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Content of Heavy Metals in the Soils of the Aragats Mountain Range

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ABSTRACT

The article considers the content and distribution patterns of heavy metals in the soils of the Aragats mountain range. The presence of heavy metals in various types of soils and migration along the soil horizons have been established based on the results of the research study. According to the content of soils, heavy metals are arranged in the following row: *Zn>Cu>Pb>Co>Mo>Cd*. The content of gross and mobile forms of heavy metals in the soils varies unevenly from top to down depending on the nature of the metals. The correlation link between the content of humus, reaction of the environment, mechanical composition of soils, gross forms of nutrients and the content of metal forms (*r=0.63±0.015 - 0.73±0.011*) has been revealed.

Introduction

Heavy metals (trace elements) play a special role in the biosphere. Existing predominantly in a scattered state, they can form local accumulations, where their concentration is hundreds and thousands of times higher than average planetary levels. Metals, being present in living organisms in negligible amounts, perform very important functions, being included as a compound of biologically active substances. The ratio of the concentrations of metals in organisms has been developed throughout the course of the evolution of the organic world (Bowen, 1979). Significant deviations from these ratios cause negative, often disastrous consequences for living organisms. Being one of the main natural resources, the main condition for the maintenance and development of modern civilization, metals form a group of the most dangerous pollutants of biosphere ecosystems. Therefore, identification of patterns (regularity) determining the content and migration of heavy metals in the biosphere, is one of the most important objectives for the protection of nature resources, including soil (Beijer, et al., 1986, Perelman, et al., 1999, Chernykh, et al., 2003, Hunanyan, et al. 2020).

Metal content in natural unpolluted soils is due to a number of factors, the main of which are the direction and intensity of soil formation process, their content in the parent rock, as well as due to the high content of heavy mineral fraction

and clay minerals, soils with heavy texture, richness in colloids and the presence of organic matters (Davtyan, et al.,1961, Mkrtchyan, et al., 2020, Perelman, et al., 2000, Sedykh, et al., 2011, Jhangiryan, 2015, Ghazaryan, et al., 2018).

It should be noted that under conditions of anthropogenic burden, the establishment of normal and toxic levels of metal content in soils is quite an urgent task.

The aim of the research is to study the heavy metal contents and their distribution throughout the soils of the Aragats mountain range.

Materials and methods

Aragats mountain range is located in the northeastern part of the Republic of Armenia at an altitude of 2000-3600 m above the sea level. The investigated territory is characterized by a cold mountain climate. The average annual air temperature is 1-3°C. Annual precipitation is 450-800 mm, which increases from bottom to top. Mount Aragats is the highest extinct volcano in Armenia (4090 m above the sea level), the lavas of which occupy a rather large area. The peak of Aragats is composed of andesite-dacites, dacites and their tuff breccias, and the slopes are covered with andesites, basalts, dacites and tuff slags (Babayan, et al., 1961, Davtyan, et al., 1961).

Mountain-meadow and meadow-steppe soils and their subtypes are widespread on the territory of the Aragats mountain range. Meadow-steppe soils are represented by two subtypes: meadow-steppe typical and meadow-steppe chernozem-like (Edilyan, 1976, Mkrtchyan, et al., 2020).

The soils of the Aragats mountain range served as a study object in this research. To study the agrochemical indicators of soils and the content of heavy metals (*HM*), stationary plots were selected at different heights and exposures, on which soil pits (profile cuts) and half-holes were laid. Analyses were carried out according to the methods generally accepted in agrochemical practice. Humus content was determined according to Tyurin method, gross nitrogen - according to Kjeldahl, phosphorus and potassium-according to Lorentz, reaction of the medium (*pH*) - with a potentiometer, the mechanical composition of soils-according to Robinson method (Arinushkina, 1970, Dospekhov, 1973).

The content of gross forms of heavy metals (HM) was determined by spectral emission, neutron activation methods (Ivanov, et al., 1979), and mobile forms - by atomic absorption method using a spectrophotometer "AAS-1" (Dueck, et al., 1984, Guidelines for the Determination of Trace Elements in Soils, Feed and Plants by the Method of Atomic Absorption Spectroscopy, 1985, Taylor, 2001).

To compare the content of HM forms, the MPC indicators (maximum permissible concentration) were taken as a basis (Chernykh, 2009, Chernikov, 2009):

Pb: gross forms - 32 mg/kg, mobile forms - 6 mg/kg,

Zn: gross forms -65 mg/kg, mobile forms -4 mg/kg,

Cu: gross forms -60 mg/kg, mobile forms-10 mg/kg,

Cd: gross forms - 2 mg/kg, mobile forms -1 mg/kg,

Mo: gross forms-10 mg/kg, mobile forms -2 mg/kg,

Co: gross forms -12 mg/kg, mobile forms-2 mg/kg.

The logarithmic function describing the change in the degree index of the heavy metal contents depending on degree variations was used as an estimating function for the studied sections (soil profiles) and the calculations were conducted using the following equation:

$$y = \log \alpha x,$$

where α is some fixed positive number, different from 1.

Results and discussions

Section 1 is located in the mountain-meadow-soddy soils at an altitude of 3171 m above the sea level on the southeastern slope of Mount Aragats, a relatively flat shield-like terrace. The vegetation is covered by a grass-forbs carpet meadow with a predominance of *Festuca ruprechtii, Campanula tridentata* and *Taraxacum stevenii*. Mountain-meadow-soddy soils are characterized by a high content of humus (organic matter) - higher in the upper layers of the soil sharply decreasing towards its depths. The reaction of the salt suspension approaches to strongly acidic (*pH* 4.1-4.4), the soil is distinguished by a light mechanical texture. The content of gross nitrogen is from 0.82 to 0.09 %, phosphorus – 0.33-0.13 % and potassium – 1.24-1.66 % (Table).

The content of gross forms of heavy metals (HM) in the soil profile is not evenly distributed, which is undoubtedly associated with the presence of humus (organic matter) and the composition of the parent rock. Thus, the content of gross copper along the soil profile ranges from 38.0 to 21.0 mg/kg, lead content - 17.2-8.6 mg/kg, zinc content – 49.0-30.2 mg/kg, cobalt – 7.6-6.6 mg/kg, molybdenum – 1.3-1.0 mg/kg, cadmium – 1.80-0.64 mg/kg. The contents of mobile forms are 5.0-2.0, 2.6-0.48, 3.9-1.6, 1.56-0.20, 0.56-0.26, 0.40-0.12 mg/kg, respectively (Figure 2).

Table. Agrochemical indicators of the soils at the Aragats mountain range*

Soil type, section №, height above the sea level	Horizon, cm	Humus, %	pH	<0.01, %	Total nutrient content, %		
					N	P_2O_5	K_2O
Mountain – meadow - soddy, 3171, № 1	0-12	20.70	4.1	25.42	0.82	0.33	1.24
	12-33	3.90	4.2	19.32	0.39	0.29	1.37
	33-60	1.50	4.4	10.94	0.09	0.13	1.66
Mountain - meadow, soddy-peaty, 3000, № 2	0-9	31.02	4.2	14.68	1.79	0.56	1.20
	9-16	11.20	4.3	23.72	1.76	0.42	1.46
	16-32	7.06	4.3	32.14	0.78	0.44	1.73
	32-43	6.15	4.4	27.86	0.41	0.50	1.20
Mountain-meadow, weakly soddy, 2800, № 3	0-15	7.9	5.3	24.75	0.75	0.42	1.06
	15-42	4.4	5.6	23.80	0.57	0.39	0.66
	42-68	2.4	5.6	23.34	0.39	0.66	1.3
	68-83	0.83	5.7	19.62	0.17	0.29	1.6
Meadow-steppe typical, 2500, №4	0-16	9.60	6.4	47.42	0.80	0.26	0.84
	16-28	6.39	6.2	31.47	0.46	0.18	0.71
	28-64	3.07	6.4	27.80	0.54	0.26	0.96

*Composed by the authors.

The correlation link between the humus content and the accumulation of HM (*r=0.63±0.015)* in the soil was identified.

Section 2 is located in the northwestern slope of Aragats mountain-meadow, soddy-peaty soils at an altitude of 3000 m above the sea level. The vegetation cover mainly contains Carex and forbs with *Taraxacum stevenii* and *Ranunculus aragazi*. In the upper horizons mountain-meadow and soddy-peaty soils are characterized by a high content of organic matters (humus), by 31.02 % sandy loamy, light and medium loamy texture, the reaction of the environment is close to weakly acidic and neutral. The amount of gross nitrogen is from 1.79 to 0.41 %, that of phosphorus - 0.56-0.42 % and potassium content - 1.73-1.20 % (Table).

The content of gross forms of heavy metals is insignificant as compared to that of in ***Section 1***, and the distribution of metals along the soil profile decreases evenly (Figure 1). The content and distribution of mobile forms of HM in the soil profile depends on the number of their gross forms (Figure 2).

Section 3 is located in mountain-meadow, weakly soddy soils at an altitude of 2800 m above the sea level, on the southern slope of Mount Aragats, with a steepness of 5-7°, a herb carpet with a predominance of *Campanula tridentata*, *Taraxacum stevenii, Carum caucasicum, Cirsium esculentu;* sometimes *Festuca ruprechtii* is also found here. The exchangeable acidity of the studied soils is quite high; in the upper horizons the humus content is much lower (7.9 %) and sharply decreases in depths. The content of gross nutrient forms (*N, P_2O_5, K_2O*) is 0.75-0.17 %, 0.66-0.29 %, 1.6-0.66 % respectively (Table). The high content of the gross forms of HM (*Cu, Pb, Co, Mo, Cd*) in the upper humus (0-15 cm) horizons is characteristic (typical) to copper, lead, zinc, cobalt, molybdenum and cadmium (Figure 1).

Section 4 is located in meadow-steppe typical soil, at an altitude of 2500 m above the sea level on the southeastern slope of Mount Aragats. Meadow-steppe typical soils are mainly characterized by medium and heavy loamy mechanical texture, high humus content (9.60 %), weakly acidic reaction medium (*pH* 6.2-6.4) (Table). Comparing to ***Section 3***, the content of gross copper is 1.02 times higher, while lead - in 1.28, zinc - 1.14, cobalt - 1.26, molybdenum -1.35, cadmium - in 1.72 times higher (Figure 1). The amount of mobile forms of the studied metals falls down with a decrease in the gross forms (Figure 2).

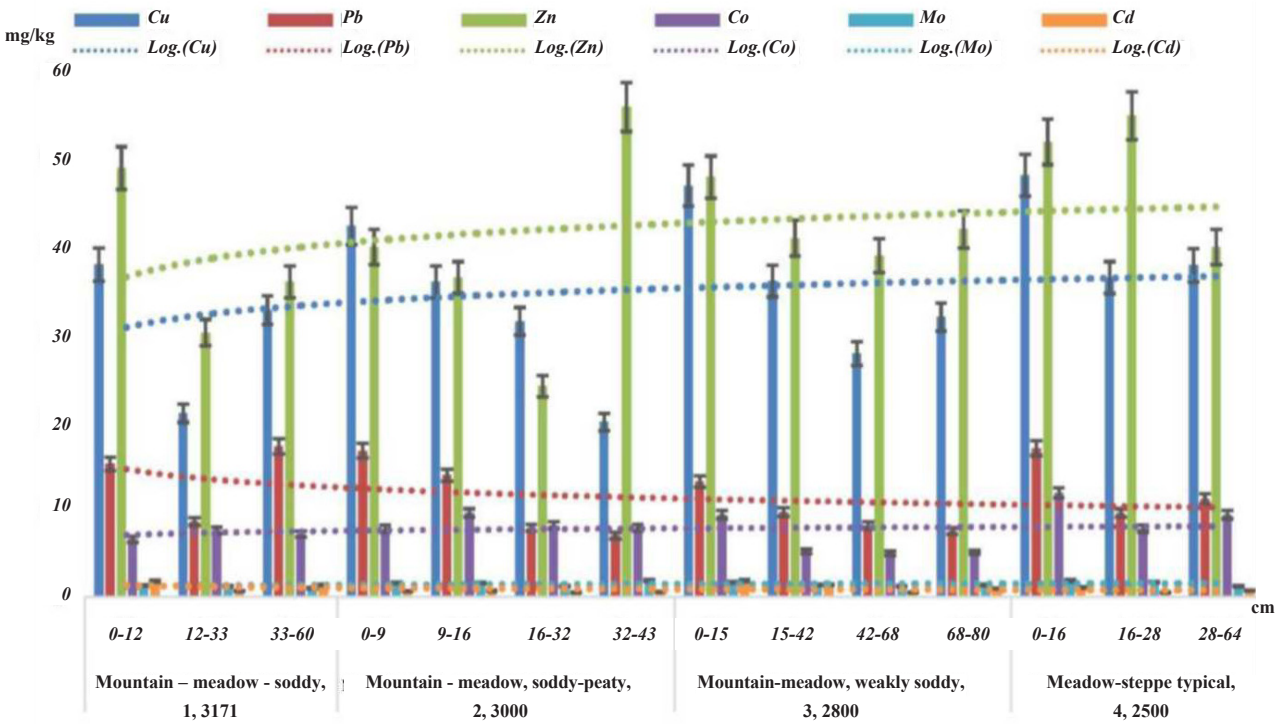

Figure 1. The content of gross forms of trace elements ((HM) mg/kg)) in the soils of the Aragats mountain range (*composed by the authors*)

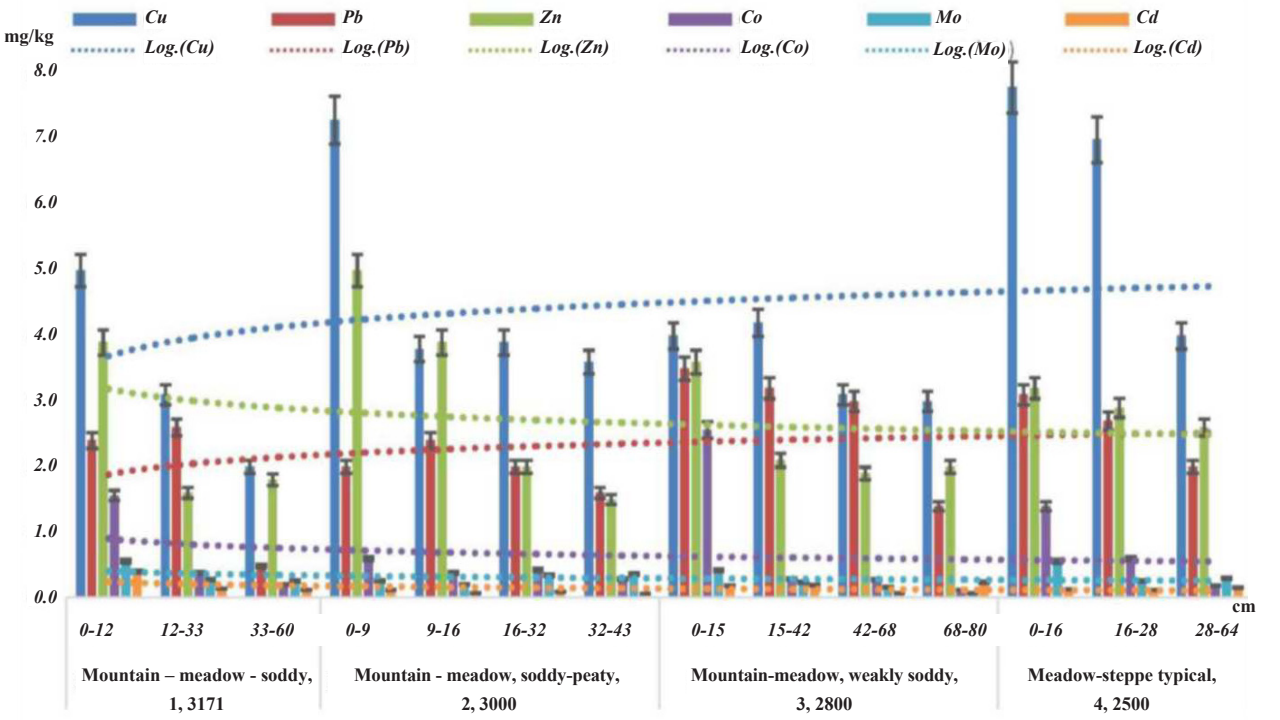

Figure 2. The content of mobile forms of trace elements ((HM) mg/kg) in the soils of the Aragats mountain range (*composed by the authors*)

There is a correlation between the content of gross and mobile forms of HM and the reaction of the environment (*r=0.73±0.011*). Correlation between the agrochemical parameters of soils and the content of HM forms (section *1-r=0.63±0.015*, section *4-r=0.73±0.011*) is typical for all studied sections.

Conclusion

Thus, based on the studies carried out, the following conclusions can be drawn:

1. The content and distribution of the forms of heavy metals in soils are mainly due to the presence of humus (organic matter), mechanical composition, reaction of the environment and the total content of nutrients.

2. According to the content of the soils of the Aragats mountain range, heavy metals are arranged in the following row: *Zn>Cu>Pb>Co>Mo>Cd.*

3. The content of gross (bulk) copper, zinc and lead increases from the top (3171 m) to down (2500 m), the amount of cadmium, molybdenum and cobalt changes uniformly/evenly.

4. The mobile forms of copper and lead are similar with the gross values. The amount of mobile zinc and cobalt decreases, and the amount of molybdenum and cadmium is evenly distributed.

5. The content of gross and mobile forms of heavy metals (*Cu, Zn, Co, Pb, Mo, Cd*) is at the MPC level.

6. The mobility of heavy metals is controlled by acid-base conditions and the amount of organic matter.

7. The bulk (basic mass) of heavy metals accumulates in the upper humus horizons (0-9 and 0-12 cm) of the soil and their content decreases towards the depth.

8. The correlation relationship between agrochemical indicators of soils and the content of heavy metal forms is *r=0.63±0.015-0.73±0.011*.

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