

**PRELIMINARY DATA CONCERNING THE CONTENTS OF HEAVY
METALS FROM THE SOILS OF THE PERIURBAN AREA OF IAȘI
MUNICIPALITY**

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Abstract

The study of the heavy metal contents in the soils of the suburban area of Iași municipality is required due to the necessity of estimating the possible hazard that they can have over health. So far, in Iași municipality, such studies had a punctual character, aiming mostly towards the neighborhoods of some industrial objectives. In order to establish the quantities of heavy metals in soils and the qualitative description of the soils there have been sampled 582 of systematic analysis, determining the contents of Zn, Cu, Mn, Pb, Cd, Co, Ni and Cr. The pollution index (PI) and integrated pollution index (IPI) indicates a reduced anthropogeneous influence. Despite this, the high heavy metal contents levels (Cu, Ni, Pb, Zn), surpassing the normal values in soils, suggests the existence of some local sources, generating pollution.

Keywords: Iași, heavy metals, soil, pollution index

Introduction

The concentration of the heavy metals in the biosphere as a result of the anthropic activity has become in the late 20th century, one of the highly studied processes of the

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natural geochemical cycle. Mostly in the periurban and urban areas, the effect over the environment is accentuated by the multitude of fix and mobile sources generating heavy metals in the soil and in the atmosphere, that are much over the natural limits (Bilos et al., 2001; Popescu and Dumitrescu, 2003; Lăcătușu et al., 2004, 2005; Ken et al., 2005).

The effect of the heavy metals from soils over the public health is manifested either indirectly, through the soils used for crops or directly through dust and/or soil inhalation, in case of the soils from the residential areas (Sakagami et al., 1982; de Miguel et al., 1997; Chen et al., 1997, 2005; Mielke et al., 1999; Bandhu et al., 2000; Rasmussen et al., 2001; Cyrus et al., 2003; Gray et al., 2003; Popescu and Dumitrescu, 2003).

Materials and methods

1. Study area

Iași municipality, situated in the N-E part of Romania (fig. 1), is documentary attested in the 15th century, but the archeological proofs shows the presence of a population even in the Paleolithic period (Cucuteni culture).

From the point of view of the population number, Iasi municipality is the second one municipality of Romania, together with the metropolitan area, the population numbering around 307377 inhabitants, to which there are also added over 60000 students. (National Institute of Statistics, 2008; City Hall of Iași, 2008). With a surface of 6700 ha, Iași municipality has a density of the population of 5373.43 inhabitants/km² (Agency for Environment Protection Iași, 2006).



Fig. 1 County and municipality Iași

Being highly industrialized within 1945-1990 (chemical industry, pharmaceutical industry, metallurgical industry and of heavy machines, textile industry, alimentary industry, energetic industry, industry of furniture), Iași county has registered a slow decrease of the industrial activity within 1991-2007. There was also registered, in the

same period, a high increase of the number of cars, as well as an intense extension of the residential areas.

From a geological point of view, Iași municipality belongs to the Moldavian Platform. Conforming to Ionesi (1994), the Moldavian Platform is made of a basement (reached at the depth of 1121m in Iași) and cover (sedimentary deposits, belonging to the superior Vendian, to Paleozoic, to Cretacic, to Paleocene, to Eocene, to the Upper Badenian, to Sarmatiane and to Meotiane periods). To these, there are also added quaternary deposits, especially the terraces that go along the hydrographic arteries.

Although there existed preoccupations concerning the impact of heavy metals over the environment in Iași municipality (Lăcătușu et al., 2004, 2005), they had no systematic character, being mostly concentrated on some industrial objectives.

2. Sampling and analysis

The studied area, situated in the northern and southern parts of Iași municipality (fig. 2), is characterized by the presence of the following types of soils (Secu, 2007): protisoils (aluviosoils = 14.1%; regosoils = 8.7%; entiantrosoils = 3.3%), cernisoils (cernozioms = 31.6%; faeozioims = 7.4%) luvisoils (preluvisoils = 2.7%), antrisoils (erodosoils = 2.9%; antrosoils = 10.8%) and soil complexes (18.5%).

As a use, the analyzed soils are part of the following classes: agricultural areas (64.2%), forests and semi-natural areas (24.3%), artificial areas (11.3%) and artificial or natural areas with water (0.2%).

The soil samples were taken from the knots of a square-like network with the side of 500 m, on an interval depth of 0.00 – 0.20 m (fig. 2). The weight of a sample varies between 1.5-2.5 kg.

Once air-dried and the ground increase of the samples done at dimensions of < 0.2 mm, there were determined the total heavy metal contents through the atomic absorption spectrometry (AAS Solar type), in air-acetylene flame, in the hydrochloric solution obtained after the digestion with a concentrated nitric and perchloric acids mixture (ICPA-București methodology).

The external control executed at Vienna University and Katowice University on a number of 57 soil samples, showed no systematic errors of analysis.

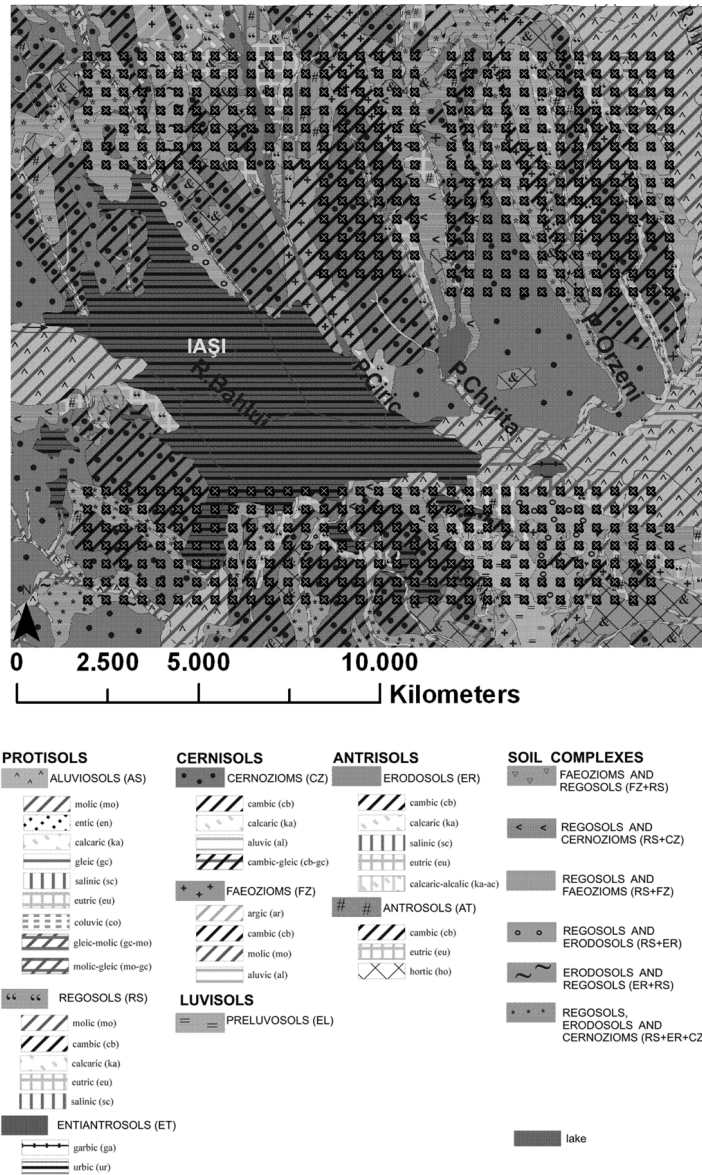


Fig. 2 Soil types and sampling in the periurban area of Iași municipality

Results

The heavy metal contents from the periurban area of Iași municipality is characterized by extended variations fields, the maximum values surpassing the normal values in soils in case of all the chemical elements (tab. 1). Despite this, the average values go over the normal values only for Cu, Pb and Ni. Even though, precaution is required in the use of the average values as a local precise estimator of the contents. This, on the one hand, due to the difference as a measuring order between the value of the average, the median and the mode, and on the other hand, due to the variation coefficient which, for some chemical elements, have relatively high values (Zn, Cu, Pb, Cd, Cr). This aspect is also sustained by the high levels of the skewness which, mostly in the case of Zn, Cu, Pb, Cd and Ni, indicates the significant weight of the reduced values of contents in comparison to the samples with high contents.

Tab. 1 Statistical parameters for heavy metals from the soils of the periurban area of Iași municipality

Statistics/Elements	Zn	Cu	Mn	Pb	Cd	Co	Ni	Cr
Mean	79.554	46.622	645.534	22.099	0.352	9.976	40.562	29.669
Geometric Mean	71.006	35.225	629.750	19.715	0.265	9.682	38.247	24.724
Median	65.964	28.112	644.000	19.650	0.276	9.600	37.498	25.050
Mode	74.000	23.800	661.000	20.000	0.200	10.100	42.800	20.500
Standard Deviation	78.896	54.191	128.038	20.406	0.422	2.592	23.934	34.213
Kurtosis	255.884	41.957	10.078	142.483	209.504	5.840	109.447	161.247
Skewness	13.991	5.066	0.667	10.886	11.889	1.594	9.607	11.328
Minimum	27.928	11.600	50.000	4.500	0.001	4.878	13.500	6.432
Maximum	1620.300	702.610	1669.000	326.330	8.150	27.900	349.600	591.600
Q1	56.502	23.800	586.946	15.300	0.181	8.300	32.500	17.800
Q3	80.150	38.923	698.750	23.842	0.377	11.100	43.025	33.662
IQR	23.648	15.123	111.804	8.542	0.196	2.800	10.525	15.862
Coefficient of variation	0.992	1.162	0.198	0.923	1.200	0.260	0.590	1.153
Count	582	582	582	582	562	582	580	582
Normal values in soil ¹	100	20	900	20	1	15	20	30

¹ – According to Order no 756/1997 of the Ministry of Waters, Forests and Environment Protection

There can be seen the fact that in the case of Cu and Ni, the values of the contents go constantly beyond the normal values in soils (fig. 3 and 4).

As far as the distribution of the heavy metal contents distribution on alignments is concerned (fig. 4), the contents values superior to the normal contents in soils appearing in a punctiform shape, with no preferential directions for their disposition.

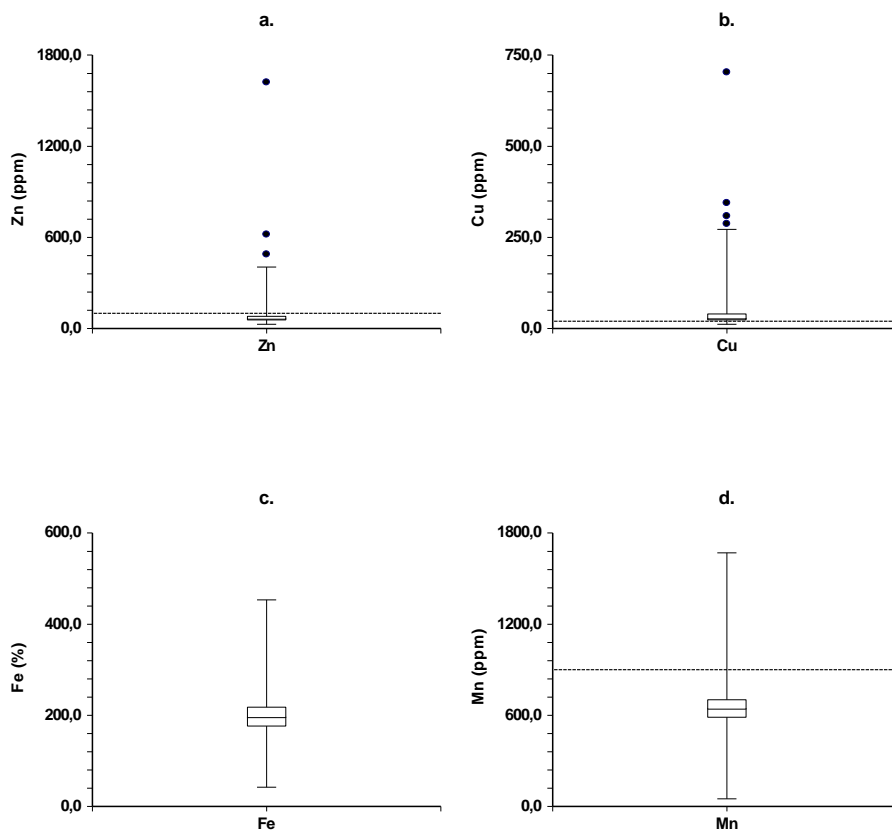


Fig. 3 The values of the heavy metal in the soils of the periurban area of Iași municipality (including the data outliers); - - - - normal value in soil

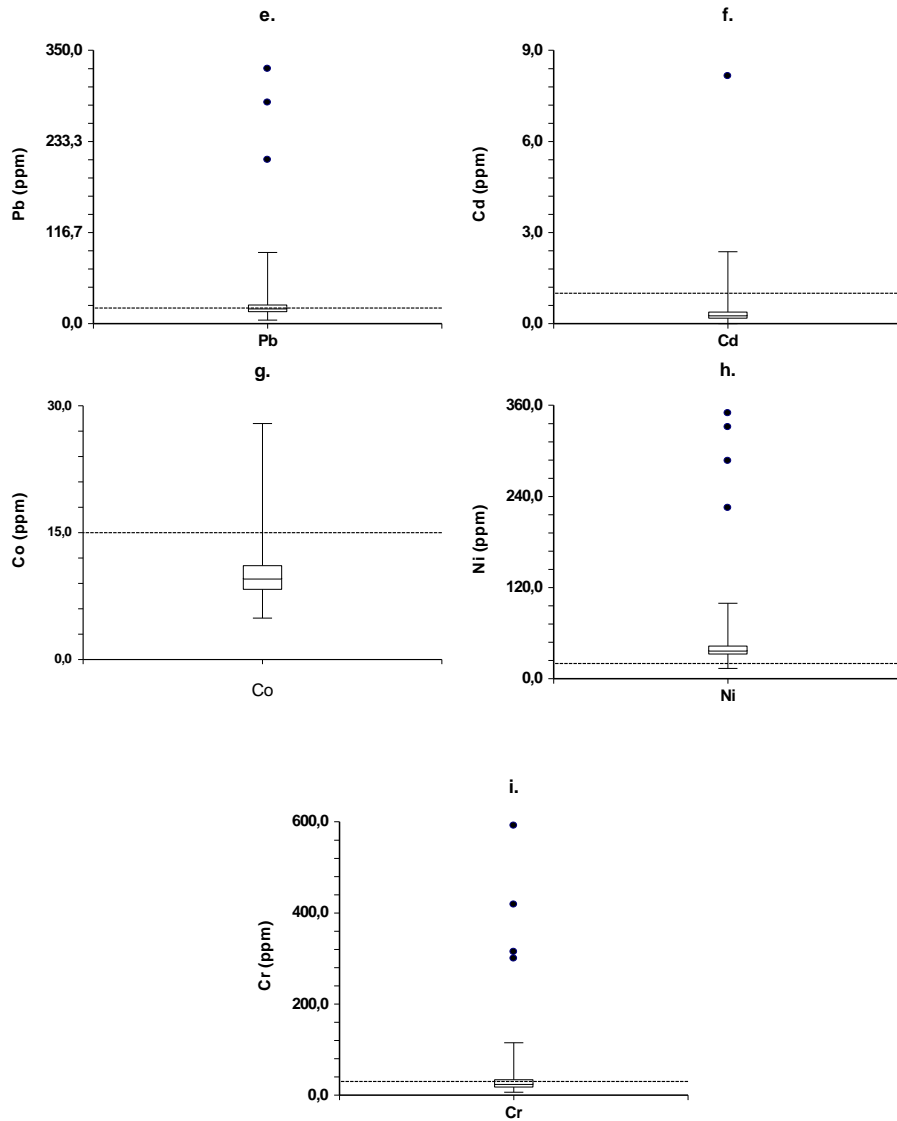


Fig. 3 (continuation) The values of the heavy metal in the soils of the periurban area of Iași municipality (including the data outliers); - - - - normal value in soil

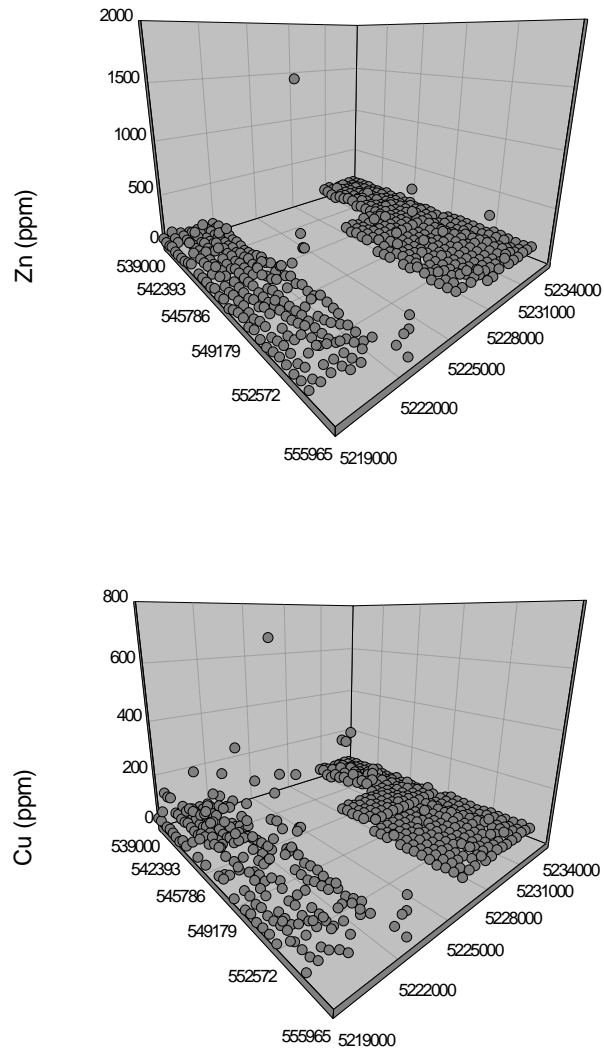


Fig. 4 The distribution on alignments of the heavy metal contents in the periurban area of Iași municipality

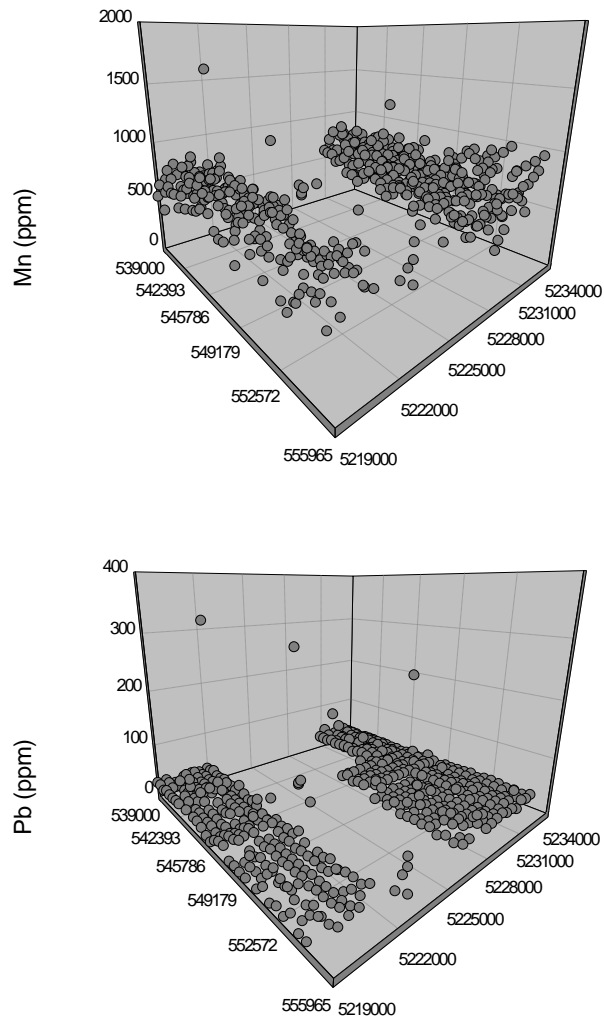


Fig. 4 (continuation) The distribution on alignments of the heavy metal contents in the periurban area of Iași municipality

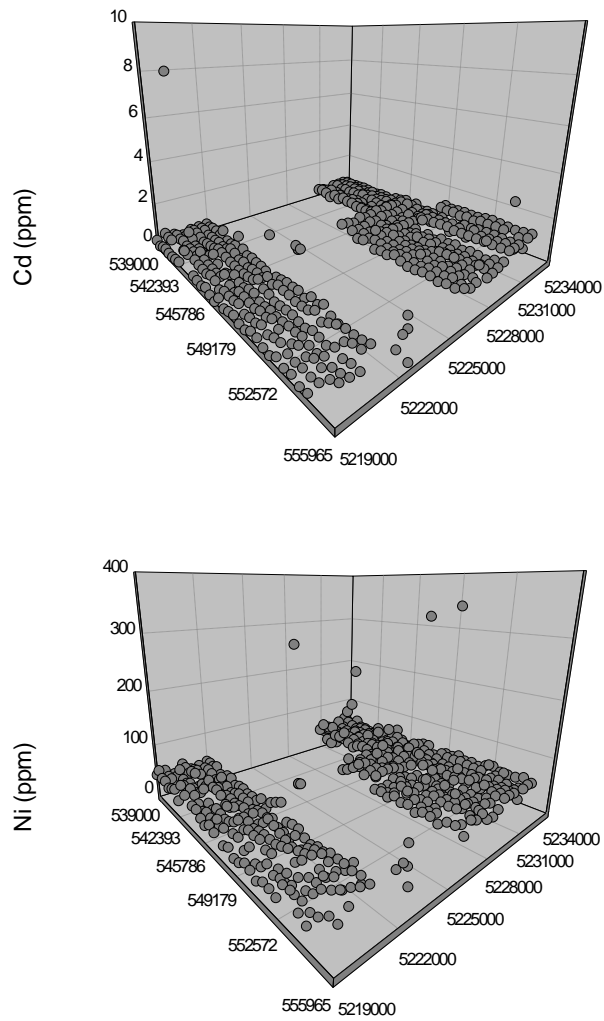


Fig. 4 (continuation) The distribution on alignments of the heavy metal contents in the periurban area of Iași municipality

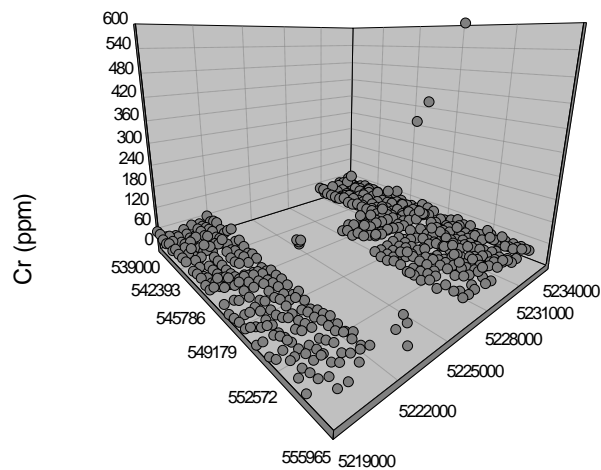


Fig. 4 (continuation) The distribution on alignments of the heavy metal contents in the periurban area of Iași municipality

The heavy metal contents varying with the soil type (fig. 5) show that their normal limits in soils are constantly over passed in the case of Cu and Ni and only for some soil types in the case of Pb (entiantrosoils, cernozioms, erodosoils, soil complexes) and Zn (prelivosoils).

In view of a characterization of the quality of each soil type, there was determined for the studied heavy metals a pollution index (PI) and an integrated pollution index (IPI) (tab. 2; fig. 6). The PI was defined as the ratio of the heavy metal concentration to the geometric mean of background concentration and the IPI was defined as the mean value of the metal's PI (Chen et al., 2005). The PI of each metal was calculated and classified as either low ($PI \leq 1$), middle ($1 < PI \leq 3$) or high ($PI > 3$). The IPI was classified as low ($PI \leq 1$), middle ($1 < PI \leq 2$) or high ($PI > 2$) (Chen et al., 2005).

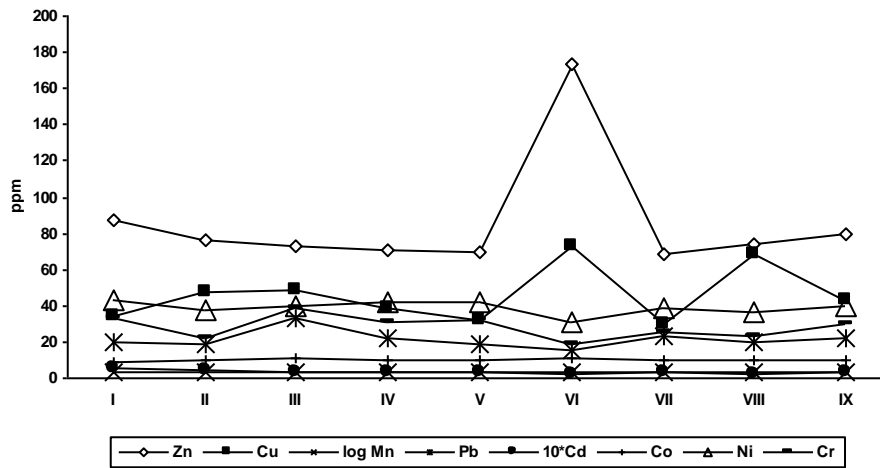


Fig. 5 The average contents of the heavy metals from the periurban area of Iași municipality varying with the soil type: I – aluviosoils; II – regosoils; III – entiantrosoils; IV – cernozioms; V – faeozioms; VI – preluvosoils; VII – erodosoils; VIII – antrosoils; IX – soil complexes

Tab. 2 Pollution index (PI) of heavy metals in the periurban area of Iași municipality

	Min	Max	Mean	Number of samples		
				Low (%)	Middle (%)	High (%)
Zn	0.393	22.819	1.120	58.4	39.2	2.4
Cu	0.329	19.946	1.324	69.9	21.6	8.5
Mn	0.079	2.650	0.825	44.3	55.7	0
Pb	0.228	16.553	1.121	50.3	48.3	1.4
Cd	0.004	30.807	1.329	49.1	39.5	11.4
Co	0.504	2.882	1.030	52.2	47.8	0
Ni	0.353	9.141	1.061	53.4	45.9	0.7
Cr	0.260	23.928	1.200	48.9	48.6	2.5

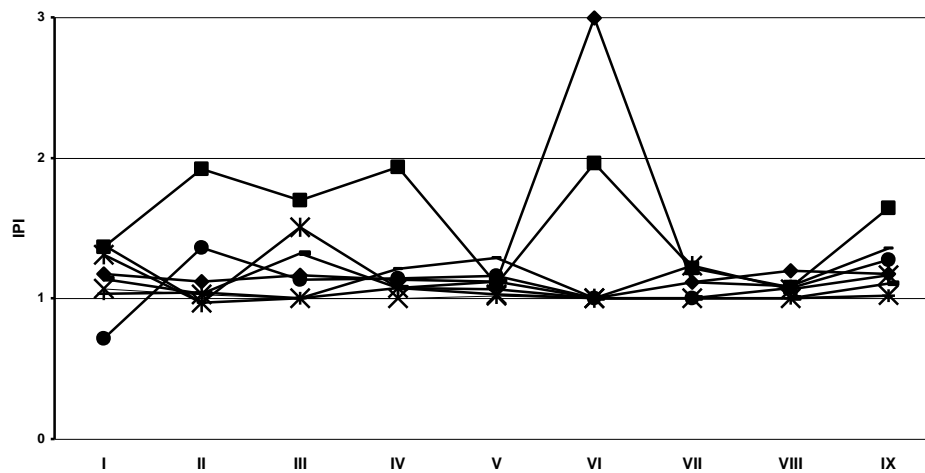


Fig. 6 – IPI varying with the soil type: I – aluviosols; II – regosols; III – entantrosols; IV – cernozioms; V – faeozioms; VI – preluvosoils; VII – erodosols; VIII – antrosols; IX – soil complexes

In the case of Mn and Co, PI presents low values, varying between 0.079 and 2.650 respectively 0.504 and 2.882. The other chemical elements presents a wide variation spectrum of the PI, remarking especially Cd (0.004–30.807) and Zn (0.393–22.819). Although the average PI values for the studied chemical elements do not indicate the possibility of a contamination with heavy metals of the suburban soils of Iași municipality, it is worth paying attention to the samples whose high level contents of Cd, Cu, Cr and Zn, although reduced, are placed in the field possibly polluted.

The IPI values allow the classification of the periurban soils of Iași municipality in the group of soils which were not highly influenced by the anthropogenic activity.

The matrix of the correlation coefficient (tab. 3) indicates the predomination of the positive correlations in comparison with the negative ones. Varying with the number of probation points and with the soil type, for a probability of 95.5%, there has been established the presence of some significant values of the correlation coefficient: a) positive: Cu-Zn; Cd-Zn; Pb-Zn; Pb-Cu; ; Cr-Ni; Cr-Mn; Cr-Cd; Cr-Co; Cr-Pb; Co-Cu; Co-Mn; Co-Pb; Ni-Mn; Ni-Zn; Ni-Cu; Ni-Pb; Cd-Mn; Cd-Pb; Pb-Cu; Ni-Co; b) negative: Ni-Co; Co-Cd; Co-Pb; Cr-Co; Mn-Cu; Pb-Mn.

Tab. 3 The matrix of the correlation coefficients for heavy metals from the soils of the periurban area of Iași municipality

	Zn	Cu	Mn	Pb	Cd	Co	Ni	Cr
Aluviosoils								
Zn	1.000							
Cu	0.277	1.000						
Mn	-0.043	0.118	1.000					
Pb	0.242	0.191	0.048	1.000				
Cd	0.206	0.008	0.003	0.139	1.000			
Co	0.023	0.059	0.073	0.068	0.107	1.000		
Ni	0.008	-0.026	0.034	0.060	0.050	0.106	1.000	
Cr	0.033	-0.024	-0.018	0.029	-0.006	0.150	0.971	1.000
Regosoils								
Zn	1.000							
Cu	0.143	1.000						
Mn	-0.070	0.133	1.000					
Pb	-0.098	0.045	0.241	1.000				
Cd	0.363	0.177	0.125	0.167	1.000			
Co	-0.022	-0.222	-0.002	0.420	0.114	1.000		
Ni	0.071	0.230	0.324	-0.148	0.063	-0.692	1.000	
Cr	-0.103	0.086	0.357	0.227	0.412	0.303	0.160	1.000
Entiantrosoils								
Zn	1.000							
Cu	0.695	1.000						
Mn	-0.273	0.191	1.000					
Pb	0.925	0.749	-0.078	1.000				
Cd	0.324	0.174	-0.122	0.403	1.000			
Co	-0.254	-0.275	-0.053	-0.211	-0.335	1.000		
Ni	0.843	0.761	0.019	0.963	0.286	-0.145	1.000	
Cr	0.370	0.243	-0.169	0.346	0.467	-0.184	0.358	1.000
Cernozioms								
Zn	1.000							
Cu	0.339	1.000						
Mn	0.029	0.068	1.000					
Pb	0.244	0.075	0.139	1.000				
Cd	0.152	-0.133	0.164	0.201	1.000			
Co	0.112	0.081	0.085	0.173	-0.222	1.000		
Ni	0.073	0.006	-0.140	0.371	0.160	0.112	1.000	
Cr	0.069	-0.070	-0.140	0.487	0.019	0.220	0.742	1.000

Tab. 3 (continuation) The matrix of the correlation coefficients for heavy metals from the soils of the periurban area of Iași municipality

	Zn	Cu	Mn	Pb	Cd	Co	Ni	Cr
Faeonzioms								
Zn	1.000							
Cu	0.162	1.000						
Mn	-0.042	0.201	1.000					
Pb	0.020	0.122	0.299	1.000				
Cd	0.415	0.067	0.324	0.128	1.000			
Co	0.050	-0.004	0.203	-0.105	-0.165	1.000		
Ni	0.013	0.080	0.064	0.203	0.182	0.009	1.000	
Cr	-0.020	-0.013	-0.075	0.326	0.067	0.211	0.362	1.000
Preluvosoils								
Zn	1.000							
Cu	0.057	1.000						
Mn	-0.155	0.298	1.000					
Pb	0.044	-0.005	0.152	1.000				
Cd	0.275	-0.291	0.196	0.125	1.000			
Co	-0.120	-0.006	0.375	0.006	0.055	1.000		
Ni	0.201	0.364	0.511	0.573	-0.081	0.022	1.000	
Cr	0.372	-0.149	-0.104	0.623	-0.087	-0.499	0.535	1.000
Erodosoils								
Zn	1.000							
Cu	0.846	1.000						
Mn	-0.434	-0.564	1.000					
Pb	0.363	0.782	-0.522	1.000				
Cd	0.217	0.184	-0.301	0.142	1.000			
Co	0.077	-0.152	0.253	-0.367	-0.407	1.000		
Ni	0.047	-0.158	0.125	-0.385	-0.072	0.623	1.000	
Cr	-0.066	-0.235	-0.027	-0.331	-0.353	0.693	0.678	1.000
Antrosoils								
Zn	1.000							
Cu	0.318	1.000						
Mn	-0.218	0.170	1.000					
Pb	0.034	-0.132	-0.075	1.000				
Cd	0.305	-0.030	-0.224	-0.030	1.000			
Co	-0.108	0.289	0.406	-0.315	-0.384	1.000		
Ni	-0.142	-0.175	-0.178	0.287	-0.089	0.146	1.000	
Cr	-0.191	-0.158	-0.073	0.371	-0.026	0.122	0.675	1.000

Tab. 3 (continuation) The matrix of the correlation coefficients for heavy metals from the soils of the periurban area of Iași municipality

	Zn	Cu	Mn	Pb	Cd	Co	Ni	Cr
Soil complexes								
Zn	1.000							
Cu	0.096	1.000						
Mn	0.070	0.125	1.000					
Pb	0.175	0.006	0.063	1.000				
Cd	0.188	-0.059	0.035	0.025	1.000			
Co	0.046	0.214	0.247	-0.019	-0.448	1.000		
Ni	-0.036	-0.054	-0.046	0.059	0.058	0.074	1.000	
Cr	-0.007	0.000	-0.058	0.127	0.017	0.128	0.952	1.000

Conclusions

At this stage of the research, one can assert that the anthropogenic activity seem to have exercised some influence over the heavy metal contents within the soils of the periurban area of Iași municipality. The contents constantly higher of Ni and Cu compared to the normal contents in soils and sometimes the contents of Pb, Zn, Cd and Cr are a proof in this respect.

There has not been established a correlation between the distribution of the contents in heavy metals and the soil type and/or the vegetation type and no preferential direction of high contents occurrence in heavy metals.

Just to have a view, there were set correlations between some pairs of chemical elements, characteristic for different types of soils.

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