Chemometric approach to the investigation of microelements and potentially toxic elements in the soil

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Abstract: The goal of this investigation was to assess the presence, content and limit concentrations of macro, 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 different depths. Samples were prepared by microwave digestion with a mixture of mineral acids. The concentration of extracted elements was 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 matrix. A chemometric 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 sampling location. Research has shown that there was no major soil contamination with toxic metals in the selected areas.

Keywords: microwave digestion, trace metals, 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 microelements and toxic elements concentrations and stocks in the forest soil, i.e., the mineral or organic (peat) soil including the ecto-organic layer (forest floor), without considering elements in the soil solution. 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, by sampling and soil analysis.

2. Materials and Methods

In 2020 on Kopaonik, in 2021 on Crni vrh and in 2022 on Mokra Gora, soil sampling and laboratory analyzes of physical and chemical parameters were carried out. The 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 were 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: exchangeable acid cations: aluminium (Al), iron (Fe), manganese (Mn), exchangeable base cations: calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), oxalate soluble iron and aluminium, elements soluble in aqua regia, macroelements od plant nutrition, essential microelements of plant nutrition, useful elements, toxic elements. 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.

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 (HNO_3) 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 HNO_3. The resulting extract was filtered through filter paper into a normal vessel and filled up to 50 ml. The amounts of the analyzed elements were determined by the ICP-OES spectrometer VARIAN VISTA-PRO and calculated to an absolutely dry sample [1].

3. Results and Discussion

Of the micronutrients extracted in the aqua regia, manganese, iron, copper, and zinc were determined on Kopaonik. The amounts of iron and manganese are high, but these two elements do not have a 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. In no 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. Among the potentially toxic nutritional elements that can be extracted in Aqua regia are mercury, cadmium, lead, arsenic, and chromium [1]. 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 the organic layer, the amount of cadmium was 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 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.

Table 1 shows the results of mean values of concentration of microelements and potentially toxic elements from soil sampled from Kopaonik, Mokra Gora, and Crni Vrh.

Table 1. The concentration of microelements and potentially toxic elements from soil - Kopaonik, Mokra Gora, and Crni Vrh.

Sampling site	Depth	Ca	Mg	K	Mn	P	Cu	Pb	Cd	Zn	Fe	Al
	cm	mg/kg										
Kopaonik	-4.5-0	625.1	70.1	46.8	121.4	104.6	3.4	22.3	< 0.1	3.1	1238.9	69.3
	0-10	106.1	139.9	51.6	44.2	80.5	5.07	23.9	0.2	3.3	2621.4	637.5
	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
Mokra Gora	-4.5-0	7074.4	8324.4	497.5	543.5	1374.2	5.1	< 0.1	< 0.1	32.5	< 0.1	< 0.1
	0-10	1671.2	40135.9	330.3	1321.5	333.6	8.1	< 0.1	< 0.1	28.7	10.97	11.4
	10-20	1519.6	40907.3	296.8	1355.5	349.4	8.3	< 0.1	< 0.1	31.7	18.8	13.8
	20-40	1837.1	42572.5	325.1	1476.1	343.1	16.9	< 0.1	< 0.1	53.9	18.8	9.6
Crni Vrh	-4.5-0	1061.9	625.98	474.9	178.3	31.93	25.0	<0.1	23.2	3031.6	4614.9	3031.6
	0-10	1250.7	653.89	487.7	164.6	24.16	26.4	<0.1	17.2	3222.2	4866.9	3222.2
	10-20	983.2	692.19	528.9	190.1	32.82	18.5	<0.1	4920.9	136.4	3127.1	136.4
	20-40	1061.9	625.98	474.9	178.3	31.93	25.0	<0.1	23.2	3031.6	4614.9	3031.6

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. It is the result of biological accumulation. 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. 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 is below the detection limit. The predominance of iron over aluminum is understandable because serpentinites are ferromagnesian silicates. The lowest concentrations of aluminum were found in the surface layers, but they slightly increase with the depth of the soil [2].

The most abundant elements on Crni Vrh 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, and arsenic are below the detection limit. Only certain amounts of lead were found, but they are also less than the lower limit values.

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.

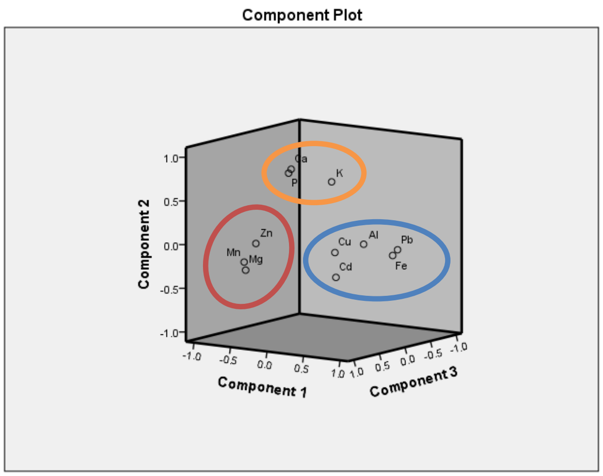

Figure 1. PCA plot of loadings of elements in soil

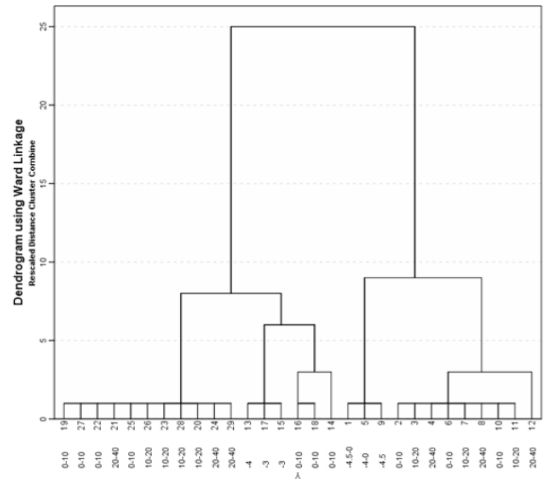

Figure 2. Dendrogram of soil samples

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 (samples marked with numbers 19-29) and Kopaonik (samples marked with numbers 13-18) at a very close Euclidean distance and continue to connect into one cluster. Mokra Gora (samples numbered from 1 to 12) is a special cluster (Figure 2).

3. Conclusions

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

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