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RESEARCH ARTICLE

Chemometrics based on the mineral content as a tool for the assessment of the pollution of top soils

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ABSTRACT

This is the first research of this type which includes the wider area of Kosovo taking into account the mineral wealth. The concentrations of 20 elements: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Si, V, and Zn were determined using ICP-OES. The ranges of concentrations of toxic elements are lead (Pb) 0.044–14.98 g/kg, arsenic (As) 0.007–0.33 g/kg, cadmium (Cd) 0.004–0.044 g/kg, and chromium (Cr) 0.053–0.245 g/kg. The spatial distribution of toxic elements was described using distribution maps. Principal component and cluster analyses were performed to reveal grouping of samples.

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Toxic elements; distribution maps; statistical analysis; soil; ICP-OES; Kosovo

Introduction

Agricultural soils and land near settlements are contaminated by the accumulation of heavy metals and metalloids due to emissions from industrial waste, mine tailings, leaded gasoline, spillage of petrochemicals, and atmospheric deposition. Most metals do not degrade microbially or chemically, and their total concentration in soils remains for a long time (Wuana and Okieimen 2009). Soil pollution by heavy metals from mining and industrial processes has been the main subject of many studies due to health risks associated with metal contamination (Abdu *et al.* 2017, Praveena *et al.* 2017). The overall goal of this study was elemental analysis of soil from the area of Kosovo (Figure 1). Elemental analysis of soils could provide information about the state of the pollution of the environment and health risk for inhabitants in this area. Contamination of soils in the province of Kosovo is caused mainly by anthropogenic activities (numerous mines, pollution as a result of postwar effects, ethnic war 1999) and geological composition of the soil.

Many papers have been published recently, which were focused on the elements contained, especially toxic, in different environmental samples from Kosovo (Veliu and Syla 2008, Rugova *et al.* 2011, Morina *et al.* 2012, Avdullahi *et al.* 2013, Šajn *et al.* 2013, Tmava *et al.* 2013, Hyseni and Musaj 2014, Zogaj *et al.* 2014, Demaku *et al.* 2015, Ferati *et al.* 2015, Maloku *et al.* 2015, Mirecki *et al.* 2015, Jusufi *et al.* 2016, Maxhuni *et al.* 2016, Rizani *et al.* 2016, Shehu *et al.* 2016, Zogaj and Düring 2016, Gashi *et al.* 2017, Gulan *et al.* 2017, Shala *et al.* 2017).

Mining and technology of refining ore in the territory of Kosovo, known as Balkan holy land, is dated from Middle Ages, thanks to the wealth of ores of Kosovo, and the advanced processing of silver and gold ore, and trade exchange throughout Western Europe (Blagojevic and Medakovic 2000). The contamination of soil due to heavy metals and health risks of inhabitants are also the consequences of war activities in Kosovo during 1999. Determination of trace metals as well as macro elements is important in toxicology in terms of binding positions at bioligands. The biohazard in soils is attributable to heavy metals (Cd, Pb, Cu, Ni, Cr, Zn, etc.). On the other hand, K, Ca, Mg are displacing metals, weakly bound electrostatistically on organic or inorganic sites. These cations have been widely employed for this purpose, generally at relatively high concentrations (Beckett 1989). In ideal systems, the relative exchangeability of trace metals is

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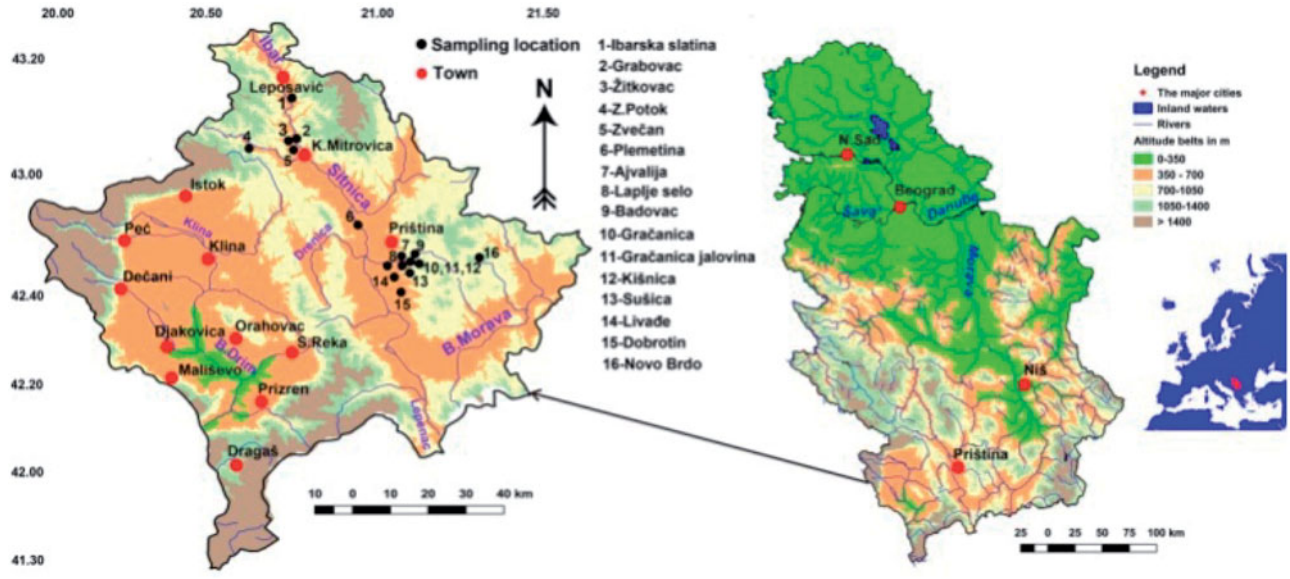

Figure 1. Geographical position of Kosovo with sampling locations and main cities.

determined by the affinity of the exchanging cation for the solid soil phase. This affinity increases with increasing valency and decreasing radius of the hydrated cation. Although heterogeneous soil systems may deviate from this ideal behavior, the selectivity of soils for cations was frequently observed to increase according to $Na < K < Mg < Ca$. Consequently, under comparable conditions (e.g. concentration, extraction time, soil/solution ratio, the efficiency of cations to exchange trace metals usually increases according to $Li < Na < K < Mg < Ca < Ba$ (Sposito 1989). As Mg is a harder Lewis acid than Ca, it was reported to displace also specifically adsorbed trace metals (Hlavay *et al.* 2004).

Differently from our previous research (Micic *et al.* 2015) related to the determination of the content of selected elements in plants in Kosovo, this paper presents an analysis of surface soil layers in the territory of Kosovo, from an environmental point, because mobility and bioavailability of toxic elements can be a risk for the environment. Samples were collected from different points, taking care of not only the environmental impact but also the impact of mineral wealth on the surface composition of the soil.

The main objectives of this study are to continue the examination process of the impact of anthropogenic and geogenic sources to elemental composition of the topsoil, especially following the chemometric analysis that enable us to detect correlations of pollutants, and the minimum number of factors that can be traced in order to effectively monitor the pollution of the area, and decrease its concentrations and influence on the animals and humans living in the investigated area.

Experimental

Instrumentation and reagents

All analyses were carried out in an iCAP 6300 Duo inductively coupled plasma optical emission spectrometer (Thermo Scientific Cambridge, UK) which used an Echelle optical design (52.92 grooves per mm, 63.5° blaze angle) and a change injection device solid-state detector (RACID86). The nebulizer was ultrasonic (CETAC U-6000). An Ultra-Scientific (North Kingstown, RI) ICP multi-element standard solution of about 20.00 ± 0.01 mg/L was used as a stock solution for calibration. The PVC containers were treated with 20% nitric acid and washed with ultra-pure water 0.05 μS/cm (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GMBH, Stockland, Niederelbert, Germany). Both nitric acid (65%) (Merck, Darmstadt, Germany) and hydrogen peroxide (30%) (Fluka, Buchs, Switzerland) were of analytical grade. All reagents used were of analytical grade.

Study area

The idea of a broader examination and comparison of the results is based on the fact that Kosovo has a specific geo-morphological composition, under the strong anthropogenic influence of mining and metallurgical activity. The current study covers the area defined by the coordinates (geographical latitude 42.00–43.25^0 N; geographical longitude 20.00°–21.75^0 N). The research area includes about 40 mines. The Mining and Metallurgical Kombinat of Lead and Zinc "Trepča" was one of the most important mining complexes of the

Table 1. Latitudes and longitudes of the investigated samples.

Geographical location	Latitude	Longitude
Dobrotin	42.529808	21.183701
Sušica	42.5789	21.2117
Laplje Selo	42.5967	21.1408
Livađe	42.56444	21.16667
Plemetina	42.7075	21.0458
Ibarska Slatina	43.0472	20.8322
Zubin Potok	42.9144	20.6897
Žitkovac	42.9311	20.8239
Grabovac	42.9336	20.8403
Zvečan	42.9075	20.8403
Novo Brdo	42.616111	21.435
Kišnica	42.602	21.218
Badovac	42.606667	21.220556
Gračanica	42.6011	21.1958
Gračanica goaf	42.605476	21.208517
Ajvalija	42.619114	21.183164

Balkan with several mine flotation concentrators (Dushi 2002). After the discovery of lead ore and mining in the nineteenth century, the area of northern Kosovo became the large center of industrial mining and smelting. Major urban centers in northern Kosovo (K. Mitrovica, Zvecan, Vucitrn) are located in the studied area, with industrial zones near K. Mitrovica and Zvecan, particularly. The study area covers eastern Kosovo with the territory of cities Priština, Lipljan, and Gnjilane. Samples were taken in the vicinity of inhabited places that are exposed to pollution from industrial sources (mines, smelting), as listed in Table 1.

Sampling and sample preparation

Composite topsoil samples were collected with manual blades at depth 0–15 cm from each sampling sites and stored in sealed polyethylene containers until further use. Samples of the surface soils from analyzed points were selected randomly from the study area. About 1 kg of each soil sample was taken by applying systematic random sampling described by IAEA-TECDOC-1415. Soil samples were air-dried indoors, at room temperature for about two weeks. Then, samples were gently disaggregated, cleaned of extraneous material, and sieved through a nylon sieve of 2 mm. The pseudo-total contents of heavy metal in the soils were obtained by wet acid decomposition in a closed system (reflux) with the addition of hydrogen peroxide (30%) (USEPA 1996).

Conditions of the operation and reliability of chemical analysis

Working parameters of plasma operation conditions were flush pump rate (100 rpm), analysis pump rate (50 rpm), RF power (1150 W), nebulizer gas (0.7 L/min), coolant gas flow (12 L/min), auxiliary gas flow (0.5 L/min), plasma view (dual mode (axial/radial)), and sample uptake delay (30 s).

Validation

The validation process of the measurements based on ICP OES technique involved precision, accuracy, the linearity of the calibration curve, detection (LOD), and quantification limits (LOQ). The accuracy and precision of the method were tested by using NIST Certificate of Analysis for CRM reference material SRM-2709 A. Method precision, evaluated as repeatability, was calculated in terms of the variation coefficient (%CV) of data obtained when three replicates of the CRM sample were analyzed (Table 2). Three blank samples were also prepared and passed through all treatment procedures as CRM samples to correct the final analytical signal. Accuracy was shown through the percentage difference between the measured concentration and the certified value in CRM (%D). Linearity was assessed by the correlation coefficients. Detection (LOD) and quantification (LOQ) limits were calculated using Equations (1) and (2) (Thomsen *et al.* 2003):

$$LOD = \bar{x}_b + 3S_b \quad (1)$$

$$LOQ = \bar{x}_b + 10S_b \quad (2)$$

respectively, where $\bar{x}_b$ is the mean blank and S_b is a standard deviation of blank responses. Both limits were expressed in ng/g. Metal concentrations were obtained using an appropriate calibration curve for each element. Selected analytical lines used for elements determination, the limit of detection, and determination with a coefficient of correlation and linearity of the calibration curves are given in Table 3.

Comparison of the concentration of elements in the CRM with those found in the study (Table 2) indicates that the concentrations of Cd and As may have been overestimated by 11% ($D \sim 89\%$), while for other elements, the difference among the measured concentrations and the expected values was below 10% ($D > 90\%$). The precision of repeatability (CV) was under 8% for all elements. Nevertheless, in all cases, the accuracy and precision were within the acceptable RSD (CV) percentages obtained from the Horwitz function (Horwitz 1982, Thompson 2004) and the AOAC Peer-Verified Methods (PVM) program (2000) on the analyte level (Gonzalez and Herrador 2007).

Statistical analyses

The principal component analysis was used as the statistical method. It was used with the aim of evaluating

Table 2. Accuracy and precision of the proposed method using certified reference material (CRM 2709a).

	Accuracy			
Element	Certified values[a] (mg/kg)	Found values[a] (mg/kg)	Accuracy D (%)[b]	Precision CV (%)[c]
Cd	0.371 ± 0.002	0.352 ± 0.005	94.88	1.42
Co	12.8 ± 0.2	12.1 ± 0.2	94.53	1.65
Pb	17.3 ± 0.3	16.1 ± 0.7	91.90	4.35
As	10.5 ± 0.3	9.9 ± 0.4	93.94	4.04
Cu	33.9 ± 0.5	32.2 ± 0.7	94.88	2.37
Cr	130 ± 9	127 ± 7	97.69	5.51
Mn	529 ± 18	525 ± 16	99.24	5.97
V	110 ± 11	108 ± 13	98.18	12.04
Zn	103 ± 4	99 ± 2	96.1	2.02
	Certified values[a] (Mass fraction, %)	Found values[a] (Mass fraction, %)	Accuracy D (%)[b]	Precision CV (%)[c]
Al	7.37 ± 0.16	7.21 ± 0.21	97.83	2.91
Ca	1.91 ± 0.09	1.95 ± 0.02	102.1	1.03
Fe	3.06 ± 0.07	3.00 ± 0.04	98.04	1.33
Mg	1.46 ± 0.02	1.39 ± 0.07	94.96	5.03
P	0.0688 ± 0.0013	0.0643 ± 0.0012	93.46	1.74
K	2.11 ± 0.06	2.05 ± 0.07	97.16	3.41
Si	30.3 ± 0.4	29.8 ± 0.6	98.32	2.01
Na	1.22 ± 0.03	1.16 ± 0.05	94.92	4.31

[a] $c_{sr} \pm u$; u: standard uncertainty, $n = 3$; s: standard deviation.
[b] [1 − (found value − certified value)/certified value] × 100%.
[c] $CV = s/c_{sr} \times 100\%$.

Table 3. Selected analyte lines with the correlation coefficient (r), limit of detection (LOD), and limit of quantification (LOQ).

Samples	Element	Wavelength (nm)	r	LOD (ng/g)	LOQ (ng/g)	Linearity µg/mL
1	Al	309.271	0.99997	6.97	23.2	0–50.0
2	As	189.042	0.99999	2.83	9.44	0–1.00
3	B	249.773	1	0.73	2.44	0–25.0
4	Ba	455.403	0.99987	0.06	0.19	0–20.0
5	Be	234.861	1	0.06	0.21	0–20.0
6	Ca	422.673	0.99995	19.5	65.0	0–500
7	Cd	226.502	0.99990	0.23	0.76	0–1.00
8	Co	228.616	1	0.34	1.12	0–2.00
9	Cr	283.563	1	0.62	2.05	0–2.00
10	Cu	324.754	0.99999	0.75	2.51	0–50.0
11	Fe	259.940	0.99995	0.66	2.20	0–50.0
12	K	766.490	0.99968	41.5	138	0–500
13	Mg	279.553	1	0.16	0.53	0–500
14	Mn	257.610	0.99992	0.12	0.39	0–25.0
15	Na	588.995	1	0.80	2.67	0–500
16	Ni	221.647	1	0.47	1.58	0–1.00
17	P	213.618	0.99933	6.93	23.1	0–500
18	Pb	220.353	0.99998	2.65	8.84	0–1.00
19	Se	196.090	0.99999	3.97	13.2	0–25.0
20	Si	251.611	1	1.84	6.15	0–100
21	V	310.230	0.99997	0.65	2.18	0–20.0
22	Zn	213.856	0.99990	0.14	4.60	0–50.0

the dataset, reducing its dimensions, and conserving most of the statistical information. PCA permits establishing the relationships among variables. The analysis was performed using data analysis and statistical applications available for Microsoft Excel® (XLSTAT 2017) (Addinsoft 2017).

GIS multiple criteria analysis

Geographical information system (GIS) was used for geospatial and geostatistical analysis for dispersion of characteristics of soils. On the basis of the obtained evaluation, it was possible to determine the characteristics of soil properties. GIS and modeling of data are very powerful tools for calculating and describing the dispersion of metals in the soils. With the purpose to analyze characteristics of metals in the soils in Kosovo, GIS software QGIS and SAGA, with tools of multidimensional calculations were used (Bíl *et al.* 2012). The satellite recordings data were downloaded from the official web page of USGS (United States Geological Survey) and the official web page Earth Explorer – LAND SAT (http://earthexplorer.usgs.gov/). The Aster Global DEM data with the exceptional view of Digital Elevation data were also downloaded (Valjarević *et al.* 2014). The downloaded data were exported to the GIS software, and the territory of Kosovo with sampling data area was cropped for the future manipulation of vectorized data. Ordinary semi-kriging and interpolation methods were employed through QGIS and SAGA (GIS) of Spatial Analyst because it includes autocorrelation or the statistical relationship among the measured points. Thus, with this method, the weights are based not only on the distance between the measured points and the prediction of location but also on the overall spatial arrangement of the measured points, and it minimizes the variance of the error of estimation.

Results and discussion

The obtained concentrations (mean ± standard deviation) of the elements determined in the soil samples are presented in Table 4.

As can be seen from Table 4, the mean concentrations of Cr (0.1122 g/kg) and Ni (0.1662 g/kg) in investigated samples are notably higher than median values for soils in European cities (Gulan *et al.* 2017, Luo *et al.* 2012), while the mean concentrations of Cr, Cu, Ni, and Pb overstepped the Dutch standard target values for soil which indicate sustainable soil quality (0.1107 g/kg, 0.0055 g/kg, 0.1663 g/kg, and 1.265 g/kg, respectively) (VROM 2000). The absence of normal distribution and high SD values are often a reliable indicator of anthropogenic activities (Manta *et al.* 2002, Mihailovic *et al.* 2014). The sample S11 (Novo Brdo) for the majority of the investigated elements shows either the highest or the lowest values of the concentrations, probably due to large ore deposits; also, it was a well-known medieval city all over Europe, dealing with the processing of silver ore.

Table 4. Contents (g/kg)[a] of the elements determined in the soil samples.

Samples	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Se	Si	V	Zn
Dobrotin (S1)	19.9 ± 0.1	0.015 ± 0.002	0.162 ± 0.003	78.9 ± 0.3	0.0038 ± 0.0001	0.019 ± 0.001	0.0697 ± 0.0003	0.0272 ± 0.0003	16.1 ± 0.3	1.78 ± 0.01	2.45 ± 0.01	0.89 ± 0.01	0.0349 ± 0.0007	0.104 ± 0.001	0.63 ± 0.02	0.0739 ± 0.0006	0.0014 ± 0.0002	0.293 ± 0.002	0.092 ± 0.001	0.075 ± 0.005
Sušica (S2)	14.4 ± 0.2	0.019 ± 0.001	0.274 ± 0.001	74.98 ± 0.01	0.0072 ± 0.0001	0.021 ± 0.001	0.0853 ± 0.0004	0.0293 ± 0.0003	16.2 ± 0.1	2.02 ± 0.01	5.57 ± 0.04	1.59 ± 0.02	0.0349 ± 0.0001	0.1725 ± 0.0001	1.17 ± 0.01	0.1539 ± 0.0004	0.0021 ± 0.0002	0.409 ± 0.004	0.076 ± 0.001	0.134 ± 0.001
Laplje Selo (S3)	29.4 ± 1.5	0.013 ± 0.001	0.69 ± 0.02	42.89 ± 0.03	0.0045 ± 0.0002	0.019 ± 0.001	0.083 ± 0.004	0.039 ± 0.002	17.2 ± 0.5	2.56 ± 0.13	5.29 ± 0.33	1.14 ± 0.06	0.0269 ± 0.0002	0.137 ± 0.008	1.079 ± 0.005	0.095 ± 0.005	0.0023 ± 0.0003	0.469 ± 0.006	0.094 ± 0.004	0.251 ± 0.015
Livađe (S4)	19.5 ± 0.2	0.084 ± 0.005	0.253 ± 0.002	44.30 ± 0.01	0.0040 ± 0.0001	0.017 ± 0.001	0.0650 ± 0.0005	0.0395 ± 0.0004	14.5 ± 0.3	2.51 ± 0.01	4.32 ± 0.02	1.03 ± 0.02	0.027 ± 0.001	0.124 ± 0.002	1.09 ± 0.01	0.089 ± 0.002	0.0024 ± 0.0004	0.527 ± 0.004	0.079 ± 0.008	0.091 ± 0.001
Plemetina (S5)	12.0 ± 0.1	0.111 ± 0.002	0.207 ± 0.002	6.24 ± 0.03	0.0035 ± 0.0001	0.023 ± 0.001	0.1163 ± 0.0005	0.0367 ± 0.0003	14.2 ± 0.2	1.67 ± 0.03	2.96 ± 0.04	1.03 ± 0.02	0.027 ± 0.001	0.019 ± 0.001	2.59 ± 0.02	0.0709 ± 0.0006	0.0021 ± 0.0004	0.621 ± 0.007	0.081 ± 0.001	0.092 ± 0.001
Ibarska Slatina (S6)	9.82 ± 0.09	0.222 ± 0.001	0.146 ± 0.001	18.27 ± 0.01	0.0157 ± 0.0001	0.022 ± 0.001	0.145 ± 0.001	0.070 ± 0.001	17.6 ± 0.2	1.13 ± 0.02	14.2 ± 0.1	2.34 ± 0.05	0.0329 ± 0.0001	0.264 ± 0.001	2.02 ± 0.01	0.672 ± 0.003	0.0030 ± 0.0002	0.569 ± 0.008	0.0685 ± 0.0006	1.41 ± 0.01
Zubin Potok (S7)	14.5 ± 0.1	0.007 ± 0.001	0.124 ± 0.002	2.80 ± 0.03	0.0039 ± 0.0001	0.0145 ± 0.0004	0.0535 ± 0.0001	0.0267 ± 0.0002	15.2 ± 0.1	1.47 ± 0.01	3.93 ± 0.03	0.681 ± 0.008	0.0249 ± 0.0002	0.067 ± 0.002	1.225 ± 0.003	0.0435 ± 0.0002	0.0024 ± 0.0005	0.674 ± 0.005	0.0689 ± 0.0006	0.0739 ± 0.0003
Žitkovac (S8)	7.64 ± 0.06	0.073 ± 0.001	0.071 ± 0.002	13.47 ± 0.01	0.0069 ± 0.0001	0.0234 ± 0.0001	0.245 ± 0.003	0.040 ± 0.001	14.9 ± 0.2	0.513 ± 0.004	20.3 ± 0.1	0.704 ± 0.003	0.0369 ± 0.0002	0.449 ± 0.003	0.098 ± 0.007	0.047 ± 0.003	0.0021 ± 0.0003	0.401 ± 0.003	0.0659 ± 0.0006	0.479 ± 0.003
Grabovac (S9)	5.53 ± 0.02	0.137 ± 0.001	0.0812 ± 0.0003	50.20 ± 0.01	0.0051 ± 0.0001	0.0189 ± 0.0001	0.190 ± 0.001	0.0647 ± 0.0006	15.7 ± 0.2	0.608 ± 0.009	15.9 ± 0.1	0.916 ± 0.008	0.0389 ± 0.0004	0.279 ± 0.001	0.091 ± 0.001	0.051 ± 0.002	0.0020 ± 0.0004	0.956 ± 0.002	0.0659 ± 0.0007	0.472 ± 0.002
Zvečan (S10)	14.5 ± 0.2	0.047 ± 0.003	0.205 ± 0.001	8.18 ± 0.08	0.0055 ± 0.0001	0.0137 ± 0.0001	0.0545 ± 0.0004	0.0526 ± 0.0005	12.9 ± 0.2	1.73 ± 0.02	3.41 ± 0.05	0.66 ± 0.02	0.0309 ± 0.0003	0.055 ± 0.001	0.166 ± 0.002	0.092 ± 0.003	0.0025 ± 0.0002	0.624 ± 0.009	0.0809 ± 0.0004	0.389 ± 0.003
Novo Brdo (S11)	0.33 ± 0.01	0.012 ± 0.001	0.0313 ± 0.0002	16.66 ± 0.01	0.0439 ± 0.0001	0.0126 ± 0.0001	0.0745 ± 0.0005	0.2209 ± 0.0007	52.8 ± 0.6	0.361 ± 0.002	0.074 ± 0.002	0.052 ± 0.001	0.0359 ± 0.0002	0.0079 ± 0.0001	0.1269 ± 0.0004	14.98 ± 0.02	0.0072 ± 0.0004	0.086 ± 0.001	0.0379 ± 0.0001	0.481 ± 0.003
Kišnica (S12)	6.55 ± 0.01	0.232 ± 0.001	0.2423 ± 0.0022	3.54 ± 0.02	0.0063 ± 0.0001	0.038 ± 0.002	0.156 ± 0.001	0.0045 ± 0.0001	20.1 ± 0.4	0.97 ± 0.01	1.40 ± 0.01	3.13 ± 0.04	0.0043 ± 0.0001	0.2805 ± 0.0007	0.409 ± 0.001	1.089 ± 0.003	0.0035 ± 0.0004	0.209 ± 0.004	0.0489 ± 0.0005	0.389 ± 0.002
Badovac (S13)	12.3 ± 0.1	0.0313 ± 0.0003	0.127 ± 0.001	2.98 ± 0.01	0.0047 ± 0.0001	0.024 ± 0.002	0.113 ± 0.001	0.0391 ± 0.0008	17.6 ± 0.1	1.24 ± 0.01	2.53 ± 0.01	1.04 ± 0.02	0.0335 ± 0.0003	0.145 ± 0.002	0.369 ± 0.002	0.189 ± 0.003	0.0021 ± 0.0001	0.369 ± 0.009	0.0469 ± 0.0002	0.1109 ± 0.0005
Gračanica (S14)	6.06 ± 0.08	0.251 ± 0.001	0.196 ± 0.004	3.52 ± 0.03	0.0072 ± 0.0001	0.0145 ± 0.0001	0.063 ± 0.001	0.0489 ± 0.0007	17.9 ± 0.1	1.04 ± 0.02	1.49 ± 0.03	3.01 ± 0.1	0.0035 ± 0.0001	0.110 ± 0.001	1.53 ± 0.01	1.40 ± 0.01	0.0036 ± 0.0002	0.69 ± 0.01	0.0379 ± 0.0006	0.711 ± 0.008
Gračanica goaf (S15)	6.97 ± 0.01	0.331 ± 0.002	0.208 ± 0.003	3.96 ± 0.01	0.0075 ± 0.0001	0.0346 ± 0.0001	0.164 ± 0.004	0.0512 ± 0.0005	21.5 ± 0.1	0.79 ± 0.01	1.64 ± 0.05	2.98 ± 0.06	0.037 ± 0.001	0.285 ± 0.005	1.08 ± 0.01	0.97 ± 0.01	0.0039 ± 0.0004	0.549 ± 0.008	0.051 ± 0.074	0.411 ± 0.005
Ajvalija (S16)	11.8 ± 0.1	0.035 ± 0.001	0.116 ± 0.002	3.13 ± 0.02	0.0042 ± 0.0001	0.0221 ± 0.0002	0.117 ± 0.002	0.0390 ± 0.0004	18.1 ± 0.3	1.21 ± 0.02	2.53 ± 0.03	1.12 ± 0.02	0.0245 ± 0.0002	0.1599 ± 0.0003	0.445 ± 0.001	0.219 ± 0.001	0.0019 ± 0.0001	0.548 ± 0.005	0.0479 ± 0.0006	0.103 ± 0.001
Min-Max	0.33–29.4	0.007–0.331	0.0313–0.69	2.80–13.47	0.0035–0.0439	0.0126–0.0380	0.0535–0.245	0.0045–0.2209	12.9–52.8	0.361–2.56	0.074–20.3	0.052–3.13	0.0035–0.0389	0.0079–0.4490	0.0910–2.5900	0.0435–14.9800	0.0014–0.0072	0.0860–0.9560	0.0379–0.0940	0.0739–1.410
Md	11.90	0.060	0.179	10.825	0.0055	0.0200	0.0991	0.0393	16.7	1.225	3.185	1.0350	0.0319	0.1410	0.8545	0.1245	0.0024	0.5375	0.0672	0.3200

[a]The values are means ± *SD*, $n = 3$.
Min: minimum; Max: maximum; Md: mediana.

Element distribution maps

In modern chemistry, GIS analysis is of significant importance. Visualization of some data was presented using distribution maps. These maps were created using GIS architecture and design. In this paper elements distribution maps were presented for four selected toxic elements (As, Cd, Cr, and Pb).

Heavy metals are elements with metallic properties and an atomic mass of >20. The most common contaminants among heavy metal(loid)s are Cd, Cr, Hg, Pb, Cu, Zn, and As. Arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) are category 1 heavy metals according to the International Agency for Research on Cancer (Kim *et al.* 2015). They are extremely toxic even in small quantities leading to diseases causing irreversible changes in the humans, especially on the central nervous system (Goyer 1996).

The first map for As shows the largest distribution in the northern and central-eastern part of Kosovo (Figure 2). Mining basins and smelting ore can be the sources of increased arsenic concentration in the environment. Arsenic is a metalloid that exists in inorganic and organic forms. According to local regulative (Official Gazette of the Republic of Serbia 2010, Official Gazette of the Republic of Serbia 2012) maximum permissible concentration (MPC) for As is 0.029 g/kg. In the analyzed samples in our study, As ranges from 0.007 to 0.330 g/kg. The surroundings of the cities Priština and Leposavić are areas with extremely high concentrations of arsenic. The highest concentrations were determined near locations Gracanica goaf (S14) and Gracanica (S15), Ajvalija (S16), Kisnica (S12), Grabovac (S9), Zvecan (S10), Zitkovac (S8), Ibarska Slatina (S6), Plemetina (S11), and Livadje (S4), and the contents of As are 0.330 g/kg, 0.250 g/kg, 0.035 g/kg, 0.230 g/kg, 0.130 g/kg, 0–050 g/kg, 0–070 g/kg, 0.220 g/kg, 0.110 g/kg, and 0.080 g/kg, respectively, over or closely MPC. All the above mentioned locations are areas nearby industrial sources of pollution (mine, smelter, and thermal power plant).

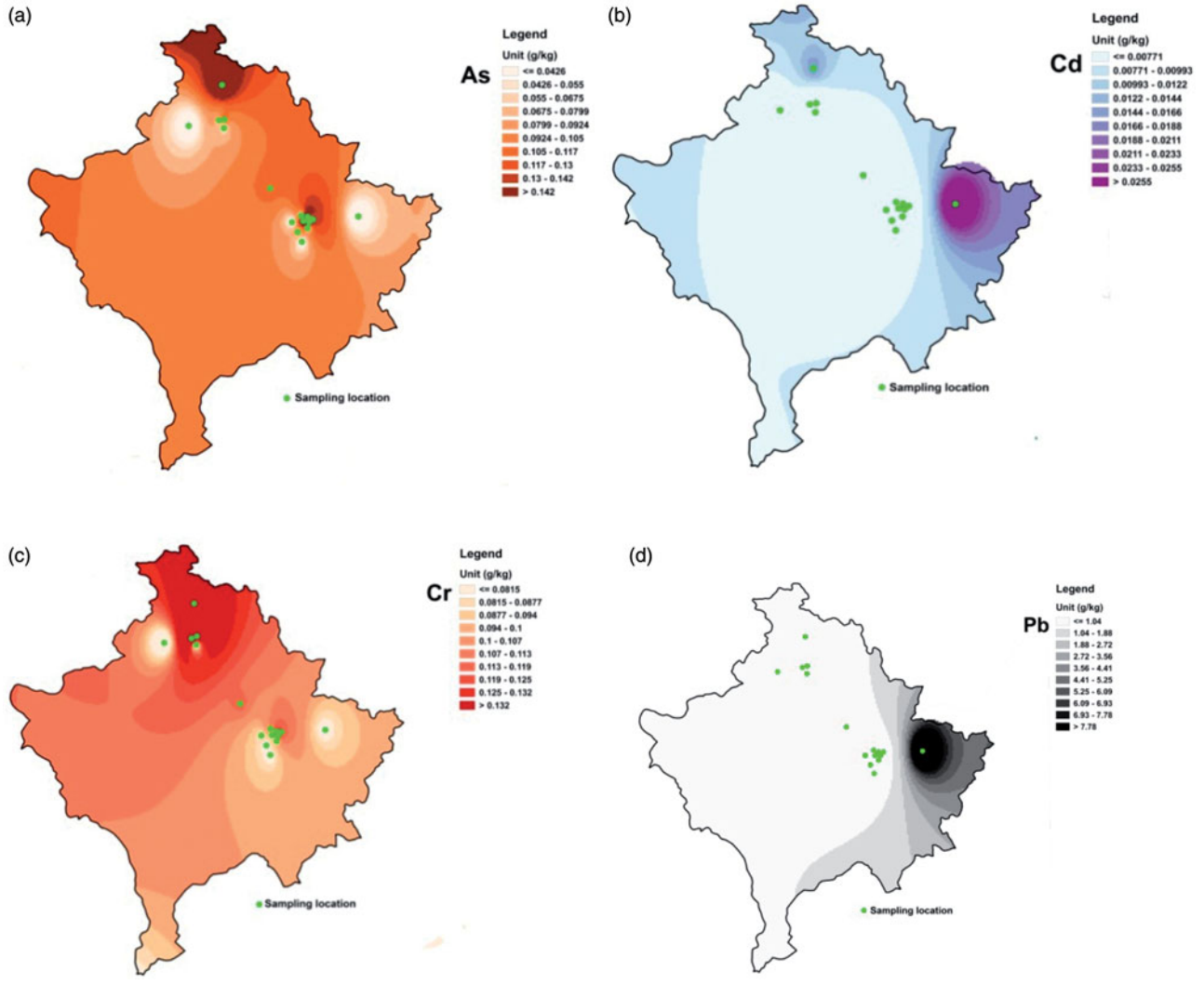

Figure 2. Distribution maps of (a) As, (b) Cd, (c) Cr, and (d) Pb in Kosovo with sampling locations.

Table 5. Results of Pearson's correlation analysis.

Variables	ln Al	ln As	ln Ba	ln Ca	ln Co	ln Cr	ln Cu	ln Fe	ln K	ln Mg	ln Mn	ln Na	ln Ni	ln P	ln Pb	ln Si	ln V	ln Zn
ln Al	**1**	**−0.756**	**0.722**	0.290	−0.323	**−0.597**	**−0.595**	−0.384	**0.880**	−0.033	−0.473	−0.443	−0.381	0.306	−0.476	−0.168	**0.705**	**−0.598**
ln As	**−0.756**	**1**	−0.490	−0.120	0.433	0.503	**0.773**	0.384	**−0.541**	−0.077	**0.666**	0.323	0.231	0.007	**0.657**	0.126	−0.503	**0.679**
ln Ba	**0.722**	−0.490	**1**	**0.708**	−0.359	−0.343	−0.294	**−0.634**	**0.648**	0.438	−0.465	−0.225	−0.353	0.207	**−0.603**	0.136	**0.938**	−0.204
ln Ca	0.290	−0.120	**0.708**	**1**	−0.104	0.088	0.067	−0.329	0.255	**0.650**	−0.163	0.158	0.207	−0.077	−0.365	0.157	**0.607**	0.113
ln Co	−0.323	0.433	−0.359	−0.104	**1**	**0.730**	0.138	−0.362	−0.108	0.513	**0.561**	0.368	0.368	0.068	0.406	−0.469	−0.217	0.135
ln Cr	**−0.597**	0.503	−0.343	0.088	**0.730**	**1**	0.451	0.351	**−0.762**	0.441	0.203	**0.644**	**0.533**	0.068	0.115	−0.117	−0.226	0.435
ln Cu	**−0.595**	**0.773**	−0.294	0.067	0.138	0.451	**1**	0.236	−0.496	0.231	0.415	0.299	0.362	−0.254	0.471	0.323	−0.344	**0.845**
ln Fe	−0.384	0.384	**−0.634**	−0.329	**0.662**	0.351	0.236	**1**	−0.317	−0.411	**0.807**	0.294	**0.530**	0.218	**0.786**	−0.336	**−0.630**	0.284
ln K	**0.880**	**−0.541**	**0.648**	0.255	−0.362	**−0.762**	−0.496	−0.317	**1**	−0.283	−0.188	**−0.516**	**−0.544**	**0.541**	−0.207	−0.110	**0.551**	**−0.551**
ln Mg	−0.033	−0.077	0.438	**0.650**	−0.108	0.441	0.231	−0.411	−0.283	**1**	−0.408	0.199	0.330	−0.367	−0.505	0.311	0.417	0.320
ln Mn	−0.473	**0.666**	−0.465	−0.163	0.513	0.203	0.415	**0.807**	−0.188	−0.408	**1**	0.227	0.322	0.438	**0.945**	−0.211	**−0.567**	0.506
ln Na	−0.443	0.323	−0.225	0.158	**0.561**	**0.644**	0.299	0.294	**−0.516**	0.199	0.227	**1**	**0.574**	−0.500	0.153	−0.472	−0.049	0.352
ln Ni	−0.381	0.231	−0.353	0.207	0.368	**0.533**	0.362	**0.530**	**−0.544**	0.330	0.322	**0.574**	**1**	−0.437	0.346	−0.256	−0.333	0.495
ln P	0.306	0.007	−0.077	0.068	−0.398	−0.254	0.218	**0.541**	−0.367	0.438	−0.500	0.153	−0.437	**1**	**1**	−0.214	0.065	−0.178
ln Pb	−0.476	**0.657**	**−0.603**	−0.365	0.406	0.115	0.471	**0.786**	−0.207	−0.505	**0.945**	0.153	0.310	0.346	**1**	−0.214	**−0.692**	**0.526**
ln Si	−0.168	0.126	0.136	0.157	−0.469	−0.117	0.323	−0.336	−0.110	0.311	−0.211	−0.472	−0.256	0.041	−0.214	**1**	0.011	0.179
ln V	**0.705**	−0.503	**0.938**	**0.607**	−0.217	−0.226	−0.344	**−0.630**	**0.551**	0.417	**−0.567**	−0.049	−0.333	0.065	**−0.692**	0.011	**1**	−0.296
ln Zn	**−0.598**	**0.679**	−0.204	0.113	0.135	0.435	**0.845**	0.284	**−0.551**	0.320	0.506	0.352	0.495	−0.178	**0.526**	0.179	−0.296	**1**

Values in bold are different from 0 with a significance level alpha = 0.05.

The second map for Cd shows the highest concentration of this metal in the east, 30 km far from the city of Priština (Figure 2). Cd is one from the group of rare earth metals which is used in high technology industries. In this study Cd ranges from 0.004 to 0.044 g/kg in the analyzed samples. It comes from industrial waste, from mines, and smelter (Trepca and Zvecan). Concentrations of Cd in all analyzed samples were higher than MPC (0.0008 g/kg). Values were especially higher in samples from Ibarska Slatina (S6) and Novo Brdo (S11), as a result of mining activities or geological composition of the soil (Figure 2).

Cr is present in considerable quantity in the Earth's crust, and its toxicity depends on its chemical state. The most well-documented reason for Cr-related toxicity is oxidative stress, causing risk of diseases such as cancer, bond damage, etc. (Kim *et al.* 2015). In analyzed samples in our study Cr ranges from 0.053 to 0.245 g/kg. The concentration of Cr was higher than MPC (0.100 g/kg) in several samples: S5, S6, S8, S9, S12, S13, S15, and S16 (0–116 g/kg, 0–145 g/kg, 0–245 g/kg, 0.190 g/kg, 0–150 g/kg, 0–110 g/kg, and 0–160 g/kg, respectively), and they are located near industrial sources of pollution, mines, and smelter (Figure 2). The third map for Cr shows the biggest concentration in the area of cities Leposavić and K. Mitrovica, as a result of the proximity of the mining complex "Trepča" and power plant "Obilić" (Figure 2).

Finally, the fourth map shows the highest concentration of Pb in the eastern part of Kosovo and 40 km far from Priština (Novo Brdo-known medieval mining center) (Figure 2). Lead is an ubiquitous metal in our environment, but it does not possess any physiologic role. Lead toxicity is an insidious hazard with the potential to cause irreversible health effects. It affects various body functions, primarily the central nervous, hepatic, hematopoietic, and renal systems causing serious disorders (Kim *et al.* 2015). MPC for Pb according to local regulative is 0.085 g/kg. Samples with higher concentrations of Pb than MPC is S2, S3, S6, S10-S16 (0.154 g/kg, 0.095 g/kg, 0.672 g/kg, 0.092 g/kg, 1.498 g/kg, 1.090 g/kg, 0.190 g/kg, 1.400 g/kg, 0.970 g/kg, and 0.220 g/kg, respectively) as could be expected in terms of mining and metallurgical activities in the area. Contents of heavy metals in soils were previously determined in 34 European cities (9954 samples), and following values were obtained (median values): 0.013 g/kg, 0.0095 g/kg, 0.0064 g/kg, 0.059 g/kg, 0.046 g/kg, 0.022 g/kg, 0.102 g/kg, 0.130 g/kg for As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, respectively (Luo *et al.* 2012). Obtained results in our study for heavy metal concentrations have been shown to be notably higher than mentioned in the previous research (Luo *et al.*

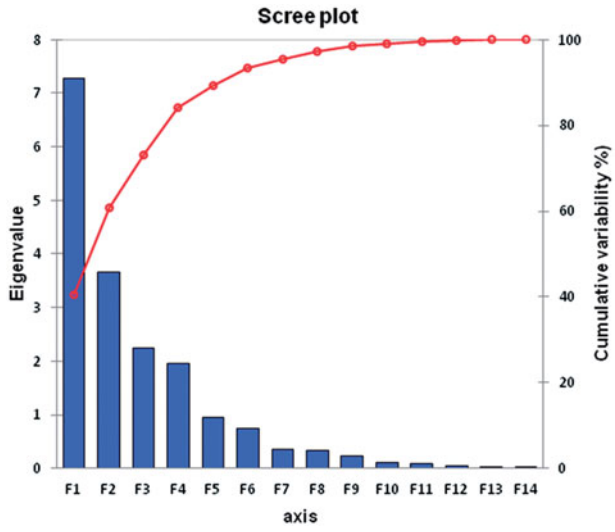

Figure 3. Scree plot.

2012). On the other side, comparison of results obtained from Gulan *et al.* (2017) for the same area, have shown good agreement for heavy metal contents with our results. All maps show the distribution of elements grouped into 10 classes.

Statistical analyses of quantities of elements in the soil

The aim of the statistical analysis of results was to find correlations among the content of elements in the soil samples.

Principal component analysis (PCA)

In the first step of statistical evaluation, the Kolmogorov–Smirnov test (the significance level α was 0.05) was used to test the normality of the concentration distribution with each investigated element. This test revealed that the original data set was not normally distributed for all samples. Therefore, the original data were *ln*-transformed and used for further analysis. The concentrations of Se were excluded from the analysis because it was not possible to normalize the data using common functions.

Pearson's correlation matrix was obtained using *ln*-transformed values of the concentrations of the investigated elements. A strong correlation (>0.7) was observed between ln Al and ln Ba, ln Al and ln K, ln Al and ln V, ln As and ln Cu, ln Ba and ln Ca, ln Ba and ln V, ln Co and ln Cr, ln Cu and ln Zn, ln Fe and ln Mn, ln Pb and ln Fe, ln Mn and ln Pb; a medium correlation (<0.7, but >0.5) was noticed in the cases of ln As and ln Mn, ln As and ln Pb, ln As and ln Zn, ln Ba and ln K, ln Ca and ln Mg, ln V and ln Ca, ln Fe and ln Co, ln Na and ln Co, ln Cr and ln Na, ln Ni and ln Cr, ln Fe and ln Ni, ln K and ln P, ln K and ln V, ln Na and ln Ni, ln Pb and ln Zn. A strong negative correlation was observed in the case of ln As and ln Al, and ln Cr and ln K (Table 5).

Before PCA analysis, the data matrix was tested to detect outliers. Grubb's test was used in the experimental data, and no outliers were found in the dataset for all investigated elements (the critical value for $\alpha = 0.05$ and $n = 16$ was 2.586), except Al, Cu, Mg, Mn, Pb, and Si (the critical value for $\alpha = 0.05$ and $n = 15$ was 2.548). Outliers were discarded from PCA analysis. Data connected to Cd were discarded from the analysis also because of the high number of the outliers.

From the shape of the scree plot, shown in Figure 3, the number of important components that were used in further calculations can be seen.

The PCA of the dataset revealed the presence of four components with characteristic (Eigen) values (7.267, 3.633, 2.243, and 1.961) exceeding 1. This four-component solution explained a total of 83% of the variance, with 40% contributed by the first component, 20% by the second component, 12% by the third component, and 11% by the fourth component.

Principal component analysis scree plot shows that samples S1-S5 (northern Kosovo), S7 and S10 have lower concentrations of aluminum, and samples S6, S8, S9, and S12-S16 (eastern Kosovo) have higher concentrations of aluminum. On the other side, S1, S4, S5, S7, S12-S16 have lower concentrations of arsenic, and samples S2, S3, S6, S8, S9, and S10 have higher concentrations of arsenic (Figure 4(a)).

Loading plot of *ln*-transformed concentrations of the investigated elements shows very similar values for a couple of elements with positives both in F1 and F2 (Cr, Na, Ni, Zn, Cu), and positive in F1, but negative in F2 (Fe, Mn, Pb) (Figure 4(b)).

To get better insight into the latent structure of the data, the correlation matrix was subjected to the Varimax orthogonal rotation with Kaiser optimization. The first factor explained the largest proportion of variance (19%). The representatives of this factor were As, Cu, and Zn with high loading values, Al, Cr, K, Mn, and Pb with moderate loading values, and Ba, Fe, Mg, Na, Ni, Si, and V with relatively low loading values. Except for Al, Ba, K, P, and V, all the investigated species had positive loading values on this factor. The key variables of the second factor were Co and Cr. This factor explained 13% of the total variance. In the first factor of the rotated principal component analysis, As, Cu, and Zn from one side and Al and K were negatively correlated, which indicated that there was a strong mutual influence. That is, if higher

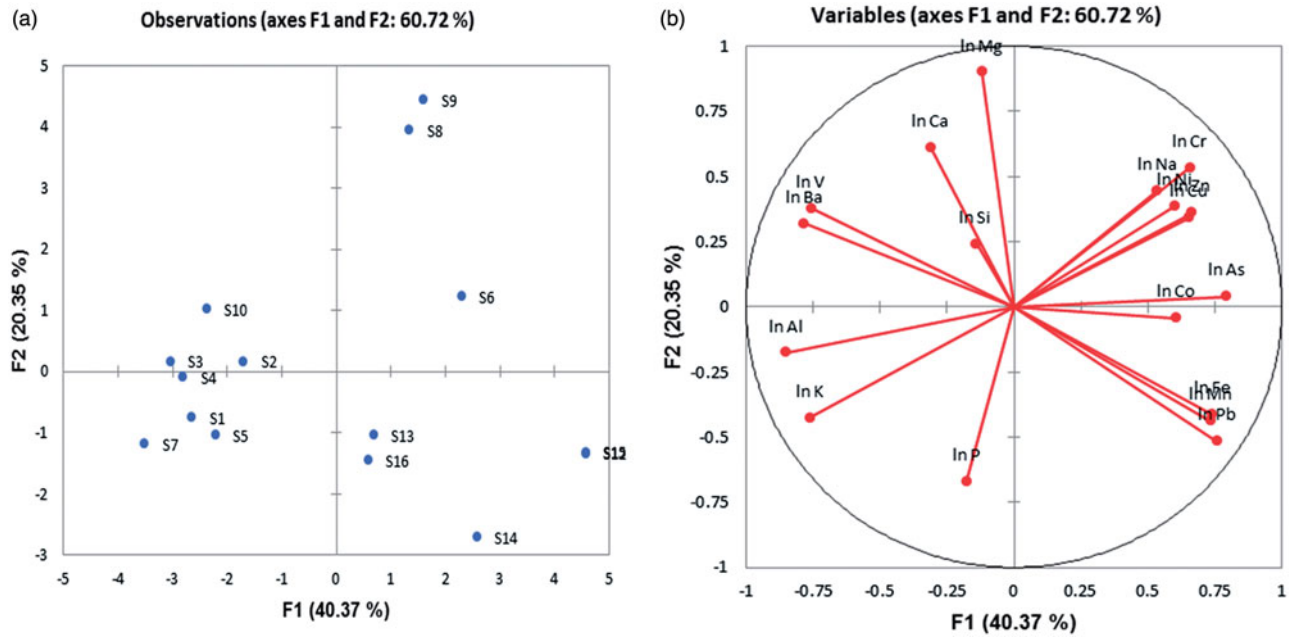

Figure 4. (a) PCA scree plot of PC1 versus PC2; (b) Loading plot.

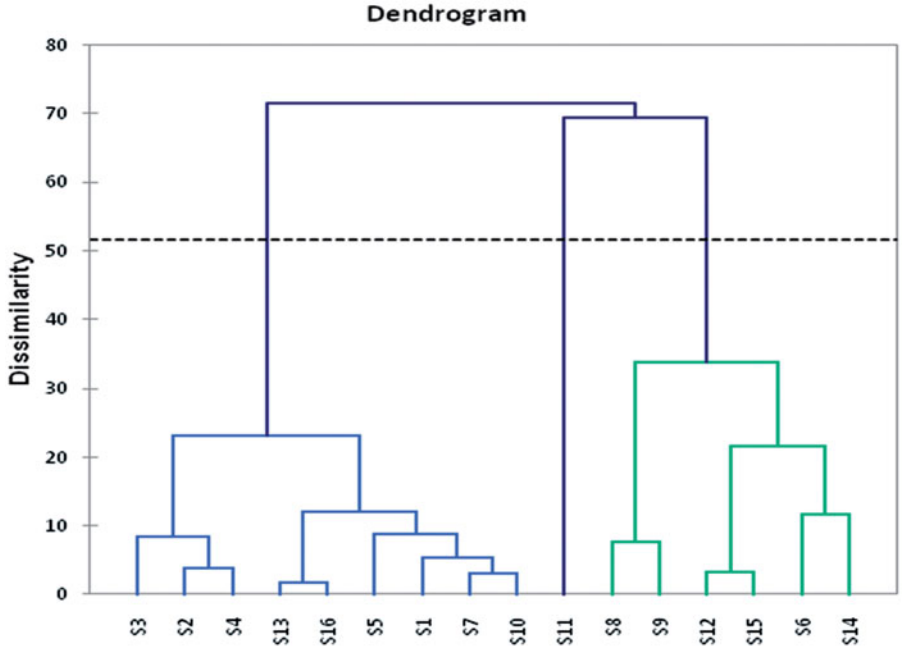

Figure 5. Dendrogram of the analyzed soil samples.

concentrations of the first elements were present, concentrations of the second elements would be lower. On the basis of performed Principal Component Analysis, it can be said that we can use only four factors-concentrations of Al, As, Ba, and Ca to effectively monitor the pollution of the investigated area of the northern and eastern part of Kosovo. Also, results of rotated Principal Component Analysis give us valuable data on the way how we can reduce the concentrations of As, Cu, and Zn in the investigated soil by increasing the concentrations of Al and K. Thus, using Principal Component Analysis, we are saving time and money in monitoring the pollution caused by elements, and obtaining information on how we can clean the area from particular metals.

Cluster analysis

An HCA of the standardized variables using the Ward method as an amalgamation rule was performed with a squared Euclidean distance as a measure of the

proximity between the samples. The obtained dendrogram presenting the clustering of the analyzed samples is presented in Figure 5.

The dendrogram in Figure 5 shows that all monitored samples could be grouped into three main clusters. Cluster I included samples with the concentrations of aluminum of more than 10 g/kg: S1–S5 (northern Kosovo), S7, S10, S13, and S16; cluster II included samples with higher concentrations of arsenic: S6, S8, S9, S12, S14, and S15 (eastern Kosovo), and cluster III included sample S11, which for the majority of the investigated elements either shows the highest or the lowest values of the concentrations.

Conclusions

The results of the study highlighted the influence of industrial and mining activities on elemental content of the soil on a wider area of Kosovo, as well as geological characteristics, in particular taking into account toxic element quantities. Also, the statistical analysis performed gave us the minimum number of factors four that can be traced to monitor the pollution of the area caused by the elements, thus saving time and money.

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