



Geochemistry of Potentially Toxic Trace Elements in Soils of Mining Area: A Case Study from Zangezur Copper and Molybdenum Combine, Armenia

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Abstract

Research was carried out to determine and assess the influence of mining industries on soil contamination with application of various pollution indices. For soil sampling 13 points were selected. Soil samples were analyzed for heavy metals by AAS. Eleven elements were determined and the greater quantities were generally observed in case of Mo and Cu. During the testing of soil pollution level pollution load index, degree of contamination (*Cd*) and geoaccumulation index were used. The correlation analysis revealed the strongest positive correlation between molybdenum and copper and that the high content of mentioned elements in soil was caused by mining industry. Assessment based on *Cd* showed that the 33.3% of A horizon soil samples referred to a very high degree of pollution. Obtained results will be useful for implementation of control measures of pollution and the remediation techniques.

Keywords Heavy metals · Soil pollution · Pollution load index · Degree of contamination · Correlation analysis · Armenia

Soil as a part of ecosystem plays a crucial role in elemental cycling and has significant function as storage, buffer, filter, and transformation compartment supporting the interrelationship between the biotic and abiotic components (Tumuklu et al. 2007). Soil pollution by heavy metals is mainly connected with human activities, such as mining, smelting, and various industrial processes (Kabala and Singh 2001; Li 2006; García-Lorenzo et al. 2012). Heavy metals are natural, non-degradable substances and remain in the environment hence the soils contamination in mining regions is a serious ecological problem (Arenas-Lago et al. 2014). In last decades, many scientists actively studied heavy metals pollution due to its diverse dangerous impact on the environment and it turned out that the mining industry is a main human source for heavy metals entered into the soils (Farmaki and Thomaidis 2008). Pollution of agricultural

areas and crops by heavy metal is giving rise to anxiety due to the possible effects on human health and the long-term sustainability of food production in contaminated regions (Praveena et al. 2015).

The aim of our research was the definition and assessment of the influence of mining activities on soil contamination using various pollution indices.

Materials and Methods

The study area is situated in the south-east of Armenia. The soils of study area belong to mountain cambisol. In this region the mean annual air temperature is 8–12°C and precipitation is 450–560 mm. Long period of soil formation process, favorable climate, the presence of supportable internal drainage system and seasonal changes of interflow directions contribute to deep and intensive weathering of primary minerals and to formation of secondary mineral substances and rather strong clayey soils.

The main task of this study was the exploration of soils around the Zangezur Copper and Molybdenum Combine. Considering the peculiarities of climate and relief 12 soil samples were taken in study area: in surroundings of processing plant (Nos. Q-F-01, Q-F-04, Q-F-11) and open

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mine (Nos. Q-OM-02, Q-OM-03, Q-OM-06, Q-OM-07) of Zangezur Copper and Molybdenum Combine, school in Lernadzor village (No. Q-LD-09), Artsvanik tailing dump (No. Q-AT-12) as well as of the surfaces of recultivated tailing dumps Darazam (No. Q-DA-05), Pkhrut (No. Q-PT-08) and Voghji (No. Q-VT-10) (Fig. 1) as well as the control sample (Q-CONT) was collected on distance 0.5 km downstream from Geghi pond as well.

The sampling in all sites was performed similarly by the method of envelope from A (0–20 cm) and B (35–55 cm) horizons of soil. The soil samples were air-dried at 20–22°C and grounded in a mortar and pestle to pass a 0.42 mm nylon mesh. Total concentration of heavy metals was determined using aqua regia digestion method. Determination of heavy metals, aluminum and some nonmetals was performed by atomic absorption spectrometry method using AAS PG990.

The degree of soil pollution by heavy metals, aluminum and some nonmetals was evaluated by contamination indices. Pollution load index (PLI), degree of contamination (Cd) and geoaccumulation index (I-geo) were used. PLI was calculated as suggested by Thomilson and co-authors through following formulas (Thomilson et al. 1980):

$$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times \dots \times Cfn} \quad (1)$$

$$Cf^i = Cs^i / Cb^i \quad (2)$$

where, *n* is the number of metals studied, *Cfⁱ* is the contamination factor calculated as described in (2), *Csⁱ* is the concentration of heavy metal *i* in the sample, *Cbⁱ* is the

background value of heavy metal. The *PLI* provides simple but comparative means for assessing a site quality.

Cd was calculated by the following formula (Håkanson 1980):

$$Cd = \sum Cf \quad (3)$$

The definition of *Cf* is given above.

I-geo was used to assess metal pollution level in the soils and was calculated as (Müller 1969):

$$I-geo = \log_2 Cs^i / 1.5 Cb^i \quad (4)$$

where *Csⁱ* is the concentration of the element *i* in the samples, *Cbⁱ* is the background value of the element *i*, and the factor 1.5 is used to take into account the possible lithological variability.

The assessment by means of *PLI*, *Cd* and *I-geo* was implemented according to Table 1 (Thomilson et al. 1980; Håkanson 1980; Müller 1969).

Results and Discussion

It is well known that mining industry has multiple negative influences on the environment since it produces large amount of ore dust and wastes that can become a source of contamination by heavy metals. In view of this fact we defined the contents of some pollutants in all soil samples. The results of statistical analysis of the contents of the range of heavy metals and nonmetals in studied soil samples are

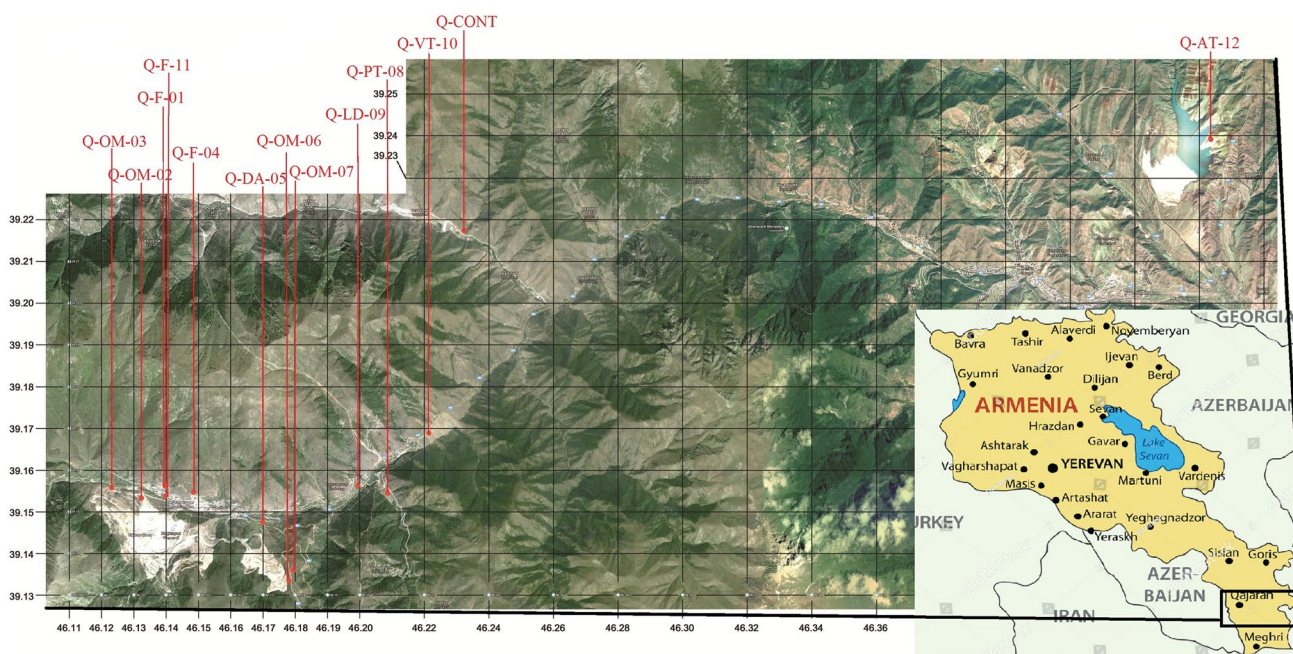


Fig. 1 Map of sampling area

Table 1 Different indices and their categories for the description of soil pollution

Model	Class	Description
<i>PLI</i>	$PLI < 1$	Perfection
	$PLI = 1$	Base line level of pollution
	$PLI > 1$	Deterioration of site quality
<i>Cd</i>	$Cd \leq 11$	Low
	$11 < Cd \leq 22$	Moderate
	$22 < Cd \leq 33$	Considerable
	$33 < Cd$	Very high
<i>I-geo</i>	$I-geo < 0$	Uncontaminated
	$0 < I-geo < 1$	Uncontaminated to moderately contaminated
	$1 < I-geo < 2$	Moderately contaminated
	$2 < I-geo < 3$	Moderately to strongly contaminated
	$3 < I-geo < 4$	Strongly contaminated
	$4 < I-geo < 5$	Strongly to very strongly contaminated
	$5 < I-geo$	Very strongly contaminated

given in Table 2. As far as the chemical composition of soil is a quite specific feature and depends on soil-forming rocks and environmental conditions, for the determination of soil contamination degree the data obtained were compared with control soil sample.

Table 2 Results of statistical analysis of heavy metals, some nonmetals and aluminum content in soils adjacent to Zangezur Copper and Molybdenum Combine (mg/kg)

Sample description	Ti	Fe	Al	As	Cu	Zn	Mo	Mn	Pb	Cr	S _{total}
Maximum value	4800	64,000	83,340	108.3	3480	106	1527	827	25.6	110.4	1634
Minimum value	3120	32,000	53,000	6.0	61	41.8	12	323	9.4	11.8	384
Mean value	4040	46,917	67,860	39.3	985	77.1	169	597	18.8	42.1	832
Median	4200	47,000	70,010	37.2	819	77.2	30	601	19.6	37.5	714
Standard deviation	478.2	8979	11,361	28.0	933	18.2	430	149	4.9	29.3	389
Q-CONT-A	4080	40,000	58,180	26.1	72	171.3	9.9	842	17.5	55.1	439
Q-CONT-B	3600	48,000	65,760	23.2	53.7	177.9	13.1	1052	19.4	51.1	741.4

According to *PLI* values (Fig. 2) of upper A horizon soils we can conclude that soil samples Q-OM-02-A (0.87) and Q-AT-12-A (0.98) were generally not polluted. The highest degree of pollution was observed in samples Q-OM-03-A (1.86) and Q-F-11-A (2.53). Such type of pollution of sample Q-F-11-A could be explained by the proximity to the processing plant, in particular to the rock mills whereas the high degree of pollution of sample Q-OM-03-A – by the nearness to the open mine and ore transportation paths (as compared to sample Q-OM-02-A), by the direction of winds and as compared with samples Q-OM-06-A and Q-OM-07-A – by lower location. According to *PLI* values of soil samples from A and B horizons (Fig. 2) almost in all sites the A horizon is more polluted than B horizon that confirms once again the fact that contamination of soils is caused by anthropogenic factors.

It should be also noted that in A horizons of almost all soil samples in comparison with control the high content of sulfur was observed which is conditioned by high content of this element in the ore.

Subsequently a correlation analysis was carried out between 13 samples of A horizon of studied territories (12 experimental areas and 1 control) in order to find out if the changes in contents of heavy metals, aluminum and some nonmetals in different sites had the same tendency.

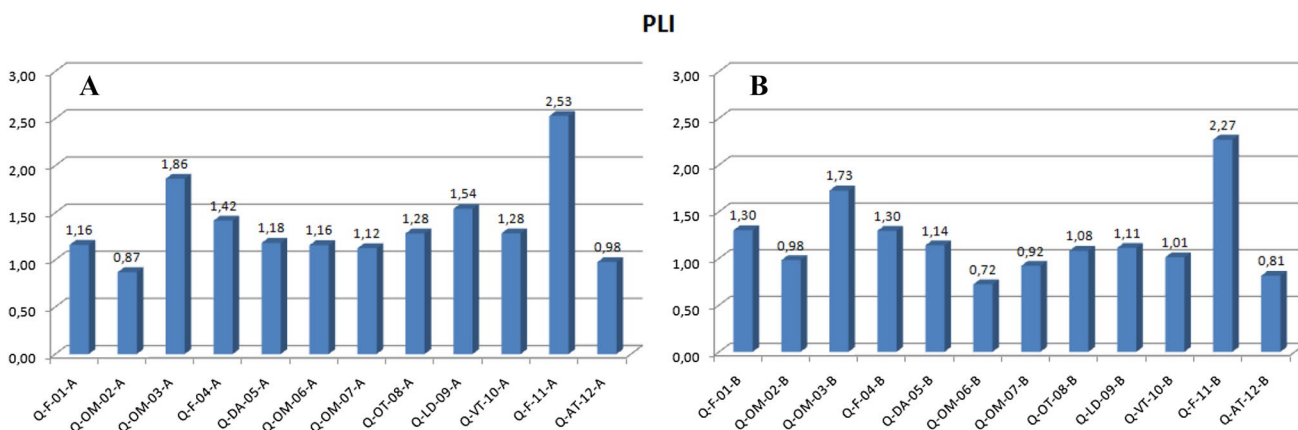


Fig. 2 Degree of pollution of soil upper A (left) and B (right) horizons by heavy metals, aluminum and some nonmetals according to pollution load index

Correlation analysis is a bivariate method which represents the degree of relationship among two random variables. The correlation coefficient of Spearman’s rank is expressed by ρ , the value of which is continuously from -1.0 to 1.0 . A high-level positive correlation coefficient (nearly 1.0) means an effective relationship among two variables, which may be an indication of the presence of a single contamination source. If the value is nearby zero it aims no relationship between them, which means that they have different sources of pollution (Ghazaryan and Chen 2016).

The strongest positive correlation in A horizon was observed between Cu and Mo ($\rho > 0.6$) (Table 3). All described above proves again that the high content of these two elements in soil is due to human activities and that they have a single source of pollution. It should be noted, that copper and molybdenum are the main metals extracted by Zangezur Copper and Molybdenum Combine and we can definitely assert that the interrelated variation of the contents of these metals in the soil is conditioned by mining industry. Strong positive correlation in A horizon is observed also between Cu and Fe, Ti and Fe, Pb and As, Ti and Mn that

may be conditioned by human activities and the similar composition of soil-forming rocks.

Pollution evaluation based on Cd is a universal method for characterization of area contamination level as far as it includes and generalizes all studied pollutants. Study results detected that among all soil samples taken from both A and B horizons the soil from sampling point Q-F-11 had the highest Cd values (215.2 and 190.8, respectively) and so a maximum Cd (Fig. 3). On the whole the 58.4% of A horizon soil samples referred to moderate Cd, 8.3% – considerable and 33.3% – very high Cd. From B horizon soils samples 16.7% had low Cd, 50.0% – moderate and 33.3% – very high Cd.

The pollution assessment by means of Cd confirms once again, that A horizon soil layer is more polluted than soil of B horizon, that is, the high content of studied elements cannot be entirely connected with high content of these elements in soil-forming rocks, but also is conditioned by external factors, in particular by mining activities. In general, according to pollution level decrease the soil samples of A horizon are arranged in the following order: Q-F-11-A > Q-F-01-A > Q-OM-03-A > Q-F-04-A > Q-LD-

Table 3 Correlation matrix of A horizon soil samples

	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S _{total}
Fe	1										
As	0.007	1									
Mo	0.629	0.175	1								
Cu	0.780	0.092	0.864	1							
Mn	0.258	0.024	0.033	-0.087	1						
Pb	-0.261	0.712	0.027	-0.127	-0.005	1					
Zn	-0.101	0.089	-0.139	-0.278	0.679	0.256	1				
Al	0.356	-0.056	0.077	0.015	0.463	-0.168	-0.113	1			
Cr	-0.552	0.343	-0.094	-0.359	-0.234	0.417	0.139	-0.612	1		
Ti	0.723	0.181	0.185	0.288	0.711	-0.069	0.299	0.567	-0.488	1	
S _{total}	0.608	0.082	0.670	0.694	0.088	0.138	-0.135	0.436	-0.545	0.287	1

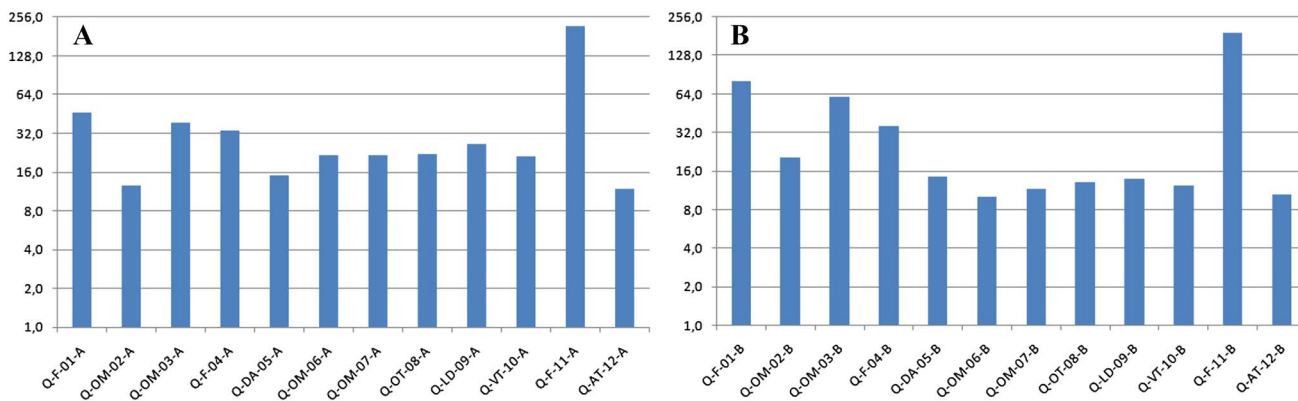


Fig. 3 Cd values of A (left) and B (right) horizons soil samples of studied sites

09-A > Q-PT-08-A > Q-OM-07-A > Q-OM-06-A > Q-VT-10-A > Q-DA-05-A > Q-OM-02-A > Q-AT-12-A, and B horizon soil samples make the line: Q-F-11-B > Q-F-01-B > Q-OM-03-B > Q-F-04-B > Q-OM-02-B > Q-DA-05-B > Q-LD-09-B > Q-PT-08-B > Q-VT-10-B > Q-OM-07-B > Q-AT-12-B > Q-OM-06-B. This rows show that the surroundings of processing plant are the most polluted areas. The territory of Q-OM-03 sample located very close to open mine is also relatively heavily polluted due to its strong influence.

For revelation of contamination level of studied regions by metals, nonmetals and aluminium we also used *I-geo* index which is widely applied in international practice. According to *I-geo* value (Table 4) the soil sample Q-F-01-A is strongly contaminated by Mo (3.1) and strongly to very strongly contaminated by Cu (4.2), the soil sample Q-OM-02-A is uncontaminated to moderately contaminated by S_{total} (0.3), Cu (0.9) and Mo (0.7), the sample Q-OM-03-A is uncontaminated to moderately contaminated by S_{total} (0.7), moderately contaminated by As (1.5), strongly contaminated by Cu (3.1) and Mo (3.1), the sample Q-F-04-A is moderately contaminated by S_{total} (1.2), moderately to strongly contaminated by Mo (2.3) and strongly contaminated by Cu (3.4), the sample Q-DA-05-A is uncontaminated to moderately contaminated by Cu (0.5) and moderately contaminated by Mo (1.2), the sample Q-OM-06-A is moderately to strongly contaminated by Cu (2.9), the sample Q-OM-07-A is uncontaminated to moderately contaminated by S_{total} (0.6) and moderately to strongly contaminated by Cu (2.9), the sample Q-PT-08-A is uncontaminated to moderately contaminated by S_{total} (0.3) and As (0.1), moderately to strongly contaminated by Cu (2.9), the sample Q-LD-09-A is uncontaminated to moderately contaminated by As (0.5), moderately contaminated by Mo (1.5) and moderately to strongly contaminated by Cu (3.0), the sample Q-VT-10-A is uncontaminated to moderately contaminated by Mo (0.4) and As (0.6), moderately to strongly contaminated by Cu

(2.7), the sample Q-F-11-A is uncontaminated to moderately contaminated by As (0.4) and Fe (0.1), moderately contaminated by S_{total} (1.3), very strongly contaminated by Cu (5.0) and Mo (6.7), the sample Q-AT-12-A is uncontaminated to moderately contaminated by Cr (0.4), Mo (0.2) and As (0.2).

According to *I-geo* value (Table 5) the soil sample Q-F-01-B is moderately to strongly contaminated by Mo (2.1) and very strongly contaminated by Cu (5.5), the sample Q-OM-02-B is moderately to strongly contaminated by Cu (3.0), the sample Q-OM-03-B is uncontaminated to moderately contaminated by Cr (0.4), moderately contaminated by As (1.1), moderately to strongly contaminated by Mo (2.3) and strongly to very strongly contaminated by Cu (4.8), the sample Q-F-04-B is uncontaminated to moderately contaminated by Mo (0.8) and strongly to very strongly contaminated by Cu (4.1), the sample Q-DA-05-B is uncontaminated to moderately contaminated by As (0.1), Mo (0.2) and Cr (0.1), moderately contaminated by Cu (1.2), the samples Q-OM-06-B and Q-OM-07-B are uncontaminated to moderately contaminated by Cu (0.8 and 0.9, respectively), the sample Q-PT-08-B is uncontaminated to moderately contaminated by As (0.2) and Cu (0.9), the sample Q-LD-09-B is uncontaminated to moderately contaminated by As (0.7), Mo (0.3), Cu (0.4) and Cr (0.3), the sample Q-VT-10-B is uncontaminated to moderately contaminated by As (0.4), Cu (0.2) and Cr (0.3), the sample Q-F-11-B is uncontaminated to moderately contaminated by As (0.4) and S_{total} (0.6), very strongly contaminated by Mo (6.3) and Cu (5.3), the sample Q-AT-12-B is uncontaminated to moderately contaminated by As (0.2) and Cr (0.5).

Summarizing and comparing the values of contamination level with heavy metals, aluminum and some nonmetals of A and B horizons of all soil samples (according to *I-geo* values), it is possible to assert unequivocally that except the titanium and chromium the high content of other pollutants in the soil is connected with human factor, particularly with mining industry developed in this area. This fact is

Table 4 The degree of pollution of A upper horizon soil samples with heavy metals, aluminum and some nonmetals according to *I-geo*

Sample description	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S_{total}
Q-F-01-A	-0.2	-1.7	3.1	4.2	-2.0	-1.5	-2.6	-0.7	-1.9	-0.7	-0.1
Q-OM-02-A	-0.9	-2.7	0.7	0.9	-1.7	-0.6	-2.4	-0.3	-1.1	-1.0	0.3
Q-OM-03-A	-0.4	1.5	3.1	3.1	-1.1	0.0	-1.6	-0.2	-1.0	-0.5	0.7
Q-F-04-A	-0.2	-1.1	2.3	3.4	-1.1	-0.3	-1.4	-0.4	-2.8	-0.6	1.2
Q-DA-05-A	-0.2	-0.3	1.2	0.5	-1.0	-0.7	-1.9	-0.2	-0.8	-0.5	-0.2
Q-OM-06-A	-0.2	-0.7	-0.3	2.9	-0.6	-0.8	-1.5	-0.1	-2.5	-0.4	0.0
Q-OM-07-A	-0.3	-1.0	-0.2	2.9	-0.6	-1.1	-1.7	-0.1	-2.6	-0.5	0.6
Q-PT-08-A	-0.5	0.1	-0.2	2.9	-0.9	-0.3	-1.7	-0.3	-1.4	-0.5	0.3
Q-LD-09-A	-0.5	0.5	1.5	3.0	-1.1	-0.1	-1.3	-0.7	0.0	-0.6	-0.4
Q-VT-10-A	-0.6	0.6	0.4	2.7	-1.1	-0.3	-1.8	-0.7	-0.6	-0.8	-0.3
Q-F-11-A	0.1	0.4	6.7	5.0	-0.9	-0.5	-1.8	-0.3	-1.2	-0.5	1.3
Q-AT-12-A	-0.8	0.2	0.2	-0.8	-1.4	-0.4	-1.8	-0.7	0.4	-0.9	-0.8

Table 5 The degree of pollution of B horizon soil samples with heavy metals, aluminum and some nonmetals according to *I-geo*

Sample description	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S _{total}
Q-F-01-B	-0.3	-1.0	2.1	5.5	-2.3	-1.3	-2.4	-0.7	-1.0	-0.5	-0.4
Q-OM-02-B	-1.0	-0.8	-0.2	3.0	-2.3	-0.7	-2.5	-0.5	-0.1	-0.7	-1.0
Q-OM-03-B	-0.7	1.1	2.3	4.8	-1.5	-0.7	-2.1	-0.4	0.4	-0.4	-0.5
Q-F-04-B	-0.3	-1.4	0.8	4.1	-0.9	-0.5	-1.4	-0.6	-1.2	-0.3	-0.6
Q-DA-05-B	-0.4	0.1	0.2	1.2	-0.8	-0.7	-1.8	-0.4	0.1	-0.2	-1.6
Q-OM-06-B	-0.5	-3.1	-0.7	0.8	-1.2	-1.7	-2.2	-0.3	-1.5	-0.2	-1.0
Q-OM-07-B	-0.5	-1.2	-0.4	0.9	-0.5	-1.4	-1.7	-0.3	-0.9	-0.1	-1.7
Q-PT-08-B	-0.8	0.2	-0.2	0.9	-0.8	-0.4	-1.9	-0.5	-0.5	-0.5	-0.8
Q-LD-09-B	-0.9	0.7	0.3	0.4	-1.1	-0.5	-1.6	-0.8	0.3	-0.5	-1.1
Q-VT-10-B	-0.7	0.4	-0.2	0.2	-1.3	-0.5	-1.9	-0.8	0.3	-0.7	-1.0
Q-F-11-B	0.0	0.4	6.3	5.3	-1.3	-0.6	-2.0	-0.4	-1.4	-0.4	0.6
Q-AT-12-B	-1.1	0.2	-0.3	-0.9	-1.4	-0.6	-2.2	-0.9	0.5	-0.7	-2.4

confirmed by the condition that among heavy metals the copper and molybdenum, constituting the staple metals, extracted from the ore in Zangezur Copper and Molybdenum Combine, are the main pollutants. The correlation analysis also demonstrated that such high content of these two metals in the soil is conditioned by human activities and that they have a single source of pollution in studied territories.

It should be noted that due to long-term mining activities as well as some physicochemical characteristics of soil (an average content of humus, not very high capacity of A horizon, eroded condition etc.) the contamination of the deeper layers of soil was also observed (Ghazaryan et al. 2013). Analyzing the results of total pollution level evaluation according to *Cd* and *PLI* it can be argued that the territories around the processing plant are the most contaminated areas and the vicinage of Artsvanik active tailing dump is the least contaminated region.

Thus the research showed that the soils around Zangezur Copper and Molybdenum Combine were widely and extremely contaminated by some trace elements as a result of long-term anthropogenic activities, and more attention should be paid to contamination as well as great efforts should be made to devise effective methods of restoration of contaminated regions, in particular, phytoremediation as the socially accepted, cost-effective and ecofriendly method.

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