Investigation of Heavy Metals Content in Airborne Particles from Ploiesti, Romania

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This study aims to evaluate the concentrations of heavy metals in airborne particulate matter (PM) collected in Ploiesti city (Romania) during the monitoring campaigns performed in 2015. Various health effects of airborne PM, from less serious to very serious ones, are often associated with its chemical speciation. The heavy metals bounded on PM may accumulate in human body by inhalation and can produce both short-term and long-term negative health effects especially in children and sensitive people. We investigated several heavy metals associated with PM$_{2.5}$ collected in 12 relevant sampling points to estimate their potential impact on urban population health. PM samples were collected on 37 mm quartz fiberglass filters using a precision optical instrument i.e., DustTrak DRX8533EP. The deposition of elements on the surface of samples was determined using a scanning electron microscope (SEM). The analysis and quantification of trace elements were performed using inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The experiments indicated that samples of PM contained heavy metals in the following order Zn > Ni > Cr > Pb > As > Cd. Monitoring of elemental composition in atmospheric particles can contribute to a better air quality management.

Keywords: PM$_{2.5}$, nickel, chromium, arsenic, air quality mapping, scanning electron microscopy

Health effects associated with Particulate Matter
The chemical composition of particulate matter (PM) is important to be determined for assessing and reducing the adverse health effects in affected population. The commonly found components of airborne PM include sulfates, nitrates, ammonium ions, hydrogen ions, other inorganic ions (i.e., Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ and Cl$^-$), particle-bound water, heavy metals (e.g., V, Cr, Cd, Co, Ni, Pb, Hg), elemental carbon, organic compounds, and crustal [1-4]. The main urban sources of these compounds associated with PM are related to anthropogenetic activities e.g., mining, building, industrial emissions, road traffic (automobiles, railways), various combustion processes, power plants, and domestic heating.

Exposure to ambient air pollution leads to negative human health impacts and contribute significantly on increasing of premature death due to cardiovascular and respiratory diseases [5-7]. Literature presents recent complex studies performed at multiple spatial scales revealing PM$_{2.5}$ (particles with an aerodynamic diameter lower than 2.5 µm) as one of the most important risk factors responsible for premature death [8,9]. Some studies, conducted by the American Cancer Society (ACS), used the size of 2.5µm as an indicator in order to assess the relationship between the exposure to airborne concentrations of PM$_{2.5}$ and mortality level [10].

The potential negative health effects of airborne fine particles (PM$_{2.5}$) are linked to their capability to penetrate into the lung, contributing to the decreasing of its functions and leading to an alteration of lung tissues [11]. Current knowledge regarding the association of health effects of fine particulates with particle size or with their chemical components is still unclear. The negative health effects are expected to affect more significantly the children, because they inhale a higher dose of airborne particulate matter compared to adults. Firstly, because children are more active than adults are, and they have higher breathing rates [12], secondarily, the particles deposited on air-tissue interface will be higher than of adults due to their lung capacity [13,14]. Consequently, exposure to PM will affect lung development in children, and will chronically reduce the lung growth rate, affecting long-term lung function [15,16].

Various health effects of PM$_{2.5}$, from less serious to very serious ones, are often associated with its chemical speciation. Even if the scientific studies do not indicate a specific component of PM that could be the cause of the observed epidemiological effects, they suggest that, at least partially, the metallic elements that are bounded on atmospheric particles contribute to the carcinogenic and toxic effects associated with exposure to PM [17,18]. In the absence of biodegradation, heavy metals bounded on PM may accumulate in human body following the inhalation. This can produce both short-term and long-term negative health effects especially for children and sensitive people [19]. Monitoring of elemental composition of atmospheric particles can play a crucial role in improving the policies regarding air pollution reduction by using the tracing of metals to identify the sources of emissions [20].

Particulate Matter Toxicity
Airborne particulates contain a complex mixture of particles that exists in the atmosphere as liquid droplets or solids that vary in size, mass, number, surface area, shape, as well as chemical composition, solubility and origin. Consequently, the identification of the toxic constituents

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of PM is a challenging task. International Agency for Research on Cancer (IARC) suggested that the toxic metal content of PM_{2.5} is one of the causative factors associated with adverse respiratory health effects and classified several metals, including chromium (Cr), cadmium (Cd), lead (Pb) and nickel (Ni), as potential carcinogenic agents.

Regarding the PM toxicity, the Central European Air Quality and Respiratory Health (CESAR) study, which was realized on the young people with age between 7 and 11 years using 17 sites from Europe, including Romania, has demonstrated that the number of lymphocytes (B, CD4+, CD8 and NK) increased in locations where the concentrations of PM were higher [21]. A positive relationship was identified between PM_{2.5} concentrations and serum IgE level as well. This relationship was not observed for PM_{10} or PM_{2.5-10}. Finally, the results of this study suggest that airborne fine particles have a more evident impact on immune defense function of human body than larger particles.

According to many toxicological studies, high metal contents of PM are directly associated with the oxidative stress and pro-inflammatory response in lung macrophages [22,23]. Research studies found a direct correlation between the viability reduction of human lung epithelial cells (A549) and the specific metallic elements as As, Cr, Zn, Cu and Mn of fine and submicrometric fractions of particulate matter [24]. In the same way, the elements such as Fe, Cd and Cr have a predominant effect in damaging DNA.

PM-induced toxicity depends on both particle composition and its source. Experimental studies conducted on animals (rats exposed at different sites and source related PM) revealed that the strongest toxic effects, especially pro-inflammatory responses, were obtained for sites having a high traffic volume [25]. According to these studies, PM originated from the urban traffic site had the strongest cytotoxic effect. Consequently, the higher pro-inflammatory responses were associated with the highest concentrations of Zn, Cu, Ni and Fe.

In Romania, some PM studies characterized several main urban areas, including Ploiesti city [26,27]. These are particularly focused on the assessment of spatial and temporal variation of PM_{2.5} or PM_{10}. There are also advanced research projects [28] that are ongoing in Romania, which use new communication technologies and a multidimensional approach to monitor and forecast the air quality. These advanced networks can complement the existing official monitoring infrastructures for air pollution control aiming a better results in protecting people health.

In this context, the present work aimed to assess the outdoor pollution with fine and submicrometric particulate matter that includes the ultrafine fraction and their heavy metals content in an urban-industrial area from Southeast of Romania, e.g., Ploiesti city (222000 permanent residents). We investigated several toxic metals i.e., Cd, Ni, Pb, Zn, Cr, and As associated with PM_{2.5} collected in the monitoring campaigns performed in 2015 in the urban area using 12 relevant sampling points.

The concentrations of these metals (ng·m^{-3}) determined in PM_{2.5} collected samples were compared with the levels reported by the Agency for Toxic Substances and Disease Registry (ATSDR), 2004/107/CE directive and other international studies e.g., European and US Environmental Protection Agencies, World Health Organization, to establish the potential impact on the respiratory problems reported in the studied area.

**Experimental part**

**Sampling method**

Monitoring campaigns were performed in 12 sampling points of Ploiesti city between January and October 2015 to assess the potential exposure of population to increased concentrations of heavy metals. The selection of 12 monitoring points envisaged a quasi-radial positioning, taking into account their proximity to the schools, and kindergartens (fig. 1).

Monitoring campaigns were performed in each month after a minimum of two or three days following a rainy day because it is well-known that an increased relative humidity reduces the PM concentrations. The PM_{2.5} measurements were performed using a precision optical portable monitoring system with a laser beam (Dusttrak^{TM} DRX 8533EP with environmental enclosure). The sampling time was one hour at each point to ensure a sufficient PM_{2.5} mass for heavy metal detection, and the log interval was 3 s. The flow rate of the external pump connected to the PM sensor was 3 L·min^{-1}, which is close to the human respiratory physiological characteristics. PM_{2.5} samples were collected on 37 mm quartz fiberglass filters (QM-A Whatman, Maidstone, Kent, UK) resulting 16 discs for each point. Before and after sampling, the filters were weighed using a thermo-analytical electronic balance with a precision of ± 1 µg to insure a proper mass detection. The fiberglass discs, mounted in specific cassettes, were stored at -20°C before their analysis.

**Analysis of PM samples**

According to US Environmental Protection Agency (EPA) method 3052 [29] with modification, the samples were digested with 9 mL HNO_{3} (67% Merck, high purity) in PTFE-PTM vessels. The mixtures were heated progressively in three steps, to 200 °C using a TOPwave Microwave-assisted
Results and discussions

Electron microscopy analysis of PM samples

Scanning electron microscopy is useful to provide supplementary information regarding the morphology, size, and elemental composition of individual particles [31]. We used such technique to explore the particularities of submicrometric fraction monitored in Ploiești urban area. Since the flow rate of the external pump was 3 L min\(^{-1}\), which is close to the human respiratory system, the mass deposition on quartz fiber discs was lower than the ones obtained using high volume samplers (flow of 68 m\(^3\) h\(^{-1}\)) or low volume samplers (2.3 m\(^3\) h\(^{-1}\)). Consequently, figures 2, 3, and 4 presents details with particulates on fiberglass filters in Ploiești showing submicrometric particles, as well as a larger particles.

Figure 2 shows the morphological structure of analyzed filters using different magnification orders. It can be observed that adsorbed particles presented different sizes and grouping in patches, clusters of particles, probably due to the atmospheric humidity or a specific deposition pattern.

Figures 3 and 4 presents SEM images of the quartz fiber filters after particle collection (e.g., P5 and P7 points) at high magnification order. It can be observed that many particles are agglomerated and embedded in the fiberglass filter.

SEM techniques allow the analyses of available data for single particles, which supports the identification of potential sources of emission or specific particle characterization using clustering algorithms [32]. Based on their classification of the sampled particles, we compared the morphology of the particles collected in Ploiești and identified metal particles. A detailed analysis of heavy metals was performed to determine their concentrations in PM.

Heavy metals content in particulate matter

The adverse effects of toxic metals on human health are well known. Heavy metals associated with fine and submicrometric PM have a clear negative influence on the biological functions affecting the normal development and growth of body tissues and their proper functioning (14,16,33). PM with less than 10 \(\mu\)m in size (especially PM\(_{10}\) or PM\(_{2.5}\)) can contain high concentrations of heavy metals with toxicological properties, e.g., Cd, Ni, Pb, Zn, Cr, As and Pb. Among the PM\(_{10}\) fraction, the alveolar fraction (PM\(_{2.5}\)) contained 90-93% of these metals, followed by the bronchial fraction (PM\(_{1-2.5}\) and PM\(_{2.5-10}\)) and trachea-pharyngeal fraction (PM\(_{10}\)).

Airborne particles with bounded heavy metals are easily driven by the wind, and they can be found, sometimes at far distances from the place of emissions into the atmosphere. Main emissions of heavy metals in Ploiești city originate from various industrial sources (especially from oil refineries) and diffuse sources such as non-industrial combustion processes, and traffic. The amount of emitted metals depends on the fuel composition (concentration of metals in fuel), the temperature of combustion, and physical and chemical properties of the element [34]. Heavy vehicles are the largest source of NO\(_x\), PM\(_{2.5}\) and heavy metals, while cars are important sources of CO, NH\(_3\) and VOCs. The experiments indicated that...
samples of PM collected in Ploiesti city during 2015, contained heavy metals in the following order based on established concentration i.e., Zn > Ni > Cr > Pb > As > Cd.

Table 1 shows the concentrations of heavy metals from PM$_{2.5}$ samples collected in 2015, using 12 monitoring points. For each metal, the concentration varied largely between sampling locations.

Monitoring campaigns were performed in 12 sampling points of Ploiesti city between January and October 2015 to assess the potential exposure of population to increased concentrations of heavy metals. The selection of 12 monitoring points envisaged a quasi-radial positioning, taking into account their proximity to the schools, and kindergartens (fig. 1).

The results indicates that Zn was one of most frequent released into the suspended particles from north metalworking activities as principal emission source (i.e., P2, P8, P9) and from the roof tops with galvanized sheets. Zinc is relatively harmless compared to several other metal ions with similar chemical properties. Exposure to elevated doses of Zn might produce toxic effects; however, acute zinc intoxications are rare events [35]. Zn did not correlate with any metal from the dataset (p > 0.05).

Table 1

<table>
<thead>
<tr>
<th>Monitoring points</th>
<th>Coordinates</th>
<th>Cd</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Cr</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Grigore Cantacuzino 44°36'17.6&quot;N 25°00'34.9&quot;E</td>
<td>0.20</td>
<td>88.24</td>
<td>2.24</td>
<td>124.76</td>
<td>16.84</td>
<td>2.21</td>
</tr>
<tr>
<td>P2</td>
<td>Elena Dosanua 44°35'33.7&quot;N 25°00'55.0&quot;E</td>
<td>0.00</td>
<td>116.24</td>
<td>0.00</td>
<td>258.72</td>
<td>25.08</td>
<td>0.00</td>
</tr>
<tr>
<td>P3</td>
<td>Sorescu Vestului 44°36'58.4&quot;N 25°59'39.5&quot;E</td>
<td>0.24</td>
<td>2.04</td>
<td>2.16</td>
<td>48.76</td>
<td>8.84</td>
<td>2.28</td>
</tr>
<tr>
<td>P4</td>
<td>8 Martie 44°35'56.6&quot;N 26°00'16.8&quot;E</td>
<td>0.23</td>
<td>2.19</td>
<td>2.28</td>
<td>49.92</td>
<td>7.16</td>
<td>2.15</td>
</tr>
<tr>
<td>P5</td>
<td>Bulevardul Bucureşti 44°35'02.3&quot;N 26°02'04.7&quot;E</td>
<td>0.26</td>
<td>2.28</td>
<td>2.25</td>
<td>84.76</td>
<td>1.20</td>
<td>2.27</td>
</tr>
<tr>
<td>P6</td>
<td>Mihai Brava 44°35'22.1&quot;N 26°02'02.5&quot;E</td>
<td>0.32</td>
<td>43.96</td>
<td>3.16</td>
<td>152.40</td>
<td>0.00</td>
<td>3.16</td>
</tr>
<tr>
<td>P7</td>
<td>Mihai Eminescu (Pediatric Hospital) 44°35'54.1&quot;N 26°01'13.7&quot;E</td>
<td>0.22</td>
<td>59.84</td>
<td>2.21</td>
<td>172.36</td>
<td>0.00</td>
<td>2.04</td>
</tr>
<tr>
<td>P8</td>
<td>Strandrului 44°35'709.0&quot;N 25°02'39.5&quot;E</td>
<td>0.32</td>
<td>26.60</td>
<td>3.19</td>
<td>223.80</td>
<td>5.48</td>
<td>3.19</td>
</tr>
<tr>
<td>P9</td>
<td>Camelița 44°35'73.7&quot;N 25°00'39.0&quot;E</td>
<td>0.16</td>
<td>1.48</td>
<td>1.33</td>
<td>230.44</td>
<td>11.48</td>
<td>1.48</td>
</tr>
<tr>
<td>P10</td>
<td>Înăriții 44°35'611.1&quot;N 25°59'02.0&quot;E</td>
<td>0.18</td>
<td>8.36</td>
<td>2.19</td>
<td>72.48</td>
<td>4.20</td>
<td>2.13</td>
</tr>
<tr>
<td>P11</td>
<td>Romană 44°35'647.3&quot;N 26°01'7.6&quot;E</td>
<td>0.17</td>
<td>101.48</td>
<td>1.57</td>
<td>162.20</td>
<td>4.60</td>
<td>1.53</td>
</tr>
<tr>
<td>P12</td>
<td>Făgăraș 44°35'54.2&quot;N 26°02'57.4&quot;E</td>
<td>0.27</td>
<td>2.39</td>
<td>2.15</td>
<td>188.48</td>
<td>7.92</td>
<td>2.16</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>0.21</td>
<td>37.93</td>
<td>2.06</td>
<td>147.42</td>
<td>7.73</td>
<td>2.05</td>
</tr>
<tr>
<td><strong>SD</strong></td>
<td></td>
<td>0.09</td>
<td>43.33</td>
<td>0.84</td>
<td>71.96</td>
<td>7.32</td>
<td>0.82</td>
</tr>
<tr>
<td><strong>CV%</strong></td>
<td></td>
<td>39.99</td>
<td>114.24</td>
<td>40.54</td>
<td>48.81</td>
<td>94.63</td>
<td>40.24</td>
</tr>
<tr>
<td><strong>Min</strong></td>
<td></td>
<td>0.00</td>
<td>1.48</td>
<td>0.00</td>
<td>48.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td></td>
<td>0.23</td>
<td>17.48</td>
<td>2.20</td>
<td>157.30</td>
<td>6.32</td>
<td>2.16</td>
</tr>
<tr>
<td><strong>Max</strong></td>
<td></td>
<td>0.32</td>
<td>116.24</td>
<td>3.19</td>
<td>258.72</td>
<td>25.08</td>
<td>3.19</td>
</tr>
<tr>
<td><strong>Skewness</strong></td>
<td></td>
<td>-1.29</td>
<td>0.83</td>
<td>-1.21</td>
<td>-0.02</td>
<td>1.32</td>
<td>-1.18</td>
</tr>
<tr>
<td><strong>Kurtosis</strong></td>
<td></td>
<td>2.95</td>
<td>-0.92</td>
<td>2.91</td>
<td>-1.27</td>
<td>1.84</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images of PM$_{2.5}$ particles (SEM at x7000 and x12000) sampled in P7 point on 26.08. 2015; right figure shows two measured particles i.e., one of 1.76 µm and one of 0.86 µm in length.
Lead (Pb) that is one of the most toxic metals contained in collected samples ranged from 0 to 3.2 ng m$^{-3}$. Common emission sources are the exhaust gases from engines internal combustion and paved road dust due to deposition from previous emissions of leaded-gasoline vehicle exhaust. The recorded levels are similar to those reported for Yosemite, Hayden and Pacheco Pass in US [36]. The values are very low compared to the ones presented by Dai et al.[37] near steel plants excepting the concentration of 4.42 ng m$^{-3}$ recorded at Port Talbot in UK [38]. Pb was determined in all sampling points excepting P2 even this sampling point was close to a street with intense traffic. The low recorded concentrations are related with the use of fuels without lead and industrial filtering installation used in refineries to comply to the current environmental standards. Pb was highly correlated with Cd and As (p < 0.001) and inversely correlated with Cr (p < 0.01).

The carcinogenic risks of Ni, Cr and Cd as well as their harmful health effects through inhalation and ingestion were demonstrated by epidemiological studies [39]. In Ploiesti, Cd potentially originates from pigment and chemical industry, as well as from tire and brakes wear. Cd showed values in the 0-0.32 ng m$^{-3}$ interval. Cr results from fossil fuel combustion and vehicle emissions [40]. Cr recorded values between 0 and 25.08 ng m$^{-3}$. The concentrations for Cd and Cr are similar to the ones reported by Querol et al.[41] for two urban sites in Spain. Cr was also inversely correlated with Cd and As (p < 0.01).

Oil combustion, oil refining, residential heating and emissions from flaring emitted Ni in the area. Ni largely ranged between 1.48 and 116.24 ng m$^{-3}$, showing elevated values in the middle of the town due to the building
disposal, traffic conditions and air circulation in the area. Ni did not correlate with any other metals contained in PM.

In Ploiesti area, arsenic might originate from the processes of purifying industrial gases (removal of sulfur) in oil refineries. As concentrations ranged between 0.0 and 3.19 ng m⁻³, values which are close to the ones reported by Querol et al.[41]. Arsenic can cause cancer and skin lesions. It has also been associated with developmental effects, cardiovascular disease, neurotoxicity and diabetes [38]. Its positive correlation with Cd and Pb suggest common sources of emissions.

For a better understanding of the spatial variations of Ni, Cr and As concentrations (ng . m⁻³), figure 5 presents the interpolated isolines using inverse distance weighting algorithm applied to the data collected from 12 sampling points in Ploiesti city during January-October 2015. The maps contain also the spatial positions of the major schools and kindergartens in Ploiesti to facilitate the children exposure assessments.

Regarding the effects on human health caused by the airborne toxic-systemic pollutants including heavy metals, they cover a wide range of disorders due to the multitude of pollutants emitted into the atmosphere and their potentiated cumulative effect. A characteristic of these pollutants is their presence both in polluted air and in food chains, so that the entering into the body has multiple ways (inhalation of air, ingestion of water and food, and contact with objects). To protect the inner residents of Ploiesti, a complex monitoring network of fine and submicrometric PM and an adjacent cyberinfrastructure able must be developed to provide early warnings and forecasting of the PM pollution episodes [28].

Conclusions
Trace elements of fine particles were determined using ICP-MS analyses, which revealed important aspects of PM chemical composition as determinants of their toxicity in the studied urban agglomeration. The samples of PM contained heavy metals in the following order Zn > Ni > Cr > Pb > As > Cd. The results indicates that Zn ranged from 48.76 to 258.72 and did not correlate with any metal from the dataset (p > 0.05). Lead (Pb), which was determined in almost all sampling points, ranged in collected samples from 0 to 3.2 ng m⁻³ and was highly correlated with Cd and As (p < 0.001) and inversely correlated with Cr (p < 0.01). Cd showed values in the 0-0.32 ng m⁻³ interval. Cr recorded values between 0 and 25.08 ng m⁻³ and was inversely correlated with Cd and As (p < 0.01). Ni largely ranged between 1.48 and 116.24 ng m⁻³, having the higher values in the middle of the town due to traffic conditions and air circulation in the area. Ni did not correlate with any other metals contained in PM. In Ploiesti area, As concentrations ranged between 0.0 and 3.19 ng m⁻³. Its positive correlation with Cd and Pb suggest common sources of emissions.

Further experiments are required in Ploiesti area to assess the levels of benzo[a]pyrene (BaP) and other dangerous SVOCs contained in the particulate matter. The use of SEM analysis of sampled discs proved to be a promising technique in classifying single particles, which facilitates the identification of the emission source.

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