

## Atmospheric fine particulate matter (PM<sub>2.5</sub>) in Bloemfontein, South Africa

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### Abstract

Indoor and outdoor pollution has become a worldwide problem; it impacts both the environment and human health. Research-driven air pollution assessment studies were done in some of the larger South African cities like Cape Town and Pretoria, but almost none in the Free State province. The purpose of the present study was to determine PM<sub>2.5</sub> levels and its chemical components over a period of more than one year in the Free State capital, Bloemfontein. Particulate matter was collected on PTFE filters, which were then analysed gravimetrically, by smoke stain reflectometry and X-ray fluorescence. The average PM<sub>2.5</sub> concentration for the study period was 11 µg/m<sup>3</sup>, which exceeded the World Health Organization (WHO) annual guideline limit (5 µg/m<sup>3</sup>), but not the annual South African National Ambient Air Quality Standard (20 µg/m<sup>3</sup>). The daily WHO guideline (15 µg/m<sup>3</sup>) was exceeded on 28 days, but not the daily South African standard (40 µg/m<sup>3</sup>). The average soot concentration was 1.2 µg/m<sup>3</sup>. The five most abundant trace elements detected in the PM<sub>2.5</sub> filter samples were K, Ca, Si, S and Fe.

**Keywords:** Smoke stain reflectometry; XRF; trace element analysis; PTFE filters; air quality standard

### 1. Introduction

Indoor and outdoor air contaminants resulting from agents with the ability to modify natural atmospheric characteristics are also known as air pollutants, which may be of biological, chemical and/or physical origins [1]. Introduction of these contaminants into the atmosphere results in 'air pollution'. Indoor and outdoor air pollution is one of the biggest environmental problems worldwide, which impacts public and individual health, as well as climate change [2].

The particulate matter (PM) component of air pollution has the ability to penetrate the human respiratory system, causing cancer, cardiovascular and respiratory diseases and dysfunctions in the central nervous and reproductive systems. In epidemiology studies, the most common air pollutants that are globally investigated and monitored by law are PM with

aerodynamic diameter of 2.5  $\mu\text{m}$  or less ( $\text{PM}_{2.5}$ ),  $\text{PM}_{10}$ , ground-level ozone ( $\text{O}_3$ ), sulphur dioxide ( $\text{SO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ), carbon monoxide ( $\text{CO}$ ) and heavy metals [3]. Carbon monoxide provokes direct poisoning when inhaled at high levels [2]. PM consists of inorganic and organic substances that are suspended in the air. The major components in this type of pollution are water, sulphate, black carbon, ammonia, mineral dust, nitrates and sodium chloride [3]. PM is reported to contribute towards climate change and global warming, affecting ecosystems, which in turn results in animal extinction, food safety issues, plant damage and iceberg melting [4,5].

Contributing sectors are agricultural, transportation, urban planning, and energy and waste management [6]. Sources of air pollution are divided into four main categories: human outdoor, natural, indoor and mobile sources. Major human sources to outdoor pollution include chemical industries, metallurgical plants, municipal incineration, fertiliser industries, industrial plants and pollutant emission from petrochemicals, power stations and refineries. Natural sources include dust storms, forest fires, agricultural burning and volcanic eruptions. Indoor sources include printing shops, domestic cooking and cleaning activities, fuel stations and dry cleaning. Mobile sources are vehicles, railways and airways.

Pollution in South Africa is primarily caused by fossil fuel burning, the largest contribution being from vehicles (ships, trucks, aircrafts and cars) powered by fossil-fuels, factories and coal-burning power plants. All these release PM and a range of carbon compounds due to incomplete combustion. In addition to the above-mentioned sources, tobacco products, fireplaces, wildfires, stoves, ovens and candles also contribute to PM pollution [7,8].

Apart from South Africa's extensive agricultural sector, production of chemicals, textiles, metal and food processing also contribute significantly. Together with the extensive mining sector, all the foregoing, to a greater or lesser degree, release PM into the atmosphere. The Mpumalanga and Free State provinces have large coal power plants which produce up to 90% of South Africa's electricity [9]. PM concentrations in the atmosphere are partly a result of long-range transport (LRT), on regional and local scale [9].

Studies conducted during 2017 and 2018 in Cape Town, Pretoria and Thohoyandou reported on  $\text{PM}_{2.5}$  levels and chemical composition [10–12]. The Pretoria study averaged a  $\text{PM}_{2.5}$  concentration of 21.1  $\mu\text{g}/\text{m}^3$  over the one-year study period, with the five most abundant elements found in related elemental analysis being sulphur, silicon, iron, potassium and calcium [13]. The Thohoyandou study averaged a  $\text{PM}_{2.5}$  concentration of 10.9  $\mu\text{g}/\text{m}^3$  over the one-year study period, with the six dominant elements being silicon, magnesium, aluminium, tin, lead and antimony. The Cape Town study averaged a  $\text{PM}_{2.5}$  concentration of 13.4  $\mu\text{g}/\text{m}^3$  over the one-year study period. Largest concentrations in Cape Town were found for the elements chlorine, aluminium, iron, magnesium, sodium, zinc, sulphur and calcium.

Only a few African countries have air quality laws, South Africa being one of them. The  $\text{PM}_{2.5}$  levels were below the South African National Ambient Air Quality Standards (SANAAQS) yearly limit of 20  $\mu\text{g}/\text{m}^3$ , but above the World Health Organization guideline (WHO) of 5  $\mu\text{g}/\text{m}^3$  [13]. Pretoria is slightly above the SANAAQS yearly limit. The difference in concentration levels can be ascribed to different geographical locations and proximity to local industries,

e.g. Pretoria is situated closer to coal-fired power stations, resulting in higher PM<sub>2.5</sub> and soot concentrations [14].

PM determination studies in the Bloemfontein (Free State) area have not been published before. The purpose of this study was to obtain more information on the ambient PM<sub>2.5</sub> concentration levels and its chemical composition in Bloemfontein. This will form part of a larger South African PM<sub>2.5</sub> study. PM<sub>2.5</sub> concentrations were determined by gravimetric analysis of the collected samples, trace elements by X-Ray fluorescence and soot content (equivalent black carbon) by absorbance measurements.

## **2. Methodology**

For the purpose of direct comparison, the methods that were used in this study were similar to those used in previous studies in South Africa [10–12]. These methods include PM<sub>2.5</sub> sampling, gravimetric analysis, smoke stain reflectometry, x-ray fluorescence and descriptive statistics.

### **2.1. Study location and PM<sub>2.5</sub> sampling**

The sampling site in Bloemfontein was selected to be at the University of the Free State (UFS) weather station (coordinates: –29.1074891, 26.188941) in the middle of a local unbuilt area of about one hectare, a few hundred metres from the city main road [15]. Bloemfontein is centrally located in South Africa, see map (Figure 1) [16]. The Bloemfontein industrial area where most industries are located is situated in Hamilton and the East End district, with the sampling site located 11 km and 6.4 km from these areas, respectively. The distance to the Bloemfontein city centre is 3.5 km, while Pelonomi, where the Municipality is sampling air pollution, is 7.6 km to the east.

A Stevenson screen meteorological instrument shelter was used as sampling station (see Figure S1), providing protection for the instruments against the elements yet allowing air throughflow. During sampling, the shelter roof overhang prevented rainwater from entering the cyclones that were mounted in the north-west outside of the shelter. The prevalent wind direction in the greater Bloemfontein area is westerly-north-westerly.

PM<sub>2.5</sub> filter samples were collected manually every third day from 26 June 2020 to 18 August 2021 (nearly 14 months). Each filter was exposed for 24 h (11:35 am to 11:35, UTC +2 h). Duplicate samples were collected after every fourth sample. The sampling schedule is included in the Supporting Information. Throughout this study, Zefon International 37 mm (2 µm pore size) PTFE membrane (part number: FPTPT237) filters were used. PTFE filters were selected in agreement with numerous other ambient PM studies. These filters are known for their durability and chemical resistance [15,17].



Figure 1. Map of Southern Africa, showing Bloemfontein centrally located [16]. Insert: Sampling site at the University of the Free State.

Three GilAir5 air sampler pumps (Sensidyne, St. Petersburg, FL, USA), provided by the School of Health Systems and Public Health (SHSPH) at the University of Pretoria (UP), were used. The flow of the GilAir 5 pumps was set to 4.0 L·min<sup>-1</sup>. The GilAir5 was extensively used in similar studies [11,12,18]. One pump was used as main air sampling pump, while the other two were used for duplicate sampling. To calibrate the GilAir5 sampler, a field calibrator (Brooks Instrument, Hatfield, PA, USA) was used.

The samples were collected using a cyclone (Figure S2). The cyclone separates the larger particles (>2.5 µm in diameter) and debris from the PM<sub>2.5</sub> particles. The period of sampling per filter was 24 h throughout. Before sampling, the flow-rate was set to 4.0 L·min<sup>-1</sup> and the rate was checked after sampling [19].

A fair correlation was observed between PM<sub>2.5</sub> levels measured on filter samples using a GilAir-5 pump and those obtained using a continuous real-time instrument during May 2018 to May 2019 in Pretoria, South Africa [12,13].

## 2.2. Gravimetric and chemical analyses

### 2.2.1. Gravimetric analysis

The filter samples' PM<sub>2.5</sub> masses were determined by an XP6 Ultra-microbalance (Mettler-Toledo, Greifensee, Switzerland, Figure S3) at the SHSPH (UP). The ambient PM<sub>2.5</sub> filters required 24 h pre-conditioning before weighing. Indoor temperature and pressure conditions at 40–55% relative humidity were 19.8–23.0°C and 101–103 kPa, respectively. All filters were weighed before and after exposure. To ensure accuracy, quality control checks were performed at the start and end of each weighing session [13]. In addition, control filters (field blank) were weighed at 10-filter increments. Filters were weighed in triplicate and handled on the outer ring (unexposed area) to ensure no contamination or loss of sample. In event of the average mass deviating by more than 15 µg, or the difference in the percentage of the minimum and maximum filter being more than 0.001%, the measurements were repeated.

The PM<sub>2.5</sub> mass ( $m$ ) was calculated using the charged referenced mass ( $m_r$ ), which was eliminated by using an ioniser, the unexposed filter mass ( $m_i$ ) and the exposed filter mass ( $m_f$ ). The analyte mass equation is expressed as follows:

$$m(\mu\text{g}) = m_f(\mu\text{g}) - m_i(\mu\text{g}) - m_r(\mu\text{g}) \quad (1)$$

PM<sub>2.5</sub> concentrations were calculated using both the flow rates (before ( $R_i$ ) and after ( $R_f$ ) sampling), the sampling volume ( $V_A$ ) and the analyte mass ( $m$ ) calculated in equation 1. Equations 2–4 show the calculation of the PM<sub>2.5</sub> concentration.

$$Q_A = \frac{R_f + R_i}{2} \quad (2)$$

$$V_A = \frac{24 * 60 * Q_A}{1000} = 1.44Q_A \quad (3)$$

$$[PM_{2.5}] = \frac{m}{V_A} \quad (4)$$

### 2.2.2. Smoke stain reflectometry

Smoke Stain Reflectometry measures the reflectance of light by particles on the PM<sub>2.5</sub> filters. In this study, the wavelength is selected to fit products produced by incomplete combustion, this is referred to as the soot analysis [20]. This was conducted with an EEL model 43D Smoke Stain Reflectometer (Diffusion Systems Ltd., London, UK, Figure S4) at the SHSPH, UP.

To maintain accuracy, measurements were done using the five-point configuration as done in other studies [10–12]. As primary control, three field blank filters were used. The instrument was calibrated using control filters. Fine adjustments were made to the readings, being set as close to 100% (on filter/white side of the plate) and 34% (on the grey part of the plate) as possible. The sample filters were measured after calibration, and the procedures were rechecked after every 20th sample. In the event of control filter deviation of more than 3%, the samples were measured again. The measurements for the determination of absorption coefficients made use of the reflectometric method (Standard Operating Procedure, SOP4.0). The guidelines used for this method were compiled from the international ISO 9835:1993 standard for determination of black smoke index. Guidelines for the SOP 4.0 (2002) were compiled using the 1993 guidelines of the international standard ISO 9835 [14].

Instrument readings were transformed to absorption coefficient ( $\alpha$ ) values as done in other studies [10–12], making use of measured reflectance values.

### 2.2.3. X-ray fluorescence (XRF)

Energy dispersive X-ray fluorescence (EDXRF) analysis was performed to determine the elemental composition of the PM<sub>2.5</sub> using an XEPOS 5 EDXRF spectrometer at the Department of Chemistry and Molecular Biology, Atmospheric Science Division, University of Gothenburg, Sweden. The advantage of this method is that it is non-destructive and PM<sub>2.5</sub> samples do not require pre-treatment. Spectra were processed and quantified using Spectro XRF Analyser Pro Software, with a total time of 3 000 s automatically divided between four analytical setup conditions [8,21,22]. The concentrations of 19 elements (Ag, Ba, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, P, S, Si, Sr, Ti, U, V and Zn) were determined and calculated. Two randomly selected filters were used for repeat analyses, showing an average precision ranging from 15% to 20%. One of the filters had a low mass loading and the other a high mass loading. All S/N ratios are listed under Supporting Information, Table S2. In the event of detected concentrations exceeding the limit of detection (LoD), uncertainties were calculated as follows,

$$Uncertainty = \frac{5 * LoD}{6} \quad (5)$$

The elements Ba, Br, Ca, Cl, Cu, Fe, K, S, Si and Zn had acceptable S/N ratios, whilst the other trace elements had very low ratios (see Tables S1 and S2). The latter were removed from the dataset to avoid overestimation of analysed trace elements.

### 2.3. Other air pollution data and meteorological data

The Mangaung Metropolitan Municipality manages the monitoring of PM<sub>2.5</sub>, PM<sub>10</sub>, PM<sub>coarse</sub> and SO<sub>2</sub> at the Pelonomi hospital ambient air quality monitoring station in Bloemfontein (Supporting Information, Figures S5–S8. NO<sub>2</sub> is not monitored here). This air quality station continuously assesses real-time levels of air pollutants by using methods equivalent to that of the United States Environmental Protection Agency and in accordance with ISO 17025 guidelines [23,24]. The station is 7.6 km east of the PM<sub>2.5</sub> sampling site of the present study. Hourly data were downloaded from the South African Air Quality Information System website [25]. Daily 24-h averages of each pollutant were calculated from the hourly data (12h00 to 12h00 the next day) where at least 18 hourly values were available.

Hourly temperature (°C), relative humidity (%), wind speed (m·s<sup>-1</sup>) and precipitation (mm) data were obtained from the South African Weather Service for the study period. The daily averages were based on at least 18 hourly values.

### 2.4. Statistical analyses

Descriptive statistics were calculated for the PM<sub>2.5</sub>, soot, trace elements, PM<sub>10</sub>, PM<sub>coarse</sub>, SO<sub>2</sub>, and meteorological variables with STATA 15 [13]. According to the Shapiro-Wilk's test, in general the air pollution and meteorological variables did not have normal Gaussian distributions and non-parametric tests were applied. Spearman rank-ordered correlation analyses were applied to investigate the correlation between air pollution and meteorological variables throughout all seasons during the study period. Seasons were defined as follows: Autumn (March–May), winter (June–August), spring (September–November) and summer (December–February). Kruskal – Wallis tests were conducted to determine whether the median air pollution levels and meteorological variables differed significantly between seasons and day of the week. Wilcoxon's rank-sum test was applied to test whether median air pollution levels and meteorological variables differed significantly between weekdays and weekends or public holidays.

## 3. Results and discussion

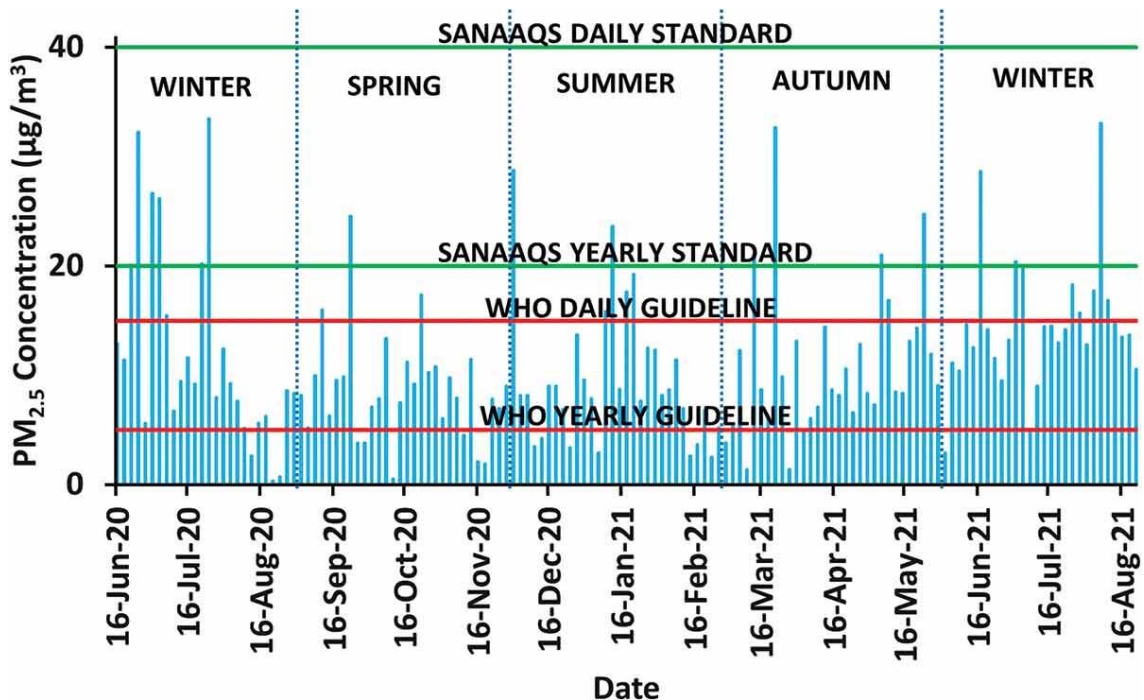
### 3.1. Gravimetric analysis

The average PM<sub>2.5</sub> concentration at the University of Free State site was found to be 11 µg/m<sup>3</sup> (ranging from 0.52 to 33 µg/m<sup>3</sup>). Table 1 gives the average PM<sub>2.5</sub> concentration (µg/m<sup>3</sup>) in Bloemfontein for each season.

**Table 1.** Average PM<sub>2.5</sub> concentration (µg/m<sup>3</sup>) in Bloemfontein for each season.

Season	Duration	Average PM <sub>2.5</sub> concentration (µg/m <sup>3</sup> )
Winter	16 June 2020–31 August 2020	12
Spring	1 September 2020–30 November 2020	8.7
Summer	1 December 2020–28 February 2021	9.6
Autumn	1 March 2021–31 May 2021	11
Winter	1 June 2021–22 August 2021	15

The time series for the sampling period is shown in Figure 2. The South African National Ambient Air Quality Standards (SANAAQS) [13] contain limits for the PM<sub>2.5</sub> concentration which are acceptable for South African population; these limits are 20 µg/m<sup>3</sup> and 40 µg/m<sup>3</sup> for yearly and daily concentration, respectively. SANAAQS limits are represented in (green horizontal lines). The yearly limit was found to be exceeded on 16 out of the 145 days. During winter, the yearly limit was exceeded eight times, once during spring, once in summer and four times during autumn. It is clear from that daily limits were never exceeded. The World Health Organisation (WHO) guideline limits for PM<sub>2.5</sub> concentrations were set at 5 µg/m<sup>3</sup> and 15 µg/m<sup>3</sup> for yearly and daily concentration limits, respectively [13]. also shows that the WHO yearly guideline (red horizontal lines) limit was exceeded on 123 out of 145 days and the daily concentration limit was exceeded on 28 days. During the winter season, the limit was exceeded fifteen times, during spring season three times, summer season five times and autumn five times. Winter seasons are prone to higher PM<sub>2.5</sub> pollution, see Table 1.



**Figure 2.** PM<sub>2.5</sub> concentrations during the sampling period. (SANAAQS = South African National Ambient Air Quality Standards. WHO = World Health Organization Guidelines).

This study forms part of a larger study being done in South Africa; the other sites were located in Pretoria, Cape Town and Thohoyandou. The PM<sub>2.5</sub> concentration in Pretoria ranged from 0 to 66.8 µg/m<sup>3</sup>, with an average of 21.1 µg/m<sup>3</sup>, Cape Town ranged from 1.17 to 39.1 µg/m<sup>3</sup> with an average of 13.4 µg/m<sup>3</sup>, and Thohoyandou ranged from 1.06 to 37.52 µg/m<sup>3</sup>, with an average of 10.9 µg/m<sup>3</sup> [10–12]. Thohoyandou and Bloemfontein results were on average on the same level, whereas Cape Town and Pretoria levels are higher than in Bloemfontein. Pretoria is situated in close proximity to local and large industries, this explains the higher PM<sub>2.5</sub> concentration levels. Thohoyandou and Bloemfontein have similar climate types, with one distinct difference: Thohoyandou is hot semi-arid and Bloemfontein is cold semi-arid. The latter explains the almost equal PM<sub>2.5</sub> concentration levels. Cape Town has a Mediterranean

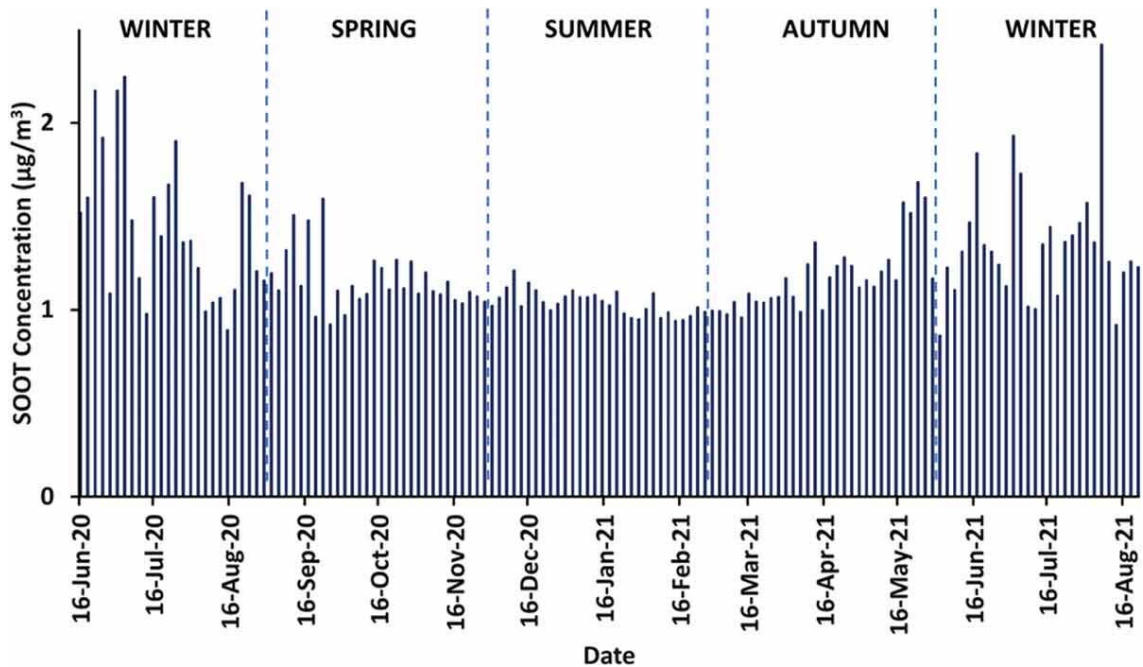


climate, and the surroundings of Cape Town are different to other studies, which explain the elemental differences found.

Data obtained at Pelonomi hospital air quality station (Pelonomi-NAQI) in Bloemfontein is given under Supporting Information (Figures S5–S8). This data is only 85.19% complete, with the average PM<sub>2.5</sub> concentration of this data being 60 µg/m<sup>3</sup>. This value is higher than found for the university site (*ca* 5 times higher), the reason being Pelonomi's closer proximity to the industrial area, thus resulting in higher PM<sub>2.5</sub> concentrations

### 3.2. Smoke stain reflectometry

Comparison of each of the exposed filters with PM<sub>2.5</sub> concentration indicates that at higher PM<sub>2.5</sub> concentrations there were higher soot concentrations as well. The seasons are summarised in Table 2 and the soot (equivalent black carbon) concentration is illustrated in Figure 3. For the winter season higher soot concentrations were observed, as was the case with the Gravimetric Analyses (GA). The average soot concentration was 1.2 µg/m<sup>3</sup> (ranging from 0.86 to 2.3 µg/m<sup>3</sup>). Seasonal average soot concentrations were as follows: winter season of 2020 (1.5 µg/m<sup>3</sup>) > winter season of 2021 (1.4 µg/m<sup>3</sup>) > autumn season of 2021 (1.2 µg/m<sup>3</sup>) > spring season of 2020–2021 (1.2 µg/m<sup>3</sup>) > summer season of 2020 (1.0 µg/m<sup>3</sup>). Winter seasons in general are prone to higher soot concentrations.



**Figure 3.** Soot concentration for sampling period. (soot = equivalent black carbon).

**Table 2.** Average PM<sub>2.5</sub> concentration (µg/m<sup>3</sup>) and soot concentration (µg/m<sup>3</sup>) in Bloemfontein for each season.

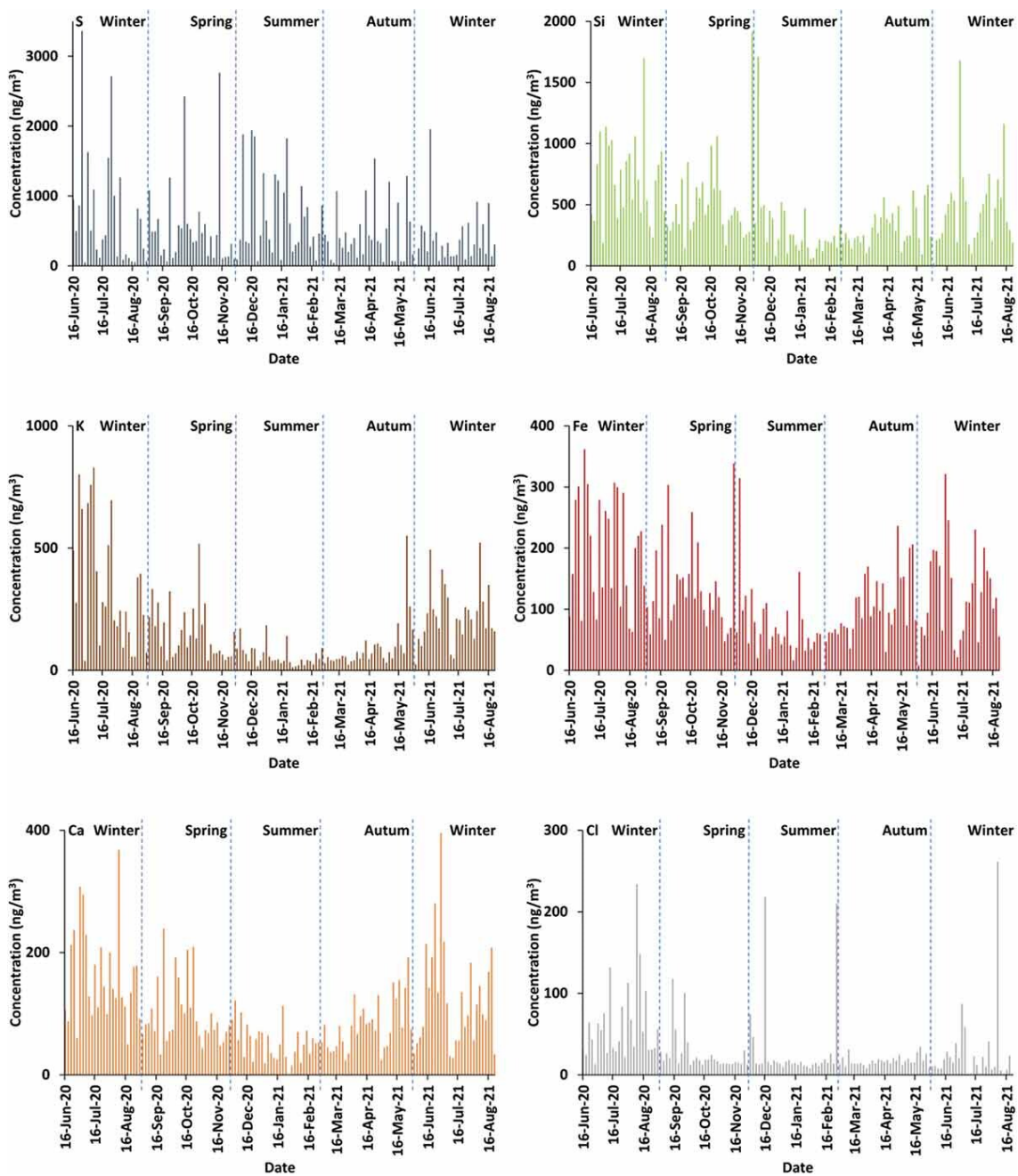
Season	Time Duration	Average PM <sub>2.5</sub> concentration (µg/m <sup>3</sup> )	Soot concentration (µg/m <sup>3</sup> )
Winter	16 June 2020–31 August 2020	12	1.5
Spring	1 September 2020–30 November 2020	8.7	1.2
Summer	1 December 2020–28 February 2021	9.6	1.0
Autumn	1 March 2021–31 May 2021	11	1.2
Winter	1 June 2021–23 August 2021	15	1.4

### 3.3. X-ray fluorescence

X-ray fluorescence is commonly used in trace element analyses [12,19]. In this study, the concentrations of 19 trace elements were analysed, i.e. the alkali metals (potassium), alkali earth metals (calcium, strontium and barium), transition metals (titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, silver), semi-metals (silicon), non-metals (phosphorus and sulphur), halogens (chlorine and bromine) and rare earths (uranium).

XRF output data (uncertainties and concentrations) are listed under Supporting Information, Table S2. These data are relevant to source apportionment studies. The yearly average concentration for S (540 ng/m<sup>3</sup>) was the highest over the sampling period. Sources that contribute to this concentration are secondary sulphates (products of SO<sub>2</sub> from gypsum dust particles, diesel, and heavy oil consumption processes) and coal burning. Other elements that are amongst the top five elements include Si – 440 ng/m<sup>3</sup>, K – 170 ng/m<sup>3</sup>, Fe – 130 ng/m<sup>3</sup> and Ca – 100 ng/m<sup>3</sup>. Sources that may contribute to K concentration include road and/or soil dust as well as biomass burning. Sources contributing to Fe concentration include road and/or soil dust and traffic. Si and Ca usually come from soil and mineral dust.

Data for the elements with an acceptable S/N ratio are summarised in Table 3, i.e. signal-to-noise ratios (S/N), average concentrations and average uncertainties of the 10 elements with an acceptable S/N ratio. The time-series graphical illustration of the six elements with highest concentrations is presented in Figure 4. In the winter season essentially, only two elements were found, namely calcium and potassium. Table S2 in the supporting information includes the summarised S/N ratios, average concentrations and average uncertainties of the 19 elements under consideration. One outlier was found in the Fe XRF results, and the value is higher than most of the Fe (Figure S9). When excluding the outlier, the yearly average Fe concentration changed from 130 ng/m<sup>3</sup> to 120 ng/m<sup>3</sup>.



**Figure 4.** Time-series XRF results of the six most prevalent elements, where *top left* is sulphur, *top right* silicon, *middle left* potassium, *middle right* iron, *bottom left* calcium and *bottom right* chlorine.

**Table 3.** PM<sub>2.5</sub> bound trace element summary of XRF results.

Element	S/N	Present in number of filters	Concentration (ng/m <sup>3</sup> )	Uncertainty (ng/m <sup>3</sup> )
S	36	178	560	13
Si	16	179	450	24
K	21	178	170	6.1
Fe	16	180	130	7.0
Ca	15	178	100	6.1
Cl	7.4	172	32	3.2
Zn	3.8	169	7.9	1.7
Ba	3.2	149	36	8.6
Cu	2.8	150	8.2	2.8
Br	2.6	148	6.1	1.5

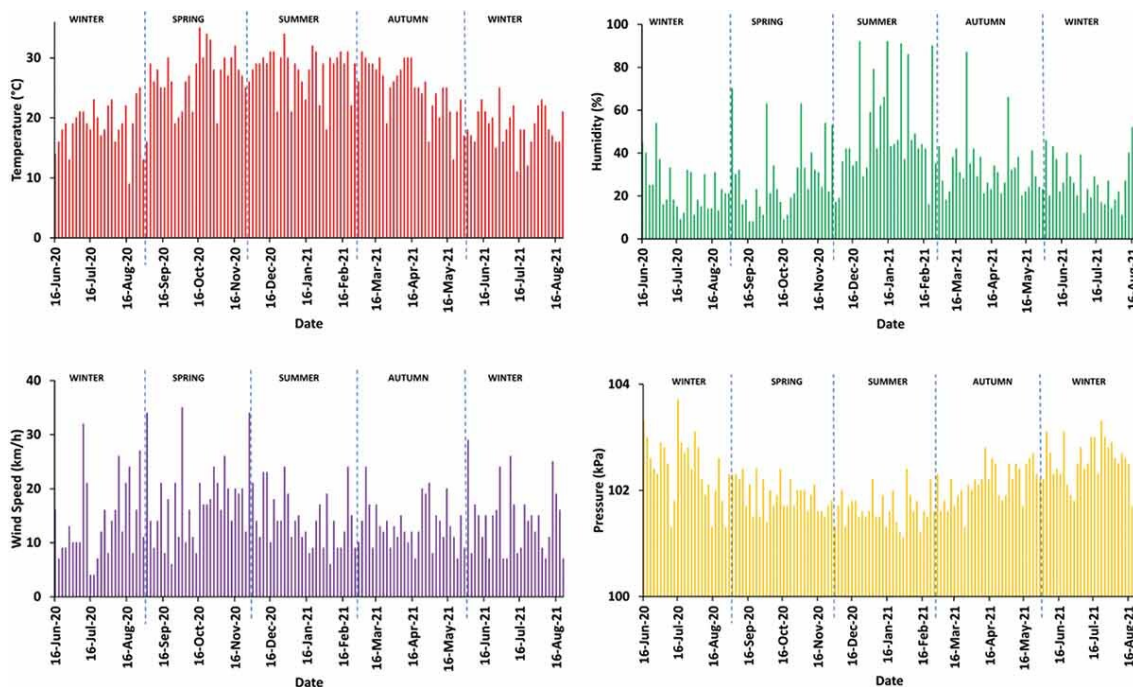
### 3.4. Meteorological

As for the present study, meteorological data (temperature, relative humidity, wind speed and pressure) were collected and are tabulated in Table S1, with seasonal averages in Table 4. The data was collected at 12h00 every day (data is only available hourly and sampling time was closer to 12h00) and compared with the PM<sub>2.5</sub> concentrations measured at the University air quality station. In general, it is seen that the lower the temperature, humidity and wind speed, the higher the PM<sub>2.5</sub> concentrations are. Lower pressures had lower PM<sub>2.5</sub> concentrations.

**Table 4.** Average PM<sub>2.5</sub> concentration (µg/m<sup>3</sup>) and meteorological data in Bloemfontein for each season.

Season	Time Duration	PM <sub>2.5</sub> concentration (µg/m <sup>3</sup> )	Temperature (°C)	Relative humidity (%)	Wind speed (km/h)	Pressure (mbar)
Winter	16 June 2020– 31 August 2020	14	19	24	14	1024
Spring	1 September 2020– 30 November 2020	8.5	27	29	18	1014
Summer	1 December 2020– 28 February 2021	9.7	28	50	14	1016
Autumn	1 March 2021– 31 May 2021	11	25	33	13	1021
Winter	1 June 2021– 23 August 2021	13	19	27	14	1025

As far as seasonal variations of PM<sub>2.5</sub> concentrations are concerned (Table 4), the winter season has the highest value, followed by autumn, summer and spring, thus in most cases having higher PM<sub>2.5</sub> concentrations at lower temperatures [26]. From October through February, average higher spring and summer temperatures were measured. PM<sub>2.5</sub> average concentrations are generally lower during this time. In the time series graph of humidity (Figure 5) the winter season has the lowest humidity, followed by spring, autumn and summer. During the summer months of January and February of 2021 humidity in Bloemfontein was higher than in both the winters before and thereafter. Again, the average PM<sub>2.5</sub> concentrations were seen to be lower over this time period.

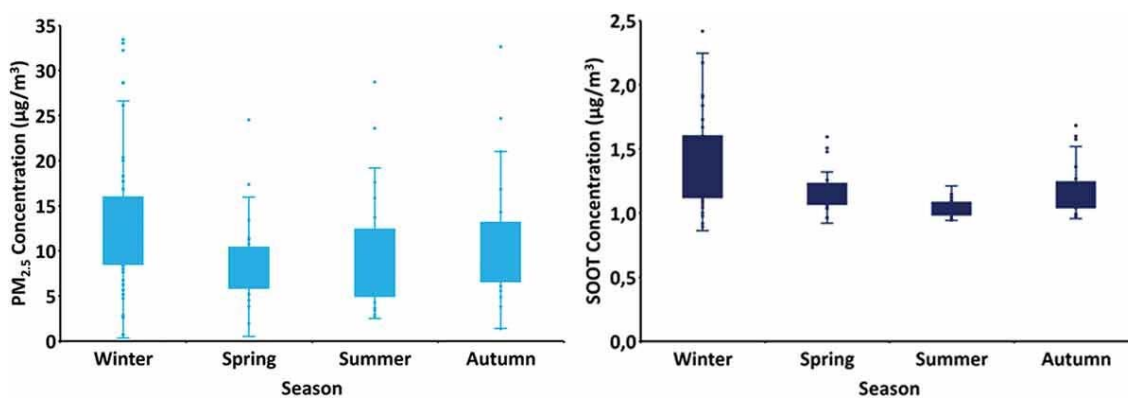


**Figure 5.** Temperature (°C), humidity (%), wind speed (km/h) and atmospheric (kPa) pressure over sampling period.

The time series wind speed graph (Figure 5) also demonstrated similar trends as found in the temperature and humidity comparisons. However, here it was noticed only in the finer day-to-day time scales. As for ambient atmospheric pressure, spring season has the lowest pressure, followed by summer, autumn and winter. It is observed that at lower pressure the PM<sub>2.5</sub> concentrations are lower in most cases. Pressure changes over the sampling period were relatively small, ranging from 101.3 to 103.7 kPa, with an average of 102.1 kPa.

### 3.5. Descriptive statistics

Descriptive statistics were applied to the collected and analysed samples. Table 5 illustrates the descriptive statistics for PM<sub>2.5</sub>, soot and trace element concentrations. The data variations of the PM<sub>2.5</sub> and soot concentrations are shown in Figure 6. Seasonal averages for the PM<sub>2.5</sub> concentrations of the 180 samples were 11 µg/m<sup>3</sup>, 14 µg/m<sup>3</sup>, 8.7 µg/m<sup>3</sup> and 9.6 µg/m<sup>3</sup> for autumn, winter, spring and summer, respectively. Seasonal averages for the equivalent black carbon (soot) concentrations in the 180 samples were 1.2 µg/m<sup>3</sup>, 1.5 µg/m<sup>3</sup>, 1.2 µg/m<sup>3</sup> and 1.0 µg/m<sup>3</sup> for autumn, winter, spring and summer, respectively. Winter had the highest PM<sub>2.5</sub> and soot levels compared to the other seasons – a Kruskal–Wallis test confirmed that the PM<sub>2.5</sub> concentrations and soot concentrations are seasonal ( $p < 0.001$ ).

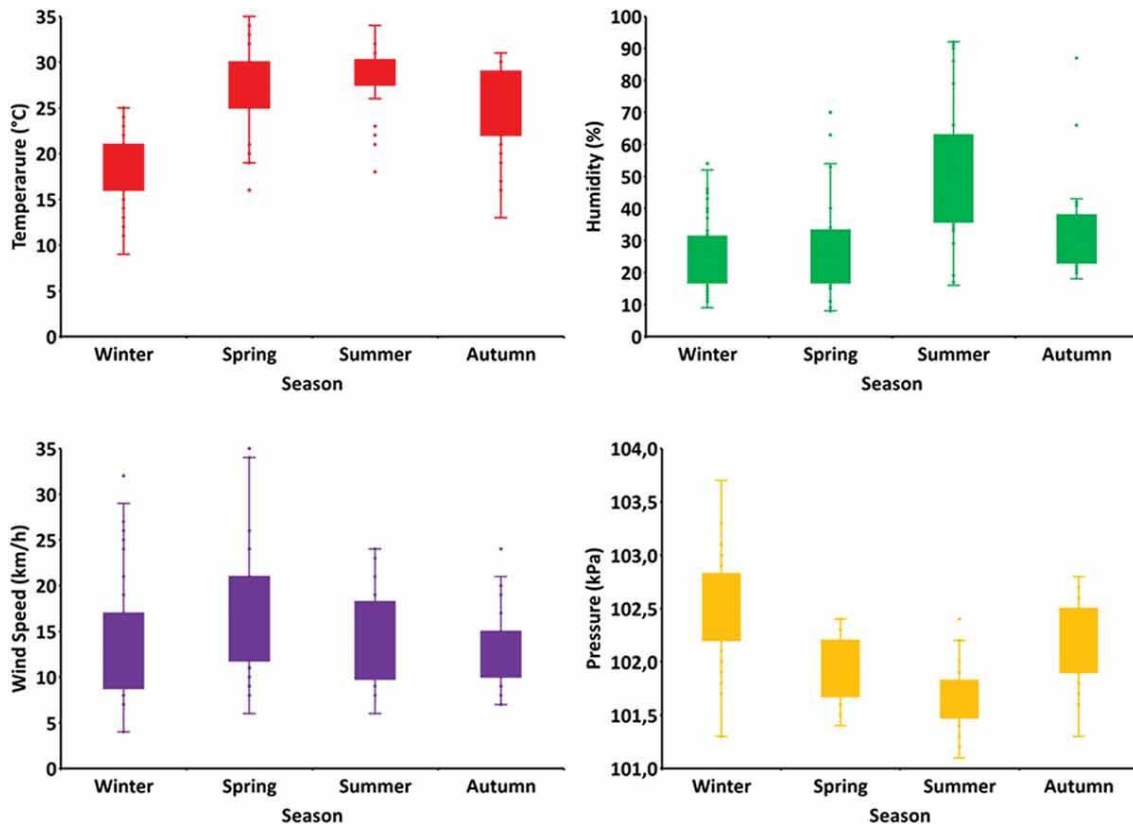


**Figure 6.** PM<sub>2.5</sub> concentration (*left*) and soot concentration (*right*) seasonal data variation.

**Table 5.** Descriptive statistics of PM<sub>2.5</sub> and its soot and trace element composition in Bloemfontein, South Africa, from 26 June 2020 to 18 August 2021 (n = 180 samples).

Variable	Mean	Std. Dev.	Median	Min	Max
PM <sub>2.5</sub> (µg/m <sup>3</sup> )	11	7.3	9.7	0.52	51
Soot (µg/m <sup>3</sup> )	1.2	0.28	1.1	0.81	2.4
Ag (ng/m <sup>3</sup> )	17	7.2	15	11	37
Ba (ng/m <sup>3</sup> )	36	19	40	0.30	67
Br (ng/m <sup>3</sup> )	5.8	6.8	3.4	0.40	47
Ca (ng/m <sup>3</sup> )	100	71	79	0.40	400
Cu (ng/m <sup>3</sup> )	8.1	3.7	7.6	2.9	17
Cl (ng/m <sup>3</sup> )	30	39	17	0.80	260
Cr (ng/m <sup>3</sup> )	2.4	6.5	0.50	0.50	46
Fe (ng/m <sup>3</sup> )	130	89	100	7.3	610
K (ng/m <sup>3</sup> )	160	170	94	6.6	830
Mn (ng/m <sup>3</sup> )	9.6	8.3	9.2	0.20	40
Ni (ng/m <sup>3</sup> )	1.6	2.8	0.90	0.20	25
P (ng/m <sup>3</sup> )	22	8.2	21	0.30	51
S (ng/m <sup>3</sup> )	540	570	360	5.0	3400
Si (ng/m <sup>3</sup> )	440	330	360	15	1900
Ti (ng/m <sup>3</sup> )	14	13	11	0.0	76
U (ng/m <sup>3</sup> )	2.4	1.7	1.8	0.0	7.3
V (ng/m <sup>3</sup> )	15	37	0.60	0.60	160
Zn (ng/m <sup>3</sup> )	7.6	5.4	5.7	2.0	33

In addition to the above, Figure 7 illustrates seasonal temperature, humidity, wind speed and pressure variations. The outcome of the descriptive statistical analysis for the seasons are illustrated in the Supporting Information, Tables S3–S7, and seasonal concentrations are graphically illustrated in Figures S10–S12.



**Figure 7.** Temperature (*top left*), humidity (*top right*), wind speed (*bottom left*) and pressure (*bottom right*) seasonal data variations.

Table 6 illustrates Spearman correlations between weather variables and PM<sub>2.5</sub> data. Correlations of 0.1 to 0.3 are considered weak, 0.3 to 0.6 are medium, and correlations above 0.6 are good. The PM<sub>2.5</sub> concentrations have a medium positive correlation with pressure, otherwise a weak negative correlation with temperature, humidity and wind speed. Temperature has a medium negative correlation, humidity has a weak negative correlation, while wind speed has a medium negative correlation with pressure. Pressure is the only variable that has a statistically significant correlation with all the variables, i.e. temperature, humidity and wind speed. The correlations in Table 6 confirm that seasons and weather patterns play a meaningful role in PM<sub>2.5</sub> air pollution, i.e. dry and cold weather patterns contribute more to air pollution than wet and warm weather patterns.

**Table 6.** Spearman correlations between weather variables and PM<sub>2.5</sub> concentrations.

	PM <sub>2.5</sub>	Temperature (°C)	Humidity (%)	Wind speed (km/h)	Pressure (mbar)
PM <sub>2.5</sub>	1				
Temperature (°C)	-0.2346*	1			
Humidity (%)	-0.1646*	0.016	1		
Wind Speed (km/h)	-0.2438*	0.0859	0.1151	1	
Pressure (mbar)	0.3974*	-0.5602*	-0.2389*	-0.4856*	1

\*Values that are statistically significant  $p < 0.05$ .

Spearman correlations for the six elements with highest prevalence (see Table 3) are listed in Table 7. PM<sub>2.5</sub> concentrations have medium positive correlations with Ca, Fe, K, S and Si and a weak positive correlation with Cl. Ca has good positive correlations with Fe, K and Si and a

medium positive correlation with S. Cl has medium positive correlations with Fe, K and Si. Fe has good positive correlations with K and Si, and a medium positive correlation with S. K has a good positive correlation with Si and a medium positive correlation with S. S has a weak positive correlation with Si.

**Table 7.** Spearman correlations between PM<sub>2.5</sub> concentrations and the top six trace elements.

	PM <sub>2.5</sub>	Ca	Cl	Fe	K	S	Si
PM <sub>2.5</sub>	1						
Ca	0.3480*	1					
Cl	0.1616	0.5681*	1				
Fe	0.3572*	0.8324*	0.5116*	1			
K	0.5076*	0.7904*	0.4764*	0.7533*	1		
S	0.3352*	0.2171*	-0.0129	0.2933*	0.3216*	1	
Si	0.3733*	0.8685*	0.5156*	0.9044*	0.7965*	0.3230*	1

\*Values that are statistically significant  $p < 0.05$ .

#### 4. Conclusions

From a comparison between the average PM<sub>2.5</sub> concentration at the Free State University site and the World Health Organization yearly and daily guideline limits, it is concluded that the level of air pollution in the Free State province may cause health problems. SANAAQ yearly and daily standards, however, do not signal dangerous levels of air pollution, since yearly limits are not exceeded, while the daily standard was exceeded only four times during the 14-month measurement period. Winter seasons were shown to have the highest PM<sub>2.5</sub> pollution, which is also true for black carbon. Elemental analyses established dust to be the main contributor to PM<sub>2.5</sub> pollution in Bloemfontein.

Follow-up future research may include black carbon analyses, organic carbon analyses, source apportionment on the chemical composition and long-range transport cluster analyses. Samples of different sizes collected in the area may be analysed by scanning electron microscopy, X-Ray fluorescence, black carbon and organic carbon analyses. These results may then be compared to the PM<sub>2.5</sub> results of the present study.

#### Disclosure statement

No potential conflict of interest was reported by the author(s).

#### Data availability statement

Additional data are available under Supplementary Material.

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