HEAVY METALS CONTENT IN THE SOIL OF THE OSOGOVO MOUNTAIN

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ABSTRACT

The article is dedicated to the ore mining footprint on the environment of Osogovo Mountain in terms of heavy metals' content in the landscapes. Some of the mountain landscapes have been damaged by mining activities in the second half of 20th century and the landscapes have responded to this through change of the geochemical structure. The geochemical status of the landscapes is evaluated on the basis of own field and laboratory research of the territory – collecting soil samples, geochemical analysis, drawing geochemical spectrums and interpretation. The investigated elements are Cu, Zn, Ni, Mn, Co, Cr, and Pb. The heavy metals' content in the selected landscapes is identified. In addition, the identified geochemical background of the mountain is compared with some neighboring mountainous areas and the major rock types in Bulgaria. The depicted geochemical status of soils as the focal point of the landscapes in the Osogovo Mountain displays the significant human impact on the environmental status of the mountain and potential threat to the health and life of people.

Keywords: landscapes, human impact, contamination, mining, geochemistry

INTRODUCTION

The complicated and unfriendly geopolitical relations between Bulgaria and the neighbouring Yugoslavia and Greece caused the isolation of the border areas (in South West Bulgaria) from the active manmade impact on the environment almost for the whole 20^{th} century. The processes of human depopulation became more intensive in the middle of the previous century. The lack of people forced recovery for many of the mountain landscapes in terms of vegetation and wildlife but not for all.

Even almost depopulated, the Bulgarian part of the Osogovo Mountain was an object of massive human impact caused by mining. The lead and zinc-rich ores in the mountain's petrography were the reason the government to start mineral extraction. This activity was as an economic act as well as an environmental damage. Even the financial collapse of the state-owned mining company operating in the mountain triggered the end of the mining (in the end of the last century) the geochemical footprint on the landscapes is still there. The environmental status of the mountain territory (in Bulgaria) has been investigated by geographers from Sofia University (2011-2018). The landscapes in the Osogovo Mountain (including soils, plants, and river sediments) have been researched for contamination with heavy metals. The presented work is a follow-up article of a long-term geochemical research of the landscapes in South West Bulgaria since 1989 [5, 6, 15].

METHODOLOGY

The geochemical research of the landscapes allows scientists to approach a lot of ongoing environmental (and social) issues. They are a tool for monitoring of nature.
The methodological base of this investigation is the (geo)system approach [11, 7]. It is conducted through the analysis of chemical elopements' content in the landscape components and the relation between neighbouring landscapes. The soil is a focal point of the landscape where all processes are "printed" and "saved" because of its property to absorb substances. The geochemical research of soil evaluates its chemical properties and there for is an environmental indicator. The lack or the overconcentration of elements may be a sign of human impact that has damaged the environment.
The chemical elements' content in the various rocks and soils does not match lithospheric clarke (the average chemical element's content in the lithosphere). That is why the coefficient of clarke concentration (CC) is used as a way of outlining the abundance or the lack of particular elements in rocks and soils. It is the proportion between the chemical element's content in a particular natural component (Ci) such as a rock, soil, water, plants, etc. and the lithospheric clarke (C). The CC value could be equal to 1 or bigger (CC = > 1). If it is bigger that means that there is concentration of a particular chemical element in comparison to the average in the lithosphere. If CC is less than 1 (CC < 1) the means that there is clarke dispersion (CD) of a particular chemical element in comparison to the average in the lithosphere.
Both CC and CD are used for interpretation of the geochemical analysis of soil samples collected in representative landscapes during a field trip in the Osogovo Mountain (2018). These two indicators are displayed by geochemical spectrums. The selected association of chemical elements includes Cu, Pb, Zn, Ni, Co, Cr, and Mn.
The collected soil samples are chemically analyzed in the Geochemistry Laboratory of Sofia University. They are dried, quartered, levigated in porcelain cup, and sift through 63 µm, burned at 500°C, and dissolved by a mixture of acids ($HClO_4$, HF, and HCl). The heavy metals content in the chemical solution is obtained by the method of atomic-absorption spectrometry (Perkin-Elmer 3030). The pH values are derived from water solution at ratio soil:water 1:2,5 after period of 18 hours.

RESULTS AND INTERPRETATION

The results of geochemical analysis of the soil samples for the content of heavy metals (a selected association) is displayed in Table 1.
The study encompasses the hypsometry between 1280 and 2251 m. The microelement chemical content of the soil types of Cambisols and Umbrosols is found. A comparison of the heavy metals content is made between the geochemical status of the Osogovo Mountain and other geographical areas (including some neighboring mountains in Bulgaria) (Table 2). Based on this data a set of geochemical spectrums is drawn.
An important element of the interpretation is the consideration of the bedrock chemistry and its influence over the microelement content of the soils. In many cases, especially in the so-called natural background areas, this correlation is the most important for the radial differentiation of heavy metals in the soil profile. The average content of some microelements in the rock types in the Osogovo Mountain are outlined in Table 3 [3]. The dominant rock complexes the mountain are either igneous rocks from the Osogovo granitoid pluton (Oligocene) or metamorphic rocks such as mica schists (Miocene) and gneisses and amphibolites (Oligocene).

Table 1. Content of heavy metals in the soils for the Osogovo Mountain (in Bulgaria)

Landscape and soil type	Location	Cu	Zn	Pb	Mn	Ni	Co	Cr	pH
Beech forest, left bank of river Eleshnitsa, (0-10 cm), Cambisols	42º8′20″N 22º33′58″E 1300 m	380	144	62	586	11	28	18	5
Beech forest, left bank of river Eleshnitsa, (30-40 cm), Cambisols	42º8′20″N 22º33′58″E 1300 m	266	104	71	386	120	19	19	5
Beech forest, left bank of river Eleshnitsa, (70-80 cm), Cambisols	42º8′20″N 22º33′58″E 1300 m	69	69	53	621	85	12	20	6
Ridge of mountain, near Shapka Peak, (0-10 cm), Umbrosols	42º10′52"N 22º34′19″E1 860 m.	19	73	51	232	31	13	28	5
Beech forest "Tsarna Reka" reserve, (0-10 cm), Cambisols	42º9′49″N 22º33′35″E 1600 m	18	159	70	749	74	11	25	5
Ridge of mountain – a watershed between catchments of river Tsarna and river Eleshnitsa, (0-10 cm), Umbrosols	42º9′28″N 22º33′14″E 1920 m	46	156	111	552	99	18	209	5
Mixed deciduous forest in the valley of Kyustendilska Bistritsa, (0-10 cm), Cambisols	42º12′13"N 22º32′45″E 1280 m	20	151	58	236	17	7	22	5
Mixed deciduous forest in the valley of Kyustendilska Bistritsa, (20-30 cm), Cambisols	42º12′13"N 22º32′45″E 1280 m	22	96	73	195	27	9	24	5
Mixed deciduous forest in the valley of Kyustendilska Bistritsa, (50-60 cm), Cambisols	42º12′13"N 22º32′45″E 1280 m	49	185	703	441	75	7	20	6
Peak Ruen, (0-10 cm), Umbrosols	42º15′80"N 22º51′63″E 2251 m	26	126	154	573	117	7	27	4
Near a tailings dam, (0-10 cm), Anthropo-genic soil substrate	42º14′12″N 22º28′15″E 930 m	92	138	1656	1018	62	2	3	3

Table 2. Average content of heavy metals in selected areas (mg/kg)

Area	**Cu**	**Zn**	**Pb**	**Mn**	**Ni**	**Co**	**Cr**
Lithosphere	47	83	16	1000	58	18	83
Soils of world[16]	20	50	10	850	40	8	100
Soils of Europe[12]	17	68	33	810	37	10	95
Soils of Bulgaria[4]	30	75	35	1000	36	20	70
Soils of Bulgaria (natural background)[8]	24	67	25	695	32	16	60
Soils of Vlahina Mountain[14]	12	350	21	688	123	41	74
Soils of Maleshevska Mountain[13, 15]	27	94	26	304	32	9	37
Soils of Ograzhden Mountain[9, 10]	19	103	41	371	45	6	36
Soils of Osogovo Mountain	91	126	141	457	66	13	41

Table. 3 Average content of heavy metals in rock groups in Bulgaria (mg/kg)

Rock groups	**Cu**	**Zn**	**Pb**	**Mn**	**Ni**	**Co**	**Cr**
Rocks in Bulgaria	32	53	26	743	77	16	108
Acidic igneous rocks in Bulgaria	8	28	30	370	6	3	8
Acidic metamorphic rocks in Bulgaria	20	50	20	287	10	11	34

The first spectrum (fig. 1) illustrates the concentration and the dispersion of microelements in the lithosphere, the soils in the world and in Europe as well as the soils in the Osogovo Mountain. It displays the accumulated association of heavy metals (Pb, Cu, Zn, Ni, and Co) in the soils of the mountain. Only Mn and Cr have values related to clarke dispersion (CD) about 2. The outlined association is related to the mineral content of the existing ore deposits in the mountain [2, 1], to the igneous and the metamorphic rocks, and to the soil-forming processes in the high altitudes.

One of the tasks of the research is the determination of the natural geochemical background of the landscapes considering the local petrochemical influence. A geochemical spectrum (fig. 2) displays the average content of heavy metals in the soils of the Osogovo Mountain compared to the average content of the soils in Bulgaria. The value of soils of Bulgaria represents the whole territory of the country while the value of the soils of Bulgaria (natural background) is related only to the landscapes in conservation zones (reserves, national parks, etc.). Generally, almost the same association of heavy metals is outlined as concentrated (except Co). Mn, Cr, and Co are with similar levels of dispersion. This comparison is another proof for the specific geochemistry of the rock complexes in the investigated mountain and their influence on the chemical content of the soil.

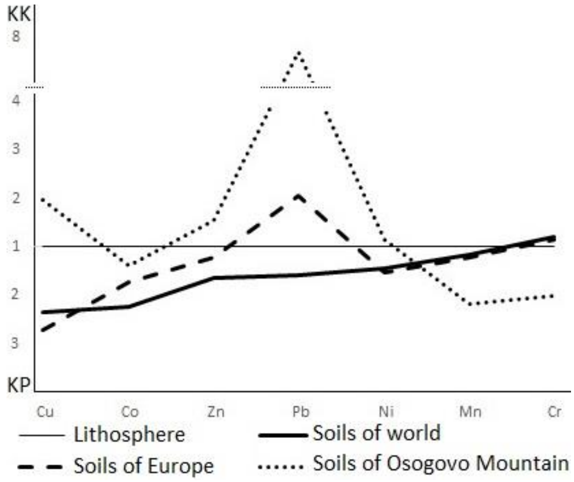

Figure 1. Geochemical spectrum of soils in the world, in Europe, and in the Osogovo Mountain

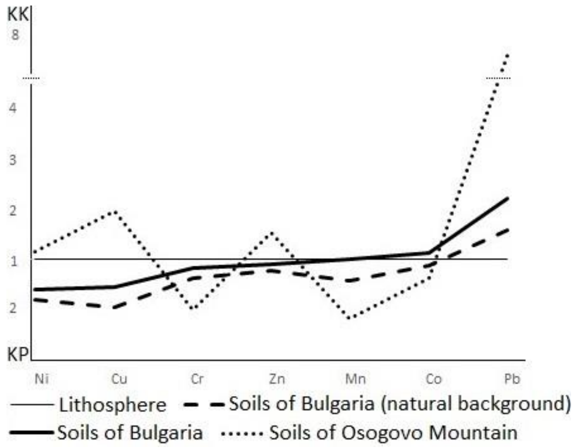

Figure 2. Geochemical spectrum of soils in Bulgaria, in Bulgaria (natural background), and in the Osogovo Mountain

The results in the Osogovo Mountain are a base for a comparative analyze to other neighboring mountains on the border between Bulgaria and North Macedonia that where investigated earlier (Vlahina Mountain, Maleshevska Mountain, and Ograzhden Mountain). The geochemical spectrum (fig. 3) displays variations of clarke concentration and clarke dispersion for heavy metals in the researched mountains. The values for Pb (CC over 8) and zinc (CC about 2) are highest in the Osogovo Mountain. The geochemical status of Osogovo Mountain is relatively close to the that in the Vlahina Mountain. The other investigated chemical elements have relevant and correlated values in all of these mountains.

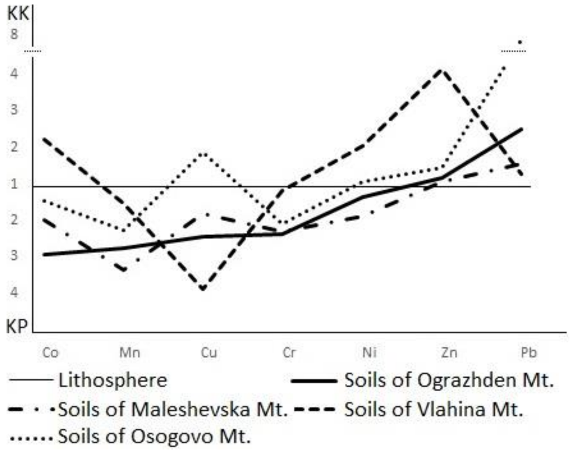

Figure 3. Geochemical spectrum for soils in mountains in South West Bulgaria

The technogenic geochemical influence is mostly visible in the analysis obtained from the soil substrate in the tailings dam around village of Gyueshevo (Table 1). The content of Pb, Zn, and Mn is relatively high and it is a probable consequence of technogenic impact on the landscapes. The high acidity and the open-air dried tailings dam are factors for heavy metals' contamination of landscapes in the area around via either water or air streams.

The radial differentiation of microelements in the soil profile of Cambisols in a beech forest at altitude of 1300 m shows the higher concentration of Zn and Cu in A horizon than in B and C horizons (Table 1). The other elements have relatively equal distribution in the profile.

CONCLUSION

The conducted geochemical research of the soil displays the special distribution of heavy metals' content in the Osogovo Mountain's landscapes. The results show the concentration and the dispersion values of heavy metals in the mountain in comparison to other geographical areas. There is well-defined association of concentrated microelements (Pb, Cu, Zn, Ni, and Co) in the soils of the mountain due to the local petrology. Some areas of the mountain are impacted by mining and there are concentrations that certify the human impact on the geochemical structure of the landscapes in the mountain.

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