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ENVIRONMENTAL RISK ASSESSMENT OF SOIL POLLUTION BY SOME TRACE ELEMENTS AROUND OPEN MINE AND TAILING DUMP OF AKHTALA MINING AND PROCESSING ENTERPRISE

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The aim of the present study was the assessment of soil pollution by some potentially toxic trace elements in the environs of Akhtala Mining and Processing Enterprise and related environmental risks. The study was implemented in 2018. The level of soil contamination with trace elements was assessed by Enrichment factor, which is widely used as a contamination index. The study revealed that the soils, almost in all studied sites, were polluted by Cu, Pb, Zn, Co and Ni. From all trace elements studied the highest contents compared with background were observed for copper. Such situation is conditioned by anthropogenic factor, in particular, by mining activities since copper is the main metal extracted in Akhtala Mining and Processing Enterprise.

Keywords: Akhtala Mining and Processing Enterprise, environmental risks, trace elements, soil, Enrichment factor.

Introduction. Trace elements in the soil are derived from the lithogenic source (natural weathering of parent rocks) and various anthropogenic sources (urbanization and industrialization including mining) [1, 2]. Among anthropogenic sources of toxic metals copper mining plays an essential role in Armenia.

The mining of metals has a long tradition in Armenia, especially in Lori Marz [3]. The mineral resources extraction such as copper, molybdenum, chromium, iron and gold was accompanied by a huge environment contamination.

Trace element contamination is hidden, dangerous, and irrecoverable; it has not only a negative influence on the air, water resources, soils and biodiversity, but also threatens the human health [4, 5]. In organisms, the toxic metals interfere with different metabolic processes, in particular by reducing the activities of some enzymes, lead to disruption of growth and development, as well as reduce the competitiveness of different species within the ecosystem [6]. So far as soil is an accumulator for trace elements dismissed from anthropogenic sources, thus understanding the distribution and availability of toxic metals in soils is of utmost significance considering the consequences for environmental health [7].

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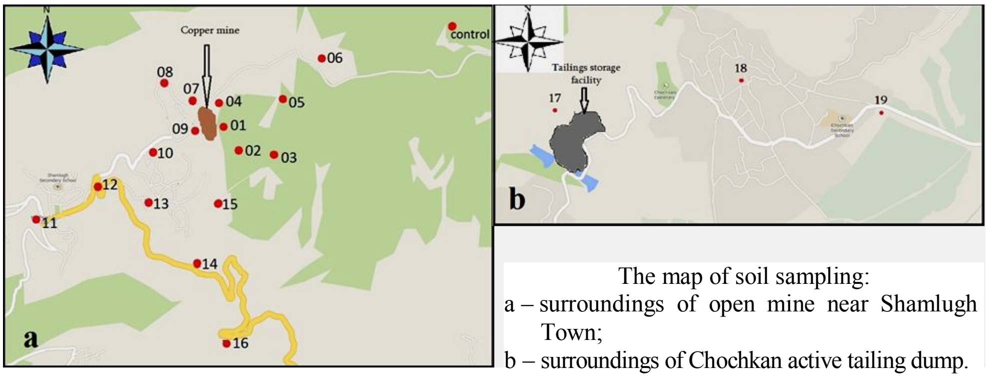
The triad approach, developed for the assessment of soil quality [8], has been recommended and successfully applied in ecological risk assessment of polluted soils [9]. The triad approach consists of three lines of evidence: chemical, ecotoxicological and ecological [10]. While stages 2 and 3 are executed to decrease uncertainties of the actual risk, stage 1 is substantially a screening phase, aiming to make the first spatial representation of the ecological risk and to define whether an area can be eliminated from higher stages of testing, or it needs to be further assessed [11, 12]. In stage 1 the chemical line of evidence comprises the comparison of the total concentrations of contaminants (particularly toxic metals) in the soils of studied area.

Due to these considerations, the objectives of this research were as follows: (1) to analyze the trace element contents in the soils of the studied area, (2) to assess the levels of soil contamination in respect to concentrations of toxic trace elements in the background (control) site, and (3) to find out the associations among different metals and their spatial distribution.

Materials and Methods.

Studied Area. The Akhtala Mining and Processing Enterprise is situated in the North-East of Armenia (Lori Marz). The soils of two high-risk sites of this region were studied (see Figure):

- surroundings of open mine near Shamlugh Town (samples №№ 1–16);
- surroundings of Chochkan active tailing dump (samples №№ 17–19).



The map of soil sampling:
a – surroundings of open mine near Shamlugh Town;
b – surroundings of Chochkan active tailing dump.

The soil type in the studied areas is the mountain cambisol with its 2 subtypes: the decalcified subtype is prevailed in the surroundings of open mine, whereas the calcareous subtype of mountain cambisol – in the surroundings of Chochkan active tailing dump.

The mountain cambisol in Armenia is distributed 500–1700 *m* above sea level (on southern arid slopes it extends up to a height of 2400 *m*) [13]. The decalcified mountain cambisol is distributed in comparatively high sites with abundant precipitation (937–1287 *m* above sea level in the territories under study). The calcareous mountain cambisol in the studied territories is spread in relatively low (705–783 *m* above sea level) and droughty sites. The relief of studied area is rather complex and disjointed, and the gradients of the slopes vary from 3 to 41 degrees.

Sample Collection. For studying purpose 19 sampling sites were selected in 2018. The background soil sample was taken in the site which was 2.5 *km* away from the open mine. During the sampling the altitude above sea level and the coordinates of sampling sites were recorded by GPS. Soil samples were taken from a depth of 0–20 *cm* by means of special sampling kit.

Pretreatment of Soil Samples and Trace Element Analysis. In the laboratory the soil samples were oven dried at 40°*C* to constant weight for a minimum of 24 *h*, then were ground and passed through a 1-*mm* mesh. Before trace element analysis the soil samples were processed appropriately [14]. Soil was ground in a mortar and pestle to pass a 0.42-*mm* nylon mesh. Total concentration of trace elements was determined using Aqua Regia ($HCl–HNO_3$, 3:1) extraction method (3 *g* of soil sample were digested for 2 *h* at 180°*C*). Determination of metals was performed by atomic absorption spectrometry method using Atomic-absorption spectrometer PG990 (PG Instruments Ltd).

Assessment of Trace Element Contamination. The degree of soil contamination by trace elements was evaluated by Enrichment factor (EF) that had a worldwide practical use. Calculation of EF is based on the standardization of a studied trace element in comparison with reference metal. A reference metal is one characterized by low occurrence changeability [15]. In our researches ferrum was used as reference metal since it is a lithophylic element and has a high chemical resistance to the weathering. The EF values were calculated by the following formula [16]:

$$\mathrm{EF} = \frac{(C_n / C_{ref})}{(B_n / B_{ref})},$$

where C_n is the concentration of trace element n in the soil; C_{ref} is the content of the reference metal in the examined environment; B_n is the content of examined trace element n in the control site and B_{ref} is the content of the reference metal in the control site. The evaluation by values of EF was implemented according to Tab. 1.

Table 1

Model and the categories for the description of soil contamination

Model	Class	Description
Enrichment factor	EF ≤ 2	depletion to minimal enrichment, suggestive for or minimal pollution
	2 < EF ≤ 5	moderate enrichment, suggestive of moderate pollution
	5 < EF ≤ 20	significant enrichment, suggestive of a significant pollution signal
	20 < EF ≤ 40	very highly enriched, indicating a very strong pollution signal
	EF > 40	extremely enriched, indicating an extreme pollution signal

Results and Discussion. The concentrations of some trace elements in the soils around the open mine and active tailing dump of Akhtala Mining and Processing Enterprise were determined (Tab. 2). The content of copper in studied soil samples ranged in the interval from 18 to 113 *mg*/*kg*. The lowest content of Cu, exceeding its content in background soil sample mere by 1 *mg*/*kg*, was detected in soil sample from the observation station № 5 whereas the maximal content of copper was observed in soil sample from the station № 15, which was 6.6 times as much comparing with background content. In all studied soil samples the lowest contents of zinc, lead, nickel and cobalt have not exceeded the contents of mentioned elements in background soil samples while their highest contents exceeded background amounts 2 (station № 2), 2.6 (station № 12), 1.8 (station № 18) and 1.8 (station № 16) times, respectively. It should be noted that the highest content of nickel was observed in the soils from the surroundings of tailing dump, and the greatest content of remaining metals was detected in the sites adjacent to open mine. From all trace elements studied the highest contents as compared with background were observed for copper. This fact is associated with anthropogenic factor; in particular it is directly conditioned by mining activities since the main metal extracted in Akhtala Mining and Processing Enterprise is copper.

Table 2

Results of statistical analysis of some trace elements content in soils adjacent to open mine and active tailing dump of Akhtala Mining and Processing Enterprise (mg/kg)

Measure	Cu	Zn	Pb	Ni	Co
Minimum value	18	400	3.4	15	10.8
Maximum value	113	800	11	37	30.4
Mean value	65.69	570	6.73	21.63	17.85
Median	60	600	6	19	17.2
Standard deviation	26.89	106.93	2.31	6.57	4.16
Control	17	400	4.3	21	16.7

The correlation analysis of the obtained data was carried out subsequently to clarify the interconnection of copper, zinc, lead, nickel and cobalt content changes in the analyzed soil samples taken from different observation stations. Correlation analysis is a bivariate method which represents the degree of relationship between two random variables. For this purpose, Spearman's rank coefficient of correlation among five trace elements, namely Cu, Zn, Pb, Ni and Co was calculated for correlation analysis as displayed in Tab. 3. The correlation analysis was implemented for the 19 studied areas to determine whether the changes of trace elements in the soil had identical trend or not in spatial distribution.

Table 3

Correlation matrix

	Cu	Zn	Pb	Ni	Co
Cu	1				
Zn	0.49	1			
Pb	0.55	0.00	1		
Ni	–0.29	–0.10	–0.15	1	
Co	0.24	0.49	0.17	–0.11	1

The correlation coefficient of Spearman's rank is expressed by q, the value of which is continuously from –1.0 to +1.0. A positive q matches to an increasing monotonic trend between two parameters whereas a negative q matches to a decreasing monotonic trend between two parameters. A high-level correlation coefficient (nearby –1.0 or +1.0) means an effective relationship between two variables. If the value is nearby zero it aims no relationship between them [17]. The noticeable positive correlation (from 0.7 to 0.5) was observed between copper and lead while the moderate positive correlation (from 0.5 to 0.3) was seen between copper and zinc as well as between zinc and cobalt. Specified results of calculation indicate that the changes in contents of all mentioned elements in sites under study have similar tendency and it is assumed that the soil pollution by these elements has the same source, in particular, the mining activities.

The pollution extent of soils by trace elements was further determined using EF index. The indicated method offers a very effective assessment technique of the soil pollution degree and has wide application in international scientific practice. The calculations showed (Tab. 4) that in case of zinc, nickel and cobalt the values of EF were no greater than 2, which pointed a minimal level of pollution while in case of lead in soil samples taken from stations № 8 and № 12 the values of EF constituted 2.05 and 2.09, respectively, that was the evidence of soils moderate pollution by this metal in mentioned sites. Concerning to copper the moderate pollution of soils by this metal was registered in all observation stations except the sites № 4, № 5 and № 8, where the pollution was minimal. The moderate pollution has direct relation to mining activities carried out in the territory under study. The highest value of EF for copper (4.83) was registered in observation station № 15 that is explained by the fact that the mentioned station is situated in the southern part of the open mine, very close to the road of ore transporting machines and has a relatively low position.

Table 4

The degree of trace element contamination of soil samples according to EF

Observation station, №	Cu	Zn	Pb	Ni	Co
1	2.71	1.30	0.85	0.70	0.96
2	2.81	1.74	0.69	0.62	1.12
3	2.94	0.83	1.10	0.67	0.74
4	1.96	1.43	1.02	0.91	0.84
5	1.05	1.23	1.58	1.41	1.11
6	2.67	1.14	0.95	0.78	0.81
7	2.79	1.05	1.15	0.89	0.90
8	1.47	1.00	2.09	1.43	1.13
9	2.85	0.93	1.30	0.80	0.82
10	3.85	1.15	1.65	0.70	0.76
11	3.04	1.15	1.55	0.63	0.78
12	4.24	1.30	2.05	0.76	0.82
13	4.52	1.15	1.79	0.55	0.99
14	4.58	1.20	1.52	0.63	1.00
15	4.83	1.09	1.52	0.76	0.47
16	4.61	1.37	1.48	0.67	1.43
17	3.48	1.36	0.97	1.43	0.94
18	3.58	1.41	1.05	1.53	0.96
19	3.23	1.35	0.95	1.24	0.89

Conclusion. Considering the results of our research it is possible to state in general that the soils in the environs of open mine and tailing dump of Akhtala Mining and Processing Enterprise are polluted by some trace elements. After the overall analysis of soil pollution degree by five trace elements in 19 observation sites the following rank of soil pollution in the decreasing order was registered: Cu > Pb > Zn > Co > Ni. Apparently, the main pollutant is copper. Such situation is associated with its high content in the extracted ore and it can be asserted unequivocally that the pollution of studied soils by copper has the anthropogenic nature.

Taking into account all mentioned above, it is absolutely essential to implement the soil restoration and remediation activities in the studied territory, in particular the phytoremediation that is considered a harmless approach for removing pollutants, especially metals, from the ambient environment, also a cost-effective and publicly acceptable method.

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