ORIGINAL PAPER

HEALTH RISKS OF POTENTIALLY TOXIC METALS BOUND $PM_{2.5}$ ACROSS AN URBAN AREA

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Abstract. *Particulate matter refers to tiny particles with a size of 2.5 µm or less. Due to their micrometric size, they easily bypass the body's natural defence mechanisms and enter the lungs and the bloodstream. In this research, potentially toxic metals (e.g., lead, cadmium, nickel, chromium, copper, manganese, zinc, aluminium, and iron) associated with* $PM_{2.5}$ *were determined in terms of concentration. This study aimed to assess the potential risk to human health from three exposure pathways: ingestion (i.e., daily intake of toxic metals), inhalation (i.e., exposure concentration), and dermal contact (i.e., dermal absorbed dose). Additionally, the hazard quotient for the above-mentioned pathways was calculated. On the other hand, the carcinogenic risk to human health of toxic metals due to inhalation was determined. The study also aimed to establish the individual pollution index for potentially carcinogenic metals (i.e, Pb, Cd, and Ni). Statistical analysis was used to highlight the relationships in similarity among the analyzed metals and to identify potential common emission sources.*

Keywords: *particulate matter; toxic metals; health risk index; urban area.*

1. INTRODUCTION

Monitoring air quality with respect to particulate matter (PM) emissions is essential for protecting human health and the environment. Thus, PM-related air pollution is one of the biggest challenges for major cities worldwide, including those in Romania. Particularly, since 2009, Romania has been notified by the European authorities that certain limit values for air pollution from suspended particles (i.e., PM_{10}) have been exceeded in several cities. On the other hand, $PM_{2.5}$ levels in most large cities in Romania exceed 16 $\mu g \cdot cm^{-3}$, which is at least three times the WHO recommendations [1-3]. Particulate matter can be emitted directly from the source (primary particles) or formed in the atmosphere through chemical reactions of gases (secondary particles). From a compositional perspective, suspended particles comprise a complex mixture of very small inorganic and organic particles, as well as liquid droplets. Particles can contain asbestos pieces (used until a few years ago on a global scale -

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carcinogenic), fibreglass, cement particles, or asphalt. These particles may also include pollutants such as sulfur dioxide, nitrogen oxides, volatile organic compounds, ammonia, and toxic metals. When the atmosphere is humid and condensation forms, water particles attract these compounds, like a magnet, making them dangerous to health. Therefore, these particles vary in size, composition, and origin, and are often classified by size (in μm) as PM_{10}, $PM_{2.5}$, and PM_1, each with specific implications for health and the environment [4]. In brief, the three categories of particles can be described as follows: *(i)* PM_{10} refers to particles with a diameter of less than 10 μm, which can penetrate the respiratory tract, causing various health problems, from eye and nose irritation to more serious respiratory problems, such as asthma or bronchitis; *(ii)* $PM_{2.5}$ refers to particles with a diameter of 2.5 μm or less and is considered particularly dangerous because it can reach the alveoli of the lungs and can even enter the bloodstream, contributing to cardiovascular and respiratory diseases and cases of cancer; *(iii)* PM_1, the finest particles, with a diameter of 1 μm or less, can penetrate deep into the lungs and are more likely to pass into the bloodstream, affecting several internal organs, including the heart and brain. The World Health Organisation (WHO) has established a series of limit values for PM concentrations in ambient air, namely: *(i)* $PM_{2.5}$: 5 $\mu g \cdot m^{-3}$ annual average, 15 $\mu g \cdot m^{-3}$ daily average; *(ii)* PM_{10}: 15 $\mu g \cdot m^{-3}$ annual average, 45 $\mu g \cdot m^{-3}$ daily average. In comparison, the European legislation [5] to which Romania is also allied [6] recommends the following limit values: *(i)* $PM_{2.5}$: 20 $\mu g \cdot m^{-3}$ annual average; *(ii)* PM_{10}: 40 $\mu g \cdot m^{-3}$ annual average, 50 $\mu g \cdot m^{-3}$ daily average.

The presence and distribution of metals in the environment are primarily determined by their occurrence in Earth's crust. At natural concentrations, metals play essential roles in many biochemical processes in living organisms, but concentrations above background levels can be toxic. As a result of anthropogenic activities, current levels are higher than under natural conditions, posing a threat to organisms, as many metals are harmful even at moderate concentrations. The toxicity of metals depends on their bioavailability and atomic and physicochemical properties. Potentially toxic metals (e.g., lead, cadmium, nickel, and chromium) can be adsorbed to the surfaces of airborne particles (PM_{10}, $PM_{2.5}$). These particles are transported over long distances and inhaled deep into the lungs, representing a major risk to human health. Major sources of PM-associated metal emissions include wastewater treatment plants, household waste, smelters, and other metal-processing activities, all of which generate numerous waste dumps. Metals released into the atmosphere from anthropogenic or natural activities are deposited at ground level, where they persist for long periods [7]. Under certain climatic conditions, e.g., a decrease in pH, metals in the soil, especially mercury and cadmium, are solubilized and reach water resources. On the other hand, metals derived from natural rock erosion or controlled mining activities are transported as suspended particles over long distances, reaching surface waters either dissolved or as part of sediments. Any activity involving the extraction or processing of metals is a source of fine metal particles that are dispersed into the atmosphere and then associated with PM [7]. Various forms of corrosion also release metals into the environment during the use or storage of metal equipment. The burning of fossil fuels or various categories of waste further releases metals into the atmosphere. However, most particles are so small that the wind can transport them over enormous distances. Road transport is also responsible for significant lead emissions due to the use of lead-containing fuel additives. In addition, metals entering the aquatic environment can dissolve in water, be stored in sediments, and later be volatilized into the atmosphere, where they are adsorbed onto fine particles and transported. These sources generate significant emissions of PM-bound metals, underscoring the broad range of factors that affect air quality [8].

The association of metals with particulate matter is critical for their uptake by organisms through various pathways (inhalation, ingestion, and dermal contact). PM can act as a carrier for metals, adsorb insoluble metal compounds over long distances, and subsequently release them into living organisms. Understanding the mechanisms of interaction between heavy metals and PM involves several aspects, such as the emission source, bioavailability (e.g., chemical forms of dissolved metals, such as complexes formed with low molecular weight organic ligands, increase bioavailability compared to ionic forms, and implicitly their toxicity), possible chemical processes (formation of free hydrated ions, e.g., for copper, cadmium and zinc, or the formation of organomercuric compounds that are toxic and liposoluble), the uptake pathways of metals, and, last but not least, climatic factors.

On the other hand, the irregular shape of suspended particles associated with PM increases the risk to humans. Several adverse health effects have been associated with exposure to PM-bound potentially toxic metals, such as worsening respiratory diseases, including asthma [9] and chronic obstructive pulmonary disease (COPD) [10], cardiac illness [11], and days of inactivity [12,13]. These adverse health effects have been reported primarily for infants, children, and older adults with preexisting cardiac or pulmonary disease [1,14,15]. In this regard, a study by Alexeeff et al. found that each 10 $\mu g \cdot m^{-3}$ increase in long-term $PM_{2.5}$-bound metals exposure is associated with a 15% increase in cardiovascular mortality [16]. Additionally, Theorell et al (2026) reported that $PM_{2.5}$ increases the incidence of primary sinonasal epithelial cells in people with chronic rhinosinusitis [17]. Another study by Hu et al. [18] found that increased exposure to $PM_{2.5}$-bound metals was associated with higher COVID-19 mortality rates, underscoring the importance of air quality during the pandemic [19]. Children, infants, and the elderly are also susceptible to inhaled metals bound to $PM_{2.5}$ [20,21], although the long-term effects are less clear [22,23].

Taking into account the above mentioned things, this research aims to contribute to a better understanding of the links and interactions between metals and particulate matters, from a medium-industrialized urban area, by determining the concentration of metals bound to $PM_{2.5}$, and assessing the potential risk of these metals on human health, given the worldwide concern regarding the potential carcinogenic effect of several metals (e.g., nickel, cadmium, chromium(VI), lead, but also copper or manganese when doses are exceeded).

2. MATERIALS AND METHODS

2.1. SAMPLING AND SAMPLE PREPARATION

2.1.1. Site Description

According to the Cooperative Program for Monitoring and Evaluation of the Long-Range Transport of Air Pollutants in Europe [24], $PM_{2.5}$ is measured with high precision across Europe, particularly in urban areas. Data show that urban $PM_{2.5}$ levels are considerably higher (15–20 $\mu g \cdot m^{-3}$) than rural levels (11–13 $\mu g \cdot m^{-3}$) [24]. It is well known that if an urban area is heavily polluted by traffic and has intense industrial activity, $PM_{2.5}$ levels are much higher (e.g., 20–30 $\mu g \cdot m^{-3}$), and the $PM_{2.5}$ chemical composition can be extremely toxic to human health. In this regard, the city of Targoviste was chosen for this study because metallurgical activity is well known to be a primary source of toxic metals bound to $PM_{2.5}$. Four locations (noted as P_1-P_4, Fig. 1) were selected based on traffic, industrial, and domestic sources that pose the highest exposure risks to air quality and human health. The European Monitoring and Evaluation Programme (EMEP) manual for chemical sampling and analysis

[24], the guide for the measurement of atmospheric pollutants [25], and the sampling procedure described by Meyer and Rupprecht [26] were used.

Briefly, point P_1 was in the western part of the city, an area characterized by industrial and commercial activities and traffic, serving as the city's entrance/exit. Point P_2 was in the northern part of the city, in a representative residential area of Targoviste. The monitored area P_3 is in the southern part of the city. Due to its location, this point can reflect the cumulative contribution of emissions from industrial activities and traffic at the city's entrances and exits. Point P_4 was selected in the southeastern area of Targoviste, which is characterized by heavy traffic at the entry and exit points to/from the city and the industrial area.

Figure 1. Sample points (P_1–P_4) in Targoviste city.

2.1.2. Sampling and Sample Preparation

$PM_{2.5}$ samples were collected with a portable air quality monitoring system (Pollusense™, Oizom, India) 1.5 m above the ground level, using laser scattering, with 0.1 $\mu g \cdot m^{-3}$ resolution, over three months of the summer of 2025. To avoid contamination, all filters were handled using powder-free Teflon materials and gloves. The collected filters were placed in Petri dishes and stored in desiccators until the analysis. The blank filters were weighed (average of three weighings) to a standard deviation of 0.00002 g, then placed in Petri dishes and stored in desiccators until the actual analysis.

All chemicals used in this research were analytical grade (Merck KGaA, Darmstadt, Germany). Deionised water (resistivity of 18.2 MΩ·cm) was obtained using a Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid (Merck KGaA, Darmstadt, Germany) was used to prepare the blank. All sample vessels, autosampler cuvettes, and other materials were washed with water, then with 10% v/v nitric acid for 24 hours and rinsed with deionised water before use. NIST SRM 1648a, *Urban Particulate Matter*, standard reference material was handled, stored, and used in accordance with the certificate of analysis. The ICP-MS calibration standard solutions were prepared by diluting 1 $mg \cdot L^{-1}$ ICP-MS standards (Sigma-Aldrich, TraceCERT, Merck KGaA, Darmstadt, Germany).

Microwave-assisted acid digestion of samples was performed using a topwave closed-vessel microwave digester (Analytic Jena, Jena, Germany). Acid digestion was performed in 50 mL PM60 PTFE digestion vessels with a mixture of HNO_3 (70% w/v) and H_2O_2 (30% w/v) in a 4:1 ratio, according to the standard method described in UNI EN 14902:2005 [27]. Thus, approximately 5 mg of sample, obtained by sampling powder from the filters, was weighed on an analytical balance with four decimal places using a watch glass. The powder was then transferred to a PTFE digestion vessel, and the acid mixture was added. The inclusion of hydrogen peroxide increases the mixture's oxidative potential and reoxidizes NO_x

to nitrate. This reaction has the added advantage of reducing the pressure generated by the digestion of organic matter in the PM sample, thereby avoiding overpressure in the digestion vessel. After 30 minutes of resting, 2 mL of 36% HCl is added, which is extremely useful for the digestion and analysis of several metals. For each digestion cycle, a reference vessel was used to monitor the temperature and pressure of the digestion process. A blank containing the same volume of reagents used in the sample vessels and 5 mg of NIST SRM 1648a - Urban Particulate Matter, was added to the reference vessel.

After mineralization (Table 1), the PTFE vessels containing the samples were cooled for 1 hour at room temperature, and then opened; the solutions were transferred to 25 mL volumetric flasks and brought to the mark with distilled water.

Table 1. Parameters and steps of the mineralization process.

Parameters	**Steps**		
	1	**2**	**3**
Temperature [°C]	145	200	200
Pressure [bar]	20	20	16
Ramp [min]	2	5	2
Time [min]	10	30	30

2.2. ANALYTICAL TECHNIQUES

Metal concentrations bound to $PM_{2.5}$ were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using an iCAP™ Qc spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The method allows the simultaneous determination of several elements (depending on the standard material used), trace and ultra-low levels, with low detection limits and high precision. The ICP-MS technique is considered a reference method for monitoring toxic metals in PM samples and other environmental matrices. The limit of detection (LOD) of nine metals (i.e., nickel, cadmium, chromium, lead, copper, zinc, manganese, aluminium, and iron) was determined using metal calibration curves, which showed good linearity over the concentration range of 0.1 to 10.0 $mg \cdot L^{-1}$, with correlation coefficients (R^2) of 0.996 to 0.999. The LOD values were calculated from Equation (1):

$$LOD = \overline{blank} + 3 \cdot SD \qquad (1)$$

where: $\overline{blank}$ is the average value of blank samples and *SD* is the standard deviation. The obtained LOD values were: Pb (10 $\mu g \cdot L^{-1}$), Cd (22 $\mu g \cdot L^{-1}$), Cr (19 $\mu g \cdot L^{-1}$), Ni (12 $\mu g \cdot L^{-1}$), Cu (11 $\mu g \cdot L^{-1}$), Mn (15 $\mu g \cdot L^{-1}$), Al (16 $\mu g \cdot L^{-1}$), Zn (18 $\mu g \cdot L^{-1}$), and Fe (12 $\mu g \cdot L^{-1}$).

Analytical curves for each analyzed element were prepared using stock standard solutions (Merck, Darmstadt, Germany). Standard reference materials (NIST SRM 1648a, Urban Particulate Matter) were used to verify the method's accuracy and traceability. On average, the recovery rate for the blank samples ranged from 91.2% for Al to 101.5% for Pb, while the recovery rate for SRM 1648a ranged from 94% for Zn to 104% for Ni. Measurements were performed in triplicate. The relative standard deviation (RSD) of the standard was 0.36%; the RSD of the samples was 1.2-2.2%, and the recovery rate was 94.2-101.4%. Concurrent interference decreased, and no substantial loss was recorded in the sample preparation process.

2.3. DATA ANALYSIS

2.3.1. Health Risk Assessment of Toxic Metals Associated with $PM_{2.5}$

Atmospheric toxic metals mainly originate from industrial emissions, mining activities, vehicle exhaust, fossil fuel combustion, waste incineration, construction, and crustal dust. Urban pollution profiles vary considerably due to differences in industrial sources [28]. This section focuses on assessing the human health risk of nine metals (Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn, and Fe) in $PM_{2.5}$ collected at P_1-P_4 points (Fig. 1). The exposure parameters related to toxic metals intake pathways (i.e., ingestion, inhalation, and dermal contact) are presented in Equations (2) – (4), developed by Zhang et al. [29] and Cha et al. [28]. The daily intake of toxic metals by ingestion (CDI_{ng}), the exposure concentration by inhalation (EC_{inh}), and the dermal absorbed dose (DAD_{derm}) were calculated for adults and children, for both carcinogenic and non-carcinogenic risks. Table 2 shows the indices and their values used in Equations (2)–(4).

$$CDI_{ng} = C_m \cdot \frac{I_{ng}R \cdot EF \cdot ED \cdot CF}{BW \cdot AT_c}\ [mg \cdot kg^{-1} \cdot d^{-1}]$$
$$CDI_{ng} = C_m \cdot \frac{I_{ng}R \cdot EF \cdot ED \cdot CF}{BW \cdot AT_n}\ [mg \cdot kg^{-1} \cdot d^{-1}] \quad (2)$$

$$EC_{inh} = C_m \cdot \frac{ET \cdot EF \cdot ED}{AT_c}\ [\mu g \cdot m^{-3}]$$
$$EC_{inh} = C_m \cdot \frac{ET \cdot EF \cdot ED}{AT_n}\ [\mu g \cdot m^{-3}] \quad (3)$$

$$DAD_{derm} = C_m \cdot \frac{SA \cdot SAF \cdot DAF \cdot EF \cdot ED \cdot CF}{BW \cdot AT_c}\ [mg \cdot kg^{-1} \cdot d^{-1}]$$
$$DAD_{derm} = C_m \cdot \frac{SA \cdot SAF \cdot DAF \cdot EF \cdot ED \cdot CF}{BW \cdot AT_n}\ [mg \cdot kg^{-1} \cdot d^{-1}] \quad (4)$$

Table 2. Indices and values used in health risk assessment models.

	Name	Unit of measurement	Value		Reference
			Children	Adults	
C_m	Metal concentration	$mg \cdot cm^{-3}$ (for CDI_{ng} and DAD_{derm}) $ng \cdot cm^{-3}$ (for EC_{inh})	-		-
$I_{ng}R$	Ingestion rate	$mg \cdot d^{-1}$	200	100	[28]
ET	Exposure time	$h \cdot d^{-1}$	12		
EF	Frequency of exposure	$d \cdot y^{-1}$	180		
ED	Exposure period	y	6	24	
CF	Conversion factor	$kg \cdot mg^{-1}$	10^{-6}		
BW	Average body mass	kg	15	70	
AT_c*	Average time (cancer)	h	613,200		[30]
AT_n*	Average time (non-cancer)	h	52,560	210,240	
SA	Skin surface	cm^2	2800	5700	[28]
SAF	Skin surface adhesion factor	$mg \cdot cm^{-2} \cdot d^{-1}$	0.2	0.07	[30]
DAF	Dermal absorption factor	-	0.001 for Cd; 0.01 for the rest of the elements		[31]

* $AT_c = 70\ y \cdot 365\ d \cdot y^{-1} \cdot 24\ h \cdot d^{-1}$; $AT_n = ED \cdot 365\ d \cdot y^{-1} \cdot 24\ h \cdot d^{-1}$

The hazard quotient (HQ) for the three exposure pathways, as well as the inhalation-related carcinogenic risk (CR_{inh}), was calculated using Equations (5) and (6), respectively. The tolerance dose values of toxic metals are presented in Table 3.

$$HQ_{ing} = \frac{CDI_{ng}}{R_f D}$$

$$HQ_{inh} = \frac{EC_{inh}}{R_f C \cdot 1000} \quad (5)$$

$$HQ_{derm} = \frac{DAD_{derm}}{R_f D \cdot GIABS}$$

$$CR_{inh} = EC_{inh} \cdot IUR \quad (6)$$

Table 3. Reference dose for the identified metals [28].

Index	**Metal**						
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Zn**
R_fD [mg·kg^{-1}·d^{-1}]	$3.50 \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	$3.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$4.00 \cdot 10^{-2}$	$1.43 \cdot 10^{-5}$	$3.00 \cdot 10^{-1}$
R_fC [mg·m^{-3}]	$3.52 \cdot 10^{-3}$	$1.50 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$9.00 \cdot 10^{-5}$	$4.02 \cdot 10^{-2}$	$5.00 \cdot 10^{-4}$	$3.01 \cdot 10^{-1}$
GIABS	1.00	0.025	0.025	0.04	1.00	1.00	1.00
IUR [mg·m^{-3}]	$1.20 \cdot 10^{-5}$	$1.80 \cdot 10^{-3}$	$8.40 \cdot 10^{-2}$	$2.60 \cdot 10^{-4}$	-	-	-

R_fD - Oral Reference Dose; R_fC - Inhalation Reference Concentration; GIABS - Gastrointestinal Absorption Factor; IUR - Inhalation Unit Risk.

To assess the impact of toxic metals on air quality and human health, the individual pollution index (PI_i) for metal-contaminated air was calculated using Equation (7).

$$PI_i = \frac{C_m}{S_i} \quad (7)$$

where: S_i represents the legal limit value of concentration for the corresponding metal (Pb = 500 ng·m^{-3}; Cd = 5 ng·m^{-3}; Ni = 20 ng·m^{-3}) [32].

2.4. STATISTICAL ANALYSIS

The experimental data on the concentrations of potentially toxic metals associated with $PM_{2.5}$ particles were analysed using descriptive statistics to assess the spatial distribution of contaminants. The statistical analysis (Pearson correlation, descriptive statistics, and hierarchical cluster analysis) was performed using IBM SPSS Statistics software (SPSS Inc., Chicago, IL, USA, 2011).

3. RESULTS AND DISCUSSION

3.1. IMPACT OF POTENTIALLY TOXIC METALS BOUND TO $PM_{2.5}$

Depending on the source of the emission, a wide range of organic and inorganic chemical species make up particulate matter, which is widely present in the environment. Mining and metallurgical operations, traffic (cars, railroads), various incineration processes, power plants, and household activities are the primary urban sources of these chemical species in particulate matter. Although natural sources account for most of the particulate matter in rural areas, anthropogenic activities also have a moderate impact. An air particle's chemical species composition varies across time and place, making it non-uniform. The concentrations of the analyzed elements (Cu, Pb, Zn, Cr, Cd, Al, Ni, Fe, and Mn) in the $PM_{2.5}$ samples are shown in Fig. 2. All metals were detected in the collected samples. From the data, Fe had the highest concentration in $PM_{2.5}$, followed by Zn > Mn > Ni > Cu > Al > Pb > Cr > Cd.

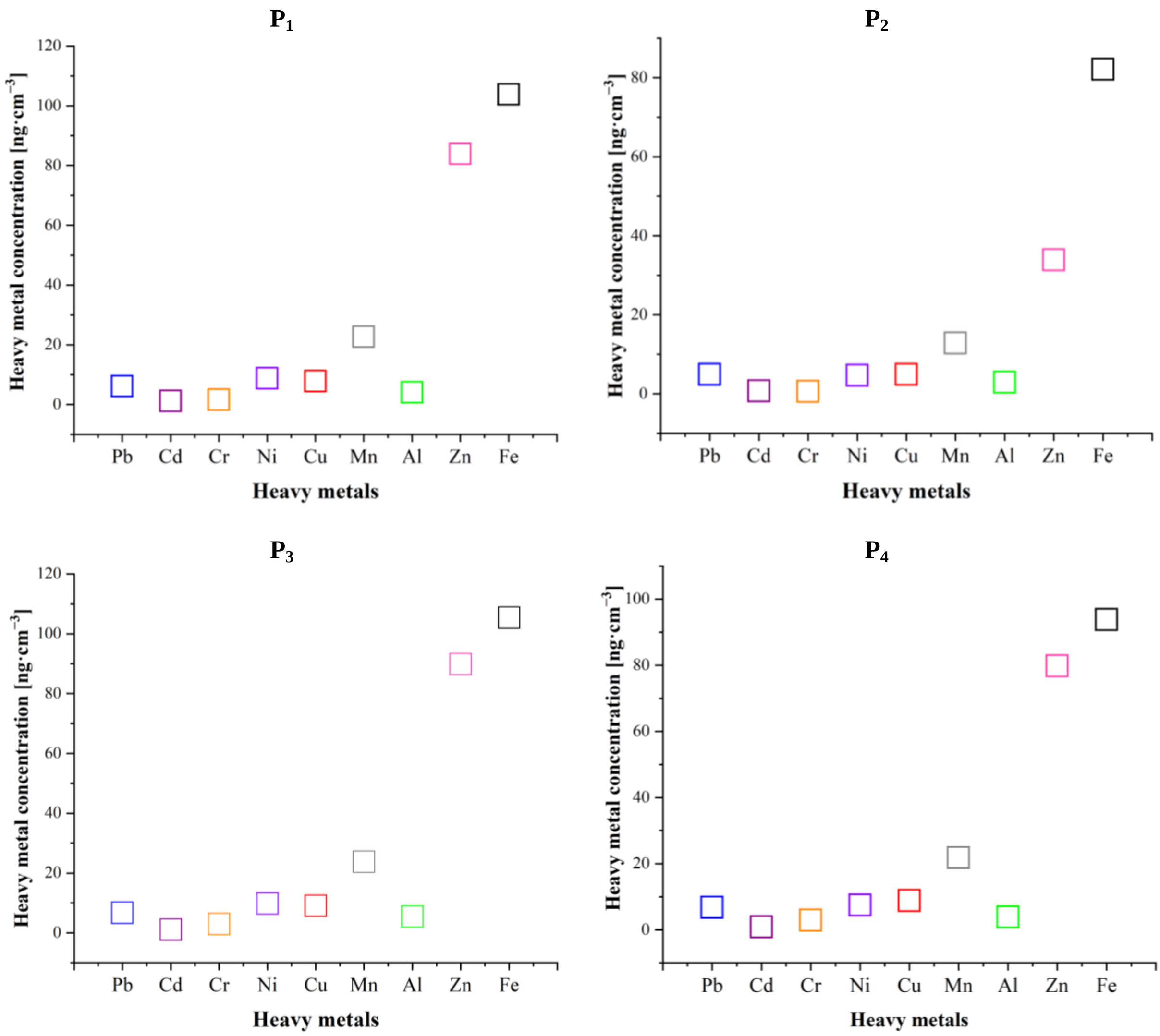


Figure 2. Toxic metal levels in monitored areas of Targoviste city: P_1 - western part, industrial area; P_2 - northern part, residential area; P_3 - southern part, industrial activities and traffic; and P_4 – southeastern part, traffic and industrial/comercial area.

The lead concentration for the four analyzed samples ranged from 4.9±1.2 ng·cm^{-3} (P_2) to 6.7±2.4 ng·cm^{-3} (P_4). For cadmium, the lowest value was recorded in sample point P_2 (0.7±0.3 ng·cm^{-3}), while the highest was in sample point P_1 (1.4±0.1 ng·cm^{-3}). Based on Cr concentration, the four analyzed samples are ranked as P_2 (0.61±0.01 ng·cm^{-3}) < P_1 (1.60±0.01 ng·cm^{-3}) < P_4 (2.80±0.4 ng·cm^{-3}) < P_3 (2.98±0.03 ng·cm^{-3}). The values of Ni and Cu are similar across the four analyzed samples; the lowest values were recorded in sample point P_2 (4.7±0.1 ng·cm^{-3} for Ni and 4.6±0.2 ng·cm^{-3} for Cr), and the highest values were recorded in sample point P_3 (9.8±0.4 ng·cm^{-3} for Ni and 9.4±0.1 ng·cm^{-3} for Cr). In sample point P_2, the lowest concentrations of manganese and aluminium were recorded (12.9±0.3 ng·cm^{-3} and 2.8±0.3 ng·cm^{-3}, respectively), while in sample point $P_{3,}$ the values were twice as high for manganese (23.8±0.1 ng·cm^{-3}) and 5.5±0.6 ng·cm^{-3} for aluminium. For zinc, the concentration in sample point P_3 (89.7±4.0 ng·cm^{-3}) was almost three times higher than in sample point P_2 (33.8±3.1 ng·cm^{-3}). The highest values were recorded for Fe, with concentrations ranging from 82.4±2.1 ng·cm^{-3} in sample point P_2 to 105.6±7.1 ng·cm^{-3} in sample point P_3. The results indicated that iron is one of the elements most readily released into suspended particles, and that the main source is industrial activity. In addition, concentrations of each metal varied among the monitored points. Most toxic metals are adsorbed onto suspended particles at the surface or incorporated into their composition through chemical processes that render them bioavailable to the exposed population. Based on the data presented previously, the concentration values of the nine metals analyzed show that in area P_2 (residential district), exposure to metals is much lower than in area P_3, characterized by high anthropogenic stationary point sources, including an industrial platform (metal smelter, metal treatment and coating), road traffic, and commercial and residential areas.

The research conducted by Kebe et al. [33] on two areas similar to P1–P4 (from the present research) reveals that the metal concentration was on the order of 10^{-3}–10^{-1} μg·m^{-3}, much lower than in the present research. Goodarzi et al. [34] investigated $PM_{2.5}$ concentrations in highly polluted urban and industrial areas of the Middle East, and their results are alarming. Indeed, the studied areas of the Middle East are highly polluted compared to the four areas of Targoviste, Romania. For example, Al ranged from 493 ng·cm^{-3} to 485 ng·cm^{-3}, and Cu values ranging from 198 ng·cm^{-3} to 212 ng·cm^{-3} were reported, while the concentration of iron ranged from 536 ng·cm^{-3} to 612 ng·cm^{-3} according to the data reported by Goodarzi et al. [35]. The study conducted by Abdulaziz et al. [35] focused on evaluating the concentration level of toxic metals in $PM_{2.5}$ in the city of Mecca in Saudi Arabia, the reported values were much higher: Mn (54.3±13.3 ng·cm^{-3}) > Pb (40.3±9.2 ng·cm^{-3}) > Ni (20.5±12.9 ng·cm^{-3}) > Cr (18.2±6.2 ng·cm^{-3}) > Cd (13.0±3.1 ng·cm^{-3}), compared to the present study (Mn > Ni > Pb > Cr > Cd). Comparing the data from the research conducted by Trako et al. [36] on the air in Sarajevo, Bosnia and Herzegovina with the average data reported in the present study, the level of toxic metals in $PM_{2.5}$ was: for Cd 2.93 ng·cm^{-3} > 0.98 ng·cm^{-3}; Cr 7.21 ng·cm^{-3} > 2.02 ng·cm^{-3}; Cu 12.02 ng·cm^{-3} > 7.65 ng·cm^{-3}; Fe 20.74 ng·cm^{-3} < 96.28 ng·cm^{-3}; Mn 20.74 ng·cm^{-3} > 20.28 ng·cm^{-3}; Ni 6.98 ng·cm^{-3} < 7.70 ng·cm^{-3}; Pb 8.74 ng·cm^{-3} > 6.13 ng·cm^{-3}; Zn 128.00 ng·cm^{-3} > 71.88 ng·cm^{-3}.

3.2. ASSESSING HEALTH RISKS FROM BIOACCESSIBLE TOXIC METALS BOUND TO $PM_{2.5}$

Toxic metals associated with $PM_{2.5}$ can enter the human body through inhalation, oral ingestion, and skin contact, accumulating over time and negatively affecting health [28].

Consequently, the assessment of health risks associated with atmospheric toxic metals has become an important research area. The assessment of health risks for adults and children across the four points of Targoviste City was conducted in high-activity areas. The daily intake of carcinogens (CDI_{ng}) (Table 4) and non-carcinogens (Table 5) for adults and children was calculated.

Table 4. Daily intake of toxic metals by ingestion (CDI_{ng} - cancerigen) for adults and children.

Sample	Toxic metals								
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**
Adults [$mg·kg^{-1}·d^{-1}$]									
P_1	$3.68·10^{-13}$	$7.25·10^{-14}$	$9.72·10^{-14}$	$5.31·10^{-13}$	$4.71·10^{-13}$	$1.37·10^{-12}$	$2.48·10^{-13}$	$5.07·10^{-12}$	$6.27·10^{-12}$
P_2	$2.96·10^{-13}$	$4.23·10^{-14}$	$3.68·10^{-14}$	$2.84·10^{-13}$	$2.96·10^{-13}$	$7.73·10^{-13}$	$1.75·10^{-13}$	$2.05·10^{-12}$	$4.96·10^{-12}$
P_3	$4.05·10^{-13}$	$6.64·10^{-14}$	$1.80·10^{-13}$	$5.92·10^{-13}$	$5.50·10^{-13}$	$1.44·10^{-12}$	$3.32·10^{-13}$	$5.43·10^{-12}$	$6.36·10^{-12}$
P_4	$4.11·10^{-13}$	$5.43·10^{-14}$	$1.75·10^{-13}$	$4.53·10^{-13}$	$5.31·10^{-13}$	$1.32·10^{-12}$	$2.36·10^{-13}$	$4.82·10^{-12}$	$5.66·10^{-12}$
Children [$mg·kg^{-1}·d^{-1}$]									
P_1	$8.59·10^{-13}$	$1.69·10^{-13}$	$2.27·10^{-13}$	$1.24·10^{-12}$	$1.10·10^{-12}$	$3.20·10^{-12}$	$5.78·10^{-13}$	$1.18·10^{-11}$	$1.46·10^{-11}$
P_2	$6.90·10^{-13}$	$9.86·10^{-14}$	$8.59·10^{-14}$	$6.62·10^{-13}$	$6.90·10^{-13}$	$1.80·10^{-12}$	$4.09·10^{-13}$	$4.78·10^{-12}$	$1.16·10^{-11}$
P_3	$9.44·10^{-13}$	$1.55·10^{-13}$	$4.20·10^{-13}$	$1.38·10^{-12}$	$1.28·10^{-12}$	$3.35·10^{-12}$	$7.75·10^{-13}$	$1.27·10^{-11}$	$1.49·10^{-11}$
P_4	$9.58·10^{-13}$	$1.27·10^{-13}$	$4.09·10^{-13}$	$1.06·10^{-12}$	$1.24·10^{-12}$	$3.07·10^{-12}$	$5.50·10^{-13}$	$1.12·10^{-11}$	$1.32·10^{-11}$

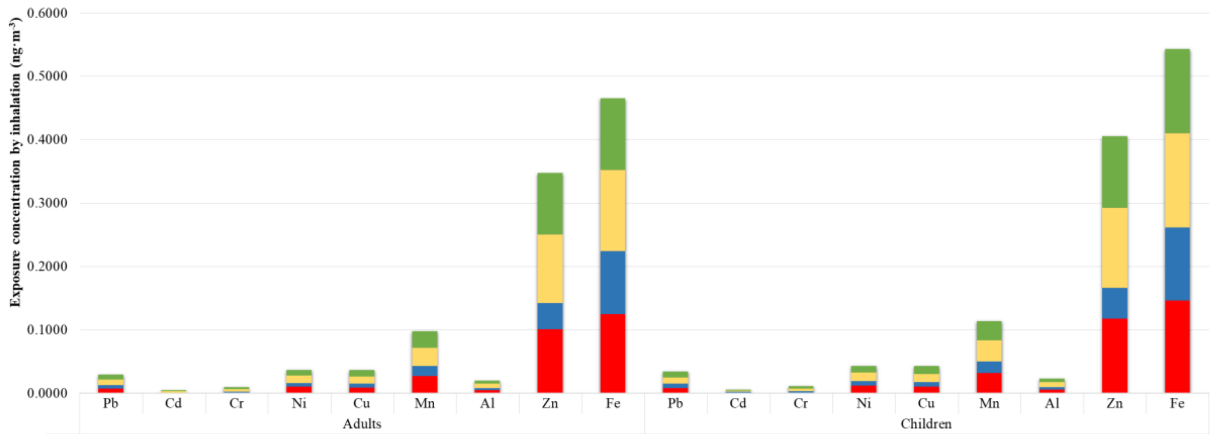
The daily carcinogenic intake from ingestion for adults ranges from $3.68·10^{-14}$ $mg·kg^{-1}·d^{-1}$ to $6.36·10^{-12}$ $mg·kg^{-1}·d^{-1}$, and for children, from $8.59·10^{-14}$ $mg·kg^{-1}·d^{-1}$ to $1.49·10^{-11}$ $mg·kg^{-1}·d^{-1}$. The CDI_{ng} – cancerigen values for adults and children do not present any risk, being a maximum of 10^{-12} $mg·kg^{-1}·d^{-1}$ for adults and 10^{-11} $mg·kg^{-1}·d^{-1}$ for children.

Table 5. Daily intake of toxic metals by ingestion (CDI_{ng} – non-cancerigen) for adults and children.

Sample	Toxic metals								
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**
Adults [$mg·kg^{-1}·d^{-1}$]									
P_1	$1.07·10^{-12}$	$2.11·10^{-13}$	$2.84·10^{-13}$	$1.55·10^{-12}$	$1.37·10^{-12}$	$4.00·10^{-12}$	$7.22·10^{-13}$	$1.48·10^{-11}$	$1.83·10^{-11}$
P_2	$8.63·10^{-13}$	$1.23·10^{-13}$	$1.07·10^{-13}$	$8.28·10^{-13}$	$8.63·10^{-13}$	$2.25·10^{-12}$	5.11·10–13	$5.97·10^{-12}$	$1.45·10^{-11}$
P_3	$1.18·10^{-12}$	$1.94·10^{-13}$	$5.25·10^{-13}$	$1.73·10^{-12}$	$1.60·10^{-12}$	$4.19·10^{-12}$	$9.69·10^{-13}$	$1.58·10^{-11}$	$1.86·10^{-11}$
P_4	$1.20·10^{-12}$	$1.59·10^{-13}$	$5.11·10^{-13}$	$1.32·10^{-12}$	$1.55·10^{-12}$	$3.84·10^{-12}$	$6.87·10^{-13}$	$1.41·10^{-11}$	$1.65·10^{-11}$
Children [$mg·kg^{-1}·d^{-1}$]									
P_1	$1.00·10^{-11}$	$1.97·10^{-12}$	$2.65·10^{-12}$	$1.45·10^{-11}$	$1.28·10^{-11}$	$3.73·10^{-11}$	$6.74·10^{-12}$	$1.38·10^{-10}$	$1.71·10^{-10}$
P_2	$8.05·10^{-12}$	$1.15·10^{-12}$	$1.00·10^{-12}$	$7.73·10^{-12}$	$8.05·10^{-12}$	$2.10·10^{-11}$	$4.77·10^{-12}$	$5.57·10^{-11}$	$1.35·10^{-10}$
P_3	$1.10·10^{-11}$	$1.81·10^{-12}$	$4.90·10^{-12}$	$1.61·10^{-11}$	$1.50·10^{-11}$	$3.91·10^{-11}$	$9.04·10^{-12}$	$1.48·10^{-10}$	$1.73·10^{-10}$
P_4	$1.12·10^{-11}$	$1.48·10^{-12}$	$4.77·10^{-12}$	$1.23·10^{-11}$	$1.45·10^{-11}$	$3.58·10^{-11}$	$6.41·10^{-12}$	$1.31·10^{-10}$	$1.54·10^{-10}$

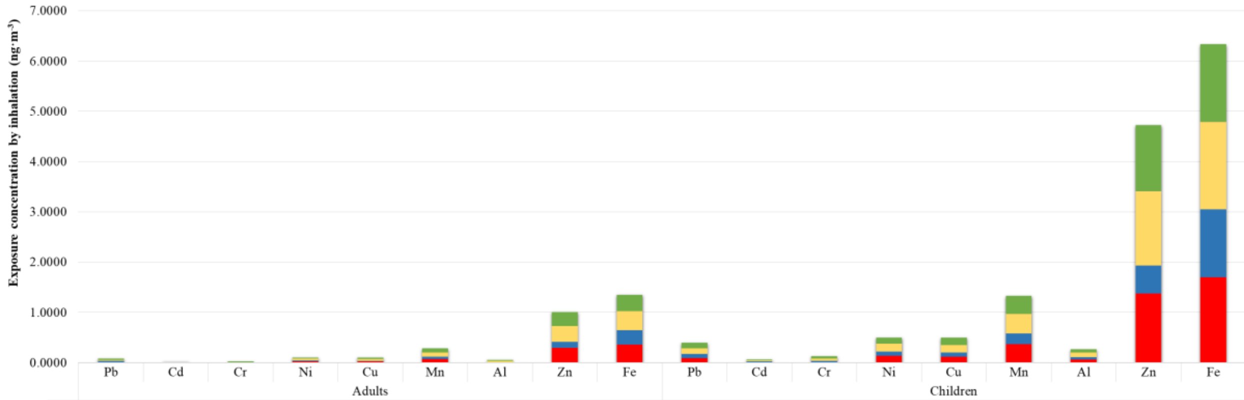
The values of the daily non-carcinogenic intake by ingestion in adults ranged from $1.07·10^{-13}$ $mg·kg^{-1}·d^{-1}$ to $1.86·10^{-11}$ $mg·kg^{-1}·d^{-1}$. The differences related to the P_1-P_4 points are small, suggesting a uniform distribution of exposure during the monitored period. In the case of children, the values ranged from $1.00·10^{-12}$ $mg·kg^{-1}·d^{-1}$ to $1.73·10^{-10}$ $mg·kg^{-1}·d^{-1}$. Pb, Cd, Cr, and Ni have values at very low levels, while the other metals follow the trend Fe > Zn > Al > Cu > Mn. For CDI_{ng} (carcinogenic and non-carcinogenic), children show a higher vulnerability to exposure than adults. The very low values of CDI_{ng} suggest that exposure through ingestion of $PM_{2.5}$ particles in the Targoviste municipality area is limited.

Inhalation exposure to toxic metals results in strong adsorption of these substances in the respiratory system and poses a significant risk to human health. Particles loaded with toxic metals can trigger respiratory, immune, and cardiovascular diseases [37].



	Pb	Cd	Cr	Ni	Cu	Mn	Al	Zn	Fe	Pb	Cd	Cr	Ni	Cu	Mn	Al	Zn	Fe
	Adults									Children								
P4	0.0082	0.0011	0.0035	0.0091	0.0106	0.0263	0.0047	0.0964	0.1133	0.0096	0.0013	0.0041	0.0106	0.0124	0.0307	0.0055	0.1124	0.1322
P3	0.0081	0.0013	0.0036	0.0118	0.0110	0.0287	0.0066	0.1086	0.1273	0.0094	0.0015	0.0042	0.0138	0.0128	0.0335	0.0077	0.1267	0.1485
P2	0.0059	0.0008	0.0007	0.0057	0.0059	0.0155	0.0035	0.0409	0.0992	0.0069	0.0010	0.0009	0.0066	0.0069	0.0180	0.0041	0.0478	0.1157
P1	0.0074	0.0014	0.0019	0.0106	0.0094	0.0274	0.0050	0.1013	0.1254	0.0086	0.0017	0.0023	0.0124	0.0110	0.0320	0.0058	0.1182	0.1463

Figure 3. Exposure concentration by inhalation (EC_{inh} – carcinogen) for adults and children.



	Pb	Cd	Cr	Ni	Cu	Mn	Al	Zn	Fe	Pb	Cd	Cr	Ni	Cu	Mn	Al	Zn	Fe
	Adults									Children								
P4	0.0240	0.0032	0.0102	0.0264	0.0310	0.0768	0.0137	0.2811	0.3304	0.1118	0.0148	0.0477	0.1233	0.1447	0.3584	0.0641	1.3118	1.5419
P3	0.0236	0.0039	0.0105	0.0345	0.0321	0.0838	0.0194	0.3167	0.3713	0.1101	0.0181	0.0490	0.1611	0.1496	0.3912	0.0904	1.4778	1.7326
P2	0.0173	0.0025	0.0021	0.0166	0.0173	0.0451	0.0102	0.1194	0.2892	0.0805	0.0115	0.0100	0.0773	0.0805	0.2104	0.0477	0.5573	1.3496
P1	0.0215	0.0042	0.0057	0.0310	0.0275	0.0800	0.0144	0.2955	0.3656	0.1003	0.0197	0.0265	0.1447	0.1282	0.3732	0.0674	1.3792	1.7063

Figure 4. Exposure concentration by inhalation (EC_{inh} – non-carcinogenic) for adults and children.

Targoviste city has a strong history in the metallurgy of special steels and related industries. The main sources of risk in areas P_1, P_3, and P_4 are direct emissions from processing plants, which release fine particles rich in metals, including lead, cadmium, chromium, nickel, and manganese, into the air. Another important cause is the resuspension of industrial dust caused by air movement. Car and rail traffic in the four studied zones also increases inhalation exposure through non-exhaust emissions from brake pads, discs, and tires, which release copper, zinc, and iron. Chromium and nickel come mostly from the corrosion of car components, while rail transport generates intense friction that releases microparticles of chromium, manganese, and iron into the atmosphere. Urban dynamics in the vicinity of commercial areas also contribute to increased inhalation exposure to metals. Central and/or densely populated commercial areas, with old, tall buildings and narrow streets between them, prevent the dispersion of pollutants carried by the wind from industrial areas or from intensive circular arteries, thereby causing the accumulation of harmful particles. Overall, the results for Exposure concentration by inhalation (EC_{inh}) indicate that inhalation exposure is dominated by Fe, Zn, and Mn, while Cd, Cr, and, to a lesser extent, Pb contributes the least to the total exposure. The differences observed between adults and children are driven by the parameters used in the exposure assessment model, not by variations in atmospheric concentrations.

The dermal absorbed dose is the mass of a contaminant that crosses the skin barrier and enters systemic circulation. This index assesses the risk arising from direct skin contact with dust or airborne particles contaminated with metals. Carcinogenic and non-carcinogenic DAD_{derm} values for adults and children are presented in Tables 6 and 7, respectively.

Table 6. Dermal absorbed dose (DAD_{derm}) carcinogenic for adults and children.

Sample	Toxic metals								
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**
Adults [$mg·kg^{-1}·d^{-1}$]									
P_1	$1.47·10^{-14}$	$2.89·10^{-16}$	$3.88·10^{-15}$	$2.12·10^{-14}$	$1.88·10^{-14}$	$5.47·10^{-14}$	$9.88·10^{-15}$	$2.02·10^{-13}$	$2.50·10^{-13}$
P_2	$1.18·10^{-14}$	$1.69·10^{-16}$	$1.47·10^{-15}$	$1.13·10^{-14}$	$1.18·10^{-14}$	$3.08·10^{-14}$	$6.99·10^{-15}$	$8.17·10^{-14}$	$1.98·10^{-13}$
P_3	$1.61·10^{-14}$	$2.65·10^{-16}$	$7.18·10^{-15}$	$2.36·10^{-14}$	$2.19·10^{-14}$	$5.73·10^{-14}$	$1.33·10^{-14}$	$2.17·10^{-13}$	$2.54·10^{-13}$
P_4	$1.64·10^{-14}$	$2.17·10^{-16}$	$6.99·10^{-15}$	$1.81·10^{-14}$	$2.12·10^{-14}$	$5.25·10^{-14}$	$9.40·10^{-15}$	$1.92·10^{-13}$	$2.26·10^{-13}$
Children [$mg·kg^{-1}·d^{-1}$]									
P_1	$2.41·10^{-14}$	$4.73·10^{-16}$	$6.35·10^{-15}$	$3.47·10^{-14}$	$3.08·10^{-14}$	$8.96·10^{-14}$	$1.62·10^{-14}$	$3.31·10^{-13}$	$4.10·10^{-13}$
P_2	$1.93·10^{-14}$	$2.76·10^{-16}$	$2.41·10^{-15}$	$1.85·10^{-14}$	$1.93·10^{-14}$	$5.05·10^{-14}$	$1.14·10^{-14}$	$1.34·10^{-13}$	$3.24·10^{-13}$
P_3	$2.64·10^{-14}$	$4.34·10^{-16}$	$1.18·10^{-14}$	$3.87·10^{-14}$	$3.59·10^{-14}$	$9.39·10^{-14}$	$2.17·10^{-14}$	$3.55·10^{-13}$	$4.16·10^{-13}$
P_4	$2.68·10^{-14}$	$3.55·10^{-16}$	$1.14·10^{-14}$	$2.96·10^{-14}$	$3.47·10^{-14}$	$8.60·10^{-14}$	$1.54·10^{-14}$	$3.15·10^{-13}$	$3.70·10^{-13}$

Table 7. Dermal absorbed dose (DAD_{derm}) non-carcinogenic for adults and children.

Sample	Toxic metals								
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**
Adults [$mg·kg^{-1}·d^{-1}$]									
P_1	$4.29·10^{-14}$	$8.43·10^{-16}$	$1.13·10^{-14}$	$6.18·10^{-14}$	$5.48·10^{-14}$	$1.60·10^{-13}$	$2.88·10^{-14}$	$5.90·10^{-13}$	$7.29·10^{-13}$
P_2	$3.44·10^{-14}$	$4.92·10^{-16}$	$4.29·10^{-15}$	$3.30·10^{-14}$	$3.44·10^{-14}$	$9.00·10^{-14}$	$2.04·10^{-14}$	$2.38·10^{-13}$	$5.77·10^{-13}$
P_3	$4.71·10^{-14}$	$7.73·10^{-16}$	$2.09·10^{-14}$	$6.89·10^{-14}$	$6.39·10^{-14}$	$1.67·10^{-13}$	$3.87·10^{-14}$	$6.32·10^{-13}$	$7.41·10^{-13}$
P_4	$4.78·10^{-14}$	$6.32·10^{-16}$	$2.04·10^{-14}$	$5.27·10^{-14}$	$6.18·10^{-14}$	$1.53·10^{-13}$	$2.74·10^{-14}$	$5.61·10^{-13}$	$6.59·10^{-13}$
Children [$mg·kg^{-1}·d^{-1}$]									
P_1	$2.81·10^{-13}$	$5.52·10^{-15}$	$7.41·10^{-14}$	$4.05·10^{-13}$	$3.59·10^{-13}$	$1.04·10^{-12}$	$1.89·10^{-13}$	$3.86·10^{-12}$	$4.78·10^{-12}$
P_2	$2.26·10^{-13}$	$3.22·10^{-15}$	$2.81·10^{-14}$	$2.16·10^{-13}$	$2.26·10^{-13}$	$5.89·10^{-13}$	$1.33·10^{-13}$	$1.56·10^{-12}$	$3.78·10^{-12}$
P_3	$3.08·10^{-13}$	$5.06·10^{-15}$	$1.37·10^{-13}$	$4.51·10^{-13}$	$4.19·10^{-13}$	$1.10·10^{-12}$	$2.53·10^{-13}$	$4.14·10^{-12}$	$4.85·10^{-12}$
P_4	$3.13·10^{-13}$	$4.14·10^{-15}$	$1.33·10^{-13}$	$3.45·10^{-13}$	$4.05·10^{-13}$	$1.00·10^{-12}$	$1.80·10^{-13}$	$3.67·10^{-12}$	$4.32·10^{-12}$

Comparing the results presented in Tables 6 and 7, it is observed that DAD_{derm} values are higher in children than in adults for all metals. The difference between adults and children is attributable to the body surface area-to-body mass ratio and the duration of exposure; therefore, children are the group most vulnerable to dermal exposure to heavy metals in $PM_{2.5}$. Across the four points where $PM_{2.5}$ samples were collected, the distribution of metals is relatively uniform and not concentrated at a single point; however, dermal exposure accounts for only a fraction of the total exposure.

The risk coefficients for ingestion, skin absorption, and inhalation are presented in Tables 8 and 9 and in Fig. 5. At HQ values below 1.0, the risk level is acceptable; however, at values above 1.0, the risk is present, and air decontamination measures and regular monitoring are required [28].

Table 8. Hazard quotient by ingestion (HQ_{ing}) for adults and children.

Sample code	Toxic metals						
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Zn**
Adults							
P_1	$3.07\cdot10^{-10}$	$2.11\cdot10^{-10}$	$9.45\cdot10^{-11}$	$7.75\cdot10^{-10}$	$3.43\cdot10^{-11}$	$2.80\cdot10^{-7}$	$4.93\cdot10^{-11}$
P_2	$2.47\cdot10^{-10}$	$1.23\cdot10^{-10}$	$3.58\cdot10^{-11}$	$4.14\cdot10^{-10}$	$2.16\cdot10^{-11}$	$1.58\cdot10^{-7}$	$1.99\cdot10^{-11}$
P_3	$3.37\cdot10^{-10}$	$1.94\cdot10^{-10}$	$1.75\cdot10^{-10}$	$8.63\cdot10^{-10}$	$4.01\cdot10^{-11}$	$2.93\cdot10^{-7}$	$5.28\cdot10^{-11}$
P_4	$3.42\cdot10^{-10}$	$1.59\cdot10^{-10}$	$1.70\cdot10^{-10}$	$6.60\cdot10^{-10}$	$3.87\cdot10^{-11}$	$2.68\cdot10^{-7}$	$4.68\cdot10^{-11}$
Children							
P_1	$2.86\cdot10^{-9}$	$1.97\cdot10^{-9}$	$8.82\cdot10^{-10}$	$7.23\cdot10^{-9}$	$3.21\cdot10^{-10}$	$2.61\cdot10^{-6}$	$4.60\cdot10^{-10}$
P_2	$2.30\cdot10^{-9}$	$1.15\cdot10^{-9}$	$3.34\cdot10^{-10}$	$3.86\cdot10^{-9}$	$2.01\cdot10^{-10}$	$1.47\cdot10^{-6}$	$1.86\cdot10^{-10}$
P_3	$3.15\cdot10^{-9}$	$1.81\cdot10^{-9}$	$1.63\cdot10^{-9}$	$8.05\cdot10^{-9}$	$3.74\cdot10^{-10}$	$2.74\cdot10^{-6}$	$4.93\cdot10^{-10}$
P_4	$3.19\cdot10^{-9}$	$1.48\cdot10^{-9}$	$1.59\cdot10^{-9}$	$6.16\cdot10^{-9}$	$3.62\cdot10^{-10}$	$2.51\cdot10^{-6}$	$4.37\cdot10^{-10}$

HQ_{ing} values are extremely low for both adults and children, ranging between 10^{-11} and 10^{-6}. The trend of the analyzed heavy metals is Mn > Ni > Pb > Cd. For Cu, Cr, and Zn, the values are even lower. Exposure to $PM_{2.5}$-bound metals through ingestion does not pose a risk to the adult or child population in Targoviste municipality across the four monitored areas.

Table 9. Hazard quotient by dermal adsorption (HQ_{derm}) for adults and children.

Sample code	Toxic metals						
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Zn**
Adults							
P_1	$1.22\cdot10^{-11}$	$3.37\cdot10^{-11}$	$1.51\cdot10^{-10}$	$7.73\cdot10^{-10}$	$1.37\cdot10^{-12}$	$1.12\cdot10^{-8}$	$1.97\cdot10^{-12}$
P_2	$9.84\cdot10^{-12}$	$1.97\cdot10^{-11}$	$5.72\cdot10^{-11}$	$4.13\cdot10^{-10}$	$8.61\cdot10^{-13}$	$6.29\cdot10^{-9}$	$7.94\cdot10^{-13}$
P_3	$1.35\cdot10^{-11}$	$3.09\cdot10^{-11}$	$2.79\cdot10^{-10}$	$8.61\cdot10^{-10}$	$1.60\cdot10^{-12}$	$1.17\cdot10^{-8}$	$2.11\cdot10^{-12}$
P_4	$1.37\cdot10^{-11}$	$2.53\cdot10^{-11}$	$2.72\cdot10^{-10}$	$6.59\cdot10^{-10}$	$1.55\cdot10^{-12}$	$1.07\cdot10^{-8}$	$1.87\cdot10^{-12}$
Children							
P_1	$8.02\cdot10^{-11}$	$2.21\cdot10^{-10}$	$9.88\cdot10^{-10}$	$5.06\cdot10^{-9}$	$8.98\cdot10^{-12}$	$7.31\cdot10^{-8}$	$1.29\cdot10^{-11}$
P_2	$6.44\cdot10^{-11}$	$1.29\cdot10^{-10}$	$3.74\cdot10^{-10}$	$2.70\cdot10^{-9}$	$5.64\cdot10^{-12}$	$4.12\cdot10^{-8}$	$5.20\cdot10^{-12}$
P_3	$8.81\cdot10^{-11}$	$2.03\cdot10^{-10}$	$1.83\cdot10^{-9}$	$5.64\cdot10^{-9}$	$1.05\cdot10^{-11}$	$7.66\cdot10^{-8}$	$1.38\cdot10^{-11}$
P_4	$8.94\cdot10^{-11}$	$1.66\cdot10^{-10}$	$1.78\cdot10^{-9}$	$4.32\cdot10^{-9}$	$1.01\cdot10^{-11}$	$7.02\cdot10^{-8}$	$1.22\cdot10^{-11}$

HQ_{derm} presents the lowest values among the three exposure routes (ingestion, inhalation, and dermal adsorption) analysed. The values are of the order of 10^{-13} to 10^{-8}. These values are approximately seven orders of magnitude below the risk limit (HQ = 1). The values of the risk coefficient by ingestion and adsorption (Tables 8 and 9) for the points P_1-P_4 fall within an acceptable risk level, being sub-unitary for both adults and children.

Taking into account the fact that EC_{inh} (Equation 3), which is the basis for establishing the inhalation risk coefficient (HQ_{inh}) according to Equation (5), the inhalation exposure concentration is expressed as $\mu g\cdot m^{-3}$, which means that the samples presented in Fig. 5 have subdimensional values.

The HQ_{inh} values (Fig. 5) calculated for inhalation exposure to heavy metals associated with $PM_{2.5}$ particles in Targoviste municipality were below the reference value (HQ = 1) for all metals analysed and for all sampling points for both adults and children. These results indicate that no non-carcinogenic adverse effects from inhalation exposure are anticipated at the contamination levels measured in the studied areas. Spatially, point P_3 presented the highest HQ_{inh} values for most metals, suggesting a more pronounced influence of local emission sources in this area. In contrast, the lowest values were recorded for point P_2, indicating a lower level of inhalation exposure.

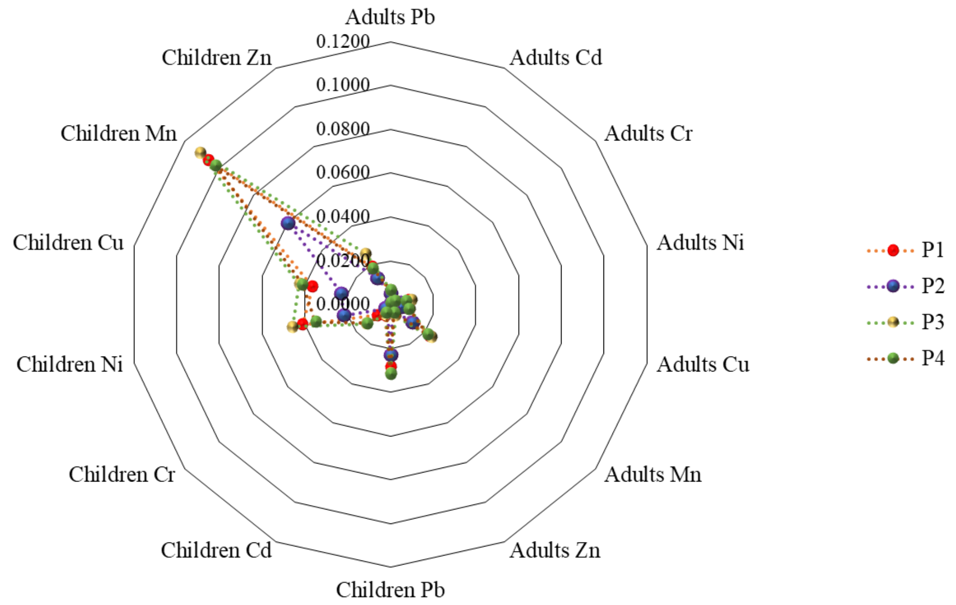


Figure 5. Hazard quotient by inhalation (HQ_{inh}) for adults and children.

The inhalation carcinogenic risk was calculated for adults and children (Table 10). In the range of 10^{-6} and $\cdot 10^{-4}$, the CR value indicates a manageable or acceptable cancer risk. If the CR is greater than 10^{-4}, it implies an unacceptable cancer risk, while CR < 10^{-6} does not indicate a significant cancer risk [38,39]. According to Table 10, the four areas analysed do not pose a carcinogenic risk requiring management and are at an acceptable level.

Table 10. Carcinogenic risk by inhalation (CR_{inh}) for adults and children.

Sample	Toxic metals							
	Pb	**Cd**	**Cr**	**Ni**	**Pb**	**Cd**	**Cr**	**Ni**
P_1	$2.58 \cdot 10^{-10}$	$5.07 \cdot 10^{-11}$	$6.81 \cdot 10^{-11}$	$3.72 \cdot 10^{-10}$	$1.20 \cdot 10^{-9}$	$2.37 \cdot 10^{-10}$	$3.18 \cdot 10^{-10}$	$1.74 \cdot 10^{-9}$
P_2	$2.07 \cdot 10^{-10}$	$2.96 \cdot 10^{-11}$	$2.58 \cdot 10^{-11}$	$1.99 \cdot 10^{-10}$	$9.67 \cdot 10^{-10}$	$1.38 \cdot 10^{-10}$	$1.20 \cdot 10^{-10}$	$9.27 \cdot 10^{-10}$
P_3	$2.83 \cdot 10^{-10}$	$4.65 \cdot 10^{-11}$	$1.26 \cdot 10^{-10}$	$4.14 \cdot 10^{-10}$	$1.32 \cdot 10^{-9}$	$2.17 \cdot 10^{-10}$	$5.88 \cdot 10^{-10}$	$1.93 \cdot 10^{-9}$
P_4	$2.87 \cdot 10^{-10}$	$3.80 \cdot 10^{-11}$	$1.23 \cdot 10^{-10}$	$3.17 \cdot 10^{-10}$	$1.34 \cdot 10^{-9}$	$1.78 \cdot 10^{-10}$	$5.72 \cdot 10^{-10}$	$1.48 \cdot 10^{-9}$
Category	**Adults**				**Children**			

According to Table 10, the four areas analysed do not present a carcinogenic risk that requires management and do not indicate a significant risk of cancer. Considering the study conducted by Haque et al. [39] for Pb, Cd, Cr and Cu, the carcinogenic risk values for adults and children in the present study are lower.

The calculation of the individual pollution index aims to assess the pollution level of each metal in a sample type and helps to identify specific sources, such as emissions from industrial activities, coal combustion, or traffic in the monitored area. Common metals assessed include lead, cadmium, and nickel (Fig. 6). Pb is often linked to vehicle emissions; Cd and Ni are often associated with industrial activity [40].

The risk levels for the individual pollution index (PI_i) are $PI_i \leq 1$ indicates clean air or low pollution; $1 < PI_i \leq 3$ indicates moderate pollution; and $PI_i > 3$ indicates strong pollution [41]. The three metals for which the PI_i was calculated are ordered as follows: for Pb > Cd > Ni, the values for Pb varying between $9.80 \cdot 10^{-3}$ (P_2) – $1.36 \cdot 10^{-2}$ (P_4), for Cd the calculated values varied from $1.40 \cdot 10^{-1}$ (P_2) to $2.40 \cdot 10^{-1}$ (P_1), and for Ni the PI_i values were recorded in the range $2.35 \cdot 10^{-1}$ (P_2) – $4.90 \cdot 10^{-1}$ (P_3).

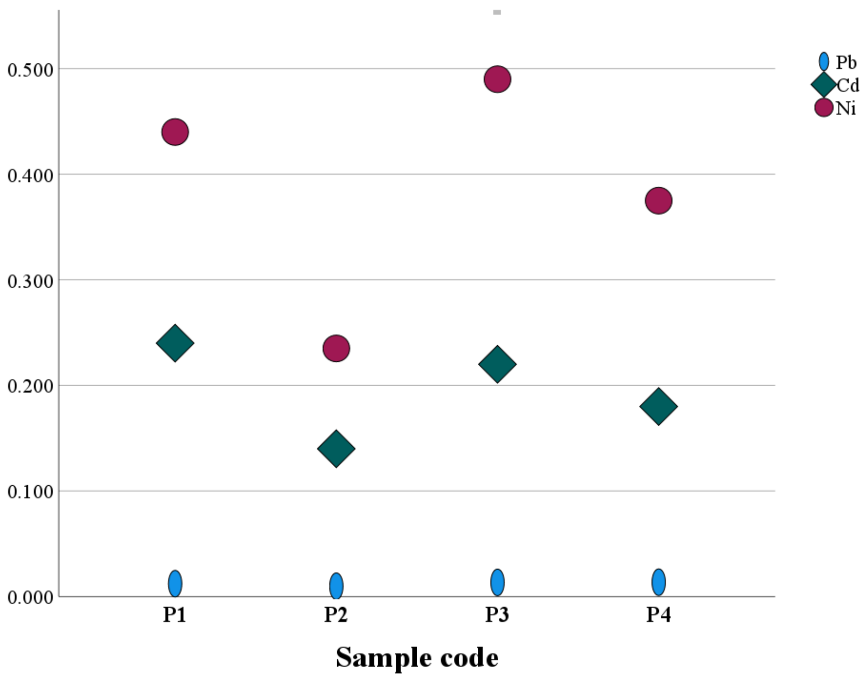


Figure 6. Individual pollution index (PI_i) for lead, cadmium, and nickel.

According to the previously presented risk levels, no area exceeds level 1, indicating that the air is clean and pollution is low. Considering that PI_i values for nickel approach 1, constant monitoring is required.

3.3. STATISTICAL ANALYSIS

Descriptive statistical analysis for the four sampling points (Table 11) highlights the variability in toxic metal concentrations. The evaluation of these differences facilitates the identification of contamination sources, separating the impact of anthropogenic activities from the natural geological background.

Table 11. Descriptive statistics of toxic metal concentrations determined in the analyzed samples.

Metal	Range [ng·cm⁻³]	Minimum [ng·cm⁻³]	Maximum [ng·cm⁻³]	Mean [ng·cm⁻³]	Mean Std. Error	Std. Deviation [ng·cm⁻³]	Variance [ng·cm⁻³]
Pb	1.90	4.90	6.80	6.12	0.43	0.87	0.76
Cd	0.50	0.70	1.20	0.97	0.11	0.22	0.04
Cr	2.37	0.61	2.98	2.02	0.56	1.13	1.28
Ni	5.10	4.70	9.80	7.70	1.10	2.21	4.88
Cu	4.20	4.90	9.10	7.65	0.95	1.91	3.67
Mn	11.00	12.80	23.80	20.27	2.52	5.05	25.50
Al	2.60	2.90	5.50	4.10	0.53	1.07	1.14
Zn	56.00	33.90	89.90	71.87	12.82	25.65	658.13
Fe	23.30	82.10	105.40	96.27	5.37	10.75	115.64

Descriptive statistical analysis highlights differences in the concentrations of toxic metals determined in the samples. The average values show that Fe presented the highest average concentration (96.28 $ng{\cdot}cm^{-3}$), followed by Zn (71.88 $ng{\cdot}cm^{-3}$) and Mn (20.28 $ng{\cdot}cm^{-3}$). The lowest average concentrations were recorded for Cd (0.98 $ng{\cdot}cm^{-3}$) and Cr (2.03 $ng{\cdot}cm^{-3}$). Regarding the dispersion of the data, the highest amplitude of the values (range) was observed for Zn (56.0 $ng{\cdot}cm^{-3}$), followed by Fe (23.3 $ng{\cdot}cm^{-3}$) and Mn

(11.0 ng·cm⁻³), suggesting a more pronounced variability of these elements between samples. This more pronounced variability suggests spatio-temporal dynamics dependent on local point sources of emissions, such as industrial activities or traffic, characteristic of the Targoviste urban area. In contrast, Cd exhibited the lowest variation (0.5 $ng \cdot cm^{-3}$), indicating a relatively uniform distribution. The standard deviation values confirm the same trend, with Zn (SD = 25.65) and Fe (SD = 10.75) showing the highest variability, while Cd (SD = 0.22) and Pb (SD = 0.87) exhibit lower dispersion.

To identify linear associations among toxic metals in the fine particle fraction ≤ 2.5 and to obtain preliminary indications of their emission sources (i.e., traffic, combustion, or industrial activities), Pearson correlation coefficient analysis was applied (Table 12).

Table 12. Pearson correlation matrix for toxic metal concentrations in samples.

Correlations										
Metal		**Pb**	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**
Pb	Pearson Correlation	1	0.607	0.971*	0.815	0.991**	0.919	0.763	0.922	0.737
	Sig. (2-tailed)		0.393	0.029	0.185	0.009	0.081	0.237	0.078	0.263
Cd	Pearson Correlation	0.607	1	0.464	0.918	0.694	0.871	0.730	0.868	0.967*
	Sig. (2-tailed)	0.393		0.536	0.082	0.306	0.129	0.270	0.132	0.033
Cr	Pearson Correlation	0.971*	0.464	1	0.748	0.955*	0.831	0.786	0.836	0.642
	Sig. (2-tailed)	0.029	0.536		0.252	0.045	0.169	0.214	0.164	0.358
Ni	Pearson Correlation	0.815	0.918	0.748	1	0.884	0.961*	0.927	0.961*	0.988*
	Sig. (2-tailed)	0.185	0.082	0.252		0.116	0.039	0.073	0.039	0.012
Cu	Pearson Correlation	0.991**	0.694	0.955*	0.884	1	0.957*	0.829	0.960*	0.817
	Sig. (2-tailed)	0.009	0.306	0.045	0.116		0.043	0.171	0.040	0.183
Mn	Pearson Correlation	0.919	0.871	0.831	0.961*	0.957*	1	0.838	1.000**	0.937
	Sig. (2-tailed)	0.081	0.129	0.169	0.039	0.043		0.162	0.000	0.063
Al	Pearson Correlation	0.763	0.730	0.786	0.927	0.829	0.838	1	0.840	0.876
	Sig. (2-tailed)	0.237	0.270	0.214	0.073	0.171	0.162		0.160	0.124
Zn	Pearson Correlation	0.922	0.868	0.836	0.961*	0.960*	1.000**	0.840	1	0.935
	Sig. (2-tailed)	0.078	0.132	0.164	0.039	0.040	0.000	0.160		0.065
Fe	Pearson Correlation	0.737	0.967*	0.642	0.988*	0.817	0.937	0.876	0.935	1
	Sig. (2-tailed)	0.263	0.033	0.358	0.012	0.183	0.063	0.124	0.065	

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

Analysis of Pearson correlation coefficients revealed strong positive relationships among most of the investigated metals, suggesting possible common sources or similar accumulation mechanisms. The strongest correlation was observed between Mn and Zn ($r = 1.000$; $p < 0.001$), indicating that the variation in the two elements across the analyzed samples was nearly identical. In addition, very strong correlations were noted between Pb and Cu ($r = 0.991$; $p = 0.009$), Ni and Fe ($r = 0.988$; $p = 0.012$), Pb and Cr ($r = 0.971$; $p = 0.029$), and Cd and Fe ($r = 0.967$; $p = 0.033$). Statistically significant correlations ($p < 0.05$) were also identified between: Cr and Cu ($r = 0.955$); Ni and Mn ($r = 0.961$); Ni and Zn ($r = 0.961$); Cu and Mn ($r = 0.957$); and Cu and Zn ($r = 0.960$). The high correlations observed in Table 12 among Pb, Cu, and Cr can be attributed to common anthropogenic sources, such as traffic and industrial activities. The association between Ni and Fe suggests contributions from emissions from combustion processes and metallurgical activities, while the very strong correlations between Mn and Zn may reflect the influence of road traffic and the contribution of suspended particles from the urban environment. Similar associations have been reported in previous studies on $PM_{2.5}$, where the Pb, Cd, and Zn group were linked to mixed anthropogenic sources (traffic, industrial and domestic activities), while the association between Fe and Ni was linked to industrial processes, fuel combustion, and particulate emissions related to traffic [42-44].

Hierarchical cluster analysis (HCA) was performed using Ward's linkage approach and Euclidean distance to identify potential commonalities in the behaviour and origins of the metals under study (Fig. 7). An association between Fe and Al can be inferred from the fact that these elements are considered markers of geogenic sources and resuspended dust [43-45]. The results of the cluster analysis are consistent with the Pearson correlation matrix, which revealed strong positive relationships among most of the investigated elements. However, the interpretation of the identified clusters should be approached with caution, given the small sample size, which may affect cluster stability. The association of Zn and Fe with other elements may suggest the predominance of geogenic sources or distinct accumulation processes, whereas the association of Pb, Cd, Cr, and Ni may be attributed to common anthropogenic sources, such as traffic, industrial and domestic activities, or combustion processes.

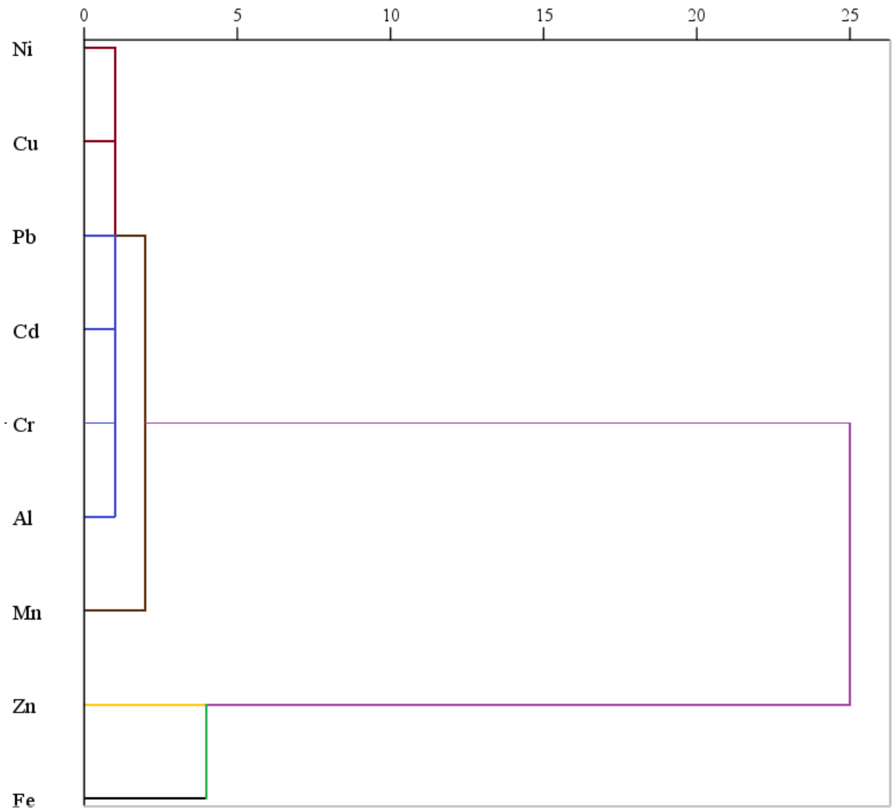


Figure 7. Hierarchical cluster dendrogram of toxic metals obtained using Ward's method and squared Euclidean distance.

The dendrogram revealed two major clusters, indicating distinct patterns of association between metals and their sources, which influence their accumulation in the environment. The first cluster includes Ni, Cu, Pb, Cd, Cr, and Mn, metals that show high spatial similarity among the sampling points (Fig. 1). The association between Ni and Cu suggests a common origin of the metals, primarily linked to industrial activities, metallurgical processes, and wear of vehicle components. High concentrations of these metals were observed, particularly at points P_1, P_3, and P_4, which are characterised by industrial activity and heavy traffic. The maximum values of heavy metal concentrations were recorded in the P_3 area, which highlights the significant influence of emissions generated simultaneously by industrial activities and road traffic. Also, the association between Pb and Cd suggests common anthropogenic sources, often linked to industrial emissions, fossil fuel combustion, and road traffic. The concentrations of these metals were consistently lower in point P_2, located in the residential area in the north of the city, while higher values were observed in points P_3 and P_4.

This distribution highlights the major influence of traffic and industrial activities on the accumulation of Pb and Cd. Chromium is frequently associated with industrial processes and traffic-generated emissions, while aluminium is often considered an indicator of urban dust resuspension. The high concentrations observed at points P_3 and P_4 indicate a high contribution from both industrial emissions and resuspension processes.

The second major cluster comprises Zn and Fe, which appear distinctly grouped and separated from the other analyzed metals. The association between these two metals indicates a dominant common source. Zinc and iron are recognised in the specialized literature as indicators of traffic-generated emissions, particularly from tire wear, braking systems, corrosion of vehicle metal components, and dust resuspension [46,47]. The HCA analysis indicates that heavy metal contamination in the monitored areas is predominantly driven by the combined effects of industrial emissions, road and rail traffic, and urban dust resuspension. The contamination gradient observed among the monitored points follows the trend $P_3 > P_1 \approx P_4 > P_2$, highlighting the dominant impact of industrial activities and traffic related to toxic metal accumulation in the urban area.

4. CONCLUSIONS

$PM_{2.5}$ pollution, in terms of metal concentrations, directly affects the quality of life in urban areas. $PM_{2.5}$ sources provide essential information for prioritising the most serious pollution risks and for adapting control strategies by targeting activities that continuously generate these pollutants. This research aims to improve understanding of how metals bound to PM2.5 collected in an urban area (with a well-established emission source) can pose a risk to human health.

Overall, the CDI_{ng} values obtained for all investigated metals are very low, ranging between 10^{-14} mg·kg^{-1}·d^{-1} and 10^{-10} mg·kg^{-1}·d^{-1}, indicating a very low daily intake of metals through ingestion of $PM_{2.5}$ particles. At the same time, the small variations in EC_{inh} values between the four samples indicate a relatively uniform distribution of metals during the monitored period. Altogether, the results suggest that the population's inhalation exposure to metals associated with $PM_{2.5}$ is reduced in both adults and children. For the investigated metals, it was observed that $PM_{2.5}$-related metals for children had higher DAD_{derm} values compared to the values obtained in adults, ranging between 10^{-16} and 10^{-13}.

Statistical analysis revealed significant associations among the analyzed metals, indicating common sources of contamination in the monitored areas (P_1–P_4). The results showed that Pb, Cd, Ni, Cu, Cr, Al, and Mn are predominantly associated with industrial emissions, road and rail traffic, and atmospheric deposition, whereas Zn and Fe are mainly associated with sources driven by mechanical wear and particle resuspension.

In the future, multi-year statistics on metals bound to $PM_{2.5}$ monitoring may reveal that additional measures are needed to meet the European Union's recommendations. It is also important to assess sources in urban areas with major industrial activities that frequently lead to environmental problems, and to combine data on potentially toxic metals associated with $PM_{2.5}$ with medical data on risk to human health. Evidence on loaded metals, $PM_{2.5}$, and potentially toxic metals can further support these assessments.

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