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ASSESSMENT OF THE CONTENT OF MACRO, MICRO AND POTENTIALLY TOXIC ELEMENTS IN THE SOIL OF THE SERBIAN MOUNTAINS BY MULTIVARIATE ANALYSIS

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Abstract: *The goal of this investigation was to assess the presence, content and limit concentrations of macro elements of plant nutrituion, trace elements, and potentially toxic elements in the soil. The research was carried out in Kopaonik, Crni Vrh and Mokra Gora during the period 2020-2022 on the different depths. Samples were prepared by microwave digestion with mixture of mineral acids. Concentration of extractedelements were measured by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES). The method of sample preparation is very important for the successful determination of elements because it is a very complex matrixChemometric approach was applied to explain the distribution of elements and potentially toxic elements in the soil by location and sampling depth. Principal Component Analysis and Cluster Analysis have proven to be excellent tools for reducing the number of measurements and for grouping data by parameters and by sampling location. Research has shown that there was no major soil contamination with toxic metals in the selected areas.*

Keywords: soil, microwave digestion, trace metals, ICP-OES, PCA, HCA

PROCENA SADRŽAJA MAKRO, MIKRO I TOKSIČNIH ELEMENATA U ZEMLJIŠTU SRPSKIH PLANINA MULTIVARIJANTNOM ANALIZOM

Sažetak: *Cilj ovog istraživanja bio je da se proceni prisustvo, sadržaj i granične koncentracije makroelemenata ishrane biljaka, elemenata u tragovima i potencijalno toksičnih elemenata u zemljištu. Istraživanja su vršena na Kopaoniku, Crnom Vrhu i Mokroj Gori u periodu 2020-2022. godine na različitim dubinama. Uzorci su pripremljeni mikrotalasnom digestijom sa mešavinom mineralnih kiselina. Koncentracija ekstrahovanih elemenata je merena induktivnospregnutom plazmom optičkomemisionom spektroskopijom (ICP-OES). Metoda pripreme uzorka je veoma važna za uspešno određivanje elemenata jer se radi o veoma složenoj matrici. Primenjen je hemometrijsk ipristup da se objasni distribucija elemenata i potencijalno toksičnih elemenata u zemljištu po lokaciji i dubini uzorkovanja. Analiza glavnih komponenti i klaster analiza su se pokazale kao odlični alati za smanjenje broja merenja i za grupisanje podataka po parametrima i lokaciji uzorkovanja.*

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Istraživanja su pokazala da na odabranim područjima nije bilo većeg zagađenja zemljišta toksičnim metalima.

Ključne reči: zemljište, mikrotalasnadigestija, metali u tragovima, ICP-OES, PCA, HCA

1. INTRODUCTION

Forest ecosystems contain pools of microelements, as well as toxic elements in virtually all forest compartments: forest floor, vegetation (trees, shrubs, ground vegetation), fauna, micro-organisms, soil and soil solution. Fluxes of these trace metals cycle along with carbon and nutrients and water (e.g. leaching). This labor focuses on macroelements, microelements (essental, and useful) and toxic elements concentrations and stocks in the forest soil, i.e. the mineral and organic layer.

The objective of this experiment was to assess the presence, content and limit concentrations of trace elements and potentially toxic elements in the soil. The research was carried out in Kopaonik, Crni Vrh and Mokra Gora, sampling and soil analysis.

2. MATERIAL AND METHODS

In 2020 on Kopaonik, in 2021 on Crni Vrh and in 2022 on Mokra Gora, soil sampling was carried out and laboratory analyzes of physical and chemical parameters were carried out according to ICP Forests Forest Soil Co-ordinating Centre methodology (Cools, De Vos 2020).

Sampling was performed on the observation plot established for soil analysis. It was performed using a probe at 30 different spots and making average samples. Probing was performed at depths of 0-10 cm, 10-20 cm and 20-40 cm.

The surface soil layer of 0–10 cm depth was sampled from 30 pits, and the deeper layers from 30 individual samples collected using a probe. An average sample was made for each layer. There were three average samples each composed of 10 individual samples. The following parameters were determined in the samples:

- ✓ Macro elements of plant nutrition (calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P))
- ✓ Microelements of plant nutrition
  - Essential microelements (copper (Cu), zinc (Zn)
  - Useful elements (manganese (Mn), iron (Fe), aluminum (Al))
- ✓ Toxic elements (lead (Pb), cadmium (Cd)).

Samples for soil analysis were prepared in the Testing Laboratory of the Department of Soil, Plant Material and Water Analysis of the Institute of Forestry.

2.1. Methods

Elements that are soluble in aqua regia are processed by wet digestion. Wet digestion is carried out in the Microwave Digestion System - Milestone Ethos LEAN, EASY in a mixture of nitric acid (HNO3) and hydrochloric acid (HCl). A sample weighing about 0.2 grams of air-dry soil was poured with 7.5 ml of HCl and 2.5 ml of HNO3. The resulting extract was filtered through filter paper into a normal vessel and filled up to 50 ml. The amounts of the macroelements of plant nutrition (K, P, Ca, Mg,), essential microelements (Cu, Zn) usefull elements (Mn, Fe, Al), and toxic elements (Pb, Cd) were determined by VARIAN VISTA PRO ICP-OES spectrometer and converted to an absolutely dry sample. (Madrid L. et al. 2006)

Statistical analyzes of the test results were performed using by the IBM SPSS Statistics Version 20 software.

3. RESULTS AND DISCUSSION

In Table 1 shows the results of average values of concentration microelements and potentional toxic elements from Kopaonik.

Table 1. *Concentrations of plant nutrients and potential toxic elements in soil at Kopaonik*

	Macro elements				**Essential micro elements**				**Useful elements**	**Toxic elements**	
Depth	Ca	Mg	K	P	Mn	Cu	Zn	Fe	Al	Pb	Cd
cm	mg/kg										
-4.5-0	625.11	70.09	46.76	104.62	121.36	3.39	3.11	1238.86	69.3	22.29	< 0.1
0-10	106.10	139.98	51.64	80.48	44.21	5.07	3.30	2621.39	637.50	23.95	0.19
10-20	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
20-40	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Limit value	-	-	-	-	-	36.00	3.00	-	-	85.00	0.80
Remediation value	-	-	-	-	-	190.00	200.00	-	-	530.00	12.00

Of the acid cations is dominated by aluminum and manganese. Of the base cations, calcium is the most abundant, followed by potassium. Their presence is highest in the organic layer, followed by the surface soil layers. As very important, macronutrients, they depend on the content of organic matter. With the depth of the soil, the amount of exchangeable forms of these elements decreases. Of the micronutrients extracted in the aqua regia, manganese, iron, copper and zinc were determined. The amounts of iron and manganese are high, but these two elements do not have defined limit and remediation values, because there are always sufficient amounts of these elements in the soil, and their high concentrations do not affect plants. Copper and zinc are essential microelements, which are necessary for plant nutrition.(Baldi E. et al. 2021) However, in very high concentrations they can be harmful to plants. In none of the collective samples, the amounts of copper and zinc do not exceed the remediation value, i.e. there are sufficient quantities of these

elements in the soil, but not in high concentrations that would be harmful to plants. Of the potentially toxic nutritional elements extractable in Aqua regia mercury, cadmium, lead, arsenic and chromium.(Borůka Lj. et al. 2005) The amounts of mercury, arsenic and chromium are extremely low and were below the detection limit, both in the organic layer and in the soil layer of 0-10 cm depth. In the horizon of organic layer, the amount of cadmium were below the detection limit. Small amounts of cadmium were found in the surface layer of the soil 0-10 cm thick, however, they are far below than the remediation value and even the lower limit value.This means that the amounts of this toxic element do not endanger plants on the sample plot. Small amounts of lead were found, both in the organic layer and in the surface layer of 0-10 cm of soil. However, the concentrations of this element are far below the remediation value, and also below the lower limit value, which means that they are far below the toxic concentrations.

In Table 2 shows the results of microelements and potentional toxic elements from Mokra Gora.

Table 2. *Concentrations of plant nutrients and potential toxic elements in soil at Mokra Gora*

	Macro elements				**Essential micro elements**				**Useful elements**	**Toxic elements**	
Depth	Ca	Mg	K	P	Mn	Cu	Zn	Fe	Al	Pb	Cd
cm	mg/kg										
-4.5-0	7074.43	8324.40	497.50	1374.23	497.50	5.13	32.50	< 0.1	< 0.1	< 0.1	< 0.1
0-10	1671.20	40135.97	330.30	333.60	330.30	8.13	28.67	10.97	11.40	< 0.1	< 0.1
10-20	1519.57	40907.30	296.83	349.37	296.83	8.33	31.70	18.80	13.80	< 0.1	< 0.1
20-40	1837.13	42572.50	325.10	343.13	325.10	16.90	53.87	18.80	9.60	< 0.1	< 0.1
Limit value	-	-	-	-	-	36.00	3.00	-	-	85.00	0.80
Remediation value	-	-	-	-	-	190.00	200.00	-	-	530.00	12.00

The most abundant element on Mokra Gora in the extract in aqua regia is magnesium. Its concentrations are the lowest in the organic horizon, but they sharply increase with the transition to the organomineral part of the solum. Its highest concentrations are in in the organic horizon, which is the result of biological accumulation. Potassium extracted in aqua regia is also significantly more abundant in the organic horizon than in the organomineral parts of the soil. The increased presence of potassium in the organic layer compared to the deeper parts of the soil is also a result of the biological accumulation of this nutrient macroelement. Manganese content in Mokra Gora is the lowest in the organic horizon, and increases strongly with depth. The amount of phosphorus in Mokra Gora is extremely low. It is the largest in the organic horizon, but it decreasesstrongly in the organomineral part of the soil. Copper soluble in aqua regia is poorly represented on Mokra Gora, both in the organic horizon and in the surface soil layers. The amount of lead and cadmium in the organic horizon and in the deeper layers of the soil on Mokra Gora are below the detection limit. The predominance of iron over aluminum is understandable because serpentinites are ferromagnesian silicates. In this case, there are no visible changes in iron concentrations at greater depths. The lowest

concentrations of aluminum were found in the surface layers, but they slightly increase with the depth of the soil. (Albanese S. et al. 2023)

In Table 3 shows the results of microelements and potentional toxic elements from Crni vrh.

Table 3. *Concentrations of plant nutrients and potential toxic elements in soil at Crni Vrh*

	Macro elements				**Essential micro elements**				**Useful elements**	**Toxic elements**	
Depth	Ca	Mg	K	P	Mn	Cu	Zn	Fe	Al	Pb	Cd
cm	mg/kg										
-4.5-0	1061.92	625.98	474.89	31.93	178.26	25.04	3031.58	4614.93	3031.58	< 0.1	< 0.1
0-10	1250.67	653.89	487.77	24.16	164.62	26.44	3222.2	4866.96	3222.2	25.04	< 0.1
10-20	983.23	692.19	528.96	32.82	190.05	18.47	136.42	3127.1	136.42	26.44	< 0.1
20-40	1061.92	625.98	474.89	31.93	178.26	25.04	3031.58	4614.93	3031.58	18.47	< 0.1
Limit value	-	-	-	-	-	36.00	3.00	-	-	85.00	0.80
Remediation value	-	-	-	-	-	190.00	200.00	-	-	530.00	12.00

The most abundant elements extracted in aqua regia are aluminum and iron, which is understandable because it is an acidic brown soil. The second most abundant element extracted in aqua regia are the alkaline earth elements calcium and magnesium. The amounts of toxic elements in the soil extracted in aqua regia – mercury, cadmium are below the detection limit. Only certain amounts of lead were found, but they are also less the lower limit values.

3.1. Chemometric approach to the distribution of microelements and potentially toxic elements in the soil

The results of the correlation analysis showed that in the Pearson correlation matrix there are not many correlation factors that are greater than 0.8, which indicates a very high degree of correlation between the elements. The strongest correlation was observed between Mn, Pb, Fe, Al and Mg, then between Cu, Fe and Al, then Ca and P.

Table 4. *Correlation Matrix*

		Ca	Mg	K	Mn	P	Cu	Pb	Cd	Zn	Fe	Al
Correlation	**Ca**	1.000	.099	.208	.190	.984	-.255	-.494	-.036	.243	-.487	-.290
	Mg	.099	1.000	-.398	.988	.140	-.306	-.781	.013	.513	-.795	-.596
	K	.208	-.398	1.000	-.336	.118	.285	.198	-.598	-.082	.180	.368
	Mn	.190	.988	-.336	1.000	.221	-.312	-.815	-.002	.496	-.822	-.597
	P	.984	.140	.118	.221	1.000	-.313	-.544	.003	.288	-.538	-.363
	Cu	-.255	-.306	.285	-.312	-.313	1.000	.396	.033	.045	.645	.861
	Pb	-.494	-.781	.198	-.815	-.544	.396	1.000	-.037	-.456	.823	.643
	Cd	-.036	.013	-.598	-.002	.003	.033	-.037	1.000	.021	.161	.056
	Zn	.243	.513	-.082	.496	.288	.045	-.456	.021	1.000	-.401	-.162
	Fe	-.487	-.795	.180	-.822	-.538	.645	.823	.161	-.401	1.000	.873
	Al	-.290	-.596	.368	-.597	-.363	.861	.643	.056	-.162	.873	1.000

By applying PCA analysis, a strong correlation was established between most of the examined elements. However, the grouping of elements according to their appearance at different depths in the soil was made into three main components, of which most of the elements are in the first component (PC1), which includes the largest part of the variance, as shown in Figure 1.

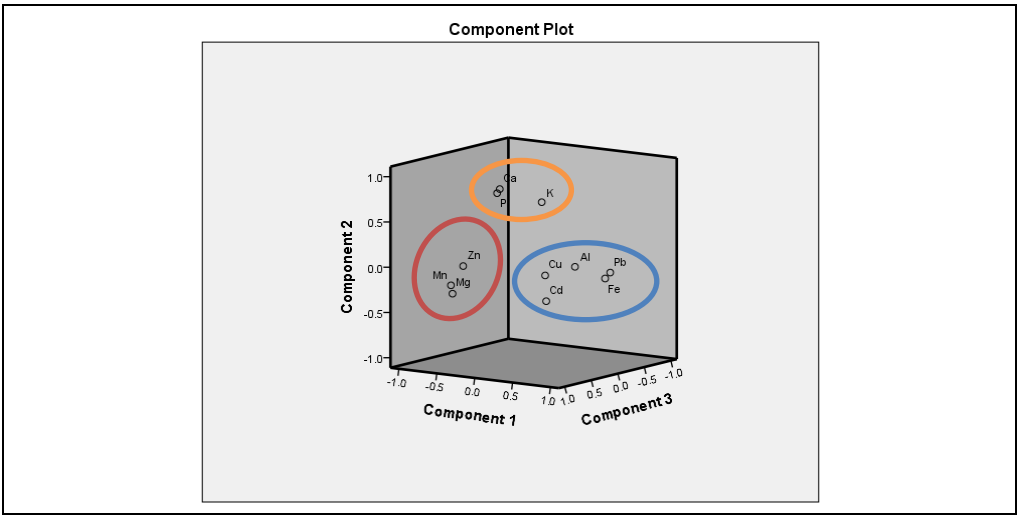

Figure 1. *PCA plot of loadings of elemets in soil*

Using hierarchical cluster analysis (HCA), the samples were grouped according to the sampling location and on the basis of the measured concentrations of elements. Three clusters can be seen on the dendrogram, the first two of which are Crni Vrh and Kopaonik at a very close Euclide distance and continue to connect into one cluster. Mokra Gora is a special cluster (Figure 2).

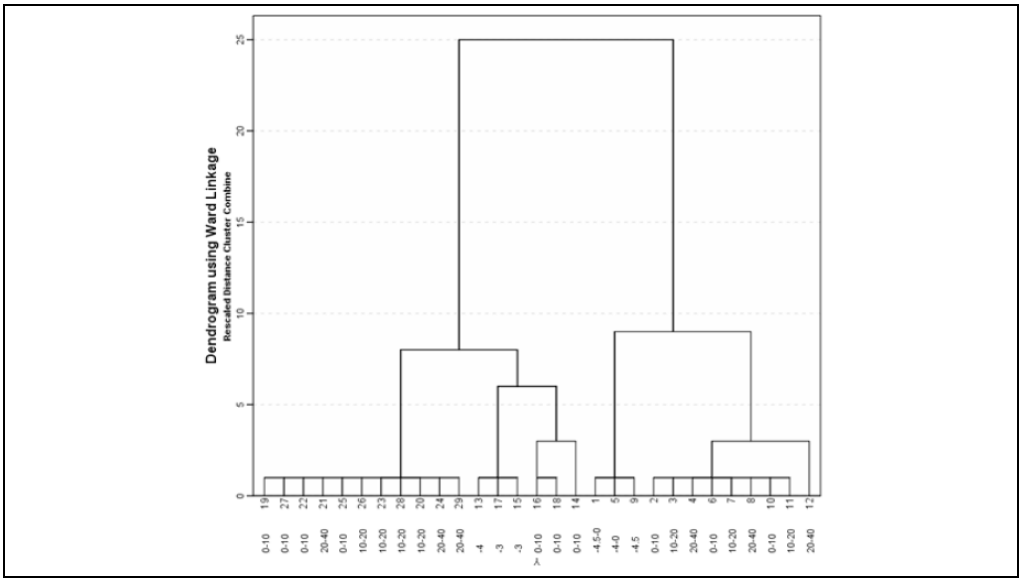

Figure 2. *Dendrogram of soil samples grouped by location*

4. CONCLUSION

Research has shown that there was no major soil contamination with toxic metals in the selected areas. As for the grouping of elements, three groups were distinguished using the PCA method: I (Fe, Al, Cu, Cd i Pb), II (Mn, Mg i Zn) and III (K, P i Ca), while the cluster analysis grouped the samples by location and depth of sampling in two clusters.

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Summary

In this research, the content of microelements and potentially toxic elements in the soil sampled on the terrain of the Serbian mountains:Kopaonik, Crni Vrh and Mokra Gora during the period 2020-2022 at different depths was examined. Preparation by microwave digestion using mineral acids was applied, and the measurement was performed using the ICP-OES technique. Using chemometric methods of multivariate analysis, correlation between elements was performed, samples were grouped according to similarity in the composition of elements by depth, elements were grouped into three main components.

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Rezime

U ovom istraživanju ispitivan je sadržaj mikroelemenata i potencijalnotoksičnih elemenata u zemljištu uzorkovanom na terenima srpskih planina Kopaonika, Crnog Vrha i Mokre Gore u periodu 2020-2022 na različitim dubinama. Primenjena je priprema mikrotalasnom digestijom pomoću mineralnih kiselina, a merenje je obavljeno ICP-OES tehnikom. Korišćenjem hemometrijskih metoda multivarijacione analize izvršena je korelacija između elemenata, uzorci su grupisani prema sličnosti u sastavu elemenata po dubini, elementi su grupisani u tri glavne komponente.