Particulate matter ($PM_{2.5}$) characterization, air quality level and origin of air masses in an urban background in Pretoria.

Adewale Adekunle Adeyemi[a,b*], Peter Molnar[c], Johan Boman[d], Janine Wichmann[a]

[a] School of Health Systems and Public Health, University of Pretoria, 31 Bophelo Road 00 01, Pretoria, South Africa.

[b] Department of Environmental Modeling and biometrics, Forestry Research Institute of Nigeria, Ibadan Nigeria.

[c] Occupational and environmental medicine, Sahlgrenska University Hospital & University of Gothenburg, Medicinaregatan 16A, SE-40530 Gothenburg, Sweden

[d] Department of Chemistry and molecular biology, University of Gothenburg Sweden.

*Corresponding author: adewale.adeyemi@up.ac.za

Abstract

Several sources have been identified as contributing to the concentration of ambient fine particulate matter, which has been associated to a variety of health issues. The chemical characteristics and sources of trace elements in $PM_{2.5}$, as well as the air quality index, were investigated in this study. 24-h fine aerosol particles were collected in an urban area in Pretoria, South Africa, from April 2017 - April 2018. Eighteen trace elements were determined using an XEPOS 5 energy-dispersive X-ray fluorescence (EDXRF) spectrometer, while black and organic carbon were estimated using an optical transmissometer from the samples collected. The HYPLIT model (version 4.9) was used to estimate air mass trajectories. Health risk was calculated by comparing it to the World Health Organization's air quality index (AQI). The overall mean $PM_{2.5}$ concentration of the collected sample equals 21µg/m^3. Majority of $PM_{2.5}$ exceedances were reported during mid-autumn and winter seasons, as compared to daily WHO guidelines and South African standards. S had the highest concentrations, greater than 1µg/m^3. Ni, Se, Br and Sb showed they were extremely enriched, (EF>10) and suggestive of anthropogenic or non crustal origin The 24-h PM, soot, BC and OC were significantly different by the geographical origin of air masses ($p<0.05$). The AQI showed that 70% of the samples showed levels above the AQI range of good and healthy air. The findings include details on the concentration, composition, and potential sources of fine $PM_{2.5}$, which is essential for policy formulation and mitigation strategies in South Africa's fight against air pollution.

Key words: Air pollution, transport cluster, particulate matter, trace elements, biomass burning, South Africa.

Introduction

Air pollution, whether outdoor (ambient) or indoor (household), continues to be a significant environmental health concern in both developed and developing countries around the world. The origin of particulate matter (PM) in the atmosphere has been traced to natural or anthropogenic sources, and it is considered a leading factor in declining ambient air quality (Parmar et al. 2001). According to WHO estimates, the combined effects of ambient and household air pollution cause approximately 7 million deaths, primarily from non-communicable diseases (WHO, 2018). According to recent estimates by Burnett et al (2018), airborne particulate matter smaller than 2.5 m causes 8.9 million deaths per year. In another global assessment, it was reported that ambient

air pollution alone contributed to about 4 to 9 million deaths per year, as well as hundreds of millions of lost years of health life, with the greatest attributable disease burden seen in low- and middle-income countries (WHO, 2018; Vohra et al. 2021). Furthermore, the unprecedented rate of increase in air pollution has a detrimental effect on the economy and quality of life, rendering it a public health emergency (WHO, 2014). The analysis of PM has grown in popularity over the last two decades due to its potential to affect local and regional air quality (Paraskevopoulou et al. 2015). It has a negative effect on visibility (Kanakidou et al. 2005), the climate system (Steinfeld, 1998), and overall humans health. Several authors have identified connections between ambient fine PM concentrations and adverse health effects in epidemiological and human exposure studies. PM exposure, both long and short term, has been related to increased cardiovascular and respiratory morbidity and mortality (Anderson et al. 2012; Brook et al. 2010; Gehring et al. 2010; Martinelli et al. 2013; Pope and Dockery, 2006).

It is therefore pertinent to study the chemical composition of atmospheric aerosol because of the health implications on human, and the impact on climate change. Investigating the contribution of natural and anthropogenic sources to PM levels and their spatial gradient, particularly in inhabited areas, as well as the information about their origin and source of emission revealed by their composition is key to this study. Many of these particles originate from anthropogenic sources either directly from a point source or by secondary formation which occurs in the atmosphere from gases such as SO_2, NO_X, and volatile organic compounds. As these particles travel from one site to another over time, the origin of air masses can be local, regional, or global. PM is known to contain heavy elements (such as Cd, As, Pb and Sb) that are harmful to human health at very low concentrations when exposed to them. Thus, the presence of definite elements or the ratio of one element's concentration to that of another may be used as signatures for emission from particular sources, which can emit both metals and other dangerous species that are less stable and harder to measure. (Boman et al. 2013).

South Africa, as a middle-income country, is confronted with poverty and deprivation, which predisposes its citizens to indoor and outdoor air pollution as a result of biomass burning, or coal for cooking and heating. People living near industrial, mining, and major roads are also affected (Albers et al. 2015; Norman et al. 2007). South Africa's air pollution has received more attention as a result of the country's strong dependence on coal mining as a main source of energy and combustion (DEAT, 2005). Despite global campaigns to shift away from high-carbon-emitting fossil fuels, South Africa's emissions increased from 2018 to 2019. South Africa leads Africa's major carbon emitters, emitting 471.6 million metric tons of carbon (MtC) in 2019, up from 464.4 million MtC in 2018 (DEAT 2019). Aside from coal mining, industrial areas like the South Durban Industrial Basin and the Vaal Triangle lead to South Africa's high emission rate (Terblanche, 1994). South Africa's National Environmental Management: Air Quality Act (AQA Act No.39 of 2004) went into effect in 2005 as a means of managing the country's air quality. Despite the passage of this act, the country currently has no ambient metal standard in place, with the exception of lead, making it impossible to protect the general public from the negative effects of pollution. WHO reported that only six countries in Sub-Saharan Africa can provide long-term data on airborne particulate matter (PM), spanning a total of 16 cities, due to a severe lack of air pollution monitoring (WHO, 2014) According to a study conducted by Tefera et al (2020) in Ethiopia, urban air quality monitoring of $PM_{2.5}$ and other pollutants is lacking, resulting in a lack of data on fine particulate matter. According to their findings, there are few studies on PM_{10}, but no studies on ambient $PM_{2.5}$, which contributes

to the lack of studies on the health effects of pollution. In addition, the annual average of $PM_{2.5}$ was three and five times higher than the Ethiopian air quality standard (15 µg/m^3) and the WHO air quality guideline, respectively. Wambebe and Duan (2020), revealed that PM pollution assessments in Abuja city of Nigeria were above WHO limits, particularly in the business area, resulting in a large gap between PM concentration assessment results and WHO set standards. In another study conducted in Ghana by Sarpong et al (2021), high concentrations of PM and total suspended particles were observed during the study period, informing the general public of what they are exposed to and the consequences for their health. Further research into the impact of environmental and other human behavioural factors on air quality is recommended by this study. On the Africa continent, only a few studies have looked at $PM_{2.5}$ levels (Gaita et al. 2014; Tshehla and Djolov 2018, Kalisa et al. 2019) and elemental composition in an urban context region with a high population density, such as Pretoria and Cape town (Novela et al. 2020; Williams et al. 2020; Adeyemi et al. 2021). As a result, the aim of this study was to determine the level of $PM_{2.5}$ in the Pretoria region, as well as its elemental composition, during four different seasons: autumn, winter, spring, and summer. Using the enrichment element, a systematic clarification of the source apportionment of present $PM_{2.5}$ aerosols' inorganic content is also possible while backward trajectory cluster was carried out using the HYSPLIT model.

Materials and Methods

Study area

Pretoria is a city in South Africa's Gauteng province, in the northern part of the country. With a population of 3.3 million people and a moderate dry subtropical climate, it is situated 50 kilometres north of Johannesburg in South Africa's northeast. Summers are hot and wet for long stretches of time, whereas winters are cool and dry for only a short period. Pretoria's average annual temperature is about 18.7°C, which is a little high considering its high elevation (1350m), and precipitation is 733mm. Because of its sheltered valley location, which acts as a heat trap and prevents the movement of cool southerly and northern-easterly air masses throughout the year, it has a warm duration. In the summer, the temperature hovers about 30°C and remains warm during the day. There are cold waves in July and August, with daytime temperatures around 20°C and night time low temperatures in recent years ranging from 2 to -5 °C (36 to 23 °F) (Mathee and Von Schirnding, 2003). South Africa has four distinct seasons: winter (June-August), summer (December-February), autumn (March-May), and spring (September-November).

$PM_{2.5}$ sampling

The sampling campaign took place on the fifth floor of the HW Snyman South building at the University of Pretoria's School of Health Systems and Public Health (SHSPH). The University Health campus is located in an urban area (Fig 1) and within 2km from a nearby major road. The sampling site was a typical urban background site (-25.73 S, 28.20 E). Urban background sites are commonly used to depict the typical exposure to the population without a dominating influence of nearby point sources. Particulate matter samples were taken every third day from April 18, 2017 to April 17, 2018, spanning four seasons, with a start and stop time of 9:00 a.m. to 9:00 a.m. the next day (due to the inability to stop the pumps at midnight, which necessitated the option of sampling time), as done in other studies (Novela et al. 2020; Williams et al. 2020; Adeyemi et al. 2021). A total of 122 $PM_{2.5}$ samples and 25 duplicates were collected on 2.0 µm PFTE (Zefon International, Inc ocala, FL34474 USA)., PTFE supports (Zefluor) 37 mm filters for 24 hours, during the sampling campaign. Important

to mention is that one duplicate sample was discarded as a result of faulty pump. A sampling pump (GilAir-5) is linked to a critical orifice that limits air flow to 4.0l/min was utilised (Novela et al. 2020; Williams et al. 2020; Adeyemi et al. 2021). Meteorological data was obtained from the South African Weather Services monitoring station located near the sampling site. It is also important to mention that rainfall data for the full study period was discarded (due to poor data quality) among the parameters collected. However, rainfall data from another nearby monitoring station was obtained, analysed and reported accordingly.

Gravimetric and Elemental Analysis Method

For gravimetric mass concentrations, all filters were weighed before and after exposure using a 1µg sensitivity ultra-microbalance (Mettler Toledo, XP6) in the SHSPH Air Quality Laboratory under climate-controlled conditions (temperature and relative humidity of 21 ± 0.5^{o}C and 50 ± 5%, respectively) as described by Adeyemi et al. (2021). The Teflon filters were weighed before and after sampling to determine the mass concentration of the collected PM. The modified version of the ULTRA research SOP was used for the weighing procedure (Pekkanen et al. 2000). Weighing batches of blank filters according to ISO/CD 15767 (ISO, 1998) was used to determine the limit of detection (LoD). The pre and post-weighed filters were kept at 4°C in the fridge.

Soot measurements

Using an M43D EEL smoke stain reflectometer (Diffusion Systems Ltd., London UK), the $PM_{2.5}$ collected on the filters were analyzed for black soot in batches of 20 filters. The procedure used also follow a SOP similar to the ULTRA study (Pekkanen et al. 2000; Götschi et al. 2002). The average reflectance resulting from the five measurements was used in the calculations. Each filter was calculated for reflectance five times on different locations according to the five-point rule (i.e., in the middle and in each quadrant). After each set of 25 filters, three filters were chosen and measured a second time to ensure that the two measurements differed by no more than 3%. By measuring the blank filter, the correction due filter was modified. According to ISO 9835 (ISO, 1993), the absorption coefficient, a, was used to express the reflectance as follows:

$a = (A/2V) \times In\ (Ro/Rs)$

Where; A is the loaded filter area (m^2), Vis the sampled air volume (m^3), Ro is the average reflectance of field blank filters (%), Rs is the average reflectance of the sampled filter (%), The absorption coefficient (a) is expressed in 10^{-5} m^{-1}

Black carbon and UPVM

A Model OT21 Optical Transmissometer was used to test black carbon (BC) and UV-PM (a proxy for organic carbonaceous (UV-PM) particulate matter absorbing UV light at 370nm) (Magee Scientific Corp., Berkeley, CA USA). The presence of biomass burning is indicated by the additional absorption of UV light at 370 nm due to organics (Samet, 2000; Sandradewi, 2008; Pope et al. 2002; Teich et al. 2017). UV-PM is a mass concentration-based analog for organic carbon species.

Elemental analysis

An XEPOS 5 energy-dispersive X-ray fluorescence (EDXRF) spectrometer (Spectro analytical instruments GmbH, Germany) was used at the Department of Chemistry and Molecular biology, Atmospheric Science Division, University of Gothenburg to determine the elemental composition of the aerosol particles on all filters. To maximize the identification of trace quantities of elements in the analytical spectrum, the analysis was performed under four different operating conditions, two of which used a He atmosphere. The EDXRF spectra were processed and quantified using the Spectro XRF Analyzer Pro application. All samples were analyzed for a total of 3000 seconds, which was divided automatically among the four analytical setup conditions. The manufacturer calibrated the EDXRF spectrometer, and the calibration was tested using the NIST SRM2783 standard reference filter. The elements Si, S, Cl, K, Ca, Ti, V, Fe, Ni, Cu, Zn, As, Se, Br, Sb, Ba, Pb, and U were quantitatively analyzed in the current $PM_{2.5}$ aerosols. According to repeated analysis (N = 5) of two randomly chosen filters, one with a low mass loading and the other with a high mass loading, the mean analytical precision was 5% (Molnar et al. 2014). Field blanks were analysed in the same way as the samples and concentrations detected above the limit of detection (LoD) were subtracted from the concentrations of the same elements in the samples. Quantitative analysis results of nineteen elements, including black carbon, were determined and converted into ng /m^3.

Transport Clusters

Daily backward trajectories from April 18, 2017 to April 17, 2018 were generated using the Hybrid Single Particle Lagrangian Integrated Trajectory software. (Draxler and Rolph, 2010; Molnár et al. 2017). 72 hours daily backward trajectories were used in the cluster analysis. The method used has been presented in detail elsewhere (Adeyemi 2020; Adeyemi et al. 2021).

Potential health risk

To determine the potential health risks that exposure to PM could pose to Pretoria residents, the potential risk analysis was conducted by comparing the calculated mean of $PM_{2.5}$ with the old and new WHO guideline of 10 and 5µg/m^3 (annual) and 25 and 15 µg/m^3 (daily), respectively. The daily and seasonal mean for $PM_{2.5}$ were used in the computation of the air quality index (AQI) using the equation below as described by Wambebe and Duan, X. (2020) and USEPA (2014).

$$\text{AQI pollutant} = \frac{\text{Pollutant concentration}}{\text{WHO Standard}} \times 100$$

According to the United States Environmental Protection Agency, the (AQI) is reported as the daily air quality index. This index indicates how clean or unhealthy the air we breathe is, as well as the level of concern and potential health consequences resulting from the air inhaled. The AQI also explains the experience an individual may face during the first few hours or days of exposure to unhealthy or polluted air. According to USEPA (2014), lower AQI values equals better air quality. Table S1 has been used to depict the air quality index rating.

The AQI table (Table S1) divides each pollutant into ranges (zero to above 300) which are then numbered and assigned with color codes, and each color indicating the level of health concern and its meaning. The daily AQI's colors correspond to the level of pollution and health concern. For example, level 1 indicates green color, implying good and healthy air quality with little or no risk of health effect, whereas level 6 indicates maroon color and a hazardous level of health concern. At this level, an emergency health warning will be activated because the population exposed to this hazardous air may be adversely harmed.

Statistical analysis

Concentrations above the limit of detection (LoD) were addressed during calculation of summary statistics. SAS System for Windows version 9.3 (SAS, 2003) was used to conduct statistical analyses. Seasons were defined as: autumn (18-April 2017 to 31-May2017 and 1-March 2018 to 16-April 2018), winter (1-June 2017 to 31-August 2017), spring (1-September 2017 to 30-November 2017) and summer (1-December 2017 to 28- February 2018). Descriptive statistics for $PM_{2.5}$, soot, BC, OC and the trace elements were reported. Since the $PM_{2.5}$ levels and meteorological variables did not have normal Gaussian distributions, non-parametric tests were used. The association between $PM_{2.5}$, BC, and trace elements were investigated using Spearman rank correlation analyses. To see whether $PM_{2.5}$ median levels varied significantly across seasons and trajectories, the Kruskal-Wallis test was used. The Wilcoxon rank-sum test was used to see whether there was a significant difference in $PM_{2.5}$ levels between weekdays and weekends.

RESULT AND DISCUSSION

Overview of $PM_{2.5}$ concentration

Table 1 shows the summary of annual and seasonal concentrations of $PM_{2.5}$, soot, BC, and OC, while Fig. 2 shows time-series graphs of $PM_{2.5}$, soot, and meteorological conditions. $PM_{2.5}$ levels ranged from 0.7 to 66.8 $\mu g/m^3$ on a daily basis, with an annual average (standard deviation) of 21.1 ± 15.0 $\mu g/m^3$. The overall average was higher than the old WHO annual air quality guideline (10 $\mu g/m^3$) (WHO, 2005) and the South African National Ambient Air Quality Standard (SA NAAQS) (20 $\mu g/m^3$) (DEA, 2005). This study's annual average was four times higher than the new WHO annual air quality guideline (5 $\mu g/m^3$) (WHO, 2021), implying that people living in Pretoria are more likely to experience health problems associated with PM exposure. During winter, the highest daily mean of 66.8 $\mu g/m^3$ was reported (2 June 2017), while the winter's median value (35.0 $\mu g/m^3$) was significantly higher than autumn's (15.4 $\mu g/m^3$), spring's (13.5 $\mu g/m^3$), and summer's (9.3 $\mu g/m^3$) values ($p<0.05$). Similar to the observed increased $PM_{2.5}$ concentration in winter months in our study, other studies (Shaltout et al. 2020; Safar and Labib, 2010) have also documented increased $PM_{2.5}$ concentration during the winter months as a result of higher frequency of inversions and reduced wind speed, which lowers particulate matter dispersion in the air, since the cold months have the lowest temperature and windspeed (Table S2). Aside from meteorological factors, biomass burning, fossil fuel burning, and agricultural activities all contribute to the increased concentration during the winter. Dust, industrial secondary sulphate and secondary organics have been reported to contribute significantly to the amount of particulate matter measured at ground level of South Africa ((Maenhaut et al. 1996; Tiitta et al. 2014), also with recent attention to the impact of regional biomass burning which also occurs from June to October (Cooke and Wilson, 1996), which originates

from the neighbouring countries mostly from Zimbabwe and Mozambique (Magi et al. 2009) and transported in stratified layers aloft (Campbell et al., 2003; Chand et al.2009).

Table 2 presents the number of days the 24h daily $PM_{2.5}$ levels exceeded the daily WHO guidelines and SA standard. No exceedances were recorded during summer when $PM_{2.5}$ concentrations were compared with the old daily WHO guideline. During other seasons, exceedances were recorded when the $PM_{2.5}$ concentrations were compared with both old and new daily WHO guideline, thus indicating that the population of Pretoria are more likely to experience health problems associated with air pollutionThe $PM_{2.5}$ median concentrations for weekdays (88days; 16.0 µg/m^3) and weekends (34days; 15.3 µg/m^3) did not differ significantly from each other ($p > 0.05$) (Table 1). This suggests that there is no variation in pollution sources between weekdays and weekends.

The monthly average mass concentration of $PM_{2.5}$ vary substantially from month to month, ranging from 10µg/m^3 in December 2017 to 41 µg/m^3 in July 2017 (Fig. 3). During June and July 2017, average monthly $PM_{2.5}$ concentrations (Fig. 3) marginally exceeded the South African air quality standard limit for $PM_{2.5}$ (40µg/m^3 for 24 hours) (DEAT, 2005). However, all months' average monthly $PM_{2.5}$ concentrations (excluding May–August 2017) exceed the World Health Organization's (WHO, 2006) and European Commission's yearly air quality standards (European commission, 2017). As done in the study of Shaltout et al. (2020), The $PM_{2.5}$ samples were divided into five particle mass ranges based on the new WHO interim objectives for daily ambient $PM_{2.5}$ concentrations (WHO 2021): <25 µg/m^3, 25–37.5 µg/m^3, 37.5–50 µg/m^3, 50–75 µg/m^3, and > 75 µg/m^3 (Fig. 4). The air quality guideline (AQG) for $PM_{2.5}$ for 24 hours (WHO, 2006) were met by 72% of the $PM_{2.5}$ mass concentrations (Fig. 4), however 28% of the $PM_{2.5}$ mass concentrations were higher, with none of the $PM_{2.5}$ mass concentrations above WHO's interim level I: 75 µg/m^3. In a study conducted by Feig et al. (2016) in Waterberg Limpopo, South Africa, the mean annual $PM_{2.5}$ values from three monitoring stations were found to be below the South African air quality standard. The mean $PM_{2.5}$ level in this study were higher than those in rural parts such as Thohoyandou (Novela et al. 2020) and Greater Tubatse of Limpopo (Tshehla and Djolov 2018), Tembisa town (Olutola et al. 2019) and major cities of South Africa which include Cape town (Williams et al. 2020) and Pretoria (Morakinyo et al. 2019). On the other hand, the overall average $PM_{2.5}$ level in an Egyptian study (Shaltout et al. 2020) was found to be three times higher than the level reported in this study. The annual average of $PM_{2.5}$ levels for all the 21 AAQM stations in South Africa has been reported to range from 4.9 – 43.3 µg/m^3 for with annual average of 24.1 µg/m^3 in the year 2012 which is slightly higher than the average annual in this study (Altieri and Keen, 2019).

The annual mean soot level for this study is 2.3 x 10^{-5} m^{-1} (Table 1). Comparing the soot level across seasons, the median soot levels in winter (4.2 x 10^{-5} m^{-1}) and autumn (2.4 x 10^{-5} m^{-1}) were significantly higher ($p < 0.05$) than summer (1.1 x 10^{-5} m^{-1}) and spring (1.0 x 10^{-5} m^{-1}), a similar observation was reported in the study of Williams et al. (2020) i.e. a consistent decline observation in the soot level was observed from July 2017 to December 2017 was observed in this study (Fig. S1). Autumn and winter had the largest variations in soot levels. This observation can be attributed to the positive correlation that exist between $PM_{2.5}$ and soot, i.e. as $PM_{2.5}$ increases, soot level also increases and vice versa. Median soot levels on weekdays (1.7 x 10^{-5} m^{-1}) and weekends (1.3 x 10^{-5} m^{-1}) ($p > 0.05$) did not differ significantly. In South Africa, no soot level standard has been set, likewise no WHO guideline is known. However, the mean level of soot in this study is higher compared to similar studies conducted as part of the bigger project in other provinces of South Africa during the same period

(April 2017 to April 2018), Cape town (1.4 x 10^{-5} m^{-1}) and Thohoyandou (0.7 x 10^{-5} m^{-1}). In comparison with the study of Gotchi et al (2002), the indoor and outdoor black smoke (BS) recorded in Athens and Prague was higher than our mean average for soot but lower than what was recorded in Basel and Helsinki, while the mean average for BC in this study was higher than the BS in all the four locations, noting that number of samples in our study is higher than the locations reported.

The annual mean for BC and OC were 3.9 µg/m^3 and 3.3 µg/m^3, respectively whereas Table 1 also summarizes the seasonal mean concentrations of BC and OC. BC and OC concentrations followed the same pattern as $PM_{2.5}$ concentrations, with the highest concentrations in winter and autumn and the lowest concentrations in spring and summer ($p<0.05$). No significant difference was also observed during weekdays and weekends for both BC and OC ($p>0.05$). A consistent decline pattern for BC and OC were observed from July 2017 to Jan 2018 (Fig. S2). The seasonality pattern identified in this study for BC and OC is consistent with Zhang et al. 2008, which employed the same sampling technique (sampling collected every 3rd day for a period of one year) and similar sampling locations e.g. urban area as our study. The higher concentrations of BC and OC in the spring compared to the summer can be due to open biomass burning, which has been associated to higher K concentrations in the spring in our study. Our findings are further corroborated by Cao et al. (2007), who found that aerosols from open biomass burning have higher BC and OC.

Risk analysis by air quality index

The daily AQI was calculated for the entire study period and seasons using the old and current WHO $PM_{2.5}$ concentration guidelines as shown in Fig S3. When the old WHO guideline was used for the AQI calculation, the lowest and highest AQI were 3 and 5, respectively, while AQI was significant when the new guideline was used, with the lowest and highest AQI being 267 and 445, respectively.

According to the old WHO annual $PM_{2.5}$ guideline, 36 days (30%) of the total number of sampling days fall within the AQI range of 0-50, indicating good and healthy air quality. According to Table S1, fifty-three (53) days (43%) of the sampling days are in the moderate range (50-100). This indicates that the population exposed to the air may face low to moderate health risks. In the instance of the new annual WHO guideline, 16 days (13%) of the sampling period were in the range of good and healthy air quality, while 40 days (33%) fell in the range of moderate air quality. Also, to be noted is that the days where good and moderate air quality were observed happen to be spring and summer days. This observation shows that the new WHO guideline is more protective than the old one as a result of the decline in the number of days of exceedances. Despite this, studies have shown that exposure at lower concentrations below the WHO guidelines can have a significant negative impact on human health (Brook et al. 2012; Burnett et al. 2018). Seasonally, using the mean values and the annual WHO guidelines (old and new) for $PM_{2.5}$, the AQI for the different seasons ranged from 107- 355 and 214 - 710 for the old and new WHO limits, respectively. Most AQI exceedances occurred during late autumn and winter, which indicates that the exposed population may be seriously affected by hazardous pollutants, thereby resulting in an emergency health condition. According to the review by the WHO, it was stated that "recent long-term studies show associations between PM and mortality at levels well below the current annual WHO air quality guideline level for $PM_{2.5}$" (WHO, 2013). Despite South Africa's progressive air quality legislation, the breath of potential health impacts associated with air quality has not been thoroughly researched

in local epidemiological studies, creating a significant research gap. Various studies have also found that inhaling particulate matter can cause immune suppression, nausea, cardiovascular infection, lung cancer, and asthma, as well as premature death (ATS, 2000; Martinelli et al. 2013; Pope et al. 2020).

Correlation coefficient between air pollution and weather variables

The spearman correlation between the air pollution and weather variables are shown in Table S3. $PM_{2.5}$ and soot had a significant positive correlation (r^2 = 0.96) and a significant negative correlation with temperature (r^2 = -0.32; -0.49) and relative humidity (r^2 = -0.22; -0.03) ($p<0.05$) Table S3. Also, BC and OC had a significant negative correlation with temperature, and a significant negative correlation with relative humidity. Wind speed had a weak positive significant correlation with $PM_{2.5}$ and OC, but a significant negative correlation with temperature. This showed that temperature, RH and wind speed had significant impact on the ambient PM. In winter, lower mean temperatures were associated with higher $PM_{2.5}$ levels, and vice versa in summer. According to studies by Cavanagh et al. (2009). and Ryu et al. (2012) air pollutants tend to increase with calm winds and stable atmospheric conditions, while air pollutant concentrations fall with increasing wind speeds and unstable atmospheric circumstances.

Elemental concentration in $PM_{2.5}$

Table S4 shows the seasonal elemental analysis data for the air particulate filter samples collected at Pretoria. The concentrations are given in ng/m^{-3}. The variability of the monthly concentration averages of eighteen elements (Si, S, Cl, K, Ca, Ti, V, Fe, Ni, Cu, Zn, As, Se, Br, Sb, Ba, Pb, and U) and black carbon (BC) in the $PM_{2.5}$ are presented in Table 3. S recorded the highest monthly concentration of 2220 $ng.m^{-3}$ in June 2017. The overall averages of the elemental concentrations showed the following pattern: S> Si> Fe> K> Ca> Ni> Cl> Zn> Ti> Br> Ba> Sb> Pb> Cu> As> V> U> Se. The high concentrations of S, Si, Fe, and K found in this study are consistent with the findings of Kilbo Edlund et al. (2021), who also found high concentrations of these elements. Except for Ca, which had the highest monthly mean concentration in August 2017, the highest monthly mean concentration for Zn and crustal elements (i.e. Si, K, Ti, and Fe) were reported in June 2017. All of these elements had their lowest monthly mean concentrations at different times of the year, and their monthly averages followed the same pattern as $PM_{2.5}$, which could have been influenced by seasonal weather conditions. The crustal elements Si, K, Ca, Ti, and Fe accounted for 45.2% of the total element concentration in $PM_{2.5}$, while S alone contributed 44.8%. Most of these elements were also highly correlated with total $PM_{2.5}$ implying that crustal elements are vital important source of $PM_{2.5}$ in Pretoria, which is also consistent with the findings of the studies conducted in Vaal Triangle and Thohoyandou (Muyemeki et al 2020; Kilbo Edlund's et al. 2021). Seasonally, except for V, Ni and Sb, all other elements recorded the highest concentrations during winter (Table S4). Across all the seasons, the presence of S in $PM_{2.5}$ was significantly high (Fig. 5), which also agrees with the study of Muyemeki et al. (2020) conducted in the same province of South Africa. This S can be attributed to coal combustion in the province as a result of power generation. A significant amount of K and a low level of Zn in $PM_{2.5}$ were recorded during winter and spring when compared to other seasons. The same observation was reported in the study by Muyemeki et al. (2020), which suggests that these elements are emitted as a result of wood and biomass burning. The significant amount of Fe and Ni observed during winter and summer is also

consistent with the finding of Muyemeki et al. (2020) conducted in the same province, thus suggestive of metallurgical industries around the province (Adeyemi et al. 2021).

The monthly difference in the sum of the of elemental concentrations, as well as BC present in $PM_{2.5}$ which corresponds to the $PM_{2.5}$ mass concentrations reveals an average concentration ranging from 2050 ng m^{-3} in November 2017 to 5970 $ng.m^{-3}$ in June 2017 with an average value of 3300 $ng.m^{-3}$ (Table 3). The overall average of the ratio between sum elemental concentrations and $PM_{2.5}$ concentration was 17%, while the monthly ratio varies between 12% in April and July 2017 and 29% in June 2017. Except for Pb, which is specified in the ambient air quality criteria in South Africa, none of the elements are currently regulated. As a result, an annual average target of 500 $ng.m^{-3}$ has yet to be promulgated. The amount of Pb identified in this study is much below the level set by the European Commission for ambient Pb annual mean levels (500 $ng.m^{-3}$). The low Pb concentrations found could be attributable to the phasing out of leaded gasoline in South Africa and other African countries since 2006.

Intra-relationship between $PM_{2.5}$, BC and other elements

The intra-element interaction, according to Manta et al. (2002), might provide crucial information regarding the likely origins and pathways for the elements detected. To explore the intra-relationship between the elements, Pearson's correlation coefficient (Table 4) was applied to the elements analyzed in $PM_{2.5}$ samples. Shaltout et al. (2011), for example, reported a high positive association when the correlation coefficients approach 1. In this study, we used Shaltout et al. (2020) definition of high positive correlation coefficients as values ranging from 0.75 to 0.99 (highlighted in bold), and moderately high correlation coefficients as values ranging from 0.50 to 0.74 in this investigation (highlighted in italic). The following elemental relationship was identified according to Table 4. $PM_{2.5}$ concentrations demonstrate a strong positive correlation with BC, Cl, Zn, As, Se, Br, and Pb, and a moderate correlation with Ca, Fe, and Si. This points to the presence of a partially mixed aerosol at the sampling site, as well as the seasonality of these elements. Secondly, Cl has a strong positive correlation with K, Zn, Pb, As, Se, and Br, but moderate to low correlation with the rest of the elements. This indicates that the source is either biomass or coal burning. Thirdly, the high correlation between the crustal elements (K, Ca, Si, Ti, and Fe) indicates that mineral dust and resuspended road dust from neighbouring roadways contribute to the source (Shaltout et al. 2020). As previously stated, sulphur had the highest concentration, indicating a potential source from coal combustion. The low correlation between S and other key elements (such as Cl and Br) associated with coal combustion suggests that coal combustion is the primary source of S in these areas. Finally, Pb had a strong correlation with Cl, Ca, As, and Br and a weak correlation with K, Fe, Zn, Si, and Ti, indicating that Pb-containing particles are complex. Except for the second source, these sources agree with Shaltout et al.'s (2020) findings, i.e $PM_{2.5}$ source composition from a similar study in residential -industrial from the Mediterranean area having similar industries around our study area, and also close to a major busy road

Enrichment Factors of Measured Elements.

PM, particularly $PM_{2.5}$ have been known to comprise mineral and elements which could originate from natural and anthropogenic sources. Enrichment factors (EFs) were therefore calculated to differentiate the sources

between natural and anthropogenic. The degree of anthropogenic contribution was determined according to the study of Yongming et al. (2006), thus assisting in the determination of the degree of contamination. The EF for an element is therefore calculated as follow. For an element X and reference crustal element Y, the EF for the element X equals:

$$EF_x = \frac{(X/Y)_{air}}{(X/Y)_{crust}} \quad (1)$$

Where (X/Y) refers to the concentration ratio of X and Y elements in the $PM_{2.5}$ aerosols or in the earth crust, respectively. Elements such as Al, Fe, Mn and Rb and also total organic carbon and grain size have been used in many studies, but in our study, Fe was used as the reference element Y. The choice of this elements was attributed to its stability in the soil and its origin is mainly by natural sources. (Barbieri, 2016). The upper continental crust chemical composition used in this study was extracted from the study by Wedepohl (1995). Our estimation of EFs was performed with the assumption that the contribution of anthropogenic sources of Fe is insignificant in Pretoria compared with the contribution from natural sources. A significant crustal source is characterised with EF values less than 10 (EF<10) while non-crustal origin i.e. anthropogenic sources were categorised as having EF greater than 10 (EF>10) (Nayebare et al. 2018). As shown in Fig 6, Si, Ca, Ti, K, Ba, V and Cl are of crustal origin (EF<10; i.e. soil and re-suspended dust), with anthropogenic having lesser influence (Hao et al. 2007). Elements such as Cu, Zn, As, , Pb, and U are moderately enriched while Ni, Se, Br and Sb are extremely enriched, (EF>10) and suggestive of anthropogenic or non crustal origin. (Xu et al. 2012; Yongming et al. 2006). The high EF values imply that these elements are present in atmospheric aerosols at levels that are too high to be explained by normal crustal weathering processes. The studies by Hsu et al. (2010) and Alghamdi et al. (2015), confirms that the sources of moderately and extremely enriched elements are suggestive emissions of combustion from mobile sources (i.e vehichle-exhaust), tire wear, fossile fuel, combustion, incinerator emmission and industrial activities. The combustion of heavy fuel oil or diesel have been known to contain S (Asaoka et al. 2019) while the presence of high EF for Cu can be attributed to anthropogenic sources which include nonferrous metal industries ,chromium plating and wear of abestos-free brake linings (Shaltout et al 2020). Since Pretoria is an inland city, studies from Duan et al. (2006) and Zheng et al. (2005) have shown from chemical analysis of $PM_{2.5}$ samples and source profiles from laboratory that Cl is an elemental tracer for coal combustion.

Seasonal Transport clusters and potential source areas

The seasonal mean of $PM_{2.5}$ and transport cluster were summarized in Table S5. Seasonally, five transport cluster with different pathways were identified based on the change in total spatial variance (TSV) output (Fig 7). The pathways in which the air masses originate can be categorized into Atlantic Ocean, Indian Ocean, Regional, National and Transboundary while the dominance of the air masses across the seasons differs from each other. During the entire study, air masses originating from cluster 2 dominated, but on distinct pathways. Air masses coming from cluster 1 dominated in winter (51.6%) and autumn (51.6%), while cluster 2 dominated in spring (60%) and summer (66.6%). The two main pathways that appeared seasonally and throughout the

investigation were North of Limpopo (NLP) and Long Indian Ocean (LIO). The 24-h PM, soot, BC and OC were significantly different by the geographical origin of air masses ($p<0.05$) (Table S6). On the other hand, the median temperature and relative humidity levels did not differ significantly by the geographical origin of air masses ($p>0.05$), however, the maximum temperature (25.3ºC) and minimum relative humidity (21.5%) were observed when the air masses originated from cluster associated Eastern inland (i.e. cluster 2).

Comparison of $PM_{2.5}$, BC level and other metals with other studies in Africa.

The results of this analysis were compared to those of other related African studies. This study's $PM_{2.5}$, trace elements, and BC concentrations were used in the comparison (Table 5). Based on the length of research, this study is comparable to Gaita et al. (2014) and Boman et al. (2009) studies in Nairobi and Cairo, respectively. The geographical positions of these countries in comparison to our study position are noteworthy. The results of the studies can also be influenced by weather conditions. Another related element in Gaita et al. (2014) analysis is the sampling location, which is an urban background.

Our annual $PM_{2.5}$ concentration was comparable to Gaita et al. (2014) $PM_{2.5}$ concentration in an urban background site in Nairobi between May 2008 and April 2010. Furthermore, the mean BC concentration in this study matches that of Gaita et al. (2014). The agreement in $PM_{2.5}$ concentrations between the two studies demonstrates the impact of the severe drought that was experienced during Gaita et al. (2014) study.'s and the low rainfall recorded during ours. The abundance of PM in the air can be seen in the study by Gaita et al. (2014), which found higher concentrations of many elements than the average concentrations in this study. In contrast, the S concentration in our study is twice that of a similar study by Gaita et al (2014).The study's high S concentration may be due to increased energy production from the power generation plants using coal during the cold season, which releases a significant amount of SO_2 into the atmosphere. The Pb concentration in our study is twice as low as that recorded by Gaita et al. (2014). This result demonstrates the impact of South Africa's 2006 ban on lead in gasoline.

This study also supports the findings by Gaita et al. (2014) who reported that air quality from other studies listed in Table 5 were largely influenced by mineral dust, combustion processes and vehicular emissions, by the presence of key elements (such as Fe, Ca, K, Ti, BC, S, Zn, Pb) that has been associated with these sources in our study. The levels of $PM_{2.5}$, BC, Pb, and K were higher in the study of Gatari et al. (2009) conducted at an industrial background when compared to the levels of the same elements in our study. Although, the S level was similar while the concentration of K in our study was 50% of what was reported in the study of Gatari et al (2009), which might have been influenced by the industrial activities. Noteworthy to mention is the high $PM_{2.5,}$ BC and other elements that were reported at the city center of Ouagadougou (Boman et al. 2009) which has been influenced by largely by mineral dust, combustion activities and vehicular emissions when compared to the semirural area of Accra (Aboh et al. 2009) and urban background in our study. High PM seen in the semirural area of the city of Accra have been reported to have been influenced by dust filled Harmattan winds blowing from the Sahara Desert to the area. Lastly, Ni and S were not reported in the study of Boman et al. (2009) and Mn in our study.

Also, Zn, Br and Pb concentrations were found to be higher in our study when compared to other two locations. The probable reasons for these differences at the locations might be partly influenced by the sampling methods

and sampling campaign period. Another source of variation can be attributed to the compositions of the $PM_{2.5}$ sampled. In comparison to Cairo urban centre, Egypt and low-income area of Accra, the concentration of $PM_{2.5}$ in our study and low-income area of Accra was 50% more of what is reported at the Cairo urban centre (Boman et al. 2013), as a result of the close proximity to the desert area. Other elements were also higher in the urban centre, with the exception of Ni, which was about 23% higher in our study compared to the urban centre.

Gaita et al. (2014) reported in their study that air quality in Egypt's desert region is partly influenced by the mineral dust originating from the desert, thus the probable reason for the increase observed for some elements such as Ca, Cl and S. The location may also be responsible for the high S and Cl concentration as Egypt is closer to the Mediterranean Sea unlike our study area which is partly influence by the emission from the surrounding power plants and industries.

Conclusion

Daily $PM_{2.5}$ samples were collected between 18/04/2017 and 17/04/2018 every third day in the urban background in Pretoria, South Africa. The annual mean for $PM_{2.5}$ (21µg/m^3) was found to breach the new WHO air quality guideline (5 µg/m^3). Seasonality was evident, with median $PM_{2.5}$ levels significantly higher in winter and autumn than in spring and summer. Autumn and winter median soot levels were significantly higher than spring and summer median soot levels. In addition, most aerosol species, such as UV-PM, BC, Pb, and Cl, had distinct seasonality, with the highest concentrations recorded during the winter season and the lowest concentrations observed during the spring and summer seasons. The daily exceedances observed indicate that the Pretoria population may suffer from a variety of health effects as a result of outdoor $PM_{2.5}$ exposure.

The origin of air masses was investigated using the transport cluster based on the HYSPLIT backward trajectory model, which revealed that the majority of pollutants reaching the study site are from local sources, particularly areas where coal is used for power generation and heating processes. High S concentration observed in the study follows the pattern of $PM_{2.5}$ which is indicative of heating and power generation source during the cold season. The low concentration of Pb recorded in this study could result from the banning of lead from gasoline in South Africa since 2006. This study found differences in the sources of elemental-containing particles ranging from soil and resuspended dust, anthropogenic activities, mobile sources and industrial activities. The assessment results revealed that $PM_{2.5}$ concentrations were above the WHO's AQI limits. The majority of AQI exceedances occurred in late autumn and winter, indicating that the exposed population may be seriously harmed by hazardous pollutants, resulting in an emergency health condition. Moreover, the findings of the study can be of help to the government in the formulation of air pollution guidelines as a measure to mitigate the effect of air pollution on the environment. In addition to this, if there is strict compliance with the already formulated regulation on the identified sources, this will further significantly reduce the effect of air pollution in our cities.

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Conflict of interest. The authors declare that they have no competing interest.

Compliance with ethical standards. The Research Ethics Committee, Faculty of Health Sciences, University of Pretoria, approved ethics approval (reference 469/2017) in 2017.

Availability of data and materials. The datasets generated and/or analysed during the current study are not publicly available due to university's intellectual property right but are available from the corresponding author on reasonable request

Authors' contributions. JW conceptualize the research**.** The research design, methodology, analysis of findings, and writing of the manuscript were all the responsibility of all authors. The statistical analyses were carried out by AA and PM. JB was responsible for the chemical analysis.

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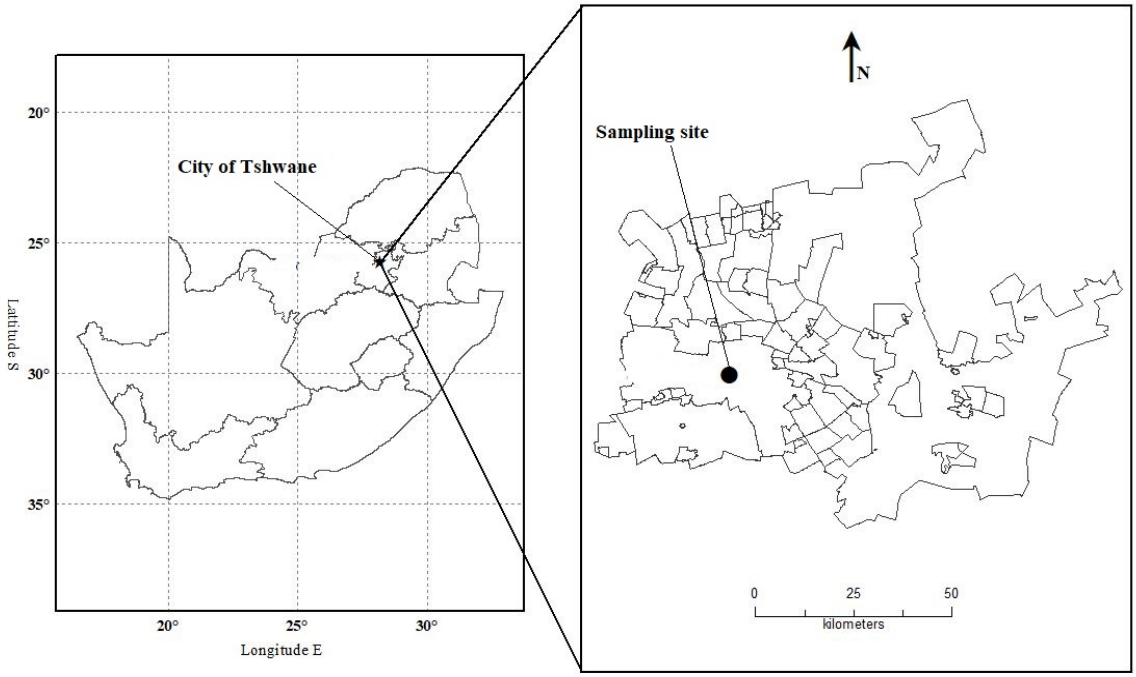
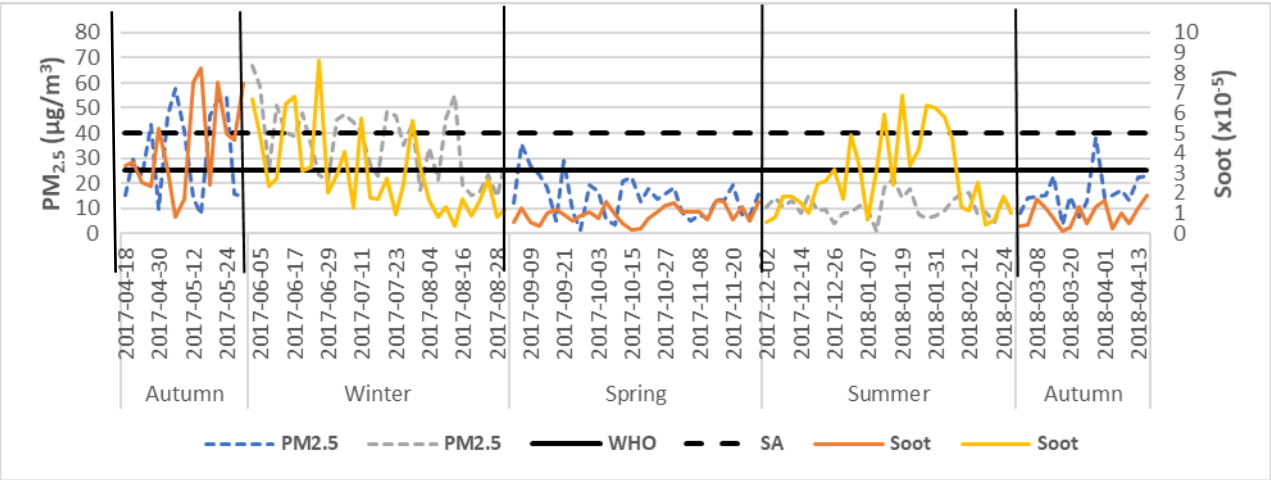


Fig. 1 Google Earth image depicting the sampling location.

(a)



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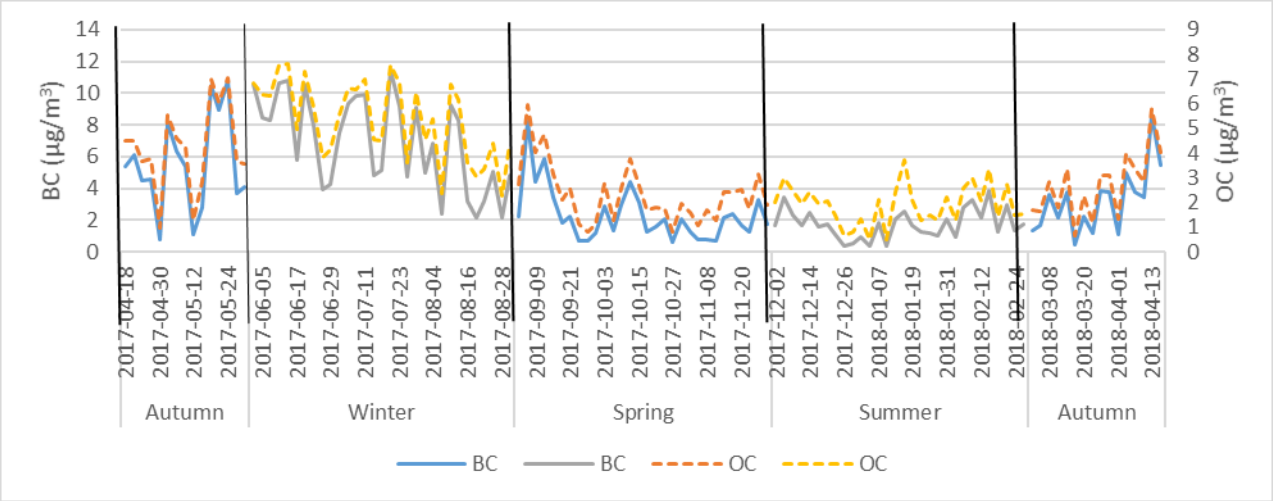

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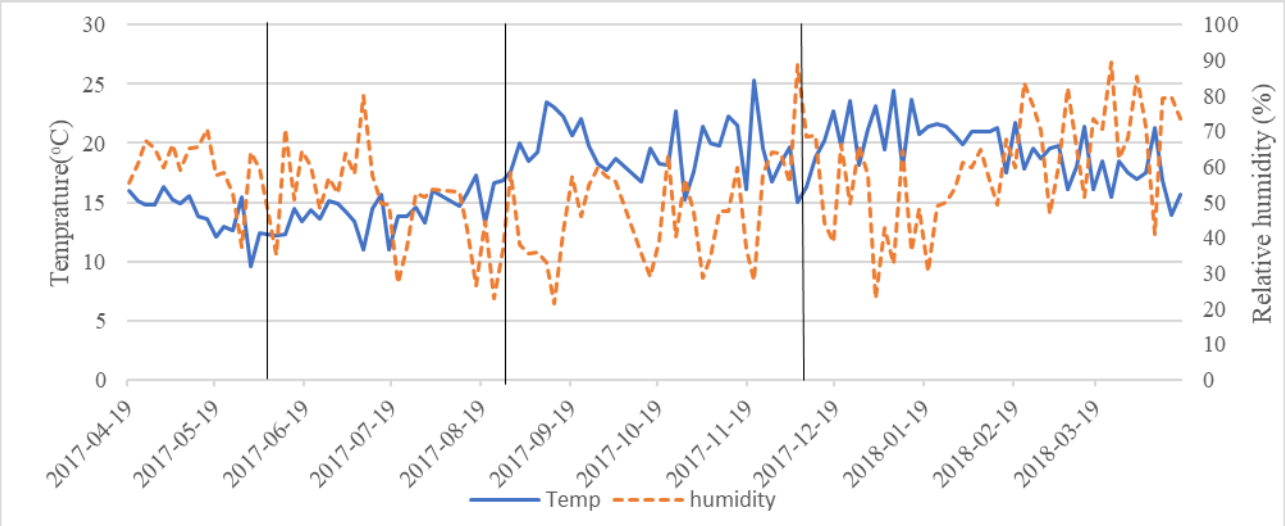

Fig. 2. Time-series graphs of (a) $PM_{2.5}$ and soot, (b) BC and OC and (c) meteorological conditions on 122 days during April 18, 2017, to April 16, 2018, in Pretoria, South Africa.

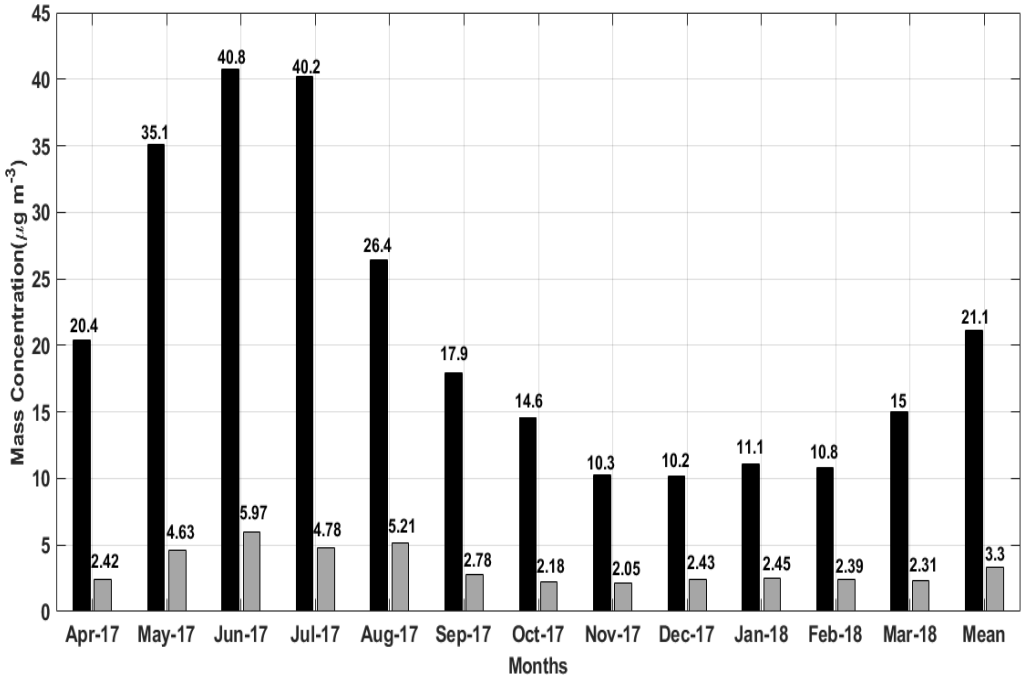

Fig. 3. Monthly averages of the total mass concentrations and total elemental concentrations in $PM_{2.5}$ during the period of study

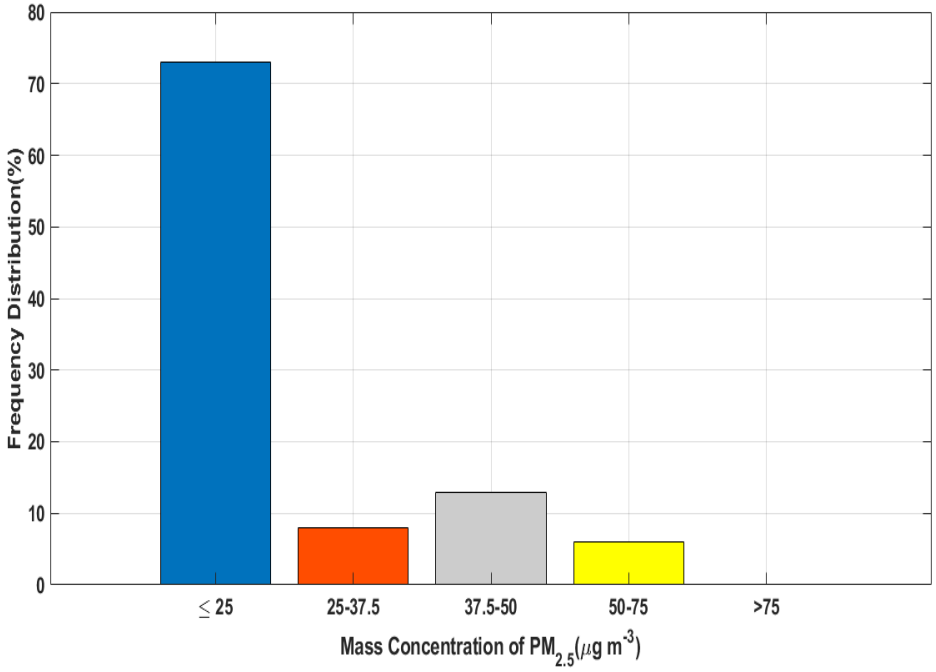

Fig. 4 Percentages of the individual $PM_{2.5}$concentrations in each particle mass range

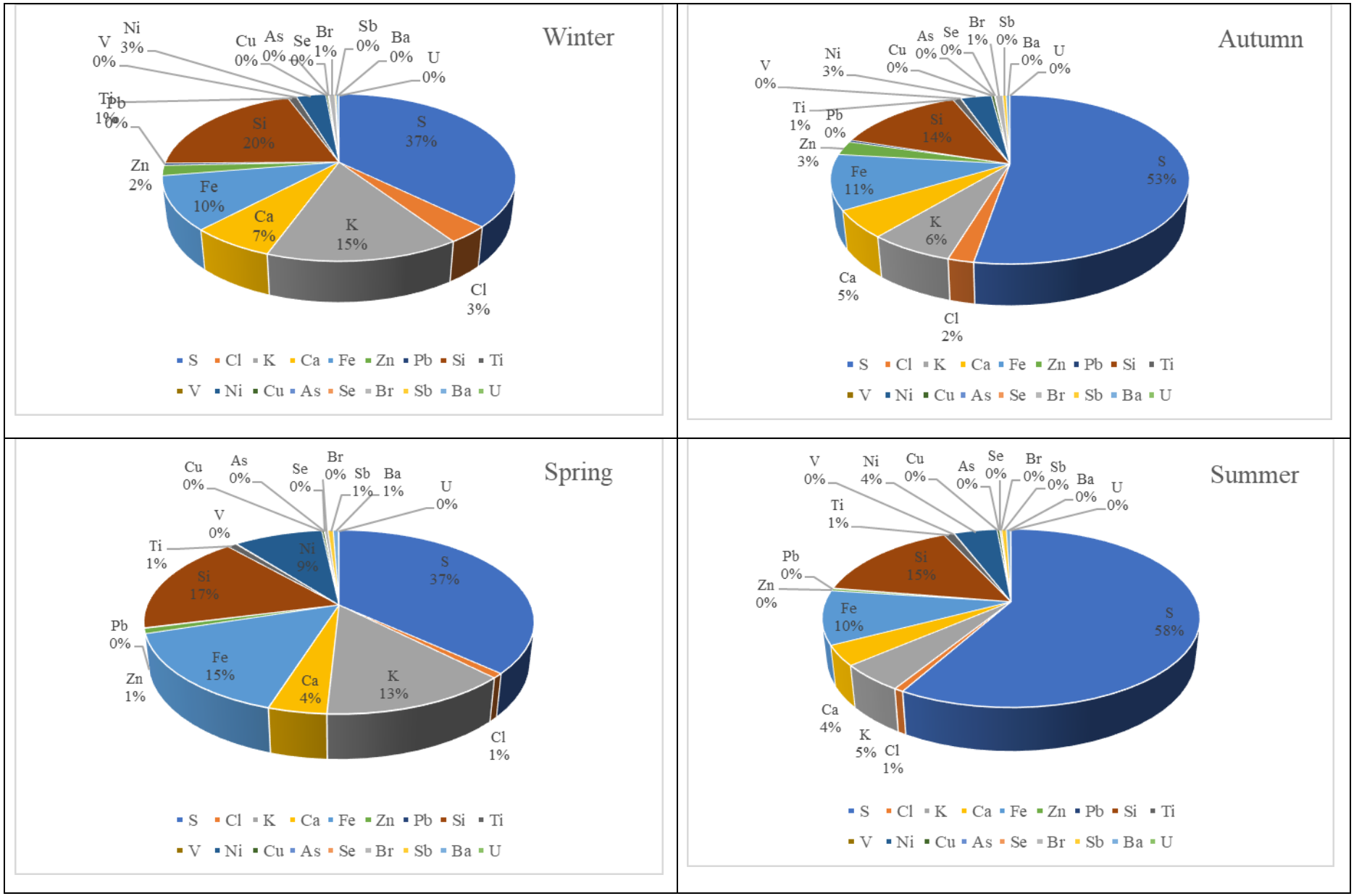

Fig. 5 Chemical profile of $PM_{2.5}$ across different seasons during the study period

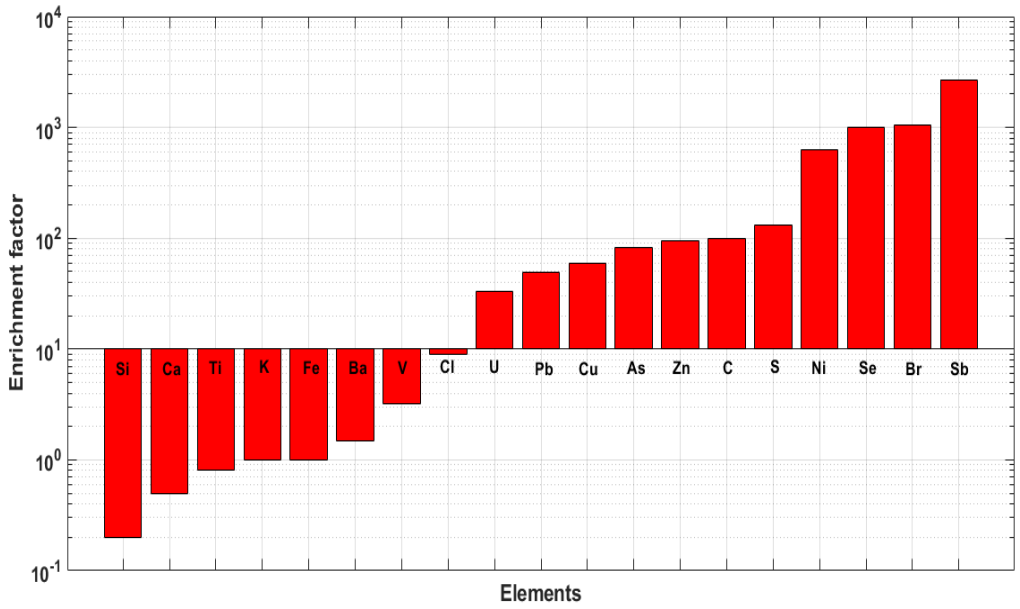

Fig. 6 Enrichment factors of the measured elements in fine aerosol samples collected form urban area, Pretoria, South Africa

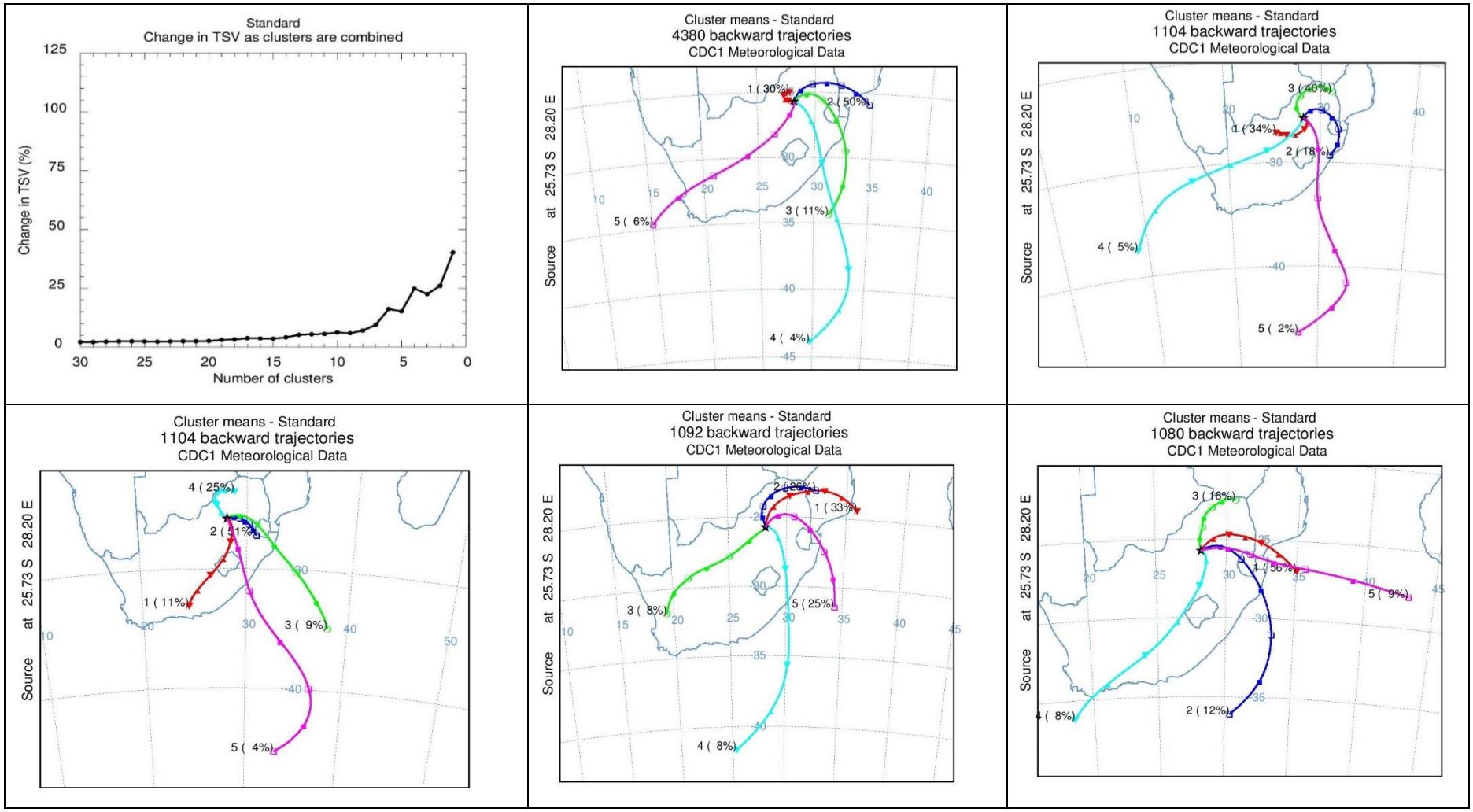

Fig. 7 Five transport pathways (cluster plots) arriving at the sampling site during 18 April 2017 and 18 April 2018 by seasons, clockwise from top left, TSV, all year, winter, autumn, spring and summer.

Table 1 Summary of $PM_{2.5}$, BC, OC concentration and soot levels for full year, seasons, weekdays and weekends in Pretoria during 18 April 2017 and 17 April 2018

Variables	N	Mean	SD	Median	Range
Full year					
$PM_{2.5}$ (μg/m^3)	122	21.1	15.0	15.6	0.7 – 66.8
BC (μg/m^3)	122	3.9	3.0	2.9	0.4 – 11.4
OC (μg/m^3)	122	3.3	1.9	2.8	0.5 – 7.6
Soot (10^{-5} m^{-1})	122	2.3	2.0	1.0	0.1 – 8.6
Autumn					
$PM_{2.5}$ (μg/m^3)	31	23.4	15.7	15.4	3.4 – 57.9
BC (μg/m^3)	31	4.3	2.9	7.5	2.1 – 11.4
OC (μg/m^3)	31	3.4	1.6	5.5	2.3 – 7.6
Soot (10^{-5} m^{-1})	31	2.7	1.9	2.4	0.5 – 8.2
Winter					
$PM_{2.5}$ (μg/m^3)	31	35.5	14.2	35.0	14.6 – 66.8
BC (μg/m^3)	31	6.9	2.8	3.8	0.5 – 10.8
OC (μg/m^3)	31	5.4	1.7	3.4	0.7 – 7.0
Soot (10^{-5} m^{-1})	31	4.3	2.2	4.2	0.9 – 8.6
Spring					
$PM_{2.5}$ (μg/m^3)	30	14.3	8.2	13.5	1.3 – 35.4
BC (μg/m^3)	30	2.3	1.7	2.0	0.6 – 8.3
OC (μg/m^3)	30	2.3	1.2	2.0	0.8 – 5.6
Soot (10^{-5} m^{-1})	30	1.3	1.1	1.0	0.4 – 5.6
Summer					
$PM_{2.5}$ (μg/m^3)	30	10.7	4.6	9.3	0.7 – 21.6
BC (μg/m^3)	30	1.8	0.9	1.7	0.4 – 3.9
OC (μg/m^3)	30	1.9	0.8	2.0	0.5 – 3.4
Soot (10^{-5} m^{-1})	30	1.0	0.5	1.1	0.1 – 1.7
Weekdays					
$PM_{2.5}$ (μg/m^3)	88	20.7	14.3	16.0	0.7 – 66.8
BC (μg/m^3)	88	4.0	3.0	3.2	0.4 – 11.4
OC (μg/m^3)	88	3.4	1.9	2.9	0.5 – 7.6
Soot (10^{-5} m^{-1})	88	2.4	2.1	1.7	0.2 – 8.6
Weekends					
$PM_{2.5}$ (μg/m^3)	34	22.1	17.0	15.3	3.4 – 57.9
BC (μg/m^3)	34	3.5	3.2	2.1	0.5 – 10.7
OC (μg/m^3)	34	3.1	2.1	2.3	0.7 – 7.6
Soot (10^{-5} m^{-1})	34	2.2	2.1	1.3	0.1 – 6.9

Table 2 Mean concentration of $PM_{2.5}$ exceedance with WHO guideline and SA air quality standard

Seasons	**No of exceedance**		
	Old Daily WHO guideline for $PM_{2.5}$ (25 µgm^{-3})	**New Daily WHO guideline for $PM_{2.5}$ (15 µgm^{-3})**	**Daily SA standard for $PM_{2.5}$ (40 µgm^{-3}).**
Summer	0	6 (20%)	0
Spring	3 (10%)	14 (47%)	0
Autumn	9 (29%)	17 (55%)	7 (23%)
Winter	21 (68%)	29 (94%)	14 (45%)
Total	**33 (27%)**	**66 (54%)**	**21 (17%)**

Table 3 the monthly average and total elemental concentrations of $PM_{2.5}$ (ng m^{-3}) at urban background site in Pretoria, South Africa

El	Apr-17	May-17	Jun-17	Jul-17	Aug-17	Sept-17	Oct-17	Nov-17	Dec-17	Jan-18	Feb-18	Mar-18	Average
Si	300±270	700±420	1220±710	760±470	1140±640	640±560	330±340	250±150	330±130	500±390	270±130	300±260	560±340
S	1230±970	2200±2000	2220±1720	1790±1070	1940±1830	710±580	820±440	1050±1000	1460±570	1120±730	1710±780	1520±1880	1480±510
Cl	30±30	140±190	180±140	280±360	80±60	30±30	20±30	9±6	8±5	30±60	10±10	11±8	70±90
K	150±80	340±290	880±450	850±380	660±290	510±440	260±150	150±80	100±40	160±140	80±40	110±80	360±300
Ca	160±110	210±150	320±190	270±170	440±230	160±160	90±100	40±20	50±40	110±40	110±60	110±40	170±120
Ti	21±10	40±20	60±40	40±20	60±30	30±20	20±10	13±9	18±7	35±20	20±10	21±12	30±20
V	4±7	0.6±0	0.6±0	0.6±0	0.6±0	0.6±0	0.6±0	5±15	4±10	0.6±0	0.6±0	0.6±0	2±2
Fe	300±120	520±140	640±240	440±160	560±160	420±190	350±100	290±70	260±50	310±90	130±60	160±80	370±160
Ni	90±100	220±25	210±20	100±110	190±70	210±20	210±30	190±50	160±15	140±50	2±1	1±0.8	140±80
Cu	12±14	11±10	15±10	11±10	10±10	8±6	5±5	3±2	4±2	4±2	12±18	5±7	10±4
Zn	70±50	140±140	140±130	140±90	40±30	20±30	40±40	11±14	6±4	8±5	16±18	40±50	60±60
As	1±1	4±6	4±4	10±10	4±10	0.7±1	0.4±0	0.4±0	0.4±0	0.4±0	0.4±0	0.5±0.1	2±3
Se	0.5±0.2	2±2	3±3	4±5	0.5±0.2	0.5±0.1	1±1	0.8±1.2	0.5±0.2	0.7±0.6	0.7±0.5	0.7±0.7	1±1
Br	15±12	55±75	40±20	40±20	20±15	12±9	8±4	5±3	5±3	4±2	4±3	8±4	20±20
Sb	11±11	20±15	7±5	7±3	11±10	11±15	12±12	14±13	15±12	13±14	8±7	8±6	10±4
Ba	13±12	10±10	10±9	10±10	23±15	15±10	10±10	11±12	8±6	11±10	101±11	12±11	12±4
Pb	10±20	20±35	15±10	30±40	30±60	3±2	3±1	2±0.1	2±0	2±0	4±6	3±2	10±10
U	1±1	1±0.5	2±3	1±1	2±2	1±1	1±1	2±1	3±2	1±0.5	1±0	1±0.5	1±1
BC	4440±2200	6180±3320	8130±2650	8090±2410	4760±2480	3070±2450	2230±1140	1600±830	1700±900	1400±700	2260±1020	2420±1250	3860±2460
∑EL	2420	4630	5970	4780	5210	2780	2180	2050	2430	2450	2390	2310	3300
$PM_{2.5}$	20400	35100	20800	40200	26400	17900	14600	10300	10200	11100	10800	15000	21100
$\sum El/PM_{2.5}$	12%	13%	29%	12%	20%	16%	15%	20%	24%	22%	22%	15%	17%

Table 4 Spearman's correlation coefficients for the concentration of detected element in $PM_{2.5}$ collected from the urban background area, Pretoria, South Africa

	$PM_{2.5}$	**BC**	**S**	**Cl**	**K**	**Ca**	**Fe**	**Zn**	**Pb**	**Si**	**Ti**	**V**	**Ni**	**Cu**	**As**	**Se**	**Br**	**Sb**	**Ba**	**U**
PM_{25}	**1.00**																			
BC	**0.96**	**1.00**																		
S	0.48	0.49	**1.00**																	
Cl	**0.90**	**0.87**	0.34	**1.00**																
K	**0.77**	*0.73*	0.32	**0.78**	**1.00**															
Ca	*0.69*	*0.70*	*0.52*	*0.54*	**0.77**	**1.00**														
Fe	*0.72*	*0.60*	0.30	*0.56*	**0.76**	*0.69*	**1.00**													
Zn	**0.90**	**0.86**	0.29	**0.83**	0.45	0.37	0.48	**1.00**												
Pb	**0.86**	**0.82**	0.40	**0.78**	*0.70*	**0.81**	*0.72*	*0.74*	**1.00**											
Si	*0.64*	*0.58*	*0.54*	*0.53*	**0.84**	**0.90**	**0.83**	0.27	*0.70*	**1.00**										
Ti	*0.62*	*0.56*	0.38	*0.56*	**0.76**	**0.89**	**0.75**	0.32	**0.75**	**0.93**	**1.00**									
V	-0.16	-0.20	-0.20	-0.21	-0.33	-0.39	-0.04	-0.01	-0.10	-0.38	-0.49	**1.00**								
Ni	0.22	0.06	0.05	0.09	0.35	0.13	**0.75**	0.05	0.15	0.44	0.26	0.30	**1.00**							
Cu	0.43	*0.56*	-0.02	0.37	0.11	0.32	0.01	*0.55*	0.48	0.00	0.18	-0.21	-0.46	**1.00**						
As	**0.91**	**0.86**	0.39	**0.93**	**0.80**	*0.72*	*0.70*	**0.79**	**0.95**	*0.69*	*0.72*	-0.17	0.16	0.39	**1.00**					
Se	**0.75**	*0.72*	0.22	**0.94**	*0.60*	0.24	0.32	**0.78**	*0.57*	0.26	0.29	-0.17	-0.03	0.30	**0.79**	**1.00**				
Br	**0.92**	**0.88**	0.45	**0.82**	*0.59*	*0.56*	0.68	**0.90**	**0.80**	*0.54*	*0.56*	-0.22	0.22	*0.50*	**0.84**	0.69	**1.00**			
Sb	-0.03	-0.16	0.27	-0.21	-0.16	-0.16	0.39	-0.06	-0.11	0.12	-0.06	0.47	**0.77**	-0.51	-0.15	-0.28	0.08	**1.00**		
Ba	0.15	0.18	*0.57*	-0.08	0.40	*0.60*	0.39	-0.23	0.12	*0.63*	0.41	-0.11	0.31	-0.29	0.04	-0.30	-0.04	0.25	**1.00**	
U	-0.18	-0.19	-0.18	-0.09	0.07	0.00	0.12	-0.27	0.11	0.07	-0.01	0.46	0.25	-0.27	0.07	-0.13	-0.22	0.13	-0.04	**1.00**

Table 5 $PM_{2.5}$, BC and trace element concentrations from this study (Pretoria) compared with concentration from other cities in Africa. Concentrations are in ng/m^3

Site/Elements	This study		**Gaita et al (2014)**		**Gatari et al (2009)**		**Aboh et al (2009)**		**Boman et al (2009)**		**Arku et al (2008)**		**Boman et al (2013)**	
	Urban background Pretoria		Urban background Nairobi		Industrial background Nairobi		Semirural area Accra		City center Ouagadougou		Low income area Accra		Urban center Cairo	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
S	1480	510	660	240	1300	400	462	290	-	-	909	267	1200	870
Cl	70	90	520	200	-	-	123	133	960	290	706	423	2200	2200
K	360	300	34	160	730	220	377	325	670	210	694	188	470	260
Ca	170	120	370	270	70	34	144	322	1400	570	57	22	2900	3200
Ti	30	20	62	27	8.7	4.4	37.5	64.8	240	81	6	3	100	89
Mn	-	-	53	23	12	3.9	7.6	11.4	61	25	6	2	24	20
Fe	370	160	730	340	130	43	289	504	3000	1400	69	27	1000	1000
Ni	140	80	4	1	2.6	1.1	3.2	2.8	-	-	-	-	6.8	1.7
Cu	10	4	12	7	3.5	2.2	4.1	3.9	19	6.4	9	15	16	9.8
Zn	60	60	120	120	100	69	6.5	5.7	45	35	32	13	200	180
Br	20	20	16	30	36	18	5.9	3.5	7.3	2.7	30	16	21	15
Rb	-	-	3	1	1.56	0.5	1.4	1.4	4.2	1.9	2	1	4.4	-
Pb	10	25	23	16	76	30	2.5	1.7	8.8	4.2	18	25	86	180
BC	3900	2500	3900	800	4800	1800	1900	1100	4900	1700	-	-	3700	2100
$PM_{2.5}$	21100	1500	21000	950	30000	9400	40800	54400	86000	42000	22700	5700	51000	39000

Source: Gaita et al 2014