393
GEOME 2
Manuscript received: December 6, 2022
Accepted: February 7, 2022

Geologica Macedonica, Vol. **37**, No. 1, pp. 15–36 (2023)
On print ISSN 0352 – 1206
On line ISSN 1857 – 8586
UDC: 631.416:550.42.08(497.721)
https://doi.org/10.46763/GEOL23371015s

Review

MULTIVARIATE STATISTICAL METHODS IN DETERMINING THE SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN SOILS (KUMANOVO REGION, NORTH MACEDONIA)

Trajče Stafilov[1]*, Robert Šajn[2], Suzana Veličkovski-Simonović[1], Claudiu Tănăselia[3]

[1]*Institute of Chemistry, Faculty of Sciences, "Ss Cyril and Methodius" University in Skopje, Arhimedova 5, 1000 Skopje, N. Macedonia*
[2]*Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia*
[3]*INCDO-INOE 2000 Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania*
*trajcest@pmf.ukim.mk

A b s t r a c t: The results of the distribution of various chemical elements in soil samples from the region of Kumanovo, North Macedonia, are presented. In order to determine the occurrence of chemical elements, soil samples were collected from a total of 51 locations. At each location, soil samples were collected from two layers, topsoil (0–5 cm) and subsoil (20–30 cm), in an area of 5×5 km^2. The soil samples were analyzed for 5 elements using two instrumental methods: inductively coupled plasma – atomic emission spectrometry (ICP-AES) for 17 macroelements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V, and Zn) and inductively coupled plasma – mass spectrometry (ICP-MS) for 38 trace elements (Ag, As, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Ti, Tm, W, Y, Yb, and Zr). Factor analysis was applied to analyze the factors affecting the linear combination variables grouped under the same factor. Spatial distribution maps for each factor as well as distribution maps for the analyzed elements were obtained by universal kriging interpolation. It was found that the distribution of most elements follows the lithology of the studied area, except for some elements (As, Pb, and Zn) whose higher contents were found in some specific parts of sub-areas, which is due to the current and past mining activities in the region.

Key words: soil pollution; potentially toxic elements; Kumanovo region; North Macedonia

INTRODUCTION

Soil is not only a geochemical reservoir for pollutants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and living organisms. Pollution of soil by potentially toxic elements (PTEs) began with anthropogenic smelting and ore processing (Kabata-Pendias & Mukherjee, 2007). The elements introduced from various sources may eventually accumulate the soil surface and their subsequent fate depends on the chemical and physical properties of the soil, especially the nature of the soil. Soil contamination is constant and lasts much longer than in other parts of the biosphere, especially contamination with PTEs, which is practically permanent. PTEs accumulated in soil are extracted from soil by their dissolution, accumulation in plants, erosion, or evaporation. The increase in soil contamination is now so high that it is possible to identify soils as urban or rural based on the content of various PTEs known to be major contaminants in cities (Kabata-Pendias & Mukherjee, 2007; Lourenço et al., 2010; Stafilov et al., 2017, 2019). Regional soil contamination occurs mainly in industrial regions and urban centres, where motor vehicle exhaust and municipal waste are the main sources of trace metals (Kabata-Pendias & Mukherjee, 2007). Due to the heterogeneity and constant change of the urban environment, the natural distribution and methods for identifying anthropogenic anomalies in the natural environment must also be determined firstly. Most studies indicate that environmental pollution with PTEs has been the subject of many studies focused on industrial areas, especially areas where minerals are mined and processed, or densely populated areas where traffic and municipal waste are the main sources of PTEs

(Stafilov et al., 2010a; Salomons et al., 2012; Acton, 2013; Jiménez-Ballesta et al., 2017).

Previous studies over the whole territory of North Macedonia, show that soil pollution with some PTEs (As, Cd, Cu, Mn, Ni, Pb, Sb, Zn) is mainly caused by mining and metallurgical activities (Balabanova et al., 2013; Bačeva et al., 2014; Stafilov et al., 2010a, 2010b, 2018a,b, 2021, 2022a; Stafilov and Šajn, 2016, 2019; Jeftimova et al., 2016). This soil pollution in turn leads to pollution of other environmental media such as air (Barandovski et al., 2008, 2012, 2015, 2020; Stafilov et al., 2018b, 2022b). water (Tomovski et al., 2018, 2019; Vasilevska et al., 2018, 2019; Bačvarovski et al., 2021) and food (Pančevski et al., 2014, 2016; Stafilov et al., 2023).

In this study, the distribution of various chemical elements in soils in the Kumanovo region, in the north of the country, was determined. For this purpose, soil samples were collected in the entire area of Kumanovo region in a grid of 5×5 km, at a total of 51 locations. The obtained results for the content of the studied elements are statistically processed using multivariate factor analysis and cluster analysis to show the correlations of the chemical elements. In addition, maps of the spatial distribution of the studied elements are prepared.

MATERIALS AND METHODS

Study area

The study area is the region around the town of Kumanovo, located in the northern part of North Macedonia (Figure 1). This region includes three municipalities: Kumanovo, Lipkovo, and Staro Nagoričane. The total area of the study area is 1206 km^2 and has a total population of 123,900 inhabitants. In the western part, there is the mountain range of Skopska Crna Gora, which consists mainly of cambisol soils, with small areas containing lithosol and regosol. The most common soil in the studied region is vertisol, which is predominant in the central and eastern parts of the region. In the southern part along the Pčinja river before the confluence with the Vardar river, the most common soil is cambisol, as well as fluvial soil. Fluvial soil is observed along all rivers in this region (Filipovski et al., 2015; Stafilov et al., 2022b).

Kumanovo has developed industry and is a center of industrial production in the northeastern part of North Macedonia, of which metal processing, textile, shoes, leather, food, and tobacco industries are the most common (Lazarevska and Markoski, 2019). It is important to mention that the source of pollution with PTEs is also the closed As-Sb-Cr mine „Lojane" and metallurgical plant in the northwestern part of the study area. This assumption is supported by high arsenic concentrations in soil and ground water detected in the vicinity of flotation tailings landfill (UNDP, 2007; Alderton et al. 2014; Đorđević et al., 2019; Stafilov et al., 2022b).

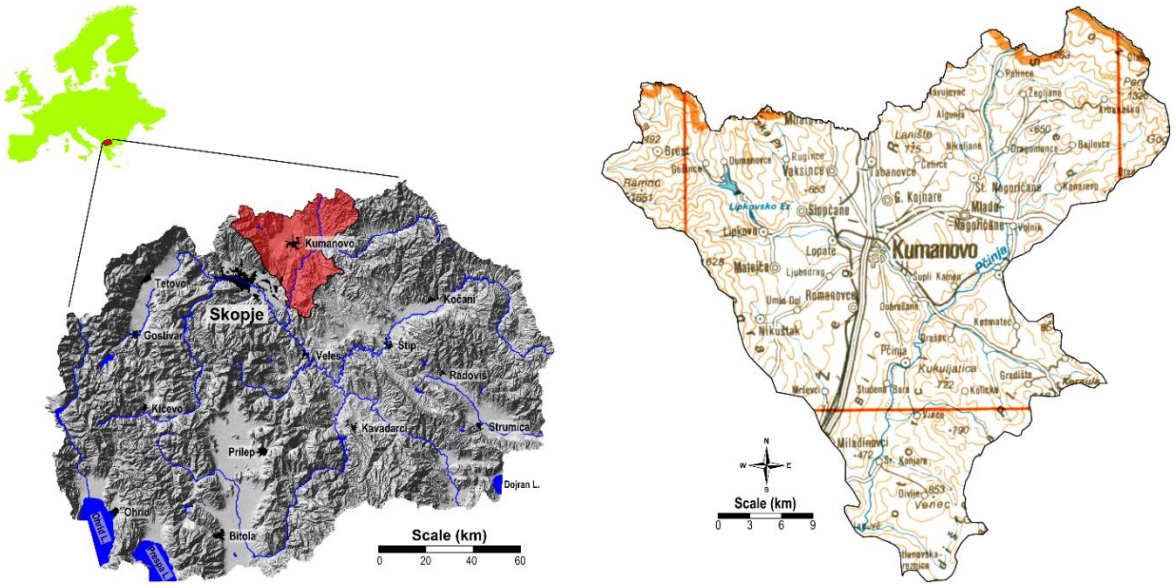


Fig. 1. Location of the study area in North Macedonia (a) and its topographic map (b)

The geological map of the study area is shown in Figure 2. In the eastern part of the region along the Pčinja river, mainly Precambrian gneisses and old granites, volcanic and magmatic rocks, and Quaternary sediments are present in the narrow course of the Pčinja river. In the central and southern parts, mainly Tertiary and Quaternary sediments are distributed with some inclusions of Paleozoic and Mesozoic carbonates, Precambrian and Paleozoic schists, and volcanic and magmatic rocks. In the northwestern part of the area (Skopska Crna Gora mountains), mainly Precambrian and Paleozoic schists and volcanic and magmatic rocks are present (Stafilov et al., 2022b).

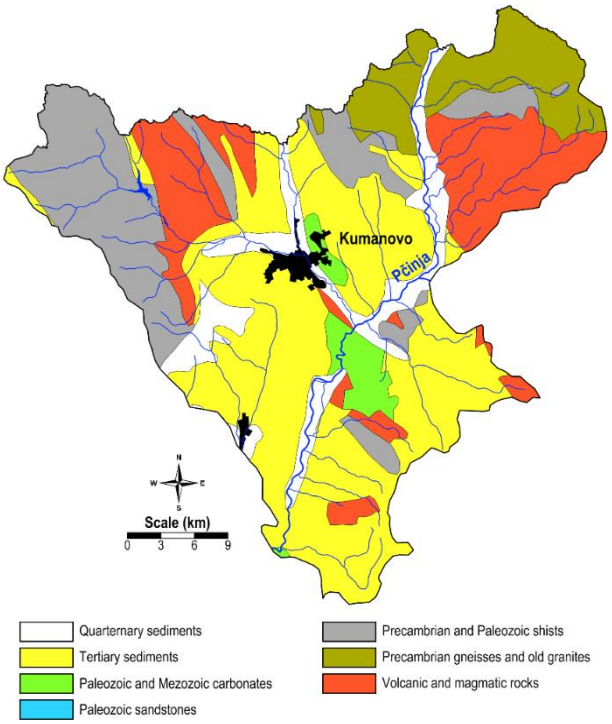


Fig. 2. Geological map of the study area

Soil sampling

The study area was covered by the same sampling grid of 5×5 km that was used for the preparation of the Geochemical Atlas of Macedonia (Stafilov & Šajn, 2016) (Figure 3). A total of 102 soil samples were collected from 51 locations. In order to distinguish possible anthropogenic contamination at the surface from the natural geochemical composition in deeper layers, samples were collected from two intervals: topsoil (0–5 cm) and subsoil (20–30 cm). To obtain representative composite samples, five subsamples were collected from each location in a 10×10 m square area. Soil samples brought to the laboratory were cleaned of plant material and stones and homogenized, dried at room temperature or in a drying oven at 40°C. They were then passed through a 2-mm sieve and ground in a porcelain mortar until they reached a final particle size of 125 μm.

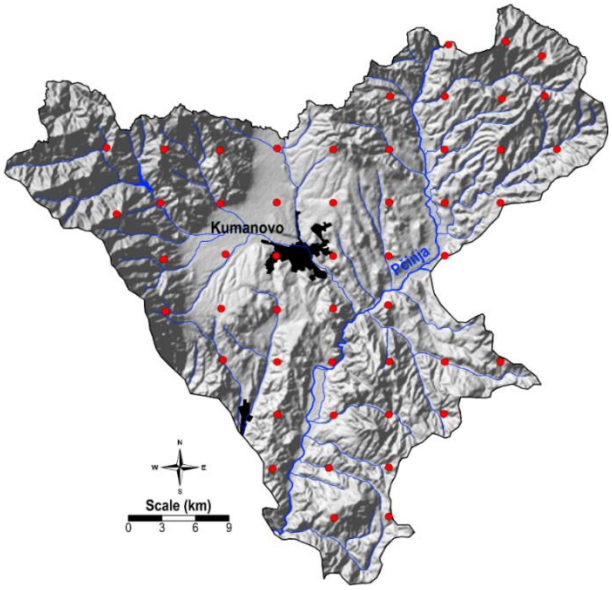


Fig. 3. Study area with soil sampling locations

Digestion and analysis of soil samples

The digestion of the soil samples was carried out by open wet digestion with an acid mixture (HNO_3, HF, $HClO_4$, and HCl was used to digest the soil samples) according to the ISO standard (ISO 14869–1:2001). The method of open digestion of a soil sample with a mixture of the mentioned acids is a generally accepted method for the preparing geological and soil samples for elemental analysis using ICP-AES and ICP-MS. Many authors point out that this method allow complete digestion even for the silicate materials prevalent in soil, and it is emphasized that for the digestion of geological samples, HF is routinely used in combination with other mineral acids (Johnson & Maxwell, 1981; Jarvis, 1990; Jenner et al., 1990; Chao & Sanzalone, 1992; Hu & Qi, 2014).

All samples were analyzed for the elements with higher content (Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V, Zn) using inductively coupled plasma – atomic emission spectrometry, ICP-AES (Varian, model 715-ES) (Balabanova et al., 2010). Trace elements (Ag, As, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Ti, Tm, W, Y, Yb, Zr) were analyzed by inductively coupled plasma – mass spectrometry (ICP-MS) measurements using SCIEX Perkin Elmer Elan DRC II ICP-MS (Canada) with quadruple and single detector setups (Bačeva et al., 2012). The

quality control of the two applied techniques was performed by the standard addition method, and the recovery for the studied elements ranged from 98.2% to 100.8%. Quality control was also performed by analyzing certified soil and geological reference samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock CRM samples undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), rock NCS DC71306 (GBW07114) (China National Analysis Centre). All elements show very low deviations from the recommended range of values, i.e. the mean of all determined elements in the standards generally differs by less than 15% of the recommended values.

Data processing and statistical analyses

Geostatistical data analysis and visualization (mapping) was performed using the following software packages: Statistica (Stat Soft, Inc.), Autodesk MAP 3D (Autodesk, Inc.), ArcInfo (ESRI, Inc.), and Surfer (Golden Software, Inc.). Parametric and nonparametric statistical methods were used and normality tests of the data distributions were performed. Multivariate cluster and R-mode factor analyses (FA) were used to reveal relationships among chemical elements (Garson, 2000, Reimann et al., 2002). Factor analysis (FA) was performed with variables standardized to zero mean and one standard deviation. The varimax method was used for orthogonal rotation. The FA, starting from the exact number of variables, yields a smaller number of new variables, called factors, representing the association of the statistically significant variables. The universal kriging method with linear variogram interpolation was used to produce maps showing the spatial distribution of factor scores and maps showing the distribution of trace elements (Davis, 1986). The base size of the grid cell for interpolation was 25×25 m. Seven classes of percentile values of the distribution of interpolated values were chosen as class boundaries (0–10, 10–25, 25–40, 40–60, 60–75, 75–90, and 90–100).

RESULTS AND DISCUSSION

The descriptive statistics for the content of elements in topsoil and subsoil samples are shown in Tables 1 and 2. The values for Al, Ca, Fe, K, Mg, and Na are given in %, the values for In are given in µg/kg, while the values for the content of the other elements are given in mg/kg. The statistics with all data of the 5 analyzed elements in the moss samples from the studied region for topsoil and subsoil samples from 51 locations are presented in Tables 1 and 2. Seventeen elements were analyzed by ICP-AES (Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V, Zn) and 38 elements (Ag, As, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Ti, Tm, W, Y, Yb, Zr) by ICP-MS. In the most cases, the content of major elements is due to the predominant geological formations of the area: Tertiary and Quaternary sediments, volcanic and magmatic rocks, and Precambrian and Paleozoic schists.

The ratio of the contents between topsoil and subsoil is shown in Table 3, where no significant differences were found except for Ag (1.81). The ratio varies from 0.89 for Al to 1.48 for Sn, indicating that there is no significant influence of anthropogenic activities.

Table 4 shows a comparative analysis of the contents of the analyzed elements in topsoil from the Kumanovo region and soils from Macedonia (Stafilov & Šajn, 2019) and Europe (Salminen et al., 2005). For the comparative analysis, the median values were used as a more stable parameter, as well as the range of contents for each element. It was found that the median content of Ba (1100 mg/kg) was higher than the median for the soil from the whole territory of Macedonia (430 mg/kg, respectively), while the contents of the other macroelements in the soil from the Kumanovo region (1.1% Ca, 2.9% Fe, 1.3% K, 0.68% Mg, 550 mg/kg Mn, 0.77% Na, 400 mg/kg P, and 0.18% Ti), are lower than in the Macedonian soil (1.3%, 3.5%, 1.9%, 0.94%, 900 mg/kg, 1.3%, 620 mg/kg, and 0.34%, respectively). The median values of the contents of most trace elements were lower in the soils from Kumanovo than in the soils from the whole state territory (Be, Bi, Cd, Ce, Co, Hf, La, Mo, Nb, Rb, Sb, Sc, Sr, Ta, W, and Y), while the values for some of them were very similar (As, Cr, Cu, Li, Ni, Pb, Sn, V, Zn, and Zr). These differences between the soil samples from the Kumanovo region and the Macedonian soils show that their distribution is consistent with the lithogenic origin of the rocks. In fact, the geology of this region is very specific and belongs to the Vardar zone as a separate tectonic unit in Macedonia (Stafilov & Šajn, 2016; Petrušev et al., 2021).

T a b l e 1

Descriptive statistics for the content of the elements in topsoil (0–5 cm), n = 51

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	0.21	0.14	0.16	0.005	0.87	0.064	0.33	0.005	0.43	0.19	0.026	88.0	1.19	1.72	–0.46	–0.58
Al	%	3.0	2.8	2.9	0.74	5.7	1.9	3.8	1.6	4.5	1.3	0.18	42.8	0.40	–0.53	–0.05	–0.59
As	mg/kg	11	9.8	9.3	1.5	33	6.8	13	4.9	19	6.5	0.91	58.6	1.51	2.77	0.04	0.54
B	mg/kg	290	46	39	23	5000	27	100	25	570	790	110	274.3	4.94	27.40	0.61	–1.10
Ba	mg/kg	1500	1100	1100	440	5500	820	1600	740	2800	1200	160	77.3	2.25	4.88	–0.18	0.16
Be	mg/kg	0.96	0.63	0.80	0.005	5.2	0.35	1.3	0.025	1.8	0.94	0.14	98.8	2.41	8.92	–0.48	0.06
Bi	mg/kg	0.10	0.060	0.085	0.005	0.53	0.015	0.15	0.005	0.21	0.097	0.014	99.3	2.13	7.67	–0.28	–0.96
Br	mg/kg	1.5	1.3	1.3	0.005	4.3	0.80	2.3	0.23	2.8	1.0	0.15	68.9	0.65	–0.06	–0.15	–0.46
Ca	%	1.7	1.2	1.1	0.16	6.5	0.51	2.8	0.34	4.0	1.6	0.23	94.1	1.35	1.10	0.16	–0.93
Cd	mg/kg	0.057	0.021	0.023	0.005	0.25	0.005	0.091	0.005	0.15	0.069	0.010	119.8	1.37	1.08	0.07	–1.73
Ce	mg/kg	9.7	8.3	8.8	0.97	27	6.2	12	2.3	17	6.0	0.90	61.9	0.74	0.37	–0.39	–0.38
Co	mg/kg	8.0	7.7	7.3	2.8	20	5.6	9.7	4.1	11	3.3	0.49	41.0	1.06	2.46	0.39	0.49
Cr	mg/kg	75	69	79	7.6	190	40	97	26	120	41	5.8	54.8	0.74	0.75	0.02	–0.23
Cs	mg/kg	1.7	1.1	1.1	0.005	20	0.74	1.9	0.37	2.6	2.9	0.43	172.3	5.97	38.47	0.17	5.69
Cu	mg/kg	23	21	22	4.8	47	15	28	11	37	9.9	1.4	43.8	0.64	0.05	–0.07	–0.20
Dy	mg/kg	0.72	0.59	0.61	0.048	1.6	0.31	1.1	0.20	1.4	0.45	0.067	62.7	0.47	–0.83	–0.59	–0.10
Er	mg/kg	0.37	0.30	0.31	0.023	0.91	0.15	0.56	0.10	0.76	0.24	0.036	64.8	0.51	–0.73	–0.64	–0.02
Eu	mg/kg	0.32	0.28	0.28	0.059	0.73	0.21	0.41	0.12	0.64	0.18	0.026	54.7	0.83	0.03	–0.27	–0.18
Fe	%	2.9	2.8	2.9	1.2	5.7	2.2	3.5	1.9	3.8	0.89	0.12	30.9	0.60	0.95	–0.04	0.03
Ga	mg/kg	6.8	6.6	6.9	3.1	12	4.5	8.8	3.6	10	2.4	0.36	36.0	0.11	–1.12	–0.11	–1.21
Gd	mg/kg	0.93	0.80	0.83	0.073	2.3	0.50	1.3	0.28	1.6	0.55	0.083	59.6	0.50	–0.58	–0.46	–0.26
Ge	mg/kg	0.11	0.088	0.084	0.053	0.45	0.074	0.12	0.061	0.21	0.078	0.012	68.7	2.63	7.73	0.22	–0.47
Hf	mg/kg	0.52	0.34	0.35	0.025	2.2	0.15	0.78	0.11	1.3	0.48	0.071	92.2	1.47	2.31	–0.25	–0.37
Ho	mg/kg	0.14	0.11	0.12	0.005	0.32	0.055	0.21	0.038	0.28	0.089	0.013	64.4	0.50	–0.76	–0.70	0.30
In	µg/kg	12	10	13	5.0	27	5.0	17	5.0	21	6.7	1.0	53.6	0.17	–1.28	–0.30	–1.73
K	%	1.4	1.3	1.3	0.66	3.7	1.1	1.6	0.90	2.1	0.55	0.078	38.7	1.82	5.00	0.15	0.24
La	mg/kg	5.2	4.2	4.4	0.55	18	3.1	6.0	1.1	11	3.8	0.57	72.8	1.54	2.60	–0.24	0.18

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Li	mg/kg	19	18	18	1.7	45	12	24	9.5	34	9.0	1.3	46.6	0.70	0.51	–0.19	0.59
Lu	mg/kg	0.076	0.053	0.063	0.005	0.36	0.028	0.11	0.016	0.15	0.066	0.010	86.6	2.00	6.50	–0.50	–0.00
Mg	%	0.80	0.72	0.68	0.16	2.2	0.50	1.2	0.32	1.4	0.44	0.062	55.1	1.04	1.07	0.02	–0.27
Mn	mg/kg	600	530	550	170	2300	410	690	310	860	320	45	54.0	3.23	16.22	–0.20	1.48
Mo	mg/kg	0.83	0.57	0.53	0.005	2.8	0.23	1.4	0.15	2.2	0.79	0.11	95.5	1.07	–0.04	–0.15	–0.34
Na	%	0.86	0.74	0.77	0.25	2.0	0.42	1.3	0.32	1.6	0.48	0.067	56.0	0.70	–0.38	–0.07	–1.06
Nb	mg/kg	4.8	4.7	4.6	0.99	8.8	3.5	5.6	2.8	7.7	1.8	0.26	36.5	0.36	–0.14	0.02	0.01
Nd	mg/kg	3.9	3.5	3.9	0.39	9.2	2.3	5.5	0.87	6.5	2.2	0.34	57.2	0.43	–0.39	–0.27	–0.57
Ni	mg/kg	57	48	49	8.3	180	24	84	15	110	38	5.4	67.7	0.93	0.73	–0.05	–0.86
P	mg/kg	480	420	400	130	1300	310	550	270	800	250	35	51.4	1.44	2.13	–0.07	0.23
Pb	mg/kg	33	30	28	5.0	110	24	37	19	45	18	2.5	53.3	2.56	8.85	–0.41	4.54
Pr	mg/kg	1.0	0.94	1.0	0.11	2.5	0.62	1.4	0.23	1.7	0.59	0.088	56.4	0.44	–0.22	–0.29	–0.48
Rb	mg/kg	25	23	24	1.9	69	16	30	11	40	13	1.9	50.1	0.89	2.35	–0.20	1.02
Sb	mg/kg	0.36	0.28	0.27	0.005	1.3	0.18	0.51	0.091	0.70	0.27	0.041	76.3	1.67	3.58	–0.70	2.00
Sc	mg/kg	5.5	4.9	5.4	1.9	13	3.3	6.9	2.2	11	2.8	0.42	51.0	0.92	0.41	–0.05	–0.76
Sm	mg/kg	0.78	0.69	0.74	0.050	1.8	0.43	1.1	0.20	1.3	0.45	0.068	57.9	0.38	–0.69	–0.41	–0.41
Sn	mg/kg	9.5	3.9	2.7	0.36	58	1.6	13	0.90	27	13	1.9	135.6	1.96	3.84	0.19	–0.92
Sr	mg/kg	69	58	52	6.3	170	39	100	19	120	43	6.4	62.2	0.72	–0.14	–0.36	–0.17
Ta	mg/kg	0.18	0.12	0.17	0.050	0.57	0.050	0.30	0.050	0.39	0.14	0.021	76.2	0.83	–0.22	–0.20	–1.64
Tb	mg/kg	0.13	0.11	0.11	0.005	0.30	0.060	0.18	0.037	0.24	0.078	0.012	61.1	0.45	–0.76	–0.62	0.17
Ti	%	0.18	0.18	0.18	0.074	0.34	0.13	0.22	0.11	0.27	0.065	0.010	35.4	0.62	–0.07	0.43	–0.31
Tm	mg/kg	0.055	0.044	0.049	0.005	0.14	0.022	0.084	0.014	0.10	0.036	0.005	65.3	0.49	–0.75	–0.60	–0.27
V	mg/kg	81	74	75	27	190	59	93	45	120	36	5.0	44.3	1.34	2.28	–0.09	0.39
W	mg/kg	0.43	0.27	0.26	0.015	2.4	0.13	0.66	0.087	1.1	0.46	0.068	105.6	2.25	6.44	–0.31	0.73
Y	mg/kg	4.8	4.5	4.6	0.40	13	3.0	6.0	2.0	8.5	2.7	0.40	54.7	0.81	0.95	–0.15	0.43
Yb	mg/kg	0.35	0.27	0.32	0.026	0.91	0.14	0.52	0.088	0.65	0.23	0.034	66.4	0.56	–0.52	–0.64	–0.23
Zn	mg/kg	81	74	72	45	190	63	93	49	120	30	4.1	36.7	1.44	2.68	0.05	–0.58
Zr	mg/kg	43	32	30	4.0	120	19	59	10	96	34	5.1	80.4	1.21	0.45	0.07	–0.52

X – geometrical mean; $X_{(BC)}$ – geometrical mean with Box-Cox method; Md – median; Min – minimum; Max – maximum; P_{10} – percentile 10; P_{90} – percentile 90; P_{25} – percentile 25; P_{75} – percentile 75; S – standard deviation; S_X – standard error of mean; CV – coefficient of variation; A – skewness; E – kurtosis; $A_{(BC)}$ – skewness after Box-Cox transformation; $E_{(BC)}$ – kurtosis after Box-Cox transformation

Table 2

Descriptive statistics for the content of the elements in subsoil (20–30 cm), n=51

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	S_x	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	0.15	0.079	0.10	0.005	0.76	0.005	0.25	0.005	0.36	0.17	0.024	113.6	1.50	2.47	0.07	–1.34
Al	%	3.3	3.2	3.2	0.90	7.6	2.4	4.2	2.2	4.9	1.3	0.18	39.2	0.67	0.91	0.05	0.14
As	mg/kg	10	8.9	9.5	2.2	31	6.2	14	3.9	18	5.8	0.81	56.8	1.06	1.64	–0.04	–0.65
B	mg/kg	470	45	34	23	8100	26	120	24	850	1400	200	301.6	4.20	18.77	0.64	–1.13
Ba	mg/kg	1800	1200	1100	580	6300	860	2200	760	4400	1500	220	86.4	1.78	2.18	0.47	–0.90
Be	mg/kg	0.78	0.44	0.49	0.005	5.8	0.11	1.0	0.028	1.4	1.1	0.15	139.3	3.39	13.43	0.20	0.30
Bi	mg/kg	0.077	0.044	0.049	0.005	0.35	0.015	0.13	0.005	0.19	0.078	0.011	101.7	1.25	1.52	–0.03	–1.31
Br	mg/kg	1.2	1.1	1.1	0.005	3.0	0.64	1.7	0.33	2.4	0.76	0.11	64.2	0.61	–0.24	–0.32	0.05
Ca	%	1.9	1.2	1.4	0.097	5.6	0.56	3.2	0.24	4.6	1.6	0.23	87.4	0.92	–0.43	–0.20	–0.87
Cd	mg/kg	0.056	0.020	0.019	0.005	0.33	0.005	0.066	0.005	0.17	0.077	0.011	137.0	2.06	4.03	0.11	–1.52
Ce	mg/kg	8.8	7.6	7.7	1.8	44	4.4	11	3.0	15	6.6	0.94	75.3	3.25	16.30	0.59	1.63
Co	mg/kg	7.4	6.9	6.6	1.0	17	4.5	9.4	3.4	12	3.6	0.51	48.8	0.59	–0.15	0.02	–0.29
Cr	mg/kg	77	72	79	7.1	200	44	97	30	120	40	5.6	52.2	0.77	1.38	–0.09	0.18
Cs	mg/kg	1.3	1.0	0.98	0.027	12	0.70	1.3	0.43	2.2	1.7	0.23	124.6	5.50	34.92	0.54	5.44
Cu	mg/kg	22	21	21	6.1	45	15	29	12	37	9.5	1.3	42.4	0.63	–0.20	0.03	–0.43
Dy	mg/kg	0.63	0.51	0.41	0.11	2.0	0.30	0.98	0.20	1.4	0.49	0.069	77.7	1.17	0.29	0.45	–0.84
Er	mg/kg	0.33	0.25	0.21	0.057	1.0	0.14	0.53	0.091	0.76	0.27	0.038	82.5	1.16	0.13	0.46	–0.93
Eu	mg/kg	0.27	0.24	0.23	0.079	0.66	0.17	0.36	0.13	0.43	0.13	0.019	49.5	0.87	0.38	0.04	–0.63
Fe	%	3.0	2.9	2.9	1.3	5.7	2.3	3.5	2.0	3.8	0.86	0.12	29.1	0.78	1.65	0.07	0.49
Ga	mg/kg	6.0	5.8	5.5	1.9	13	4.3	7.7	3.3	8.9	2.3	0.33	38.4	0.66	0.35	0.18	–0.15
Gd	mg/kg	0.82	0.70	0.63	0.16	2.8	0.44	1.1	0.28	1.7	0.57	0.080	69.0	1.27	1.43	0.36	–0.55
Ge	mg/kg	0.12	0.088	0.087	0.045	0.57	0.066	0.14	0.059	0.21	0.10	0.014	82.2	3.20	11.71	–0.05	–0.57
Hf	mg/kg	0.46	0.26	0.22	0.033	1.8	0.11	0.82	0.070	1.3	0.49	0.070	106.3	1.34	0.83	0.17	–1.08
Ho	mg/kg	0.12	0.096	0.078	0.021	0.39	0.053	0.19	0.037	0.28	0.099	0.014	81.5	1.18	0.24	0.50	–0.87
In	µg/kg	11	8.8	11	5.0	24	5.0	16	5.0	21	6.3	0.89	57.9	0.56	–1.11	0.10	–1.77
K	%	1.4	1.3	1.3	0.62	3.3	1.1	1.7	0.94	2.1	0.49	0.069	34.5	1.32	2.92	–0.18	0.49
La	mg/kg	4.5	3.8	4.1	0.86	20	2.5	5.3	1.5	6.8	3.5	0.49	76.5	2.68	8.95	0.40	1.17
Li	mg/kg	20	19	19	3.5	50	13	26	9.5	37	9.9	1.4	48.3	0.92	0.67	0.22	0.03

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	S_x	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Lu	mg/kg	0.058	0.041	0.031	0.005	0.22	0.021	0.083	0.016	0.14	0.052	0.007	90.8	1.31	0.80	0.32	–0.81
Mg	%	0.83	0.75	0.70	0.19	2.0	0.49	1.1	0.39	1.4	0.42	0.059	50.9	0.74	–0.16	–0.05	–0.43
Mn	mg/kg	610	540	560	230	2400	410	720	280	930	340	48	56.2	3.20	15.44	0.16	0.63
Mo	mg/kg	0.73	0.44	0.32	0.005	3.5	0.21	1.0	0.005	1.9	0.79	0.11	108.6	1.49	2.04	–0.07	–0.57
Na	%	0.91	0.77	0.76	0.25	2.3	0.43	1.4	0.32	1.6	0.55	0.076	59.8	0.56	–0.89	0.01	–1.40
Nb	mg/kg	4.4	4.3	4.2	1.5	8.4	3.3	5.1	2.2	6.5	1.6	0.22	36.4	0.40	0.17	0.07	–0.04
Nd	mg/kg	3.4	3.1	2.8	0.74	10	2.1	4.6	1.1	5.9	1.9	0.28	57.3	0.96	1.28	0.18	–0.37
Ni	mg/kg	59	50	53	6.3	190	23	83	16	110	40	5.6	67.7	0.99	0.81	–0.08	–0.60
P	mg/kg	420	360	370	120	1300	260	500	200	670	250	34	58.2	1.74	3.14	0.14	0.03
Pb	mg/kg	31	28	28	12	95	21	34	18	44	15	2.0	47.6	2.44	8.05	0.59	1.42
Pr	mg/kg	0.91	0.83	0.80	0.20	2.6	0.52	1.2	0.31	1.5	0.50	0.071	55.4	0.91	1.35	0.12	–0.33
Rb	mg/kg	23	22	21	3.1	72	17	29	11	39	13	1.8	56.0	1.61	3.77	0.56	1.52
Sb	mg/kg	0.32	0.23	0.21	0.039	1.9	0.12	0.44	0.085	0.66	0.34	0.048	105.7	2.77	9.81	0.61	0.31
Sc	mg/kg	5.6	4.6	4.5	1.2	31	3.3	6.7	2.0	10	4.5	0.63	79.6	3.71	19.32	0.16	0.91
Sm	mg/kg	0.68	0.60	0.53	0.15	2.1	0.36	0.97	0.23	1.3	0.42	0.060	62.3	1.05	1.02	0.26	–0.56
Sn	mg/kg	5.8	2.6	2.0	0.083	36	1.6	4.8	0.82	17	8.2	1.2	141.4	2.17	4.35	–0.19	1.37
Sr	mg/kg	60	51	56	9.9	270	27	72	20	93	45	6.4	75.7	2.51	8.93	0.62	0.90
Ta	mg/kg	0.15	0.093	0.050	0.050	0.61	0.050	0.26	0.050	0.41	0.15	0.021	94.2	1.32	0.84	0.42	–1.57
Tb	mg/kg	0.11	0.094	0.081	0.021	0.36	0.057	0.17	0.038	0.24	0.083	0.012	73.0	1.17	0.57	0.44	–0.73
Ti	%	0.17	0.16	0.16	0.067	0.34	0.12	0.20	0.084	0.26	0.063	0.009	37.8	0.56	–0.07	0.35	–0.33
Tm	mg/kg	0.047	0.035	0.030	0.005	0.15	0.020	0.080	0.013	0.11	0.040	0.006	84.9	1.16	0.10	0.30	–0.71
V	mg/kg	84	76	74	28	200	60	94	48	130	38	5.4	45.8	1.40	2.11	0.08	0.31
W	mg/kg	0.34	0.22	0.17	0.041	1.3	0.11	0.45	0.085	0.82	0.32	0.045	95.5	1.52	1.85	0.23	–0.93
Y	mg/kg	4.2	4.0	3.6	1.1	10	2.7	5.5	2.0	6.6	2.0	0.28	47.1	0.72	0.20	0.24	–0.55
Yb	mg/kg	0.30	0.22	0.18	0.057	0.99	0.13	0.53	0.077	0.74	0.26	0.037	86.0	1.18	0.09	0.48	–0.98
Zn	mg/kg	78	72	75	41	210	59	88	50	110	29	4.0	36.8	2.26	8.49	–0.01	–0.00
Zr	mg/kg	36	28	31	4.6	140	16	41	8.0	89	29	4.1	80.7	1.55	2.46	0.06	–0.54

X – geometrical mean; $X_{(BC)}$ – geometrical mean with Box-Cox method; Md – median; Min – minimum; Max – maximum; P_{10} – percentile 10; P_{90} – percentile 90; P_{25} – percentile 25; P_{75} – percentile 75; S – standard deviation; S_X – standard error of mean; CV – coefficient of variation; A – skewness; E – kurtosis; $A_{(BC)}$) – skewness after Box-Cox transformation; $E_{(BC)}$) – kurtosis after Box-Cox transformation

T a b l e 3

Concentration ratios (FO) of the average contents of the elements (Box-Cox transformed) in topsoil vs. subsoil (T/S)

Element	Unit	Topsoil	Subsoil	FO(T/S)	T-test	Sign	F-ratio	Sign	R(T/S)	Sign
Ag	mg/kg	0.14	0.079	1.81	2.18	*	1.21	*	0.35	*
Al	%	2.8	3.2	0.89	-1.45	NS	1.10	NS	0.62	*
As	mg/kg	9.8	8.9	1.09	0.77	NS	1.03	NS	0.64	*
B	mg/kg	46	45	1.04	0.24	NS	1.07	NS	0.77	*
Ba	mg/kg	1100	1200	0.92	-0.87	NS	1.07	NS	0.7	*
Be	mg/kg	0.63	0.44	1.42	1.26	NS	1.05	NS	0.46	*
Bi	mg/kg	0.060	0.044	1.36	1.18	NS	1.01	NS	0.29	*
Br	mg/kg	1.3	1.1	1.21	1.20	NS	1.38	NS	0.37	*
Ca	%	1.2	1.2	0.93	-0.36	NS	1.15	NS	0.89	*
Cd	mg/kg	0.021	0.020	1.02	0.07	NS	1.08	NS	0.43	*
Ce	mg/kg	8.3	7.6	1.09	0.62	NS	1.27	NS	0.2	NS
Co	mg/kg	7.7	6.9	1.11	1.12	NS	1.41	NS	0.46	*
Cr	mg/kg	69	72	0.97	-0.31	NS	1.05	NS	0.92	*
Cs	mg/kg	1.1	1.0	1.10	0.48	NS	1.74	NS	0.81	*
Cu	mg/kg	21	21	1.00	0.03	NS	1.10	NS	0.97	*
Dy	mg/kg	0.59	0.51	1.17	0.97	NS	1.09	NS	0.23	NS
Er	mg/kg	0.30	0.25	1.18	1.02	NS	1.06	NS	0.22	NS
Eu	mg/kg	0.28	0.24	1.17	1.38	NS	1.42	NS	0.41	*
Fe	%	2.8	2.9	0.97	-0.49	NS	1.14	NS	0.92	*
Ga	mg/kg	6.6	5.8	1.13	1.53	NS	1.04	NS	0.22	NS
Gd	mg/kg	0.80	0.70	1.14	0.90	NS	1.13	NS	0.21	NS
Ge	mg/kg	0.088	0.088	1.00	0.00	NS	1.28	NS	0.18	NS
Hf	mg/kg	0.34	0.26	1.28	1.12	NS	1.22	NS	0.47	*
Ho	mg/kg	0.11	0.096	1.17	0.96	NS	1.11	NS	0.23	NS
In	µg/kg	10	8.8	1.15	1.12	NS	1.06	NS	0.21	NS
K	%	1.3	1.3	0.99	-0.18	NS	1.09	NS	0.91	*
La	mg/kg	4.2	3.8	1.11	0.74	NS	1.42	NS	0.19	NS
Li	mg/kg	18	19	0.95	-0.55	NS	1.03	NS	0.97	*
Lu	mg/kg	0.053	0.041	1.30	1.38	NS	1.25	NS	0.22	NS
Mg	%	0.72	0.75	0.96	-0.40	NS	1.11	NS	0.91	*
Mn	mg/kg	530	540	0.98	-0.18	NS	1.01	NS	0.91	*
Mo	mg/kg	0.57	0.44	1.28	0.98	NS	1.18	NS	0.56	*
Na	%	0.74	0.77	0.96	-0.31	NS	1.18	NS	0.86	*
Nb	mg/kg	4.7	4.3	1.11	1.31	NS	1.16	NS	0.46	*
Nd	mg/kg	3.5	3.1	1.14	1.03	NS	1.33	NS	0.24	NS
Ni	mg/kg	48	50	0.95	-0.32	NS	1.01	NS	0.98	*
P	mg/kg	420	360	1.17	1.63	NS	1.19	NS	0.91	*
Pb	mg/kg	30	28	1.05	0.58	NS	1.41	NS	0.67	*
Pr	mg/kg	0.94	0.83	1.13	0.99	NS	1.36	NS	0.24	NS
Rb	mg/kg	23	22	1.07	0.64	NS	1.03	NS	0.53	*
Sb	mg/kg	0.28	0.23	1.21	1.06	NS	1.02	NS	0.56	*
Sc	mg/kg	4.9	4.6	1.06	0.51	NS	1.47	NS	0.47	*

Element	Unit	Topsoil	Subsoil	FO(T/S)	T-test	Sign	F-ratio	Sign	R(T/S)	Sign
Sm	mg/kg	0.69	0.60	1.14	0.99	NS	1.24	NS	0.21	NS
Sn	mg/kg	3.9	2.6	1.48	1.51	NS	1.09	NS	-0.16	NS
Sr	mg/kg	58	51	1.15	0.98	NS	1.20	NS	0.54	*
Ta	mg/kg	0.12	0.093	1.27	1.47	NS	1.07	NS	0.24	NS
Tb	mg/kg	0.11	0.094	1.14	0.88	NS	1.15	NS	0.21	NS
Ti	%	0.18	0.16	1.11	1.37	NS	1.02	NS	0.38	*
Tm	mg/kg	0.044	0.035	1.23	1.20	NS	1.02	NS	0.18	NS
V	mg/kg	74	76	0.97	-0.30	NS	1.01	NS	0.94	*
W	mg/kg	0.27	0.22	1.22	1.02	NS	1.20	NS	0.36	*
Y	mg/kg	4.5	4.0	1.12	1.00	NS	1.71	NS	0.49	*
Yb	mg/kg	0.27	0.22	1.20	1.06	NS	1.08	NS	0.2	NS
Zn	mg/kg	74	72	1.03	0.45	NS	1.07	NS	0.89	*
Zr	mg/kg	32	28	1.17	0.92	NS	1.07	NS	0.71	*

Comparing the median values of the soils from the Kumanovo region with those of European soils (Table 4), it was noted that the contents of some elements (Ba, Ca, Cr, Cu, Mg, Ni, and V), which are characterized by increased values in the soils of the Vardar zone (Stafilov & Šajn, 2016; Petrušev et al., 2021), are higher in the soils of the Kumanovo region than in European soils (Salminen et al., 2005), while the content of many trace elements (Cd, Ga, Ge, Hf, In, Nb, Sb, Sc, Y, and Zr) and all rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb) is significantly lower in the soils of the Kumanovo region than in European soils.

It is important to note that, with the exception of Ba, the median value for all elements included in the New Dutch List, such as As, Cd, Co, Cr, Cu, Pb, Mo, Ni, and Zn (http://www.contaminatedland.co.uk), is lower than the action values, while some of these elements (As, Be, Cr, Cu, Ni, Pb, V, and Zn) exceed the target values in some sub-areas, mainly due to the lithogenic origin of these elements in soils from the Vardar tectonic zone (Stafilov & Šajn, 2016).

The degree of correlation between the concentrations of the chemical elements in the soil samples was evaluated using the Pearson correlation coefficient (r). Qualitatively, it was considered that the absolute values of r between 0.5 and 0.7 indicate a good association, which means that the coefficient of determination is in the range between 25% and 50%, and that when $r > 0.70$, there is a strong association between the elements due to the very similar distribution of the elements. The values for the content of each element were correlated with the values for the content of the other elements (Reimann et al., 2002). All correlation coefficients between all 17 elements for the elements determined by ICP-AES are listed in the matrix of correlation coefficients in Table 5. Due to the large number of variables (5 chemical elements analyzed), factor analysis was performed only for the 17 elements analyzed by ICP-AES. The matrix of correlation coefficients was constructed based on the previously standardized and Box-Cox transformed values (Box and Cox, 1964) of element contents in topsoil and subsoil. The Factor analysis considered data from 51 topsoil samples (0–5 cm) and 51 subsoil samples (20–30 cm). The matrix of rotated factor loadings is shown in Table 6. Five factors were identified – Factor 1 (Cr, Li, and Ni), F2 (B, Ba, and Na), F3 (Al, Ca, Mg, and P), F4 (K, and Pb), and F5 (Cu, Fe, Mn, V, and Zn), which are interpreted as factors F1–F5 and account for 82.3% of the total variability of the treated elements.

The dendrogram obtained by applying the cluster analysis to the data of the elements determined by ICP-AES is shown in Figure 4. In the dendrogram, the elements are divided into four subclusters according to their degree of correlation. The first sub-cluster includes the same elements included in Factor 3 of the factor analysis (Al, Ca, Mg, and P) (Table 6). The second sub-cluster consists of Cr, Ni, and Li, which are also included in Factor 1 of the factor analysis. The third sub-cluster consists of Cu, Zn, Mn, Fe, and V, which are included in Factor 5, the fourth sub-cluster includes B, Ba, and Na, which belong to Factor 2, and the fifth subcluster includes K, and Pb, which are included in Factor 4.

T a b l e 4

Comparison of the median, minimal and maximal values of the content of the analyzed elements in topsoil from the Kumanovo region with soils from North Macedonia and Europe

Element	Unit	The New Dutch list		Kumanovo region (this work)		North Macedonia (Stafilov & Šajn, 2019)		Europe (Salminen et al., 2005)	
		Target	Action	Md	Min–Max	Md	Min–Max	Md	Min–Max
Ag	mg/kg		15	0.16	0.005–0.87	–	–	0.27	0.01–3.15
Al	%			2.9	0.74–5.7	6.6	0.09–11	5.8	0.70–14.1
As	mg/kg	29	55	9.3	1.5–33	10	1.0–720	7.03	0.32–282
B	mg/kg			39	23–5000	–	–	–	–
Ba	mg/kg	200	625	1100	440–5500	430	6–2900	375	30–1870
Be	mg/kg	1.1	30	0.80	0.005–5.2	2.0	<1.0–8.0	<2.0	<2.0–18.4
Bi	mg/kg			0.085	0.005–0.53	0.3	<0.1–15	<0.5	<0.5–9.57
Br	mg/kg			1.3	0.005–4.3	–	–	–	–
Ca	%			1.1	0.16–6.5	1.3	0.05–35	0.66	0.019–34.3
Cd	mg/kg	0.8	12	0.023	0.005–0.25	0.30	0.01–110	0.145	<0.01–14.1
Ce	mg/kg			8.8	0.97–27	56	1.0–180	48.2	2.45–267
Co	mg/kg	20	240	7.3	2.8–20	17	0.50–150	7.78	<3.0–249
Cr	mg/kg	100	380	79	7.6–190	88	5.0–2700	60	<3.0–6230
Cs	mg/kg			1.1	0.005–20	–	–	3.71	<0.5–69.1
Cu	mg/kg	36	190	22	4.8–47	28	1.6–270	13.0	0.81–256
Dy	mg/kg			0.61	0.048–1.6	–	–	3.42	0.18–44.9
Er	mg/kg			0.31	0.023–0.91	–	–	1.98	0.12–26.0
Eu	mg/kg			0.28	0.059–0.73	–	–	0.77	0.05–6.99
Fe	%			2.9	1.2–5.7	3.5	0.03–12	2.45	0.11–15.6
Ga	mg/kg			6.9	3.1–12	–	–	13.5	0.54–34.3
Gd	mg/kg			0.83	0.073–2.3	–	–	3.85	0.20–36.0
Ge	mg/kg			0.084	0.053–0.45	–	–	–	–
Hf	mg/kg			0.35	0.025–2.2	1.0	<0.10–6.6	5.55	<0.2–21.2
Ho	mg/kg			0.12	0.005–0.32	–	–	0.68	0.03–9.16
In	µg/kg			13	5.0–27	–	–	50	<10–410
K	%			1.3	0.66–3.7	1.9	0.02–5.3	1.59	0.022–5.09
La	mg/kg			4.4	0.55–18	25	0.60–88	23.5	1.10–143
Li	mg/kg			18	1.7–45	26	1.8–210	–	–
Lu	mg/kg			0.063	0.005–0.36	–	–	0.30	<0.02–3.21
Mg	%			0.68	0.16–2.2	0.94	0.12–13	0.46	<0.006–14.8
Mn	mg/kg			550	170–2300	900	17–10000	503	31–6025
Mo	mg/kg	10	200	0.53	0.005–2.8	0.90	<0.10–51	0.62	<0.1–21.3
Na	%			0.77	0.25–2.0	1.3	0.013–6.0	0.59	0.03–3.30
Nb	mg/kg			4.6	0.99–8.8	11	0.30–2000	9.68	0.45–134
Nd	mg/kg			3.9	0.39–9.2	–	–	20.8	1.14–132
Ni	mg/kg	35	210	49	8.3–180	46	2.1–2500	18	<2–2690
P	mg/kg			400	130–1300	620	110–3900	720	62–7440
Pb	mg/kg	85	530	28	5.0–110	32	1.2–10000	22.6	5.32–970
Pr	mg/kg			1.0	0.11–2.5	–	–	5.6	0.29–31.6
Rb	mg/kg			24	1.9–69	86	0.7–390	80	<2.0–390
Sb	mg/kg			0.27	0.005–1.3	0.80	<0.10–630	0.60	0.02–31.1

Element	Unit	The New Dutch list		Kumanovo region (this work)		North Macedonia (Stafilov & Šajn, 2019)		Europe (Salminen et al., 2005)	
		Target	Action	Md	Min–Max	Md	Min–Max	Md	Min–Max
Sc	mg/kg			5.4	1.9–13	12	<1.0–39	8.21	<0.5–54.1
Sm	mg/kg			0.74	0.050–1.8	–	–	3.96	0.23–30.0
Sn	mg/kg		900	2.7	0.36–58	2.6	<0.10–680	3.00	<2.0–106
Sr	mg/kg			52	6.3–170	140	21–1400	89.0	8.0–3120
Ta	mg/kg			0.17	0.050–0.57	0.70	<0.10–30	0.68	<0.05–6.78
Tb	mg/kg			0.11	0.005–0.30	–	–	0.60	0.03–7.01
Ti	%			0.18	0.074–0.34	0.34	0.004–1.2	0.34	0.0126–3.27
Tm	mg/kg			0.049	0.005–0.14	–	–	0.30	0.05–4.03
V	mg/kg	42	250	75	27–190	89	1.0–470	60.4	2.71–537
W	mg/kg			0.26	0.015–2.4	1.3	0.20–18	<5.0	<5.0–14
Y	mg/kg			4.6	0.40–13	18	0.30–110	21	<3.0–267
Yb	mg/kg			0.32	0.026–0.91	–	–	1.99	0.09–25
Zn	mg/kg	140	720	72	45–190	83	8.0–10000	52	<3–2900
Zr	mg/kg			30	4.0–120	35	0.80–210	231	5.0–1060

Md – median; Min – minimum; Max – maximum

T a b l e 5

Pearson correlation coefficients between element contents in soils from the Kumanovo region, n = 102 (2×51), group of 17 elements determined by ICP-AES. Values in the range of 0.5–0.7 (good association) are underlined and in the range of 0.7–1.0 (strong association) are bolded. Box-Cox transformed values used.

Element	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	V	Zn
Al	1.00																
B	0.12	1.00															
Ba	0.01	0.49	1.00														
Ca	0.75	0.03	-0.08	1.00													
Cr	0.40	0.03	0.06	0.29	1.00												
Cu	0.36	0.14	0.28	0.13	0.60	1.00											
Fe	0.61	0.08	-0.03	0.37	0.61	**0.70**	1.00										
K	-0.27	-0.02	0.46	-0.36	-0.43	-0.14	-0.40	1.00									
Li	0.18	0.00	0.29	0.03	0.50	0.55	0.20	0.11	1.00								
Mg	**0.79**	0.03	-0.01	0.66	0.68	0.51	0.69	-0.39	0.23	1.00							
Mn	0.53	0.08	0.10	0.37	0.61	**0.71**	**0.75**	-0.24	0.34	0.65	1.00						
Na	0.12	0.69	0.58	-0.09	-0.12	0.06	0.04	0.24	-0.17	0.00	0.02	1.00					
Ni	0.35	-0.09	-0.02	0.32	**0.93**	0.49	0.45	-0.39	0.54	0.65	0.54	-0.29	1.00				
P	0.42	0.15	0.05	0.48	0.00	0.13	0.34	0.08	-0.20	0.39	0.40	0.14	-0.06	1.00			
Pb	-0.01	0.06	0.28	-0.04	-0.11	0.04	0.09	0.49	0.04	-0.02	0.12	0.13	-0.07	0.19	1.00		
V	0.46	0.16	-0.03	0.26	0.46	0.65	**0.92**	-0.45	0.06	0.54	0.60	0.11	0.28	0.27	-0.01	1.00	
Zn	0.32	0.02	0.23	0.06	0.41	**0.71**	**0.72**	0.02	0.31	0.37	0.61	0.05	0.30	0.30	0.32	0.62	1.00

T a b l e 6

Matrix of rotated factor loadings, n = 102 (2×51), 17 selected elements determined by ICP-AES. Box-Cox transformation used

Element	F1	F2	F3	F4	F5	Comm
Cr	**0.74**	–0.02	0.25	–0.28	0.42	86.3
Li	**0.85**	0.01	–0.06	0.19	0.11	77.9
Ni	**0.81**	–0.17	0.27	–0.22	0.24	87.1
B	–0.04	**0.89**	0.07	–0.10	0.07	80.4
Ba	0.29	**0.73**	–0.06	0.45	0.00	82.0
Na	–0.20	**0.89**	0.03	0.10	0.07	85.2
Al	0.17	0.10	**0.81**	–0.08	0.29	79.2
Ca	0.09	–0.05	**0.91**	–0.13	0.01	85.9
Mg	0.37	0.00	**0.74**	–0.16	0.40	86.5
P	–0.33	0.07	**0.67**	0.30	0.27	72.1
K	–0.05	0.15	–0.21	**0.85**	–0.26	86.1
Pb	–0.05	0.02	0.05	**0.78**	0.16	63.6
Cu	0.49	0.15	0.06	0.05	**0.74**	82.3
Fe	0.15	0.00	0.35	–0.12	**0.88**	94.3
Mn	0.34	0.02	0.41	0.06	**0.68**	74.4
V	–0.02	0.09	0.20	–0.25	**0.89**	90.8
Zn	0.19	0.01	0.05	0.32	**0.84**	84.1
Prp.Totl	16.3	13.0	17.7	12.0	23.3	82.3
EigenVal	6.32	2.72	2.08	1.51	1.36	
Expl.Var	2.77	2.21	3.01	2.04	3.95	

F1, F2, F3, F4, and F5 – factor loadings of Factors 1, 2, 3, 4, and 5; Comm – communality (%);
Prp.Totl – total amount of the explained system variance; Expl.Var – particular component variance; EigenVal – Eingene value

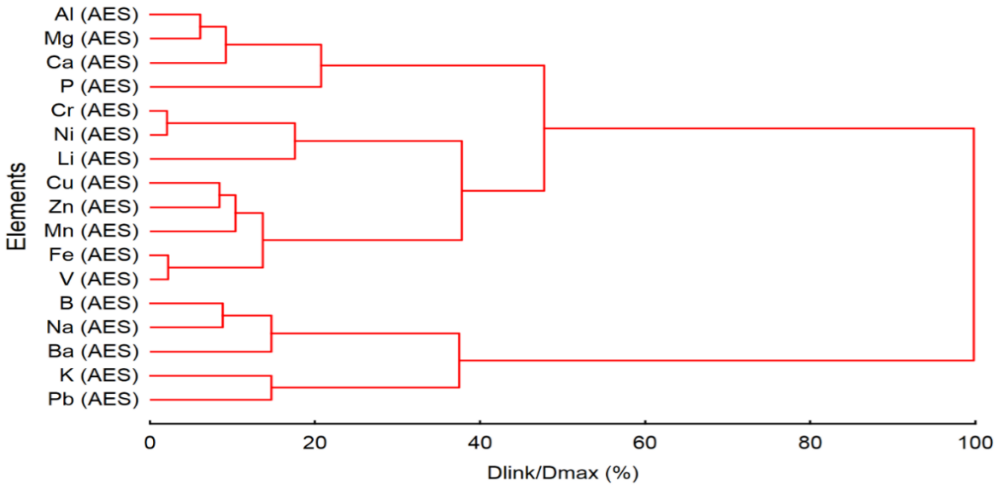


Fig. 4. Dendrogram from the cluster analysis of the results for the elements determined by ICP-AES

Pearson correlation coefficients between element contents in soils from the Kumanovo region determined by ICP-MS as a group of 23 elements and 12 rare earth elements (REEs) as a group are presented in Table 7. Bivariate statistics was also applied for REEs determined by ICP-MS. The matrix of correlation coefficients is presented in Table 8, where the correlation is shown for the content of the following 14 REEs: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb. It is obvious that the correlation coefficients for all REEs are very high ranging from 0.72 to 0.99.

Table 7

Pearson correlation coefficients between element contents in soils from the Kumanovo region, n = 102 (2×1), group of 23 elements and 12 REEs as one group determined by ICP-MS. Values in the range of 0.5–0.7 (good association) are underlined and in the range of 0.7–1.0 (strong association) are bolded. Box-Cox transformed values used.

Element	Ag	As	Be	Bi	Br	Cd	Co	Cs	Ga	Ge	Hf	In	Mo	Nb	Rb	Sb	Sc	Sn	Sr	Ta	Ti	W	Y	Zr	REEs
Ag	1.00																								
As	0.28	1.00																							
Be	0.60	0.31	1.00																						
Bi	0.54	0.46	**0.86**	1.00																					
Br	0.03	0.62	0.10	0.22	1.00																				
Cd	0.59	0.31	0.46	0.48	0.06	1.00																			
Co	0.54	0.47	0.41	0.57	0.27	0.47	1.00																		
Cs	0.57	0.40	0.68	0.52	0.17	0.42	0.30	1.00																	
Ga	0.64	0.39	**0.81**	**0.81**	0.18	0.54	0.61	0.56	1.00																
Ge	0.17	0.25	0.39	0.44	0.30	0.23	0.32	0.11	0.35	1.00															
Hf	0.65	0.44	**0.70**	**0.71**	0.25	**0.75**	0.59	0.53	**0.76**	0.28	1.00														
In	0.57	0.47	0.60	0.69	0.24	0.49	0.69	0.46	**0.82**	0.28	0.63	1.00													
Mo	0.18	-0.21	0.09	-0.02	-0.04	0.38	-0.05	0.08	0.00	0.20	0.26	-0.03	1.00												
Nb	**0.73**	0.30	**0.79**	0.64	0.17	0.51	0.38	**0.70**	**0.77**	0.26	0.67	0.65	0.17	1.00											
Rb	0.51	0.28	**0.73**	0.50	0.07	0.34	0.10	**0.83**	0.62	0.17	0.45	0.45	0.11	**0.76**	1.00										
Sb	0.55	0.45	0.47	0.51	0.18	0.54	0.57	0.48	0.51	0.19	0.68	0.51	0.31	0.54	0.40	1.00									
Sc	0.12	0.49	0.17	0.39	0.60	0.18	0.69	0.01	0.42	0.33	0.37	0.47	-0.15	0.11	-0.12	0.32	1.00								
Sn	0.29	0.11	0.54	0.62	0.28	0.15	0.32	0.22	0.36	0.53	0.29	0.25	0.20	0.40	0.19	0.33	0.30	1.00							
Sr	0.30	0.32	0.52	0.51	0.51	0.39	0.25	0.41	0.53	0.25	0.66	0.39	0.28	0.45	0.39	0.29	0.36	0.34	1.00						
Ta	0.61	0.46	**0.80**	**0.83**	0.13	0.59	0.56	0.55	**0.88**	0.24	**0.76**	**0.78**	-0.04	**0.71**	0.57	0.53	0.34	0.28	0.47	1.00					
Ti	0.55	0.41	0.53	0.64	0.29	0.48	**0.79**	0.28	**0.79**	0.41	0.61	**0.77**	-0.04	0.53	0.21	0.37	0.63	0.33	0.38	0.69	1.00				
W	0.63	0.48	**0.84**	**0.81**	0.07	0.52	0.48	**0.74**	**0.83**	0.19	**0.72**	**0.70**	-0.09	**0.75**	**0.71**	0.57	0.20	0.28	0.41	**0.86**	0.57	1.00			
Y	0.30	0.52	0.41	0.57	0.60	0.23	0.54	0.29	0.54	0.38	0.39	0.64	-0.08	0.45	0.28	0.31	0.68	0.47	0.47	0.52	0.65	0.38	1.00		
Zr	0.57	0.29	0.46	0.39	0.31	0.69	0.45	0.42	0.47	0.25	**0.87**	0.37	0.49	0.57	0.30	0.63	0.28	0.28	0.64	0.42	0.39	0.38	0.26	1.00	
REEs	0.53	0.62	0.69	**0.80**	0.42	0.47	0.66	0.54	**0.82**	0.31	**0.70**	**0.80**	-0.13	0.63	0.53	0.48	0.61	0.35	0.59	**0.83**	**0.75**	**0.75**	**0.83**	0.41	1.00

T a b l e 8

Pearson correlation coefficients between rare earth elements (REEs) contents in soils from the Kumanovo region, n = 102 (2×51). Values in the range of 0.7–1.0 (strong association) are bolded. Box-Cox transformed values are used.

Element	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Yb
Ce	1.00													
Dy	**0.84**	1.00												
Er	**0.82**	**1.00**	1.00											
Eu	**0.72**	**0.76**	**0.76**	1.00										
Gd	**0.91**	**0.98**	**0.97**	**0.78**	1.00									
Ho	**0.82**	**1.00**	**1.00**	**0.76**	**0.98**	1.00								
La	**0.95**	**0.80**	**0.78**	**0.72**	**0.87**	**0.78**	1.00							
Lu	**0.77**	**0.91**	**0.92**	**0.87**	**0.89**	**0.91**	**0.74**	1.00						
Nd	**0.97**	**0.92**	**0.90**	**0.76**	**0.97**	**0.90**	**0.94**	**0.82**	1.00					
Pr	**0.98**	**0.89**	**0.87**	**0.75**	**0.95**	**0.87**	**0.96**	**0.80**	**1.00**	1.00				
Sm	**0.94**	**0.96**	**0.95**	**0.78**	**0.99**	**0.95**	**0.90**	**0.87**	**0.99**	**0.97**	1.00			
Tb	**0.88**	**1.00**	**0.99**	**0.77**	**0.99**	**0.99**	**0.83**	**0.90**	**0.94**	**0.92**	**0.98**	1.00		
Tm	**0.82**	**0.99**	**0.99**	**0.78**	**0.96**	**0.99**	**0.78**	**0.95**	**0.89**	**0.86**	**0.94**	**0.98**	1.00	
Yb	**0.82**	**0.99**	**0.99**	**0.78**	**0.96**	**0.99**	**0.78**	**0.95**	**0.89**	**0.86**	**0.94**	**0.98**	**0.99**	1.00

The dendrogram from the cluster analysis of the results for the elements determined by ICP-AES and ICP-MS is shown in Figure 5. It was found that some of the trace elements determined by ICP-MS are contained in sub-clusters formed by the elements determined by ICP-AES. This is the case of As and Br, which together with Al, Mg, Ca, and P are contained in the sub-cluster corresponding to Factor 3. It can be seen that the macroelements determined by ICP-AES (which include the trace elements As, Br, and Mo) from one of the two main clusters. The second main cluster in the dendrogram includes all other trace elements determined by ICP-MS. They are divided into several distinct sub-clusters. Thus, the first sub-cluster with Ag, Pt, Be, Bi, Ga, Ta, and W, and the second with Cs, Rb, and Nb form a sub-cluster that is included in another sub-cluster together with the third core sub-cluster of Cd, Hf, Zr, Sb, and Sr. The next sub-cluster includes the remaining macroelements with two sub-sub-clusters, one with Co, Ti, In, Sc, Y and all analyzed RREs, and the second with Ge, and Sn.

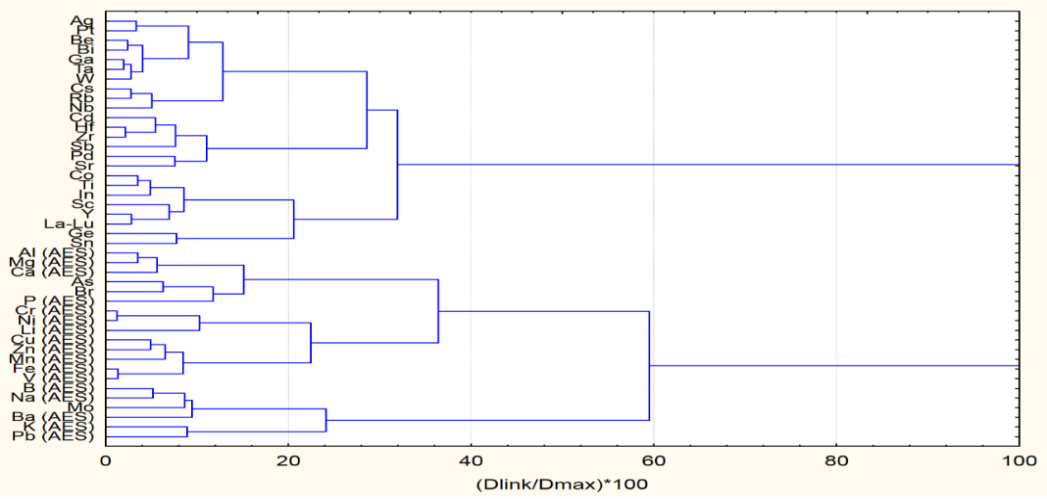


Fig. 5. Dendrogram from the cluster analysis of the results for the elements determined by ICP-AES and ICP-MS

Factor 1 (F1) includes Cr, Li, and Ni, and accounts for 16.3% of the total variability. This group represents chemical elements that are likely to be naturally distributed. The spatial distribution of the factor scores of F1 and the spatial distribution of the elements from this factor association are shown in Figure 6. High contents of the elements of the F1 association are typical for the northwestern part (with dominant Precambrian and Mesozoic carbonates) and the southwestern and central parts of the study area with the dominant occurrence of Tertiary sediments along the Kumanovska and Pčinja rivers. It should be emphasized that the high content of chromium and nickel in the soil samples from the central part of the study area, especially along the river of Tabanovska Reka, is also due to the emission of particles enriched with these elements originating from the flotation tailings dump near the village of Lojane (UNDP, 2007; Alderton et al., 2014; Đorđević et al., 2019). Higher concentrations of these elements are also found in the samples in the area of the town of Kumanovo, which is due to industrial and urban activities. The lowest contents of these elements were found in soil samples from the northeastern part of the area (upper reaches of the Pčinja river), where volcanic and magmatic rocks, as well as Precambrian gneisses and old granites are predominated.

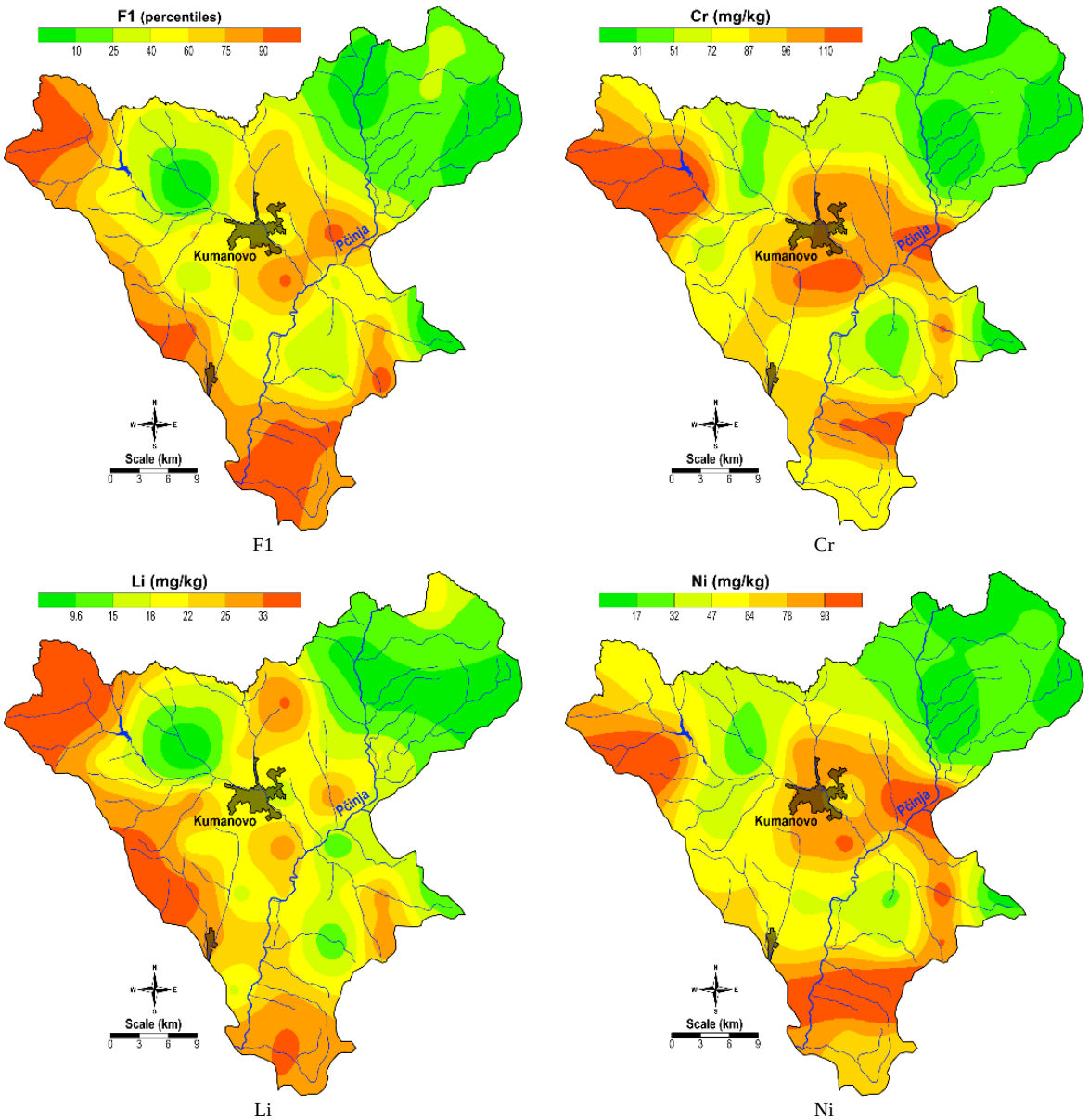


Fig. 6. Spatial distribution of factor values and the content of the elements from the Factor 1 (Cr, Li, and Ni) – ICP-AES analytical method

The maps of spatial distribution of the factor scores of the factor F2 and the maps of spatial distribution of elements of this factor (B, Ba, and Na), presented in Figure 7, show that these elements are present in higher contents in soils in the northwestern part of the study area and in the northeastern part of the area (upper reaches of the Pčinja river), where volcanic and magmatic rocks as well as Precambrian gneisses and old granites predominate. The lower content of these elements was found in the central part of the study area where Tertiary sediments predominate.

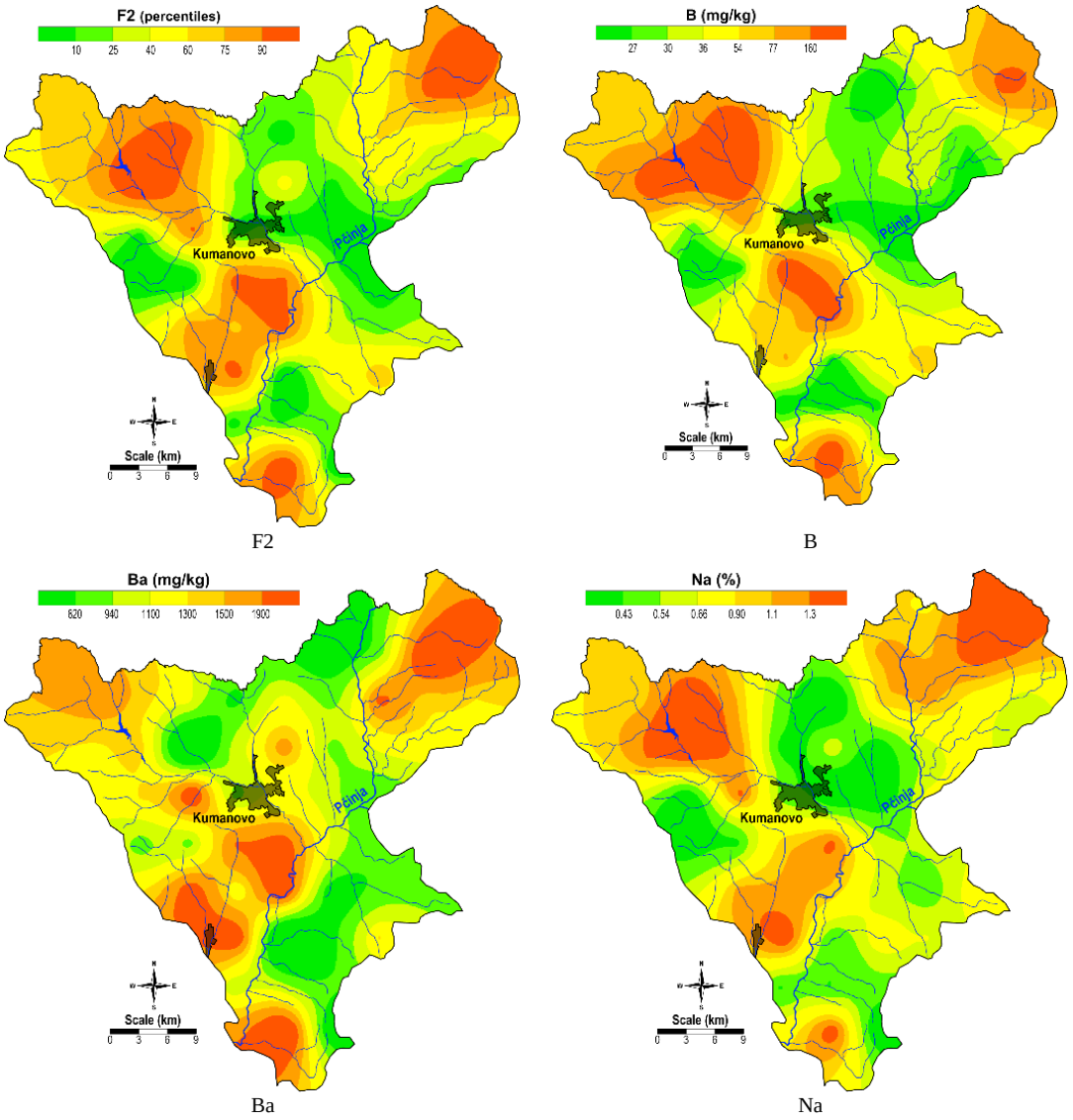


Fig. 7. Spatial distribution of factor values and the content of the elements from the Factor 2 (B, Ba, and Na) – ICP-AES analytical method

Factor 3 includes Al, Ca, Mg, and P. Soil samples from the central part of the study area, where Tertiary sediments predominate (Figure 8), have the highest contents of these elements. The contents of these elements along the Pčinja, Tabanovska, and Kumanovska rivers are significantly high, indicating the transport of materials and their deposition in the sedimentary material of the study area. The increased contents of Al and Mg are also characteristic for part of the soils from the northwestern part of the study area, where the contents of Cr and Ni in the soil are also high, indicating a similar origin and geological substrate with these elements.

From the dendrogram shown in Figure 5, it is evident that As and Br are included in a subcluster together with Al, Mg, Ca, and P, which corresponds

to a Factor 3. This is also confirmed by the similarity of the distribution of the contents of these elements (Figure 9). It should be added that elevated arsenic contents are also observed in the north-central part of the study area, due to pollution from the transport of arsenic-bearing minerals and concentrates from the abandoned flotation dump and concentrates from an As-Sb-Cr mine near the village of Lojane (UNDP, 2007; Alderton et al. 2014; Đorđević et al., 2019).

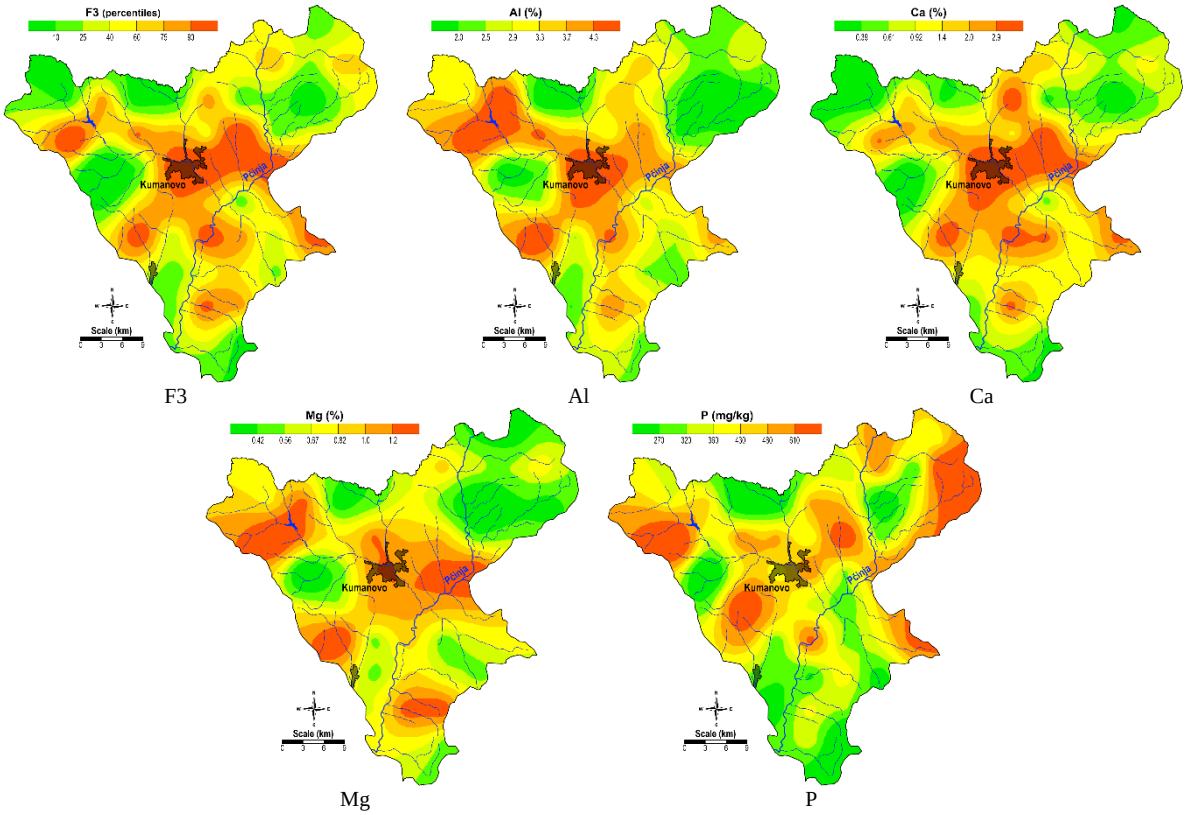


Fig. 8. Spatial distribution of factor values and the content of the elements from the Factor 3 (Al, Ca, Mg, and P) – ICP-AES analytical method

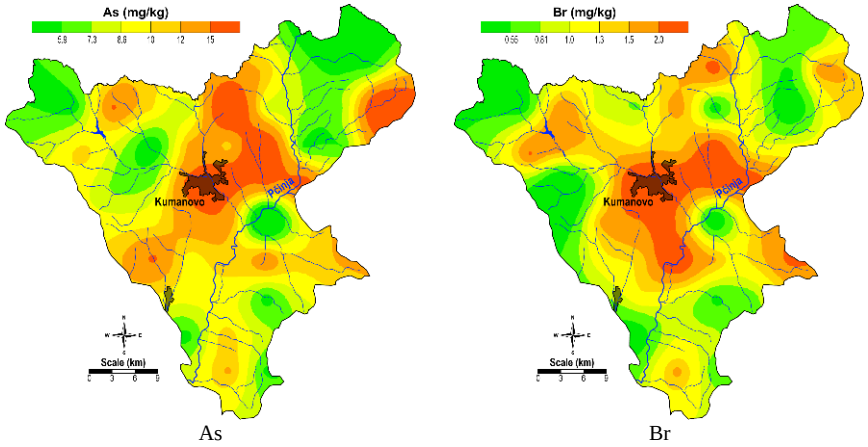
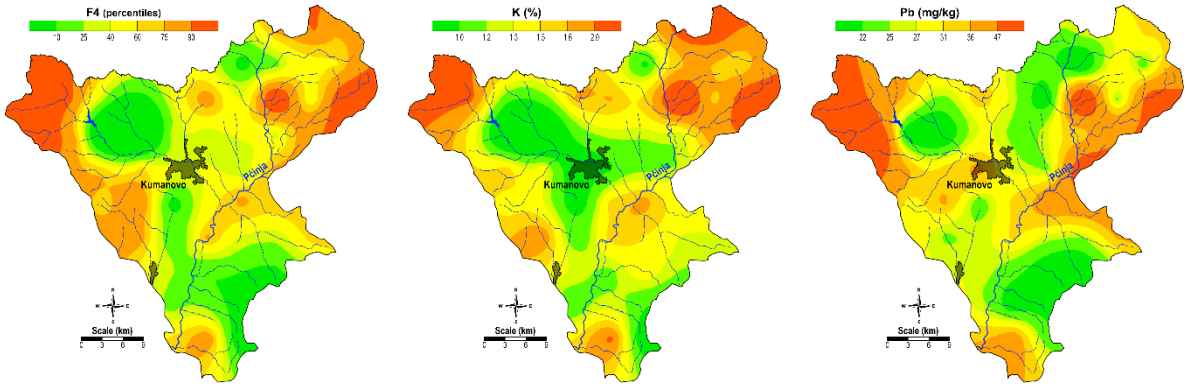


Fig. 9. Spatial distribution of the contents of As and Br determined by ICP-MS included in sub-clusters which correspond to Factor 3

The maps of spatial distribution of factor scores of Factor 4 and elements of this factor (K and Pb) (Figure 10) show that these elements are present in higher contents in the moss samples from the mountainous areas of the study area, such as Skopska Crna Gora mountains (with the predominant

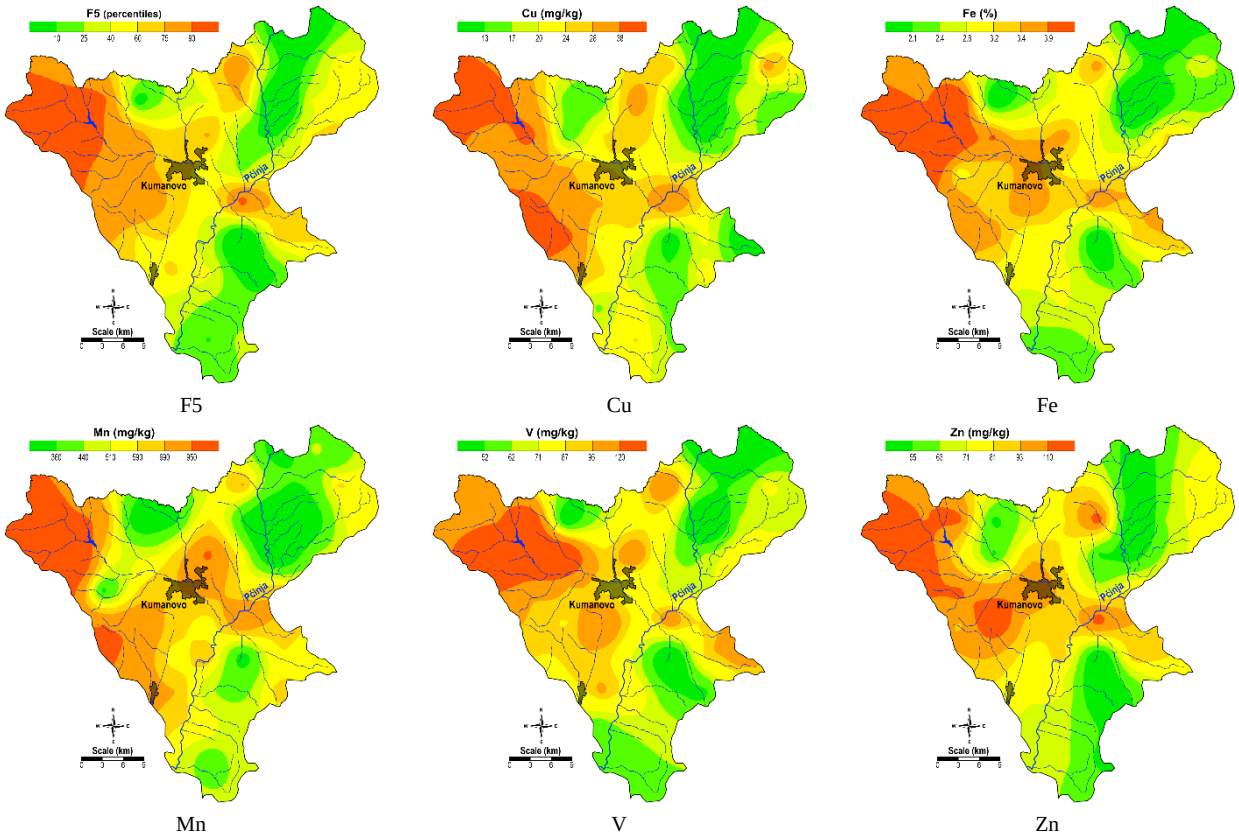
Precambrian and Paleozoic schists) in the west, and Mt. Kozjak in the northwest (with also predominant volcanic and magmatic rocks and Precambrian and Paleozoic schists). Some increase in lead content is also observed in Quaternary sediments of the Pčinja river after the mouth of the Kriva Reka river, whose waters and sediments are contaminated with Pb due to the operation of the "Toranica" mine and flotation near the town of Kriva Palanka (Stafilov et al., 2018b).



F4 K Pb

Fig. 10. Spatial distribution of factor values and the content of the elements from the Factor 4 (K and Pb) – ICP-AES analytical method

Factor 5 (F5) includes Cu, Fe, Mn, V, and Zn. The distribution maps of the factor scores of F5 and the individual elements of F5 are shown in Figure 11. Elevated contents of these elements are observed mainly in the soils of the northwestern part of the study area (Skopska Crna Gora mountains), where Precambrian and Paleozoic rocks predominate.



F5 Cu Fe

Mn V Zn

Fig. 11. Spatial distribution of factor values and the content of the elements from the Factor 5 (Cu, Fe, Mn, V, and Zn) – ICP-AES analytical method

CONCLUSION

A study was conducted on the distribution of 5 chemical elements in soil samples from the Kumanovo region, North Macedonia. The soil samples collected from 51 locations were analyzed by two spectroscopic techniques: inductively coupled plasma – atomic emission spectrometry (ICP-AES) for major elements, and inductively coupled plasma – mass spectrometry (ICP-MS) for trace elements. Cluster and R-mode factor analyses were used to identify and characterize element associations, and five associations of macroelements were determned using the multivariate statistics method. The spatial distribution of the content of the elements showed that the distribution of the elements was mainly due to the geogenic origin. The higher content of some potentially toxic elements (As, Pb) in certain parts of the subareas is due to the current and past mining activities and urban activities in the region.

Acknowledgement: Data processing partially supported by the Slovenian research Agency under the research program Groundwater and Geochemistry (P1-0020)

REFERENCES

Acton, Q. A. (2013): *Issue in Environmental Health and Pollution*. Scholarly Editions: Atlanta, Georgia.

Alderton, D., Serafimovski, T., Burns, L., Tasev, G. (2014): Distribution and mobility of arsenic and antimony at mine sites in FYR Macedonia. *Carpathian Journal Earth and Environmental Sciences*, **9**, 43–56.

Bačeva, K., Stafilov, T., Šajn, R., Tănăselia, C. (2012): Moss biomonitoring of air pollution with heavy metals in the vicinity of a ferronickel smelter plant. *Journal of Environmental Sciemce and Health, Part A*, **47**, 645–656.

Bačeva, K., Stafilov, T., Šajn, R., Tănăselia, C., Makreski, P. (2014): Distribution of chemical elements in soils and stream sediments in the area of abandoned Sb-As-Tl Allchar mine, Republic of Macedonia. *Environmental Research*, **133**, 77–89.

Bačvarovski, D., Šajn, R., Stafilov, T. (2021): Distribution of chemical elements in sediments and alluvium soils from the Pčinja river basin, North Macedonia. *Geologica Macedonica*, **35** (2), 95–113.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2010): Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *Journal of Environmental Sciemce and Health, Part A*, **45**, 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2013): Spatial distribution and characterization of some toxic metals and lithogenic elements in topsoil and subsoil from copper mine environs, *International Journal of Environmental Protection*, **3** (9), 1–9.

Barandovski, L., Cekova, M., Frontasyeva, M. V., Pavlov, S. S., Stafilov, T., Steinnes, E., Urumov, V. (2008): Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. *Environmental Monitoring and Assessment*, **138**, 107–118.

Barandovski, L., Frontasyeva, M. V., Stafilov, T., Šajn, R., Pavlov, S., Enimiteva, V. (2012): Trends of atmospheric deposition of trace elements in Macedonia studied by the moss biomonitoring technique. *Journal of Environmental Science and Health, Part A*, **47**, 2000–2015.

Barandovski, L., Frontasyeva, M. V., Stafilov, T., Šajn, R., Ostrovnaya, T. (2015): Multi-element atmospheric deposition in Macedonia studied by the moss biomonitoring technique. *Environmental Science and Pollution Research*, **22**, 16077–16097.

Barandovski, L., Stafilov, T., Šajn, R., Frontasyeva, M. V., Bačeva Andonovska, K. (2020): Atmospheric heavy metal deposition in North Macedonia from 2002 to 2010 studied by the moss biomonitoring technique. *Atmosphere*, **11**, 929.

Box, G. E. P., Cox, D. R. (1964): An analysis of transformations. *Journal of the Royal Statistical Society, Series B (Methodological)*, **26**, 211–243.

Chao T. T., Sanzolone, R. F. (1992): Decomposition techniques. *Journal of Geochemical Exploration*, **44**, 65–106.

Davis, J. C. (1986): *Statistic and Data Analysis in Geology*. Wiley, New York.

Đorđević, T., Kolitsch, U., Serafimovski, T., Tasev, G., Tepe, N., Stöger-Pollach, M., Hofmann, T., Boev, B. (2019): Mineralogy and weathering of realgar-rich tailings at a former As-Sb-Cr mine at Lojane, North Macedonia. *The Canadian Mineralogist*, **57**, 403–423.

Filipovski, G., Andreevski, M., Wasilevski, K., Milevski, I., Markoski, M., Mitkova T., Mitrikeski, J., Mukaetov, D., Petkovski, D. (2015). *Pedological (Soil) Map*. Institute of Agriculture, Ss. Cyril and Methodius University: Skopje.

Garson, D. (2000): *Factor analysis. PA 765: Quantitative Research in Public Administration*. North Carolina State University, Raleigh, 20, 8763–8779.

Hu, Z., Qi, L. (2014): Sample Digestion Methods. Volume **15** (5), In: Holland, H. D., Turekian, K. K. (Eds.). *Treatise on Geochemistry*, Second Edition, Elsevier Ltd., Amsterdam, p. 87–109.

Jarvis, K. E. (1990): A critical evaluation of two sample preparation techniques for low-level determination of some geologically incompatible elements by inductively coupled plasma – mass spectrometry. *Chemical Geology*, **83**, 89–103.

Jeftimova, M., Stafilov, T., Šajn, R., Bačeva Andonovska, K., Karadjova, I. (2016): Spatial distribution of chemical elements in soil samples in the Veles region, Republic of Macedonia, *Geologica Macedonica*, **30** (2), 103–114.

Jenner, G. A., Longerich, H. P., Jackson, S. E., Fryer, B. J. (1990): ICP-MS – A powerful tool for high-precision trace-element analysis in earth sciences: Evidence from analysis of selected U.S.G.S. reference samples. *Chemical Geology*, **83**, 133–148.

Jiménez-Ballesta, R., García-Navarro, F. J., Bravo, S., Amoros, J. A., Pérez-De-Los-Reyes, C., Mejias, M. (2017): Environmental assessment of potential toxic elements contents in the inundated floodplain área of Tablas de Daimiel Wetland (Spain). *Environmental Geochemistry and Health*, **39**, 1159–1177.

Johnson, W. M., Maxwell, J. A. (1981): *Rock and Mineral Analysis*. 2nd ed., Wiley, New York, p. 489.

Kabata-Pendias, A., Mukherjee, A. B. (2007): *Trace Elements from Soil to Human*. Springer, Heidelberg.

Lazarevska, M., Markoski, B. (2019): Chronology of the urban expansion of Kumanovo, *International Scientific Conference „GEOBALCANICA 2019*, 13–-14 June 2019, Sofia, Bulgaria, *Proceedings*, pp. 573–589.

Lourenço, R. W., Barbosa Landim, P. M., Rosa, A. H., Roveda, J. A. F., Martins, A. C. G., Fraceto, L. F. (2010). Mapping soil pollution by spatial analysis and fuzzy classification. *Environmental Earth Sciences*, **60**, 495–504.

Pančevski, Z., Stafilov, T., Bačeva, K. (2014): Distribution of heavy metals in some vegetables grown in the vicinity of lead and zinc smelter plant. *Contribution, Section of Natural, Mathematical and Biotechnical Sciences, Macedonian Academy of Sciences and Arts*, **35** (1), 25–36.

Pančevski, Z., Stafilov, T., Bačeva, K. (2016): Distribution of heavy metals in the garden soil and vegetables grown in the vicinity of lead and zinc smelter plant. *Journal of Scientific and Engineering Research*, **3** (3), 94–104.

Petrušev, E., Stolić, N., Šajn, R., Stafilov, T. (2021): Geological characteristics of the Republic of North Macedonia. *Geologica Macedonica*, **35** (1), 49–58.

Reimann, C., Filzmoser, P., Garrett, R. G. (2002): Factor analysis applied to regional geochemical data: problems and possibilities. *Applied Geochemistry*, **17**, 185–206.

Salminen, R., Batista, M. J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., KleinP., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P. J., Olsson, S. Å., Ottesen, R. T., Petersell, V., Plant, J. A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. (2005): *Geochemical Atlas of Europe*, Part 1*: Background Information, Methodology and Maps*, Geological Survey of Finland, Espoo.

Salomons, W., Förstner, U., Mader, P. (2012): *Heavy Metals: Problems and Solutions*. Springer Science & Business Media, Heidelberg.

Stafilov, T., Šajn, R., Pančevski, Z., Boev, B., Frontasyeva, M. V., Strelkova, L. P. (2010a): Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia. *Journal of Hazardous Materials*, 175, 896–914.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., Lepitkova, S. (2010b): Distribution of some elements in surface soil over the Kavadarci region, Republic of Macedonia. *Environmental Earth Sciences*, **61**, 1515–1530.

Stafilov, T., Šajn, R. (2016): *Geochemical Atlas of the Republic of Macedonia*. Faculty of Natural Sciences and Mathematics, Skopje.

Stafilov, T., Šajn, R., Ahmeti, L. (2017*): Geochemical Atlas of Skopje*. Faculty of Natural Sciences and Mathematics, Skopje.

Stafilov, T., Šajn, R., Arapčeska, M., Kungulovski, I., Alijagić, J. (2018a): Geochemical properties of topsoil around the coal mine and thermoelectric power plant. *Journal of Environmental Science and Health, Part A*, **53**, 793–808.

Stafilov, T.; Šajn, R.; Barandovski, L.; Bačeva Andonovska, K.; Malinovska, S. (2018b). Moss biomonitoring of atmospheric deposition study of minor and trace elements in Macedonia. *Air Quality, Atmosphere & Health*, **11**, 137–152.

Stafilov, T., Šajn, R. (2019): Spatial distribution and pollution assessment of heavy metals in soil from the Republic of North Macedonia. *Journal of Environmental Science and Health, Part A*, **54**, 1457–1474.

Stafilov, T., Šajn, R., Ahmeti, L. (2019): Geochemical characteristics of soil of the city of Skopje, Republic of Macedonia. *Journal of Environmental Science and Health, Part A*, **54**, 972–987.

Stafilov, T., Šajn, R., Damčevska, D., Tănăselia, C. (2021): Use of multivariate statistical methods to determine spatial distributions of chemical elements in soils (Mariovo region, North Macedonia), *Geologica Balcanica*, **50** (3), 37–53.

Stafilov, T., Šajn, R., Blaževska, C., Tănăselia, C. (2022a): Assessment of natural and anthropogenic factors on the distribution of chemical elements in soil from the Skopje region, North Macedonia. *Journal of Environmental Science and Health, Part* A, **57** (5), 357–375.

Stafilov, T., Šajn, R., Veličkovski-Simonović, S., Tănăselia, C. (2022b): Moss biomonitoring of air pollution with potentially toxic elements in the Kumanovo region, North Macedonia. *Journal of Environmental Science and Health, Part A*, **57** (8), 694–708.

Stafilov, T., Stojanova, K., Tašev, K., Bačeva Andonovska, K. (2023): Accumulation and distribution of heavy metals in soil and food crops in the Pb-Zn mine environ. Case study: Region of Probištip, North Macedonia. *Journal of Environmental Science and Health, Part A*, Published online: 06 Feb 2023. https://doi.org/10.1080/10934529.2023.2174331.

Tomovski, D., Stafilov, T., Šajn, R., Bačeva Andonovska, K. (2018): Distribution of chemical elements in surface waters from the Crna River basin, *Contributions, Section of Natural, Mathematical and Biotechnical Sciences, Macedonian Academy of Sciences and Arts*, **39** (1), 31–49.

Tomovski, D., Bačeva Andonovska, K., Šajn, R., Karadjov, M., Stafilov, T. (2019): Distribution of chemical elements in sediments and alluvial soil from the Crna Reka river basin. *Geologica Macedonica*, **33** (2), 125–145.

UNDP (2007): *Feasibility Study for Lojane Mine, Macedonia – Final Report*. UNDP, Deconta, Bratislava.

Vasilevska, S., Stafilov, T., Šajn, R. (2018): Distribution of chemical elements in surface water from Crn Drim river basin, Republic of Macedonia. *Water Research and Management*, **8** (1), 3–15.

Vasilevska, S., Stafilov, T., Šajn, R. (2019): Distribution of trace elements in sediments and soil from Crn Drim river basin, Republic of Macedonia. *SN Applied Sciences*, **1**, 555, 1–16.

Р е з и м е

МУЛТИВАРИЈАНТНИ СТАТИСТИЧКИ МЕТОДИ ВО ОПРЕДЕЛУВАЊЕТО НА ПРОСТОРНАТА РАСПРЕДЕЛБА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВАТА (КУМАНОВСКИ РЕГИОН, СЕВЕРНА МАКЕДОНИЈА)

Трајче Стафилов[1]*, Роберт Шајн[2], Сузана Величковски-Симоновиќ[1], Клаудиу Танаселија[3]

[1]Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“ во Скопје, Архимедова 5, 1000 Скопје, С. Македонија
[2]Геолошки завод на Словенија, Димичева 14, 1000 Љубљана, Словенија
[3]INCDO-INOE 2000 Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania
*trajcest@pmf.ukim.mk

Клучни зборови: загадување на почва; потенцијално токсични елементи; Кумановски регион; Северна Македонија

Презентирани се резултатите од дистрибуцијата на различни хемиски елементи во примероци почва од Кумановскиот регион, Северна Македонија. За да се утврди застапеноста на хемиските елементи, земени се примероци почва од вкупно 51 локација. На секоја локација примероците почва беа земени од два слоја, површинска (0–5 cm) и длабочинска почва (20–30 cm), на површина од 5×5 km^2. Беа анализирани 57 елементи со примена на два инструментални метода: индуктивно спрегната плазма – атомска емисиона спектрометрија (ICP-AES) за 17 макроелементи (Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V и Zn) и индуктивно спрегната плазма – масена спектрометрија (ICP-MS) за 38 елементи во траги (Ag, As, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Ti, Tm, W, Y, Yb и Zr). Применета е факторната анализа за да се анализираат факторите кои влијаат врз линеарните комбинациски променливи групирани во секој фактор. Картите на просторна дистрибуција за секој фактор, како и карти на дистрибуција за анализираните елементи, се добиени со универзална кригинг интерполација. Утврдено е дека дистрибуцијата на повеќето елементи ја следи литологијата на испитуваната област, освен некои елементи (As, Pb и Zn) чии повисоки содржини се застапени во некои специфични делови од подобластите, што се должи на сегашните рударски активности и рударските активности во минатото во регионот.