Heavy metals assessment in street dust and soil of Botosani city, Romania

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Abstract. In urban areas, increased human activities generate toxic heavy metals emissions that contaminate the environment and affect human health. Street dust and soils nearby the streets receive metals especially from road traffic. A total of 50 samples of street dust and soil were collected from Botosani city during one sampling campaign. The samples were categorized according to the urban function of space: gas stations, industry, commercial parking lots, intersections, green areas and municipal waste deposit. Samples were analyzed using flame absorption spectrometry for Cr, Cu, Co, Fe, Mn, Zn, Pb and Ni detection. Results of the street dust samples showed more elevated values of metals than in urban soil, indicating that road traffic is one of the main source responsible for heavy metals emissions in the city. For both types of samples, the concentrations of Cr, Ni, Pb, Cu and Zn exceeded the maximum allowed limit established by the Romanian authorities. For street dust samples, the categories which were identified with the highest concentrations of metals were the industrial area, intersections and institutions. For soil samples, the highest metal concentrations were detected in the following categories: industry, institutional areas, parking lots of commercial areas and green areas.
Key words: street dust, soil, flame atomic absorption spectrometry (FAAS), metals, Botosani.

Introduction. Road surfaces are a site of deposition for particles from a wide variety of sources: exhaust particles, de-icing salt and grit, biogenic and geogenic material. This deposited material is referred to as road dust (Thorpe & Harrison 2008). Street dust and soil serve as one of the most important sink for trace metal contaminants in the terrestrial ecosystem, seen as indicators that reflect the quality of the environment (Yeung et al 2003).

Street dust receives heavy meals emissions from stationary and mobile sources such as soil erosion by wind and rainfall, road traffic, industrial activities, power plants combustions, residential combustion, waste incineration, corrosion of construction materials, corrosion of asphalt, concrete and paint (Lu et al 2010; Ordóñez et al 2015).

Various studies state that one of the most important sources of heavy metals in the urban environment is represented by road traffic emissions (Charlesworth et al 2003; De Miguel et al 2007; Tositti et al 2014; Ordóñez et al 2015). Emissions from major highways contain different kinds of contaminants such as metals, polycyclic aromatic hydrocarbons and road salts which can occur in both particulate and dissolved form. In particular, metals are of great concern because they cannot be decomposed by micro-organisms and have a long term toxicity for plants, animal and human. Emissions resulting from traffic are caused mainly by tire wear off, break lining, wear of individual vehicular components such as the car body, clutch or motor parts and exhaust (Lindgren 1996).

Pollutants released by motor vehicles may also originate from the residues from incomplete fuel combustion, oil leaking from engine and hydraulic systems, and fuel additives. Road abrasion, pavement leaching, traffic control device corrosion and road maintenance are also relevant sources of pollution (Hjortenkrans et al 2007; Kluge & Wessolek 2012).

The aim of this study was to analyze the concentrations of Cr, Cu, Co, Fe, Mn, Zn, Pb and Ni in street dust and soil samples in Botosani City and to compare the results between street dust and soil samples in order to establish if road traffic can be considered as an important source of metals emissions in the city.

Material and Method

Description of the study area. Located in the North Eastern Romania and situated at the contact of Moldavian Plain with Suceava Plateau, Botosani city is documentary attested since the XV century. Botosani city is located in the central-western part of the county with the same name, at the intersection of 47°44´N with 26°41´E, at an average elevation of 170 m above the sea level (Figure 1). It is considered a medium-sized town, with an administrative area of 4136 ha (0.85% of the county's surface). The built territory occupies 1968 ha (Vieru 2014).

From a geological point of view, Botosani city belongs to the Moldavian Platform, which is made by a lower level consisting with a bedrock of Precambrian crystalline rocks and an upper level consisting in old Paleozoic and Mesozoic sedimentary rocks, covered by a Quaternary thin cover rocks.

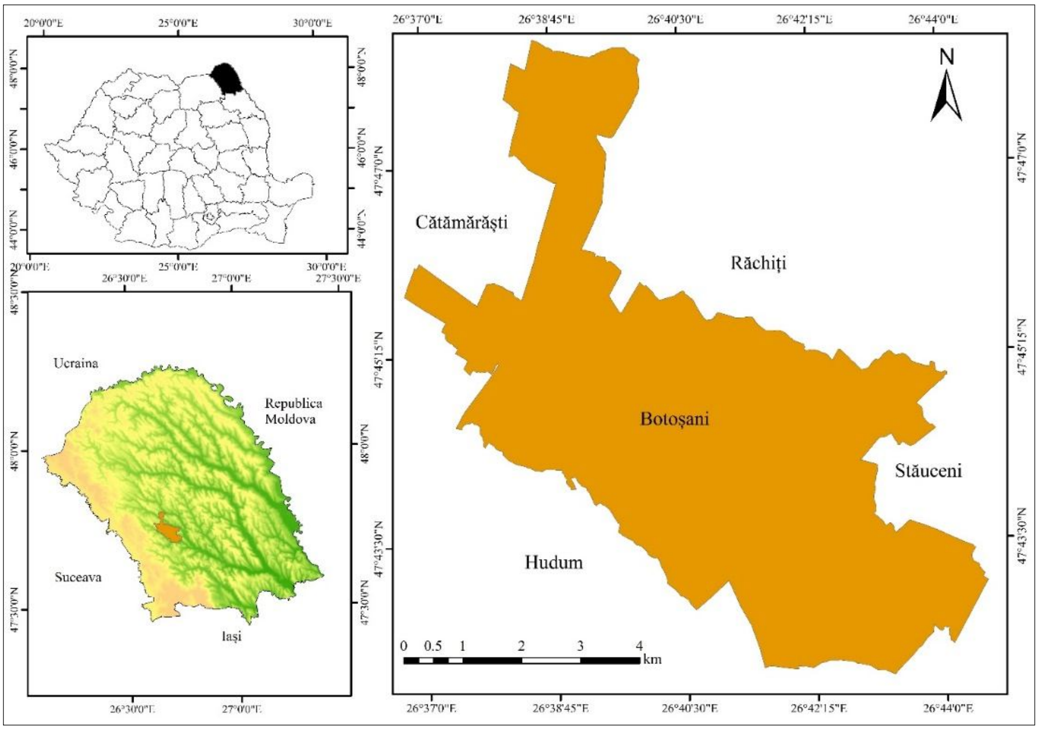

Figure 1. Spatial localization of Botosani City.

As of 2011, approximately 100.890 people lived in the city. The city consists with 12 districts, 253 traffic roads and 139 km of street.

During the communist period, the city experienced a rapid industrialization followed by a process of urbanization until 1989. After the communism collapse, most of the industrial activity was shut down and the industrial area is nowadays undergoing through a process of urban renewal, the surfaces being used for commercial spaces and other activities. Existing industrial activities account for chemical industry of synthetic and artificial fibers, machine and electrical devices industry, food and drinks processes, textile industry and metallic construction activities. Also, the city has a thermal plant that generates heat and hot water for the residential and industrial buildings. Many of these industrial activities are locates in Manolești-Deal district (58.4% of the district's surface) (Vieru 2014).

Located next to the border of two countries (Ukraine and Republic of Moldova), the high tonnage traffic receives new dimensions, given by the fact that many trucks and cars are using the county's customs.

According to National Community Service for Vehicle Registration (2016), county's road network contains 9 routes of national roads, 29 county roads and 175 rural roads. In Botosani City, the number of cars has grown during recent years as: 31885 vehicles in 2013, 33446 vehicles in 2014 and 34958 vehicles in 2015.

Experimental. For this study, a number of 25 street dust samples and 25 soil samples were collected from Botosani City after two weeks without rainfall, in compliance with standard procedures (Figure 2). A soil sample was collected for each street dust sample, in order to obtain a comparison for results between the two types of samples. The dust samples were collected from the main streets of the city and the soil samples were collected as well from the areas next to the street. Samples were analyzed using a Perkin Elmer flame and graphite furnace atomic absorption spectrometer, PinAAcle 900T model.

In the laboratory, samples were sieved, dried and milled. All samples were subjected to chemical extraction using 37% HCl and 65% HNO_3, followed by an under pressure digestion of the samples that were kept in a microwave system for two hours. The last step consisted in filtering the extraction solution using a filter paper with a porosity of 2 µm. The final solutions were then analyzed by PinAAcle 900T spectrometer.

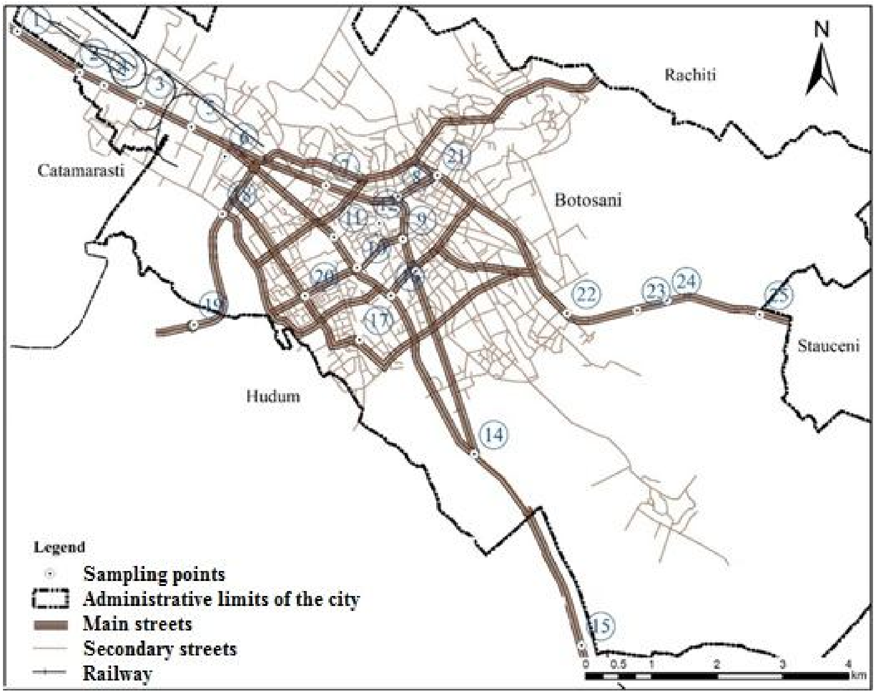

Figure 2. Location of the sampling points.

Results and Discussion. The concentration of metals in street dust and soil is shown in Table 1. The highest average values were recorded in street dust for Cr, Ni, Pb, Cu, Fe and Zn, while for soil samples, the highest average values were recorded for Co and Mn. These results indicate the fact that road traffic can be considered a main source of metals present in the environment. Street dust samples are more likely to contain emissions generated during last days or hours, while the soil samples can indicate cumulative emissions that have occurred during past years. Street dust is permanently removed by the air flow, wind, other cars or rainfall. The variable number of cars passing through one point adds to the constant urban or industrial constructions as a constant source of contaminants in street dust.

Samples were categorized according to the use of the spaces as: gas stations, industry, parking lots of commercial areas, intersections, green areas and municipal waste deposit (Figure 3).

Table 1
Statistical values of heavy metal concentration in street dust and soil samples (mg kg^{-1})

Metal	*Type of sample*	*Min.*	*Max.*	*Average*	*Median*	*Skewness*
Cr	Street dust	22.97	**77.80**	**43.29**	40.10	0.74
	Soil	18.06	45.60	34.21	33.80	-0.35
Ni	Street dust	14.14	31.72	**24.11**	24.72	-0.32
	Soil	14.52	**34.67**	25.55	24.47	0.03
Pb	Street dust	5.22	**191.47**	**49.64**	33.98	2.30
	Soil	22.58	56.85	37.58	34.34	0.54
Cu	Street dust	8.55	**220.48**	**85.27**	74.52	0.66
	Soil	14.20	94.58	35.79	31.49	2.09
Co	Street dust	2.41	9.25	4.30	3.83	1.94
	Soil	4.18	**10.96**	**7.23**	6.80	0.51
Mn	Street dust	320.95	799.69	431.15	411.33	2.92
	Soil	373.94	**1043.40**	**593.74**	573.20	0.89
Fe	Street dust	10250.70	**24690.70**	**19433.90**	18840.10	-0.52
	Soil	10125.30	24358.20	18089.53	17461.20	0.12
Zn	Street dust	30.41	**297.28**	**151.63**	149.08	0.21
	Soil	42.71	193.55	111.12	98.80	0.53

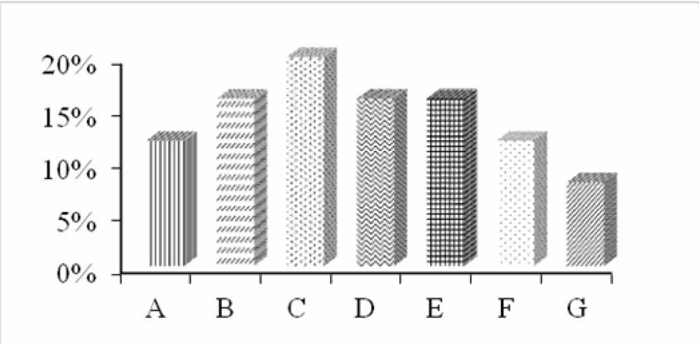

Figure 3. Distribution of the samples as categories: A – gas stations, B – industry, C – institutions, D – parking lots of commercial areas, E – intersections, F – green areas, G – waste deposit.

Cobalt values in street dust samples were recorded within the range of 2.4-9.2 mg kg^{-1}, while in soil samples cobalt values were recorded within the range of 4.18-10.9 mg kg^{-1} (Figure 4). These values indicate that they do not exceed the maximum allowed limit (15 mg kg^{-1}) set by the Romanian authorities (Order no. 756/1997). Values higher than 5 mg kg^{-1} were recorded in the industry, institutions and green areas categories for street dust samples, while for soil samples in gas stations and intersections.

Figure 4. Spatial distribution of cobalt concentrations in street dust (A) and soil (B).

The analyses indicated that chromium had the highest values in the street dust samples; 88% of the street dust samples and 76% of the soil samples exceeded the maximum allowed limit set by the national authorities (30 mg kg^{-1}). The highest values in the street dust samples (more than 60 mg kg^{-1}) were pointed out in intersections (Figure 5). The highest values of chromium in soil samples were pointed out in the following categories: industry, green areas and waste deposit. Mihai Eminescu Park, located in a place without industrial activities is a sampling point that indicated the biggest value of chromium in soil.

Figure 5. Spatial distribution of chromium concentrations in street dust (A) and soil (B).

96% of the dust samples and 92% of the soil samples exceed the maximum allowed limit set by the authorities for copper (20 mg kg^{-1}). The highest values of copper in street dust (more than 130 mg kg^{-1}) were recorded in the categories of industry and intersections (especially one intersection in Bucovina district). Almost all dust samples had more elevated concentrations of copper compared with the soil samples (Figure 6). For the soil samples that indicated lower values of copper compared with those of dust, high values were recorded in the industrial area of the city.

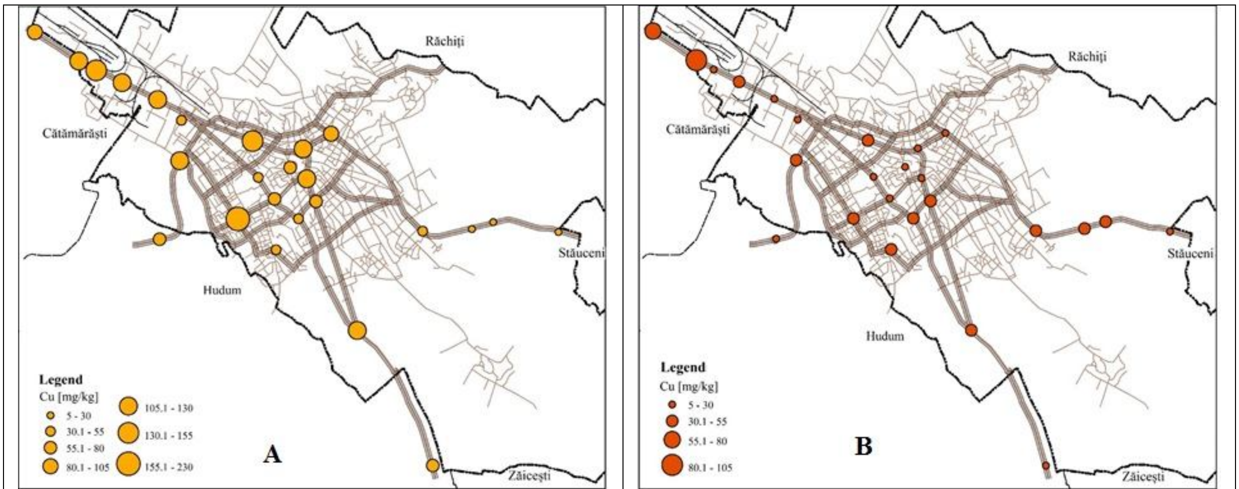

Figure 6. Spatial distribution of copper concentrations in street dust (A) and soil (B).

The highest values of manganese were recorded in soil samples, with only 8% of them exceeding the maximum allowed limit set by the authorities (900 mg kg^{-1}). Street dust samples did not exceeded the maximum allowed limit. The highest values of manganese in soil (more than 925 mg kg^{-1}) were recorded in the following categories: industry and institutions (Figure 7).

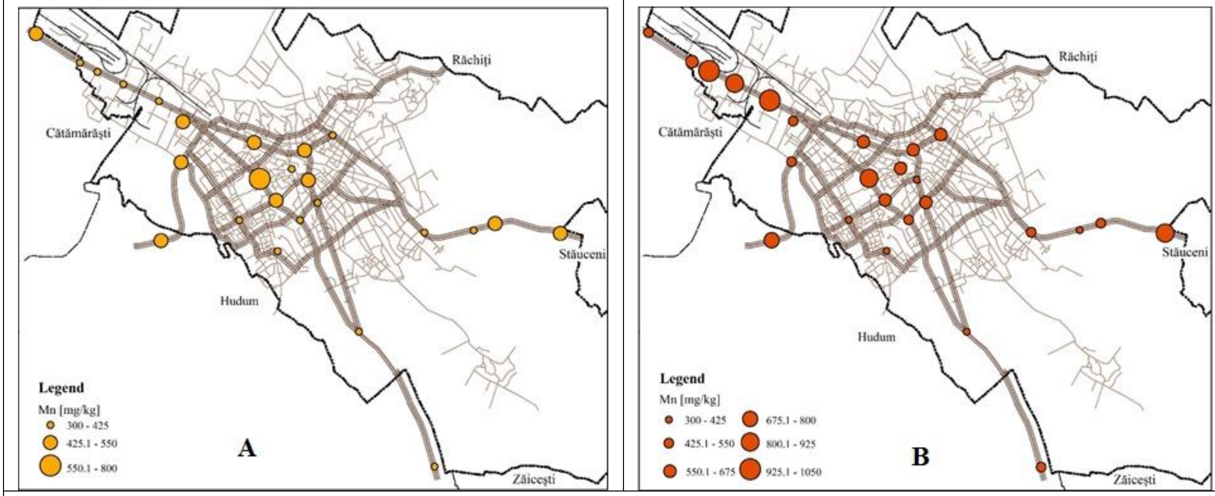

Figure 7. Spatial distribution of manganese concentrations in street dust (A) and soil (B).

Nickel was recorded with high values both in street dust and soil samples, with a proportionate spatial distribution (Figure 8). 80% of the soil samples and 84% of the street dust samples exceed the maximum allowed limit set by the authorities (20 mg kg^{-1}). The highest values of nickel in dust samples and soil samples were recorded in the following categories: industry, institutions, and parking lots of the commercial areas. The highest value of Ni in dust sample was recorded close to Mihai Eminescu Park (31.72 mg kg^{-1}).

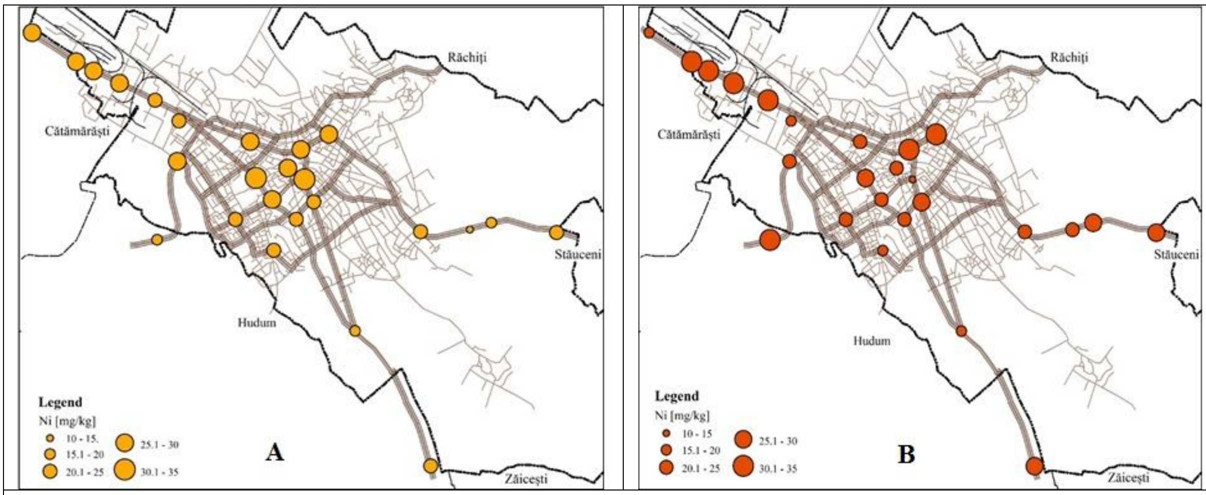

Figure 8. Spatial distribution of nickel concentrations in street dust (A) and soil (B).

The highest values of zinc were recorded in the street dust samples. 84% of the street dust samples an 56% of the soil samples exceed the maximum allowed limit (100 mg kg^{-1}). The highest concentration of zinc was recorded in a street dust sample close to Mihai Eminescu Park, same as for chromium and nickel. The highest values of zinc in street dust samples corresponds to industry and intersection categories whilst for soil samples the highest values were recorded in institutional areas, intersections and parking lots of the commercial areas (Figure 9)

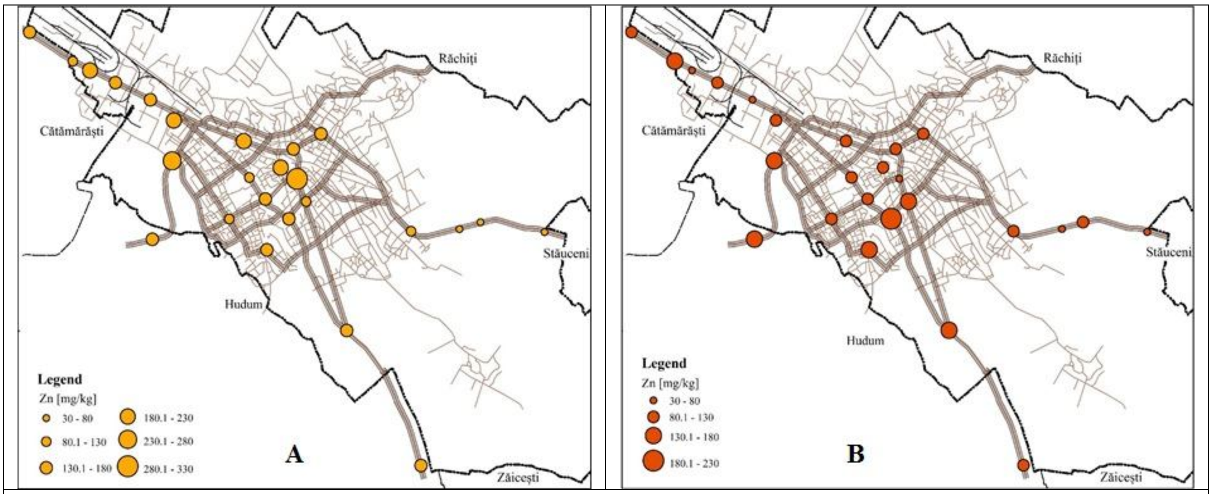

Figure 9. Spatial distribution of zinc concentrations in street dust (A) and soil (B).

Lead was recorded with the highest values in the street dust samples, 80% of them exceeding the maximum allowed limit (20 mg kg^{-1}). The highest values were recorded within the categories institutions and intersections (more than 80 mg kg^{-1}). All the soil samples exceed the maximum allowed limit, some of them exceeding the alert threshold for sensitive soils: 50 mg kg^{-1}). The highest values of lead were recorded within the categories: gas stations, institutions, commercial parking lots and green areas. The fact that lead had a higher concentration close to the gas stations can be explained by the fact that for many years, gasoline containing lead was used. Repeated refill of car's gas tanks and a big number of cars that pulled in one day at gas stations contributed to lead emission in the environment, especially close to this type of spaces (Figure 10).

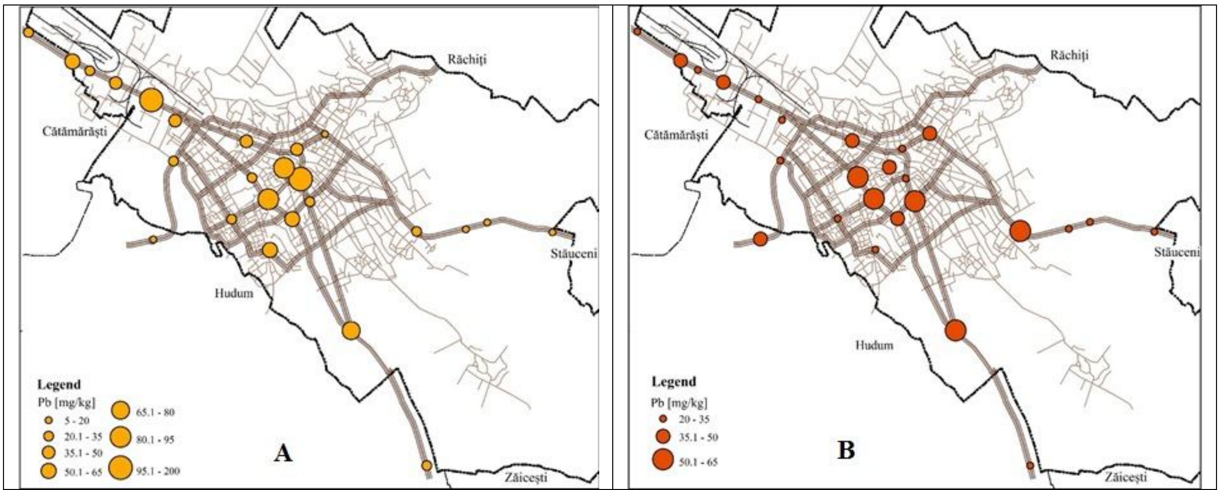

Figure 10. Spatial distribution of lead concentrations in street dust (A) and soil (B).

The national legislation does not set a limit value for iron. Data obtained indicated that iron sets on a broad range of values for both street dust and soil samples. The concentrations for all samples ranged 10.000-24.700 mg kg^{-1}. The highest values were recorded within the categories: gas stations, waste deposit, institutions and industry (Figure 11).

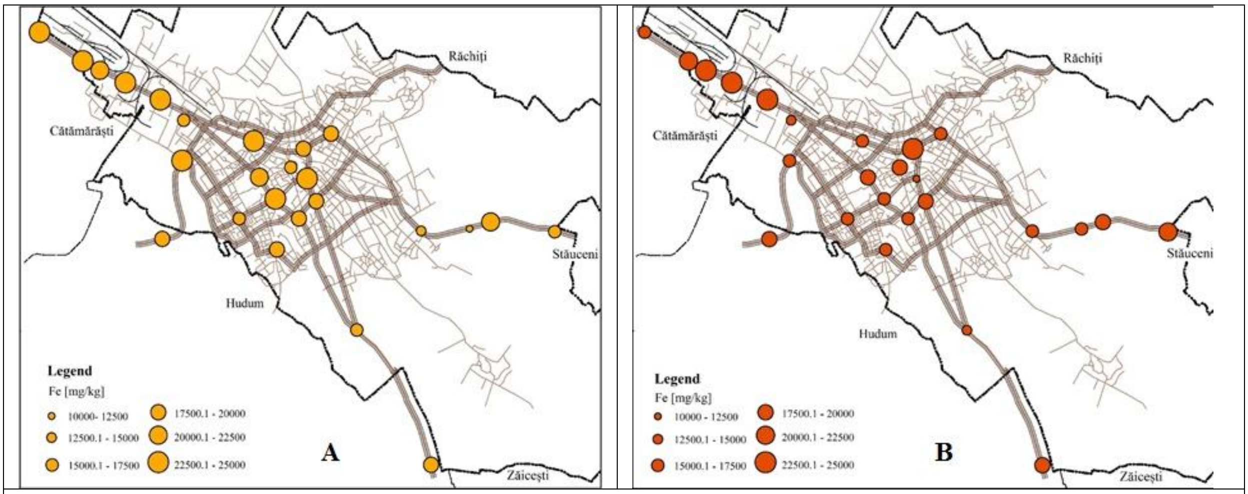

Figure 11. Spatial distribution of iron concentrations in street dust (A) and soil (B).

Urban soils have a different distribution of metals compared to street dust. Usually, metals accumulate in soil for a longer time, originating from anthropogenic sources. On the other hand, street dust can reflect a load of metals that comes mostly from traffic and asphalt. Various metals are used extensively in brake lining materials, and several studies have sought to determine the metal content of brake linings and brake wear particles, due to the toxicological effects associated with exposure to metals (Table 2). Iron, copper, lead and zinc appear to be ubiquitous and have been repeatedly reported to show high concentrations in brake linings (Kennedy & Gadd 2003; Schauer et al 2006).

Table 2

Summary of key components in vehicle's brake lining materials
(Eriksson et al 1999; Chan & Stachowiak 2004)

Component	*Purpose*	*Example ingredients*
Fibers	Provide mechanical strength	Various metals, carbon, glass, Kevlar, occasionally ceramics
Matrix-binder	Holds the components together and provides thermal stability	Phenolic and modified phenolic resins, rubber compounds sometimes added
Friction modifiers	Provide the desired frictional properties, control wear rates	Metal sulphides, metal oxides, silicates, graphite, brass, bronze
Abrasives	Increase the friction coefficient and remove oxide coatings that may form on the disc/drum surface.	Zirconium oxide, zirconium silicate, aluminium oxide, chromium oxide
Fillers	Improve manufacturability and reduce costs.	Various inorganics – barite, calcite, mica, vermiculite. Organic substances – cashew dust, rubber particles.

The present study indicates that high concentrations of metals were identified close to residential buildings and different types of institutions: schools, hospitals, city hall. The highest concentrations of metals were identified in the city center and not close to the waste deposit as it was normally expected. Recently, commercial areas and parking lots were constructed on soils which hosted past for industrial activities. This type of spaces did not benefit by decontamination measures and can expose population's health to an important risk.

Beside direct health implications of metals presence in the environment, an indirect consequence of trace metal contamination of the urban environment include the subsequent migration of the pollutants to receiving bodies of water via urban runoff, resulting in the trace metal enrichment of sediments (Sutherland & Tolosa 2000). This may affect the quality of aquatic ecosystems and increase the body loadings of aquatic organisms through bioaccumulation and biomagnification, potentially causing trace metal contamination of the food chain (Callender & Rice 2000).

Conclusions. In this study it was pointed out the fact that in Botosani City street dust contains higher concentrations of metals than soils. Overall, analysis indicated the fact that Cr, Ni, Pb, Cu, Fe and Zn had higher concentrations in street dust, while for soil samples, the highest were recorded for Co and Mn.

Statistical analysis indicated that the categories which had the highest concentrations of metals were the industrial area, intersections and institutions for street dust. The fact that elevated concentrations of metals correspond to places where car traffic is very intense points out the role of traffic among anthropic sources of emission. For soil samples, statistical analysis indicated that elevated concentrations of metals were detected in the following categories: industry, institutions parking lots of commercial areas and green areas.

One sampling point was identified corresponding to Mihai Eminescu Park located close to the city center. Maximum recorded values of Cr, Ni and Zn correspond to this sampling point. The fact that this point is located close to a pedestrian area, far from the main industrial points indicates car traffic as main responsible source.

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