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Assessing sources and contaminates of soil in public parks and playgrounds of Romanian cities located on the external side of the Carpathian mountain chain

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Abstract. The Romanian cities, especially in the proximity of the Carpathian mountain chain, are acknowledged for the natural resources and for the intense anthropogenic activities related to their exploitation and processing. Nevertheless, the effects of these activities on urban soil quality have not been yet consistently assessed. In this regard the present paper aims at identifying contamination levels, sources of origins and components of urban soil in public parks and playgrounds strongly related to anthropogenic activities in 11 Romanian cities. Twenty five different elements concentrations were determined in order to identify their source in soil and whether or not they can be considered as contaminants. The study has been carried out at 59 urban parks and playgrounds, using analytical procedures, multivariate statistical and mathematical methods. Results highlight concentrations for contaminants such as Cr, Cu, Zn, As, Cd, Sb, Hg, Pb and Mo that recurrently exceed alert thresholds established for Romania, denoting extensive pollution in public urban recreational areas. In 15% of the locations punctual severe contamination has been identified, mainly by Hg, As, Pb and Cr. Both principal components and factor analyses indicate anthropogenic activities (mainly metallurgy and traffic) as sources for these contaminants.

Key Words: recreational urban areas, soil contamination, principal component analysis, positive matrix factorisation, enrichment factors, geochemistry.

Introduction. Anthropogenic soil contamination represents a worldwide concern due to the serious risks for human health and ecosystem quality (Norra & Stuben 2003; Braz et al 2013). Although a number of elements occur naturally in soils, the anthropogenic impact in urban areas has increased their concentrations in topsoil layers converting them to contaminates (Hursthouse et al 2004; Chen et al 2005; Ristic & Marjanovic 2006; De Miguel et al 2007). The Romanian territory, especially in the proximity of the Carpathian mountain chain, is acknowledged for the natural mineral resources (metallic and non-metallic) and energetic resources (coal, gas and radioactive elements) (Borcoş & Udubaşa 2012) and for the intense anthropogenic activities related to their exploitation and processing (Bird et al 2005; Máthé et al 2012; Weindorf et al 2013). Taking into account the deficient environmental regulations and lack of land use planning procedures, it is expected that soil in urban areas of Romania may be severely contaminated. Nevertheless, the presence of a number of elements in top soils may not necessarily represent pollution. In this regard, assessing sources of origin of contaminants in soil represents an important step in understanding their provenience and behaviour. This is essential in order to properly limit future soil contamination and to be able to decide upon suitable mitigation and remediation actions for existing contaminated sites.

This study aims at identifying pollutants levels, sources of origin and components of soil in public parks and playgrounds strongly related to anthropogenic activities in 11 Romanian cities situated on the external side of the Carpathian Mountains. Twenty five different chemical species concentrations are determined in order to identify their source of provenience in soil and whether or not they ca be considered as contaminants. Soil samples were collected in urban parks and playgrounds, due to the fact that risks posed by the presence of contaminants in these areas are increased by the vulnerability of children, and by the increased uptake of soil particles that occurs during outdoor activities.

Due to the large geographical domain under study, geochemical composition of sediments is very heterogeneous as the bed-rock material. Also, special attention must be given to the fact that urban soils have great horizontal and vertical variability, disruptions in natural parental rock, atypical mineralogy, low porosity, the presence of a crust, restricted aeration and permeability, incomplete nutrients cycle and frequent exposure to contamination sources (Craul 1985).

Therefore we used a combination of analytical procedures, multivariate statistical and mathematical methods (similarly to receptor modelling studies in air quality sciences), allowing to discloses concentrations of urban recreational area soil components, sources of species origination and highlights cases of anthropogenic contamination in urban settlements located in the external side of the Carpathian mountain chain. The results of this study are disseminated in order to supplement the scientific research previously conducted on the topic, and to shed specific insights of Romania's present situation in terms of urban soil contamination.

Material and Method

Study area and sampling. The cities selected for the present study are located on the external side of the Carpathian mountain chain. The selection was made in order to maintain as much as possible the same geological characteristics for all urban areas included in the analysis. On this behalf the present research was focused on 11 Romanian cities: Baia-Mare, Botosani, Bacau, Vaslui, Buzau, Braila, Slatina, Craiova, Timisoara, Arad and Oradea.

The recreational areas within these cities, selected in order to assess soil contamination, are some of the most frequented among residents. Soil samples from 59 different parks and playgrounds were collected for subsequent chemical analyses. The sampling locations were chosen based on their position, importance and frequency of utilisation by children (Figueiredo et al 2011). From each location subsamples were collected, mixed and reduced to the weight of 300 g by repeated quartering (De Miguel et al 2007). Only topsoil samples were considered for the present analysis and were collected from the first top 15 cm. Soil sampling was conducted based on the requirements stipulated in the Romanian Ministry of Waters, Forests and Environmental Protection's Order number 184/1997, combined with recommendations within scientific profile publications (De Zorzi et al 2008; Ruan et al 2008; Faithfull 2002). The samples were collected using sterile equipment, individually labelled and transported in polyethylene bags. Sample storage before analysis has been done at room temperature. Additional precaution measures, such as individual packaging, and use of appropriate, sterile sampling equipment, were taken during sampling, transportation and storage in order to limit external contamination and assure the integrity of existing contaminates (Kulmatiski & Beard 2004; De Zorzi et al 2008). The sampling took place in April, May and June 2014 and the samples were analysed between June and August 2014 using the methodologies and equipment of the National Institute for Research and Development of Isotopic and Molecular Technologies pf Cluj-Napoca and Institute of Environmental Assessment and Water Research (IDÆA-CSIC) of Barcelona.

Sample treatment and analytical procedures. First, the recreational area soil samples were dried for 24 hours at ambient temperature and coarse pieces of organic matter were removed. Subsequent, samples were shredded to reduce agglomeration, re-dried at 110^oC using a laboratory oven, homogenised, disintegrated and passed through 2 mm sieves. During this phase the concentration of volatile elements such as Hg may have been diminished. Second, in order to obtain homogeneous and representative split of the samples, the soil sample were downsized by repeated quartering (De Miguel et al 2007) for subsequent analysis. Samples were acid digested at ambient temperature for 16 hours using aqua regia in sterile laboratory vessel. The substance obtained was boiled under reflux for 2 hours, cooled, filtered and diluted using nitric acid. Solutions were then analysed using inductively coupled plasma mass spectrometry (ICP-MS) and concentrations for 25 elements (Li, Na, Mg, K, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Cs, Mo, Cd, Sb, Ba, Ce, Ta, W, Hg, Tl and Pb) were determined. For quality control, standard coal fly ash was analysed using the same digestion procedure providing recovery rates ranging from 90% and 95%.for the analysed elements.

Data evaluation

Descriptive statistics and correlation assessment. Descriptive statistics comprising range, mean, standard deviation, coefficient of variance and Skewness (Dean & Illowsky 2012) have been calculated in order to better describe concentration characteristics. A correlation assessment was conducted in order to analyse whether there are relationships between contaminants.

Principal Component Analysis (PCA). The multivariate PCA is a data reduction technique applied successfully in environmental and contamination studies in order to ease the visualization of the relationships existing between analysed elements enquired in high dimension data sets (Thurston & Spengler 1985; Passos et al 2010). Using the PCA technique similar patterns between chemical concentrations have been identified, grouping the analysed elements accordingly. The differences between groups are related to the elements' main sources of origination in the urban soil environment. The principal components, commonly named factors, explaining the variance of the data, are interpreted as possible sources for the presence of elements within soil samples. These factors are the result of linear combinations between concentrations values of the considered elements.

In the present study the multivariate PCA was applied to the collection of elements concentration data. The purpose of this analysis is to illustrate the clustering of elements and to identify their sources in the analysed environments. The PCA technique was applied to a data set of 1475 values representing concentrations (mg kg^{-1}) of 25 different elements identified in 59 locations. The analysis was performed using the Statistica for Windows software (version 4.0).

Positive Matrix Factorisation (PMF). After identifying potential contamination sources of soil in urban recreational parks and playgrounds and verifying correlations between elements, a PMF technique (Paatero & Tapper 1994) was applied in order to apportion elements concentrations to distinct sources/factors (Pekey & Dogan 2013). PMF is a multivariate factor analysis that implements non-negativity constraints and makes use of individual data uncertainties (Paatero & Tapper 1994). This type of analysis strengthens previous interpretations or highlights new aspects of interest as missing and below-detection limit data can be handled more effectively (Comero et al 2009). The PMF was applied using US EPA's Positive Matrix Factorization Model software, Version 5.0 (Norris et al 2014).

A total (dependent) variable was set as "Soil" with a constant value of 1,000,000 mg kg^{-1} for all samples. The first input data matrix contains the 25 elements concentrations identified using ICP-MS in urban parks and playgrounds in Romania. The second data matrix represents the individual data uncertainty associated with each value presented in the first matrix. For all elements with concentrations above the detection limit the uncertainty was expressed as 10% of the element concentration plus one third of the detection limit. For elements with concentration below or equal to the detection limit, uncertainty was expressed as 0.83 times the detection limit.

The elements introduced in the PMF analysis were categorised based on their signal-to-noise ratio (Paatero & Hopke 2003). Species were defined as strong when the signal to noise ratio exceeds a value of 2. The distribution of residuals, G-space plots, F peak values and Q values were explored for solutions with number of factors varying between 3 and 7.

Enrichment factor (EF) calculation. The EF is further utilized to assess the degree of contamination (Uduma & Awagu 2013) of urban recreational soil with different analysed species identified as occurring from anthropogenic sources (Yongming et al 2006). The EF method normalises the measured contaminants content with respect to a sample reference element (Duan et al 2010). The reference element must be a conservative, stable one, characteristic for the Earth's crust, with no high variations between analysed samples. Most appropriate element to be used as reference vary among authors. Most common elements suggested and used are Al, Fe (Abraham & Parker 2008), Mn, Sc, Ti (Yongming et al 2006), Li and Zr (Szolnoki et al 2013).

For the present research EF is calculated as the concentration ratio of the analysed element and Mn within a recreational area soil sample, divided by the same ratio in earth crust using the formula:

$$EF = (X / Mn)_{sample} / (X / Mn)_{uncontaminated\ soil}$$

where X represents the analysed species concentration and Mn has been chosen the reference element based on its identified concentration and source of origination. Previously PCA and PMF analysis were conducted in order to evaluate if Mn concentrations can be assigned to natural sources. The concentrations attributed to the earth's crust are the reference values assigned to uncontaminated soil (normal values) stipulated in Ministerial Order 184/1997 emitted by the Romanian Ministry of Waters, Forests and Environmental Protection.

Results and Discussion

Descriptive statistics and correlation assessment. The range, mean, standard deviation, coefficient of variance and Skewness, reference value attributed to uncontaminated soil (normal values), and alert values established by Ministry of Water, Forests and Environmental Protection of Romania for assessing soil contamination are shown in Table 1. For Li, Na, Mg, K, Fe, Rb, Sr, Cs, Ta and W reference values have not been established through the Ministerial Order 184/1997 emitted by the Romanian Ministry of Waters, Forests and Environmental Protection.

Table 1

Descriptive statistics (min, max, mean, std. deviation, variance normal and alert value for analysed element in mg kg^{-1})

	Min.	*Max.*	*Mean*	*Std. deviation*	*Coefficient of variance*	*Skewness*	*Normal value**	*Alert value**
Li	7.1	43.0	19.0	7.3	0.37	0.55		
Na	173	2967	824	615	0.75	1.71		
Mg	2498	38879	14535	7442	0.51	0.98		
K	1405	18635	7249	3033	0.42	1.17		
V	16	154	93	34	0.37	-0.19	50	100
Cr	58	400	173	93	0.54	0.82	30	100
Mn	275	1262	721	214	0.30	0.04	900	1500
Fe	7206	28592	18660	5439	0.29	-0.38		
Ni	12	50	27	7.8	0.28	0.34	20	75
Cu	13	156	38	26	0.69	2.46	20	100
Zn	35	433	126	70	0.56	1.88	100	300
As	4.3	74.0	26.0	11	0.42	1.58	5	15
Rb	8.6	32.0	20.0	6.2	0.31	-0.15		
Sr	12	109	45	21	0.46	0.74		
Mo	1.8	6.3	3.4	0.92	0.26	0.75	2	5
Cd	0.10	2.20	0.40	0.38	0.95	3.03	1	3
Sb	0.06	7.20	1.40	1.6	1.14	2.26	5.00	12.50
Cs	0.44	6.00	1.40	0.76	0.55	3.99		
Ba	49	172	108	28	0.26	-0.28	200	400
Ce	14	48	33	8.7	0.27	-0.22		
Ta	0.00	0.01	0.01	0.00	0.56	-1.27		
W	0.06	1.60	0.44	0.22	0.50	3.02		
Hg	0.12	5.00	0.54	0.66	1.22	5.82	0.10	1.00
Tl	0.08	0.61	0.19	0.09	0.48	2.69	0.10	0.50
Pb	12	570	67	91	1.35	3.82	20	50

* Normal and alert values expressed for contaminants in soils, Order 756/3.11.1997/ Ministry of Water, Forests and Environmental Protection of Romania.

As shown in Table 1, mean concentrations for Cr, As and Pb are 173, 26 and 67 mg kg^{-1}. Also, he maximum values of V (154 mg kg^{-1}), Cu (156 mg kg^{-1}), Zn (433 mg kg^{-1}), Mo (6.3 mg kg^{-1}), Hg (5 mg kg^{-1}), and Tl (0.6 mg kg^{-1}) exceed both alert thresholds established for Romania and concentrations levels presented in other similar studies conducted on parks and playgrounds of China, Brazil, Chile, Australia and Sweden (Chen et al 2005; Figueiredo et al 2011; Tume at al 2008; Taylor et al 2010; Ljung et al 2006) denoting severe anthropogenic pollution in urban areas. In 54 out of the 59 locations analysed values surpassing the alert threshold for at least one of the above mentioned elements have been identified. Furthermore, mean As and Hg concentrations are more than 5 times higher than the normal reference values attributed to uncontaminated soil, that may pose serious threats for users' welfare. The same situation is encountered with Pb, where identified mean concentrations exceed 3 times the normality threshold established by legislation. For Cu and Zn the normal values are exceeded by 1.9 and respectively 1.3 times. Skewness values reveal distributions that differ from normality for most elements. In addition, the low coefficient of variance for Li, Mg, Fe, and Ni in the soil samples, suggest natural sources as a main origin for these elements.

Correlation analysis was conducted aiming to evaluate the relationships between chemical elements (Table 2). Positive high correlations (r = 0.67 to r = 0.78) can be identified among Mn (a typical crustal component), Li, Fe, and Rb indicating a major crustal origin in parks and playgrounds in Romania. Furthermore relatively high and positive correlations (r = 0.50 and r = 0.54) among Mn , Ba, and Tl) are also identified suggesting that the presence of these elements in parks and playground soils can be partially attributed to crustal and anthropogenic sources. Copper, Zn, Cd, Sb, As, Hg, and Pb are strongly and positively correlated among them and weekly correlated with Mn (r = 0.10 to 0.32). Both the high correlation among Zn, Cd, Sb, As, Hg, Tl and Pb and their high concentration in soil samples (often exceeding normal references values) indicate potential cases of soil contamination by anthropogenic sources. The significant but not so strong correlation (mean r = 0.20) of these group of elements with Cs may be further explained by differences between their sources of origination.

The high correlation between Na and Mg (r = 0.68) reveals a common source, most probably in soil salts and/or from the spreading of non-skid saline materials in winter periods as will be discussed later.

Table 2

Correlation coefficients between analyzed species

	Li	*Na*	*Mg*	*K*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*As*	*Rb*	*Sr*	*Mo*	*Cd*	*Sb*	*Cs*	*Ba*	*Ce*	*Ta*	*W*	*Hg*	*Tl*
Li																								
Na	-0.20																							
Mg	0.16	0.83																						
K	0.59	0.07	0.46																					
V	0.84	-0.27	-0.06	0.47																				
Cr	0.29	-0.45	-0.25	0.43	0.31																			
Mn	0.82	0.08	0.32	0.52	0.66	0.15																		
Fe	0.89	0.03	0.31	0.52	0.76	0.06	0.88																	
Ni	0.86	0.11	0.46	0.54	0.63	-0.04	0.69	0.82																
Cu	0.37	-0.18	-0.14	0.06	0.40	0.20	0.47	0.51	0.11															
Zn	0.36	-0.08	0.01	0.11	0.35	0.17	0.48	0.48	0.18	0.87														
As	0.53	-0.18	-0.11	0.18	0.68	0.27	0.57	0.52	0.19	0.76	0.68													
Rb	0.76	0.28	0.51	0.63	0.60	-0.09	0.81	0.85	0.78	0.22	0.26	0.29												
Sr	0.34	0.37	0.63	0.35	0.04	-0.08	0.26	0.27	0.60	-0.13	0.02	-0.03	0.36											
Mo	0.08	-0.34	-0.32	0.08	0.13	0.80	0.10	-0.09	-0.15	0.19	0.23	0.17	-0.21	-0.06										
Cd	0.21	-0.12	-0.12	0.07	0.20	0.35	0.45	0.26	-0.16	0.80	0.74	0.75	0.09	-0.17	0.37									
Sb	0.24	-0.24	-0.23	0.04	0.34	0.39	0.31	0.28	-0.07	0.79	0.68	0.67	0.08	-0.24	0.38	0.73								
Cs	0.47	0.06	0.16	0.27	0.42	0.29	0.75	0.59	0.25	0.46	0.42	0.54	0.53	0.03	0.31	0.57	0.38							
Ba	0.53	0.24	0.47	0.42	0.30	-0.06	0.71	0.71	0.59	0.29	0.34	0.17	0.71	0.48	-0.02	0.18	0.03	0.58						
Ce	0.58	0.31	0.50	0.61	0.47	-0.18	0.59	0.72	0.69	0.06	0.02	0.02	0.89	0.20	-0.38	-0.15	-0.08	0.25	0.56					
Ta	0.63	-0.08	0.19	0.51	0.58	0.07	0.47	0.63	0.63	0.03	0.03	0.11	0.63	0.16	-0.20	-0.18	-0.08	0.25	0.53	0.64				
W	0.06	-0.06	-0.08	0.10	0.19	0.56	0.26	0.14	-0.18	0.50	0.54	0.45	0.00	-0.12	0.66	0.60	0.52	0.66	0.24	-0.24	-0.08			
Hg	-0.01	-0.05	-0.08	0.00	0.01	0.20	0.00	0.08	-0.13	0.73	0.69	0.37	-0.11	-0.04	0.23	0.50	0.52	0.09	0.03	-0.17	-0.18	0.42		
Tl	0.51	-0.01	0.12	0.39	0.48	0.34	0.74	0.59	0.17	0.70	0.61	0.78	0.51	-0.03	0.23	0.84	0.63	0.83	0.45	0.27	0.19	0.57	0.28	
Pb	0.15	-0.16	-0.18	0.05	0.17	0.31	0.33	0.20	-0.21	0.80	0.72	0.73	0.05	-0.22	0.26	0.94	0.76	0.41	0.05	-0.14	-0.25	0.51	0.54	0.78

Principal Component Analysis. In order to further assess the above stated hypothesis a PCA was conducted (Table 3). By applying this technique to the database of potential soil contaminate concentrations in urban recreational areas of Romania, principal components are identified.

Table 3

Factor loadings obtained by PCA. Values above 0.6 are in bold

	Factor 1	*Factor 2*	*Factor 3*	*Factor 4*	*Factor 5*
Li	**0.93**	0.22	-0.07	0.14	-0.06
Na	-0.08	-0.09	**0.83**	-0.30	0.19
Mg	0.28	-0.10	**0.89**	-0.14	0.04
K	**0.66**	-0.03	0.27	0.34	-0.01
V	**0.81**	0.25	-0.32	0.13	0.03
Cr	0.12	0.16	-0.23	**0.89**	0.01
Mn	**0.78**	0.36	0.18	0.08	0.34
Fe	**0.90**	0.33	0.10	-0.08	0.11
Ni	**0.90**	-0.05	0.24	-0.05	-0.24
Cu	0.20	**0.95**	-0.09	0.01	0.00
Zn	0.19	**0.90**	0.09	0.07	-0.08
As	0.34	**0.77**	-0.19	0.09	0.16
Rb	**0.86**	0.10	0.31	-0.15	0.23
Sr	0.34	-0.10	**0.68**	0.13	-0.39
Mo	-0.11	0.19	-0.12	**0.90**	0.05
Cd	-0.02	**0.87**	-0.02	0.21	0.34
Sb	0.06	**0.80**	-0.22	0.19	0.09
Cs	0.40	0.39	0.16	0.30	**0.66**
Ba	**0.61**	0.16	0.49	0.04	0.20
Ce	**0.78**	-0.11	0.24	-0.31	0.15
Ta	**0.80**	-0.17	-0.07	-0.04	0.03
W	-0.07	0.51	0.10	**0.63**	0.36
Hg	-0.17	**0.76**	0.11	0.12	-0.37
Tl	0.38	**0.68**	0.07	0.19	0.53
Pb	-0.08	**0.89**	-0.09	0.11	0.24
Cumul. Eigenval	**0.93**	0.22	-0.07	0.14	-0.06
Cumul. Var %	-0.08	-0.09	**0.83**	-0.30	0.19

The PCA results highlight five factors, explaining a cumulative variance of 84% using the information contained in the original set of soil data. Also the first two factors explain a cumulative variance in the data of 62% signalling major sources of chemical elements in urban recreational area soils.

Factor 1 is dominated by elements such as K, Li, V, Mn, Fe, Ni, Rb, Ba, Ce and Ta with mean concentrations close to the value of the natural thresholds established for Romania. Due to the fact that these elements can be naturally encountered in the Earth's crust, *Factor 1* can be associated with natural sources and background rock composition. This factor explains a cumulative variance of 37% of the input data.

Conversely *Factor 2*, explaining 25% of the cumulative variance, is dominated by elements such as Pb, Hg, Zn, Cu, Sb, As and Cd. In Romania, mining and milling processes, smelting industry, fossil fuel combustion and traffic contribute significantly to soil contamination (Bird et al 2005; Máthé et al 2012; Weindorf et al 2013; Maftei et al 2014) with elements comprised in *Factor 2*. Each of these elements can come from one or more of the above mentioned sources, depending on the location. Taking this into account *Factor 2* can be described mostly as an industrial and secondary as traffic related contamination source.

Factor 3 is dominated by elements like Na, Mg, and Sr, elements that indicate towards a soil rich in salts. In Romanian urban areas, saline soils can be either linked to salt deposits in soil or to the practice of spreading non-skid saline materials in winter periods.

Elements such as Cr, Mo and W are grouped under *Factor 4*. This indicates a clear source of anthropogenic soil contamination from metallurgical and electronics manufacturing industry.

The presence of Cs in soils, as the dominant element in *Factor 5*, may suggest usage of nuclear and radioactive technologies. However, in the present research, extensive Cs contamination has been identified in the soil of one playground in the city of Baia Mare, a former large mining city in Romania. Here, mining companies frequently operate radioactive sources emitting gamma radiation from Cs 137 in mining related projects. Evidence of their activity was enclosed in the Risk Assessment and Response Plans of Maramureş County, as some of these companies are listed as economic operators considered a source of nuclear and radiologic risk, with permanent activity. Nevertheless, due to the fact that extremely high Cs contamination was found punctually in only one location, it can be assumed that it was accidental. The other four recreational areas investigated from the city of Baia Mare did not reveal elevated Cs levels. Another aspect that should not be omitted is the association of Cs with Tl and W in *Factor 5*. This indicates that at some extent the presence of Cs, Tl and W in soil be attributed to the high temperature processes such as ceramic or cement industry (Querol et al 2007). This hypothesis is also applicable in the city of Baia Mare where economic activities in the ceramics sector have been conducted.

Positive Matrix Factorisation analysis. The most reliable solution identified by applying PMF highlights 4 main factors/sources responsible for the elements concentrations in soils. These are represented in Table 4 compared to the results obtained previously when applying PCA, and can be visualised in Figure 1.

Table 4

Result comparison between PCA and PMF analysis

PCA		*PMF*	
Factor profiles	*Major elements*	*Factor profiles*	*Major elements*
Factor 1 – Crustal	K, Li, V, Mn, Fe, Ni, Rb, Ba, Ce, Ta	Factor 1 – Crustal	Li, V, Mn, Fe, Ni, Ba, As, Cs
Factor 2 - Mining, Industry and Traffic	Pb, Hg, Zn, Cu, Sb, As, Cd	Factor 2 - Mining, Industry and Traffic	Cu, Zn, Cd, Sb, Hg, Pb
Factor 3 - Saline Mineralogical Background	Na, Mg, Sr	Factor 3 - Metallurgical and Electronic Manufacturing Industry	Cr, Mo,W
Factor 4 - Metallurgical and Electronic Manufacturing Industry	Cr, Mo,W	Factor 4 – Saline Mineralogical Background	Na, Mg
Factor 5 - High temperature processes and usage of nuclear and radioactive technologies	Cs, Tl	-	-

Figure 1 shows the factor profiles identified by PMF. The result is comparable to the one generated by the PCA analysis and sources of elements explaining the presence of the analysed elements in soils encountered in parks and playgrounds of Romania could be properly explained.

Factor 1 is similar to PCA and accounts for crustal sources. It is representative for elements such as Li, Mn, Fe and Ni. The presumption that As and Cs can be at some extent attributed to natural sources is strengthened, as *Factor 1* contributes with 58% of the As and 41% of the Cs in soils. The second factor is traced by Cu, Zn, Cd, Sb, Hg and

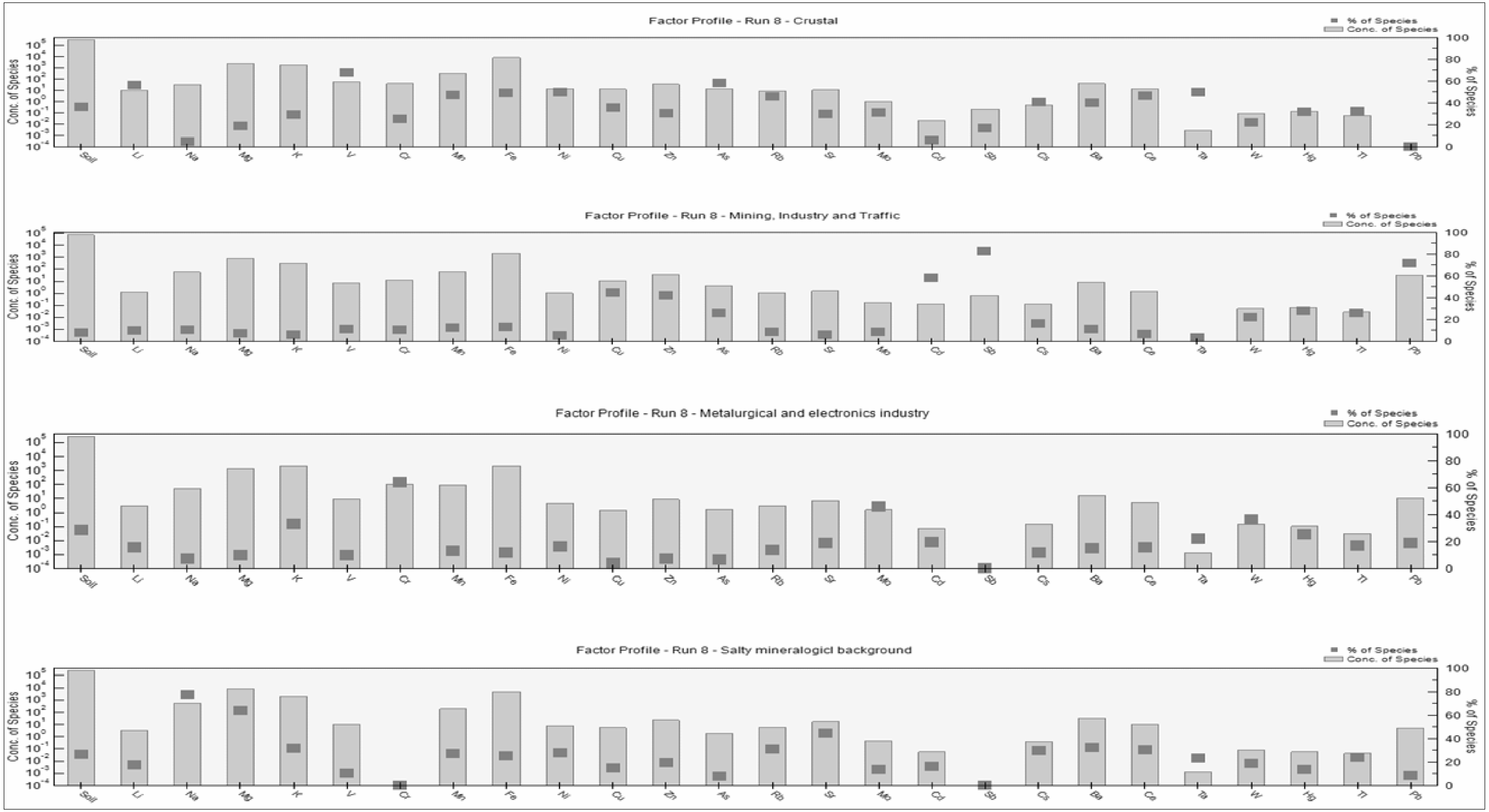
Pb signalling anthropogenic sources of urban soil contamination. Also 30% of the As can be attributed to this factor. Since the above mentioned elemental species can be related to more than one anthropic activity *Factor 2* is associated to mining, industry and traffic as in the PCA analysis. *Factor 3* is associated with Cr, Mo and W and it is similar to Factor 4 identified previously using the PCA. In the metallurgical industry in Romania, Cr, W and Mo are intensively used in a series of alloys and steels, while in the electronic industry these species are a result of the manufacture of semi-conductors, cables and other electrical compounds. *Factor 4* generated by the PMF analysis explains Na and Mg origination. This factor is similar to *Factor 3* identified with PCA and is linked to natural salt deposits common within the Romanian territory, where rock salt accumulations have been intensively exploited and to the spreading of salts in winter period.

By comparing the results obtained when applying both PCA and PMF analysis to the recreational area soil data, it can bee seen that four factors are common, meaning that the species characterising each factor have similar provenience and are strongly associated with one another. The sources for these species are clear and it can be easily distiguished which of the elements could pose contamination issues in urban parck and playground soils of Romanian cityes. PCA *Factor 5* suggesting a different source for the presence of Cs in soil has not been identified by PMF being 29% of the Cs attributed to the antropogenic sources, the rest accounting for background material as the correlation with Li and Mn suggests. Nevertheless, punctual Cs contamination signaled by the PCA results is still possible in the city of Baia Mare, originating either from historical presence of ceramic industry within the city or from present mining prospection activities undertaken in the area.

Aiming to ensure the robustness of the conclusions, a bootstrap analysis (Efron & Tibshirani 1986) was also performed. This type of analysis was conducted in order to explore the rotational ambiguity of the PMF solution. Two hundred bootstrap runs were performed and results are illustrated in Figure 2. Particular interest was granted to the overlapping of the base run solution within the generated interquartile range. It was observed that all 25 species have their base run within or extremely close to the assigned interquartile range suggesting that the proposed solution is stable. Taken this into account Figure 3 was utilized to summarize relative contribution of each factor to the analysed elements.

In Figure 3 it can be seen that from the 25 analysed species, the ones that can be strongly associated with anthropogenic contamination are Pb, Cr, Cd, Sb, W and Hg and to a lower extent Cu, Zn, As and Tl.

Special focus was given to *Factor 2*, representing mining, industry and traffic sources as it stands for 67% of the Pb encountered in Romanian parks and playgrounds. It also explains 78 % of the Sb, 54 % of the Cd, 42 % of the Cu and 39 % of the Zn and close to 30% of As. The origination of the above mentioned species in soil of urban recreational areas can be attributed to a high extent to anthropogenic activities. On this behalf, the elevated concentrations, surpassing reference value associated with uncontaminated soil in Romania can be linked directly to soil contamination. Special attention should be paid to the fact that 90% of the parks and playgrounds analysed in the present study present to some extent soil contamination issues with the above mentioned species. Moreover, *Factor 3* is also associated with anthropogenic pollution, mainly occurring from metallurgical and electronic industry discharges in the atmosphere. This factor explains 58 % of the Cr, 40 % of the Mo and 31% of the W found in urban soils of the recreational areas analysed.



Factor Profile - Run 8 - Crustal

Factor Profile - Run 8 - Mining, Industry and Traffic

Factor Profile - Run 8 - Metalurgical and electronics industry

Factor Profile - Run 8 - Salty mineralogicl background

Figure 1. Explained variance of the elements in each factor obtained with PMF.

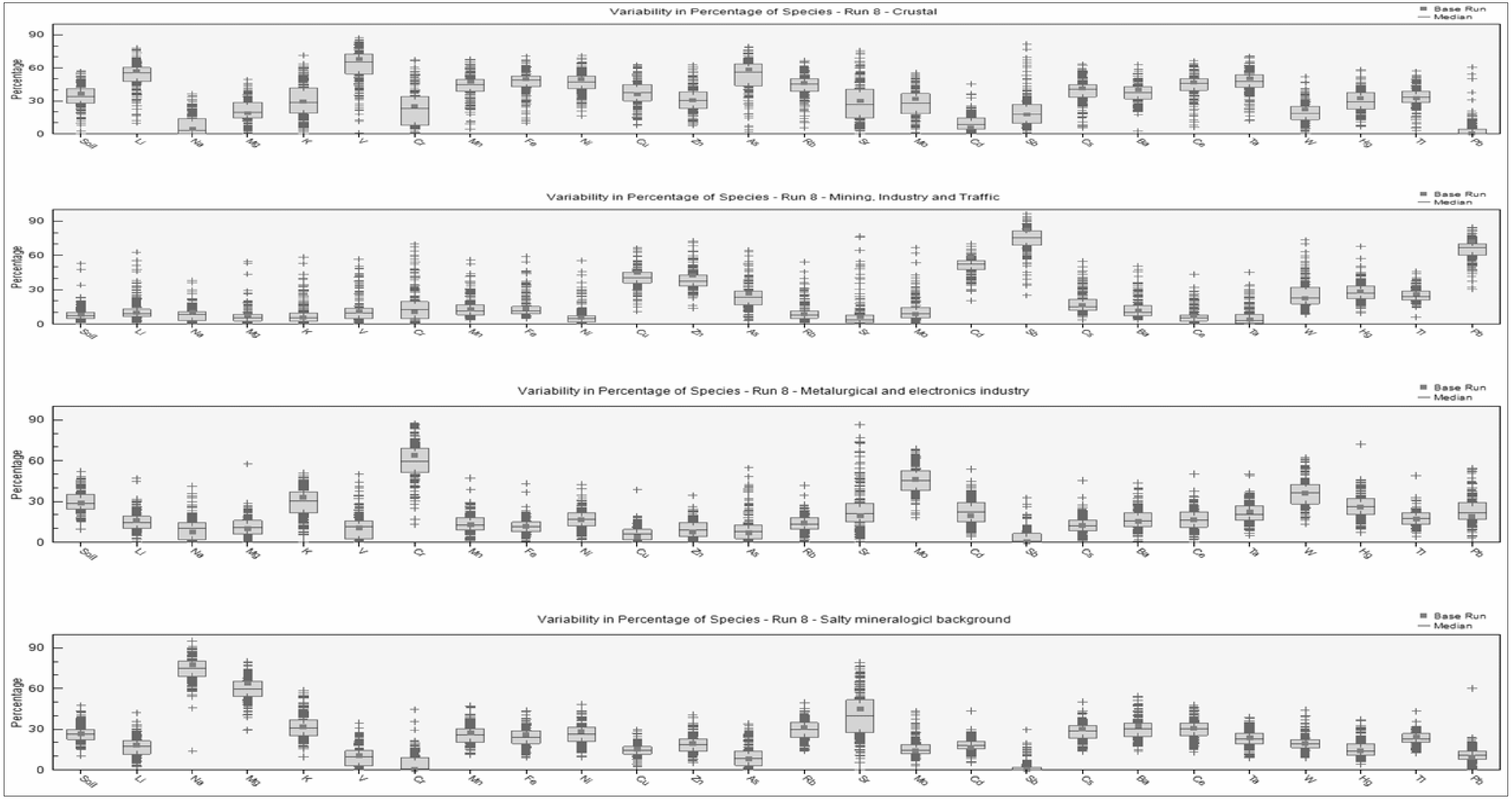


Figure 2. Bootstrap results of the identified PMF solution.

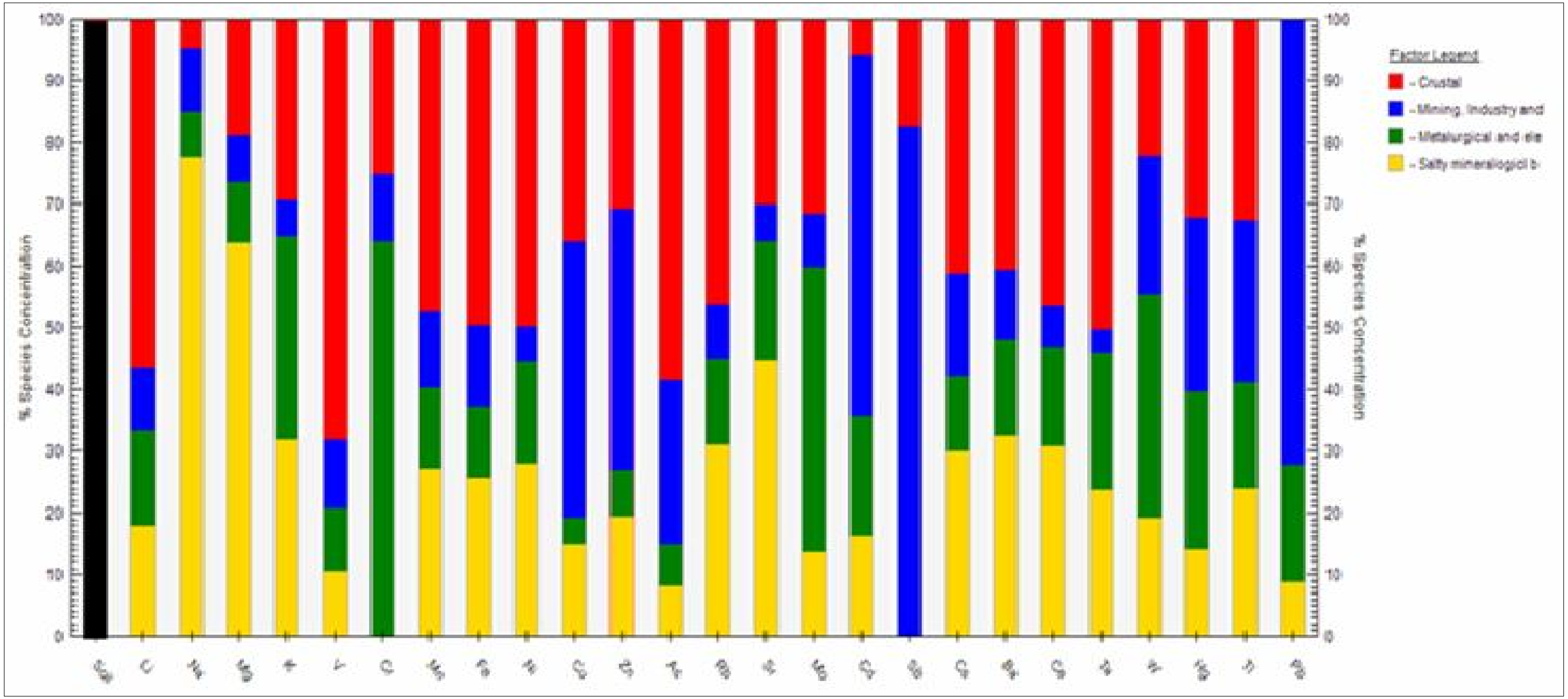


Figure 3. Relative contribution of different sources to elements as identified by PMF.

Corroborating sources of these metals with the identified concentrations it can be stated that even if these species also occur naturally in soils, as clearly deduced for As, their concentrations are highly increased by anthropogenic pollution in recreational areas of Romania. The particular case of soil contamination with Pb, Cr, As, Sb, Zn, Cu, Cd, and Hg must also be analysed as these are contaminants that may pose significant risks to human health. The neurotoxicity and potential carcinogenic effects of the aforementioned pollutants, especially for children have been acknowledged by the scientific community (Zubero et al 2010; Liu et al 2013; Li et al 2013). In the case of the 59 parks and recreational areas analysed, alert reference values expressing severe contamination have been exceeded in 55 locations for As, in 45 locations for Cr, in 16 locations for Pb, in 6 locations for Hg, in 4 for Mo and in 2 for Zn. Concentration values for Cd and Sb are below alert reference values in all analysed locations. For these locations additional health and impact assessments are highly recommended and remediation measures must be applied accordingly.

Mn, Fe and Ni are also species investigated in relation with potential harmful health effects (Pandelova et al 2012). Even if they are considered essential metals, necessary for the development and normal functioning of the human organism, it is admitted that at excessive intake may lead to serious toxic effects (Zhu et al 2011). However, in parks and playgrounds within the analysed Romanian urban areas these three metals do not present reasons of concern. *Factor 1*, associated with natural origination from crustal sources stands for 61 % of the Ni, 61% of the and Fe, 58% of the Mn. Identified concentrations similar to those attributed to uncontaminated soil in Romania have been identified in all locations under analysis. In addition, 78 % of the Na concentration, 64 % of the Mg and 25 % of the Mn concentration can be explained due to natural rich in salt parental material or winter salting described by *Factor 4*. On this behalf, it can be stated that high concentrations of salts in some urban parks and playgrounds soil may be further assessed taking into account environmental effects such as plant growth, rather than in correlation with anthropogenic pollution and health risks.

Contaminant EF in urban recreational area soils. As the PCA and the PMF analysis conducted show, Mn is one of the elements most strongly associated with earth crust and composition of background material. Near 83 % of the Mn, identified in the urban parks and playgrounds soils is explained by *Factor 1* and *Factor 4* in the PMF analysis, both factors associated with natural origination of elements.

The EF analysis was applied to species identified as being influenced by anthropogenic sources. In this regard, EF were calculated for Cr, Cu, Zn, As, Cd, Sb, Hg, Pb and Mo in order to identify severity of urban recreational area contamination of soil with these species in Romanian cities located on the external side of the Carpathian mountain chain.

The mean calculated EF decreases following the sequence Hg > As > Cr > Pb > Mo > Cu > Zn > Cd > Sb.

The value of the EF is used as a highlighter of anthropogenic origination of elements and presence of pollution. The scales used to assess EF are not unitary and can contain several categories from no enrichment to extremely sever enrichment (Lu et al 2009; Yongming et al 2006; Rodriguez-Barroso et al 2010; Qiao et al 2013). Nevertheless, it is generally accepted that an EF around 1 or slightly below explains species that are not enriched in the topsoil. A value between 1 and 2 can be attributed to both natural enriched background and anthropogenic activities, while a value above 2 points towards soil contamination (Szolnoki et al 2013). EF values between 2 and 5 suggest moderate enrichment, values between 5 and 20 represent significant enrichment and values exceeding 20 represents high or severe enrichment (Yongming et al 2006; Qiao et al 2013). The contamination level is considered to be directly proportional to the value of EF identified for an analysed component.

The mean EF obtained for Hg (EF = 7.5) and for As (EF = 6.7) highlights significant enrichment. Punctual severe EFs (over 20) with Hg and As was identified at five of the 59 locations. Corroborating this with the potential health effects of these two species and with the increased vulnerability of the majority of parks and playgrounds users, it can be stated that the presence of these pollutants in recreational areas may pose serious risks and needs to be better monitored and managed by Romanian local authorities.

Two other species can be further considered as contaminates of the assessed urban soils as their mean EF exceeds a value of 4. This is the case of Cr (EF = 4.8) and of Pb (EF = 4.3). Punctual values over 20 indicating high or severe enrichment with Pb have been identified in three locations indicating the necessity of implementing remediation measures.

Mean EF calculated for Mo (EF = 2.4), Cu (EF = 2.4) and Zn (EF = 1.6) suggest moderate soil contamination due to anthropogenic activities, but can also be explained in some of the cases by natural background enriched in these elements. Nevertheless, EF exceeding the value 2 for Zn has been identified in 7 locations, indicating the possibility of local soil contamination with this metal.

Cd and Sb reveal no enrichment as their mean EF calculated value does not exceed the value 1. EFs above 1 for these two elements were identified in 6 of the 59 analysed locations reflecting the low soil contamination with two species in the urban recreational areas studied.

Conclusions. Analytical determinations, correlation analysis, PCA and PMF highlighted similarities in behaviour and concentration distributions within the 25 analysed elements, grouping them based on possible common source of origin. The PCA and the PMF analysis indicated four common factors for these elements: (1) crustal sources, (2) mining and milling processes, smelting industry, fossil fuel combustion and traffic, (3) atmospheric depositions from metallurgical and electrical manufacturing industries and (4) parental rock background enriched in salts. Pb, Hg, Zn, Cu, Sb, Cd, Cr, Mo and to some extent As have been associated with anthropogenic sources. The presence of Cs and Tl in soils of parks and playgrounds of Romanian cities was taken under discussion as they were attributed to a fifth factor by the PCA and to crustal affiliation by the PMF. Therefore, it can be concluded that the origin of these elements can be attributed mainly to natural sources, but without overlooking the case of the city Baia Mare where punctual Cs contamination may occur either from high temperature process industries within the city or from present mining prospection activities undertaken.

As the PCA and the PMF analysis highlight, Pb, Hg, Zn, Cu, Sb, Cd, Cr, Mo and to some extent As are 9 species among the 25 analysed that are strongly connected to anthropogenic sources of origination. Soil contamination with these species in urban public parks and playgrounds was evaluated and the mean EF calculated. EFs decreases as following: Hg > As > Cr > Pb > Mo > Cu > Zn > Cd > Sb with values ranging between 7.5 for Hg to 0.4 for Sb. These results point to significant contamination with Hg and As, moderate contamination with Cr, Pb, Mo, Cu, low contamination with Zn. Cd and Sb are not enriched in the analysed locations. Nevertheless, due to the fact that in 15% of the locations analysed punctual severe contamination has been identified, mainly with Hg, As, Pb and Cr it is considered that special attention should be paid to the quality of soils in public parks and playgrounds in Romanian cities as there are locations that may pose serious risks to their users.

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