



GENERAL CHARACTERISTIC AND POLLUTION LEVEL OF SOILS IN ECOLOGICALLY VULNERABLE MINING AREAS AROUND KAPAN TOWN IN ARMENIA

K. A. Ghazaryan, H. S. Movsesyan and K. V. Grigoryan

Yerevan State University, Republic of Armenia

N. P. Ghazaryan

State Committee of Science, Ministry of Education and Science, Republic of Armenia

G. A. Gevorgyan

National Academy of Sciences, Republic of Armenia

Kapan town is situated in the south-east of the Republic of Armenia. The lands of the area belong to the type of mountain cambisols and fluvisols. The studies revealed that the surface of soils was well covered by vegetation in this area and the naked soils generally made only 0-32% in all. Studied soils were basically weakly eroded and the degree of erosion was fluctuating within the range from non-eroded to medium eroded. They were classified from fine to coarse according to texture. In some soil samples much stoniness has been observed. At the time of studies the root systems in soil samples were classified from bad to well developed. The pH of studied soil samples was from slightly acidic to slightly alkaline and ranged from 6.71 to 8.04. The content of humus ranged from 1.13 to 10.53% in the upper A horizon, and from 0.74 to 5.60% in the B horizon. The study of pollution of soils with heavy metals and metalloids revealed the significant increase in contents of As and the following metals: Fe, Mn, Co, Ni, Cu, Zn, Cr, Hg, Sb, Mo, Cd, Pb compared with control sample. Experiments have led us to the assumption that pollution of soils with mentioned elements in studied territory is conditioned by human activities, particularly by mining and smelting industries.

Keywords: Heavy metals, Soil pollution, Land degradation, Mining and metallurgical industries.

Introduction

Mining industry is developed in the Republic of Armenia. The mining industry has been the mainstay of the economy of Armenia for over 20 years. Since the late 20th century, the mining and beneficiation of minerals, particularly copper and gold, have been the driving force behind economic development, particularly in Kapan town. Kapan town is situated in the south-east of Armenia. Nowadays, the pressures of human activities on natural landscapes has reached such a level that their qualitative and quantitative properties are affected significantly. Mining

operations give rise to a number of serious environmental effects. In most cases, the impact of mining on the environment is at both regional and local level. This economic sphere is the main source of soil pollution with heavy metals/metalloids (Pb, Cu, Ni, Cd, Mo, As etc.) which are considered as dangerous pollutants causing the desertification of soils [4, 5, 8]. One of significant environmental problems is the heavy metal pollution of soil, which affects soil characteristics negatively and leads to the limitation of productive and environmental functions. In particular, heavy metal pollution of soils due to intense industrialization and urbanization has become a serious concern in many developing countries because of its toxicity and threat to human life and the environment [2, 6]. Heavy metals are natural, nondegradable substances and aren't broken down in the environment. Heavy metals also occur naturally, but rarely at toxic levels. Toxic heavy metals entering an ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications [2]. The accumulation of these contaminants in the environment and health risks to humans and living organisms regarding it have become a serious concern [7, 9]. Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Excessive concentrations of heavy metals may induce the serious metabolic changes and disturbance of metabolic processes, and these lead to the lowering of the organism resistibility, the disturbance of allergic and somatic status and the dysfunction of diverse organs and systems.

That is why, the determination of heavy metal concentrations in soils, the establishment of appropriate land-use systems and soil remediation technologies to deal with soil pollution are very important.

The aim of the present work was to implement the monitoring study of soils in ecologically vulnerable mining areas around Kapan town in Armenia. The problem under the study in this region is very urgent and actual because it concerns the preservation of sensitive natural resources, the prevention of the inadmissible contamination of food products and the protection of the health of inhabitants in this region.

Materials and methods

The lands of the study area belong to the type of mountain cambisol. In Armenia, this soil type is distributed 500-1700 meters above sea level, and on arid southern slopes, it reaches up to 2400 meters [1]. The soils of two riskiest sites of this region were investigated (Figure 1):

1. around the Kapan copper-molybdenum combine (samples №№ 01-06);
2. around the tailings storage facility of Geghanush (samples №№ 07-12).

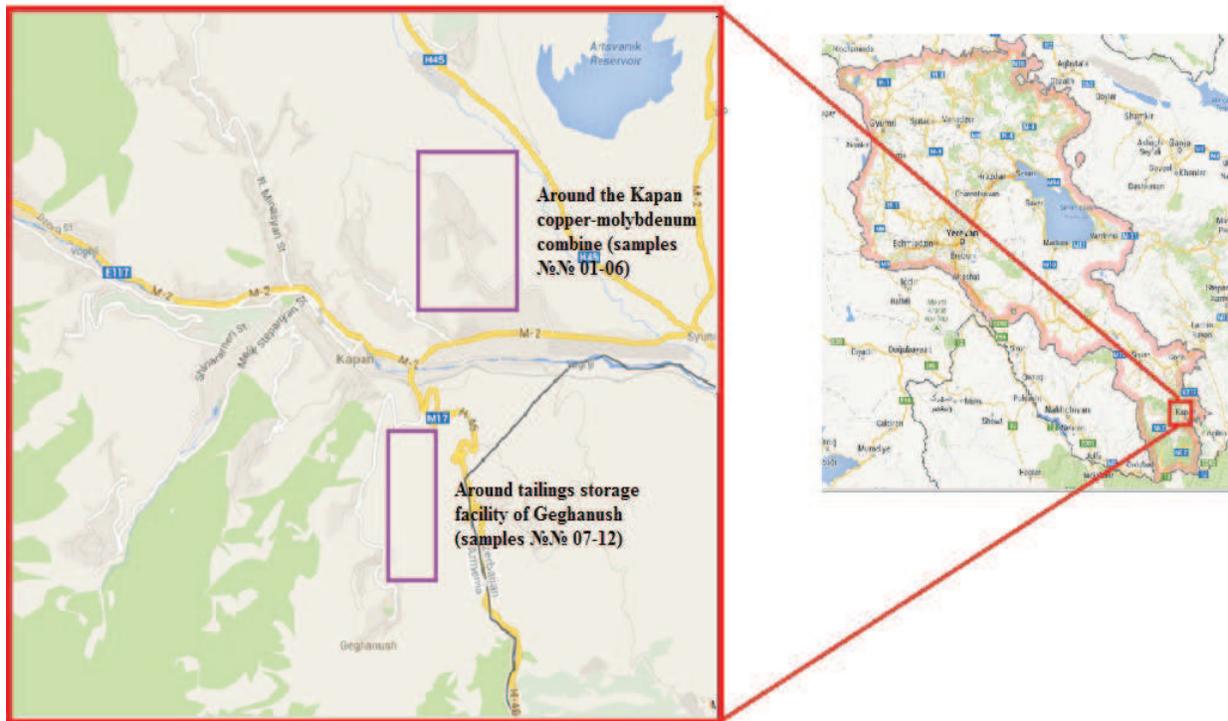


Figure. 1 The map of Armenia showing two sampling areas.

The 12 sections in the horizon A of soil (0-22 cm) were made in selected sites in 2013. The control section was made in the site which was 4 km away from the Kapan copper-molybdenum combine. The sections were made manually. The coordinates of the sampling sites were determined by GPS.

The sampling of the soils was carried out in a traditional way, well-known in soil science. All labware and sampling apparatus were pre-soaked in 5% nitric acid solution followed by distilled water for a day prior to sampling for removing the trace concentrations of metals.

The samples of the soils were taken from a depth of 0-20 cm at 5 m intervals on a grid measuring 20 m x 20 m and with the center point of the grid at the sample location. After the homogenization and removal of unwanted content (stones, plant material, etc.), the samples were air-dried at room temperature, sieved to pass a 1 mm mesh and stored in an all-glass jar for the analysis of their properties.

The pH of the soil was measured potentiometrically with the pH-meter (Hanna, Checker). The determination of the soil texture was carried out by “Feel Method”.

The content of heavy metals was determined by the mass spectrometric method using “ELAN 900” inductively coupled plasma mass spectrometer (ICP-MS).

Geo-accumulation index (I_{geo}) was used to calculate metal contamination level in the soils. The geo-accumulation index (I_{geo}) was originally defined by Müller in 1969, in order to determine and define metal contamination in sediments, by comparing current concentrations with pre-industrial levels. The index is calculated as [2, 3]:

$$I_{geo} = \log_2 C_n / 1.5 B_n,$$

Where C_n is the concentration of the element in the samples, B_n is the background value of the element, and the factor 1.5 is used to take into account the possible lithological variability.

The geoaccumulation index scale consists of seven grades (0–6) ranging from unpolluted to very strongly polluted. These seven descriptive classes are as follows: < 0 = unpolluted; $0 - < 1$ = unpolluted to moderately polluted; $1 - < 2$ = moderately polluted; $2 - < 3$ = moderately to strongly polluted; $3 - < 4$ = strongly polluted; $4 - < 5$ = strongly to very strongly polluted and ≥ 5 = very strongly polluted.

Results and discussion

The data of the field studies indicated that the 13 sections of the soils can be classified into types and subtypes. The soil types in the studied territory were the mountain cambisol with its subtypes and fluvisol:

- a) calcareous mountain cambisol (samples № 01, 02, 03, 06, 08, 11, 12 and control sample),
- b) decalcified mountain cambisol (samples № 04, 07, 09, 10);

fluvisol (sample № 05).

The properties of the studied objects are described hereinafter (Table 1). Calcareous mountain cambisol is the first subtype. This subtype of soil in the studied territories is distributed 821-1001 meters above sea level, on the gradients of 0-30 degrees. The microrelief is smooth, or there are small mounds, except the sample № 11, where there are mounds. Decalcified mountain cambisol is the second subtype. This subtype of soil in the studied territories is distributed 816-894 meters above sea level, on the gradients of 20-34 degrees. The microrelief is smooth, or there are small and medium mounds. Fluvisol is the next type of soil. This type of soil in the studied territories is located on 848 meters above sea level, on the gradient of 0 degrees. The microrelief has small mounds.

The description of each section and their general properties clarified during the field studies are presented in Table 1. According to the data of the studies, the soil surface was well covered by plants, and 0 - 20% of the soil surface was naked, except the sections № 03, 06, 10 and 11, where 30 - 32% of the soil surface was uncovered. The main vegetation in the surroundings of the sections № 02, 03, 04, 05, 06, 07, 08, 09, 11, 12, and the control section was presented by herbage, and the main vegetation near the sections № 01 and 10 was presented by trees and shrubs. The studied soils were basically weakly eroded, except the sections № 05 and 08 where due to sufficient vegetation and 0% surface gradient, the erosion processes weren't developed. Erosion degree in the sections № 09, 10 and 11 was medium, which was conditioned by comparatively high slope gradient (higher than 20 degrees), bad vegetation cover, stoniness as well as anthropogenic load.

Table 1. The general characteristic of the sampling areas.

Sample number	Soil type and subtype	Basin	Surface altitude above sea level (m)	Surface gradient	Microrelief	Exposition	Soil surface cover	Erosion degree (0-4)
01	Calcareous mountain cambisol	Khalaj river	1001	30°	Smooth	NE	Trees - 40%, shrubs - 25%, herbage - 35%	1
02	Calcareous mountain cambisol	Khalaj river	945	16°	Smooth	E	Herbage - 80%, naked soil - 20%	1
03	Calcareous mountain cambisol	Khalaj river	915	12°	Smooth	SE	Herbage - 65%, naked soil - 32%, stones - 3%	1
04	Decalcified mountain cambisol	Khalaj river	894	21°	Smooth	N	Shrubs - 15%, herbage - 80%, naked soil - 5%	1
05	Fluvisol	Khalaj river	848	0°	Small mounds	-	Trees - 30%, shrubs - 20%, herbage - 50%	0
06	Calcareous mountain cambisol	Voghchi river	889	10°	Small mounds	S	Herbage - 70%, naked soil - 30%	1
07	Decalcified mountain cambisol	Geghanush river	860	20°	Small mounds	ENE	Trees - 5%, shrubs - 25%, herbage - 65%, naked soil - 5%	1
08	Calcareous mountain cambisol	Geghanush river	827	0°	Small mounds	-	Herbage - 100%	0
09	Decalcified mountain cambisol	Geghanush river	833	23°	Small mounds	SW	Shrubs - 10%, herbage - 50%,	2

							naked soil - 20%, stones - 20%	
10	Decalcified mountain cambisol	Geghanush river	816	34°	Mounds	SW	Shrubs - 20%, herbage - 15%, naked soil - 30%, stones - 35%	2
11	Calcareous mountain cambisol	Geghanush river	831	27°	Mounds	SSE	Shrubs - 20%, herbage - 35%, naked soil - 30%, stones - 15%	2
12	Calcareous mountain cambisol	Geghanush river	821	5°	Small mounds	-	Herbage - 100%	0
Control	Calcareous mountain cambisol	Khalaj river	986	12°	Smooth	NE	Herbage - 85%, naked soil - 15%	1

The general characteristic of the studied soils is presented in Table 2. The best ratio of clay – sand - silt was observed in the soil samples №01, 02, 03, 04, 06, 08, 11,12 and control sample. Comparatively worse ratio was observed in the soil samples №05, 07, 09 and 10. The soil samples of first row according to texture classification were characterized as good soils while the soils of second range were characterized as moderately coarse and coarse soils. Much stoniness was observed in the samples №09, 10, 11 and 12. Comparatively well-developed root systems were observed in almost all soil samples, and they were rated as ample, only in the section № 09, root system was weakly developed. The pH of the studied soil samples, except the soil sample 07 that was slightly acidic (pH = 6.97), was slightly alkaline and ranged from 7.27 to 7.85. The content of humus ranged from 2.13 to 5.35% in the upper A horizon. The highest content of humus was observed in the section №05. The lowest content of humus was in the section №06.

Table 2. The general characteristic of the studied soils

Sample number	Color		Texture	Texture classification	Stones	Roots	pH	Humus content, %
	Dry	Wet						
01	Dark brown	Dark brown	Silty Clay	Good	very few, 2-5 mm	Ample	7.83	3.59
02	Dark brown	Dark brown	Silty Clay	Good	no	Ample	7.68	2.82

03	Dark brown	Dark brown	Clay	Good	2-5 mm	Medium	7.85	2.2
04	Dark brown	Gray-dark brown	Clay	Good	no	Medium	7.53	3.01
05	Gray-brown	Gray-dark brown	Sandy Loam	Moderately Coarse	no	Ample	7.61	5.35
06	Brown	Brown	Clay	Good	few	Medium	7.65	2.13
07	Brown	Dark brown	Sandy Loam	Moderately Coarse	1-7 cm	Ample	6.97	3.93
08	Dark brown	Dark brown	SiltyClayLoam	Good	little, 2-3 cm	Ample	7.27	3.29
09	Brown	Brown	Sand	Coarse	a lot, 3-5 cm	Little	7.37	2.73
10	Light brown	Light brown	Sand	Coarse	moderately stony, 1-5 cm	Medium	7.35	2.78
11	Dark brown	Dark brown	SiltyClayLoam	Good	moderately stony, 1-5 cm	Ample	7.65	3.75
12	Dark brown	Dark brown	Silty Loam	Good	moderately stony, 1-7cm	Ample	7.73	3.17
Control	Dark brown	Dark brown	Silty Clay	Good	very few, 2-5 mm	Ample	7.79	3.38

The concentrations of Cr, Mn, Ni, Cu, Zn, As, Mo, Cd and Pb in the soils around the Kapan copper-molybdenum combine and the tailings storage facility of Geghanush were determined, and the degree of the heavy metal pollution in the soils was assessed. The content (mg/kg) of some heavy metals in the studied samples of soil is presented in Table 3. Since the contents of metals in soils are specific and depend on the compound of rocks producing soil and the conditions of soil formation, for determination of pollution level, the obtained results were compared to the control sample which was considered as a background. Geo-accumulation index (Igeo) was used to calculate metal contamination level in the soils. The geo-accumulation index values showed that the investigated soils were moderately to strongly polluted with copper, unpolluted to strongly polluted with molybdenum, unpolluted to moderately polluted with manganese, nickel, chromium, zinc, arsenic, cadmium and lead (Table 4).

Table 3. The content (mg/kg) of some heavy metals in the studied samples of soil.

Sample number	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb
01	99.45	1557.61	118.52	67.36	127.13	16.53	1.14	0.45	16.82
02	73.91	1244.73	90.55	44.3	86.51	10.21	0.50	0.26	12.20
03	57.47	1017.25	72.93	44.14	84.34	10.39	0.50	0.27	10.64
04	43.16	939.46	58.85	32.57	65.98	6.86	0.25	0.25	8.74
05	23.32	813.23	36.83	72.76	90.30	9.11	0.55	0.23	4.02
06	17.54	1162.19	26.40	46.11	126.67	22.49	0.93	0.52	22.43
07	47.43	1447.88	45.95	60.93	84.43	6.11	0.32	0.16	5.44
08	47.14	1504.61	52.31	55.38	97.67	7.17	0.53	0.23	7.13
09	18.57	1611.49	20.52	86.74	86.45	2.74	0.34	0.14	3.48
10	31.14	1587.89	26.63	100.42	63.04	4.03	0.12	0.19	2.64
11	27.68	854.38	32.59	37.84	56.15	3.44	0.28	0.12	2.95
12	43.74	1185.99	56.05	58.68	82.86	7.77	0.40	0.21	6.97
Control	43.20	527.70	26.40	8.97	75.50	7.48	0.18	0.24	10.26

Table 4. The degree of the heavy metal pollution of the soil samples according to the Geo-accumulation index (Igeo).

Sample number	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb
01	0.6	1.0	1.6	2.3	0.2	0.6	2.1	0.3	0.1
02	0.2	0.7	1.2	1.7	-0.4	-0.1	0.9	-0.5	-0.3
03	-0.2	0.4	0.9	1.7	-0.4	-0.1	0.9	-0.4	-0.5
04	-0.6	0.2	0.6	1.3	-0.8	-0.7	-0.1	-0.5	-0.8
05	-1.5	0.04	-0.1	2.4	-0.3	-0.3	1.0	-0.6	-1.9
06	-1.9	0.6	-0.6	1.8	0.2	1.0	1.8	0.9	0.5
07	-0.5	0.9	0.2	2.2	-0.4	-0.9	0.2	-1.2	-1.5
08	-0.5	0.9	0.4	2.0	-0.2	-0.6	1.0	-0.6	-1.1
09	-1.8	1.0	-0.9	2.7	-0.4	-2	0.3	-1.4	-2.1
10	-1.1	1.0	-0.6	2.9	-0.8	-1.5	-1.2	-0.9	-2.5

11	-1.2	0.1	-0.3	1.5	-1	-1.7	0.1	-1.6	-2.4
12	-0.6	0.6	0.5	2.1	-0.5	-0.5	0.6	-0.8	-1.1

Conclusion

The monitoring of the soils in the mining territories around Kapan town revealed that some negative changes, especially the intensification of erosion processes and pollution with some heavy metals occurred due to human activity. Natural climatic conditions, the steep gradient of slopes, rather bad cover with vegetation, the texture and stoniness of soils as well as huge anthropogenic load caused erosion processes. As a result of human activities, due to the operation of technique and soil pollution (particularly with heavy metals), the growth of vegetation and the formation of strong root system were partially reduced, and the soil became more vulnerable to erosion processes.

Contamination assessment based on Geo-accumulation Index (Igeo) showed that the soils in the investigated territory were highly polluted with copper and molybdenum. The 12 soil samples were moderately to strongly polluted with copper, unpolluted to strongly polluted with molybdenum. Such high degree of pollution with copper and molybdenum was conditioned by the high content of these metals in ores.

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References

1. Edilyan R. A. Atlas of Soils of the Republic of Armenia. Yerevan, 1990, 70 p. (In Russian).
2. Fagbote E. O. and Olanipekun E. O. Evaluation of the status of heavy metal pollution of soil and plant (*Chromolaena odorata*) of Agbabu Bitumen deposit area, Nigeria // *American-Eurasian Journal of Scientific Research*, 5 (4), 2010, p. 241 – 248.
3. Forstner, U., Ahlf W., Calmano W. Sediment quality objectives and criteria development in Germany // *Water Science and Technology*, 28, 1993, p. 307-316.
4. Ghazaryan K., Movsesyan H., Ghazaryan N., Grigoryan K. The ecological assessment of soils around Agarak town. *Biological Journal of Armenia*, 65 (1), 2013, p. 39-43.
5. Grzebisz W., Ciesla L., Komisarek J., Potarzycki J. Geochemical assessment of heavy metals pollution of urban soils. *Polish Journal of Environmental Studies*, 11 (5), 2002, p. 493-499.
6. Hu Y., Liu X., Bai J., Shih K., Zeng E. Y. and Cheng H. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization // *Environ. Sci. Pollut. Res.*, 20, 2013, p. 6150 – 6159
7. Nagajyoti P. C., Lee K. D., Sreekanth T. V. Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chemistry Letters*, 8 (3), 2010, p. 199–216.
8. Rafiei B., Bakhtiari Nejad M., Hashemi M. and Khodaei A.S. Distribution of heavy metals around the Dashkasan Au Mine. *Int. J. Environ. Res.*, 4 (4) 2010, p. 647-654.

9. Walker C. H., Sibly R. M., Hopkin S. P., Peakall D. B. Principles of Ecotoxicology. CRC Press, New York, 2012, 386 p.