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Chemical Properties of Serpentine Soils from Kosovo

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Abstract

Ultramafics represent magmatic or metamorphic rocks which are characterized by high concentrations of Mg, Fe, Ni, Cr and Co and low concentrations of macronutrients. They contain less than 45% silica (SiO_2). Throughout the territory of Kosovo there are many basic and ultra-basic rocks. The aim of this study was to determine the content of heavy metals and other macro elements in some of serpentine soils of Kosovo and finding out bioavailable Ca/Mg relationship as well, which is very important indicator for plants development. The sampling was conducted on June 2014. Three serpentine areas have been surveyed and 7 soil samples in total have been taken in different depth of soil profiles. The serpentine soils at all sites were characterized by elevated levels of heavy metals such as, Fe, Ni, Cr, Cd, Mn that show typical properties of ultramafic environments. Total Ni availability at studied areas varied from 1543 to 2570 mg kg^{-1}, whereas bioavailable Ni is on range of 37.71 mg kg^{-1} and 101.04 mg kg^{-1} respectively. On the other hand concentration of bioavailable macroelements such as Ca, K is very low and varied from 874 up to 3822 mg kg^{-1} for Ca and from 16.5 to 91.1 mg kg^{-1} for K, which is also characteristics of ultramafic soils, while Cu, Zn, and Pb concentrations in analyzed serpentine soil samples fall within the ranges for normal soils. The Ca/Mg ratio varied from 0.63 to 3.17, which is one more indicator of ultramafic soils.

Keywords: Serpentine soils, heavy metals, ultramafics, metals bioavailability.

1. Introduction

Ultramafics represent magmatic or metamorphic rocks which are characterized by high concentrations of Mg, Fe, Ni, Cr and Co and low concentrations of Ca, and K and contain less than 45% silica (SiO2).

The term "serpentine" strictly speaking refers only to the serpentine group of minerals (including antigorite and chrysolite) which have the general formula ($Mg_3Si_2O_5(OH)_4$ and which are important constituents of weathered "ultramafic rocks". These minerals are derived from the "serpentinization" of ultramafic rocks. Rocks which are rich in serpentine minerals derived from alteration of previously existing olivines and pyroxenes are known as "serpentinites". Serpentinites are rocks that form as a result of metamorphism or metasomatism of primary magnesium–iron silicate minerals.

Throughout the territory of Kosovo there are many basic and ultra-basic rocks, which are known by their common name as "serpentine". The aim of this study was to determine the content of heavy metals and other macro elements in some of serpentine soils of Kosovo and finding out bioavailable Ca/Mg relationship as well, which is very important indicator for normal plants development.

The studied area of serpentine soils includes three separate zones with an area of 15.67 km^2 which is 7.66 % of total serpentine soils of Kosovo

1.1. Chemical properties of serpentine soils - the serpentine factor

The serpentine factor may be defined as the causal factor or factors (physical or chemical) related to the infertility of serpentine soils. The general infertility of serpentine soils may also be defined as the serpentine problem" Brooks [4] and Kazakou [6] presented three of the most popular hypotheses to explain the edaphic factors which may control serpentine floras: 1) Low availability of calcium relative to magnesium; 2) Deficiency of essential macronutrients; 3) High levels of phytotoxic heavy metals (Ni, Cr, Co, Mn).

a) The toxicity of Magnesium

The high level of Magnesium was considered to be one of the most likely negative causes of the

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serpentine problem. This subject has been presented in detail by Krause [7] and has been known over past 150 years. Part of this toxicity comes from the very high magnesium concentration of some soils, which can be up to 36% MgO. According to my results at studied areas content of total Mg is in range of 16-19.4% [13].

b) Deficiency of Calcium

The concentration of calcium in serpentine soils is extremely low and in some cases is <100 mg/kg. However, low calcium levels are not the primary cause of serpentine infertility, since the low Ca/Mg quotients is the main cause of the serpentine syndrome. Experiments which were done by Proctor [11] have proved that addition of calcium can largely reduce the incidence of nickel toxicity symptoms in vegetation. Ca content in serpentine soils of Kosovo is 628.83-5422.27 mg kg^{-1}[13].

c) Unfavorable Ca/Mg Quotient

Loew & May [9] first reported that poor productivity of serpentine sites is due to the low Ca:Mg ratio present in serpentine soils. From their experiments, they concluded that the Ca:Mg ratio must be at least unity for optimal growth. The bioavailable Ca/Mg ratio in studied serpentine soils of Kosovo is in range of 0.63-3.17 [13].

2. Materials and Methods

The sampling was conducted on June 2014. Three serpentine areas have been surveyed and 7 soil samples in total have been taken in various depths of soil profiles. Soil samples were chosen by eye based on the presence of the plants. All soil samples were air-dried ground and sieved to 2 mm, then transported in polyethylene bags to the laboratory for analyzing

Those samples were analyzed for total Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb, Fe and Zn. Results showed that each site exhibited a high concentration of one or more heavy metals.

The first site that was investigated is Vejshtine that is situated in west-south of Kosovo. This area lies at an altitude of 632 m. above sea level and belongs to continental climate. The average annual precipitation attains 604 mm. The average temperature is 10 ^{0}C with minimum -1.3 ^{0}C on January and maximum 20.4 ^{0}C on July. The zone is vegetated with a poor coverage of plants. In this area one soil profile was opened and 2 soil samples were taken one for each horizon. The depth of profile was 0.6 m under which there was bedrock. The second investigated area is Çabër that is situated in south part of Kosovo at an elevation of 587 m.

In this area was also opened one soil profiles and 3 soil samples taken. The third area is called Radoniq a location that is situated in the western part of Kosovo, at an elevation of 455 m. In this sampling site was opened one soil profile and 2 soil samples were taken at two different horizons. All soil samples were air-dried ground and sieved to 2 mm. Then they were mineralized with a microwave digester. Conditions for mineralization were 6 ml HCl, 2 ml HNO_3, and 3 ml H_2O_2, per 0.5-g soil. Soils were air-dried and sieved to 2 mm. Total major (Ca, Mg) and trace elements (Ni, Cr, Cu, Zn, Co, Pb, Cd, Fe and Mn) were determined in mineralization solution by atomic absorption spectrophotometry. Ni, Ca, Mg and K bioavailability in different soil samples was extracted by Mechlich 3 method.

3. Results and Discussions

a)Trace elements

The serpentine soils at all sites were characterized by elevated levels of heavy metals that show typical properties of ultramafic environments

Results showed that each site exhibited a high concentration of at least one heavy metal. The maximum concentrations of Cd in soils dry matter (DM) were 108.9 mg kg^{-1} it is varied between 8.9 and 108.9 mg kg^{-1}.

DM and was relatively high compared to the values generally observed in non-serpentine soils and considered as toxic according to Kabata-Pendias [5]. The highest value was observed at Çabër location.

Cr concentrations in soils were also elevated and varied from 218 to 1206 mg kg^{-1} DM.

Total Ni availability at studied areas varied from 1543 and 2570 mg kg^{-1} respectively, whereas bioavailable Ni is on range of 37.71 mg/kg and 101.04 mg/kg respectively (Çabër).

The Mn content at all sites was quite homogenously distributed and varied between 508-1013 mg kg^{-1}

Co presence on soil varied from 49.5-95.8 mg kg^{-1} and is within the normal range for mafic rocks. Relatively easy interactions of Co with all metals that are associated geochemically or biochemically with Fe have a significant impact on its behavior in soils and its phytoavailability [5].

Iron concentration at all sampling sites show typical ultramafic characteristics and varied from 2.43-6.28%

While most of the total Cu, Zn, and Pb concentrations in analyzed serpentine soil samples fall within the ranges for normal soils

Robinson *et al.* [12] and Brooks [4] suggested that high levels of phytotoxic elements such as nickel, chromium and cobalt in serpentine soils were responsible for their infertility.

There are several factors that contribute to phytotoxicity of heavy metals and their mobility through the soil horizons. One of the most important factors is pH of the soil. In this study pH of the samples is predominantly basic and varies from 7.58 to 8.64, which shows that heavy metals mobility through the horizons of soil profile is very low as regards pH readings.

If we refer the papers published by Bani [1, 2, 3] serpentines soils of Albania do not show any big difference on Ni concentration (1370-3240 mg kg^{-1} and 1658-3077 mg kg^{-1}) compare to Kosovo's serpentine regions (1543-2570 mg kg^{-1}). Also if we compare the general presence of heavy metals in soils of Albania based on Shallari's [14] paper, there is no big difference on their concentrations.

Table 1. Heavy metals concentrations and pH in soils

Site	mg kg^{-1} DM								
	Zn	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**Mn**	**Cr**	**pH**
Vejshtine HA	32.7	8.9	62.9	24.0	1543	21.7	1013	1150	8.58
Vejshtine HB	26.6	84.3	71.5	21.4	2008	9.1	780	1206	8.64
Çaber HA	39.0	103.1	82.8	14.4	2235	11.2	910	680	7.95
Çaber HB	31.7	108.9	95.8	10.0	2570	9.2	898	218	7.88
Çaber HC	25.7	94.8	54.2	5.4	1865	9.0	563	260	7.97
Radoniq HA	31.7	67.2	78.8	9.2	2234	20.7	965	770	7.58
Radoniq HB	20.4	66.8	49.5	8.3	1576	9.3	508	399	7.79

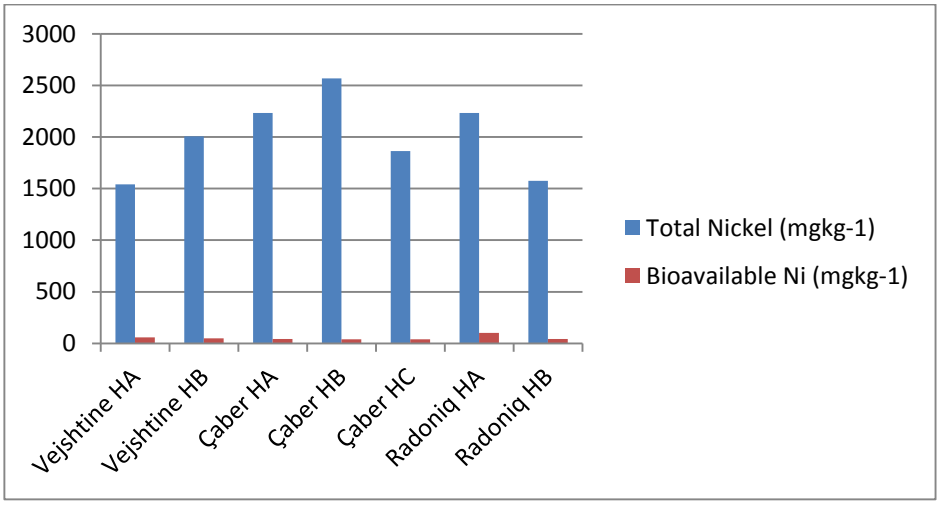

Figure 1. Total and Bioavailable Nickel proportion on serpentine soils

b) Macroelments

Concerning the concentrations of major elements (N, P, K Fe, Ca, and Mg) in soil samples (Table 2), the soils were more or less of typical ultramafic composition.

The table 2 below which represents macronutrients on first horizon of the sampling site show very low level of nitrogen in serpentine soils of Kosovo. Nitrogen content varied from 440 to 2560 mg kg^{-1}

The serpentine soils were also rich in Mg, but deficient in Ca. The concentrations of total Mg varied from 16 -19.4 % Mg and from 0.06 to 0.54% Ca on a DM basis. The phosphorus concentration varied from 95 to 1640 mg $kg^{-1.}$ Concerning the concentration of P and K, most of the soil samples are characterized by low level of these nutrients, which is a general characteristics of ultramafic soils [4, 15]

The low concentrations of available phosphorus in serpentine soils may possibly be connected to the high affinity of soluble phosphates to serpentine [4].

Potassium content is given in table 2 and show very low level of this essential element for the normal flora development.

Moreover content of bioavailable macro elements such as Ca, K is also very low and varied from 874 and 3822 mg kg^{-1} for Ca and from 16.5 to 91.1 mg kg^{-1} for K, which is also a characteristic of ultramafic soils. The available Ca/Mg ratios in four soil samples are relatively low (0.63–0.92), while in three serpentine soil samples higher values of bioavailable Ca compared to Mg (Ca/Mg ratios 1.70 and 3.17) would indicate lower Ca deficiency stress for the plants.

Table 2. Macronutrients in soil

Site	mg kg^{-1} DM			% DM		
	N	P	K	Fe	Ca	Mg
Vejshtine HA	440	105	104.71	4.87	0.37	17.90
Vejshtine HB	-	-	88.63	5.06	0.54	18.70
Çaber HA	510	95	471.75	5.15	0.18	17.80
Çaber HB	-	-	140.91	4.50	0.07	19.20
Çaber HC	-	-	52.26	3.65	0.17	19.30
Radoniq HA	2560	1640	382.63	3.93	0.18	16.00
Radoniq HB	-	-	149.53	2.43	0.06	19.40

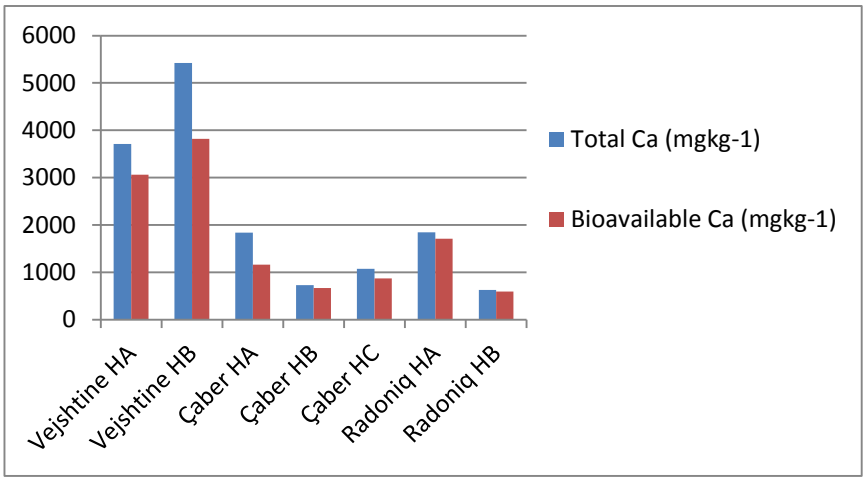

Figure 2. Total and Bioavailable Calcium concentration on serpentine soils

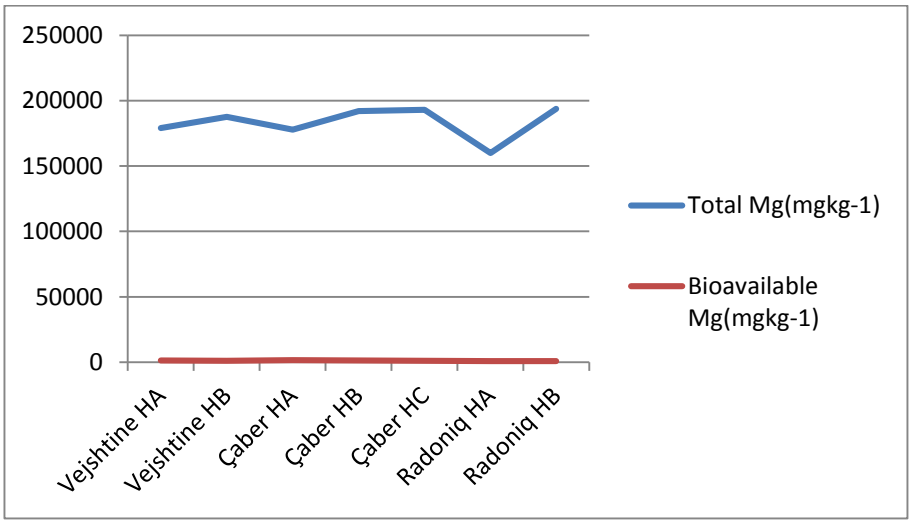

Figure 3. Total and Bioavailable Magnesium proportion on serpentine soils

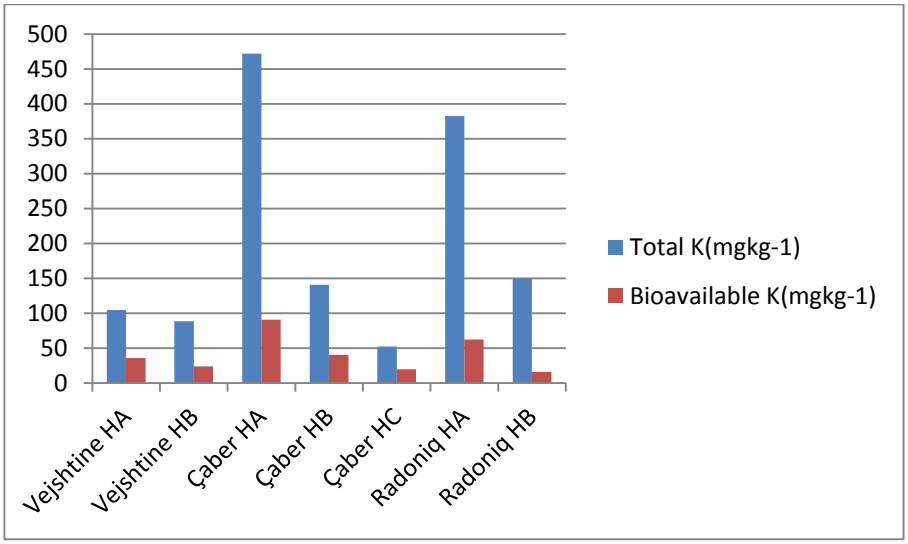

Figure 4. Total and Bioavailable Potassium concentration on serpentine soils

4. Conclusions

Results from the field proved that all of three most popular hypothesis presented by Kazakou [6] are met such as: Low availability of calcium relative to magnesium; Deficiency of essential macronutrients and High levels of phytotoxic heavy metals (Ni, Cr, Co, Mn, Co)

Serpentine soils have properties that are highly unfavorable for most plants. Among these, heavy metal tolerance, especially to Ni, is considered as a crucial factor for plant survival on certain serpentine soils [8, 11]. One strategy to cope with high levels of metals shown by serpentine plants is hyperaccumulation.

As a conclusion the serpentine soils in Kosovo are more or less similar in terms of physical and chemical soil properties to other serpentine soils in Balkans Peninsula.

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