al K Ca Ti V Cr Mn Fe Co Ni Cu Zn As Se Sr Mo Pd Cd Sb Ba Pt Au Tl Pb U

(b)



PM$_{1\text{-}2.5}$ [μg m^{-3}]
5
0.01
0.1
0.01
0.001
0.0001
0.00001
Be B Na Mg Al K Ca Ti V Cr Mn Fe Co Ni Cu Zn As Se Sr Mo Pd Cd Sb Ba Pt Au Tl Pb U

(c)



(d)

Figure 2: Box and whisker plots of trace metal concentrations in the (a) PM_{10} (sum of trace metal concentrations in the three size fractions), (b) PM_1, (c) $PM_{1-2.5}$, and (d) $PM_{2.5-10}$ size fractions. The red line indicates the median concentrations, the blue rectangle of the boxplot represents the 25th and 75th percentiles, while the whiskers indicate ± 2.7 times the standard deviation

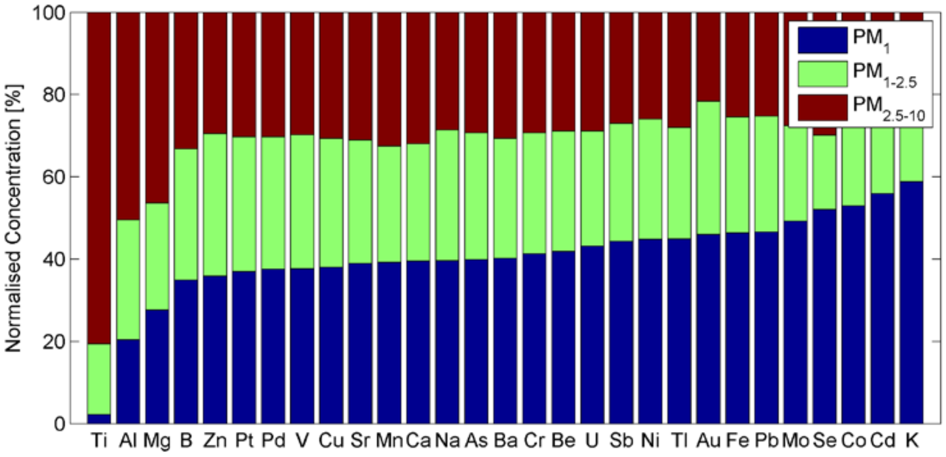


Figure 3: Mean size distributions of individual trace metal species detected. Species are arranged by increasing concentration in the PM_1 size fraction

Table 1: Annual mean PM$_{10}$ trace metal concentrations measured at Welgegund, annual average standards, as well as annual average trace metal levels determined in other studies in South Africa, China and Europe. Concentration values are presented in μg m^{-3}

PM$_{10}$ annual average	ICP detection limits (x10^{-5})	Welgegund (This study)	Annual standard	South Africa			Beijing, China (Duan et al., 2012)	West coast of Portugal (Pio et al., 1996)	Spain (Querol et al., 2007)
				Marikana (Van Zyl et al., 2014)	Rustenburg (Kgabi, 2006)	Vaal Triangle (Kleynhans, 2008)			
Be	0.293	**0.0002**		0.020			0.100		<0.001
B	4.415	**0.28**		1.300					
Na	8.515	**0.38**		1.410		2.800	1.450		
Mg	3.504	**0.23**		2.040		1.000	0.637		
Al	6.960	**0.17**		1.280			2.180	0.200	
K	12.98	**0.14**		0.680		1.300	1.170		
Ca	19.88	**1.1**		1.080			0.996		
Ti	5.729	**0.072**		0.120	0.180	0.020	0.069		0.019
V	1.736	**0.037**	$1.000^{(b)\#}$	0.040	0.160			<0.001	0.005
Cr	0.233	**0.50**	$2.5\text{x}10^{-5(a)*}$	0.240	1.370	0.050	0.022	<0.001	0.001
Mn	2.064	**0.026**	$0.15^{(a)}$	0.060	4.390	0.120	0.036	0.002	0.005
Fe	15.86	**1.2**		2.540	9.760	1.280	1.090	0.028	
Co	0.8146	**0.0035**		0.140			<0.001		<0.001
Ni	4.000	**0.079**	$0.020^{(b)}$	0.330	0.770	0.040	0.020	<0.001	0.003
Cu	3.529	**0.0069**		0.180	0.210	0.050	0.010	0.003	0.008
Zn	14.13	**0.053**		0.490	0.340	0.090	0.027	0.003	0.026
As	4.730	**0.0084**	$0.006^{(b)}$	0.260			0.003	0.002	<0.001
Se	10.51	**0.0074**		0.580			0.001	<0.001	0.001<

Table 1: continued...

Sr	0.819	**0.0017**					0.010		0.005
Mo	0.421	**0.015**					0.007		0.004
Pd	7.394	**0.0018**		0.410					
Ag	1.030	***0.0005***					<0.001		
Cd	0.637	**0.0004**	0.005 (a)(b)	0.030			<0.001	<0.001	<0.001
Sb	0.444	**0.0013**					<0.001		<0.001
Ba	3.194	**0.0040**		0.140			0.018		<0.008
Pt	6.962	**0.0016**		0.350					
Au	7.340	**0.0031**		0.380					
Hg	9.971	***0.0002***	1.000(a)	0.550					
Tl	4.917	**0.0007**		0.270					<0.001
Pb	2.592	**0.0078**	0.5 (a)(b)(c)	0.080	0.420	0.040	0.053	0.003	0.009
U	8.527	**0.0009**							

** WHO guideline for Cr(VI) concentrations associated with an excess lifetime risk of 1:1 000 000*
 # 24-h limit value
a) *WHO air quality guidelines for Europe,* b) *European Commission Air Quality Standards, c) National Air Quality Act of the South African Department of Environmental Affairs*

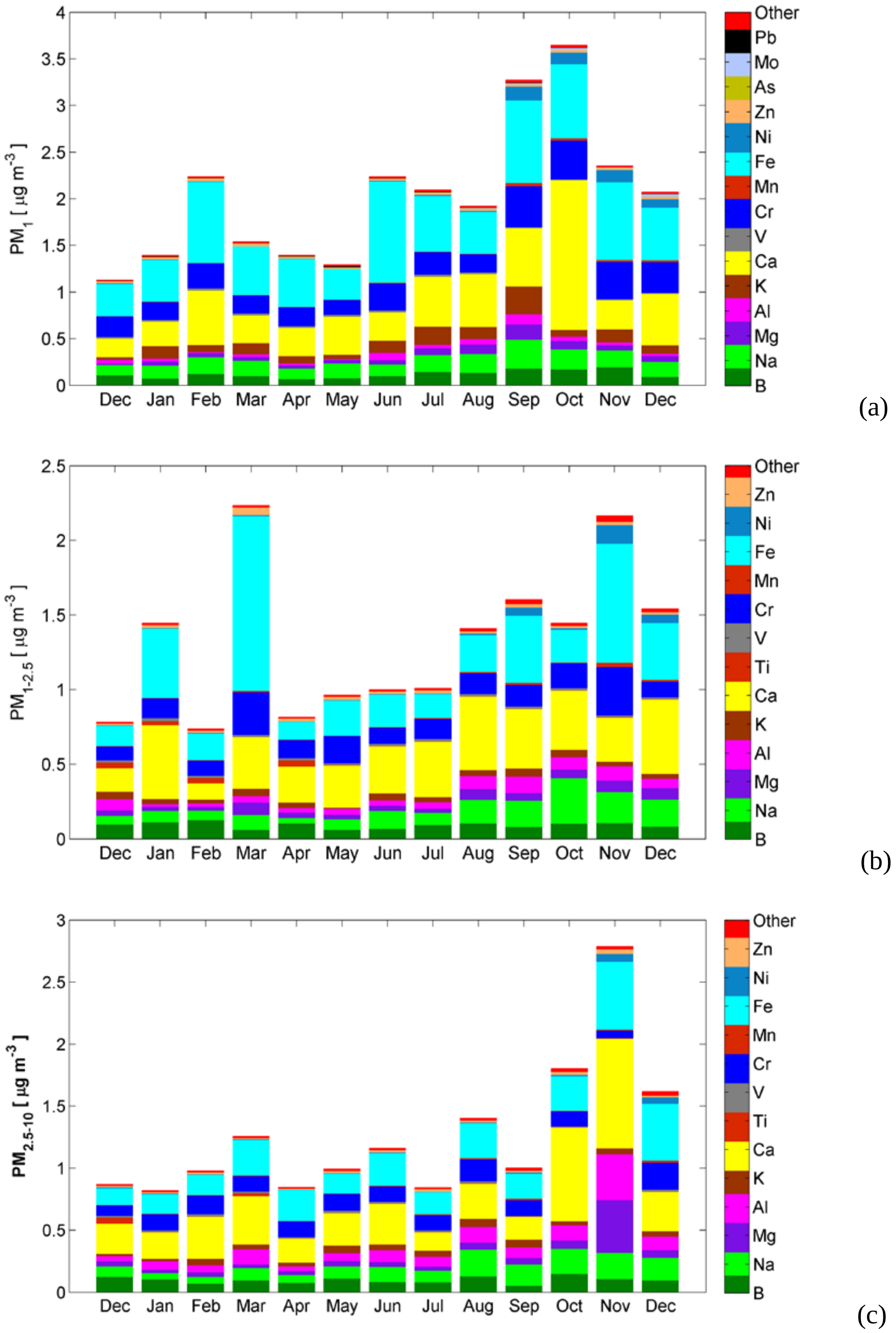


Figure 4: The monthly median trace metal concentrations in the PM$_1$ (a), PM$_{1–2.5}$ (b) and PM$_{2.5–10}$ (c) size fractions

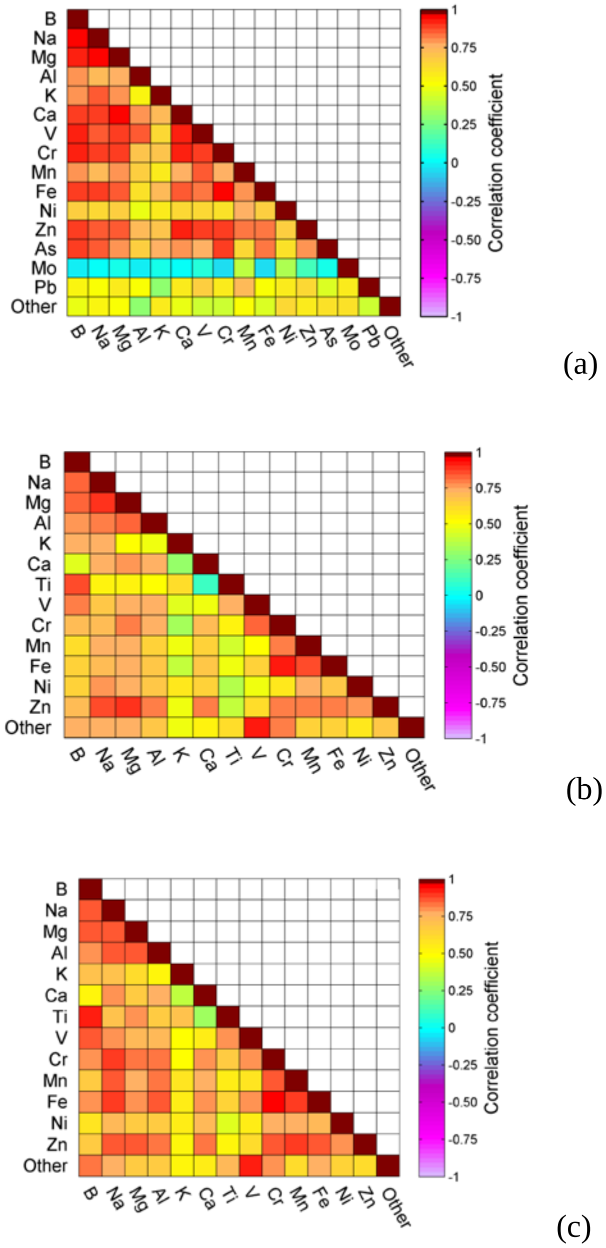


Figure 5: Spearman correlations of trace metal species in the PM_1 (a), $PM_{1\text{-}2.5}$ (b) and $PM_{2.5\text{-}10}$ (c) size fractions

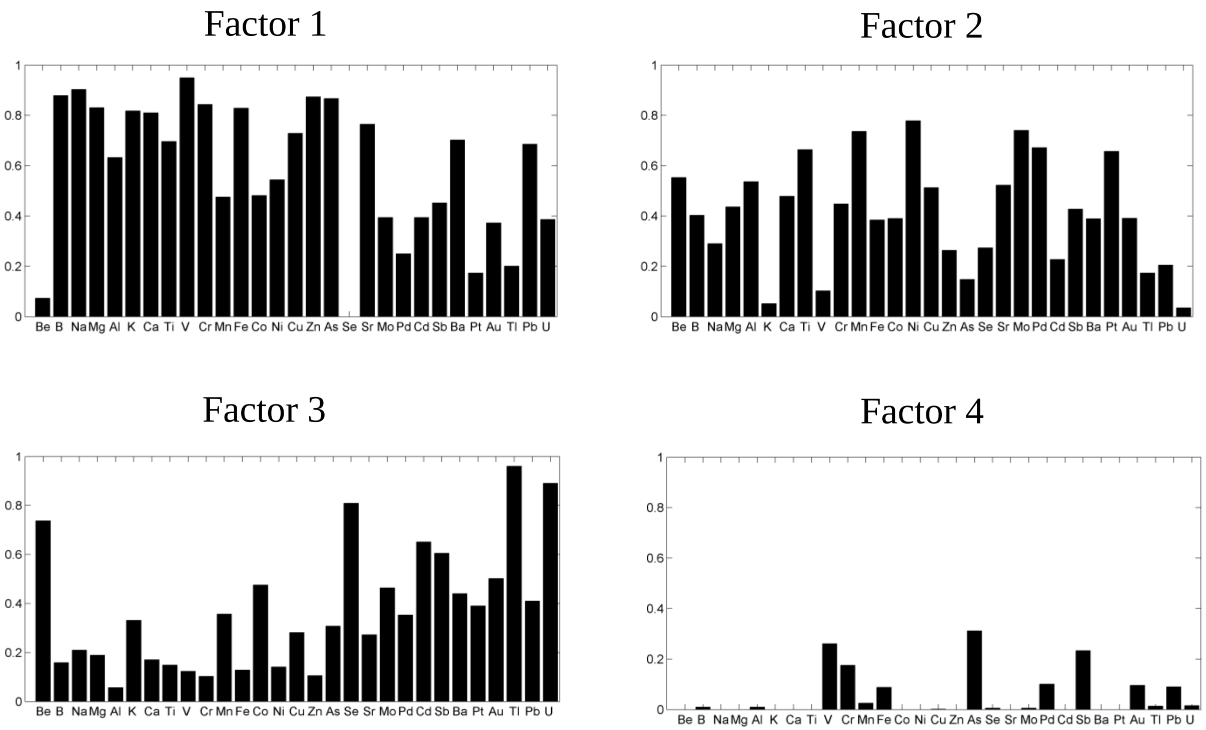


Figure 6: PCFA of the trace metal concentration in the PM_1 size fraction. Four dominant factors are identified

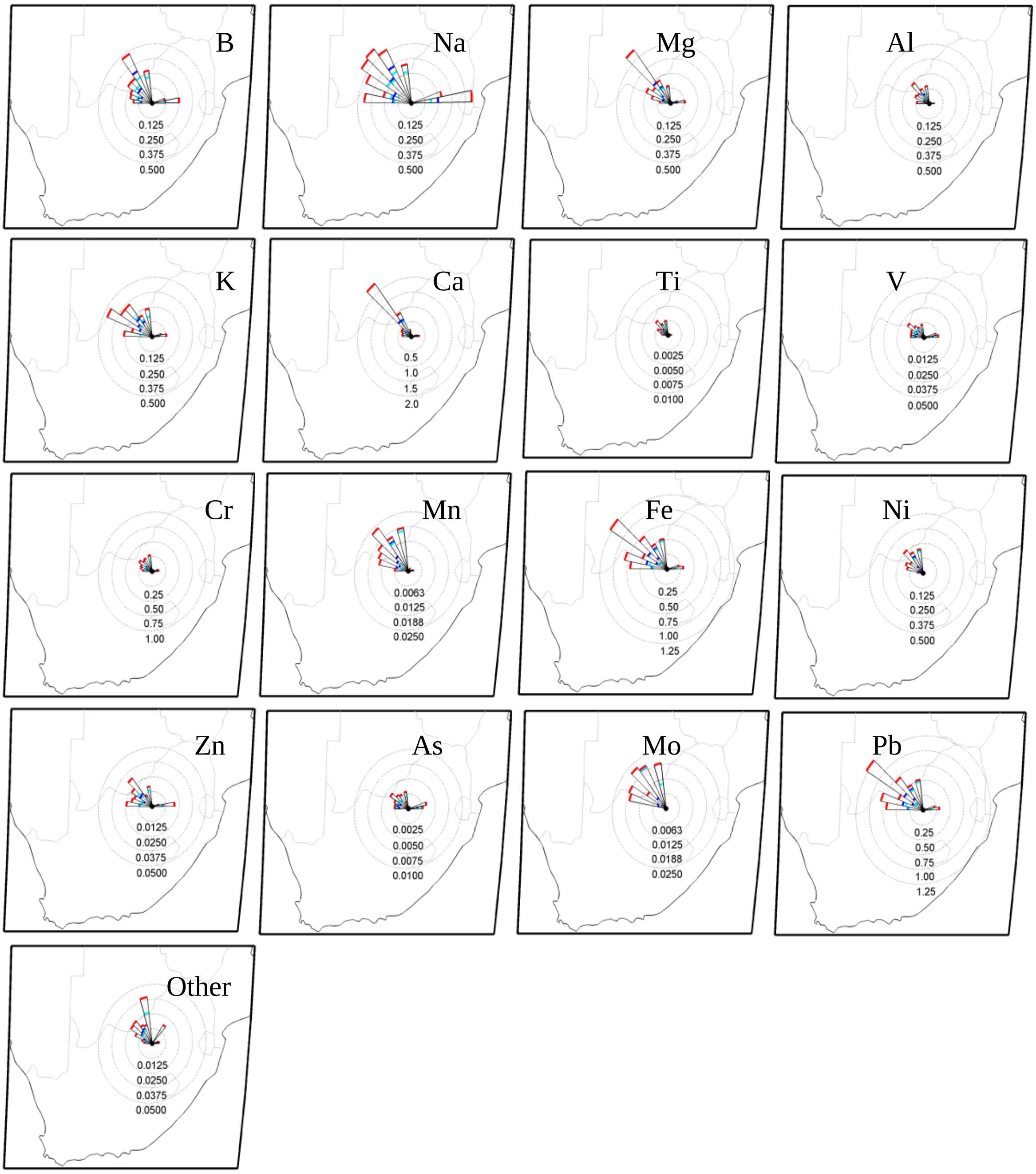


Figure 7: Pollution roses of trace metal species that were 25% or more of the time detected with the analytical technique