Source Apportionment of $PM_{2.5}$ and $PM_{2.5}$-Bound Trace Elements in Pretoria, South Africa

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Abstract

Outdoor $PM_{2.5}$ samples were collected for 34 months in Pretoria, South Africa from 18 April 2017 to 28 February 2020. The average total $PM_{2.5}$ concentration was 23.2 ± 17.3 µg.m^3 (0.69–139 µg.m^{-3}), with the highest mean recorded during winter and the lowest during summer ($p < 0.05$). The sources were determined by means of cross referencing the US EPA PMF 5.0 program and the NOAA HYsplit model. The sources of the total $PM_{2.5}$ were mining (33%), resuspended dust (24%), industry (15%), general exhaust (12%), vehicular emissions (12%) and biomass burning (4%). Sources of air pollutants are both ubiquitous and seasonal.

Highlights

- In central Pretoria, the largest contributing sources of $PM_{2.5}$ are resuspended dust matrix and mining from surrounding areas;
- A winter analysis was run where As, Se and Pb was included in the dataset, confirming biomass burning sources which were typically higher during the winter season; and
- Air quality management policies should address both ubiquitous and seasonal sources.

Keywords: PMF; HYsplit; $PM_{2.5}$; trace elements; seasonal; ubiquitous sources

Introduction

“Aerosolized” particulate matter (PM), found in air streams, is a complex mixture of both chemical and biological components (Cao et al. 2014; Liang et al. 2014; Pascal et al. 2013). The constituents of ambient PM include biological organisms (e.g., bacteria, fungi and viruses), organic compounds (e.g., polycyclic aromatic

hydrocarbons [PAHs] and their nitro-derivatives [NPAHs]), nitrates, sulfates, trace metals (e.g., iron, copper, nickel, zinc and vanadium) (Kalisa et al. 2018, 2019; Shi et al. 2016) and carbon compounds (black carbon [BC] and organic carbon [OC]).

These components vary substantially according to time, location, season and climate (Safari-Kagabo et al. 2020). Suspended particulates are further defined by size. Coarse particulates have a diameter between 2.5 and 10 $\mu g.m^{-3}$, whilst fine particulates ($PM_{2.5}$) have a diameter smaller than 2.5 $\mu g.m^{-3}$ (Ruuskanen et al. 2001).

The chemical composition and its relative proportions differ between urban and rural locations as either locations are subject to not only different characteristic variations in source strength but also to shifting meteorological conditions over time and space (Eklund et al. 2014; Tramuto et al. 2011; Djolov and Tshehla 2018; Tshehla and Wright 2019) (Chimidza and Moloi 2000; Dimitriou and Kassomenos 2014; Hao et al. 2019).

In 2020, Pretoria had an overall population of 2,566,000 (Stats 2020). Geographically, Pretoria is situated approximately 55 km (34 mi) north-northeast of Johannesburg in the northeast of South Africa, in a transitional belt between the plateau of the Highveld to the south and the lower-lying Bushveld to the north. Pretoria is situated at an altitude of about 1339 m (4393 ft) above sea level surrounded by the hills of the Magaliesberg range with agricultural and mining activities in the surrounds. Pretoria experiences summer rainfall and very dry winter seasons.

Soot, BC and UV-PM are an ever-present feature in urban societies in both developed and developing countries (Nazarpour et al. 2019; Ngo 2013; Novakov et al. 2005; Zhi et al. 2021; Zhou et al. 2013, 2020). In the United States, the Congress on Black Carbon, US EPA defines BC as the “carbonaceous component of PM that absorbs all wavelengths of solar radiation” (hence, the appropriateness of the term “black”) (Long, Nascarella, and Valberg 2013). In its 2012 report, the *Joint World Health Organization (WHO)/Convention Task Force on Health Aspects of Air Pollution* similarly describes BC as “an operationally defined term, which describes carbon as measured by light absorption” (Singh et al. 2014; Venter et al. 2012).

Although the composition of BC particles was not investigated in this project, it is interesting to note that BC has variable chemical compositions depending on their sources. These are sometimes primarily elemental carbon (EC), but often existing as complex mixtures of EC, OC and other non-carbon species such as ionic species and trace metals (Long, Nascarella, and Valberg 2013; Singh et al. 2014; Wichmann and Voyi 2012). Maritz et al. (2015) and Sahu et al. (2011) established the seasonal and diurnal variations of BC and UV-PM where the mean concentrations were higher during dry seasons (Sahu et al. 2011). In South Africa, this will not be the case due to winter biomass burning (Adeyemi et al. 2021; Djolov and Tshehla 2018).

Positive Matrix Factorization (PMF) has been used extensively for source apportionment of ambient PM in environmental studies, where the goal is to resolve the mixture of sources that contributes to PM samples (Hopke et al. 2020; Molnár, Johannesson, and Quass 2014).

An advantage of PMF when working with environmental data is it forces all the values in the solution profiles and contributions to be nonnegative, which is more realistic than solutions from methods like principal components analysis (PCA) (Norris et al. 2014).

Assigning sources to the factors are subjective and the relative percentage presence of BC, UV-PM and the tracer elements are relied upon. The objectives of the project were to

- investigate if there were any temporal trends in $PM_{2.5}$ and their trace element content; and
- establish potential sources of emissions by means of trace elemental combinations.

Methods

$PM_{2.5}$ Sampling Site

The site was located at the School of Health Systems and Public Health (SHSPH), University of Pretoria, and aerosol samples were collected approximately 20 m above ground, on the roof of HW Snyman South Building, Prinshof Campus (S25° 43′ 57″ E28° 12′ 10″). The study site can be characterized as an urban background area. Activities surrounding the site are large educational institutions, two governmental hospitals and industries in the northern and north-western areas including metal and motor manufacturing, ferrochrome smelters and mining (Djolov and Tshehla 2018) (Figure 1).

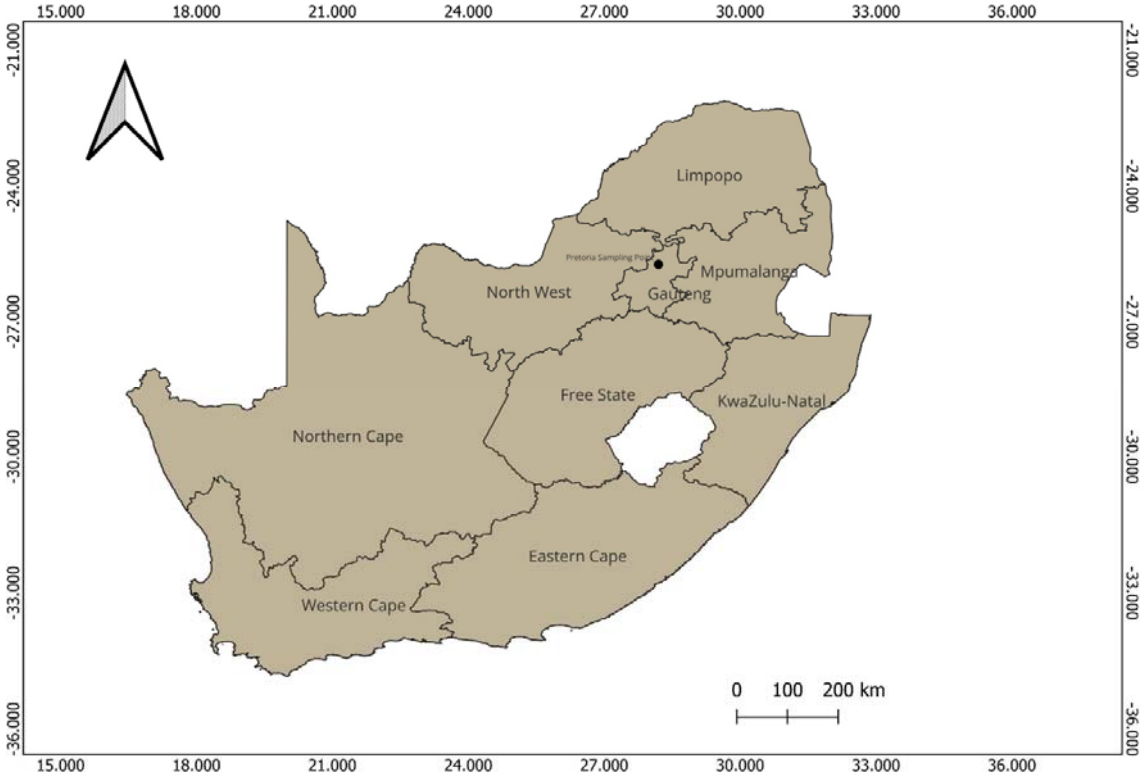

Figure 1. •••

$PM_{2.5}$ Sampling

This project used the same sampling methodology as in previous South African studies (Adeyemi et al. 2021; Howlett-Downing et al. 2022; Novela et al. 2020; Williams, Petrik, and Wichmann 2020). Of 24-h samples were collected every third day from 9:00 to 9:00 am the next day using GilAir-5 personal air samplers with 2.0 µm PFTE (Zefluor) 37 mm filters (Zefon International, Inc., Ocala, FL34474), between 18 April 2017 and 28 February 2020. The total dataset included 350 $PM_{2.5}$ filter samples with 59 duplicate samples.

Gravimetric and Chemical Analysis of Filters

Gravimetric analyses of $PM_{2.5}$ filters were carried out using a 1 µg sensitivity microbalance (Mettler Toledo, XP6) under climate-controlled conditions (temperature and relative humidity were maintained at 21 ± 0.5 °C and 50 ± 5%, respectively) at the Air Quality Laboratory, SHSPH. The elemental composition of aerosol particles on all filters was determined using an XEPOS 5 energy-dispersive X-ray fluorescence (EDXRF) spectrometer (Spectro Analytical Instruments GmbH, Kleve, Germany) at the Department of Chemistry and Molecular Biology, Atmospheric Science Division, University of Gothenburg. BC and UV-PM were measured using a Model OT21 Optical Transmissometer (Magee Scientific Corp., Berkeley, CA) (Boman et al. 2009; Molnár, Johannesson, and Quass 2014; Molnár et al. 2017).

Source Apportionment

PMF is a multivariate receptor modeling concept that uses a weighted least square approach to estimate source profiles and contributions (Paatero et al. 2014; Paatero and Hopke 2003, 2009). The Environmental Protection Agency program EPA PMF version 5.0 was used to conduct the source apportionment study (Molnár et al. 2017). An iterative process is used to minimize a residual function for optimization of the calculations. In the case of missing data, the median was substituted and the uncertainty was calculated using four times the median (Reff, Eberly, and Bhave 2007).

Back Trajectory Calculations

The origins of air masses passing through Pretoria, South Africa, were used as a proxy for the long-range transport of air pollutants from distant sources. The HYbrid Single Particle Lagrangian Integrated Trajectory (HYsplit) program was used to generate backward trajectories for each year of the sampling campaign (i.e., 18 April 2017 to 16 April 2018, 19 April 2018 to 22 April 2019 and 25 April 2019 to 28 February 2020) (Figure 2). Every 6 h (0:00; 6:00; 12:00; 18:00), an analysis field (resolution 2.5° × 2.5° and 17 vertical levels) was generated, and the wind field was interpolated linearly between each analysis. Since a single backward trajectory has a significant uncertainty and is of little importance, as in previous studies, this study used an ensemble of trajectories with a 500 m starting height and a fixed offset grid factor of 250 m (i.e., 250 m and 750 m). For cluster analysis, the average daily trajectories were estimated backwards for 72 h. For the study period, 13,512 backward trajectories were generated (Howlett-Downing et al. 2022).

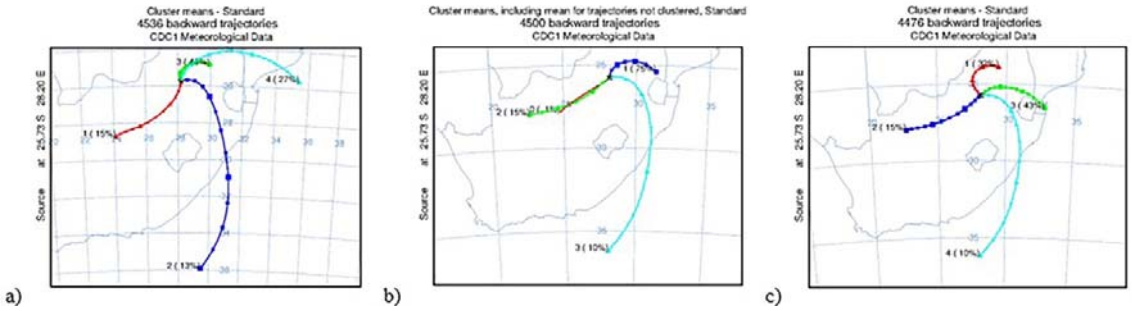

Figure 2. •••

Data Preparation

There is no standard rule on what species to select or leave out in multiple-year studies where the range of species varies per year (Reff, Eberly, and Bhave 2007). For the main 34-month dataset used in the PMF model, trace elements above the level of detection (LoD) was included. Two sensitivity studies were then run where a winter analysis and a dataset including an adjusted Ni was performed. The winter analysis included As, Se and Pb which were below the LoD for the 34-month study but were above the LoD during the winter months.

Statistical Analysis

The factors were tested for independence and seasonality by means of a Kruskal–Wallis test (H0: $\mu_1 \neq \mu_2 \neq \mu_3 \neq \mu_4$) using STATA version 15 (StataCorp LLC, College Station, TX). A Spearman's Rank Correlation test was performed to test for correlations between constituents of total $PM_{2.5}$, BC, UV-PM and trace elements.

Results

A summary of descriptive statistics of meteorological conditions, $PM_{2.5}$, soot, BC, OC and trace elemental concentrations during the measurement period from 18 April 2017 to 28 February 2020 is given in Table 1.

Table 1. Descriptive statistics of 24-h $PM_{2.5}$, soot, black carbon, organic carbon and trace elemental levels and meteorological conditions on 350 d at the School of Health Systems and Public Health, University of Pretoria during 18 April 2017 and 28 February 2020.

Factor		Constituents	PMF contribution (%)
1	Mining	$PM_{2.5}$, BC, UV-PM, Ti, Fe, Cu, Br and U	33
2	Resuspended dust matrix	$PM_{2.5}$, BC, UV-PM, Ca, Ti and Cu	24
3	Industry	$PM_{2.5}$, Ti, Fe, Ni and Si	15
4	Exhaust	S and Si	12
5	Vehicular emissions	Cl, Zn and Br	12
6	Biomass burning	Cl and K	4

Correlations between Variables

$PM_{2.5}$, soot, BC and UV-PM were correlated by means of a Spearman's Rank correlation test ($p < 0.001$) (Table S4). The strongest correlation was observed

between BC and UV-PM, whilst soot had the weakest correlations with $PM_{2.5}$, BC and UV-PM.

Br is positively correlated with Cl, K and Ti (rho = 0.64, 0.65 and 0.56, $p < 0.001$, respectively). These were the coarse particulates and seasonal ($p < 0.001$), which implies winter biomass burning as well as urban industrial activities (Adeyemi et al. 2021; Pachon et al. 2013; Srivastava, Goel, and Agrawal 2016; G. Thurston, Ito, and Lall 2011; Zhang, Chen, and Xu 2020). Further coarse particulate correlations include Si and Ti (rho = 0.60, $p < 0.001$). Ni was poorly correlated with S and Si (rho = 0.14 and 0.17, $p < 0.001$, respectively). K, S and Si are correlated (rho = 0.53 and 0.50, $p < 0.001$, respectively). K, S and Si are tracers for the burning of coal and other exhaust emissions (Adeyemi et al. 2021; Pachon et al. 2013; Srivastava, Goel, and Agrawal 2016; G. Thurston, Ito, and Lall 2011; Zhang, Chen, and Xu 2020).

PMF Analysis of the Total Dataset

The PMF analysis was performed for 4, 5 and 6 factors. In the four-factor run, coal and biomass burning, secondary S and the resuspended dust matrix were separated while industry and vehicular emissions shared a factor. In the five-factor run, the industry and vehicular emissions factor were delineated. It was decided to select the six-factor configuration where industry was separated from mining and vehicular emissions, $p < 0.05$ (Table 2 and Figure 3). The presence of $PM_{2.5}$, BC, UV-PM, Ti, Fe, Cu, Br and U was attributed to mining for the first factor. This factor constituted the largest factor in the PMF modeling process with 33% of the total $PM_{2.5}$. This could be due to the proximity to surrounding mining activities as well as dust from legacy mines (Davy et al. 2012; Thurston and Spengler 1985). The large BC, UV-PM percentage contribution could be attributed to industrial exhaust emissions and accrued dust from industry and mining (Kim, Hopke, and Edgerton 2003).

Table 2. A summary of the constituents of each factor configuration for the full dataset above LoD from 18 April 2017 to 28 February 2020 as modeled by PMF.

Factor		Constituents	PMF contribution (%)
1	Mining	$PM_{2.5}$, BC, UV-PM, Ti, Fe, Cu, Br and U	33
2	Resuspended dust matrix	$PM_{2.5}$, BC, UV-PM, Ca, Ti and Cu	24
3	Industry	$PM_{2.5}$, Ti, Fe, Ni and Si	15
4	Exhaust	S and Si	12
5	Vehicular emissions	Cl, Zn and Br	12
6	Biomass burning	Cl and K	4

The second factor, being the resuspended dust matrix factor contributed 24% to the total assessed $PM_{2.5}$ in the PMF modeling process. The constituents of this factor were $PM_{2.5}$, BC, UV-PM, Ca, Ti and Br. The Ni-U combination in the third factor was attributed to industry from the surrounding areas contributing 15% to the total assessed $PM_{2.5}$ (Moreno et al. 2010; Djolov and Tshehla 2018; Venter et al. 2012; Wang et al. 2006). Here, 90% of the total Fe mass was attributed to this factor, this implies a strong influence from pyrometallurgical activities in the surrounds of Pretoria (Van Zyl et al. 2014; Venter et al. 2012). The presence of S and Si was attributed to general exhaust fumes and contributed 12% to the total assessed $PM_{2.5}$ by the PMF process. The presence of Cl, Zn and Br was attributed to vehicular emissions and the

fifth factor contributes 12% to the total assessed $PM_{2.5}$ by the PMF process (G. D. Thurston, Ito, and Lall 2011; Zhou et al. 2013).

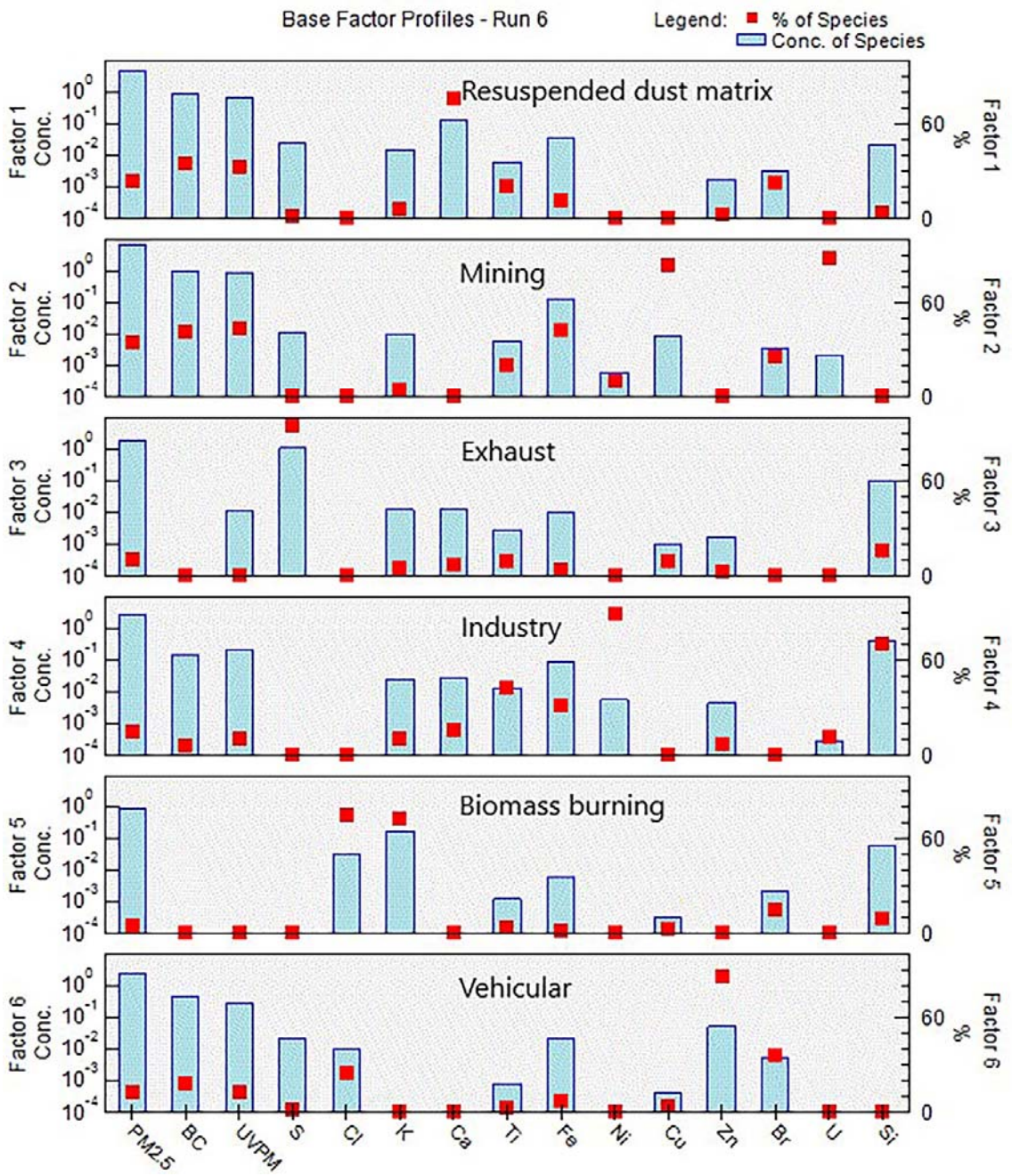

Figure 3. •••

Vehicles can contribute to air emissions by means of combustion as well as a range of non-exhaust particulates including wear of brake pads and tires (Chan et al. 2008; Iijima et al. 2008, 2009; Wahlin, Berkowicz, and Palmgren 2006). The presence of a Cl and K combination was attributed to coal/biomass burning and the sixth factor contributes 4% to the total assessed $PM_{2.5}$ by the PMF process. The factor contains 75 and 73% of the Cl and K contributions, respectively.

PMF Analysis for Winter Months

The ambient mass concentrations for As, Se and Pb were above the LoD during the winter months but not as an annual average over the 34 months. When running a winter analysis, the six-factor configuration for the PMF analysis, including As, Se and Pb in the analysis, resulted in the sources coal burning (29%), industry (24%), general exhaust (13%), mining (12%), vehicular emissions (12%) and fossil fuel burning (9.7%). It is interesting to note that during winter, the factor for coal burning could be demarked from other fossil fuel sources due to the inclusion of As and Pb. (Bartkowiak, Lemanowicz, and Breza-Boruta 2017; Fernández-Camacho et al. 2012; Jeong and Ra 2021) The Cu–Pb–Zn combination supported the assigning of a coal-burning factor.

HYsplit, Sources and Seasons for Full Study

Four main transport clusters were decided upon for the 34-month analysis when amalgamating the three individual years model output. Of the four-cluster configuration, 42% of the three-year wind trajectories are from the westerly direction (W). The other three main clusters are from the easterly direction, 29% from the north easterly (NE), 15% from the south easterly (SE) and 14% from the long-range Indian Ocean (LRIO) direction. Notably, the highest concentration of total $PM_{2.5}$ is transported *via* the western and south-eastern cluster with 48 and 51 observations respectively. The three separate years are presented in

(Howlett-Downing et al. 2022).

Discussion

PMF Analysis of the Total Dataset

The 6-factor source contribution according to the PMF analysis is shown in Table 2. The assigning of sources to factors is a subjective practice (Hopke 2000; Hopke et al. 2006, 2020). It is standard practice to assign sources based on previous PMF outcomes (Mathuthu, Dudu, and Manjoro 2019; Molnár, Johannesson, and Quass 2014; Srivastava, Goel, and Agrawal 2016; G. Thurston, Ito, and Lall 2011; Wahlin, Berkowicz, and Palmgren 2006; Willis, Ellenson, and Conner 2001; Yin et al. 2010) as well as studies on the prevalence of the $PM_{2.5}$ constituents in known processes (Genchi et al. 2020; Gieré, Kaltenmeier, and Pourcelot 2012; Jaszczak et al. 2017; Jayasekher 2009; Ngo et al. 2015; Novak et al. 2016; Quincey 2007; Ruuskanen et al. 2001; Singh et al. 2014; Thorpe and Harrison 2008; Visschedijk et al. 2013; Wien et al. 2001; Yu et al. 2018; Zychowski et al. 2018). The main determinants of the sources in this study were proximity to industry and coal-fuelled power stations, proximity to ocean or inland areas, geomorphology of landscape, rural or urban settlements (Maritz et al. 2015; Djolov and Tshehla 2018; Venter et al. 2012).

In this study, the sum of BC and UV-PM constitute approximately 11% and 9%, respectively, of the total $PM_{2.5}$ concentration (Howlett-Downing 2022). According to Junker and Liousse (2008), biomass burning and biofuel emissions usually have higher UV-PM/BC ratios than fossil fuel sources. Bove et al. (2014) allocated the burning of diesel to an OM (organic matter) – BC ratio of about 1.8. A similar ratio of

UV-PM/BC in the Pretoria study (1.4) was determined, implying vehicle and industrial sources of air pollutants near the sampling site.

Vehicular and resuspended dust have ratios of 1.4 and 1.2, respectively, whilst exhaust and mining have ratios of approximately 1. A ratio of 1.55 was attributed to vehicular emissions, implied fresh gasoline exhaust fumes contributed to the exhaust factor (Guhirwa 2018; Maritz et al. 2015; Ruuskanen et al. 2001; Safari-Kagabo et al. 2020). In Europe, vehicular emissions (Belis et al. 2013) have been identified as the highest source targeted for abatement measures, in developing countries it was exhaust fumes (Naidja, Ali-Khodja, and Khardi 2017) and emissions from burning of coal, which should be targeted (Karagulian and Belis 2012; Karagulian et al. 2015).

In Europe, vehicular emissions (Belis et al. 2013) have been identified as the source targeted for abatement measures, in developing countries it is exhaust fumes in general (Naidja, Ali-Khodja, and Khardi 2017) and emissions from burning of coal which should be targeted (Karagulian and Belis 2012; Karagulian et al. 2015).

Two sources can be attributed to vehicles, exhaust fumes as well and the tyre and break lining which is attributed to non-exhaust vehicular emissions (Thorpe and Harrison 2008). In this project, these are aligned to the vehicular emissions factor but exhaust emissions may also contribute to the exhaust factor due to the presence of a low Cu–Zn combination (9% and 3%).

The resuspended dust matrix was seasonal ($p < 0.001$), with the highest mean concentration in winter (8.2 $\mu g.m^{-3}$) and during summer, was four times the mean $PM_{2.5}$ (1.9 $\mu g.m^{-3}$). The exhaust factor was the highest during autumn and summer (2.4 and 1.1 $\mu g.m^{-3}$, respectively) which tentatively supported the allocation of the contributing percentage of S to exhaust rather than to secondary sulfur due to the photochemical process (Ito, Xue, and Thurston 2004; Thorpe and Harrison 2008; G. Thurston, Ito, and Lall 2011). The highest mean concentration in winter (9.2 $\mu g/m^3$) could be allocated to processes which rely on coal combustion (Li et al. 2017; Sandradewi et al. 2008; G. Thurston, Ito, and Lall 2011; Yu et al. 2013; Zhang, Chen, and Xu 2020). The presence of Cl was higher in the winter months ($p < 0.001$) possibly due to the burning of coal and biomass as a domestic source of fuel (Luo et al. 2019).

Recently, Muyemeki et al. (2021) studied three sites in the Vaal Triangle Airshed Priority Area (VTAPA) which was situated in a highly industrialized region south of Gauteng, South Africa. The highest seasonal median concentrations of $PM_{10-2.5}$ (116 $\mu g.m^{-3}$) and $PM_{2.5}$ (88 $\mu g.m^{-3}$) were observed in Sharpeville during the winter. The lowest median concentrations of $PM_{10-2.5}$ (25 $\mu g.m^{-3}$) and $PM_{2.5}$ (18 $\mu g.m^{-3}$) were detected in Zamdela during the summer/autumn period. At all sites, there was an abundance of crustal elements in $PM_{10-2.5}$ and a dominance of coal and biomass combustion-related elements in $PM_{2.5}$. The Positive Matrix Factorization receptor model identified dust-related and secondary aerosols as the major contributing sources of $PM_{10-2.5}$. $PM_{2.5}$ contributions were predominantly from coal burning for Sebokeng and Sharpeville and from industry, wood and biomass burning, and secondary aerosols for Kliprivier and Zamdela (Muyemeki et al. 2021).

Similar results were determined by Djolov and Tshehla (2018) in the Greater Tubatse Municipality in Limpopo where three ferrochrome smelters and over fifteen operational

mines which are mining chromium, platinum or silica. The allocated source factors where agriculture/wood combustion, coal combustion, crustal/road dust, ferrochrome smelters and vehicle emissions as the main sources in the area (Djolov and Tshehla 2018).

When considering collinearity during the assigning of sources (Belis et al. 2013), there were combinations that were repeated in other factors. The Ti–Fe combination was attributed to both mining and industry. The presence of the Cl–Br combination was a tracer for both coal burning and biofuel (Huang et al. 2021; Wahlin, Berkowicz, and Palmgren 2006). The S–Ti–Si combination was attributed to exhaust emissions with the strong possibility of the presence of secondary S during autumn and summer (Ito, Xue, and Thurston 2004; Srivastava, Goel, and Agrawal 2016; G. Thurston, Ito, and Lall 2011; Venter et al. 2012). The large 94% contribution of S within the exhaust factor could have accrued from several sources including coal burning (Molnár et al. 2017) and secondary sulfur production due to photochemical activities in the atmosphere in warmer temperatures (Kim, Hopke, and Edgerton 2003). The high Ni content (90%) attributed to industry could be attributed to pyrometallurgy activities, non-ferrous activities as well as oil combustion in industry (Belis et al. 2013; Molnár et al. 2017). The exhaust factor was referred to as an activity rather than as a point source or particular industry due to the innate heterogenous nature of industrial emissions (Belis et al. 2013).

PMF Analysis for Winter Months

There are strengths and limitations to removing or keeping in trace elements in a study (Ganser and Hewett 2010; Hornung and Reed 1990). Three trace elements including As Se and Pb were included in the main dataset to support the factor allocation as these were seasonal.

The three trace elements were above the LoD during winter and tracers for coal, wood and biomass burning (Eklund et al. 2014; Safari-Kagabo et al. 2020; Szidat et al. 2009). This was evident in the factors that were modeled by the PMF model.

The exhaust factor which was characterized with the high S content and could include both industrial exhaust emissions and coal-burning emissions during winter. The As–Pb combination is a tracer for coal burning (Agency 1998; Saikia et al. 2013). The As–Se combination is a tracer for soils, coal or biofuels during winter (Wen and Carignan 2007). The inclusion of the tracer elements did not affect the more ubiquitous factors including vehicular emissions, mining and resuspended dust matrix but do confirm the factors assigned to exhaust and biofuel emissions.

HYsplit, Sources and Seasons for Full Study

The transport analysis by means of HYsplit approximated the transport clusters by means of meteorological data (de Hoogh et al. 2014; Leelőssy et al. 2014; Stein et al. 2015). This project does not explore the deposition rates of the heavier metals which could account for selective loss or the selective gains in constituent $PM_{2.5}$ due to chemical formation or condensation (Belis et al. 2013).

The trace element Ti featured in all six factors but largely in resuspended dust matrix (20%), mining (21%) and in industry (43). Titanium is a crustal size particulate and a tracer for natural dust; however, titanium is mined in South Africa (Richards Bay and the west coast). The high mean concentration of 4.5 and 4.3 $\mu g.m^{-3}$ attributed to coarse particulates was transported by cluster 2 (SE) with only 52 observations and cluster 4 (LRIO) with 48 observations. These transport clusters originated or traveled near mining activities (Chimidza and Moloi 2000; Venter et al. 2012, 2017). Zn, Cu, Ni and Pb will deposit in soils and in turn be present in the form of resuspended dust (Bartkowiak, Lemanowicz, and Breza-Boruta 2017) (Table 4).

During winter the high mean concentration contribution was equal for three clusters, NE, SE and W (30.7, 30.1 and 29.5 $\mu g.m^{-3}$, respectively) and higher for the LRIO with 36.1 $\mu g.m^{-3}$. Resuspended dust and exhaust emissions have the highest mean concentrations in cluster 2 (SE). The Vaal priority area could contribute to these sources. The platinum mining activities in the Rustenburg area and the bushveld igneous complex could contribute to these sources (Maritz et al. 2015; Djolov and Tshehla 2018; Tshehla and Wright 2019; Van Zyl et al. 2014; Venter et al. 2012; Yu et al. 2018) (Table 3).

Table 3. Summary of the seasonal mean and range for $PM_{2.5}$ levels ($\mu g.m^{-3}$) as measured at the School of Health Systems and Public Health, University of Pretoria from 18 April 2017 to 28 February 2020.

	Full study (350 observations)		Autumn (77 observations)		Winter (91 observations)		Spring (92 observations)		Summer (90 observations)		Kruskal–Wallis
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	p^*
$PM_{2.5}$ (Observed)	23.0	0.7–138	22.4	5.17–48.5	24.8	7.04–57.9	22.7	0.7–66.8	21.4	1.35–47.9	$p < 0.05$
Resuspended matrix	4.3	0–30.1	3.3	0–17	8.6	0–31	3.5	0–19	1.9	0–19	$p < 0.05$
Mining	6.4	0–127	6.5	0–127	9.2	0–32	7.3	0–27	2.9	0–27	$p < 0.05$
Exhaust	1.9	0–21.0	3.1	0–21.2	1.8	0–19	1.0	0–13	2.0	0–13	$p < 0.05$
Industry	2.8	0–24.0	2.5	0–14.2	4.0	0–24	2.8	0–14	1.9	0–14	$p < 0.05$
Biomass burning	0.8	0–13.0	0.7	0–5.0	1.9	0–13	0.5	0–3.2	0.2	0–3.2	$p < 0.05$
Vehicular	2.3	0–38	2.5	0–23	5.2	0–38	1.1	0–13	0.4	0–13	$p < 0.05$

*$\alpha = 0.05$.

Table 4. The mean concentration of $PM_{2.5}$ ($\mu g.m^{-3}$) within a cluster per season, as estimated by the positive matrix factorization model as modeled by the NOAA HYSPLIT.

	Cluster (observations)	Seasons (observations)	Resuspended matrix	Mining	Exhaust	Industry	Biomass burning	Vehicular
1	NE (103)	Autumn (25)	3.9	4.4	**4.0**	3.4	1.0	3.3
		Winter (28)	**9.3**	**9.2**	1.2	**3.7**	**1.8**	**5.4**
		Spring (22)	4.3	7.2	0.4	2.4	0.4	1.2
		Summer (28)	1.8	2.8	1.3	2.0	0.2	0.5
2	SE (52)	Autumn (14)	4.1	4.8	**4.1**	1.6	0.7	2.7
		Winter (14)	**8.9**	**9.9**	1.2	**4.9**	**1.0**	**4.2**
		Spring (10)	2.7	7.5	1.5	3.9	0.6	0.7
		Summer (14)	1.6	2.7	1.9	1.1	0.2	0.3
3	W (148)	Autumn (35)	2.5	**9.1**	2.1	2.3	0.6	2.0
		Winter (38)	**7.6**	**8.8**	2.0	**3.7**	**2.1**	**5.2**
		Spring (36)	3.9	7.8	1.0	3.2	0.5	1.3
		Summer (39)	1.9	2.5	**2.5**	2.2	0.1	0.3
4	LRIO (48)	Autumn (4)	4.4	2.3	**2.5**	2.2	0.2	0.9
		Winter (11)	**9.7**	**9.9**	**3.3**	**4.4**	**2.5**	**6.4**
		Spring (24)	2.5	6.4	1.3	2.1	0.5	0.8
		Summer (9)	2.7	4.7	2.3	1.8	0.3	0.2

Sampled at the School of Health Systems and Public Health, University of Pretoria from 18 April 2017 to 28 February 2020.
Bold are the highest scores per season per cluster.

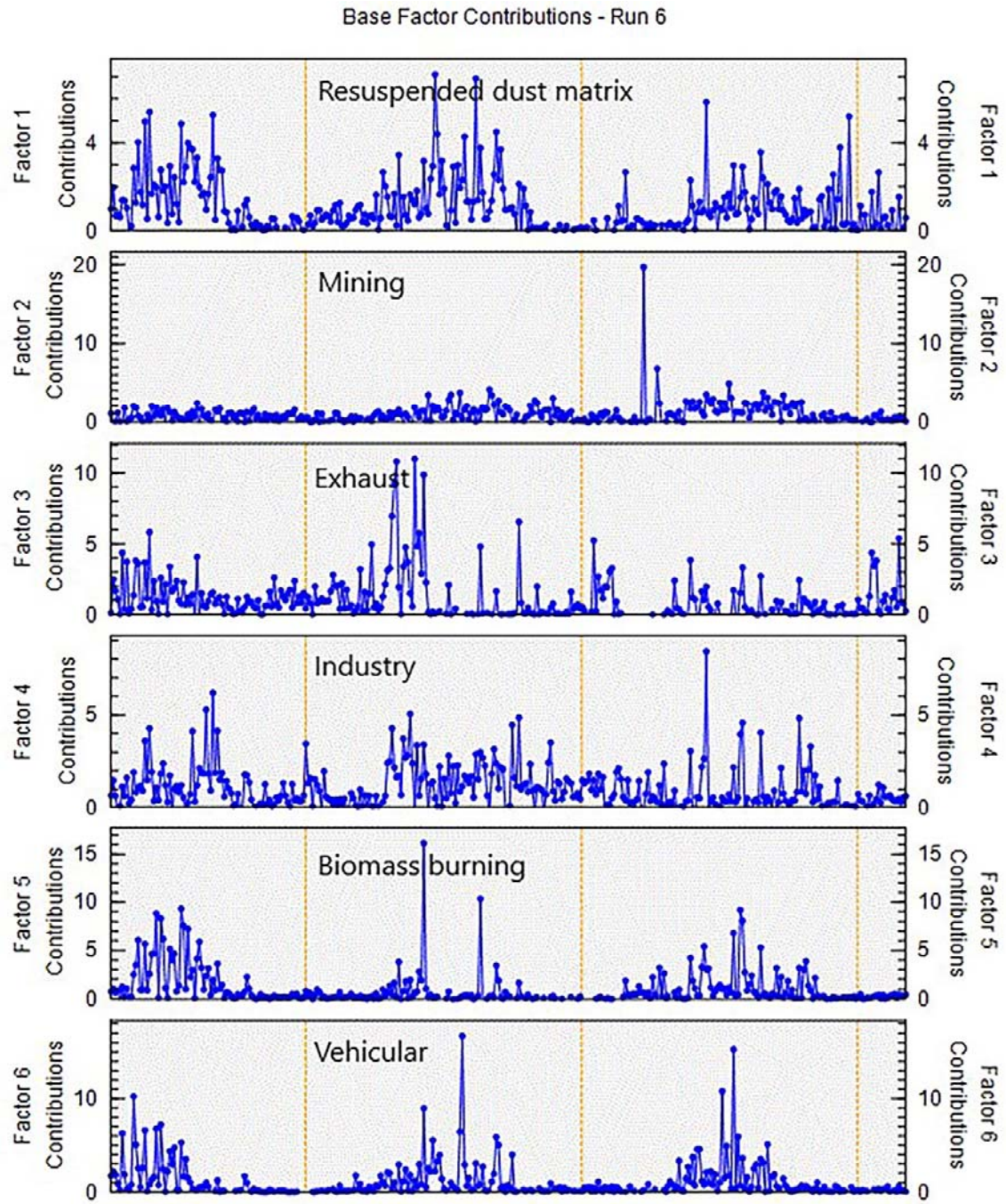

Figure 4. •••

The seasonal Trend of the Sources

The mean seasonal concentration for all six individual sources was the highest during winters (Table 4 and Figure 4). All factors demonstrated seasonality ($p < 0.05$). This could be attributed to winter fuel sources (Luo et al. 2019) as well as temperature, relative humidity and wind speed (Macdonald 2003; Stein et al. 2015). The sum of mean concentrated $PM_{2.5}$ modeled by the PMF is 30.8 $\mu g.m^{-3}$ in winter compared to 9.2 $\mu g.m^{-3}$ in summer. All sources except for exhaust emissions are higher in winter

than in summer. Vehicular emissions were 10 times higher (5.2 $\mu g.m^{-3}$) in winter than in summer (0.4 $\mu g.m^{-3}$). Industry with coarse heavy metal tracers including Ti, Fe, Ni and Si had a mean concentration of 1.4 $\mu g.m^{-3}$ in winter and 0.68 $\mu g.m^{-3}$ in summer. The high contribution of Si could be attributed to soil dust (Yu et al. 2013), road dust (Thorpe and Harrison 2008) and tail pipe particulates (Yu et al. 2013). The inversion layer as well as deposition mechanisms may account for this trend (Leelőssy et al. 2014; Macdonald 2003; Stein et al. 2015). The heavy metals in the mining source where the mean seasonal concentration was 3x higher in winter (9.2 $\mu g.m^{-3}$) than in summer (2.9 $\mu g.m^{-3}$) could also follow the above trend (Figure 5).

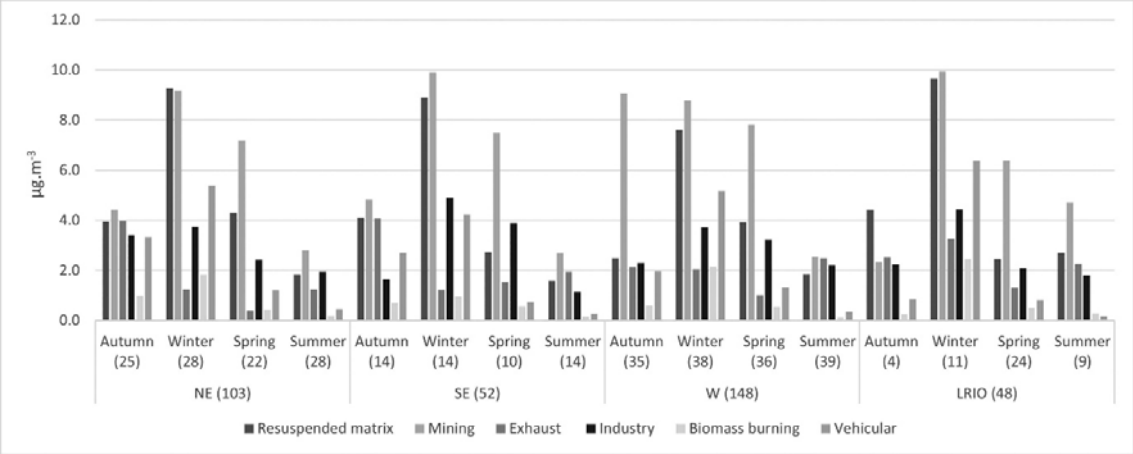

Figure 5. •••

Chlorine is tracer for biomass burning during winter (Luo et al. 2019) with seasonal average concentrations for the 34-month study, being 0.7 $\mu g.m^{-3}$ (77 observations) in autumn, 0.5 $\mu g.m^{-3}$ (91 observations) in spring, 0.2 $\mu g.m^{-3}$ (90 observations) in summer and 1.9 $\mu g.m^{-3}$ (90 observations) in winter. Potassium was also seasonal with 0.50 $\mu g.m^{-3}$ in winter, 0.075 $\mu g/m^3$ in summer, 0.02 $\mu g.m^{-3}$ in spring and autumn. The K–Br (15%) and Cl–Br combinations were reported to be tracers for wood burning during the winter months (Pachon et al. 2013). The presence of Cl (75%) has previously been attributed to coal burning during winter by Wahlin, Berkowicz, and Palmgren (2006). Biomass sources peak in June (2.3 $\mu g.m^{-3}$) and this corresponded to the highest triannual Cl (1.3 $\mu g.m^{-3}$) and K (1.9 $\mu g.m^{-3}$) concentrations (Figure 5).

The exhaust factor was 3 × higher in autumn (3.1 $\mu g.m^{-3}$) than in spring (1.0 $\mu g.m^{-3}$). Sulfur had the highest total mean concentration sampled at the SHSPH (1.16 $\mu g.m^{-3}$). The mean concentration for S in autumn was double (1.7 $\mu g.m^{-3}$) that of the summer mean average (0.7 $\mu g.m^{-3}$). The mean seasonal windspeed for summer was 1.2 ms^{-1} and for autumn, 0.96 $m.s^{-1}$ (Figure 5).

The highest recorded Si concentrations occurred from May to August in all three years (1039, 1160 and 688 $ng.m^{-3}$). The high presence of the total annual contribution of Ti could come from mining as well as natural sources. The dust matrix is more than 4 × in winter (8.6 $\mu g.m^{-3}$) than in summer (1.9 $\mu g.m^{-3}$).

In terms of the number of observations of sources per cluster, cluster 3 (W) has the least variability ranging from 34 counts in autumn to 39 in summer. Cluster 4 (LRIO) displays the most variability, ranging from 3 counts in autumn to 24 in spring.

Conclusion

The 34-month study corresponds very well with the 12-month study done previously by Adeyemi et al. (2021) in a single city study (Adeyemi et al. 2021). Trace elements constituted 20% of the total $PM_{2.5}$ load. The reliance of metal trace elements only during receptor source apportionment could result in overestimation. Biomass burning is a major source of $PM_{2.5}$ in European studies since strong policies for vehicular and industrial emissions are well implemented. By contrast, in Pretoria, industrial, mining and resuspended dust matrix sources were ubiquitous and biomass burning was seasonal. The sensitivity analysis for the adjusted Ni marginally confirmed the allocation of factors since the majority of Ni was allocated to the industrial source in both instances. Secondary compounds including SO_2 and NO_2 were not analyzed. Allocating secondary S products as a source to a factor was a thus a tentative allocation. The S–Pb combination due to combustion was a more reliable tracer for coal in this study. Pb was below the LoD in an all-year mean but above the LoD during the winter months. A winter season analysis was beneficial since coal burning could be delineated from biofuel burning. It is recommended that parallel studies, and an analysis of local soils complement the source apportionment study.

Ethics Approval

The Research Ethics Committee, Faculty of Health Sciences, University of Pretoria, approved ethics approval (reference 300/2020) in 2020.

Author Contribution

JW conceptualized the research. The research design, methodology, analysis of findings and writing of the manuscript were all the responsibility of CHD. The statistical analyses were carried out by CHD. JB was responsible for the chemical analysis. PM did the data management of the trace elements results prior to statistical analysis and PMF application. All authors read and approved the final manuscript.

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Disclosure Statement

The authors declare that they have no conflict of interest.

Data Availability

The datasets generated and/or analyzed during this study are not publicly available due to university's intellectual property right but are available from the corresponding author on reasonable request.

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