RISKS ASSESSMENT OF HEAVY METALS ON PUBLIC HEALTH ASSOCIATED WITH ATMOSPHERIC EXPOSURE TO $PM_{2.5}$ IN URBAN AREA

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Risk assessments can provide reliable information for medical investigations and especially in understanding PM-related health effects. Particulate air pollutants have been associated with increased respiratory, cardiovascular and cancer mortality and morbidity, and with other health problems. The fine fraction includes particles with aerodynamic diameters of < 2.5 μm, and is referred to as $PM_{2.5}$. These $PM_{2.5}$ has shown a closer association with human adverse health effects than either particle < 10 μm (PM_{10}) or total suspended particles (TSP). In addition, several studies suggest an association between motorized traffic-related air pollution and diminished pulmonary function and/or increased respiratory symptoms in children. It is well known that fine particles have high concentrations of many potentially toxic trace metals, such as cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc that can be incorporated into the body through inhalation. The purpose of this study was to evaluate the concentrations of $PM_{2.5}$, and a series of toxic metals, including Pb, Cd, Cr, Ni, Cu, Mn, Al, Sr, Fe and Zn, from eleven sampling points in Targoviste during spring period of 2013 in order estimate the potential impact on urban population health.

Key words: particulate matter, heavy metal, GFAAS.

1. INTRODUCTION

Fine particulate matter can represent a hazard to human health [1, 2]. Health effects can be associated with the number or the surface of the particles. Generally, the fine particles such as $PM_{2.5}$ are the result of the transition of the elements from the gas phase in the form of nuclei, which have condensed at a low equilibrium of the vapor [3]. The major components of airborne particulate matter 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, elemental carbon, organic compounds, and crustal material [4–6].

The main urban sources of these compounds in particulate matter are related to mining and metallurgical activities, traffic (automobiles, railways), various incineration processes, power plants, and domestic activity.

The $PM_{2.5}$ is formed by a series of chemical reactions of a free gas, which can be absorbed or dissolved. Most of the fines $PM_{2.5}$ are formed by condensation of the vapors produced by chemical reaction of several precursors in the gas phase. Thus these particles can be newly formed particles or can result from the addition of particulate elements formed from pre-existing particles [2]. The atmospheric lifetime of $PM_{2.5}$ varies from the order of days to weeks and they can be transported hundreds to thousands of kilometers [3].

Fine fraction of the particulate matter are mostly associated with respiratory, cardiovascular and cancer diseases. Size of 2.5 μm was used as an indicator for fine particles during some studies such as the one conducted by the American Cancer Society (ACS) in order to assess the relationship between exposure to airborne concentrations of $PM_{2.5}$ and mortality level [7]. Various health effects of $PM_{2.5}$, from less serious to very serious ones, are associated with its specific chemical and physical (but mostly chemical) components. Several studies [9, 10] pointed out the existence of an association between traffic pollution and diminished pulmonary function in children observable especially by the increase of the respiratory symptoms. In urban area $PM_{2.5}$ are mainly produced by particles emitted directly into the atmosphere and particles formed in the air from the chemical transformation of gaseous pollutants (secondary particles).

The toxic metal content of $PM_{2.5}$ has been suggested as causative factors associated with adverse respiratory health effects according to the International Agency for Research on Cancer (IARC), which classified several metals, including chromium, cadmium, lead and nickel, as potential cancer agents. Several studies [11, 12] showed that especially young population may have a genetic predisposition to lung damage and is more susceptible to toxic metal exposure from airborne particulate matter. One of the most known studies, coordinated by G.S. Leonardi [13], is CESAR study (Central European Air Quality and Respiratory Health). This study was achieved in 17 sites form Europe, including Romania, on the young people with age between 7 and 11 years. First of all, blood samples from these children were collected. The results showed that the number of lymphocytes increase in the same time with the exposure of PM concentrations. Lymphocytes such as B, $CD4^+$, CD8 and NK increased as the concentration of PM were higher. A positive relationship was identified between $PM_{2.5}$ and serum IgG level as well. This relationship was not observed for PM_{10} or $PM_{10\text{-}2.5}$. Finally, the results of this study suggest that airborne fine particles have a more powerful action than larger

particles on immune defense function of human. Other study [14] achieved in Germany, Munich, on the children with age up to two years, exposed at $PM_{2.5}$ between 11.9 and 21.9 μg/m^3, showed a cough without an infection and a dry cough at night. However the presence of wheezing, respiratory infections and rhinorrhea were not correlated with levels of $PM_{2.5}$ in the air. It can concluded that children's who are exposed at high concentrations of particulate matters can have serious health problems such as decrease of pulmonary ventilatory performance [15, 16], accentuation of bronchitis [17], increasing the blood viscosity [18] and thus the occurrence of serious cardiac diseases [19–21]. ACS study pointed out that the long-term exposures to $PM_{2.5}$ were strongly associated with mortality attributable to ischemic heart disease, dysrhythmias, and heart failure [22].

In this study several toxic metals (*i.e.* Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn, Fe and Sr) from $PM_{2.5}$ collected in 2013 from polluted urban area were investigated. The levels of these metals (ng/m^3) determined in $PM_{2.5}$ samples collected in Targoviste city were compared with levels reported by the Agency for Toxic Substances and Disease Registry (ATSDR), 2004/107/CE directive and other international studies (*i.e*. EPA, EEA, WHO) in order to establish if these metals could be responsible for respiratory problems reported in the studied area.

2. EXPERIMENTAL PART

2.1. SITE DESCRIPTION

According with the Convention's Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) [23] the $PM_{2.5}$ are measured carefully in Europe, especially in urban areas because the data showed that the urban level of $PM_{2.5}$ are considerably higher (15–20 μg/m^3), as compared to data from rural area (11–13 μg/m^3). If the urban area, which mostly are polluted by traffic, has an intense industrial activity, then the level of $PM_{2.5}$ are much higher (*e.g*. 20–30 μg/m^3) and the composition of $PM_{2.5}$ can be very toxic for human health. In this respect, in this study, Targoviste city was chosen, being well-known that metallurgical activity is the main cause of heavy metals load in $PM_{2.5}$. Eleven significant points were selected to investigate the children exposure in the urban area (in the proximity of kindergartens, schools, hospital, health clinic). These include locations (*e.g.* P1-P11, Fig. 1) in the proximity of traffic, industrial and domestic sources as well. $PM_{2.5}$ can be significantly higher near such sources, increasing the risk of adverse health effects.

Fig. 1 – $PM_{2.5}$ sampling points in Targoviste city.

2.2. SAMPLING PROCEDURE

A portable monitoring system that uses an infrared beam projected in a measuring chamber provided the $PM_{2.5}$ measurements, which were performed in eleven representative monitoring points of the Targoviste urban area (*e.g.* kindergartens, schools etc., Fig. 1). GPS measurements established their exact position, and facilitated digital maps production. Samples were collected in accordance with EMEP manual for sampling and chemical analysis [23] and Guidelines for the Measurement of Ambient Air Pollutants [24] as well as the sampling methods presented in [25, 26]. The samples were collected during the spring period of 2013 year. Each filter contained the material collected in a 24-h period. Filters were stored in Petri dishes and kept in desiccators until the conditioning process was achieved. Filters were weighted (mean of tree weights) until a standard deviation of 0.00002 g was achieved.

2.3. GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY TECHNIQUE

The collected filters were analyzed through laboratory methods (*i.e.*, GFAAS techniques) to determine the heavy metal composition of captured fine particulates. Graphite furnace atomic absorption spectrophotometry (GFAAS) is an analytical technique designed to perform the quantitative analysis of metals in a wide variety of samples (*e.g.* liquids, solids). Certainly, for GFAAS was necessary some preparation requirements of collected samples including extraction, digestion, dilution [23–29]. The samples were digested on a hot plate by using a Berghof Microwave digestion. After digestion acidified extracts were filtered through a

Whatman 41 filter paper, previously rinsed with 1% HNO_3. The metals were analysed by a graphite furnace atomic absorption spectrometry (GFAAS) using ZEEnit 700 P spectrometer. This spectrometer combines the furnace with powerful background correction (*i.e.* Deuterium and Zeeman background correction) which besides forms the basis for optimal results. The calibration curves for all three metals demonstrated good linearity over the concentration range (0.1 to 10.0 mg/L) with correlation coefficients, R^2 in the range of 0.996 to 0.999. The precision among the values of each calibration data point (replicate analysis) was calculated with the help of 95% confidence intervals based on triplicate measurements. The determination of the LOD is very important for metals under investigation. LOD here means the lowest concentration that can be detected with GFAAS. In this study the LODs of all metals were determined by using the calibration data; y-intercept and standard deviation of the regression (Table 1). The accuracy and precision of the results were further evaluated by measuring a certified reference sample (*i.e.* NIST SRM 1648a, *Urban Particulate Matter*). On average, recoveries from spike blanks fluctuated from 91% for Sr to 101% for Pb, while recoveries for the SRM 1648 ranged from 94% for Zn to 104% for Ni. No substantial loss occurred in the sample preparation process.

Table 1

Correlation LOD with coefficients, R^2

Metal	R^2	LOD [µg/L]
Pb	0.999	10
Cd	0.999	22
Cr	0.998	19
Ni	0.997	12
Cu	0.999	11
Mn	0.996	15
Al	0.997	16
Zn	0.996	18
Fe	0.996	12
Sr	0.999	20

3. RESULTS AND DISCUSSION

Different components of $PM_{2.5}$ may be involved in eliciting the diverse effects. Several $PM_{2.5}$ components were shown to be able to induce oxygen radical formation. However, the surface and composition of $PM_{2.5}$ seem to be more important determinants of particle effects than mass. Several metals, including chromium, lead, nickel and cadmium, but also metal-free ultrafine particles, are strong inducers of inflammation. Concerning the potential effect of air pollution, particularly PM, on children's health, the most frequent clinical diagnostics

recorded from hospital admissions of children in Targoviste Emergency Hospital in 2013 were bronchiolitis, interstitial acute pneumonia with wheezing, recurrent wheezing and asthma.

Mostly, heavy metals occur in particulate matter in an easy soluble form, which makes them bioavailable to the exposed young peoples. Thus, it is well known that the gaseous chromium is rarely encountered in the environment and this is due to the high boiling point of chromium [30]. But, in the environment, chromium occurs as particle-bound chromium or chromium dissolved in water droplets. The compounds of chromium from environment can be chromium (VI) trioxide (chromic acid) or soluble chromium (VI) salt aerosols. These soluble forms of chromium may produce serious health effects than insoluble forms. Studies showed that the exposure to chromium (VI) trioxide lead to some problems to the nasal mucosa and even perforation of the nasal septum [30]. Thus, from Fig. 2 and Table 2 it can be seen that the average of cadmium concentration was high for the P1 sample, 1.2 ± 0.1 ng/m^3, (where occurs an intense industrial activity, intense automobiles and railway traffic, commercial, and residential heating), and lower for P8 sample (residential district), such as 0.61 ± 0.01 ng/m^3. Cadmium might occurs in air particles as inorganic and organic soluble or insoluble salts [30, 31]. As example, chromium chloride has a high solubility in water, but cadmium oxide and cadmium carbonate, which are relatively insoluble in water (but may be dissolved at pH gastric fluid), has a high toxicity similar with the soluble cadmium salts. The average of chromium concentration for all sampling points collected from Targoviste ranged between 2.88 ± 0.03 ng/m^3 in P10 sample (with high anthropogenic stationary point sources steel plant, *e.g.* metal smelter, metal treatment and coating, commercial, and residential heating) and 0.68 ± 0.01 ng/m^3 in P4 sample (only traffic, domestic activity, residential heating had influence on the metal levels). The industrial activities from Targoviste are the main cadmium sources released in to the air. Strontium is released into the atmosphere as a result of natural sources, especially from soil. Strontium oxide (SrO) is the principal chemical species in the air. This oxide reacts quickly with water from atmosphere forming ions such as Sr^{2+} and $SrOH^+$. The average concentration of strontium in the analyzed samples ranged between 0.23 ± 0.03 ng/m^3 in P10 and 0.14 ± 0.01 ng/m^3 in P11. The average value for strontium levels obtained in the urban area of Targoviste was lower than average strontium concentration (*i.e.* 20 ng/m^3), in United States urban air measured in 1985 [30].

Based on these aspects it can be concluded that the average concentrations of Cr, Cd and Sr, in the six samples (*i.e.*, P1, P2, P3, P5, P6 and P10, Figs. 1, 2 and Table 2) which were consistently higher during the spring months (March-May) can be attributed to the soluble or insoluble forms of these metals, which occurred due to the traffic and domestic activities, but in equal measure to the industrial activity.

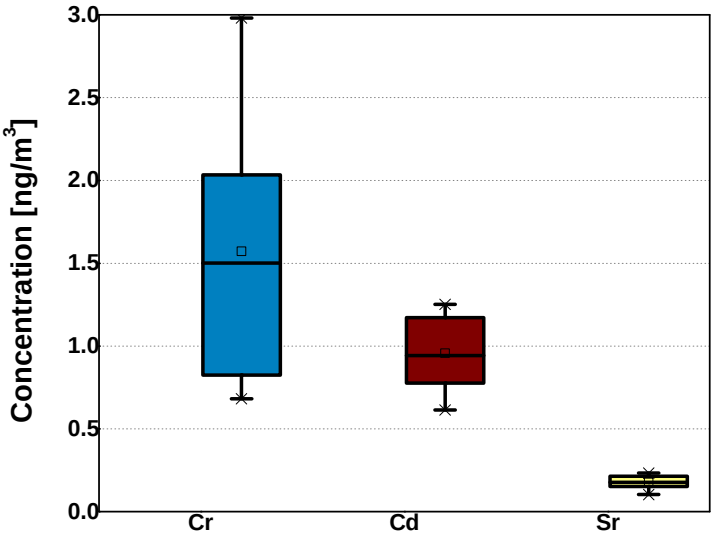

Fig. 2 – Average of Cr, Cd and Sr concentrations in $PM_{2.5}$ collected from eleven points of Targoviste city.

The form of nickel emitted to the atmosphere varies according to the type of source. Nickel species associated with combustion, incineration, and metals smelting and refining are often salts, including nickel oxides, nickel sulfate, nickel silicate, nickel sulfide, and nickel chloride [32]. In this study the average of nickel concentration ranged between 9.8 ± 0.4 ng/m^3 in P10 (industrial platform of Targoviste) and 4.6 ± 0.1 ng/m^3 in P8 (residential district). According with EPA data, the average ambient air nickel concentrations in the United States measured during 1977–1982 ranged between 7 and 12 ng/m^3 [33] and a recent estimation of nickel concentrations in the United States based on data collected in 1996 was 2.22 ng/m^3 [32]. According to ATSDR, the recent data confirmed that nickel concentrations in airborne particulate matter in U.S. urban area were in the ranges of 0.01–60, 0.6–78, and 1–328 ng/m^3, respectively [30]. As compared to these data, it can be concluded that the average of airborne nickel concentration in Targoviste (Fig. 3 and Table 2) was lower than nickel concentration estimate by ATDSR and EPA agency. Global atmospheric natural and anthropogenic emissions of copper have been assessed to be 35×10^6 and 28×10^6 kg/year, respectively [34]. Copper released into the atmosphere may exist in particulate matter in the elemental form or in the oxide, sulfate, or carbonate form [30]. In most cases [35] copper is associated with fine particles (< 1 μm) which result from fuel combustion. Thus, the average airborne copper concentration ranged between 9.1 ± 0.5 ng/m^3 in the same industrial point P10 and 4.9 ± 0.1 ng/m^3 which corresponded to P4 point (residential area with intense traffic) according to the data presented in Fig. 3 and

Table 2. These data were lower compared to the average copper concentration in air samples of United States which ranged from 0.02 to 10 μg/m^3 [30]. Aluminum occurs in particulate matter from natural and anthropogenic sources. The major anthropogenic sources of aluminum-containing particulate matter in Targoviste city include industrial activities, such as smelting, that process crustal minerals. The average airborne aluminum concentration in the studied urban area ranged from 5.1 ± 0.6 ng/m^3 in the same industrial area P10, to 2.9 ± 0.5 ng/m^3 in residential P4 area (Fig. 3 and Table 2). In the air, lead is in the form of particles and is removed by rain or gravitational settling [30]. The solubility of lead compounds in water is a function of pH, hardness, salinity, and the presence of humic material. If the medium is highest in soft, acidic water, solubility increases. Anthropogenic sources of lead in Targoviste include the manufacture of lead-containing products, combustion of coal and oil, and waste incineration. The average concentration of lead in Targoviste city ranged from 6.1 ± 1.5 ng/m^3 in P1 (automobiles and railway traffic, comercial and domestic fuel combustion, industrial activity, being one of the main entrances of the city) to 4.5 ± 0.7 ng/m^3 in P3 site coresponding to University campus (Fig. 3 and Table 2).

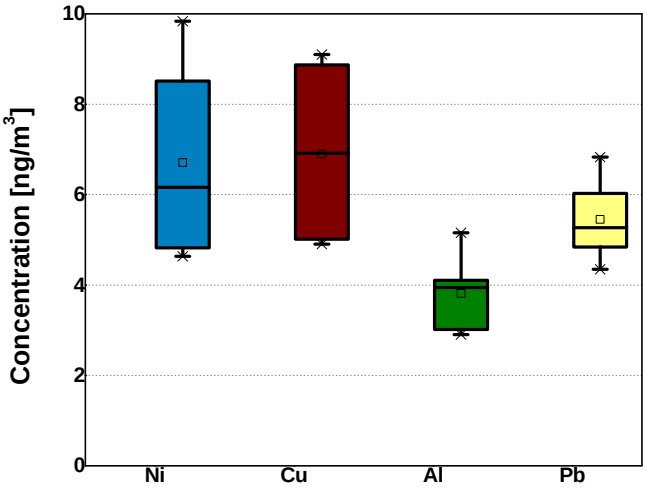

Fig. 3 – Average of Ni, Cu, Al and Pb concentrations in $PM_{2.5}$ for eleven sampling points of Targoviste city.

Manganese is one of the most common elements from environment. The human is exposed from both natural and anthropogenic activities, which involves the presence of manganese. The primary sources of manganese released to the air are industrial emissions, combustion of fossil fuels, and reentrainment of manganese-containing soils [30, 32]. The average concentration of manganese in urban areas based on measurements obtained of 102 United States cities was approximately 40 ng/m^3 [31]. Also, a survey of ambient airborne concentrations of

manganese in $PM_{2.5}$ in rural areas of United States and in several urban areas in California indicated that during five years (*i.e.* 1988 to 1993), the ambient concentrations of manganese ranged from 1 ng/m^3 in rural areas to 3 ng/m^3 in urban areas [30]. In Targoviste area, the average concentration of manganese in the air $PM_{2,5}$ estimated to range between 23.8 ± 0.1 ng/m^3 in P10 industrial site and 12.7 ± 0.1 ng/m^3 in P4 residential district (Fig. 4 and Tabel 2). These estimated values of manganese concentration obtained in the urban area of Targoviste were higher than the ones obtained in California urban area during the five years of observation. Zinc and its compounds were released in the atmosphere of Targoviste city mainly by anthropogenic sources such as industrial activity (*e.g.* steel production, processing of zinc-bearing raw materials, zinc production facilities, material incineration) as well as coal and fuel combustion and commercial and domestic activities. The survey of National Air Pollution Surveillance (NAPS), estimated that the average concentration of zinc in the air of urban remote areas range from < 0.003 to 0.027 μg/m^3 [36]. In this study the average of zinc concentration ranged from the higher value 89.9 ± 4.2 ng/m^3, which corresponded to P10 (intense industrial activity) to the low value, such as 33.9 ± 3.4 ng/m^3 which corresponed to residential district site, P4 (Fig. 4 and Table 2). In the same way, the average concentration of iron in studied urban area was high in P10 point (105.4 ± 5.2 ng/m^3) – an expected value due to the intense industrial activity correlated with traffic and fuel combustion as well. The low value (81.8 ± 3.4 ng/m^3) was observed in P8 point coresponding to the residential district (Fig. 4 and Table 2).

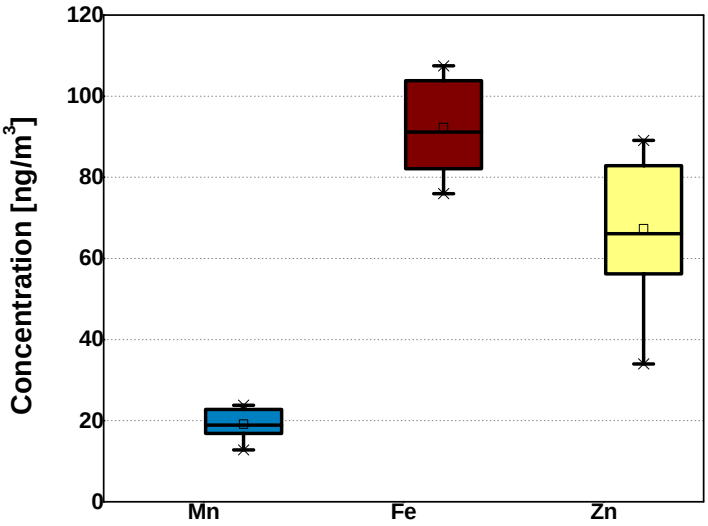

Fig. 4 – Average of Mn, Fe and Zn concentrations in $PM_{2.5}$ for eleven sampling points of Targoviste city.

Table 2

Averages of heavy metal concentrations ($n = 6$) contained in $PM_{2.5}$ samples [ng/m^3]

Sampling point	Heavy metals									
	Pb	**Cd**	**Cr**	**Ni**	**Cu**	**Mn**	**Al**	**Zn**	**Fe**	**Sr**
P1	6.1±1.5	1.2±0.1	1.61±0.01	8.8±0.5	7.8±0.1	22.7±0.1	4.1±1.0	83.9±2.1	103.8±6.5	0.15±0.01
P2	5.2±0.6	1.2±0.5	1.43±0.15	7.8±0.1	6.9±0.5	16.8±0.1	3.9±0.5	52.1±4.4	91.6±4.4	0.19±0.01
P3	4.5±0.7	0.9±0.5	1.66±0.01	6.1±0.5	6.1±0.4	18.9±0.4	3.9±0.7	61.8±2.6	94.9±4.5	0.18±0.01
P4	4.9±1.5	0.7±0.3	0.68±0.01	4.7±0.1	4.9±0.1	12.8±0.1	2.9±0.5	33.9±3.4	82.1±3.1	0.17±0.01
P5	6.8±2.1	0.9±0.2	2.9±0.5	7.5±0.2	8.8±0.1	21.8±0.3	3.9±0.1	79.8±2.1	93.8±3.4	0.15±0.01
P6	4.8±1.1	0.9±0.2	2.3±0.1	8.5±0.2	8.9±0.5	23.5±0.1	4.1±0.9	82.8±3.2	107.8±5.1	0.21±0.01
P7	5.1±1.0	0.8±0.1	0.76±0.03	5.1±0.5	6.4±0.2	17.9±0.4	3.1±0.7	63.3±4.5	75.9±4.3	0.22±0.01
P8	5.8±1.5	0.61±0.01	0.82±0.01	4.6±0.1	5.1±0.4	15.8±0.2	2.9±0.9	56.9±3.6	81.8±3.4	0.13±0.05
P9	4.3±0.5	1.1±0.5	1.51±0.01	4.8±0.5	7.6±0.7	16.9±0.6	3.9±0.4	66.1±3.3	90.8±3.5	0.16±0.01
P10	6.2±1.4	1.1±0.4	2.88±0.03	9.8±0.4	9.1±0.5	23.8±0.1	5.5±0.6	89.9±4.2	105.4±5.2	0.23±0.03
P11	5.9±1.1	0.7±0.2	0.98±0.05	5.7±0.2	5.1±0.3	19.6±0.2	3.9±0.4	71.9±2.1	89.5±4.1	0.14±0.01
Blank LVS (Low Volume Sampler): 34–41 mm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

4. CONCLUSIONS

Eleven significant sampling points were chosen to investigate the relevance of children exposure in various urban areas considered as vulnerable receptors (the proximity of kindergartens, schools, hospitals, health clinics, and playgrounds). Concerning the obtained results, the average of Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn, Fe and Sr, were compared to the concentration values recorded by the Agency for Toxic Substances and Disease Registry (ATSDR). A slight decrease of strontium, nickel and zinc levels as compared to ATSDR values was observed. According to ATSDR data, the estimated concentration of manganese obtained in Targoviste city, with values ranging between 12.7 ± 0.1 and 23.8 ± 0.1 ng/m^3, was higher than 3 ng/m^3 obtained in the urban areas from U.S. Taking into account the results, it can be concluded that average concentrations of heavy metals including, Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn, Fe and Sr, in the six sampling point (*i.e.* P1, P2, P3, P5, P6 and P10) which were consistently higher during the spring months (March-May) can be attributed to the soluble or insoluble forms of these metals. This is due to

the traffic and domestic activities, but in equal measure to industrial activity and fuel combustion. The levels of metal in $PM_{2.5}$ can be significantly higher near pollution sources, which can increase the risk of adverse health effects.

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