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

The primary aim of the study was the determination and evaluation of the impact of mining activity on soil pollution with application of various pollution indices. In this study we selected 8 zones basing on soil maps and marked 13 points for soil sampling. Soil samples were analyzed for heavy metals using Atomic-absorption spectrometer PG990. During the study 11 metals and nonmetals were analyzed and the greater quantities, as compared with control sample, were observed generally in case of copper and molybdenum. These data were obtained by means of both Contamination factors (*Cf*) and Geoaccumulation index (*I-geo*) during the testing of soil contamination level. The correlation analysis revealed the strongest positive correlation between Cu and Mo and that the high content of these two elements in soil is caused by human activities and the presence of a single pollution source. Contamination assessment based on Degree of contamination (*Cd*) showed, that the 58.4% of A horizon soil samples referred to a moderate degree of contamination, 8.3% - to a considerable degree and 33.3% - to a very high degree of contamination. Obtained results will be useful for implementation of control measures of pollution and the remediation techniques in the study area.

Keywords: heavy metals, soil contamination, Degree of contamination, Geoaccumulation index, Armenia

1. Introduction

Soil being the important part of ecosystem plays a vital role in elemental cycling and has significant function as storage, buffer, filter, transformation compartment, and sustains the interaction between the biotic and abiotic components (Kabata-Pendias and Sadurski 2004). Pollution of soil with heavy metals to the greatest extent is connected with anthropogenic activity, such as mining, smelting, and various industrial activities (Callender 2005; Li *et al*. 2007). Since heavy metals are natural, non-degradable substances and remain in the environment, heavy metal contamination of soils around open mines and processing plants is a serious ecological problem (Ettler *et al*. 2005). In recent decades, many scientists actively explored heavy metals contamination due to its diverse hazardous influences on the environment, and many studies show that mining industry is one of the most substantial human sources for heavy metals entered into soils (Burt *et al*. 2003). Heavy metal pollution of agricultural lands and crops is giving rise to anxiety due to the eventual effects on human health and the possible long-term sustainability of food production in polluted areas (Fernández-Caliani *et al*. 2009). The main aim of our study was the determination and evaluation of the impact of mining activity on soil pollution using various pollution indices.

2. Materials and methods

2.1. Description of sampling area

The study area is situated in the watershed of Voghji River. The soils of study area (surroundings of Zangezur Copper and Molybdenum Combine) belong to mountain cambisol. The relief in the area of distribution of mountain brown forest soils is multifarious and is characterized by many heights (mountain ranges and water-divider mountain peaks) as well as trenches which descend to canyons and floodplains. The degraded structures of porphyrites, dolomites, limestone, conglomerates, sand, granodiorites are the main soil-producing rocks of mountain brown forest soils. In this region the mean annual air temperature is 8-12°C, in August it can increase up to 37°C and in January decrease to -23°C. Mean annual precipitation ranges to 450-560 mm. Warm, mild and variable damp climate, long duration of soil formation active period, the availability 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, as well as to formation of rather strong clayey soils.

2.2. Soil sampling and analysis

The main task of this study was the exploration of soils in surroundings of processing plant of Zangezur Copper and Molybdenum Combine, school in Lernadzor village, Artsvanik tailing dump as well as of the surfaces of recultivated tailing dumps Darazam, Pkhrut and Voghji:

1. surroundings of processing plant (№№ Q-F-01, Q-F-04, Q-F-11),

2. surroundings of open mine (№№ Q-OM-02, Q-OM-03, Q-OM-06, Q-OM-07),
3. Darazam recultivated tailing dump (№ Q-DA-05),
4. Pkhrut recultivated tailing dump (№ Q-PT-08),
5. surroundings of school in Lernadzor village (№ Q-LD-09),
6. Voghji recultivated tailing dump (№ Q-VT-10),
7. surroundings of Artsvanik tailing dump (№ Q-AT-12).

Considering the peculiarities of climate and relief 12 soil samples were taken in study sites as well as one control sample (Q-CONT) was collected on distance 0.5 km downstream from Geghi pond. Sampling was performed from A and B horizons of soil. During the soil sampling the coordinates of sampling sites as well as the altitude of sites above sea level were recorded by GPS. The landscape, relief, location of slopes, vegetation, stoniness, extent of erosion, type and structure of soils, turfing, carbonate content and soil texture were recorded in laboratory and field registration books. The sampling in all sites was performed by method of envelope. After the removal of unwanted content (stones, plant material, etc.) in laboratory the samples were air-dried at room temperature (20–22°C). Before analysis the samples were processed appropriately. Soil was grounded in a mortar and pestle to pass a 0.42 mm nylon mesh. Total concentration of heavy metals was determined using Aqua Regia (HCl-HNO_3, 3:1) extraction method (3g of soil sample were digested for 2h at 180°C). Determination was performed by atomic absorption spectrometry method using Atomic-absorption spectrometer PG990 (PG Instruments LTD).

2.3. Calculation of Cf, Cd and I-geo

The level of soils contamination by heavy metals was assessed by contamination indices. Contamination factors (*Cf*), Degree of contamination (*Cd*) and Geoaccumulation index (*I-geo*) were used.

Cf and *Cd* were calculated as suggested by Håkanson through following formulas (Håkanson, 1980):

$$Cf^i = Cs^i / Cb^i$$

$$Cd = \Sigma Cf$$

where, Cs^i is the measured concentration of the examined metal *i* in the soil sample and Cb^i is the background value of heavy metal *i* in the uncontaminated soil (control). Håkanson suggested four classes of *Cf* to evaluate the metal contamination levels as shown in Table 1 (Håkanson, 1980). Four categories of *Cd* also were used to determine metal contamination levels (Table 1). If the *Cd* value exceeds 33, then it is necessary to take immediate contrary measures to lower heavy metal contamination in the soil. Geoaccumulation index (*I-geo*) was used to evaluate metal contamination level in the soils. The geoaccumulation 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 (Müller, 1969):

$$I\text{-}geo = \log_2 Cs^i / 1.5\ Cb^i$$

where Cs^i is the concentration of the element *i* in the samples, Cb^i is the background value of the element *i*, and the factor 1.5 is used to take into account the possible lithological variability. The rank of values of *I-geo* and its implication is shown in Table 1.

3. Results

3.1. Chemical properties of soil horizons and contamination assessment based on Cf

It is well known that mining industry has numerous negative impacts on the environment since it produces the huge amount of ore dust, useless rocks and wastes that can become a source of pollution by heavy metals. In view of this fact we determined the contents of some metals and nonmetals in all soil samples. The results of statistical analysis of the contents of the range of heavy metals and nonmetals in studied soils are presented 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 determination of soil pollution level the data obtained were compared with control soil sample. We used *Cf* for this purpose (Table 3). From studied metals and nonmetals the greater quantities, as compared with control sample, were observed generally in the case of copper and molybdenum. Particularly, in the vicinity of open mine (sample Q-F-11) in horizon A the *Cf* value in the case of copper was 48.6, in the case of molybdenum 154.0, and in horizon B – 58.4 and 121.8, respectively. This circumstance is explained by high content of mentioned metals in the ore and by the fact that the point Q-F-11 is situated on distance 250-300 meters from ore mill of processing plant and is exposed to strong influence of anthropogenic factor. 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.

3.2. Correlation analysis

This is a bivariate method which represents the degree of relationship among two random variables (Srivastava and Ramanathan 2008). The correlation analysis was carried out between 13 samples of both A and B horizons 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 have the same tendency. The strongest positive correlation in A horizon is observed between Cu and Mo (ρ>0,6), and in horizon B it dropped measuring 0,58 (Tables 4 and 5). All described above proves again that the high content of these two elements in soil is due to human activity and that they have a single pollution source. 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 activity, and the similar composition of soil-forming rocks.

3.3. Contamination assessment based on Cd

Cd is more universal method for characterization of area pollution degree as far as it includes and generalizes all studied pollutants. As a result of study data analysis it was found out that from soil samples of both A and B horizons the most pollution had Q-F-11 sampling point (215.2 and 190.8) and it corresponded to a very high degree of contamination (Fig. 1, 2). On From B horizon soils

samples 16.7 % had low degree of contamination, 50.0% - moderate and 33.3% - very high degree of contamination. 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-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 zone. The territory of Q-OM-03 sample located very close to open mine is also relatively heavily polluted due to its strong influence. *3.4. Geoaccumulation index*

For revelation of pollution degree of studied areas by metals and nonmetals we used *I-geo* index which is widely applied in international practice (Tables 6). According to *I-geo* value the soil sample Q-F-01-A is strongly contaminated by Mo (3.07) and strongly to very strongly contaminated by Cu (4.18), the soil sample Q-OM-02-A is uncontaminated to moderately contaminated by Mo (0.70),

Table 1. Different types of model and the categories for the description of soil contamination

Model	Class	Description
Cf	*Cf<1*	Low
	1<*Cf*<3	Moderate
	3 <*Cf*< 6	Considerable
	6 <*Cf*	Very high
Cd	*Cd≤11*	Low
	11 <*Cd*≤ 22	Moderate
	22 <*Cd*≤ 33	Considerable
	33 <*Cd*	Very high
I-geo	*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

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

Sample description	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S_{total}
Minimum value	32000	5,96	12,3	61,4	323,1	9,35	41,85	53000	11,8	3120	384,4
Maximum value	32000	108,3	1526,5	3480,3	826,5	25,6	106	83340	110,4	4800	1633,8
Mean value	46916,7	39,3	169,0	985,2	596,7	18,8	77,1	67860,0	42,1	4040,0	832,3
Standard deviation	8979,4	28,0	429,6	932,8	149,3	4,9	18,2	11361,3	29,3	478,2	389,4
Median	47000	37,15	29,64	818,8	601,1	19,55	77,15	70010	37,45	4200	713,95

Table 4. Correlation matrix of A horizon soil samples

	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S_{total}
Fe	1										
As	0,01	1									
Mo	0,63	0,17	1								
Cu	0,78	0,09	0,86	1							
Mn	0,26	0,02	0,03	-0,09	1						
Pb	-0,26	0,71	0,03	-0,13	-0,01	1					
Zn	-0,10	0,09	-0,14	-0,28	0,68	0,26	1				
Al	0,36	-0,06	0,08	0,02	0,46	-0,17	-0,11	1			
Cr	-0,55	0,34	-0,09	-0,36	-0,23	0,42	0,14	-0,61	1		
Ti	0,72	0,18	0,19	0,29	0,71	-0,07	0,30	0,57	-0,49	1	
S_{total}	0,61	0,08	0,67	0,69	0,09	0,14	-0,13	0,44	-0,54	0,29	1

Table 5. Correlation matrix of B horizon soil samples

	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S_{total}
Fe	1										
As	-0,25	1									
Mo	0,65	0,21	1								
Cu	0,64	0,13	0,58	1							
Mn	0,12	-0,15	-0,10	-0,52	1						
Pb	-0,24	0,55	0,09	-0,15	0,10	1					
Zn	0,05	-0,10	-0,11	-0,31	0,68	0,31	1				
Al	0,41	-0,22	0,30	0,07	0,36	-0,49	-0,06	1			
Cr	-0,71	0,71	-0,35	-0,33	-0,24	0,45	-0,14	-0,54	1		
Ti	0,49	-0,29	0,05	0,03	0,51	-0,53	-0,02	0,75	-0,48	1	
S_{total}	0,72	0,16	0,87	0,74	-0,17	0,12	0,03	0,25	-0,49	-0,02	1

Table 3. The degree of pollution of A and B horizons soil samples with heavy metals, aluminum and some nonmetals according to *Cf*

Sample description	Fe	As	Mo	Cu	Mn	Pb	Zn	Al	Cr	Ti	S_{total}
Q-F-01-A	1.3	0.5	12.6	27.3	0.4	0.5	0.2	0.9	0.4	0.9	1.4
Q-OM-02-A	0.8	0.2	2.4	2.8	0.5	1.0	0.3	1.2	0.7	0.8	1.8
Q-OM-03-A	1.2	4.2	13.0	12.4	0.7	1.5	0.5	1.3	0.7	1.1	2.4
Q-F-04-A	1.3	0.7	7.3	16.1	0.7	1.3	0.6	1.2	0.2	1.0	3.4
Q-DA-05-A	1,3	1.3	3.5	2.2	0.8	0.9	0.4	1.3	0.9	1.1	1.3
Q-OM-06-A	1.4	0.9	1.2	11.4	1.0	0.9	0.5	1.4	0.3	1.2	1.5
Q-OM-07-A	1.2	0.7	1.3	11.4	1.0	0.7	0.5	1.4	0.2	1.1	2.2
Q-PT-08-A	1.1	1.6	1.3	10.9	0.8	1.3	0.5	1.2	0.6	1.1	1.8
Q-LD-09-A	1.1	2.1	4.2	11.7	0.7	1.4	0.6	0.9	1.5	1.0	1.2
Q-VT-10-A	1.0	2.3	1.9	9.4	0.7	1.3	0.4	0.9	1.0	0.9	1.2
Q-F-11-A	1.6	2.0	154.0	48.6	0.8	1.1	0.4	1.2	0.7	1.1	3.7
Q-AT-12-A	0.9	1.7	1.7	0.9	0.6	1.1	0.4	0.9	2.0	0.8	0.9
Q-F-01-B	1.3	0.7	6.6	66.7	0.3	0.6	0.3	0.9	0.8	1.1	1.1
Q-OM-02-B	0.8	0.9	1.3	11.8	0.3	0.9	0.3	1.0	1.4	0.9	0.7
Q-OM-03-B	0.9	3.3	7.1	41.9	0.5	0.9	0.4	1.1	2.0	1.1	1.0
Q-F-04-B	1.3	0.6	2.6	25.0	0.8	1.1	0.6	1.0	0.7	1.2	1.0
Q-DA-05-B	1.2	1.6	1.7	3.3	0.8	0.9	0.4	1.1	1.7	1.3	0.5
Q-OM-06-B	1.1	0.2	0.9	2.7	0.7	0.4	0.3	1.2	0.5	1.3	0.8
Q-OM-07-B	1.0	0.7	1.2	2.8	1.0	0.6	0.5	1.2	0.8	1.4	0.5
Q-PT-08-B	0.9	1.7	1.3	2.8	0.9	1.1	0.4	1.1	1.1	1.1	0.9
Q-LD-09-B	0.8	2.5	1.8	2.0	0.7	1.1	0.5	0.9	1.9	1.1	0.7
Q-VT-10-B	0.9	2.0	1.3	1.7	0.6	1.0	0.4	0.9	1.8	0.9	0.8
Q-F-11-B	1.5	2.0	121.8	58.4	0.6	1.0	0.4	1.2	0.6	1.1	2.3
Q-AT-12-B	0.7	1.7	1.2	0.8	0.6	1.0	0.3	0.8	2.1	0.9	0.3

Cu (0.90) and S_{total} (0.29), the sample Q-OM-03-A is uncontaminated to moderately contaminated by S_{total} (0.67), moderately contaminated by As (1.47), strongly contaminated by Mo (3.12) and Cu (3.05), the sample Q-F-04-A is moderately contaminated by S_{total} (1.16), moderately to strongly contaminated by Mo (2.29) and strongly contaminated by Cu (3.43), the sample Q-DA-05-A is uncontaminated to moderately contaminated by Cu (0.53) and moderately contaminated by Mo (1.24), the sample Q-OM-06-A is moderately to strongly contaminated by Cu (2.93), the sample Q-OM-07-A is uncontaminated to moderately contaminated by S_{total} (0.56) and moderately to strongly contaminated by Cu (2.93), the sample Q-PT-08-A is uncontaminated to moderately contaminated by As (0.09) and S_{total} (0.25), moderately to

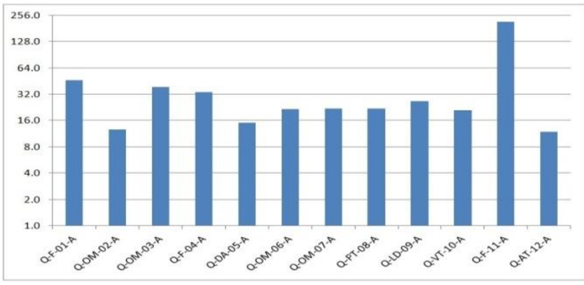

Fig. 1. *Cd* values of A horizon soil samples of studied sites

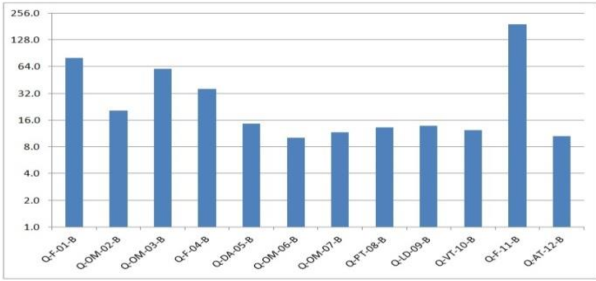

Fig. 2. *Cd* values of B horizon soil samples of studied sites

Table 6. 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	-0.18	-1.70	3.07	4.18	-1.97	-1.49	-2.62	-0.72	-1.89	-0.67	-0.11
Q-OM-02-A	-0.91	-2.71	0.70	0.90	-1.69	-0.55	-2.35	-0.27	-1.10	-0.97	0.29
Q-OM-03-A	-0.38	1.47	3.12	3.05	-1.14	-0.04	-1.59	-0.20	-1.03	-0.50	0.67
Q-F-04-A	-0.21	-1.14	2.29	3.43	-1.07	-0.26	-1.37	-0.36	-2.81	-0.58	1.16
Q-DA-05-A	-0.21	-0.26	1.24	0.53	-1.00	-0.66	-1.87	-0.16	-0.77	-0.50	-0.16
Q-OM-06-A	-0.15	-0.74	-0.27	2.93	-0.64	-0.81	-1.51	-0.10	-2.47	-0.35	-0.03
Q-OM-07-A	-0.32	-1.00	-0.18	2.93	-0.61	-1.14	-1.65	-0.07	-2.60	-0.50	0.56
Q-PT-08-A	-0.45	0.09	-0.22	2.86	-0.87	-0.25	-1.73	-0.33	-1.37	-0.50	0.25
Q-LD-09-A	-0.45	0.51	1.47	2.97	-1.07	-0.10	-1.28	-0.66	-0.02	-0.58	-0.36
Q-VT-10-A	-0.58	0.61	0.35	2.65	-1.14	-0.25	-1.75	-0.70	-0.58	-0.77	-0.34
Q-F-11-A	0.09	0.39	6.68	5.02	-0.93	-0.46	-1.82	-0.31	-1.18	-0.50	1.31
Q-AT-12-A	-0.82	0.18	0.19	-0.81	-1.39	-0.39	-1.84	-0.71	0.42	-0.87	-0.78

strongly contaminated by Cu (2.86), the sample Q-LD-09-A is uncontaminated to moderately contaminated by As (0.51), moderately contaminated by Mo (1.47) and moderately to strongly contaminated by Cu (2.97), the sample Q-VT-10-A is uncontaminated to moderately contaminated by As (0.61) and Mo (0.35), moderately to strongly contaminated by Cu (2.65), the sample Q-F-11-A is uncontaminated to moderately contaminated by Fe (0.09) and As (0.39), moderately contaminated by S_{total} (1.31), very strongly contaminated by Mo (6.68) and Cu (5.02), the sample Q-AT-12-A is uncontaminated to moderately contaminated by As (0.18), Mo (0.19) and Cr (0.42).

4. Conclusions

Summarizing and comparing the values of pollution degree with heavy metals, aluminum and some nonmetals of A and B horizons of all soil samples (according to *Cf* and *I-geo*), it is possible to assert unequivocally that except the chromium and titanium the high content of other elements in the soil is connected with anthropogenic factor, particularly with mining industry developed in this region. It should be noted that due to continuous mining activity as well as soil condition, texture and some physicochemical peculiarities (not very high capacity of A horizon, an average content of humus, eroded condition etc.) the pollution of the deeper layers of soil was also observed. Analyzing the results of total contamination degree assessment according to *Cd* it can be argued that the territories around the processing plant are the most polluted sites and the vicinage of Artsvanik active tailing dump is the least polluted area. Thus the study showed that the soils around Zangezur Copper and Molybdenum Combine were widely and extremely polluted by some heavy metals as a result of long-term industrial activities, and more attention should be paid to pollution as well as the great efforts should be made to devise effective methods of restoration of polluted lands, in particular, phytoremediation as the most efficient, cost-effective and environmentally safe method.

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