

Article

Temporal Variability and Evolution of PM_{2.5} Sources in an Urban Environment: A PIXE–PMF Study in Vilnius, Lithuania

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Abstract

This study investigates the long-term variability and evolution of particulate matter with an aerodynamic diameter of $<2.5\ \mu\text{m}$ (PM_{2.5}) sources in Vilnius, Lithuania, during the period 2013–2021. Source apportionment was performed using Positive Matrix Factorization (PMF) based on elemental composition data obtained through particle-induced X-ray emission (PIXE) analysis. The results revealed substantial year-to-year variability in the chemical profiles of the identified sources. Crustal/mineral dust was characterized by high contributions of lithogenic elements, including Si, Ca, Ti, and Fe, while soil dust exhibited elevated proportions of Al, Ca, and Fe. Traffic non-exhaust emissions were marked by elevated Cu, Zn, and Pb in 2013–2015, whereas exhaust emissions in 2019–2021 were characterized by sulfur-rich aerosols. Industrial and oil combustion sources showed enhanced contributions of Ni, V, and Cr, particularly in 2016, 2018, and 2020. Biomass/wood burning represented a major seasonal source, reaching peak intensity in 2018–2019 and characterized by elevated K and Zn contributions. A notable long-term trend was the increasing importance of soil-derived particles, as reflected by Al contributions rising to 91.2% by 2021. Overall, the major PM_{2.5} source categories remained relatively stable, while their chemical fingerprints and relative importance exhibited substantial temporal variability.

Keywords: PM_{2.5}; source apportionment; PMF; PIXE; urban air quality; long-term trends

1. Introduction

1.1. PM_{2.5} Pollution

Air pollution remains one of the leading environmental risk factors for premature mortality worldwide [1]. Despite decades of research and regulatory efforts, air quality in many regions remains a critical concern (Figure 1). This analysis highlights the complex interplay of multiple emission sources contributing to atmospheric pollution. According to the World Health Organization (WHO), approximately 99% of the global population is exposed to ambient air pollution levels exceeding the WHO Air Quality Guideline value of $5\ \mu\text{g m}^{-3}$, with the highest pollutant concentrations and associated health risks occurring in low- and middle-income countries [2]. To promote progressive air quality improvement in regions with persistently elevated concentrations of particulate matter with an aerodynamic diameter less than $2.5\ \mu\text{m}$ (PM_{2.5}), the WHO has defined four interim

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targets at 35, 25, 15, and 10 $\mu\text{g m}^{-3}$, providing a stepwise pathway toward the recommended annual guideline value of 5 $\mu\text{g m}^{-3}$. Despite this framework, approximately 36% of the global population remains exposed to $\text{PM}_{2.5}$ levels exceeding the least stringent interim target (35 $\mu\text{g m}^{-3}$), while fewer than 1% of people worldwide currently live in areas where the WHO annual guideline level of 5 $\mu\text{g m}^{-3}$ is achieved [3].

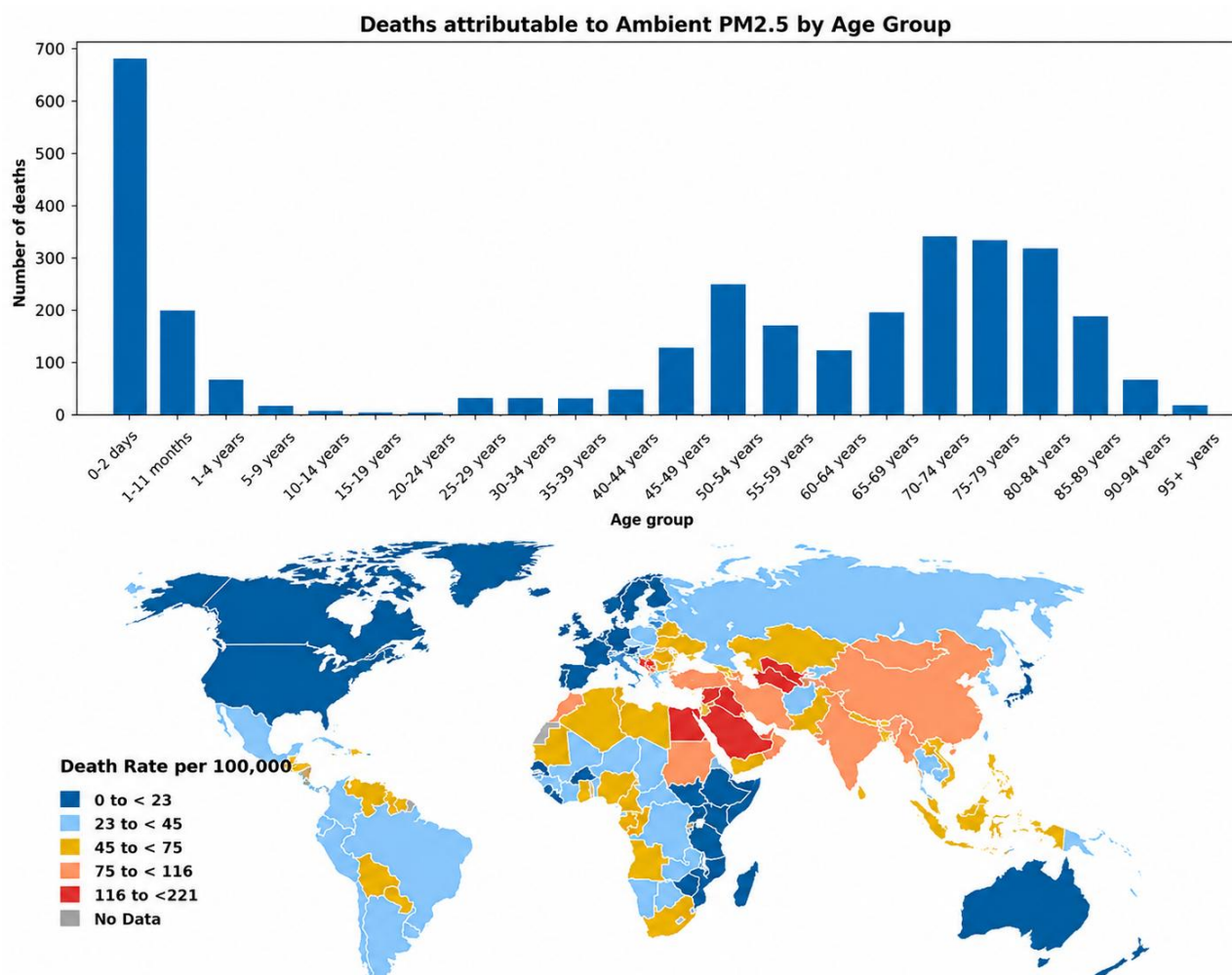


Figure 1. Distribution of deaths in 2023 attributable to ambient $\text{PM}_{2.5}$ and household air pollution, by age, and global distribution of deaths attributable to ambient $\text{PM}_{2.5}$ exposure by country in 2023 per 100,000 population [3].

Air pollution represents a major global environmental challenge and is associated with substantial mortality and morbidity. The highest mortality rates attributable to air pollution (75–221 deaths per 100,000 population) are observed in regions with elevated air pollution levels, particularly in South Asia, the Middle East, and parts of North and West Africa [3].

Notably, countries such as India, China, and several Middle Eastern nations fall within the highest mortality categories, reflecting both high $\text{PM}_{2.5}$ exposure and population vulnerability (Figure 1). Particulate matter, especially $\text{PM}_{2.5}$, is recognized as a critical pollutant due to its ability to penetrate deep into the respiratory system and potentially enter the bloodstream. Fine particulate matter originates from natural sources like fugitive dust but is also heavily emitted by human activities [4]. Air pollution not only leads to respiratory diseases [5,6] but also has a significant adverse effect on the cardiovascular system [7–11]. The WHO notes that deaths from poor air quality are increasing, but in

2023, it lowered the threshold for air pollution in crowded areas. Overall, noncommunicable diseases (NCDs) account for approximately 6.8 million deaths (~86%) of the total mortality burden attributable to air pollution, underscoring its dominant role in the global NCD burden as reported by the WHO and the Global Burden of Disease framework [3]. Air pollution was responsible for 7.9 million deaths in 2023, with the largest health impacts seen in low- and middle-income countries, where 95% of air pollution-attributable deaths in adults over the age of 60 are due to NCDs like chronic obstructive pulmonary disease, dementia, diabetes, and cardiovascular and lung disease [3].

1.2. PMF Analysis of Pollution Sources

Various receptor modelling approaches, including Positive Matrix Factorization (PMF), Principal Component Analysis (PCA), and Monte Carlo simulations, are widely employed for source apportionment of atmospheric PM and for assessing associated environmental and health risks [12]. However, these PMF outcomes have exhibited inconsistencies, particularly regarding the specific sources identified and their relative contributions to PM mass concentrations, leading to significant discrepancies across studies [13]. Source profiles vary among countries and environments; therefore, a nuanced understanding of local emission profiles is crucial for effective mitigation strategies [14]. Research across various megacities highlights distinct regional source profiles. In practice, PMF studies on PM_{2.5} and PM₁₀ most often resolve a recurring set of source categories: secondary inorganic aerosol, traffic, dust/crustal material, industry/metallurgy, biomass burning, coal or oil combustion, and, in some environments, sea salt, shipping, and cooking-related aerosol [4,5,15]

Although the PMF model is a well-established method for PM_{2.5} source apportionment and has been widely applied in previous studies, many investigations have relied on relatively short-term datasets. The novelty of the present study lies in the analysis of long-term PM_{2.5} measurements collected over eight years (2013–2016 and 2018–2021), enabling more robust identification of source-related factors and a better understanding of their temporal variability. This long-term approach provides deeper insight into the dominant sources influencing PM_{2.5} concentrations and their evolution over time. In Vilnius, annual mean PM_{2.5} concentrations in 2022 ranged from 6.1 to 10.8 $\mu\text{g m}^{-3}$ [16], indicating relatively moderate pollution levels compared with major European urban hotspots, where annual mean concentrations can exceed 25 $\mu\text{g m}^{-3}$. Similar PM_{2.5} levels were observed at other Lithuanian urban and regional background stations, with annual means generally between 7.2 and 13.3 $\mu\text{g m}^{-3}$. Although no exceedances of the European Union annual limit value for PM_{2.5} (20 $\mu\text{g m}^{-3}$) were recorded, PM_{2.5} concentrations at all monitoring locations remained above the WHO annual guideline value of 5 $\mu\text{g m}^{-3}$, indicating persistent population exposure to elevated PM levels. Since 2013, when annual PM_{2.5} levels in Vilnius reached approximately 23 $\mu\text{g m}^{-3}$, a pronounced long-term decline has been observed. This substantial reduction highlights the effectiveness of emission control measures, while the continued exceedance of the WHO guideline values underscores the need for a detailed investigation of PM source contributions and their temporal dynamics [2].

2. Materials and Methods

2.1. Site Description

Data were collected in the urban area of Vilnius, as shown in Figure 2.

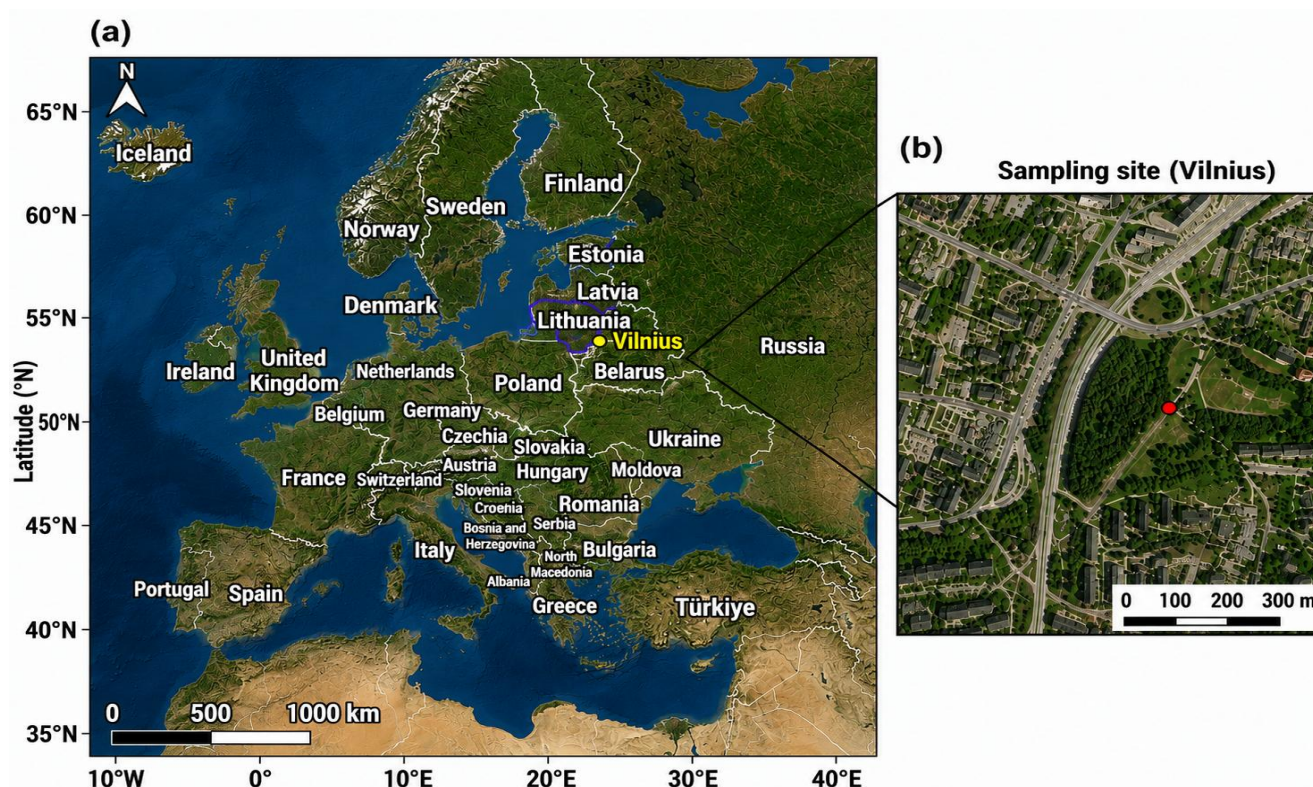


Figure 2. Study area location: (a) Geographic position of Lithuania within Europe, shown using a Lambert Conformal Conic projection. The red marker denotes Vilnius (b). High-resolution aerial view of the PM_{2.5} sampling site in Vilnius.

The measurement location (54.685987° N, 25.210866° E), indicated by the red marker, is situated within a vegetated park area characterized by tree cover and open grassland. The distance from this location to the nearest busy road (Laisvės pr.) is 190 m. The nearest park, Pasakų Parkas, is located approximately 500 m from the sampling site and is dominated by coniferous trees. Vingis Park is located approximately 600 m from the sampling site. The city center is located approximately 5 km away; therefore, the sampling location is likely influenced by PM_{2.5} originating from urban emissions.

2.2. Sampling and Analysis

A total of 485 PM_{2.5} samples were collected on polytetrafluoroethylene (PTFE) filters and analyzed using broad-beam particle-induced X-ray emission (PIXE) with 1.9 MeV protons. PIXE is a rapid ion beam analytical technique capable of multi-elemental analysis with detection limits in the ppm range [17]. Figure 3 presents a schematic diagram of the vacuum chamber employed for PIXE measurements. A proton beam, accelerated using a Tandatron 4110A particle accelerator (General Ionix Corp., Boston, MA, USA) and collimated to a diameter of 5 mm, was used to irradiate the samples. A single spectrum was collected for each PM sample, and elemental concentrations at the ppm levels were determined assuming homogeneous deposition of PM on the filters. X-ray spectra were recorded using a CANBERRA model SL30165 Si(Li) detector (Mirion Technologies, Inc., Atlanta, GA, USA) with 165 eV energy resolution at 5.894 keV and a Canberra DSA1000 Multichannel Analyzer (MCA) (Mirion Technologies, Inc., Atlanta, GA, USA). Data acquisition was performed with Genie 2000 software version 4.0.

The distance between the sample and the detector was 59.5 mm (8.5 msr). A total charge of 0.9 ± 0.07 μ C was collected from each sample during a 600 s acquisition period. Prior to each measurement, the proton beam fluence was determined using a Faraday cup.

Furthermore, because the proton beam passes through the PM filter during analysis, a sample-specific relative fluence value was used to compensate for beam current fluctuations.

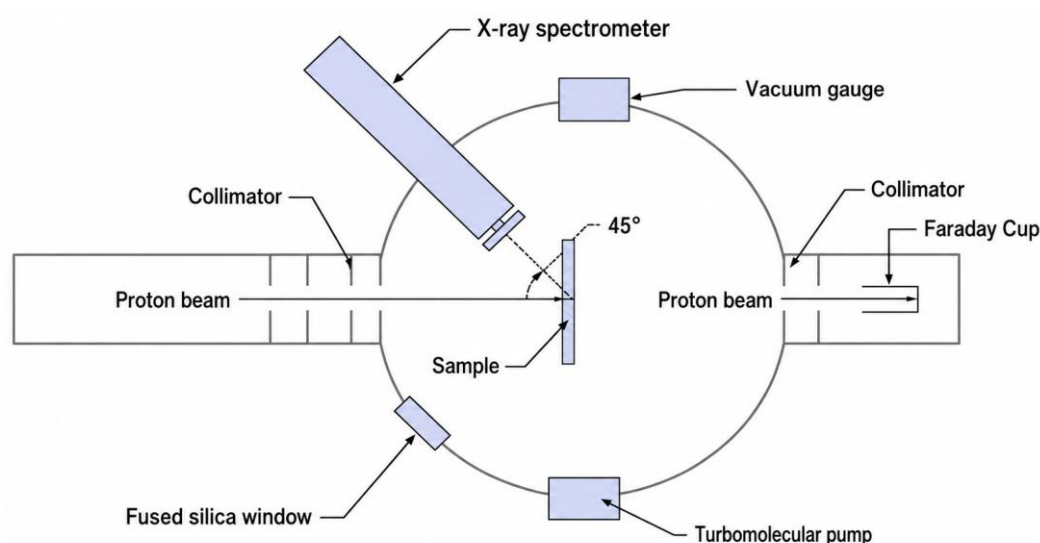


Figure 3. Schematic diagram of the analytical chamber used for PIXE measurements.

X-ray spectra were fitted using the GupixWin software version V package for quantitative elemental analysis [18], using the default uncertainty values: 1% of absorber thickness, 1% of the area of any overlapping peaks, etc. The standard reference material of the National Institute of Standards and Technology (NIST), NIST-2783 (airborne PM_{2.5} deposited on a polycarbonate filter), was used to calibrate X-ray yields to ppm concentrations [19]. The correlation between the certified NIST values and those determined using our setup is depicted in Figure 4.

The filters were analyzed in batches of four, and each registered yield underwent blank correction, subtracting elemental areal densities (ng/cm²):

$$CA = C_{Aero} - C_{blank} \quad (1)$$

LOD is estimated for each particular element in each spectrum. It is calculated on the basis of 3 standard deviations of the background areas over a 1 FWHM. In ppm, the LOD is extracted using the following:

$$LOD(\text{ppm}) = \frac{(3\sqrt{B})}{((Q \times H \times Y \times \varepsilon \times T))} \quad (2)$$

where B —background area in one FWHM region, Q —charge in μC , H —instrumental constant for conversion of area to concentration (contains the solid angle), Y —theoretical yield of X-rays, ε —relative detector efficiency, and T —transmission of X-ray through absorber.

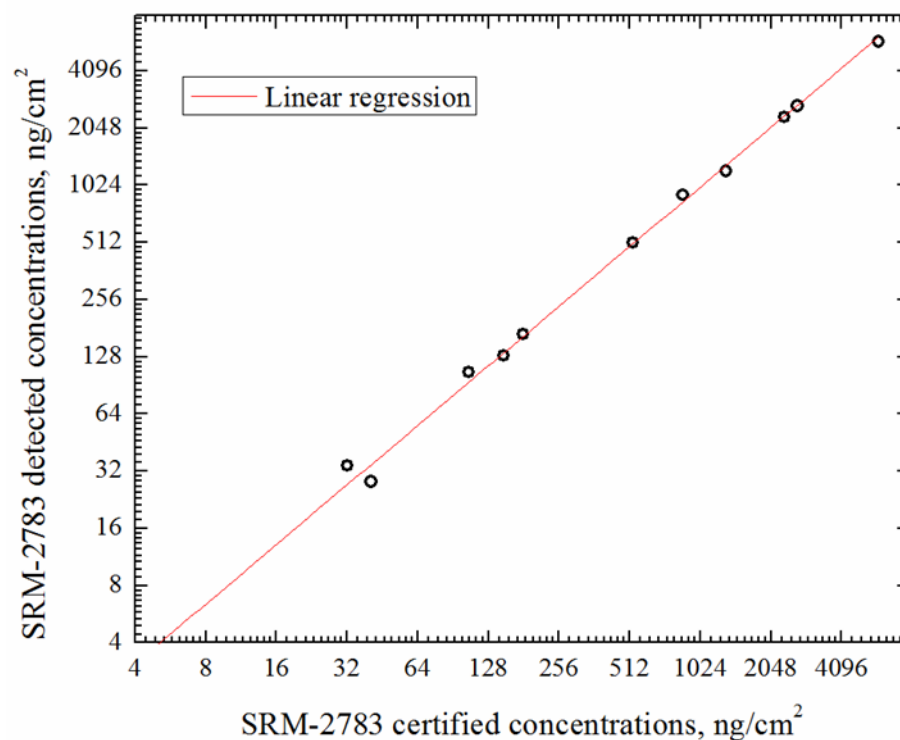


Figure 4. Concentration of detected certified elements.

2.3. Source Stability Index Analysis

To quantify the temporal stability of PMF-resolved source fingerprints, a Source Stability Index (SSI) was calculated for each source category over the period 2013–2021. For each year, PMF factor profiles were expressed as normalized elemental contributions (%), ensuring that comparisons reflected chemical composition rather than absolute concentration levels. SSI was computed using pairwise similarity between source fingerprints of the same source in consecutive years, applying cosine similarity to assess the degree of overlap between elemental vectors. For each source, SSI values were averaged across all available year-to-year comparisons, and the resulting mean values were used to classify sources into stability categories (moderate, high, and very high). Sources that appeared only in selected years (e.g., industrial emissions and road salt) were evaluated only for the years in which the factor was resolved.

2.4. Matching of PMF Factors Between Years

Because PMF analyses were performed independently for each year, factor numbering and factor structure were not expected to remain identical across annual solutions. Therefore, factors were matched between years based on the similarity of their dominant elemental fingerprints and established source tracers rather than on factor number or factor order. Source identification relied on the combined occurrence of multiple tracer elements and the overall factor profile. For example, factors enriched in Cu, Zn, Pb, P, and Fe were associated with non-exhaust traffic emissions, whereas factors characterized by elevated S together with Pb, Cr, and Zn were interpreted as traffic-related combustion or S-rich traffic-influenced aerosols. Since PMF may resolve source splitting or merging differently among years, temporal comparisons were conducted at the level of broader source families (e.g., traffic, crustal dust, soil dust, biomass burning, industrial emissions, and road salt aerosol) rather than through direct one-to-one comparison of individual PMF factors.

2.5. Source Occurrence Frequency and Turnover Analysis

Source occurrence frequency and turnover were assessed to distinguish persistent sources from episodic or seasonal contributors. For each year, the presence of a source was determined based on PMF results and the identification of a chemically coherent factor characterized by established diagnostic tracers. A source was considered present each year if its dominant tracer elements showed clear and interpretable contributions within a resolved PMF factor. The total number of years in which each source appeared was then counted over the 2013–2021 period. Based on their frequency of occurrence, sources were classified as persistent (present in all years), seasonal/variable (present in most but not all years), or episodic (present intermittently). This approach provides a qualitative but systematic assessment of source turnover and complements the quantitative SSI analysis.

2.6. Hierarchical Clustering

For each source family (e.g., crustal dust, soil dust, traffic non-exhaust, traffic-related S-rich aerosol, biomass burning, industrial/oil combustion, and road salt), a representative centroid fingerprint was calculated as the mean of normalized elemental contributions (%) across all years in which the source was resolved. This approach reduces the influence of year-specific PMF factor splitting or merging and emphasizes chemically coherent source characteristics. Hierarchical clustering was performed using Ward's minimum variance method with Euclidean distance, applied to the centroid fingerprints expressed in a common elemental space (Si, Al, Ca, Fe, Ti, Cu, Zn, Pb, S, K, Ni, V, Cl, Na). The resulting dendrogram was used to identify clusters corresponding to major source families and to assess inter-source similarity. The resulting dendrogram was used to identify clusters corresponding to major source families and to assess inter-source similarity.

3. Results

3.1. Sampling

PM_{2.5} samples were analyzed by means of PIXE to quantify trace element concentrations used as input for the model EPA PMF 5.0 [20]. The dataset included key source tracers such as lithogenic elements (Si, Al, Ca, Ti, Fe), combustion markers (S, K, Zn), industrial metals (Ni, V, Cr, Mn), and traffic-related elements (Cu, Zn, Pb). These elements accounted for a substantial portion of PM_{2.5} mass, enabling robust source attribution. PMF solutions with 4–6 factors were tested, and the five-factor solution was selected as the most interpretable and statistically satisfactory, with $Q_{\text{true}}/Q_{\text{exp}} = 3.3$. The resulting factor fingerprints were used to identify source categories based on characteristic elemental enrichments. The results highlight a stable but dynamically modulated mixture of emission sources, with robust tracer-based evidence supporting the interpretation of long-term trends. Although absolute mass contributions were not evaluated, the relative elemental fingerprints allow quantitative assessment of changes in dominant chemical signatures between 2013 and 2021. For the purpose of long-term interpretation, annual PMF factors were grouped into recurring source families according to their characteristic elemental fingerprints. Consequently, the source evolution discussed below refers to changes in recurring source families and their chemical signatures rather than direct comparison of individual PMF factor numbers between years.

The PMF-resolved source categories and their predominant elemental tracers for each year are summarized in Table 1. Across the study period, five recurring source families were consistently identified: crustal/soil dust, traffic-related emissions (exhaust and non-exhaust), industrial/oil combustion, biomass burning, and chloride-rich aerosol associated with road salt. The correspondence between annual PMF factors and the source families used in the long-term analysis is provided in Supplementary Table S1.

Table 1. PMF-resolved factors, source-family assignments, and predominant elemental tracers by year (2013–2021).

Year	Factor 1 (Pre-dominant Elements)	Factor 2 (Pre-dominant Elements)	Factor 3 (Pre-dominant Elements)	Factor 4 (Pre-dominant Elements)	Factor 5 (Pre-dominant Elements)
2013	Crustal (Soil) (Si, Ca, Ti, Fe)	Traffic-related S-rich anthropogenic aerosol (S, Cr)	Industrial emissions (Mn, Fe, Zn)	Traffic dust (Cu, Zn, Pb)	Wood/biomass burning (K, Zn)
2014	Crustal (Soil) (Al, Si, Ca, Ti, Fe)	Traffic dust (Cu, Pb, Zn)	Ca-rich mineral dust (Ca, Fe)	Traffic-related S-rich anthropogenic aerosol (Zn, S)	Traffic dust (Cu, Pb)
2015	Traffic dust (Cu, Zn, Pb)	Vehicle emissions/secondary sulfate (S)	Crustal (Soil) (Si, Ca, Fe)	Chloride-rich aerosol/road salt (Cl, Na)	Soil dust (Al)
2016	Wood/biomass burning (K, Zn)	Industrial emissions (Zn, Ni)	Soil dust (Al, Mg, Ca)	Crustal (Soil) (Al, Ca, Ti, Fe)	Traffic-related S-rich aerosol (S, Cr)
2017	Not enough data	Not enough data	Not enough data	Not enough data	Not enough data
2018	Industrial/oil combustion (Ni, Cr, V)	Traffic non-exhaust/lubricant-related (P, Cu)	Crustal (Soil) (Al, Si, Ca, Ti, Fe)	Wood/biomass burning (K, Zn)	Traffic dust (Cu, Zn)
2019	Vehicle emissions/mixed traffic aerosol (S, Cu, Pb)	Wood/biomass burning (K, Zn)	Soil dust (Ca, Al, Mg, Fe)	Chloride-rich aerosol/road salt (Cl, Na)	Crustal (Soil) (Si, Ti, Fe)
2020	Traffic-related S-rich anthropogenic aerosol (S, Pb, Zn)	Wood/biomass burning (Zn, Ca, K)	Soil dust (Ca, Fe, Al)	Industrial/oil combustion (V, Ni)	Chloride-influenced crustal dust (Cl, Ti)
2021	Crustal (Soil) (Fe, Ca, Ti)	Industrial emissions (Zn, V, Cr)	Wood/biomass burning (K, Zn)	Vehicle emissions (Pb, S, Cu)	Soil dust (Al, Ca)

Annual PM_{2.5} concentrations exhibited pronounced interannual variability during the study period (2013–2021). Although PM_{2.5} measurements were available for 2017, the number of observations was insufficient to support robust PMF analysis; therefore, PM_{2.5} concentration data for 2017 are presented, whereas PMF results for this year are not discussed further (Figure 5). The highest annual mean concentration was observed in 2013 (19.09 µg m⁻³; *n* = 16), followed by 2014 and 2015, which showed similar annual means of 13.77 µg m⁻³ (*n* = 43) and 13.76 µg m⁻³ (*n* = 48), respectively. A marked decline was evident by 2016, when the annual mean decreased to 10.68 µg m⁻³ (*n* = 73), after which lower concentrations predominated. During the later period (2018–2021), annual mean PM_{2.5} concentrations ranged from 7.03 to 9.42 µg m⁻³, corresponding to a 51–61% reduction relative to the 2013 baseline. Mean concentrations were 8.67 µg m⁻³ in both 2018 (*n* = 69) and 2019 (*n* = 100), decreased to 7.38 µg m⁻³ in 2020 (*n* = 73), and increased slightly to 9.42 µg m⁻³ in 2021 (*n* = 72). Overall, the annual mean declined by approximately 51% between 2013 and

2021, corresponding to an average linear decrease of about $1.21 \mu\text{g m}^{-3}$ per year, or an average annual reduction rate of approximately 6% per year.

Median $\text{PM}_{2.5}$ concentrations followed a similar downward pattern, decreasing from $17.44 \mu\text{g m}^{-3}$ in 2013 to $7.84 \mu\text{g m}^{-3}$ in 2021, indicating a reduction of approximately 55%. Despite these substantial improvements, annual mean and median $\text{PM}_{2.5}$ concentrations remained above the WHO annual guideline value of $5 \mu\text{g m}^{-3}$ in all years with available data. Although the magnitude of exceedance decreased markedly over time, long-term $\text{PM}_{2.5}$ exposure levels did not reach the WHO guideline threshold during the study period.

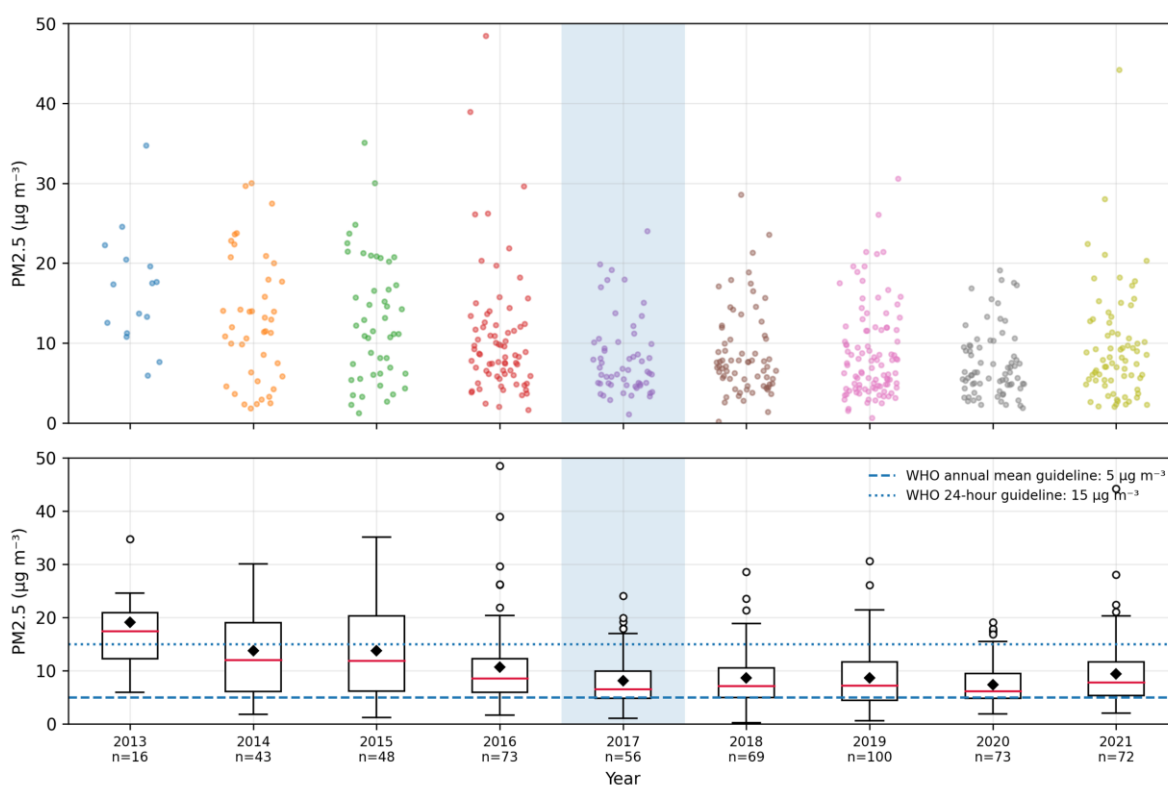


Figure 5. $\text{PM}_{2.5}$ time series (upper panel) and annual distributions (lower panel) for 2013–2021. Boxes show interquartile ranges, horizontal lines denote medians, diamonds indicate annual means, and numbers below boxes represent sample sizes. The dashed horizontal line indicates the WHO annual mean $\text{PM}_{2.5}$ guideline ($5 \mu\text{g m}^{-3}$). The dotted line represents the WHO 24 h guideline ($15 \mu\text{g m}^{-3}$) and is shown for contextual comparison only.

3.2. Aerosol $\text{PM}_{2.5}$ and Trace Element Concentration Levels and Input Data for PMF

Over the period 2013–2021 (with 2017 excluded due to insufficient data for PMF), a total of 485 $\text{PM}_{2.5}$ filter samples collected at the urban background site in Vilnius were chemically characterized by means of PIXE and used as input to the PMF model. The analyzed elemental concentrations (e.g., Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Na, Mg, P) accounted for a substantial fraction of the $\text{PM}_{2.5}$ mass, ensuring that the main primary and secondary sources were captured. To explore the most appropriate source structure, PMF solutions with 4 to 6 factors were tested. The choice of the final solution was based on the physical interpretability of factor profiles (elemental fingerprints), the temporal behavior of factor contributions, the distribution of residuals, and the goodness-of-fit parameter Q , comparing theoretical (Q_{exp}) and calculated (Q_{true}) values. The five-factor solution was selected as the best compromise between statistical performance and interpretability. The Q ratio of 3.3 indicated an acceptable fit between observed and modelled concentrations. The factor fingerprints, illustrating the relative contributions of

each element to the resolved sources, are shown in Figures 6–13. These figures were used to identify diagnostic tracers and to attribute each factor to a specific emission source.

Across all analyzed years, the PMF analysis consistently resolved five factors that were attributed to recurrent source categories. These included crustal material, dominated by lithogenic elements such as Si, Al, Ca, Ti, and Fe; soil dust, characterized by elevated contributions of Al, Ca, Mg, and Fe and linked to mechanically disturbed or wind-eroded soils; traffic-related emissions, which were subdivided into traffic-related S-rich aerosol (S, Pb, Cu, Cr, Zn, reflecting exhaust emissions, lubricant contributions, and secondary sulfate formation) and traffic non-exhaust dust (Cu, Zn, Pb, associated with brake and tire wear and road dust resuspension); industrial emissions, identified by Ni, V, Cr, Fe, Mn, and Zn, indicative of industrial combustion and metallurgical activities; and biomass/wood burning, marked by K together with Zn, associated with residential heating.

A key finding of this study is the persistent dominance of crustal and soil-related source fingerprints, which were present in every year and consistently exhibited very high contributions of lithogenic tracers. For example, Si reached 100% in the crustal factor in both 2013 and 2019, while Ca exceeded 68–76% in multiple years (2013, 2015, 2016, and 2018). The influence of soil-related tracers increased over time, culminating in exceptionally high Al contributions in later years—82% in 2015, 46.6% in 2020, and 91.2% in 2021—indicating an increasing representation of soil-related elemental tracers within the resolved PMF fingerprints in the urban aerosol. Similar trends have been reported across northern and central Europe, where climate-driven changes have amplified natural dust emissions in urban environments. While traffic-related emissions, particularly non-exhaust sources such as brake and tire wear, remained a stable background contributor throughout the study period, the growing prominence of soil and crustal dust indicates that natural and mechanically driven sources are becoming increasingly influential relative to exhaust emissions. These findings underscore the importance of considering soil and mineral dust processes alongside anthropogenic sources when assessing long-term trends in urban particulate matter.

Clear interannual differences in the intensity of PMF-resolved sources are highlighted in Table 2. Crustal mineral dust was the most persistent and dominant contributor, showing strong influence in all years, while soil dust increased in importance toward the later period, becoming a strong source in 2020–2021. Traffic-related emissions were present throughout the study, with non-exhaust sources more prominent in earlier years and combustion-related aerosol strengthening in later years. Industrial emissions appeared episodically, with pronounced contributions in 2016, 2018, and 2020, whereas biomass burning showed strong year-to-year variability, peaking during colder years. The road salt factor was confined mainly to winter-affected years, reflecting the seasonal impact of road de-icing practices on urban aerosol composition.

Table 2. Qualitative intensity of major PMF-resolved sources by year (the intensity scale provides a qualitative synthesis of PMF-resolved sources, where filled circles (●) indicate years with strong and chemically well-defined factor contributions, open circles (○) denote moderate presence or partial mixing, and dashes (–) indicate weak or absent sources).

Source/Year	2013	2014	2015	2016	2018	2019	2020	2021
Crustal mineral dust (Si-Ca-Ti-Fe)	●	●	●	●	●	●	●	●
Soil dust (Al-Ca-Mg-Fe)	○	○	●	○	○	○	●	●
Traffic non-exhaust (Cu-Zn-Pb)	●	●	●	○	○	●	○	○

Traffic-related S-rich aerosol (S–Pb–Cu–Zn)	○	○	○	○	○	●	●	●
Industrial/oil combustion (Ni–V–Cr)	○	○	–	●	●	–	●	○
Biomass/wood burning (K–Zn)	○	–	–	●	●	●	○	●
Road salt/chloride-rich aerosol Na–Cl)	–	–	●	–	–	●	●	–

Based on the dataset covering the period 2013–2021 (with 2017 excluded due to insufficient data for PMF), PMF was applied to identify the predominant sources of atmospheric particulate matter and their characteristic elemental tracers. Yearly PMF results obtained in 2013–2021 were systematically analyzed, and the results of this analysis are presented below, described in detail for each year. **2013:** The PMF analysis resolved five factors, which were attributed to specific emission sources based on their elemental composition and supported by earlier source apportionment research (Figure 6, Table 3).

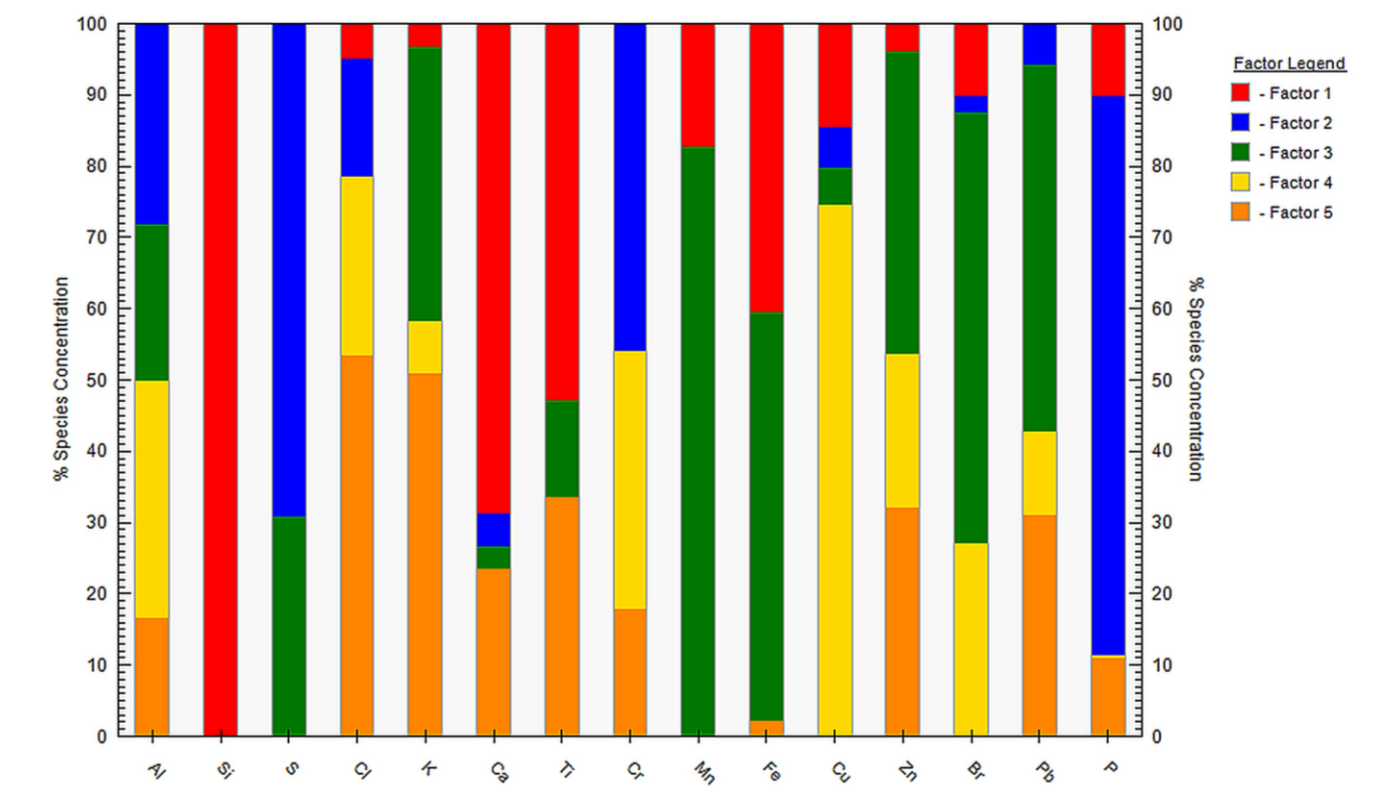


Figure 6. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2013.

Factor 1 was associated with crustal material (soil/mineral dust), as it exhibited strong loadings of lithogenic elements, including Si (100%), Ca (68.8%), Ti (52.8%), and Fe (40.6%).

Table 3. Factor profiles of aerosol sources based on elemental composition (%) for 2013.

Factors\Elements	Si	Ca	Ti	Fe	S	Cr	Mn	Zn	Cu	Pb	K
Silicate-rich soil/road mineral dust	100	68.8	52.8	40.6							
Traffic-related S-rich anthropogenic aerosol					69.2	45.9					
Metal-rich anthropogenic/industrial dust				57.3			82.7	42.5			
Traffic non-exhaust (brake/vehicle wear)								21.4	74.5	11.7	
Mixed crustal-combustion aerosol		23.5						32.2			50.9

This elemental pattern is characteristic of natural soil resuspension and mineral dust, commonly reported in urban environments [21]. Factor 2 was assigned to vehicular-related anthropogenic emissions, primarily characterized by elevated contributions of S (69.2%) and Cr (45.9%). The presence of sulfur indicates secondary sulfate formation from combustion-related emissions, while chromium suggests contributions from traffic-related wear and high-temperature combustion processes [22]. Factor 3 was interpreted as a metal-rich anthropogenic factor, marked by high contributions of Mn (82.7%), Fe (57.3%), and Zn (42.5%). This elemental combination is consistent with emissions from industrial activities and mechanically generated metal particles associated with urban infrastructure and fuel combustion processes [23].

Factor 4 was attributed to traffic-related dust from non-exhaust sources, dominated by Cu (74.5%) with additional contributions from Zn (21.4%) and Pb (11.7%). These elements are widely recognized indicators of brake abrasion, vehicle component wear, and resuspension of road dust [24]. Factor 5 was associated with combustion-related emissions influenced by biomass burning, as indicated by contributions of K (32.2%) together with Zn (23.5%). Potassium is a well-established tracer of biomass combustion, while zinc suggests mixing with urban anthropogenic sources, particularly during colder periods [20]. Notably, Zn and Pb exhibited partial overlap across Factors 3–5, indicating mixed contributions from industrial activities, non-exhaust traffic emissions, and combustion-related sources.

2014: The PMF analysis resolved five factors, which were attributed to specific emission sources based on their elemental composition and supported by earlier source apportionment studies (Figure 7, Table 4).

Factor 1 was associated with crustal material (soil/mineral dust), as it exhibited strong loadings of lithogenic elements, including Al (85.4%), Ca (14.5%), Ti (16.5%), and Si (48.4%).

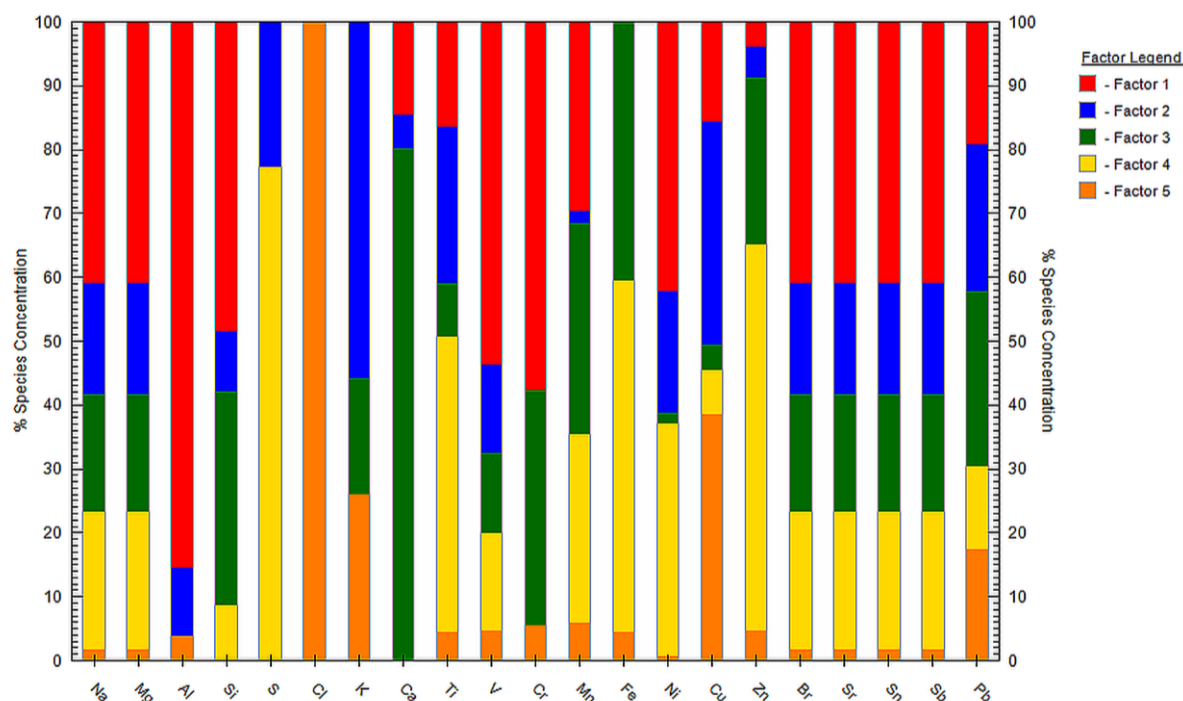


Figure 7. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2014.

Table 4. Factor profiles of aerosol sources based on elemental composition (%) for 2014.

Factors\Elements	Al	Ca	Ti	Fe	Zn	Cu	Pb	S	Si
Soil/road mineral dust (Al–Si rich)	85.4	14.5	16.5						48.4
Traffic non-exhaust (brake/vehicle wear)					4.8	34.9	23.1		
Ca-rich mineral dust		80.2		40.6					
Traffic-related S-rich anthropogenic aerosol (Zn–S rich)					60.5			77.2	
Traffic exhaust						38.7	17.5		

This elemental pattern is characteristic of natural soil resuspension and mineral dust, commonly observed in urban environments due to wind-driven resuspension and mechanical disturbance activity [24]. Factor 2 was attributed to traffic non-exhaust emissions, characterized by elevated contributions of Cu (34.9%), Pb (23.1%), and Zn (4.8%). These elements are well-established tracers of brake wear, tire wear, and vehicle-related mechanical abrasion, particularly in urban areas with significant traffic activity [24]. Factor 3 was identified as Ca-rich mineral dust, dominated by Ca (80.2%) and Fe (40.6%). This factor likely represents construction- and building-material-related dust, including cement, concrete, and plaster particles, as well as resuspended mineral material from paved and unpaved surfaces. Such sources are frequently resolved in urban PMF studies and may be enhanced by construction activities and indoor–outdoor resuspension processes. Factor 4 was interpreted as a sulfur-rich anthropogenic aerosol, marked by high contributions of Zn (60.5%) and S (77.2%). The coexistence of sulfur with zinc suggests a mixture of

secondary sulfate aerosol and Zn-rich urban emissions, likely reflecting the atmospheric aging processes and the influence of mixed combustion and industrial sources rather than a single primary emission source. Factor 5 was attributed to traffic-related dust from non-exhaust sources, dominated by Cu (38.7%) with a notable contribution from Pb (17.5%). This profile is consistent with brake abrasion, mechanical vehicle wear, and the resuspension of road dust, which are recognized as major contributors to urban particulate matter independent of exhaust emissions [24].

2015: The PMF analysis resolved five factors, which were attributed to specific emission sources based on their elemental composition and supported by earlier source apportionment studies (Figure 8, Table 5).

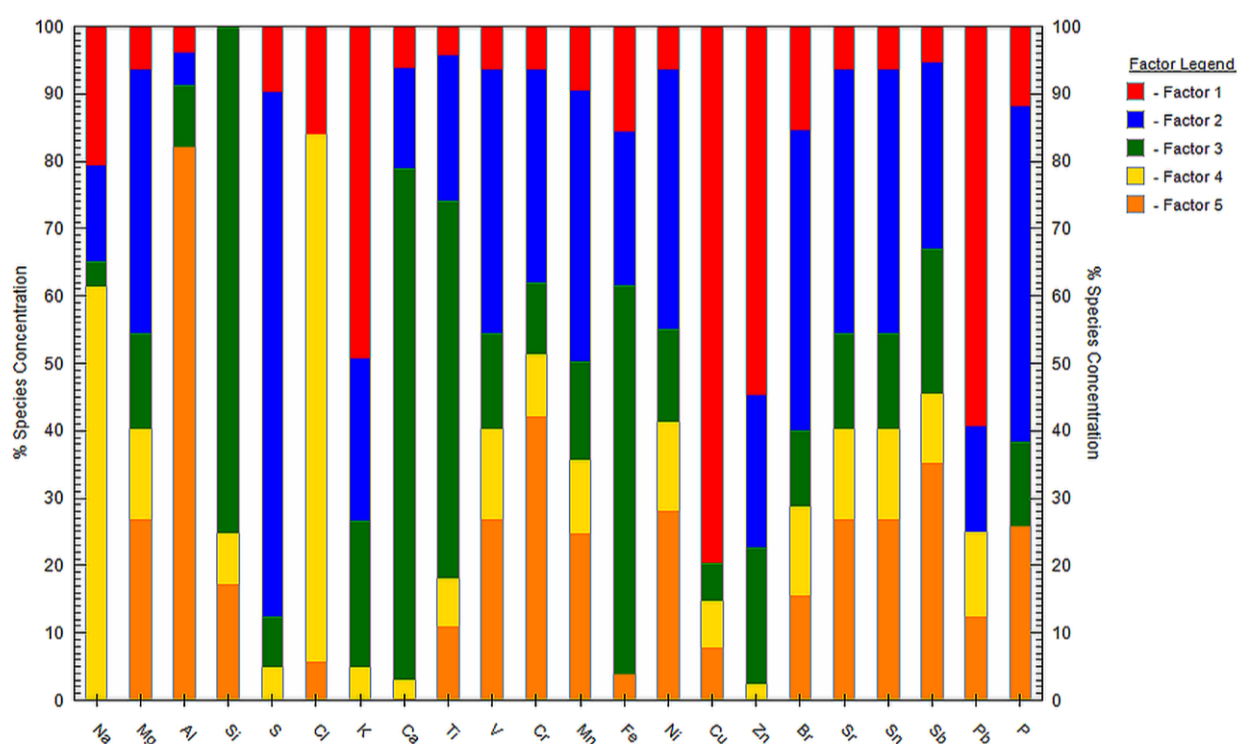


Figure 8. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2015.

Factor 1 was interpreted as traffic-related dust from non-exhaust sources, dominated by Cu (79.6%) and further influenced by Zn (54.7%) and Pb (59.2%).

Table 5. Factor profiles of aerosol sources based on elemental composition (%) for 2015.

Factors\Elements	Cu	Zn	Pb	S	Si	Ca	Fe	Cl	Na	Al
Traffic non-exhaust (brake/vehicle wear)	79.6	54.7	59.2							
Traffic-related S-rich anthropogenic aerosol				78						
Soil/road mineral dust					75.1	75.9	57.7			
Road salt/chloride-rich aerosol								78.3	61.3	
Crustal mineral dust (Al-rich)										82

These elements are well-recognized indicators of brake abrasion, tire wear, and the resuspension of road dust, reflecting a strong contribution from non-exhaust traffic emissions emissions [24]. Factor 2 was assigned to secondary anthropogenic aerosol, primarily characterized by a high contribution of S (78%). This profile is consistent with secondary sulfate formation resulting from atmospheric oxidation of S-containing emissions associated with fuel combustion and vehicular activity, indicating the influence of regionally transported aerosol [22]. Factor 3 was linked to crustal material (soil or mineral dust), as it exhibited strong loadings of lithogenic elements such as Si (75.1%), Ca (75.9%), and Fe (57.7%). This elemental composition confirms its origin from natural soil and road dust resuspension processes in the urban environment [25]. In contrast to 2013 and 2014, Ti was not a significant contributor to this factor in 2015, suggesting some variability in the mineral dust composition. Factor 4 was attributed to a chloride-rich aerosol, dominated by Cl (78.3%) and Na (61.3%). This combination is characteristic of salt-related particles and is most plausibly associated with road de-icing salt application and subsequent resuspension, particularly during colder periods. Factor 5 was identified as an Al-rich crustal dust factor, characterized by a very high contribution of Al (82%). Aluminum is a common constituent of mineral dust originating from soil resuspension, and its presence in urban air can be further enhanced by mechanical disturbance of surfaces and the mixing of natural crustal material with anthropogenic activities such as construction and traffic-related resuspension [26].

2016: The PMF analysis resolved five factors, which were attributed to specific emission sources based on their elemental composition and supported by earlier source apportionment research (Figure 9, Table 6).

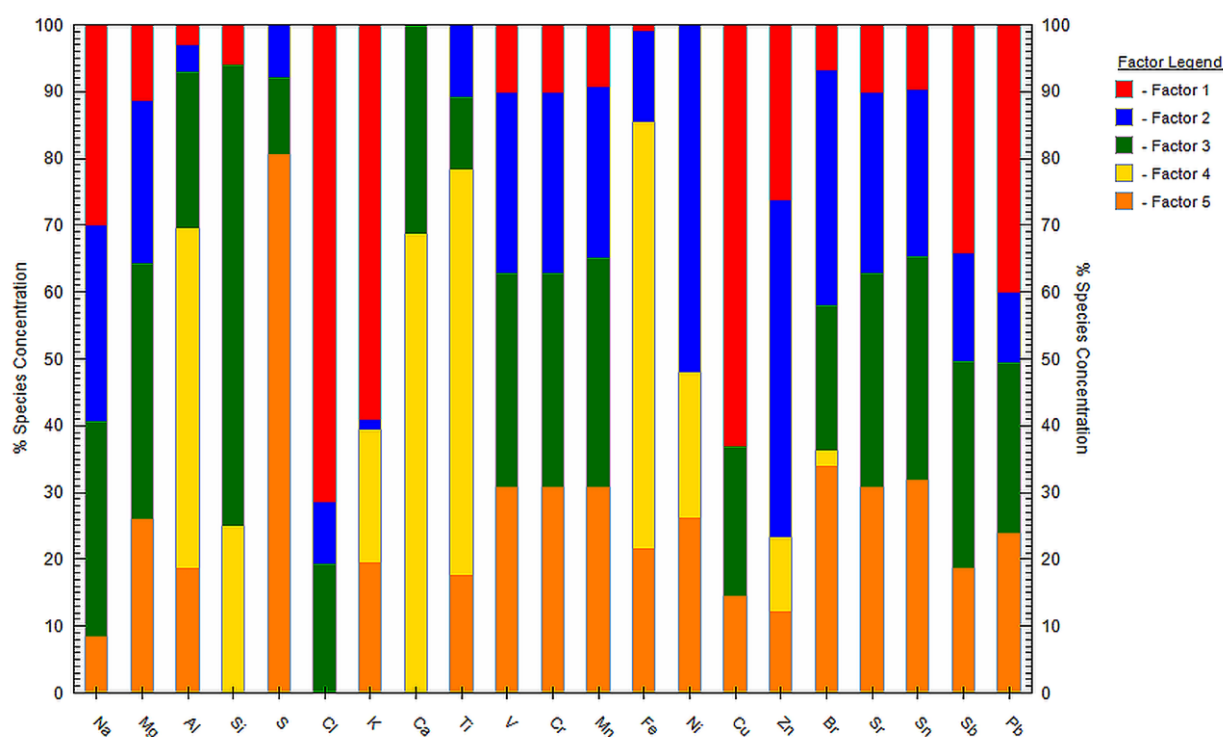


Figure 9. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2016.

Factor 1 was attributed to biomass combustion, as indicated by elevated contributions of K (59.2%) together with Zn (26.2%). Potassium is a well-established tracer of residential wood and biomass burning, while zinc reflects mixing with urban combustion-related emissions, particularly during colder periods [25].

Table 6. Factor profiles of aerosol sources based on elemental composition (%) for 2016.

Factors\Elements	K	Zn	Ni	Al	Mg	Ca	Ti	Fe	Pb	Cr	S
Biomass/solid-fuel combustion	59.2	26.2									
Metal-rich anthropogenic/industrial emissions		50.5	51.9								
Mineral dust (mixed crustal)				23.4	38.5	31.2					
Ca-rich mineral dust (construction/building materials)				50.9		68.8	60.7	63.9			
Traffic-related S-rich anthropogenic aerosol										30.9	80.7

Factor 2 was interpreted as a metal-rich anthropogenic factor, marked by high contributions of Zn (50.5%) and Ni (51.9%). This elemental combination is characteristic of industrial emissions and high-temperature combustion processes, including manufacturing activities and oil combustion, as reported in previous source apportionment [23]. Factor 3 was identified as mixed mineral dust, characterized by contributions of Al (23.4%), Ca (31.2%), and Mg (38.5%). This factor likely represents resuspended soil and road dust influenced by mechanical disturbance and wind erosion in the urban environment. Factor 4 was linked to crustal material (soil/mineral dust), as it exhibited strong loadings of lithogenic elements such as Al (50.9%), Ca (68.8%), Fe (63.9%), and Ti (60.7%). This elemental profile confirms its origin from natural soil resuspension and mineral dust, which is commonly observed in urban background aerosol [23,25]. Factor 5 was assigned to secondary anthropogenic aerosol associated with vehicular-related emissions, primarily characterized by S (80.7%) and Cr (30.9%). The dominance of sulfur indicates secondary sulfate formation from combustion emissions, while chromium suggests contributions from traffic-related wear and high-temperature processes, reflecting transport-related S-rich and mixed urban emissions [22].

2018: Factor 1 reflected industrial and fuel-combustion-related activity, marked by elevated contributions of Ni (55.8%), Cr (55.8%), and V (55.8%) (Figure 10, Table 7).

This elemental combination is characteristic of oil combustion and industrial high-temperature processes, commonly reported in source apportionment studies [23,26].

Factor 2 was attributed to traffic non-exhaust emissions with a lubricant-related signature, characterized by very high P (86.1%) and a notable contribution of Cu (12.7%). Phosphorus is widely associated with engine lubricant additives, while copper reflects vehicle wear processes, indicating a traffic-related mechanical source rather than agricultural activity. Factor 3 was linked to crustal material (soil/mineral dust), as it exhibited strong loadings of lithogenic elements such as Al (44.4%), Si (50.4%), Ca (76.6%), Fe (36.1%), and Ti (41.1%), confirming its origin from natural soil resuspension and mineral dust [15,25]. Factor 4 was attributed to biomass combustion, as evidenced by enrichment in K (67.4%) together with Zn (64.6%), both considered diagnostic tracers of residential

wood and biomass burning, particularly during colder periods [19]. Factor 5 was interpreted as traffic-related dust from non-exhaust sources, dominated by Cu (45.7%) and further influenced by Zn (13.3%). These elements are well-recognized indicators of brake abrasion, mechanical vehicle wear, and resuspension of road dust in urban environments [23].

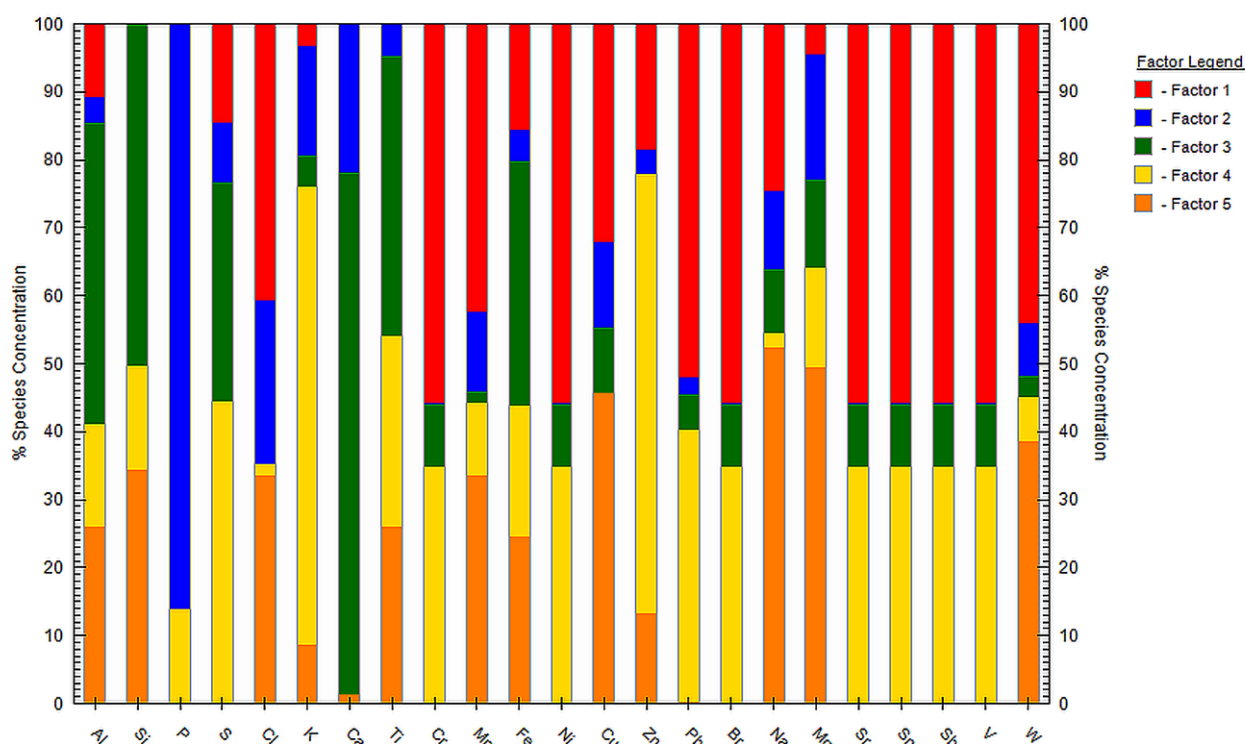


Figure 10. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2018.

Table 7. Factor profiles of aerosol sources based on elemental composition (%) for 2018.

Factors\Elements	Ni	Cr	V	P	Cu	Al	Si	Ca	Ti	Fe	K	Zn
Oil combustion/industrial combustion	55.8	55.8	55.8									
Traffic non-exhaust/lubricant-related emissions (P–Cu)				86.1	12.7							
Mineral dust (mixed crustal)						44.4	50.4	76.6	41.1	36.1		
Biomass burning											67.4	64.6
Traffic non-exhaust					45.7							13.3

2019: Factor 1 was attributed to traffic-related anthropogenic emissions, primarily characterized by elevated contributions of S (61.9%), Cu (49.7%), and Pb (30.7%) (Figure 11, Table 8).

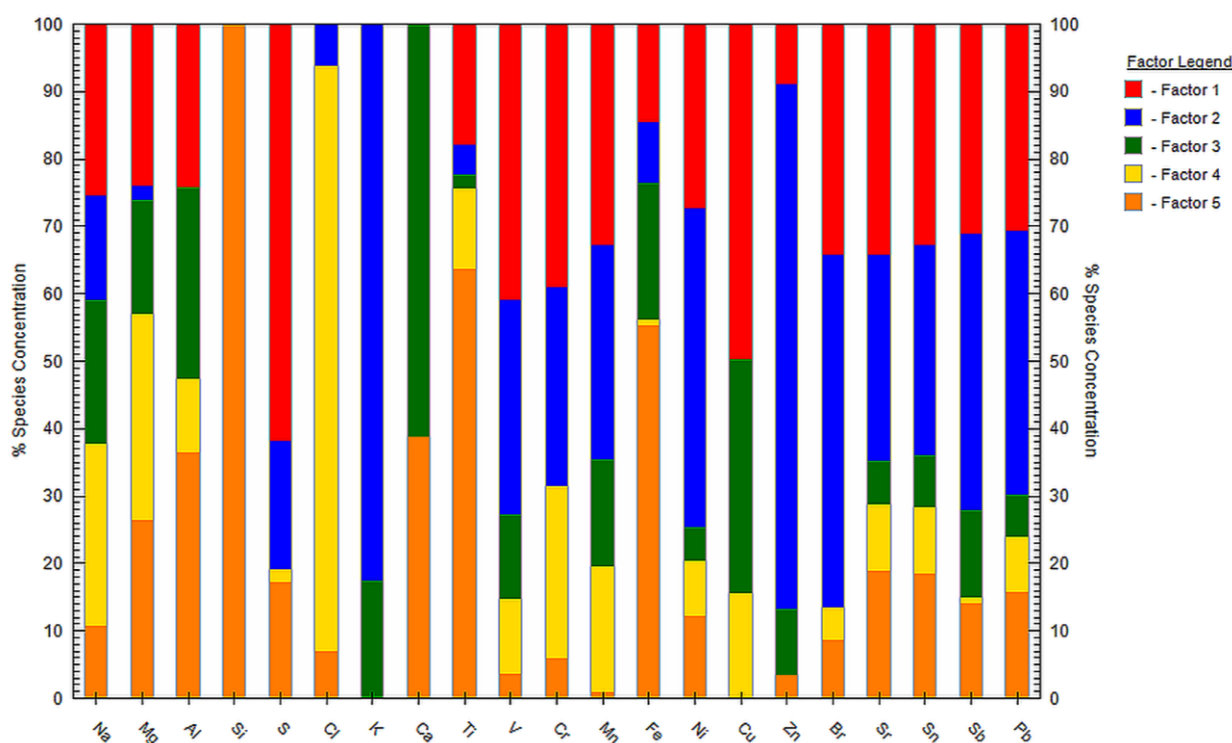


Figure 11. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2019.

The dominance of sulfur indicates secondary sulfate formation from combustion emissions, while copper and lead suggest contributions from traffic-related processes, reflecting a mixture of exhaust and non-exhaust vehicular influences [21].

Table 8. Factor profiles of aerosol sources based on elemental composition (%) for 2019.

Factors\Elements	S	Cu	Pb	K	Zn	Ca	Al	Mg	Fe	Cl	Na	Si	Ti
Traffic exhaust	61.9	49.7	30.7										
Biomass burning				82.5	77.8								
Ca-rich mineral dust						61.2	28.4	17.0	20.3				
Road salt/chloride-rich aerosol										86.9	27.1		
Silicate-rich soil/road dust (mineral crustal)									55.4			100.0	63.7

Factor 2 was assigned to biomass combustion, as evidenced by strong enrichment in K (82.5%) and Zn (77.8%), both of which are widely recognized as diagnostic tracers of residential wood and biomass burning, particularly during colder periods [24]. Factor 3 was identified as Ca-rich mineral dust, characterized by notable contributions of Ca (61.2%), together with Al (28.4%), Mg (17.0%), and Fe (20.3%). This elemental composition is consistent with resuspended mineral material, including soil particles and building-related dust, influenced by mechanical disturbance and wind-driven resuspension. Factor 4 was attributed to road de-icing salt and subsequent resuspension, dominated by Cl (86.9%) and Na (27.1%). This factor reflects the influence of chloride-rich salt aerosols, which are typical of urban environments during winter conditions. Factor 5 was linked to silicate-rich soil and road dust, as it exhibited strong loadings of lithogenic elements such as Si

(100.0%), Ti (63.7%), and Fe (55.4%), confirming its origin from natural soil resuspension and mineral dust [15,25].

2020: Factor 1 was attributed to traffic-related anthropogenic emissions, primarily characterized by elevated contributions of S (48.1%), Pb (75.6%), and Zn (23.9%) (Figure 12, Table 9).

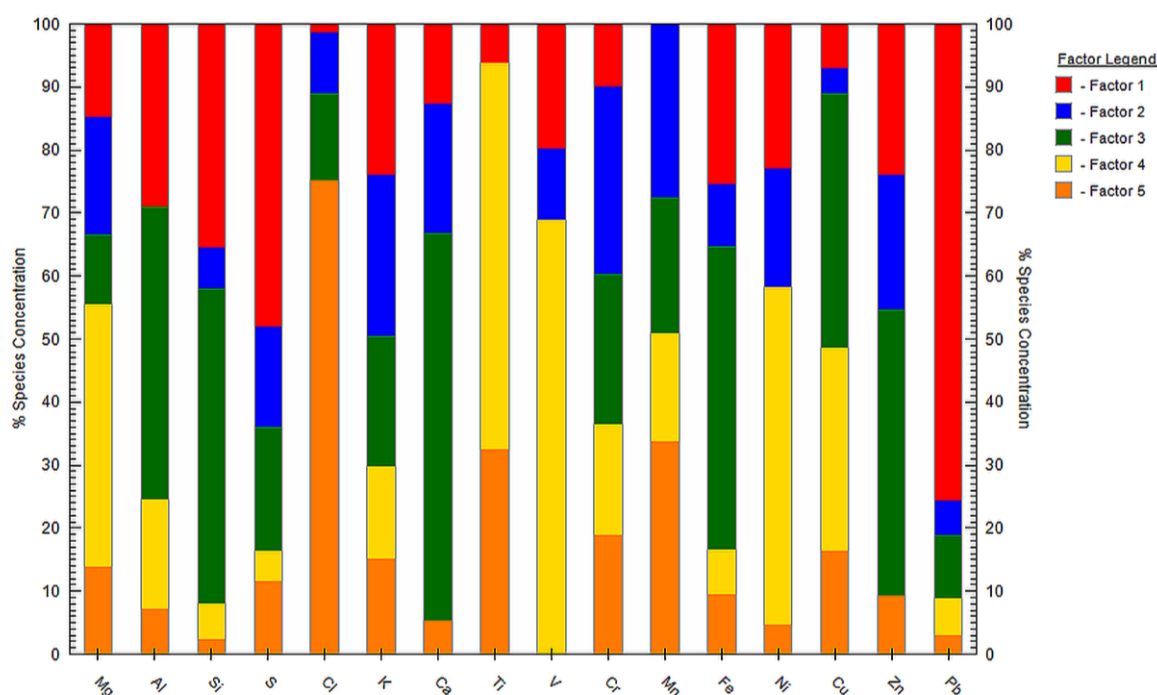


Figure 12. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2020.

The dominance of sulfur indicates secondary sulfate formation from combustion emissions, while lead and zinc reflect mixed influences from vehicular exhaust and traffic-related wear processes [21].

Table 9. Factor profiles of aerosol sources based on elemental composition (%) for 2020.

Factors\Elements	S	Pb	Zn	Ca	K	Fe	Al	V	Ni	Cl	Ti
Traffic exhaust	48.1	75.6	23.9								
Mixed combustion/biomass-influenced aerosol			21.4	20.6	25.5						
Ca-rich mineral dust				61.4		48.1	46.6				
Oil combustion								69.0	53.6		
Road salt										75.2	32.5

Factor 2 was assigned to biomass combustion, as indicated by contributions of K (25.5%), together with Zn (21.4%) and Ca (20.6%). Potassium is a widely recognized tracer of residential wood and biomass burning, while zinc and calcium suggest mixing with urban background aerosol, particularly during colder periods [24]. Factor 3 was identified as Ca-rich mineral dust, characterized by elevated contributions of Ca (61.4%), Al (46.6%), and Fe (48.1%). This elemental composition is consistent with resuspended mineral material, including soil- and construction-related dust, influenced by mechanical disturbance and wind-driven resuspension [25]. Factor 4 reflected industrial and fuel-combustion-

related emissions, marked by high contributions of V (69.0%) and Ni (53.6%). This elemental pairing is a well-established tracer of oil combustion and industrial fuel use, commonly reported in urban and regional source apportionment [15,25]. Factor 5 was attributed to chloride-rich mineral aerosol, dominated by Cl (75.2%) with a contribution from Ti (32.5%). This factor likely represents salt-influenced crustal particles, such as resuspended road de-icing salt mixed with mineral dust, rather than a purely natural soil source [15,25].

2021: Factor 1 was linked to crustal material (soil or mineral dust), as it showed strong loadings of lithogenic elements such as Fe (65.0%), Ca (33.2%), and Ti (33.8%), confirming their origin from natural soil resuspension and mineral dust [15,25] (Figure 13, Table 10).

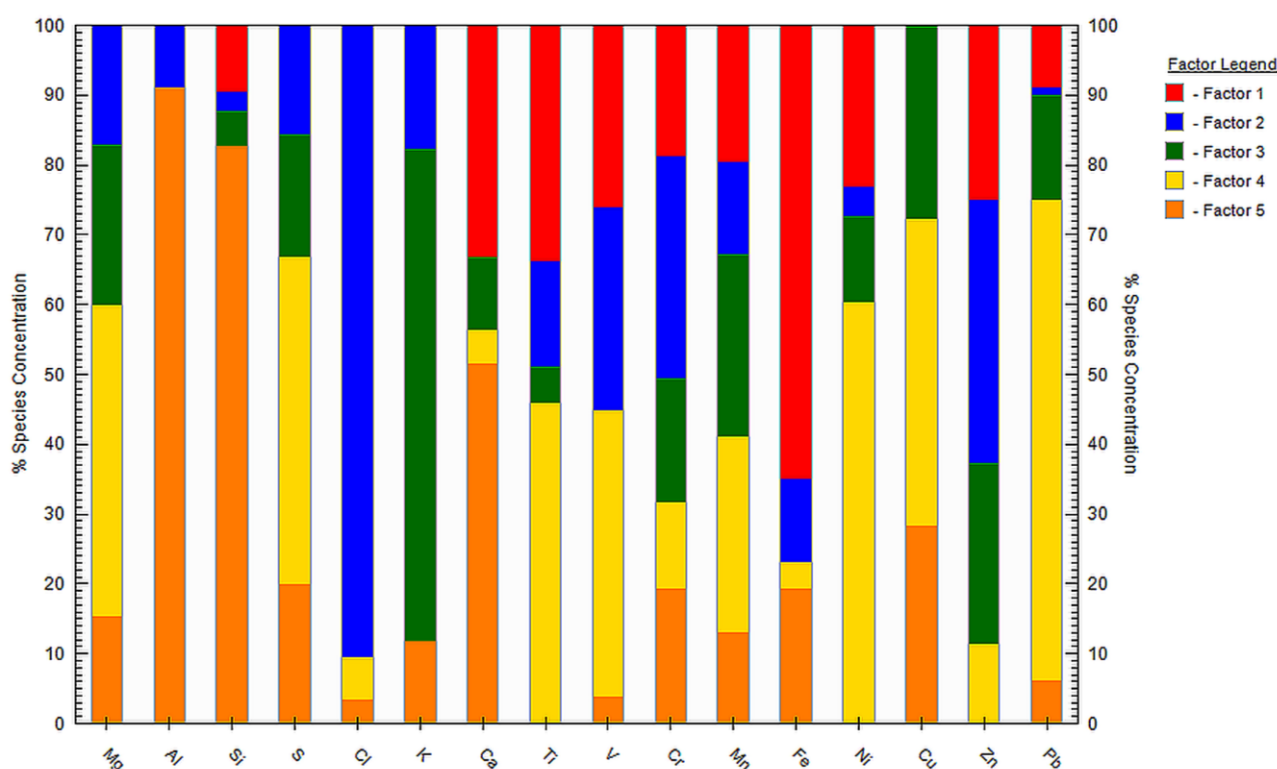


Figure 13. Source apportionment fingerprints of PM_{2.5} based on the relative contribution of elemental species across identified factors for 2021.

Factor 2 reflected industrial activity, marked by elevated contributions of Zn (37.7%), V (29.2%), and Cr (31.7%), reflecting emissions from manufacturing activities and oil combustion [22,26].

Table 10. Factor profiles of aerosol sources based on elemental composition (%) for 2021.

Factors\Elements	Fe	Ca	Ti	Zn	V	Cr	K	Pb	S	Cu	Al
Crustal (Soil)	65.0	33.2	33.8								
Industrial Emissions				37.7	29.2	31.7					
Wood Burning				26.0			70.5				
Vehicle Emissions								68.9	46.8	43.9	
Soil Dust		51.5									91.2

Factor 3 was attributed to wood/biomass burning, as evidenced by enrichment in K (70.5%) and Zn (26.0%), all of them considered diagnostic tracers of residential biomass combustion, particularly during colder months [24]. Factor 4 was assigned to vehicular emissions, primarily characterized by S (46.8%), Pb (68.9%), and Cu (43.9%), consistent with fuel combustion and vehicular wear processes, as well as being indicative of secondary sulfate formation from combustion processes [21]. Factor 5 was designated as soil dust. The origin of this dust is related to soil erosion, that is, the removal of various elements from the soil by wind. In our case, the removal of elements such as Al (91.2%) and Ca (51.5%).

3.3. Multi-Year Trend and Similarity Analysis Based on Factor Fingerprints (2013–2021)

Across the 2013–2021 period, the PMF results demonstrate a high degree of interannual similarity in factor fingerprints, indicating that the same fundamental emission sources persist over time, while their relative strengths vary substantially between years. The source structure remains stable, but contributions evolve toward greater dominance of soil/crustal dust and traffic-related S-rich anthropogenic aerosol, with episodic industrial events and variable biomass burning superimposed on this long-term shift. In the early part of the study period (2013–2015), the PMF results indicate a stronger dominance of anthropogenic sources, particularly traffic non-exhaust emissions and metal-rich industrial factors (Table 11). This is evidenced by very high Cu (74.5–79.6%), Zn (42.5–54.7%), and Pb (59.2%) contributions in traffic-related factors and strong Mn–Fe–Zn or Ni–Cr signatures in industrial factors. From 2016 onward, the relative importance gradually shifts toward natural and mechanically driven sources, with crustal and soil dust factors becoming increasingly dominant.

Table 11. Maximum tracer contributions by source and year.

Source	Key Tracer	Max%	Year
Crustal	Si	100	2013, 2019
Soil dust	Al	91.2	2021
Biomass	K	82.5	2019
Traffic NE	Cu	79.6	2015
Industrial	V	69.0	2020

3.3.1. Crustal (Soil) and Soil Dust

Crustal and soil-related sources represent the most stable and dominant contributors throughout the entire study period. In 2013, the crustal factor was characterized by extremely high lithogenic contributions, with Si reaching 100%, Ca 68.8%, Ti 52.8%, and Fe 40.6%, a pattern that reappeared in 2019 when Si again reached 100% with Ti 63.7% and Fe 55.4%. Similarly, high Ca contributions were observed in multiple years, including 80.2% in 2014, 75.9% in 2015, 68.8% in 2016, and 76.6% in 2018, confirming the persistent influence of mineral dust resuspension. In parallel, a distinct soil dust component intensified over time, as reflected by rising Al contributions, from 82% in 2015 to 46.6% in 2020, culminating in 91.2% in 2021, indicating a strengthening role of mechanically disturbed and wind-eroded soils in the later years.

3.3.2. Traffic-Related Sources: Exhaust and Non-Exhaust

The trend analysis reveals a clear decoupling between traffic exhaust and non-exhaust emissions. Non-exhaust traffic sources dominate the early years (2013–2015), as shown by extreme Cu–Zn–Pb contributions, but their relative intensity decreases after 2016. In contrast, S-rich traffic-related aerosol becomes increasingly important after 2018

(S = 61.9% in 2019; 48.1% in 2020; 46.8% in 2021), reflecting enhanced secondary sulfate formation and atmospheric aging of traffic emissions. This shift mirrors broader European trends where exhaust emissions decline due to regulation, while non-exhaust emissions remain persistent and secondary processes gain importance. Non-exhaust traffic sources were particularly strong in 2013 (Cu 74.5%, Zn 21.4%, Pb 11.7%) and 2015, when Cu reached 79.6%, Zn 54.7%, and Pb 59.2%, indicating intense brake and tire wear contributions. In contrast, traffic-related S-rich anthropogenic aerosol factors were more pronounced in later years, with high sulfur contributions such as S 61.9% in 2019, 48.1% in 2020, and 46.8% in 2021, accompanied by elevated Pb and Cu, reflecting increasing importance of secondary sulfate formation and mixed exhaust–non-exhaust influences.

3.3.3. Industrial Emissions

Industrial and oil combustion sources appeared episodically but with highly consistent chemical fingerprints when present. Strong industrial signatures were observed in 2016 (Ni 51.9% and Zn 50.5%), in 2018 (Ni, Cr, and V each 55.8%), and in 2020 (V 69.0% and Ni 53.6%). These near-identical tracer contributions point to a well-defined industrial or heavy-oil combustion source, likely influenced by episodic industrial activity or favorable transport conditions rather than continuous local emissions. Industrial and oil combustion sources showed no monotonic trend, instead appearing as episodic peaks with remarkably stable chemical fingerprints.

3.3.4. Wood/Biomass Burning

Biomass burning exhibited the greatest interannual variability while maintaining a stable chemical identity. The biomass factor was relatively weak in 2014–2015 but intensified markedly in 2016 (K 59.2%), 2018 (K 67.4%, Zn 64.6%), and especially 2019, when K reached 82.5% and Zn 77.8%, indicating strong residential wood combustion. After a moderate contribution in 2020 (K 25.5%), biomass burning rebounded in 2021, with K 70.5%, consistent with variability in heating demand and winter severity.

3.4. Hierarchical Clustering of Factor Fingerprints (2013–2021) and Source Stability

Hierarchical agglomerative clustering was performed using Ward's linkage and Euclidean distance to evaluate the similarity of PMF-resolved factor fingerprints across all years (Figure 14). The resulting dendrogram reveals several distinct and interpretable clusters that reflect both the chemical nature of the emission sources and their temporal evolution.

To evaluate the chemical similarity and temporal consistency of PMF-resolved sources, a quantitative hierarchical clustering analysis was applied to source-family fingerprints derived from the PMF results for the period 2013–2021 (Figure 15). The quantitative dendrogram shows a clear separation of source families based on their dominant chemical signatures. Crustal and soil dust form a closely related but distinct sub-branch, reflecting shared lithogenic tracers (Si, Al, Ca, Fe) with different relative weighting. Traffic-related sources split into two neighboring branches corresponding to non-exhaust emissions (Cu–Zn–Pb) and traffic-related aerosol (S-rich), indicating partial chemical similarity but distinct source processes.

The hierarchical clustering analysis confirmed the chemical distinctiveness of biomass burning (K, Zn), industrial/oil combustion (Ni, V, Cr), and road salt (Cl, Na) sources, which formed separate branches in the dendrogram. Traffic-related and crustal sources showed shorter linkage distances, indicating greater similarity in their elemental compositions.

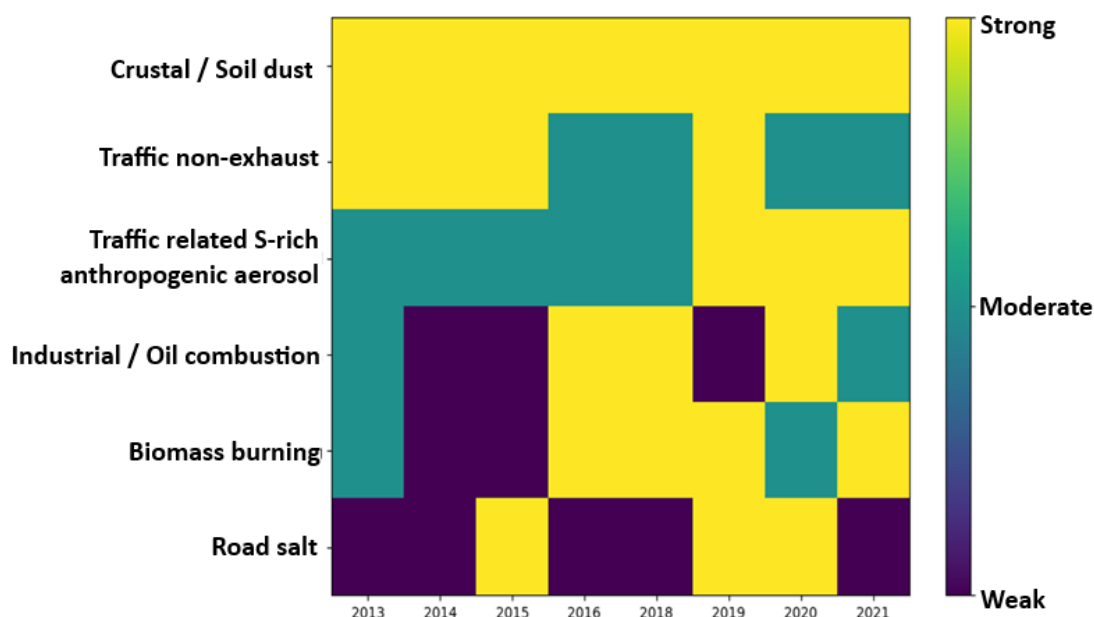


Figure 14. Source persistence and qualitative intensity matrix of PMF-resolved factors for the period 2013–2021. Colors indicate the relative strength of each source (absent/weak, moderate, strong) based on factor fingerprints and dominant tracer contributions.

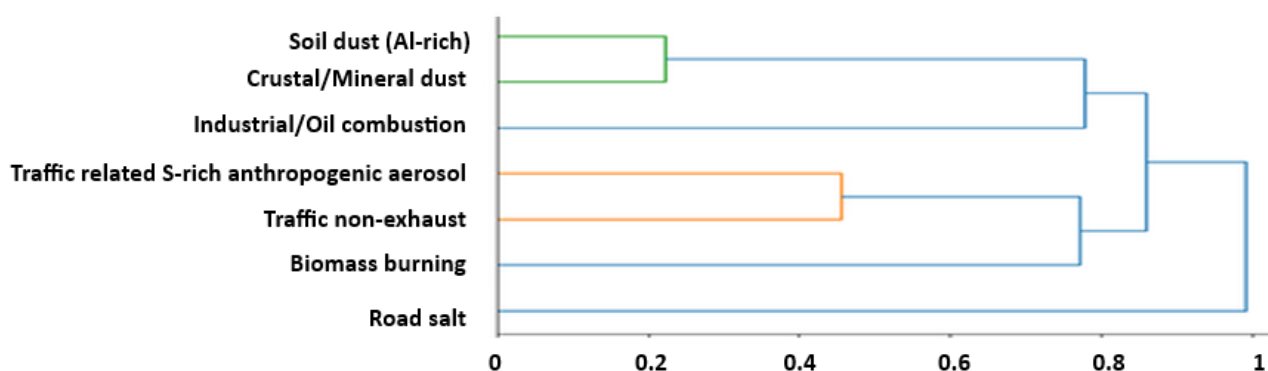


Figure 15. Hierarchical clustering dendrogram.

Analyses confirm that the majority of PMF-resolved source families are both internally coherent and externally well separated. Mineral dust and soil dust clusters exhibit high compactness, with partial overlap reflecting natural compositional variability. Traffic-related sources clustered more closely with crustal and soil dust sources, indicating similarities with their elemental composition and potential mixing processes. In contrast, biomass burning, industrial/oil combustion, and road salt sources were clearly separated from remaining source families due to their distinctive elemental fingerprints. These results independently support the PMF source attribution. Table 12 presents the Source Stability Index) calculated for each PMF-resolved source over the period 2013–2021, providing a quantitative assessment of the temporal consistency of factor fingerprints. Crustal and soil-related sources exhibited the highest stability, with SSI values generally exceeding 0.85, reflecting the chemically invariant nature of mineral dust and resuspended soil particles across years. These high SSI values confirm that the observed interannual variability of mineral sources is driven primarily by changes in source intensity rather than by changes in chemical composition.

Table 12. Source Stability Index for PMF-resolved sources (2013–2021).

Source Category	Dominant Tracers	Mean SSI	Stability Class
Crustal/silicate dust	Si, Al, Ca, Ti, Fe	0.88–0.92	Very high
Soil dust (Al/Ca-rich)	Al, Ca, Mg, Fe	0.84–0.90	Very high
Traffic non-exhaust	Cu, Zn, Pb	0.70–0.78	Moderate
Traffic-related S-rich anthro-pogenic aerosol	S, Pb, Cu	0.75–0.82	Moderate–high
Biomass burning	K, Zn	0.80–0.87	High
Industrial/oil combustion	Ni, V, Cr	0.86–0.93	Very high
Road salt	Cl, Na	0.89–0.95	Very high

Biomass burning also showed relatively high stability (SSI $\approx$ 0.80–0.87), indicating a robust and well-defined chemical signature dominated by potassium and zinc, despite strong year-to-year variability in contribution strength. Traffic-related sources displayed moderate to high stability, with traffic non-exhaust emissions showing slightly lower SSI values ($\approx$ 0.70–0.78) compared to traffic-related S-rich anthropogenic aerosol ($\approx$ 0.75–0.82). This reduced stability reflects enhanced source mixing, mechanical wear variability, and atmospheric aging processes affecting traffic-derived particles.

Industrial and oil-combustion-related sources exhibited very high SSI values when present (often >0.85), underscoring their distinct and chemically consistent fingerprints characterized by Ni, V, and Cr. Similarly, road salt showed very high stability (SSI > 0.90) in years when it was resolved, consistent with its unique Na–Cl chemical profile. Overall, the SSI analysis demonstrates that PMF-resolved sources are chemically robust across years, reinforcing confidence in source identification and supporting the interpretation that long-term trends reflect evolving emission strengths rather than shifting source identities.

The urban aerosol is structurally dominated by mineral and traffic-related sources, while biomass burning, industrial emissions, and road salt contribute episodically, driven by seasonality and specific activity patterns. Table 13 summarizes the occurrence frequency and temporal persistence of the PMF-resolved sources over the period 2013–2021, highlighting clear differences between structurally persistent and episodic contributors to urban particulate matter. Crustal and soil-related sources were resolved in all analyzed years (8/8), confirming their role as permanent components of the urban aerosol and reflecting continuous soil resuspension and mechanically disturbed mineral material.

Table 13. Source occurrence frequency and turnover (2013–2021).

Source Category	Years Present (of 8)	Occurrence Type
Crustal/soil dust	8/8	Persistent
Soil dust (Al-rich)	8/8	Persistent (intensifying)
Traffic non-exhaust	8/8	Persistent (declining)
Traffic-related S-rich anthropogenic aerosol	8/8	Persistent (strengthening)
Biomass burning	6/8	Seasonal/variable
Industrial/oil combustion	4/8	Episodic
Road salt	3/8	Seasonal (winter-only)

Traffic-related sources, including both non-exhaust emissions and traffic-related S-rich anthropogenic aerosol, were also present throughout the entire study period, although their relative importance varied over time, indicating evolving traffic activity and atmospheric processing rather than changes in source identity. In contrast, biomass

burning exhibited seasonal and interannually variable behavior, appearing in six out of eight years, with pronounced contributions during colder periods. Industrial and oil-combustion-related emissions were distinctly episodic, occurring in only half of the analyzed years (4/8), suggesting sporadic influences linked to specific industrial activities, fuel-use patterns, or meteorological conditions favoring regional transport. Road salt was the least persistent source, detected only in three years (3/8), consistent with its association with wintertime de-icing practices. Overall, the turnover analysis demonstrates that while the urban aerosol source structure is dominated by persistent mineral and traffic-related emissions, episodic sources introduce substantial interannual variability and can strongly influence particulate composition during specific years.

The correlation matrix of elemental concentrations across all PM_{2.5} factor fingerprints and years provided a comprehensive overview of the co-variation structure among elements and offered valuable insight into their shared emission origins. Strong positive correlations were observed among lithogenic elements, including Al, Si, Ca, Ti, Fe, and Mg, reflecting their common geochemical origin in crustal and soil dust. The persistence of these correlations across the entire 2013–2021 period highlights the chemical stability of mineral dust contributions in the urban environment and supports the consistent resolution of crustal factors by PMF.

The correlation matrix provides insight into which elements tend to co-occur across all PMF factor fingerprints and years (Figure 16).

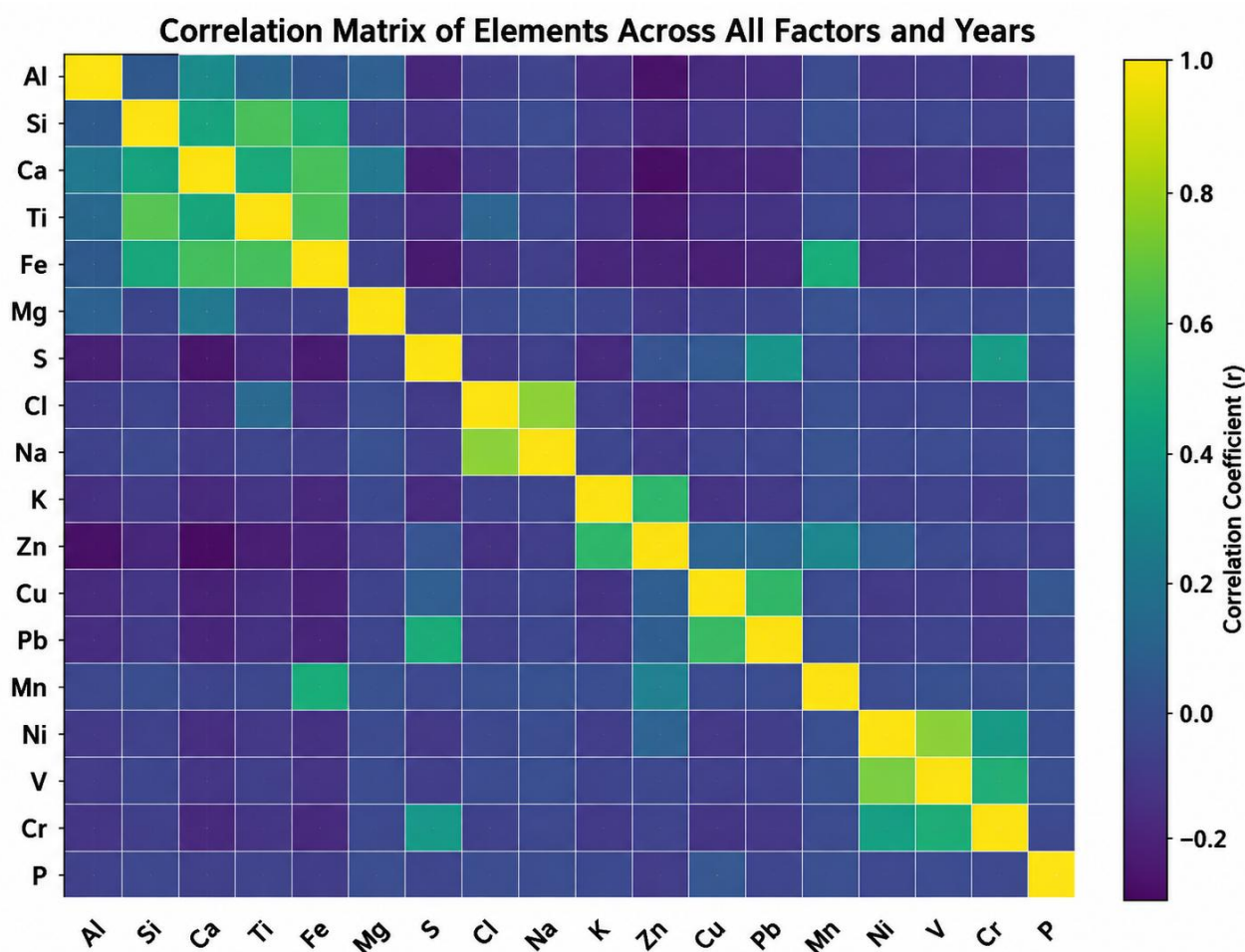


Figure 16. Correlation matrix of elements across all factors and years.

A distinct cluster of industrial metals, most notably Ni, V, and Cr, also exhibited strong inter-element correlations. These elements are characteristic of industrial

combustion processes and metallurgical activities, and their coherent behavior corroborates the episodic industrial factors detected in specific years. The strength of these correlations suggests that industrial emissions are associated with a well-defined and chemically uniform signature in the ambient aerosol. Moderate correlations were found between K and Zn, both of which are frequently associated with biomass burning emissions. This relationship reflects the characteristic composition of residential wood combustion, particularly during heating seasons. Traffic-related elements such as Cu, Zn, and Pb showed weaker but still discernible correlations, consistent with the variable nature of non-exhaust traffic emissions that depend on driving patterns, brake and tire wear intensity, and resuspension of legacy materials. Elements associated with road salt, particularly Na and Cl, formed another correlated pair, reflecting their common origin—the use of de-icing agents during winter. In contrast, sulfur displayed weak or even negative correlations with most other elements, suggesting that sulfate-rich emissions and secondary aerosol formation processes operate largely independently of the primary sources that dominate the other elemental clusters.

Although some variations in elemental composition were observed among studies, likely reflecting differences in local emission sources, geographical conditions, and analytical approaches, the overall consistency of the identified source profiles demonstrates that the factors obtained in this study are comparable to those reported in other regions worldwide (Table 14). But some differences were observed. The soil dust and crustal factors showed variations in dominant elements, reflecting regional geological characteristics. The biomass burning factor in this study was mainly represented by K and Zn, whereas other studies also reported significant contributions of OC and EC.

Table 14. Comparative table of elements included in the factors.

Factors	This Study	(Heze, China August 2015–April 2016) [27]	Baengnyeong Is- land (BNI) (2020–2021) [28]	Seoul Metropol- itan Area (SMA) (2020–2021) [28]	Taranto, Italy (2004) [29]
Soil Dust	Al (46.6%), Ca (61.4%), Mg (17%), Fe (91.2%)	Si (42.7–54.4%), Ca (16.3–27.9%), Mg (9.4–48.3%), Al (45.3–55.5%), Fe (16.7–26.9%)	Ca (90%), Ti (65%), Fe (50%)	Ca (80%), Ti (65%), Fe (48%)	Al (82%), Si (71%), Ti (42%)
Biomass Burning	K (59.2%) Zn (82.5%)	OC (Organic Carbon) (18.7–30.5%), EC (Elemental Carbon) (11.1–17.4%), K (33.6–88.8%)	Pb (49%), K (45%),	OC (65%), EC (52%), K (70%)	
Vehicle Emissions	Cu (79.6%), Zn (54.7%), Pb (59.2%)	OC (38.8–48.2%), EC (35.4–47.6%), Cu (24–28.5%), Zn (21.8–48.8%)	OC (69%), EC (48%), Br (50%)	Cu (70%), OC (48%), EC (45%)	Cu (80%), Zn (35%), Pb (79%)
Industrial	Ni (55.8%), V (69%), Cr (55.8%)	Cr (24.3–67.4%), Cu (32–48.6%), Fe (31.8–47.7%), Mn (23.4–35.8%), Ni (33.3–65%), Ti (33.8–50.9%), V (27.3–75.5%),	Cr (62%), Mn (70%), Fe (55%), Zn (72%), Br (58%)	Pb (69%), Zn (50%), Mn (58%), Cr (49%)	Fe (78%), Mn (50%)
Crustal	Si (100%), Ca (68.8%), Ti (52.8%), Fe (40.6%)	Ca (52.6–60.8%)			Zn (67%), Ca (58%), Pb (49%)

Vehicle emissions were characterized by Cu, Zn, and Pb, indicating a stronger influence of non-exhaust traffic emissions compared to studies where OC and EC were dominant. The industrial factor was associated with Ni, V, and Cr, differing from other regions

where Fe, Mn, Zn, or Pb were more prominent. These differences likely result from variations in local emission sources, environmental conditions, and analytical approaches.

4. Conclusions

This study presents an eight-year (2013–2021, except 2017) PM_{2.5} source apportionment in Vilnius based on PIXE elemental analysis (485 samples) and EPA PMF 5.0. The results show that urban PM_{2.5} is driven by a chemically stable but dynamically varying mixture of sources, with pronounced interannual changes in source influence rather than source identity. Across the analyzed years, Vilnius PM_{2.5} composition was consistently characterized by persistent mineral (Si–Ca–Ti–Fe) and soil dust (Al-rich) sources, with evidence of increasing soil influence in 2020–2021 (Al contributing up to 91.2%). Traffic remained present throughout the study period but shifted from dominant non-exhaust wear signatures in early years (Cu contributing up to 79.6% and Pb up to 59.2%) to traffic-sulfate-influenced anthropogenic aerosol factors in later years (S contributing up to 61.9%). Industrial/oil combustion appeared intermittently yet with highly consistent tracers (V contributing up to 69.0%; Ni and Cr up to ~56%), while biomass burning varied strongly year-to-year (K up to 82.5%) and road salt emerged only in winter-affected years (Cl contributing up to 86.9%). Chloride-rich aerosol associated with road de-icing salt occurs intermittently during winter periods.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos17070645/s1>, Table S1: Correspondence between annual PMF factors and source families used for long-term interpretation.

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