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Elemental composition of surface soils in Nature Park Shumen Plateau and Shumen City, Bulgaria

Vanya Koleva[1], Teodora Koynova[1], Asya Dragoeva[1], Nikolay Natchev[1,2]

[1]*Faculty of Natural Sciences, University of Shumen, 115 Universitetska str., Bulgaria*
[2]*Department for Integrative Zoology, Vienna University, Althanstrasse 14, Vienna 1090, Austria**
e-mail: vanyakolleva@gmail.com

Abstract: *Anthropogenic activities cause environmental pollution and alter biogeochemical cycles. Soils in cities and their vicinity are exposed to different pollutants. Nature Park Shumen Plateau is a protected area situated in the proximity of Shumen (Bulgaria). The aim of this research was to compare elemental composition of surface soil samples from Nature Park with two* areas *in Shumen city.*

Soil samples from seven sites on the territory of Nature Park and from two urban sites were collected. The elemental composition of the samples was determined using Energy Dispersive X-Ray Fluorescence technique. Principal component analysis and cluster analysis were performed to interpret the complex data.

The content of 24 elements was determined: Br, Y, Zr, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce Si, K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr, and Pb. Results presented here and previously showed that concentrations of heavy metals Cu, Zn, Cd and Pb are below the upper limit according to Bulgarian legislation. Concentrations of Mn and Fe in samples from Nature Park were comparable to the literature data reported for unpolluted areas. Principal component analysis and cluster analysis show similarity of the content of 24 elements between samples from Nature Park and from Shumen city. These findings are in accordance with our previous positive results from Allium-test: cytogenetic endpoints showed a presence of harmful compounds in Nature Park soils.

The content of heavy metals in the surface soils studied show a lack of environmental risk for Nature Park. However, a similar distribution pattern of the investigated elements in the park and two anthropologically influenced areas in Shumen city indicated a potential hazard in Nature Park.

Keywords: Nature Park Shumen Plateau, multi-elemental analysis, soil samples

Introduction

Nature Park Shumen Plateau (NP) provides important ecosystem services to local residents. Our previous findings illustrate great social benefits of park as a green space for outdoor recreation [1]. Such green areas are perceived as "clean of pollution", but several studies revealed that they can be affected by accumulation of harmful compounds [2], [3]. It should be noted that pollution of recreational areas poses a risk for human health.

Corresponding author: vanyakolleva@gmail.com

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The forest areas are endangered from the harmful effect of soil pollutants emitted into the terrestrial environment [4], [5]. Worldwide soils are analyzed for the presence of heavy metals. Results from other studies provided in Bulgaria show that the content of heavy metals in surface soils from Bulgarka Natural Park, Pirin National Park and industrial zone of Devnya, exposed to different level of anthropogenic influence, do not exceed the maximum permissible concentrations according to Bulgarian legislation [5], [6]. So, the soils studied are considered unpolluted with heavy metals. In the case of NP, the end-of-the-century data does not indicate the presence of acute contamination in Shumen region [7], [8], but over the past 11 years winter air pollution in the city of Shumen has been reported. The soil acts as a conservative matrix for the accumulation of atmospheric deposition [4], [9]. The town of Shumen is located at the northern and eastern foot of the Nature Park. Since the prevailing wind direction is northeast, it is assumed that the city could be a source of pollution to the park.

Environmental risk evaluation of contaminated land usually is based on guideline values derived from the ecotoxicological properties of specific chemicals. A major limitation of this approach is that the most of dangerous compounds in soil are unknown. Most of available soil ecotoxicological data are focused on relatively few compounds [10], [11]. In this context, the multi-elemental analysis provides information for many elements, including non-metals and trace elements [12], [13]. The application of methods such as energy dispersive X-ray fluorescence spectrometry (EDXRF) for direct multi-elemental analysis of soil samples has increased over the last few years [14], [15], [16]. This is a promising analytical technique, which is an alternative to the classical analytical methods, such as Atomic Absorption Spectrometry [17].

The aim of this research was to compare elemental composition of surface soil samples from NP with two anthropogenically influenced areas in Shumen city.

Materials and methods

Study sites and soil sampling

Study sites in present investigation are Nature Park Shumen Plateau (NP) and Shumen city, located in northeastern part of the Bulgaria. Soil samples from seven sites on the territory of NP (SNP) and from two urban sites (grassy area along the Simeon Veliki Avenue in Shumen city (SU) and City Park in Shumen (SCP)) were collected [18], [19].

Physico-chemical analyses

pH analysis. Soil samples were suspended in deionized water in ratio of 1:2 (w/v). pH of filtrate was measured by pH meter (Hanna Instruments 8314) [19].

Total elemental analysis. Direct quantification of total element concentration in soils using EDXRF technique was provided at Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences. The spectrometric systems with detectors Ketek and PGT, DSP, software for PFA were used. Excitation sources were Fe^{55}, Pu^{238} and Am^{241}. Samples were triplicate excited for 2000 s, 2500 s and 3000 s.

Statistical analyses

Mean data of pH in soil samples were calculated. Results from elemental analysis were expressed as mean value. A multivariate analysis of the results was done using principal component analysis (PCA) and cluster analysis (CA). All calculations were performed using the statistical package IBM SPSS Statistics 22.0.

Results and discussion

Physico-chemical analyses

Corresponding author: vanyakolleva@gmail.com

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Soil quality is important feature of recreational areas. People are exposed to surface soil contaminants during outdoor physical activities [20]. The occurrence of toxic compounds in soils can be natural or due to anthropogenic activities. Thus, we compared pH and elemental concentrations of the surface layer of the NP and anthropogenically influenced urban soils. The content of 24 elements (Si, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr, Y, Zr, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce and Pb) were detected in varied among (Table 1). Data presented in Table 1 include also previously reported by us content of Cu, Zn, Cd and Pb in samples from NP and SU [19]. Only 12 elements were found in detectable amount in all soil samples studied – Si, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Zr, Ba and Pb.

Table 1. The pH values and total element concentrations in surface soils in Nature Park Shumen Plateau and two urban sites at Shumen city.

Element (mg/kg)	**Sample**								
	SNP-1	**SNP-2**	**SNP-3**	**SNP-4**	**SNP-5**	**SNP-6**	**SNP-7**	**SU**	**SCP**
pH	7.38*	6.52*	5.89*	7.20*	7.82*	7.64*	7.49*	7.90*	7.98
Si	97500	86000	14700	99000	85300	113000	114000	137000	97000
K	9100	10600	12900	12300	11800	12000	13800	11900	11400
Ca	4700	11900	3400	14000	47300	10000	6900	91000	50000
Ti	2050	3800	4900	4050	2900	4230	4220	2500	2760
Mn	410	600	1600	720	450	520	600	250	390
Fe	12100	24000	13500	18700	20600	21200	24600	14600	18700
Cu	nd*	nd*	nd*	nd*	nd*	20*	28*	24*	23
Zn	57*	83*	68*	93*	113*	78*	92*	108*	80
Br	nd	nd	nd	nd	nd	18	nd	nd	nd
Rb	63	83	97	81	63	77	74	41	52
Sr	50	65	89	72	200	95	63	243	140
Y	20	40	36	42	nd	25	28	nd	18
Zr	230	280	440	290	183	333	329	170	225
Mo	nd	nd	nd	nd	nd	6	nd	nd	7
Ag	nd	nd	nd	nd	nd	2	2	nd	nd
Cd	nd*	3*	nd*	3*	nd*	2*	2*	3*	2
Sn	3	4	nd	nd	4	nd	4	6	6
Sb	3	nd	nd	nd	nd	nd	nd	nd	nd
I	10	16	nd	15	11	9	10	7	nd
Cs	4	nd	nd	nd	nd	nd	4	nd	nd
Ba	400	330	376	320	305	362	368	280	300
La	17	28	22	22	16	22	27	nd	13
Ce	47	75	87	77	57	80	82	nd	60
Pb	44*	47*	52*	23*	21*	44*	42*	26*	40

nd – not-detectable; *[19]

Corresponding author: vanyakolleva@gmail.com

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Bulgarian soil pollution standards determine maximum permissible concentrations for 9 heavy metals – As, Cd, Cu, Cr, Ni, Pb, Zn, Hg and Co [21]. As noted by Duffus [22] there are different terms and lists of “heavy metals” in the scientific publications and in legal regulations. This term is often used as a group name for metals, semimetals (metalloids) and metal compounds that have been associated with contamination, negatively affecting people's health and environment [22]. Most studies of soil contamination over the last decade included Pb, Zn, Cu, Cr, Cd, Ni, Mn, As, Co, Fe and Hg [23], [24], [25], [26], [27], [28], [29]. Total content of six heavy metals (Mn, Fe, Cu, Zn, Cd and Pb) was detected in nine surface soil samples tested by EDXRF technique (Table 1). Among them, detectable amounts of four heavy metals (Mn, Fe, Zn and Pb) were found in all investigated areas. Cadmium and copper were detected in SNP-6 and SNP-7 and in both urban samples. Cadmium was also detected in SNP-2 and SNP-4.

Concentrations of detected heavy metals Cu, Zn, Cd and Pb in surface soil samples studied were below the upper limit according to Bulgarian legislation [19]. The values are below or close to value of such elements in surface soil of unpolluted areas of Bulgarka Nature Park and Pirin National Park [5], [6]. Only Zn content of SNP-5, SU and SCP is slightly higher than this in the other protected parks. Accumulation of zinc in the environment usually is a consequence of mining operations [30]. Road traffic also is frequently mentioned [31]. Zinc is the 24th most abundant element in the earth’s crust and has a rage of <1–180 mg/kg in limestones [32]. According to Klimek [33] forest soils containing 140 mg/kg zinc are uncontaminated. Considering the above-mentioned, we can conclude that studied by as soil samples are not Zn-polluted.

Total content of Mn in top soil samples studied (except SNP-3) varied from 250 to 720 mg/kg. According to Fan et al. [34] this range value does not suggest Mn soil contamination. The content of Mn in SNP-3 (Reserve “Bukaka” – *Fagus sylvatica* ssp. *Moesiaca* forest) is 1600 mg/kg (pH 5.89). Manganese is an essential microelement important for all living organisms [35] but overexposure to this metal can be toxic [36]. It is known that *F. sylvatica*is is very tolerant to the surplus of Mn [37]. Therefore, Mn abundance in topsoil will not adversely affect the beech forest. Absorption of Mn by different exposure routes (inhalation or oral) adversely affects nervous system in adults can cause developmental neurotoxic effects in children [36]. However, the topsoil of the NP beech forest is covered by a thick layer of ivy, which probably limits inhalation of Mn-rich dust. So, it could be assumed that that there is no elevated risk to the health of frequent visitors.

Iron is the second most abundant metal on the earth’s crust [38]. It is an essential element in human nutrition [39]. In NP samples tested Fe concentrations range from 12 100 to 24 600 mg/kg. Fe content in urban samples was 14 600 mg/kg (SU) and 18 700 mg/kg (SCP). Iron is abundant in soil and therefore for its content doesn`t exist maximum permissible concentration [40], [41]. Iron compounds in soils are relatively insoluble [39], [41], [42]. Fe-toxicity may occur in acidic soils (pH <3.2) [39]. The pH values of filtrates of NP and urban sites are in range from 5.89 to 7.98. So, there is no important factor for Fe-toxicity in the studied areas. Actually, Fe is the major limiting factor for plant growth [43]. As pointed at OSWER Directive 9285.7-69 [42] “From an ecological perspective, the concern is not direct chemical toxicity *per se*, but the effect of iron as a mediator of the geochemistry of other (potentially toxic) metals.” For example, the iron-manganese interaction is well known: Fe decreases Mn-uptake in plants [44].

Principal component analysis and cluster analysis of the total elemental concentrations

Corresponding author: vanyakolleva@gmail.com

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Principal component analysis is the powerful multivariate method to identify data patterns and to express their similarities and differences [45], [46], [47]. So, in order to clarify the relationships between the soil elemental distributions in investigated sites we performed PCA. The two-dimensional plane formed by the two first principal components is the most informative in PCA [45]. The first two principal components of factor analysis describe a total of 94.89% of the variability of our data. The loading plots display the relationships among the sites [46]. The sample sites on the PCA-score plot formed four distinct groups of soil samples: 1) SNP-1, SNP-2, SNP-4, SNP-6 and SNP-7; 2) SNP-5 and SU; 3) SNP-3; 4) SCP (Figure 1).

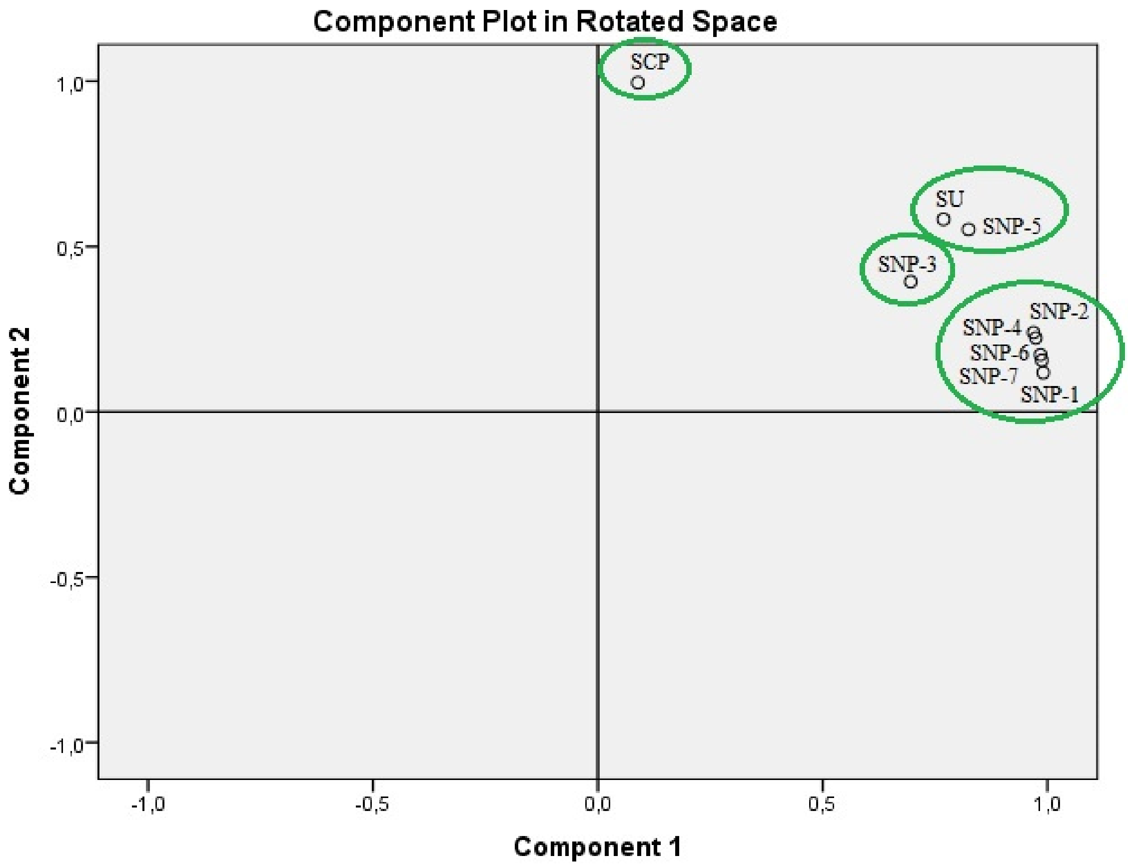

Figure 1. Score plot of PC1 vs. PC2 of the surface soil samples from Nature Park Shumen Plateau and Shumen city. Analysis included total 24 elements detected.

Cluster analysis was performed in order to confirm the results obtained by PCA and to create groups of variables with similar characteristics [48], [49], [50]. The results obtained by CA are presented by dendrogram where the distance axis represents the degree of association between groups of variables, i.e. the lower the value on the axis, the more significant the association (Figure 2). The results of CA are similar to PCA, revealing three large clusters. Cluster 1 is composed by two sub-clusters – six NP samples (SNP-1, SNP-2, SNP-4, SNP-5, SNP-6 and SNP-7) and SNP-5. Cluster 2 included only soil sample SU. Cluster 3 grouped soils from SNP-3 and SCP.

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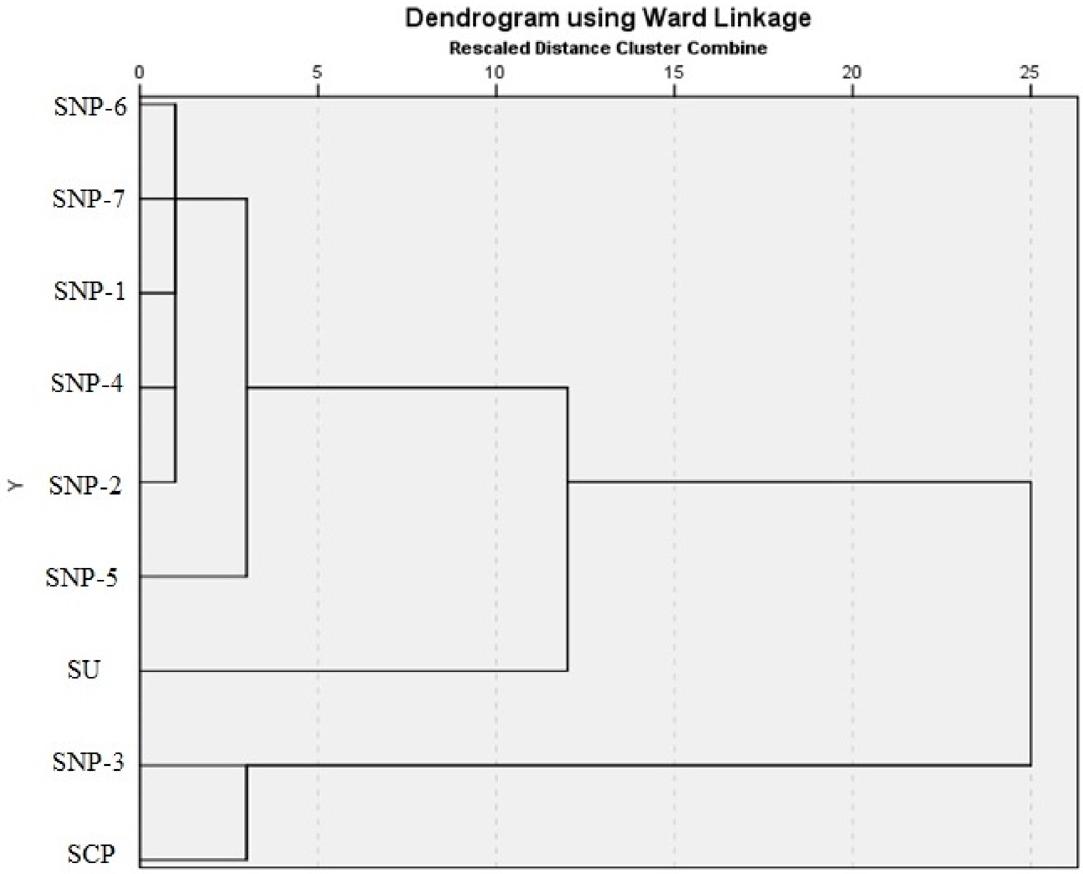

Figure 2. Dendrogram from hierarchical cluster analysis of the surface soil samples from Nature Park Shumen Plateau and Shumen city. Analysis included total 24 elements detected.

As can be seen PCA separated SNP-5 and SNP-3, CA separated only SNP-3 from other SNPs. However, CA also separated SNP-5 in a sub-cluster. PCA data showed similarity between SNP-5 and SU, but CA – between SNP-3 and SCP. Separation of SNP-3 resulted from high value of Mn and low value of Si and Ca; separation of SNP-5 resulted from high value of Ca and Sr in comparison with other SNP samples. The significance of the high values of Mn for beech forest and for visitors` health was discussed earlier. SNP-5 is an open meadow near a large parking, a road and a big monument built of concrete. The enrichment of Ca probably is strongly influenced by anthropogenic activity.

Despite of some differences between total content of few elements, all investigated areas are plotted on the positive side of the axis for both PCA components and formed clusters with low distance (less than 5) (Figure 1 and Figure 2). These results indicated similarities between nine sites investigated. These findings are in accordance with our previous positive results from *Allium*-test: cytogenetic endpoints showed a presence of harmful compounds in NP soils [19].

Conclusions

The content of heavy metals in the surface soils studied show a lack of environmental risk for Nature Park. However, a similar distribution pattern in the park and two anthropologically influenced areas in Shumen city indicated a potential hazard in Nature Park.

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Corresponding author: vanyakolleva@gmail.com

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