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Spatial distribution and assessment of heavy metal pollution in the soils of Copou Park, Iasi, Romania

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Abstract

The parks and green spaces from large urban areas, whose positive social, economic and environmental impact is recognized nowadays throughout the world, are subject to the actions of anthropic factors. As part of the present study, the authors determined the Fe, Mn, Cr, Co, Ni, Cu, Zn, Pb, As and Cd contents of 42 samples collected from the soils of Copou Park and 7 soil samples collected from the green area between the pavement bordering Copou Park and the road adjacent to it. The statistical parameters, the geochemical background and the geo-accumulation index allowed the emphasizing of heavy metal contents which, according to the national soil quality standards, exceed the alert thresholds (Cr, Cu, Zn, Pb, As) and/or the intervention thresholds (Zn, Pb, As), which may be attributed to anthropogenic inputs. The spatial patterns were analyzed with the help of semivariograms, whose parameters were used in the kriging method in order to estimate heavy metal contents in the locations not subjected to measurements.

Keywords: Copou Park, heavy metal contamination, geo-accumulation index, spatial variability, Iasi, Romania.

Introduction

The intense process of urbanization and the activities related to it, such as the intensification of vehicular traffic, the production of electric and/or thermal power, and the appearance of deposits of urban waste, have, in most cases, led to the accumulation of potentially toxic elements in urban soils, and, implicitly, to the degradation of the environment. The interaction between human beings and the environment they live in is extremely complex and difficult to quantify. Among the various types of interactions, that with the soil plays an essential role, the contact between humans and soil being (a) directly or (b) indirectly achieved through the inhalation of soil-derived dust.

The main chemical elements generated through anthropic activity which have a

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powerful impact upon the natural geochemical background of urban soils are Cu, Pb, Zn, Cd, Co, Mn, As, Cr and Ni (Alloway, 1994; Li et al., 2001; He et al., 2005; Bounds and Johannesson, 2007; Papafilippaki et al., 2008; Fong et al., 2008; Cannon and Horton, 2009; Oprea et al., 2010; Zaady et al., 2010; Fordyce et al., 2012; Guo et al., 2012).

Within the urban environment, green spaces – public parks, in particular – play a very important role, both from an aesthetic point of view, but also through their positive influence upon human health (Richardson et al., 2010). Unfortunately, anthropic activities have a negative impact upon the soil of green spaces (Hursthouse et al., 2004; Lăcătuşu et al., 2004; Chen et al., 2005; Marjanović et al., 2009; Jien et al., 2011), with undeniable negative consequences regarding public health.

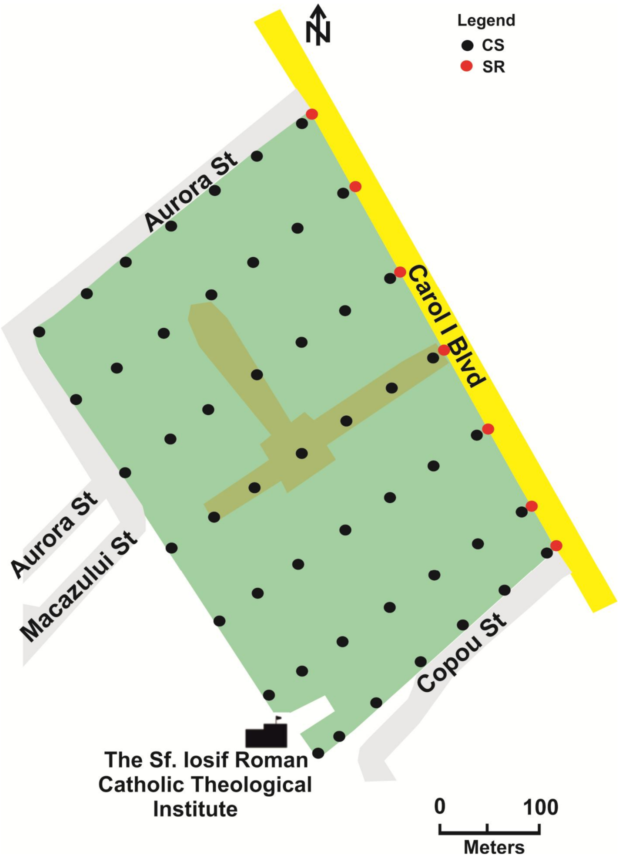


Fig. 1 Sampling network.

Materials and methods

1. Study area

Situated on Copou hill and serving the over 300,000 inhabitants of the city of Iași, Copou Park was created between 1753 and 1852, through the orders of princes Matei Ghica and Mihai Sturdza. Completed, from a stylistic point of view, at the beginning of the 20th century by the Austrian landscape architect Rebhun, Copou Park represented, at the time, a hybrid between the English and French styles (Iliescu, 2006; Tofan, 2008).

According to the provisions of Law 24/2007, Copou Park, which covered an initial area of 20 ha, but currently occupies only 10 ha, is inscribed in the category of public parks (the Official Journal of Romania, 2007).

The soil of Copou Park is of the cambic chernozem type, covered by a strongly anthropic supply (Lăcătuşu et al., 2005).

2. Soil sampling

A number of 42 samples (CS) from 7 alignments perpendicular to Carol I Boulevard were collected from the soil of Copou Park (Fig. 1). In order to underline the direct impact of vehicular traffic upon the soil, 7 additional soil samples (SR) were collected from the soil of the green area situated between the pavement bordering Copou Park and the adjacent road (Fig. 1). The sampling depth was within the 0.0–0.30 m range, while the weight of the samples varies between 1.5 and 2.0 kgs.

3. Analytical procedure

The Fe, Mn, Cr, Co, Ni, Cu, Zn, Pb, As and Cd contents were determined through X-ray Fluorescence Spectrometry (EDXRF Epsilon 5), within the Department of Geology.

Statistical treatment

1. Descriptive statistics

The statistical study, performed using SPSS 19 software, has focused on the main statistical parameters which characterize the heavy metal contents of the soils in the studied area (Tab. 1).

The type of distribution – normal or lognormal – implies the further use, in calculations, of either the arithmetic mean or the geometric mean.

A hierarchy of the average heavy metal content values for the soils in the studied area (Tab. 1; Fig. 2) allows the following observations:

a. CS: Cd < As < Co < Cu < Ni < Pb < Cr < Zn < Mn < Fe
b. SR: Cd < Co < As < Ni < Cu < Cr < Zn < Pb < Mn < Fe
c. quantitatively, CS IS richer in Co, Fe, Mn, Ni and Zn, while SR exhibits higher contents of As, Cd, Cr, Cu and Pb;

When compared to the average heavy metal content values obtained for the soils of the city of Iasi and its surrounding areas by Iancu and Buzgar (2008) and Apostoae and Iancu (2009) (Tab. 1; Fig. 2), the average values obtained for the perimeter studied point to the following:

a. high average values:
  a$_1$. CS and SR: Zn and Pb
  a$_2$. CS: Fe, Cr, Co and Ni
  a$_3$. SR: Cu
b. lower average values:
  b$_1$. CS and SR: Cd

The explanation for the differences noticed lies in the fact that, among the soils described by Iancu and Buzgar (2008) and Apostoae and Iancu (2009), those upon which the anthropic impact has been either reduced or entirely absent (farming areas, forests and semi-natural areas) are predominant (over 72%), while the soils from Copou Park are subjected to continuous stress (largely as a result of vehicular traffic).

Compared to the normal values in soils (NVS) (the average concentration of iron (Fe) in the upper crust, respectively), the heavy metal contents of the soils studied (Tab. 1, Fig. 3) reveal the following:

a. high values:
  a$_1$. CS and SR: Ni, Cu, Zn, Pb and As
  a$_2$. CS: Cr and Co
b. similar values:
  b$_1$. CS: Fe and Mn
  b$_2$. SR: Co
c. low values:
  c$_1$. CS and SR: Cd
  c$_2$. SR: Fe and Mn

The sensible alert thresholds (SAT) and the sensible intervention thresholds (SIT), established by means of Law 756/1997 (the Official Journal of Romania, 1997) (Tab. 2; Figs. 4, 5), are exceeded by the contents of Cr, Cu, Zn, Pb and As (SAT), and Zn, Pb and As (SIT), respectively, indicating a correlation with the road and the residential buildings adjacent to Copou Park.

Table 1 Descriptive statistics parameters of soil heavy metals

	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Background (mg/kg)	Coefficient of Variation	Geometric Mean	Distribution type	Normal value in soils (NVS)[1] (mg/kg)
a.*CS and SR (soil samples = 49)*								
Fe	18604.509	36719.425	29431.208	33234.017	0.146	29079.781	Normal	30890[2]
Mn	557.605	921.597	810.171	893.203	0.113	804.473	Normal	900
Cr	60.825	184.383	94.504	106.899	0.272	91.621	Normal	30
Co	9.659	24.951	18.637	21.855	0.196	18.204	Normal	15
Ni	22.28	51.912	41.116	47.293	0.182	40.307	Normal	20
Cu	28.399	135.167	47.809	44.697	0.567	43.051	Lognormal	20
Zn	75.86	3526.045	211.754	156.204	2.300	143.549	Lognormal	100
Pb	20.73	897.344	66.778	52.66	1.879	46.702	Lognormal	20
As	9.956	54.088	13.79	13.544	0.441	13.248	Normal	5
Cd	0.026	0.437	0.08	0.089	0.731	0.071	Normal	1
b. CS (soil samples = 42)								
Fe	18604.509	36719.425	30556.224	33994.795	0.113	30327.701	Normal	30890[2]
Mn	580.838	921.597	834.932	895.025	0.084	831.684	Normal	900
Cr	60.825	154.407	91.639	84.261	0.247	89.265	Normal	30
Co	9.659	24.951	19.620	18.497	0.147	19.349	Normal	15
Ni	22.881	51.912	43.343	44.645	0.122	42.945	Normal	20
Cu	28.399	66.921	37.488	42.604	0.195	36.902	Lognormal	20
Zn	75.861	3526.045	216.891	158.972	2.429	138.341	Lognormal	100
Pb	20.730	215.396	46.698	50.391	0.726	41.335	Lognormal	20
As	10.223	19.159	13.104	14.682	0.120	13.021	Normal	5
Cd	0.026	0.437	0.077	0.039	0.801	0.067	Normal	1

	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Background (mg/kg)	Coefficient of Variation	Geometric Mean	Distribution type	Normal value in soils (NVS)[1] (mg/kg)
c.*SR (soils samples = 7)*								
Fe	19723.577	25179.034	22681.114	-	0.091	22599.614	-	30890[2]
Mn	557.605	735.728	661.602	-	0.096	658.916		900
Cr	76.969	184.383	111.693	-	0.334	107.123		30
Co	9.967	15.233	12.744	-	0.144	12.628		15
Ni	22.280	32.179	27.750	-	0.126	27.556		20
Cu	80.203	135.167	109.735	-	0.155	108.540		20
Zn	145.449	227.172	180.931	-	0.151	179.186		100
Pb	45.171	897.344	187.256	-	1.674	97.161		20
As	9.956	54.088	17.904	-	0.893	14.694		5
Cd	0.063	0.152	0.100	-	0.320	0.096		1
d.*Soils of Iaşi city and the suburban areas (Iancu and Buzgar, 2008; Apostoae and Iancu, 2009)*								
Fe	4215.00	54111.00	20442.06	-	0.210	20012.260	-	30890[2]
Mn	50.00	1669.00	628.82	-	0.180	616.43		900
Cr	0.00	591.60	36.00	59.166	0.77	31.10		30
Co	4.88	27.90	9.28	11.802	0.24	9.28		15
Ni	13.50	349.60	38.13	46.991	0.55	36.33		20
Cu	11.60	702.61	45.36	48.624	1.02	36.29		20
Zn	10.10	5624.00	114.78	139.349	2.37	83.55		100
Pb	4.50	1995.43	27.73	43.755	2.41	21.32		20
Cd	0.00	15.44	0.49	0.841	1.53	0.35		1

[1] Law 756/1997, Romanian Ministry of Waters, Forests and Environment Protection

[2] average concentration of Fe in the upper crust (Reimann et al., 2008

Table 2 The distribution of the heavy metals reported to NVS[1], SAT[1] and SIT[1]

	[0 ; NVS)	%	[NVS ; SAT)	%	[SAT ; SIT)	%	[SIT ; +∞)	%
a.*CS and SR*								
Mn	46	93.877	3	6.123	0	0	0	0
Cr	0	0	34	69.387	15	30.613	0	0
Co	9	18.367	40	81.633	0	0	0	0
Ni	0	0	49	100	0	0	0	0
Cu	0	0	44	89.795	5	10.205	0	0
Zn	5	10.204	42	85.714	1	2.041	1	2.041
Pb	0	0	35	71.428	11	22.45	3	6.122
As	0	0	46	93.877	2	4.082	1	2.041
Cd	49	100	0	0	0	0	0	0
b.*CS*								
Mn	39	92.857	3	7.143	0	0	0	0
Cr	0	0	30	71.428	12	28.572	0	0
Co	42	100	0	0	0	0	0	0
Ni	0	0	42	100	0	0	0	0
Cu	0	0	42	100	0	0	0	0
Zn	5	11.905	35	83.333	1	2.381	1	2.381
Pb	0	0	34	80.952	6	14.286	2	4.762
As	40	95.238	2	4.762	0	0	0	0
Cd	42	100	0	0	0	0	0	0
c.*SR*								
Mn	7	100	0	0	0	0	0	0
Cr	0	0	4	57.143	3	42.857	0	0
Co	6	85.714	1	14.286	0	0	0	0
Ni	0	0	7	100	0	0	0	0
Cu	0	0	2	28.571	5	71.429	0	0
Zn	0	0	7	100	0	0	0	0
Pb	0	0	1	14.286	5	71.428	1	14.286
As	0	0	6	85.714	0	0	1	14.286
Cd	7	100	0	0	0	0	0	0

[1] Law 756/1997, Romanian Ministry of Waters, Forests and Environment Protection

The coefficients of variation (CV) for CS and SR (Tab. 1, Fig. 6) are within the [0.113÷2.300] interval, a hierarchy of values indicating the following: Mn < Fe < Ni < Co < Cr < As < Cu < Cd < Pb < Zn.

A comparison with the CV values calculated for the heavy metal contents in the soils of the city of Iasi and its surrounding areas (Buzgar and Iancu, 2008; Apostoae and Iancu, 2009) approximately indicates the same order (Tab. 1; Fig. 6). The CV values for CS and SR in the case of Cu (0.567) and, in particular, Pb (1.879) and Zn (2.300) suggest a supplementary contribution of Cu, Pb and Zn, which, in the case of the soils studied, is due to anthropic activity. Pb and Zn have CV values higher than 1.2, justifying a lognormal distribution (Knudsen, 1988; in Moon et al., 2006).

A detailing of CV values for the soil samples analyzed reveals the following:

a. low CV:

a_1. CS and SR: Fe, Mn, Ni, Co, Cu and Cr

a_2. SR: Zn and Cd

a_3. CS: As

b. average-to-high CV:
b_1. CS: Pb and Cd
b_2. SR: As

c. very high CV:
c_1. CS: Zn
c_2. SR: Pb

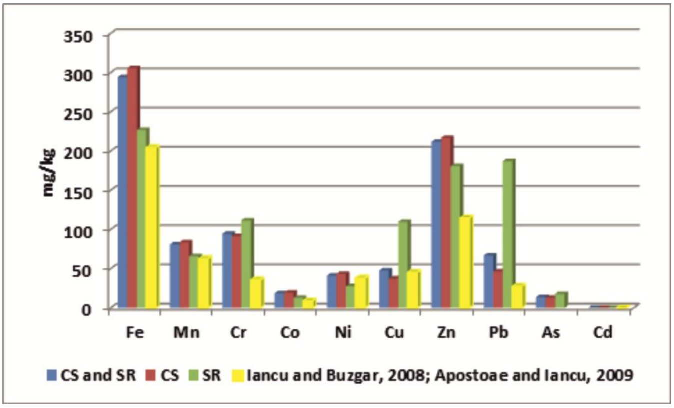


Fig. 2 Average values of the heavy metals contents (Fe × 10^{-2}; Mn × 10^{-1}).

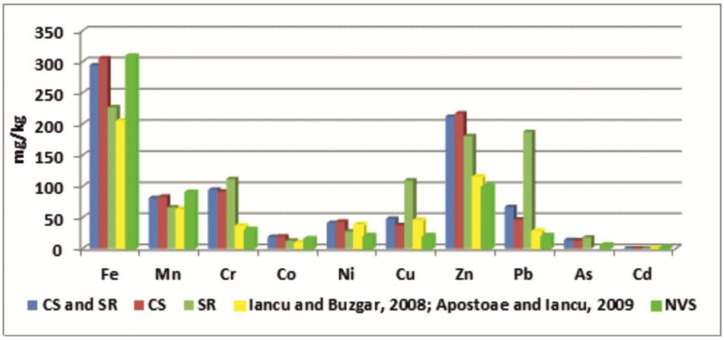


Fig. 3 NVS versus average values of the heavy metals (Fe × 10^{-2}; Mn × 10^{-1}).

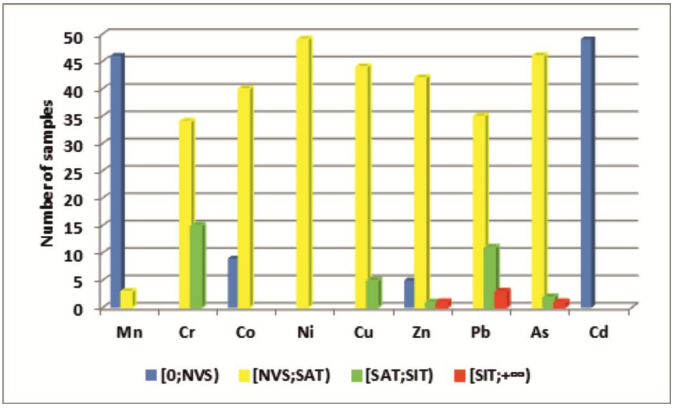
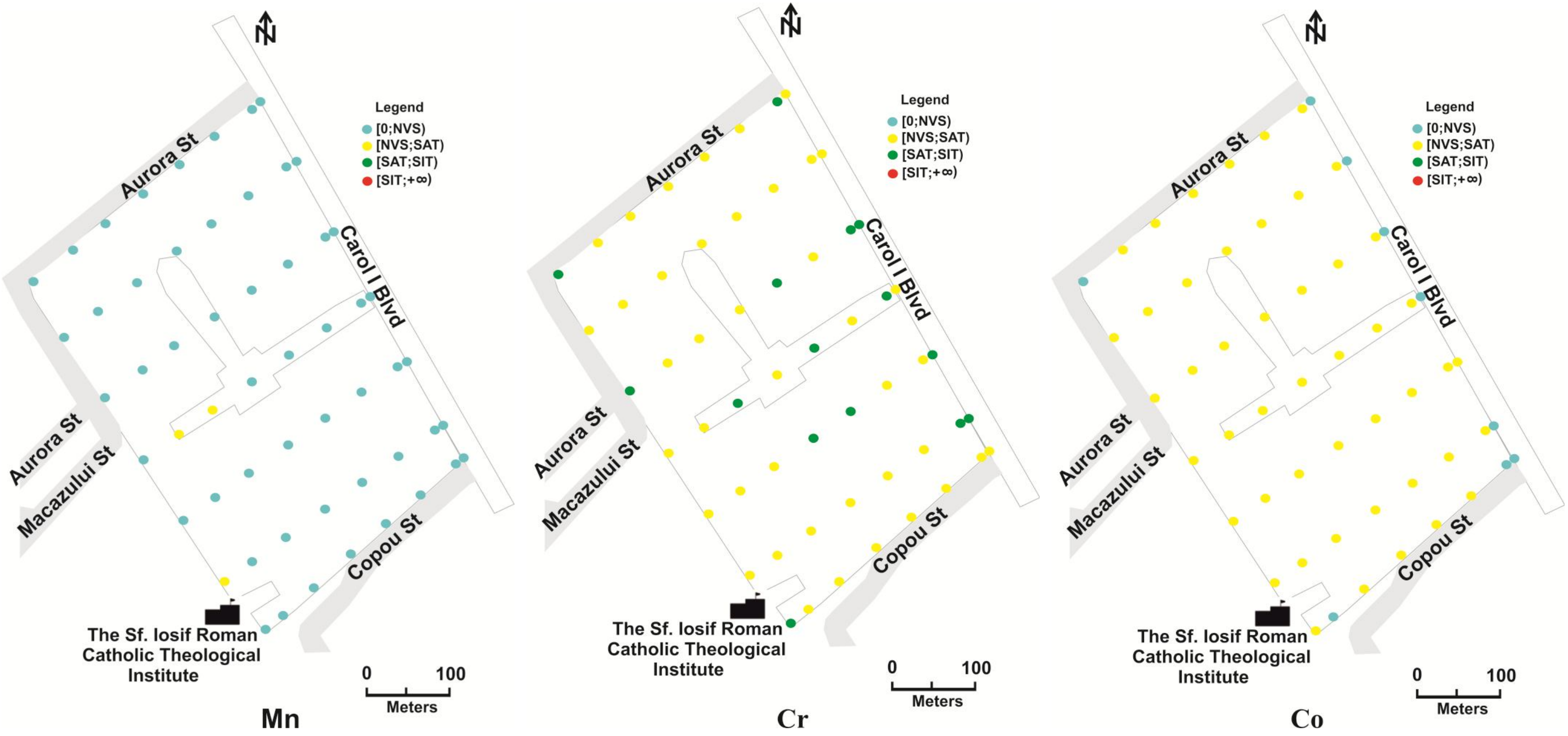
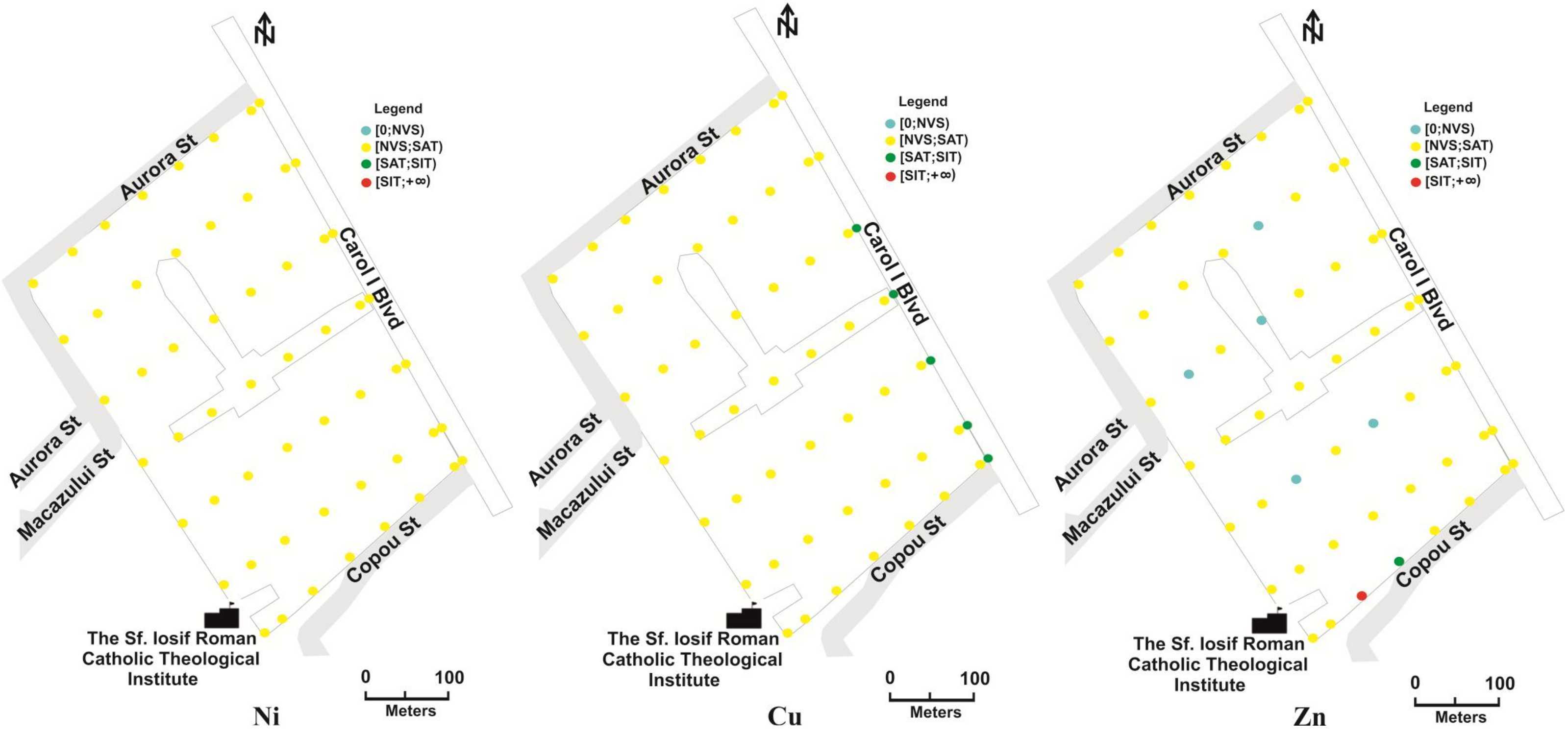


Fig. 4 The contents of the heavy metals reported to NVS, SAT and SIT.



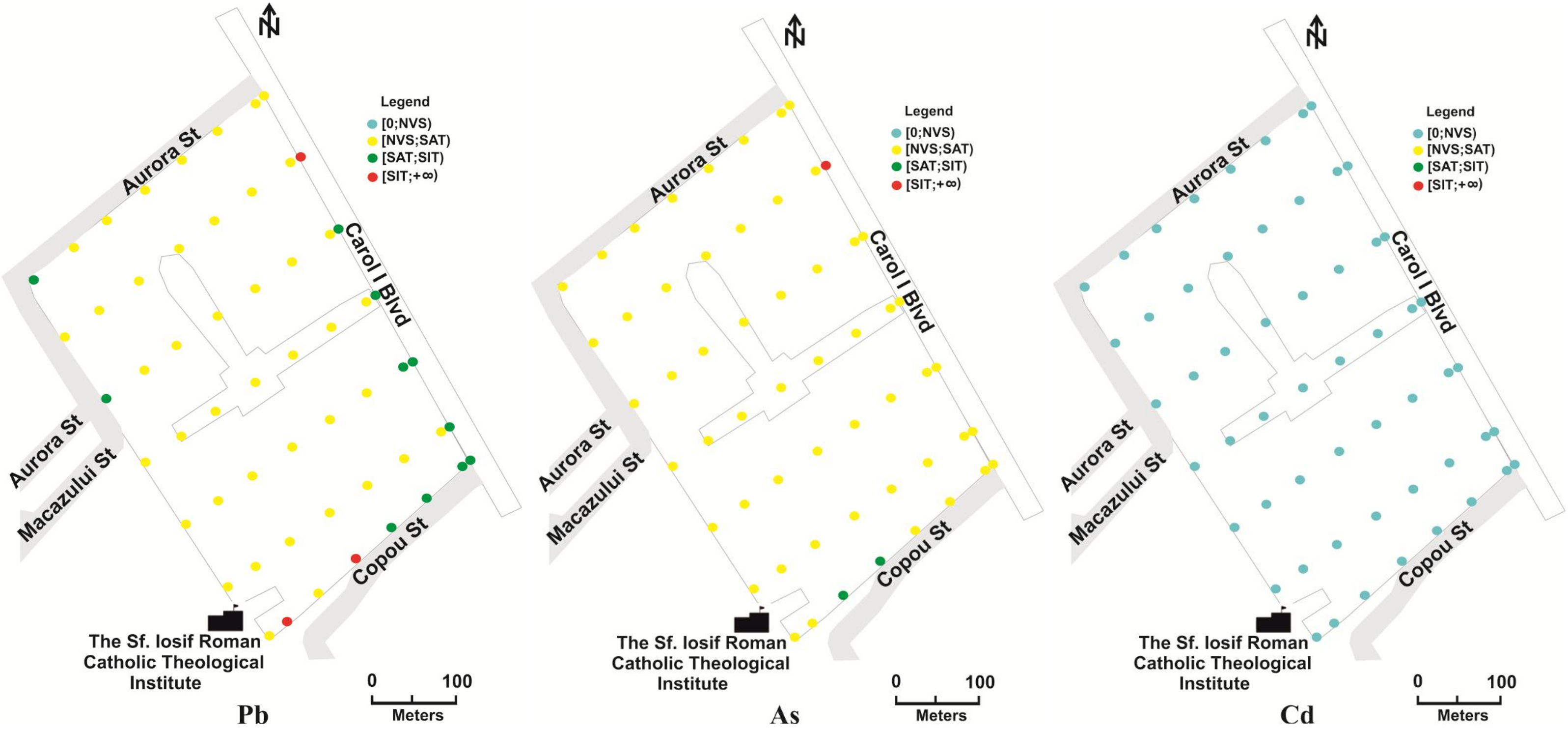
(1) (2) (3)

Fig. 5 The distribution of the heavy metals reported to NVS, SAT and SIT.



(4) (5) (6)

Fig. 5 *(continued)*



(7) (8) (9)

Fig. 5 *(continued)*

Table 3 The Spearman’s rank correlation coefficients of soil heavy metals

a.*CS and SR*

	Fe	Mn	Cr	Co	Ni	Cu	Zn	Pb	As	Cd
Fe	1									
Mn	0.713^{**}	1								
Cr	0.136	-0.076	1							
Co	0.945^{**}	0.623^{**}	0.143	1						
Ni	0.828^{**}	0.551^{**}	0.251	0.827^{**}	1					
Cu	-0.447^{*}	-0.362	0.436^{*}	-0.282	-0.186	1				
Zn	-0.603^{**}	-0.223	0.009	-0.586^{**}	-0.558^{**}	0.331	1			
Pb	-0.795^{**}	-0.428^{**}	0.047	-0.738^{**}	-0.637^{**}	0.138	0.848^{**}	1		
As	-0.103	0.295	0.038	-0.092	0.067	0.051	0.218	0.287	1	
Cd	-0.227	-0.289	-0.047	-0.148	-0.260	-0.089	0.133	0.287	-0.142	1

b.*CS*

	Fe	Mn	Cr	Co	Ni	Cu	Zn	Pb	As	Cd
Fe	1									
Mn	0.650^{**}	1								
Cr	0.121	-0.012	1							
Co	0.949^{**}	0.623^{**}	0.073	1						
Ni	0.841^{**}	0.551^{**}	0.190	0.827^{**}	1					
Cu	-0.213	-0.083	0.037	-0.236	-0.189	1				
Zn	-0.577^{**}	-0.059	-0.038	-0.533^{**}	-0.504^{**}	0.536^{**}	1			
Pb	-0.790^{**}	-0.311	-0.033	-0.726^{**}	-0.690^{**}	0.429^{**}	0.829^{**}	1		
As	-0.140	0.192	0.106	-0.215	-0.087	-0.083	0.359^{*}	0.295	1	
Cd	-0.191	-0.194	-0.054	-0.131	-0.206	0.301	0.077	0.177	-0.039	1

Table 3 *(continued)*

c.*SR*

	Fe	Mn	Cr	Co	Ni	Cu	Zn	Pb	As	Cd
Fe	1									
Mn	0.929**	1								
Cr	0.750	0.643	1							
Co	0.964**	0.857*	0.714	1						
Ni	0.893**	0.929**	0.643	0.857*	1					
Cu	0.857*	0.857*	0.679	0.821*	0.964**	1				
Zn	0.429	0.214	0.036	0.393	0.321	0.357	1			
Pb	-0.071	-0.143	0.429	-0.214	-0.071	0.001	0.001	1		
As	0.144	0.090	0.721	0.054	0.126	0.180	-0.252	0.883**	1	
Cd	0.321	0.393	0.679	0.286	0.214	0.143	-0.607	0.286	0.649	1

******: correlation is significant at the 0.01 level

*** :** correlation is significant at the 0.05 level

Table 4 Total variance explained and component matrices for the soil heavy metals

Total variance explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.078	50.781	50.781	5.078	50.781	50.781	4.659	46.593	46,593
2	1.567	15.671	66.451	1.567	15.671	66.451	1.916	19.162	65,755
3	1.346	13.456	79.907	1.346	13.456	79.907	1.415	14.152	79,907
4	0.874	8.743	88.650						
5	0.554	5.543	94.193						
6	0.336	3.358	97.551						
7	0.119	1.191	98.742						
8	0.072	0.715	99.457						
9	0.038	0.376	99.833						
10	0.017	0.167	100.000						

Component matrix

Element	Component matrix			Rotated component matrix		
	1	2	3	1	2	3
Fe	0.968	0.148	0.022	0.960	-0.175	-0.084
Mn	0.914	0.181	0.064	0.924	-0.135	-0.031
Cr	-0.267	-0.077	0.858	-0.211	-0.143	0.865
Co	0.911	0.269	-0.069	0.940	-0.028	-0.148
Ni	0.900	0.110	0.214	0.898	-0.223	0.107
Cu	-0.666	-0.158	0.371	-0.650	-0.003	0.428
Zn	-0.564	0.393	-0.047	-0.400	0.554	0.087
Pb	-0.855	0.363	-0.177	-0.694	0.642	-0.008
As	-0.001	0.723	0.553	0.284	0.572	0.649
Cd	-0.321	0.767	-0.277	-0.064	0.866	-0.116

Extraction Method: Principal Component Analysis (PCA)

Based on CV values (Yongming et al., 2006), the soils for which the heavy metal contents were calculated can be divided into two groups:

a. soils not affected by anthropic sources of heavy metals:
  a_1. CS and SR: Fe, Mn, Cr, Ni and Cu
  a_2. SR: Cd
b. soils affected by pollution from anthropic sources:
  b_1. CS and SR: Pb
  b_2. CS: Zn and Cd
  b_3. SR: As

2. Spearman's rank *correlation* coefficients (RCC)

Very robust in relation to outliers (Pan and Harris, 2000), RCC (ρ) exhibit the following significant values (Tab. 3):

a. positive:
  a_1. CS: Fe-Mn-Co-Ni; Mn-Co-Ni; Co-Ni; Cu-Zn-Pb; Zn-Pb-As
  a_2. SR: Fe-Mn-Co-Ni-Cu; Mn-Co-Ni-Cu; Co-Ni-Cu; Ni-Cu; Pb-As;
b. negative:
  b_1. CS: Fe-Zn-Pb; Co-Zn-Pb; Ni-Zn-Pb

The same coefficients determined for the heavy metals of CS and SR (Tab. 3) indicate the following significant values, as well:

a. positive: Fe-Mn-Co-Ni; Mn-Co-Ni; Cr-Cu; Co-Ni; Zn-Pb
b. negative: Fe-Cu-Zn-Pb; Mn-Pb; Co-Zn-Pb; Ni-Zn-Pb

By interpreting the values obtained, it may be estimated that Fe, Mn, Co and Ni reflect the natural geochemical background of the soils studied, which exhibit either no anthropic contribution or only a slight one. On the contrary, the RCC for Cu, Pb and Zn suggest both an anthropic input in the case of CS, and a possible common source.

3. Principal components analysis (PCA)

PCA indicates that the heavy metal contents from the soils studied may be reduced to 3 components, which account for over 79% of the total variation (Tab. 4). The commonalities (Jackson, 2003) between the heavy metal contents studied indicate the following: Zn (0.475) < Cu (0.606) < Cd (0.768) < Cr (0.814) < As (0.829) < Ni (0.867) < Mn (0.873) < Pb (0.893) < Co (0.907) < Fe (0.960).

The initial component matrix (Tab. 4) indicates that Fe, Mn, Co and Ni associate, an aspect highlighted by the high values in the F1 component. As and Cd associate in the second component (F2), displaying comparable values, while Cr and As associate in the third component (F3). The presence of As both in F1 and in F2 reflects the natural background of the soil studied, an anthropic contribution being associated, as well.

The rotated component matrix (Tab. 4; Fig. 7) suggests the possible source of the heavy metals from the soils studied. F1 shows high positive factor loadings of Fe, Mn, Co and Ni, an aspect also emphasized by the RCC ($\rho_{\text{Fe-Mn}} = 0.713$; $\rho_{\text{Fe-Co}} = 0.945$; $\rho_{\text{Mn-Co}} = 0.623$; $\rho_{\text{Fe-Ni}} = 0.828$; $\rho_{\text{Mn-Ni}} = 0.551$), and moderately negative loadings of Cu, Zn, Pb ($\rho_{\text{Fe-Cu}} = -0.447$; $\rho_{\text{Mn-Cu}} = -0.362$; $\rho_{\text{Fe-Zn}} = -0.603$; $\rho_{\text{Mn-Zn}} = -0.223$; $\rho_{\text{Fe-Pb}} = -0.795$; $\rho_{\text{Mn-Pb}} = -0.428$). Kabata-Pendias and Pendias (2001) and Kabata-Pendias and Mukherjee (2007) have underlined the fact that, in soils, the oxides and hydroxides of Fe and Mn play a crucial role in the precipitation of heavy metals. By corroborating this observation with that of Reimann et al. (2008), who regard Mn as the conservative lithogenic reference element, we may conclude that the Fe and Mn from the soils studied are derived from parent materials, an observation which is also valid for Co and Ni.

F2 displays moderate positive loadings of Zn and Pb, which, correlated with the moderate negative loadings of the same chemical elements in F1, indicate variable degrees of anthropic contribution superposing over the natural geochemical background. The strong positive loading of Cd and the negative correlations with Fe and Mn ($\rho_{\text{Fe-Cd}} = -0.227$; $\rho_{\text{Mn-Cd}} = -0.289$) suggest an independent source.

F3 exhibits a strong loading in the case of Cr, which reflects a strong anthropic contribution ($\rho_{\text{Fe-Cr}} = 0.136$; $\rho_{\text{Mn-Cr}} = -0.076$). The average positive loadings registered in the case of Cu and As, corroborated with the presence of the two chemical elements in F1 and F2, reflect a purely anthropic contribution, which affects the natural geochemical background of the soils studied.

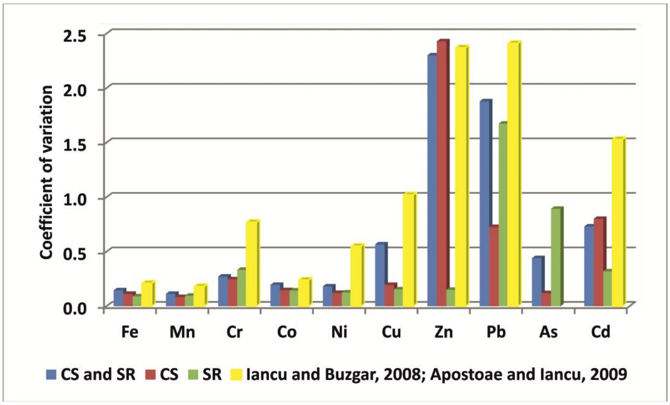


Fig. 6 CV of soil heavy metals.

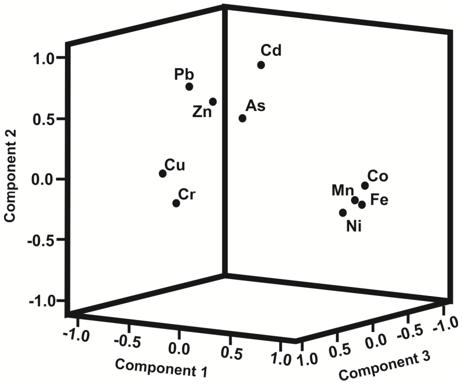


Fig. 7 The Component plot in rotated space for the heavy metals (according to the distribution type)

Geochemical background (GB)

The local GB for the heavy metals from CS was calculated using the Ouellette and Morissette method (2007). In the case of SR, due to the reduced number of samples, the values of the local GB were regarded as equal to the geometric mean.

The first aspect worth pointing out is the fact that, for the heavy metals studied, with the exception of Mn and Cd, the local GB exceeds the NVS (the average concentration of Fe in the upper crust, respectively) (Tab. 1; Fig. 8).

At the same time, compared to SR, CS is characterized by values of the local GB which are higher in the case of Fe, Mn and Co. In the case of As, the local GBs from the two areas are approximately equal.

The ratios between the local GBs calculated for the studied area (CS and SR) and the GB calculated for the heavy metal contents in the soils of the city of Iasi and its sub-urban areas (Apostoae and Iancu, 2009) indicate super unitary values, with the exception of Cu and Cd. This aspect is explained by the fact that the soils studied by Apostoae and Iancu (2009) include, on the one hand, soils over which the anthropic impact has been either reduced or absent, and, on the other hand, soils in which extremely high contents of Cu (vineyards and orchards) and Cd (waste dumps) were determined.

Soil pollution estimation method

The method through which the degree of pollution caused by heavy metals in the soils studied was estimated is based on the geo-accumulation index (I_{geo}) (Müller, 1969):

$$I_{geo} = log_2 \frac{C_i}{1.5B_i}$$

where: C_i = the measured concentration of the heavy metal in the soil;

B_i = the geochemical background value;

1.5 = the background correction factor due to lithogenic effects (Chen et al., 2007).

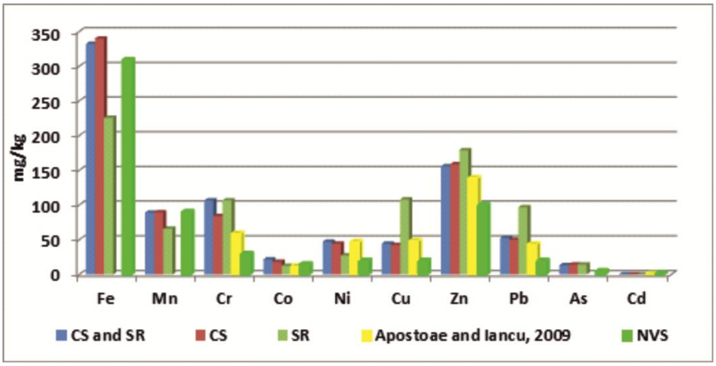


Fig. 8 GB for heavy metals (Fe × 10^{-2}; Mn × 10^{-1}).

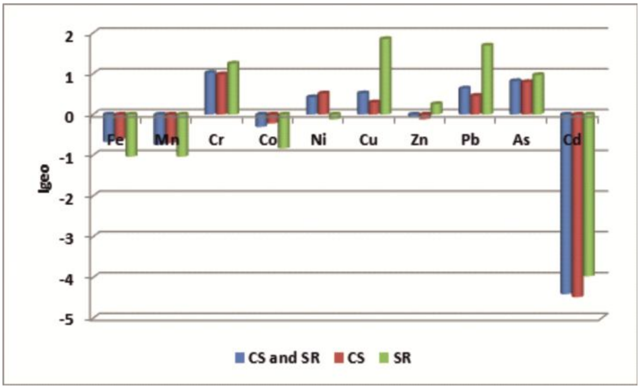


Fig. 9 The average values of I_{geo} for heavy metals.

Given that, in our opinion, one cannot completely eliminate the anthropic effects from the calculated GB, the determination of the I_{geo} was carried out using the following formula:

$$I_{geo} = log_2 \frac{C_i}{1.5\text{NVS}}$$

where: C_i = the measured concentration of the heavy metal in the soil;

B_i = the normal value in soil (the average concentration in the upper crust in the case of Fe);

1.5 = the background correction factor due to lithogenic effects (Chen et al, 2007).

The values of the I_{geo} (Fig. 10) are theoretically inscribed within the (-∞; +∞) domain, the identification of the degree of pollution being achieved through the help of critical intervals such as: I_{geo} € (-∞÷0]: unpolluted soil; I_{geo} € (0÷1]: unpolluted to moderately polluted soil; I_{geo} Є (1÷2]: moderately polluted soil; I_{geo} Є (2÷3]: moderately to strongly polluted soil; I_{geo} Є (3÷4]: strongly polluted soil; I_{geo} Є (4÷5]: strongly to very strongly polluted soil; I_{geo} Є (5÷ +∞]: very strongly polluted soil.

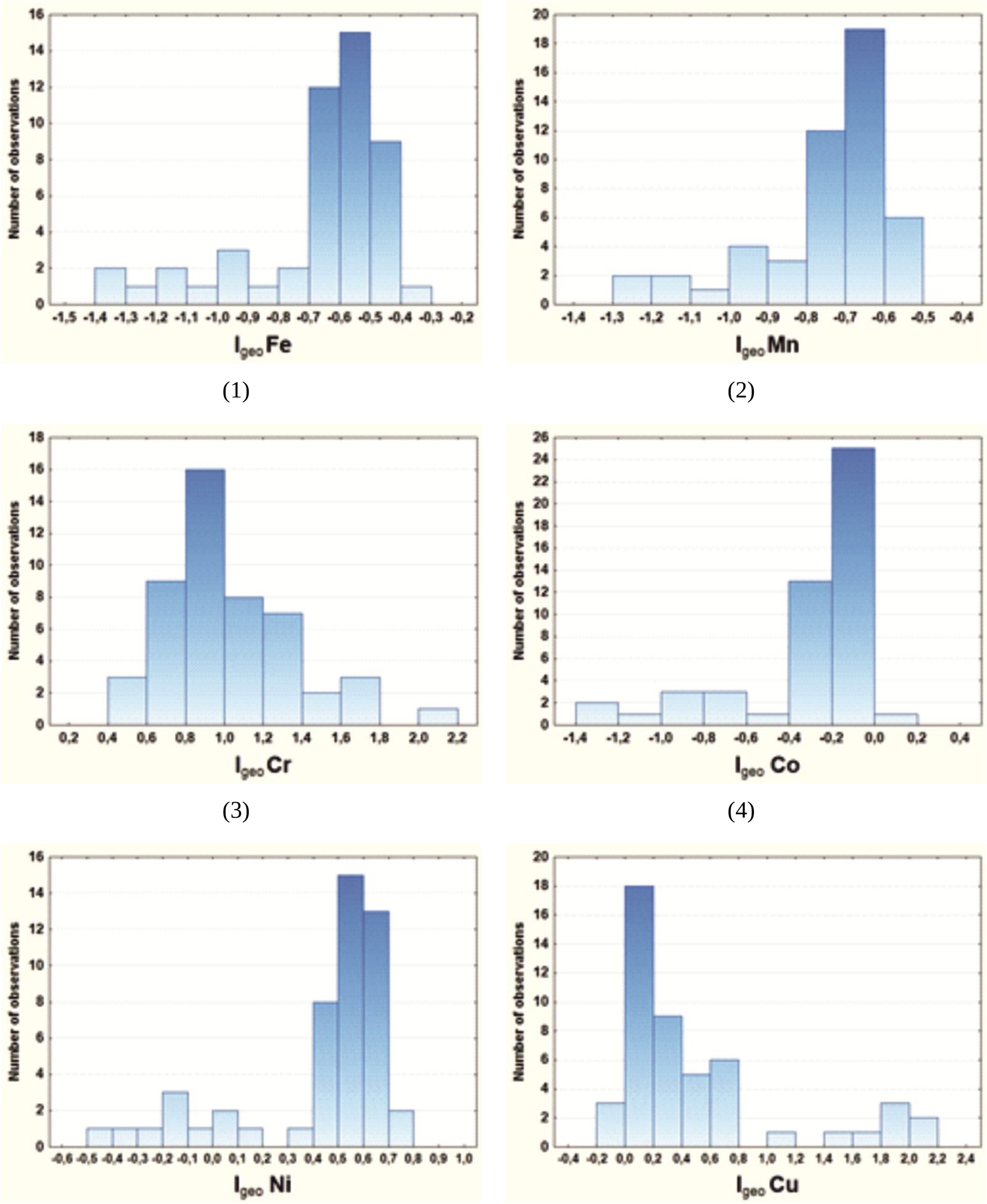


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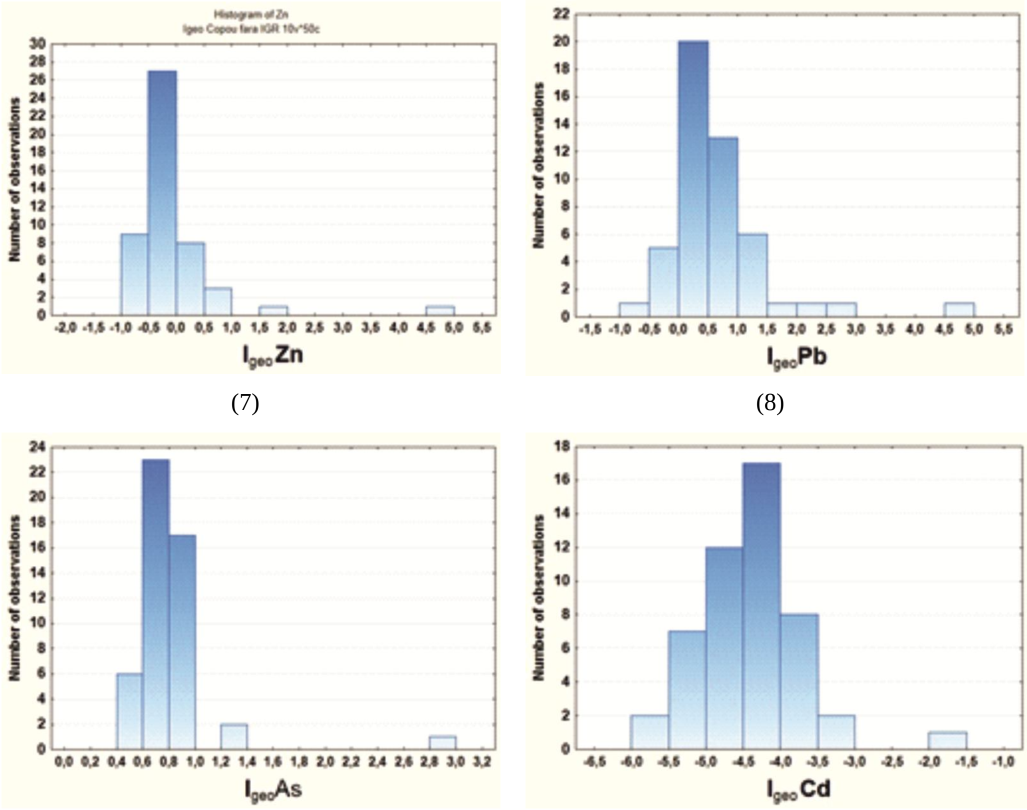
Fig. 10 The values of I_{geo} for heavy metals.



(7) (8)

(9) (10)

Fig. 10 *(continued)*

The average values of the I_{geo} (Tab. 5; Fig. 9) indicate that CS and SR may be characterized as follows:

a. unpolluted with Fe, Mn, Co, Zn and Cd;
b. unpolluted to moderately polluted with Ni, Cr, Pb and As;
c. moderately polluted with Cr.

A detailing of the average values obtained for the I_{geo} (Tab. 5) leads to the degree of pollution being within the following categories:

a. unpolluted:
  $a_{1.}$ CS: Zn
  $a_{2.}$ SR: Fe, Mn, Co, Cd and Ni
b. unpolluted to moderately polluted:
  $b_{1.}$ CS and SR: As
  $b_{2.}$ CS: Cr, Ni, Cu and Pb
  $b_{3.}$ SR: Zn
c. moderately polluted:
  c_1. SR: Cr, Cu and Pb

Spatial Structure Analysis

Webster and Olivier (2007) regard the heavy metals in soils as typical regionalized variables. The experimental semivariogram, the main instrument in the study of regionalized variables, measures the average dissimilarity between data separated by a vector h (Goovaerts, 1997). The value of the experimental semivariogram for a separation distance of h is half the average squared difference between the value at $Z(x_i\ )$ and $Z(x_i+h)$:

Table 5 I_{geo} values for the soil heavy metals

	< 0	%	0 - 1	%	1 - 2	%	2 - 3	%	3 - 4	%	4 - 5	%	> 5	%	Mean
a.*CS and SR (soil samples = 49)*															
Fe	49	100	0	0	0	0	0	0	0	0	0	0	0	0	-0.672
Mn	49	100	0	0	0	0	0	0	0	0	0	0	0	0	-0.747
Cr	0	0	28	57.143	20	40.816	1	2.041	0	0	0	0	0	0	1.026
Co	48	97.959	1	2.041	0	0	0	0	0	0	0	0	0	0	-0.306
Ni	7	14.286	42	85.714	0	0	0	0	0	0	0	0	0	0	0.426
Cu	3	6.122	38	77.551	6	12.245	2	4.082	0	0	0	0	0	0	0.521
Zn	47	95.918	0	0	1	2.041	0	0	0	0	1	2.041	0	0	-0.063
Pb	6	12.245	33	67.346	7	14.286	2	4.082	0	0	1	2.041	0	0	0.639
As	0	0	46	93.877	2	4.082	1	2.041	0	0	0	0	0	0	0.821
Cd	49	100	0	0	0	0	0	0	0	0	0	0	0	0	-4.409
b.*CS (soil samples = 42)*															
Fe	42	100	0	0	0	0	0	0	0	0	0	0	0	0	-0.611
Mn	42	100	0	0	0	0	0	0	0	0	0	0	0	0	-0.699
Cr	0	0	26	61.905	16	38.095	0	0	0	0	0	0	0	0	0.988
Co	41	97.619	1	2.381	0	0	0	0	0	0	0	0	0	0	-0.218
Ni	2	4.762	40	95.238	0	0	0	0	0	0	0	0	0	0	0.518
Cu	3	7.143	38	90.476	1	2.381	0	0	0	0	0	0	0	0	0.299
Zn	35	83.333	5	11.905	1	2.381	0	0	0	0	1	2.381	0	0	-0.117
Pb	6	14.286	32	76.190	2	4.762	2	4.762	0	0	0	0	0	0	0.462
As	0	0	40	95.238	2	4.762	0	0	0	0	0	0	0	0	0.796
Cd	42	100	0	0	0	0	0	0	0	0	0	0	0	0	-4.482

Table 5 *(continued)*

	< 0	%	0 - 1	%	1 - 2	%	2 - 3	%	3 - 4	%	4 - 5	%	> 5	%	Mean
c.*SR (soil samples = 7)*															
Fe	7	100	0	0	0	0	0	0	0	0	0	0	0	0	-1.036
Mn	7	100	0	0	0	0	0	0	0	0	0	0	0	0	-1.035
Cr	0	0	2	28.571	4	57.143	1	14.286	0	0	0	0	0	0	1.251
Co	7	100	0	0	0	0	0	0	0	0	0	0	0	0	-0.833
Ni	5	71.429	2	28.571	0	0	0	0	0	0	0	0	0	0	-0.123
Cu	0	0	0	0	5	71.429	2	28.571	0	0	0	0	0	0	1.855
Zn	1	14.286	6	85.714	0	0	0	0	0	0	0	0	0	0	0.256
Pb	0	0	1	14.286	5	71.429	0	0	0	0	1	14.286	0	0	1.695
As	0	0	6	85.714	0	0	1	14.286	0	0	0	0	0	0	0.970
Cd	7	100	0	0	0	0	0	0	0	0	0	0	0	0	-3.971

$$\gamma(h) = \frac{1}{2}Var[Z(x+h) - Z(x)]$$

$$\gamma(h) = \frac{1}{2\mathrm{N(h)}}\sum_{i=1}^{N(h)}[Z(x_i) - Z(x_i+h)]^2$$

where: *N(h)* is the total number of pairs of sampling points separated by the lag distance *h*;

Z(xi) is the measured sample value at point *i*;

Z(xi + h) is the measured sample value at point *i* + *h*.

Experimental semivariograms represent the variance of the sample value (in the present case, the values of the I_{geo}) at different separation distances, and are characterized by nugget (C_o), sill ($C+C_o$) and range (Armstrong, 1998; Pan and Harris, 2000).

The theoretical models which correspond to the experimental semivariograms set up for the I_{geo} calculated for the heavy metal contents from the soils studied are the following: a) the exponential model (Ni, Cu, Zn, Pb and Cd); b) the Gaussian model (Fe, Mn, Co and As); c) the spherical model (Cr).

The I_{geo} calculated for the heavy metal contents (Tab. 6) varies within the 49.08 m (Cr) ÷ 250.23 m (Fe) interval. The ranges of Fe (250.23 m), Mn (244.93 m), Ni (249.21 m) and Co (242.41 m) are very closely related to these values, suggesting both a good spatial correlation, and the fact that the natural geochemical background is either not affected or only slightly affected by anthropic sources.

Tab. 6 Semivariogram models and parameters for the soil heavy metals

Parameter/ Element	Model	C_o	C	Major axis range (m)	Co/(C+Co) (%)
Fe	Gauss	0.021	0.070	250.23	23.07693
Mn	Gauss	0.011	0.050	244.93	18.03279
Cr	Sph	0.094	0.138	149.08	40.51724
Co	Gauss	0.043	0.139	242.41	23.62637
Ni	Exp	0.011	0.175	249.21	5.913978
Cu	Exp	0.467	0.696	175.67	40.15477
Zn	Exp	0.441	1.191	205.48	27.02206
Pb	Exp	0.393	0.790	173.15	33.22063
As	Gauss	0.165	0.211	218.42	43.88298
Cd	Exp	0.121	0.361	221.74	25.10373

The [Co/(Co+C)] ratio, expressed in percentages (Tab. 6), is regarded as a criterion for the classification of the spatial dependence of soil characteristics (Cambardella et al., 1994). If the ratio is less than 25% (Fe, Mn, Co and Ni), the variable has a strong spatial dependence. If the ratio is between 25% and 75% (Cr, Cu, Zn, Pb, As and Cd), the variable has moderate spatial dependence. When the ratio exceeds 75%, the variable displays weak spatial dependence.

The maps of the distribution of the I_{geo} calculated for heavy metals (Fig. 11) were devised by means of ArcGis 9.3, through the kriging method, using the parameters of the semivariograms (Tab. 6).

Analysis of pollutant sources

The possible sources which generate the anthropic stress to which the soils from the area of Copou Park studied have been and continue to be subjected are the following:

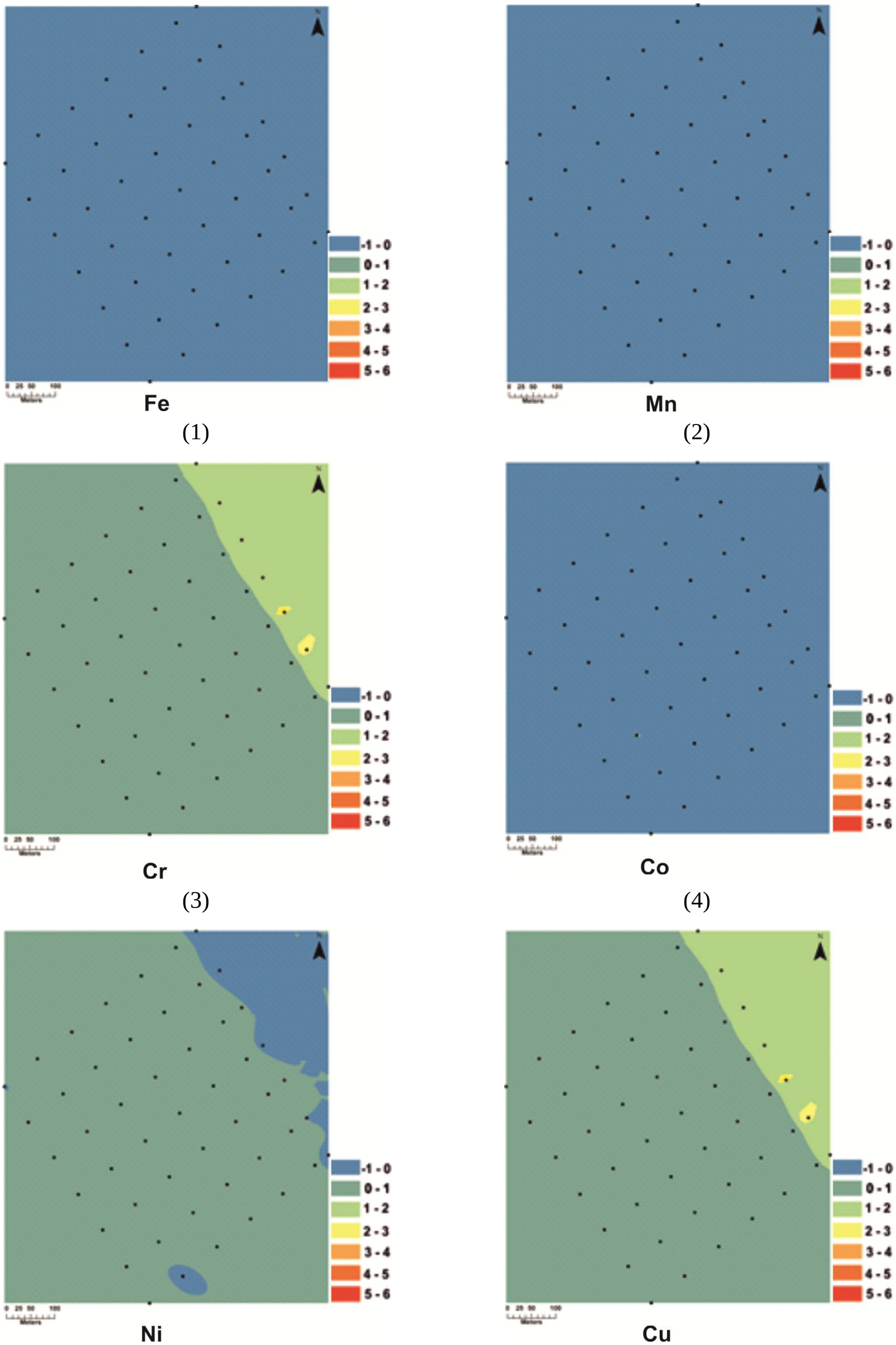


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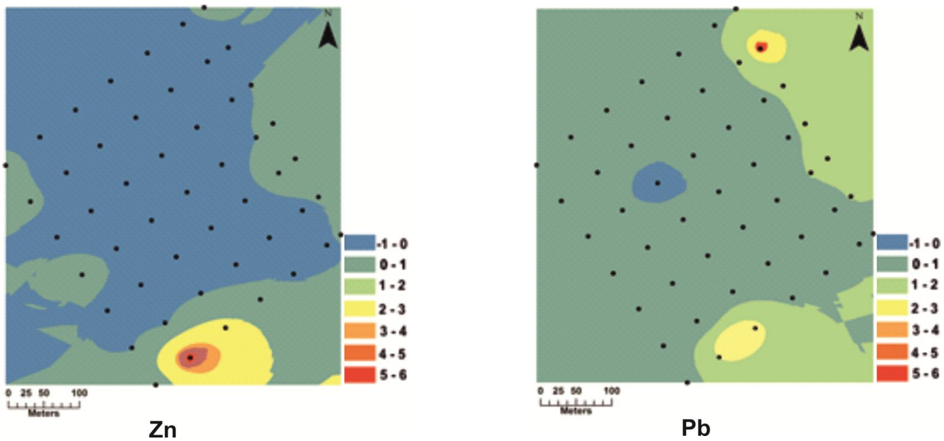
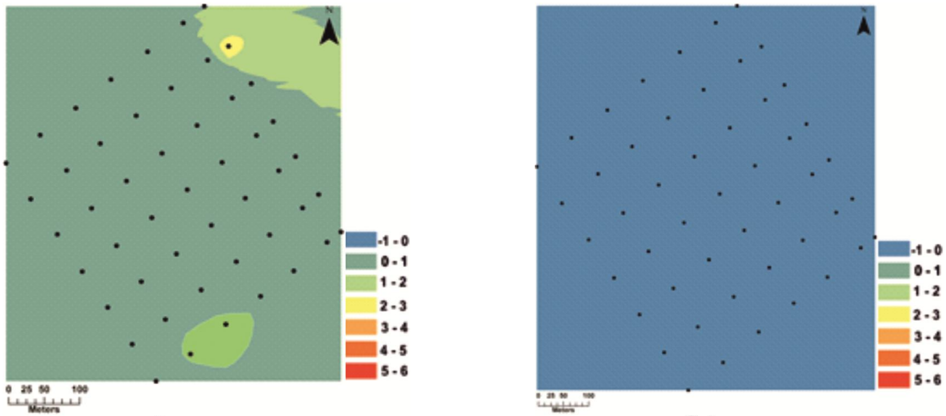
Fig. 11 The soil pollution map



Zn (7) **Pb** (8)



As (9) **Cd** (10)

Fig. 11 *(continued)*

a). the age of the park, which entails a multitude of factors with a variable evolution over time, factors that are, therefore, difficult to quantify. From the point of view of its age, according to Chen et al. (2005), Copou Park is included in Group B, which consists of parks with a history exceeding 100 years;

b). the intense traffic (cars, trams) on the streets adjacent to the park – Carol I Boulevard, in particular;

c). the maintenance works being carried out on the green spaces (chemical fertilizers, fungicides, insecticides);

d). the general urbanization process, which entails the building of residential complexes, some of them equipped with fossil-fuel-based heating systems, in the close proximity of Copou Park;

e). the works carried within the "Road network development in the cultural, historic and touristic areas of the city of Iasi" project (www.primaria-iasi.ro), which generate large quantities of dust;

f). the pollution caused by industrial activities, which has, indeed, diminished to a great degree since 1989.

The impact of the traffic on the streets adjacent to Copou Park, which generates airborne heavy metals, is especially noticeable in the case of Cu, Pb and Zn (Figs. 5, 10). Although leaded gasoline has been forbidden in Romania since 2005 (the admissible limit for the concentration of Pb in gasoline is, presently, 0.005 g/l (Government Resolution 689/2004)), the high average contents of Pb found in the soils studied reflect its accumulation as a result of the long-term use of Pb as additive in gasoline. Cu, used in the braking devices and radiators of vehicles, and Zn, used in the composition of lubricants and protection alloys for means of transportation like cars and trams, generate, through mechanical corrosion, important quantities of metals, which modify the natural GB of the soils.

The average RCC values, which are significantly positive, as well as the distribution of the values of the I_{geo} in the soils studied, suggest a common source for Cu, Pb and Zn. Although Kelly et al. (1996) regard Cu, Pb and Zn as having an identical behavior in soils affected by vehicular traffic, in the case of CS, the average Zn content is higher, compared to that of SR. This is due to an exceptional sample (sensu Sinclair and Blackwell, 2002), collected from CS, from a sampling point approximately 10m from a residential complex covered with galvanized metal sheets, whose Zn content was measured at 3526.045 mg/kg. Chen et al. (2005) correlate the age of parks with the heavy metal contents found in their soils, specifying the important role played by the application of dyes containing heavy metals. For the soils of Copou Park, this aspect is difficult to estimate, given the lack of information related to the type of dyes used from the 18th century onward.

Chromium, a chemical element which is found in additive-enriched gasoline in the form of chromium hexacarbonyl, in the metal alloys used for certain components of vehicles, as well as in fungicides and insecticides, displays a set of contradictory aspects in the soils studied. Thus, although it exceeds the NVS both in the case of CS and in that of SR, it does not exhibit significant RCC with any of the other chemical elements studied, except Cu ($_{\rho Cr\text{-}Cu}$ = 0.436). This aspect, together with the CV and the distribution of the values of the I_{geo}, suggest an anthropic source of Cr which is different from that of Pb and Zn. This source seems to lie in the mechanical usage of the components of trams and cars and the rehabilitation works being carried out on the road network, which are added (and totally subordinated) to the fungicides and insecticides applied to the vegetation from Copou Park.

Nickel, a chemical element which enters the composition of several alloys, rechargeable batteries, certain detergents (nickel sulphate hexahydrate) and fungicides, is regarded by Cannon and Horton (2009) as exceeding normal values in the soils where it is associated with Pb, Zn and Cu. However, in the soils studied, with the exception of SR, where $\rho_{Ni\text{-}Cu} = 0.964$, the RCC highlights significantly negative correlations between Ni-Pb-Zn. This indicates that the source of Ni lies in the mechanical deterioration of the alloys of Cu and Ni used in the braking devices, hydraulic suspension systems and cooling systems of cars, or in the works being carried out within the road rehabilitation project. The average contents, as well as the values of the I_{geo} calculated for the soils studied, indicate a reduced-to-moderate degree of pollution with Ni, which is in contradiction with the observaions formulated by Chen et al. (2005) and Onder et al. (2007) in relation to parks and green spaces from China and Turkey, where contents exceeding the natural GB were not noticed.

Cobalt, whose anthropic source may be correlated with the burning of fossil fuels (coal and oil), the mechanical deterioration of metallic alloys and the use of cobalt-based paints, seems to be associated with Cu, Ni, Mn and As (MEE, 2001). This is partially verified in the case of the soils studied, the RCC indicating significantly positive values only in the case of Fe, Mn, and Ni. In these soils, the average Co contents are similar in relation to the values of the NVS, the I_{geo} indicating a lack of pollution, an aspect which is in agreement with the observations made by Onder et al. (2007).

Arsenic, which is currently used in paints, pesticides, herbicides and fertilizers, in metal alloys, semiconductors, medicines and wood preservatives, is considered one of the most dangerous chemical elements when it comes to human health (Henke, 2009; Henke and Atwood, 2009). Presently, due to anthropic sources, arsenic is found in some urban soils in quantities which exceed the legal limits (Järup, 2003; Onweremadu et al., 2008; Oprea et al., 2010; Zhang et al., 2011). In parks and green areas, arsenic is present in quantities which vary from insignificant (Mäntylahty and Laakso, 2002) to high (Xu and Thornton, 1985; Peryea, 1999; Jien et al., 2011), which is probably due to the use of lead arsenate as insecticide (Peryea, 1999). In the soils studied, the average values of As exceed the NVS, and the values of the I_{geo} indicate a degree of pollution which varies from unpolluted to moderately polluted, with the exception of certain samples collected from SR, in whose case the pollution is included in the moderately-to-strongly polluted category.

What is interesting is that As displays RCC with significant values only with Zn ($\rho_{As\text{-}Zn)}$ = 0.359) in the case of CS, and with lead (Pb) in the case of SR ($\rho_{As\text{-}Pb}$ = 0.833). These aspects, in conjunction with the CV values of As (which are low in the case of SR), suggest a double anthropic contribution, namely the use of lead arsenate and/or zinc arsenate as pesticides (Reigart and Roberts, 1999), on the one hand, and vehicular traffic, on the other.

In relation to the last aspect, Brandão et al. (2006) and Trindade et al. (2006) established the presence of certain quantities of As in gasoline and Onweremadu et al. (2008) determined high quantities of As in the proximity of an automobile servicing station.

Cadmium, presently found in alloys, rechargeable nickel-cadmium batteries, phosphate fertilizers, anticorrosion agents, as pigment in paints or as stabilizer for polyvinyl chloride (PVC), constitutes one of the main environmental pollutants, especially when cadmium-containing products are incinerated (Järup, 2003). Other generators of Cd are the corrosion of galvanized-metal structures and the deterioration of old facades or recently redecorated walls (Charlesworth et al., 2011). Regarding the soils of parks and green spaces in urban areas, studies indicate both the absence of pollution (Li et al., 2001; Jien et al., 2011) and a reduced-to-average level of pollution with Cd (Yang et al., 2009; Marjanović et al., 2009). CS and SR exhibit average contents of Cd, clearly inferior to the NVS, which points to their inclusion, according to the I_{geo}, into the unpolluted soils group.

The average contents calculated for Fe and Mn do not exceed the NVS for average content in the upper crust. Therefore, Reimann et al. (2008) regard Mn as the conservative lithogenic reference element. The RCC calculated for the soils studied suggest the association of Fe and Mn with Co and Ni, and different sources for Cu, Zn and Pb.

Conclusions

The study of the distribution of heavy metals in the soils of Copou Park has highlighted the importance of the proximity of potential anthropic sources of pollution. If the Fe, Mn, Co, Ni and Cd contents seem to be typical for the natural geochemical background, unaffected by anthropogenic inputs, Cr, Cu, Zn and As are characterized by an I_{geo} which varies from moderately polluted to strongly polluted, but is, still, in agreement with SAT and SIT values. Although the heavy metal contents of the soils of Copou Park are not highly dangerous for human health, a constant monitoring of the area, which would allow efficient solutions to be implemented in the future, is desirable.

Acknowledgements

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