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# **Mineralogy and Geochemical Speciation of Heavy Metals in some Serpentine Soils of Serbia**

## **Minéralogie et spéciation géochimique des métaux lourds dans quelques sols à Serpentine de Serbie**

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### **Introduction**

Serpentine soils in Serbia occur in the hilly and mountain regions, covering a large area of about 250 000 ha. A selection of samples from Kopaonik, Zlatibor, Maljen, Fruska gora, Miroc and Deli Jovan Mts., was taken to represent the most important soils. The soil type is ranker and humous or brunified rankers.

Their low fertility, susceptibility to erosion and physical and chemical soil properties reflect competing effects of inhibited biological activity and parent rock mineralogy and geochemistry. Previous studies have shown the importance of the following processes in ultramafic pedogenesis: redistribution of magnesium and nickel in soil profiles (Alexander, 1988), transfer of heavy metals from primary silicate minerals to secondary iron oxides and hydroxides (Miura et al, 1988), and alteration of ferromagnesian minerals present in ultramafic rocks to smectite and vermiculite (Bain 1977). Studies of slightly weathered serpentinite soils (Rankers and Brunisols), have shown an increased redistribution of cobalt, nickel, manganese and iron from primary minerals within soil profiles. Release of chromium was not observed in these soils.

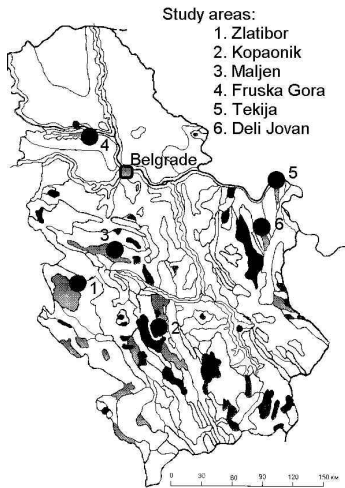
### **Material and methods**

During a large scale soil sample collection for the project, financed by the Ministry of Science and technology, Republic of Serbia, an orthogonal regular grid was used. Sampling was based on a 3 x 3 km cell and a selection of serpentine soil samples from Kopaonik, Zlatibor, Maljen, Fruska gora, Miroc and Deli Jovan Mts., was taken to represent the most important soils. After collection the samples were air-dried and sieved to pass a 2 mm sieve. A 50 g subsample of < 2mm soil was obtained by coning-and-quartering and ground to less than 150# in an all-agate ball-mill.

Chemical analyses for major elements were carried out on samples of bulk material by X-ray fluorescence spectrometry. Samples were fused into a lanthanum borate pressed glass disc and analysed with a PHILIPS multi-channel XRF instrument.

Total heavy metals were analysed by ICP following dissolution of samples in the aqua-regia. In order to ascertain bioavailability of heavy metals chemical speciations

of the elements were carried out according to the EC Protocol. Methods used to characterize the mineralogy and some physical and chemical properties of soil samples included X-ray diffraction (XRD), particle size analysis, separation and sedimentation techniques and standard chemical tests for soils were carried out according to Klute (Ed) 1986.



**Table 1 . Climatic characteristics of study area**

	<b>Altitude (m)</b>	<b>MAT (° C)</b>	<b>MAP (mm/y)</b>
<b>Kopaonik</b>	1700	3.5	905
<b>Zlatibor</b>	1030	6.5	960
<b>Maljen</b>	960	7.0	910
<b>Deli Jovan</b>	690	8.0	860
<b>Tekija</b>	180	11.0	830
<b>Fruska Gora</b>	475	9.5	525

Figure 1. Location of the study areas

The mineralogy of bulk soil samples was obtained by X-ray diffraction analysis (XRD) of random-packed powder mounts, after they were grind and freeze-dried. Separation of the clay ( $< 2 \mu\text{m}$ ) fraction was accompanied by wet sieve and centrifugal sedimentation technique. The samples were disaggregated by ultrasonic treatment (3 min. at 100 W). Characterization of clay minerals was performed on each  $< 2 \mu\text{m}$  specimen as follows: air dried, ethylene glycol solvated, potassium saturated, and progressive heat treatments ( $300^{\circ}\text{C}$  and  $500^{\circ}\text{C}$ ) of samples (Brown and Brindly, 1980). XRD patterns were obtained by using SIMENS 2 kW diffractometer, with iron filtered  $\text{Co K}\alpha$  radiation. DRX Win 1.4c (1996) computer package was used to identify and quantify soil mineralogy. All data obtained were statistically analyzed by computer package STATISTICA for Windows 4.3b (1993).

### Study area

Figure 1. shows the location of the study areas. Zlatibor and Kopaonik Mountains are amongst the largest areas of serpentinised peridotites in Europe. The peridotite and serpentinised peridotite rocks are parts of the tectonically disrupted ophiolite complex belt (Dimitrijevic, 1995). The lithology consists of dark, massive and occasionally sheared serpentinite derived from peridotite of lherzolitic, verlitic and harzburgitic composition and rarely dunite. The rocks have a hypidiomorphic-granular texture and consist of olivine, monoclinic and orthorhombic pyroxene, serpentine minerals, amphiboles, talc, chlorite, opaque minerals (picotite, chromite and magnetite) and minor amounts of carbonate. Olivine and pyroxenes are altered along the cleavages to serpentine, whilst chlorite, hornblende and tal fill the fractures within the rock. The degree of serpentinisation is lowest around summits of Zlatibor Mt., while in other studied areas it is relatively uniform.

Table 1. provides climate data for the study areas. The climate of the region is continental temperate, but changes with altitude to a colder mountain regime. Climate diversity is caused by the change in elevation which causes moisture division and induces precipitation and temperature gradients along steep slopes. On the mountains winters are long and very cold with maximum precipitation, frosts are frequent in early autumn and late spring and summers are dry and cool with occasional storms.

Vegetation of meadows on serpentinitised peridotites is xerophile grass associations eg.: *As. Poeto Molierii - Plantaginerum carinatae*, *As. Fetusceto sulcatae - Potentillentum zlatiborensis*, *As. Koelerietum montanae*, as well as *Trifolium, Fetusca and Bromus* which covers almost 90% of area ( Zivkovic, 1952). On lower elevations there are remnant forests of *Quercus pubescens, Flaxinus ornus and Pinus nigra*, while solitary trees of *As. Pinetum nigrae - silvstris* and *As. Quercus sesiliflora* frequently occur on higher elevations, above 1000m.

## Soils

Study sites were selected to represent peridotite parent rocks weathered under various climatic conditions and to reflect soils on stable portions of landscape. Table 2. provides average information of selected soils. The soils have small depth of profile, since they are derived from serpentinitised peridotite residue. They could be classified as rankers, humous and brownised rankers (Orthic Brunisols). The ranker and humous ranker colours are variable from pale brown (5 YR 5/4), moderate brown (7.5 YR 4/4 and 10 YR 3/4-4/4) to dusky brown (5 YR 2/1-3/3 and 10 YR 2/2-3/2). Brownised ranker colours are more reddish and change to dusky reddish brown (10 R 3/2) and moderate reddish brown (10 R 3/4-4/6). The organic C content of the soils in the wet environment was slightly higher than for soils developed in the dry environment. The serpentinitised peridotite parent material have shown slightly acidic to near neutral pH

**Table 2 . Average properties of investigated serpentine soils**

Horizon Depth (cm)	pH (H <sub>2</sub> O)	C-org (%)	CaCO <sub>3</sub> (%)	Moisture (%)
A <sub>n</sub> (0 - 15)	5.84 ± 0.273 (5.56 - 6.15)	9.23 ± 0.950 (8.32 - 10.57)	2.67 ± 1.150 (1.05 - 3.65)	3.40 ± 0.323 (2.86 - 3.68)
(C) (15 - 40)	6.04 ± 0.314 (5.64 - 6.59)	8.01 ± 2.261 (4.58 - 10.60)	3.11 ± 1.482 (1.52 - 5.87)	3.33 ± 0.729 (1.96 - 4.84)

N.B. Average ± St. Dev, (Range)

values. The pH values in upper parts of soil are more acidic for proper rankers, indicating that slight acid weathering and base leaching are important soil forming processes in more wet environments. On the other side humous and brownised rankers have shown near neutral pH values reflecting a lower weathering intensity and leaching in drier environments.

## Mineralogy

The soils are consisted mostly of secondary minerals: serpentine with various proportions of chrysotile and antigorite, chlorite and minor to trace amounts of pyrixene, hornblende, talc, rare olivine, goethite, carbonate and clay minerals indicating

that parent rocks were highly serpentinised. All soils have shown the presence of minor to trace amounts of feldspars, quartz and illite introduced as an eolian addition. Magnetite, chromite, ilmenite and other un-serpentinised (olivine, piroxene) minerals are found in heavy mineral fractions. The major weathering process in the soil in a wet, slightly acidic environment involved the disappearance of chlorite from the surface horizons, and its conversion to expandible minerals such as vermiculite and smectite (Kodama, 1979). The degree of chlorite alteration correlated with the development of brownised and humous rankers in samples from Zlatibor and Kopaonik Mts.

Clay fraction of the soils consisted of serpentine-antigorite, which is the soil type (Brindley, 1980), chlorite, talc, illite, illite/smectite, chlorite/vermiculite, nontronite and minor amounts of disordered kaolinite and quartz. Disordered kaolinite was developed from feldspars and was identified only by infra-red spectroscopy spectrum 3700 and 3620  $\text{cm}^{-1}$  bands. The persistence of talc and serpentine in fine clay throughout the profiles could suggest a high stability of these minerals within soils in strongly leaching and weathering conditions. Slightly acidic conditions and the presence of chlorite could indicate favourable conditions for HI - smectite/vermiculite forming. The occurrence of Al-vermiculite/smectite was confirmed by XRD analysis of  $\text{NH}_4\text{NO}_3$  and Na-citrate treated specimens, (Zivkovic, 1966).

### Geochemistry

The chemical composition of the soils is given in Table 3. Considering the chemical composition of the soil horizons, it is evident that the leaching of MgO proceeded in a greater degree, while the amounts of silica, alumina, alkalis and calcium are increased. Iron has shown only slight leaching and is the major colouring matter in brownised soils. Titania was shown to be a stable element within the soil profiles.

The MgO and LOI contents of deeper horizons reflect the degree of serpentinisation of the parent rock. Higher contents of silica and alumina as well as alkalis and calcium may indicate minor eolian additions of orthoclase and plagioclase feldspars to the soils. Relative enrichment of minerals during weathering and nutrient cycling by vegetation may account for slightly higher CaO,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$ .

**Table 3 . Total elemental analysis of serpentine soils by XRF (%)**

Sample	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	CaO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
A <sub>h</sub>	49.46 ± 5.27 (40.60-55.36)	0.38 ± 0.09 (0.25-0.53)	10.43 ± 2.16 (6.37-13.90)	17.82 ± 5.12 (12.27-25.21)	17.06 ± 3.93 (12.12-24.50)	2.09 ± 0.82 (1.06-3.15)	0.53 ± .17 (0.20-0.84)	0.62 ± 0.26 (0.20-1.07)
(C)	47.63 ± 5.17 (40.10-52.32)	0.34 ± .07 (0.22-0.44)	9.21 ± 2.12 (5.54-11.94)	18.27 ± 6.12 (12.71-28.11)	20.65 ± 4.06 (16.45-28.21)	2.52 ± 0.54 (1.87-3.10)	0.44 ± 0.13 (0.23-0.59)	0.45 ± 0.25 (0.15-0.86)

N.B. Average ± St. Dev. (Range)

Table 4. shows that soil contained slightly more Mn and Cr and slightly less Ni than parent material and these differences were greater for soils from wet environments (Kopaonik and Zlatibor). The insolubility of chromium ions in a wide range of soil environments is restricting for Cr mobility. Nickel is present as a hydrated ion in soil solutions at  $\text{pH} < 8$ , and is liable to leaching. The abundance of other minor elements is illustrative for soils derived from ultrabasic rock residue. Higher Cu, Zn and Pb values in Kopaonik and Deli Jovan soils could be a sign of possible pollution of soils by neighbouring mining and smelting activities.

**Table 4. Heavy metals content of the soils (mg/kg)**

SAMPLE	CU	ZN	PB	NI	CO	CR	MN
<b>A<sub>h</sub> (0 - 15)</b>	25 ± 23 (18-80)	95 ± 36 (58-171)	61 ± 32 (24-116)	1187 ± 254 (947-1620)	132 ± 19 (110-176)	1410 ± 1080 (506-4150)	2088 ± 646 (1130-2988)
<b>(C) (15 - 40)</b>	21 ± 21 (4-66)	88 ± 47 (45-163)	60 ± 41 (5-110)	1355 ± 340 (1006-1978)	129 ± 22 (108-172)	1640 ± 1245 (548-4080)	1866 ± 626 (1230-2920)

N.B. **Average ± St. Dev.** (Range)

Results of sequential dissolution analysis of soil materials are expressed as proportions of total element contents and are presented in Table 5. Investigated soils contained large residual Cr and Fe fractions. Only 0.16% Cr and 0.25% Fe in soils were present in extractable forms. Limited mobility of chromium occurred due to resistance to weathering of primary oxide minerals (chromite, picotite, magnetite) where it substituted for iron. Iron had almost equal proportions present as oxide and organic forms. The results of the sequential extraction for Co were similar to the results for Mn, while Ni and Zn have shown similar results. These soluble elements were depleted from soil horizons and significant quantities were present in extractable forms. Smaller proportions of the elements were also found in oxide and organic fractions. Significant proportions of Zn and Ni and smaller ones of Co and Mn were present as residue fraction of soils. These elements could be removed from secondary minerals as chlorite as well as from poorly crystallised weathering products. Copper and lead have shown completely different results from other elements. The majority of copper has remained in residual form, but about one third was found as organic fraction, strongly suggesting a biophilic cycling of copper. The most of lead was leached and migrated to oxide, with only 34 percent remaining as residual fraction.

**Table 5. Chemical Speciation of Heavy Metals in Serpentine Soils (%)**

	CR	FE	CU	ZN	NI	CO	MN	PB
<b>EXCH</b>	0.67 ± 0.416	0.92 ± 0.700	3.92 ± 2.472	17.12 ± 2.077	25.89 ± 4.350	51.18 ± 4.543	52.74 ± 1.796	0.16 ± 0.078
<b>OXHY</b>	0.33 ± 0.285	8.90 ± 1.399	2.61 ± 1.196	16.40 ± 4.922	10.32 ± 2.686	12.02 ± 2.0635	13.96 ± 1.382	62.69 ± 8.344
<b>ORG</b>	1.12 ± 0.234	7.18 ± 1.474	24.00 ± 5.128	8.17 ± 2.010	14.83 ± 2.594	2.46 ± 2.132	6.12 ± 2.089	3.00 ± 1.877
<b>RES</b>	97.88 ± 0.728	83.00 ± 2.045	69.42 ± 4.379	58.31 ± 4.804	48.96 ± 6.014	34.34 ± 3.949	27.18 ± 2.573	34.25 ± 7.410

N.B. **Average ± Standard Deviation**

In order to investigate physical speciation and particle size fraction, in which heavy metal concentrations tend to be high as possible metalliferous minerals, a particle size analysis was carried out on soil samples. The soil from Deli Jovan Mt., (DJV 121/2) was split into five fractions, as follows: sand (2-0.2mm; 17.90%), coarse silt (0.2-0.053mm; 23.97%), fine silt (0.053-0.002mm; 38.73%), coarse clay (0.002-0.0005mm; 14.66%) and fine clay (< 0.0005mm; 4.74%). Table 6. provides results of the ICP analysis of micro elements in studied soil. The greatest influx of heavy metals was identified for Cr, Fe and Ni, which are found in the coarse (sand and silt) fractions,

**Table 6. Physical Speciation of Heavy Metals in DJV - 121/2 Soil (%)**

	<b>FE</b>	<b>CR</b>	<b>NI</b>	<b>CO</b>	<b>MN</b>	<b>ZN</b>	<b>CU</b>	<b>PB</b>
<b>Sand</b>	15.24	54.32	14.90	13.48	9.71	13.84	4.31	9.30
<b>C. Silt</b>	22.10	32.75	24.59	19.67	19.04	15.38	5.17	6.98
<b>F. Silt</b>	37.06	10.12	35.47	38.76	40.88	35.38	45.70	34.88
<b>C. Clay</b>	18.40	2.18	18.72	20.76	21.69	24.63	31.03	34.88
<b>F. Clay</b>	7.20	0.63	7.13	7.30	8.68	10.77	13.79	13.95

where chlorite, olivine, picotite, chromite, hornblende and other minor silicate minerals dominate. In medium (silt and coarse clay) fractions Mn, Co and Zn dominate, where secondary minerals (serpentine, smectite, illite, goethite and minor psyllomelane) comprise the most of these fractions. Copper and lead are associated with fine silt and clay fractions, in which secondary minerals (smectite and serpentine) are associated with poorly crystallised Fe - Mn hydroxides and their organo-mineral complexes.

### **Conclusions**

The chemical properties, mineralogy and geochemistry of the serpentine soils have reflected only slight differences due to the regional climate. The mineralogical analysis has shown that the parent rock minerals were altered during weathering. X-ray diffraction analysis has shown that the clay mineral assemblage of the soils was altered during pedogenesis: chlorite was converted to smectites and HI-vermiculites; eolian additions of micas, illite and feldspars were altered to illite/smectite, and disordered kaolinite. Inherited serpentinite (chrysotile and antigorite) and talc in the clay fraction of the serpentine soil suggests their considerable stability in soil environments with high weathering and leaching intensities.

Geochemical analyses have indicated that dissolution of parent rock mineral assemblages was an important process in all soils. Release of heavy metals, particularly Mn, Co, Fe and Ni and to a lesser extent Zn, Cu and Pb, and mobilisation of their soluble weathering products could be contributed to climate and precipitation. Chromium has remained in residual form and was retained in coarse fractions within heavy minerals, while Mn, Co, Fe and Ni were depleted from A horizons of the soils.

Low fertility of these soils could be attributed to high phytotoxic concentrations of bioavailable, exchangeable and easy mobile forms of elements such as: Mn, Co, Ni, in slightly acidic environments, low Ca/Mg ratio, small depth of the soils and consequently adverse water regime within the soil profile.

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