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Geospatial analysis of soil pollution by Hurtful materials in the Vršac Mountains, Serbia –Case study: Landscapes of Outstanding Features "Kula"

Miško MILANOVIĆ[1*], Dragan ČAKMAK[2], Veljko PEROVIĆ[2], Orhideja ŠTRBAC[3], Saša BAKRAČ[4]

[11]University of Belgrade, Faculty of Geography, Belgrade, Serbia
[2]Institute of Soil, Belgrade, Serbia,
[3]Public Enterprise "Varoš" Vršac, Vršac, Serbia
[4]Military Geography Institute, Belgrade, Serbia

Abstract. The subject of this work is the protection zone and the "Kula" area of outstanding features in Vršac Mountains. Soil samples were taken at certain locations and were later detailed laboratory processed. Regarding the site of the "Kula area" and degree of protection, the main goal of this study was to determine the degree of degrading soil covering surface. For the studied territory, the presence of high Fe and Mn and low Cu in the samples is proven.

Keywords: geospatial, analysis, soil, pollution, hurtful materials, Vršac

[*] Miško Milanović> milanovic.misko@gmail.com

1 Introduction

Locality "Kula" is a region of the outstanding features of the Vršac Mountains, the subject of this research, is located in the eastern part of Vojvodina (Serbia). Locality "Kula" – the first level of protection, is located in the western region of Vršac Mountains and covers an area of about 3.171 ha.

According to its geographical position, orographic layout, geological features and flora and fauna, Vršac Mountains represent a specific area of Vojvodina and Serbia. The total protected area is 44.08 km^2, the first level of protection is 1.90 km^2, under a second degree of protection is 29.36 km^2, and the third level of protection is 12.82 km^2 [8]. In geological terms, they represent the earliest period of geological history and different tectonic phases, which are the only in the region of Vojvodina that can be explored and observed. The initial geological foundation of igneous and metamorphic rocks was changed due to passage of time, so now we have either blocks or smaller forms. Indigenous flora and fauna are natural values, which should be preserved by natural or deliberately caused disasters. Also, different types of life of indigenous communities can be observed here. The Vršac Mountains became officially internationally significant in 2000, when there are established as an Important Bird Area in Europe. The development of civilization requires less or more serious human intervention in the environment. The consequences are increasingly obvious, deep and attract the attention of increasing number of investigations in various scientific fields. At present, anthropogenic influences of various types and intensities, distributed within traditional appropriating of new arable lands, disturb complex ecosystems and change a character, a direction and mutual relations of natural pedogenic processes. This anthropogenic soil tranformation is dependent on its initial characteristics, characteristics of natural conditions of pedogenesis, as well as on the character of the anthropogenic influence. The available experience shows that the human activity mainly caused the degradation of soil and the soil cover as a whole.

According to the Article 129 of the Law of Environmental Protection [13], Vršac Mountains are defined as the region of the outstanding features. This is the specific area of Serbia, with different geological and geomorphologic forms and the soil and the vegetation cover. Precisely for this reason, the authors have done an analysis of land, studying the samples taken at 10 sites in the zone of the protection and "Kula"area, which is the subject of this work. The main task is to determine the degree of pollution in the "Kula area". As the parameter for determining the degree of pollution, we used the relevant Serbian regulations, which define the maximum value for organic production [14], as well as the maximum allowable concentrations of hazardous and harmful substances in the soil in Serbia [12]. The subject and the task of the function of the target are to prevent further degradation and suggest measures for further protection. Fig. 1 shows the elevation zones of Vršac Mountains, where the subject of this article - Locality Kula, belongs to.

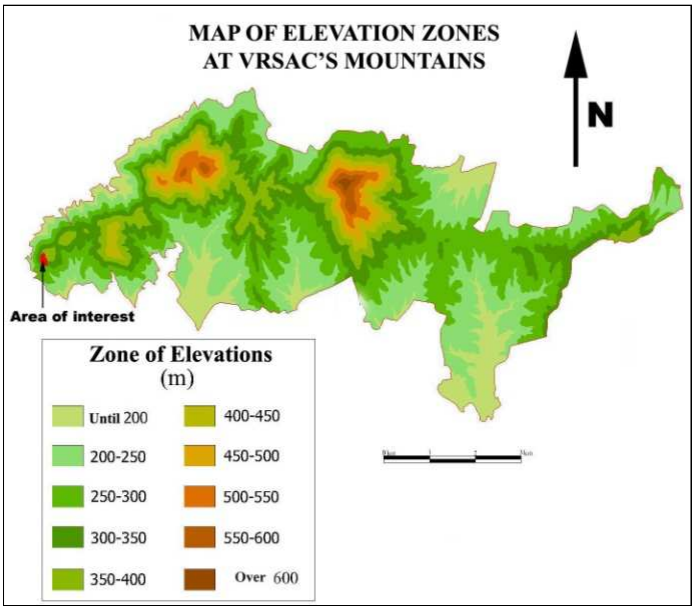


Figure 1. Map of elevation ones in Vršac Mountains with area of interest ("Kula" area), Serbia

2 Material and methods

Environment landscapes of the outstanding features, Vršac Mountains, has been compromised in the first degree of protection – "Kula" area. The main problem discussed in this paper, the degradation and destruction of the environmental elements, is present in the entire system surrounding the region of the outstanding features of Vršac Mountains. The work on this subject should provide methodological adjustments in order to obtain a more precise way to get to the actual situation of soil protected area. We presented the related the theoretical methods, the concrete methods and the methods of evaluation of the environment with the methods of geographic information systems (GIS). By modeling these features, we presented the geospatial areas of the Vršac Mountains.

The largest part of the "Kula" area, is composed of crystalline schists, which easily fall apart, crumble, and therefore there are observable gullies and occasional streams. In the "Kula" area one can observe two dominant soil types: automorphic and hydromorphic soil types. The automorphic soil types were detected at the initial soil that is undeveloped in nature and transient. The hydromorphic soil types are represented by alluvial and gley soil. Fig. 2 shows the level of protection of the Locality Kula.

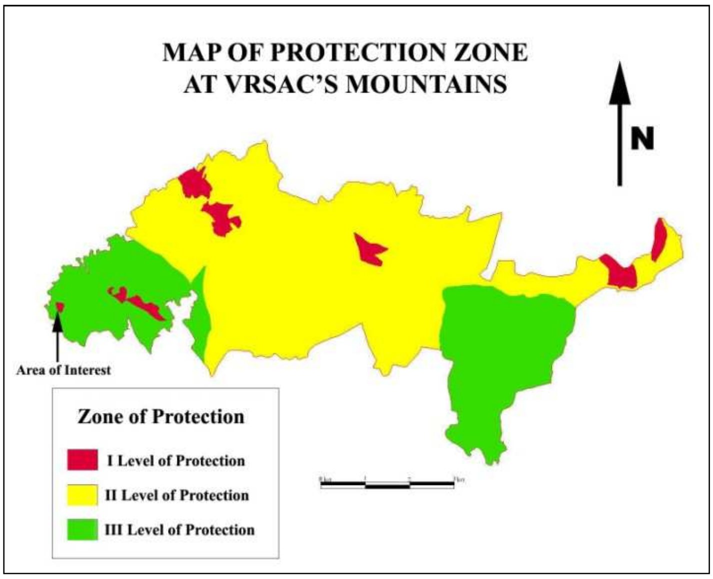


Figure 2. Map of protection zones in Vršac Mountains with the area of interest ("Kula" area), Serbia

The collected soil samples were stored in polyethylene bags for transportation and storage, and were air–dried, than sieved through a 2.0 mm mesh sieve. Soil pH was determined with a glass electrode pH meter, MA 5703, Iskra–Kranj, Slovenia. Soil total C and N were measured with an elemental CNS analyzer, Vario model EL III (ELEMENTAR Analysasysteme GmbH, Hanau, Germany), [11]. Available P_2O_5 and K_2O were determined by the Al–method of Egner-Riehm, where 0.1 N ammonium lactate (pH=3.7) was as an extract. After the extraction, potassium was determined by flame emission photometry (photometer, FLAPHO 4, Carl Zeiss, Jena) and phosphorous by spectrophotometry (spectrophotometer, UV–160A, UV–Visible Recording, CHIMADZU) after colour development with ammonium molybdate and $SnCl_2$ [3]. Soil Ca and Mg were extracted by ammonium acetate and determined with a SensAA Dual atomic adsorption spectrophotometer (GBC Scientific Equipment Pty Ltd, Victoria, Australia), [16]. Instrumental detection limits (mg kg-1) were: for Ca and Mg 0.01. Trace elements were determined with an ICAP 6300 ICP optical emission spectrometer (Thermo Electron Corporation, Cambridge, UK), after the soils were digested with concentrated HNO3 for extraction of hot acid–extractable forms, and by DPTA for extraction of DTPA extractable elements [15]. The instrumental detection limits (μ l-1) were: for Zn, Hg, and Cr 0.01., for Ni, Cu, Pb, Co and As 0.1.

All chemical analyses were performed in two analytical replications. The MERCK standards were used for the determinations on ICP and SensAA Dual. Before the determinations the blank samples were read, which allowed to correct the results. For the verification of the results the referent soil sample was determined for all studied elements. The ArcGIS software was used as the basic analysis tool for spatial data management and manipulation.

Locations of the soil samples were determined by

GPS receivers. According to required accuracy of the spots where the samples were taken, differential GPS (DGPS) was used as a measuring method. Coordinates were obtained within World Geocentric System 84 (WGS84). On the other hand, available maps that were used as a basis for GIS were created within Serbian national datum (transversal Mercator projection on Bessel ellipsoid), which significantly differs from WGS84. In order to match GPS measurements with the maps, we calculated a set of transformation parameters. Seven parameters transformation (three translations, three rotations and the scale) was chosen, because it describes the best the changes between two coordinate systems [7].

Table 1: The maximum allowable concentration of the hazardous and harmful substances in the soil in Serbia [12]

Elements	Cd	Pb	Hg	As	Cr	Ni	F	Cu	Zn	B
mg/kg	3	100	2	25	100	50	300	100	300	50

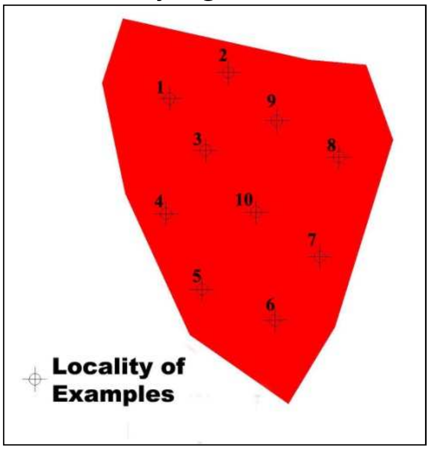
Table 2: Maximum value for organic production [14]

No.	Metal	mg/kg of air-arid soils
1	Cd	0.8
2	Hg	0.8
3	Pb	50
4	Zn	150
5	Cr	50
6	Ni	30
7	Cu	50
8	PAH	1
9	Mo	10
10	As	10
11	Co	30

3 Results and Discussion

The soil belongs to the category of highly acidic; with three samples belonging to a group of acid (1, 5 and 9). The soil is without carbonate. The average organic matter content is high; the samples 2, 4, and 7 are within the mean values, while the sample 6 is low.

Figure 3. Case study region–"Kula" area, Serbia



In accordance with the samples, we measured a high content of nitrogen, except for samples No. 6 and 7, where the content of nitrogen is medium. Phosphorus content is very heterogeneous from the very low (samples no. 7 and 10), low (samples No. 6 and 9) middle (samples 1, 2 and 5) to high (samples of 3, 4 and 8). Potassium was high in all samples except in samples No. 6 and 7 where low or medium content of this element is noticed.

Table 3: Coordinates for the case study region –"Kula" area, Serbia;

No.	Coordinates of the case study region	
	X	Y
1	7534776.41	4996707.32
2	7534815.41	4996724.53
3	7534800.50	4996672.92
4	7534774.12	4996630.49
5	7534798.21	4996580.03
6	7534846.39	4996559.39
7	7534876.23	4996601.82
8	7534888.85	4996668.33
9	7534847.54	4996692.42
10	7534833.77	4996631.63

Table 4: Base attribute of soil for the locality of speciment (Soil analysis done by Čakmak, D.)

No.	pH nKCl	C %	O.M %	N %	P_2O_5 mg/100g	K_2O mg/100g	Ca mg/100g	Mg mg/100g	Ca:Mg
1	5.4	3.32	5.81664	0.29	10.47	40	192	35	3.3
2	4.3	2.16	3.78432	0.22	14.66	36	105	21	3.00
3	3.7	3.1	5.4312	0.3	17.41	29.6	82	16	3.2
4	4.1	2.72	4.76544	0.3	18.6	29.2	138	20	4.2
5	5.2	5.86	10.26672	0.49	12.16	32.8	280	43	4
6	3.75	0.34	0.59568	0.07	9.23	8	100	27	2.3
7	4	1.3	2.2776	0.11	0.58	15.7	29	8	2.2
8	4.2	7.43	13.01736	0.6	27.28	40	206	23	5.6
9	4.65	4.01	7.02552	0.37	8.14	38.5	172	31	3.4
10	4.5	3.86	6.76272	0.34	5.4	24.8	134	19	4.3
average	4.38	3.41	5.97432	0.309	12.393	29.46	143.8	24.3	3.55

Commuted calcium content is average in most samples, with the maximum in the sample No. 5 and the minimum in the samples 3 and 7. Commuted magnesium content is high, except in the sample number 7, where the lowest content is measured.

Content of hot acid extractible micronutrients in the tested samples are low, far below the maximum allowable amount (MDK-MAC-maximal concentrations allowed) [12].

Content of (DTPA-extractible) iron in the tested samples is very high and manganese in the samples, except 6 and 7, where it is low or very low .

In the sample 7, copper content is low by MAC (maximal concentrations allowed), samples 4 and 8 have a high content of copper and, at other locations, copper content is within the limits of high. Zinc content is high (samples 1, 3 and 10) and others are very high except for sample number 7, which is low.

Table 5: Hazardous and harmful substances for locality of speciment, first measuring (Soil analysis done by Čakmak, d.)

No.	As	Hg	Cd	Cr	Ni	Pb	Cu	Zn	Co	Mn
1	3.8	0.063	0.3	16	12	18	9	45	7.3	394
2	4.1	0.084	0.36	17	13	19	8	45	8.2	439
3	4.4	0.071	0.26	19	13	22	7	45	7.1	325
4	5	0.065	0.45	27	17	22	12	74	9.9	565
5	5.6	0.062	0.39	19	13	21	9	59	10.5	705
6	3.9	0.037	0.29	26	17	12	8	57	10	460
7	6.4	0.03	0.25	24	13	14	8	42	7.6	164
8	7.9	0.079	0.46	20	12	33	11	67	6.4	440
9	3	0.057	0.34	8	6	19	6	37	4.6	532
10	3.7	0.068	0.27	10	7	20	6	37	5	329
average	4.78	0.0616	0.337	18.6	12.3	20	8.4	50.8	7.66	435.3

A great impact on the content of the substrate microelements (trace elements) is expressed throughout the case study area especially for underdeveloped shallow, skeletal soils in the fall rankers and regosols. For these reasons eventual anthropogenic pollution is easily noticeable. Results obtained from the studied samples indicate that the content of harmful elements not increased compared to the parent material and granite rocks [2]. Measured value samples are mostly in the average boundary, except for cadmium, which is slightly enlarged. The obtained quantities are also in line with the average amount identified for the land in the world where the content of Cr, Ni, Pb, Cu and Zn below average [1]. On the other hand if we consider the average content of soil in Serbia [10], the amount determined for all examined elements multiples below average. It should be noted that the concentration in the samples were well below the MAC for the soil of Serbia [12], and they are below the legal limit for land intended organic production[14]. Solubility of some trace elements of the tested samples is somewhat more expresssed due to increased soil pH [5], particularly lead, but only the extraction tool used in the methodology allows for such amount and ratio of the total soluble fractions [4]. Therefore, there is no danger that any of the increased quantities appear in any significant content in the food chain.

Table 6: Hazardous and harmful substances for locality of speciment, second measuring (Soil analysis done by Čakmak, D.)

No.	Cd	Cr	Ni	Pb	Cu	Zn	Co	Mn	Fe
1	0.11	0.017	0.5	3.1	0.9	3.0	0.12	33.0	70.0
2	0.18	0.025	1.0	4.5	0.9	4.8	0.39	58.0	144.0
3	0.09	0.022	0.5	8.4	1.6	2.4	0.78	46.0	254.0
4	0.17	0.018	0.8	4.4	1.5	4.4	0.28	44.0	184.0
5	0.16	0.020	0.5	3.0	1.2	8.2	0.07	51.0	83.0
6	0.03	0.003	0.3	0.8	0.9	7.0	0.09	5.0	74.0
7	0.02	0.009	0.1	2.1	0.3	0.5	0.08	2.0	38.0
8	0.26	0.031	0.7	12.6	1.5	11.1	0.31	76.0	335.0
9	0.19	0.033	0.6	4.7	1.1	6.0	0.16	76.0	126.0
10	0.13	0.022	0.6	6.2	0.8	3.6	0.17	47.0	125.0

The quality of the structure [6], and of the soil itself, depends on the influence of many factors participating in aggregation, as for instance, of organic matter content, clay, iron and aluminum oxides and plant root activity.

4 Conclusion

Taking into consideration the natural values of the Vršac Mountains and putting it in range of the protected area, there is a need for a higher level of protection, control and management. Due to authenticity of the mountains of Vršac, condition, representation, diversity, integrity and landscape–environmental values must create the conditions for the protection for the Vršac Mountains. If we take into account the proximity of borders with Romania, then the considered problem may has the interstate significance in the environmental management. This will be an excellent basis for the international cooperation between Serbia and Romania.

The results of the research showed that the influence of degrading soil and hazardous pollutants and is apparent, especially in the western parts of the analyzed area. Argument of this is the immediate vicinity of the settlements of Vršac municipality, as well as use of forests, water sources, tourism and recreation within the first protection zone. It was determined that the land can be categorized as sour to very sour. Organic matter is present due to the exceptional biodiversity in some habitats. However, the comparative analysis has found that the native plant species are dying in such soil, and the animal species from the "Kula" area gravitate towards the northern and northeastern parts of the Vršac Mountains. Because of this, it is necessary to mark the boundaries of I, II and III degree of protection zones to prevent further degradation of the environment and all its elements. For the protection of the said premises, there is a need for a special act on the internal order (within the laws the environment issues), development plans and programs for the protection and harmonization of the same [9]. For the purpose of the further protection, the authors start with the construction of an ecological information system of Vršac Mountains, which will hopefully, in the near future, be one of the tools for the control and the verification elements of the environment. The environment information system has become an integral part of the applied informatics. On the other hand, new and provoking environmental requirements arise, stimulating research and development of the informational methodology and the applications. It should be emphasized that environmental informatics not only explores the potential benefit from the informational technologies when troubleshooting environmental problems, but also sees its responsibility considering the negative environmental impact. Constitution of the information systems of environment is one of the basic entrances for solution in conform to the management of the life environment.

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