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Heavy Metal Pollution of the Soils Around the Mining Area Near Shamlugh Town (Armenia) and Related Risks to the Environment

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Abstract: *The heavy metal pollution of the soils around the mining area near Shamlugh town and related risks to human health were assessed. The investigations showed that the soils were polluted with heavy metals that can be ranked by anthropogenic pollution degree as follows: Cu>Pb>As>Co>Ni>Zn. The main sources of the anthropogenic metal pollution of the soils were the copper mining area near Shamlugh town, the Chochkan tailings storage facility and the trucks transferring ore from the mining area. Copper pollution degree in some observation sites was unallowable for agricultural production. The total non-carcinogenic chronic hazard index (THI) values in some places, including observation sites in Shamlugh town, were above the safe level (THI<1) for children living in this territory. Although the highest heavy metal enrichment degree in the soils was registered in case of copper, however the highest health risks to humans especially children were posed by cobalt which is explained by the fact that heavy metals have different toxicity levels and penetration characteristics.*

Keywords: *Armenia, copper mine, soil, heavy metal pollution, health risks.*

1. Introduction

Rapid urbanization and industrial development have caused the degradation of air, water and soil quality in most countries of the world [1].

During the last decades of the twentieth century, there was an awareness of the importance of soil as an environmental component and the recognition of need to maintain or improve its capacity to allow it to perform its various functions. At the same time, there was a confirmation that soil is not an inexhaustible resource, and if used improperly or poorly managed, its characteristics can be lost in a short period of time, with limited opportunities for regeneration [2].

Heavy metal pollution of surface soils due to intense industrialization and urbanization has become a serious concern in many parts of the world especially in developing countries [3].

Soil pollution with heavy metals is derived from anthropogenic activities, mainly associated to industrial activities and natural processes [2].

Industrial development has led to an increase in the production and emission of heavy metals. Some metals are essential micronutrients for microorganisms, plants and animals, but they have strong toxic effects and pose an environmental threat at high concentrations [4].

Although researches involving soil quality are facing an important technologic challenge with several actions being taken in order to assess, correct and reduce the risks of contaminants in soil, standardized monitoring combined with remediation strategies are still needed [2].

Metallurgical industry is a developed branch of Armenian economy. Since the last decades of the twentieth century, the mining and beneficiation of a variety of minerals have been driving force behind economic development, particularly in Syuniq marz and Lori marz (administrative districts) of the Republic of Armenia. Shamlugh town is situated in the north-east of Armenia (Lori marz) where metallurgical industry is developed [5]. This economic sphere is a potential source of soil pollution with heavy metals. Heavy metals are considered as dangerous pollutants which may cause environmental and health hazards [6, 7].

Therefore, the investigation of the heavy metal pollution of the soils and related health risks in this territory is required.

The aim of the present study was to investigate the heavy metal pollution of the soils around ecologically vulnerable mining areas near Shamlugh town and related risks to the environment.

2. Materials and Methods

The soils around the copper mining area near Shamlugh town were studied in September, 2014.

25 observation sites were chosen in and near Shamlugh town, and a control site was selected in a place which was 4 km away from the mining area near Shamlugh town and wasn't under anthropogenic influence (Fig. 1).

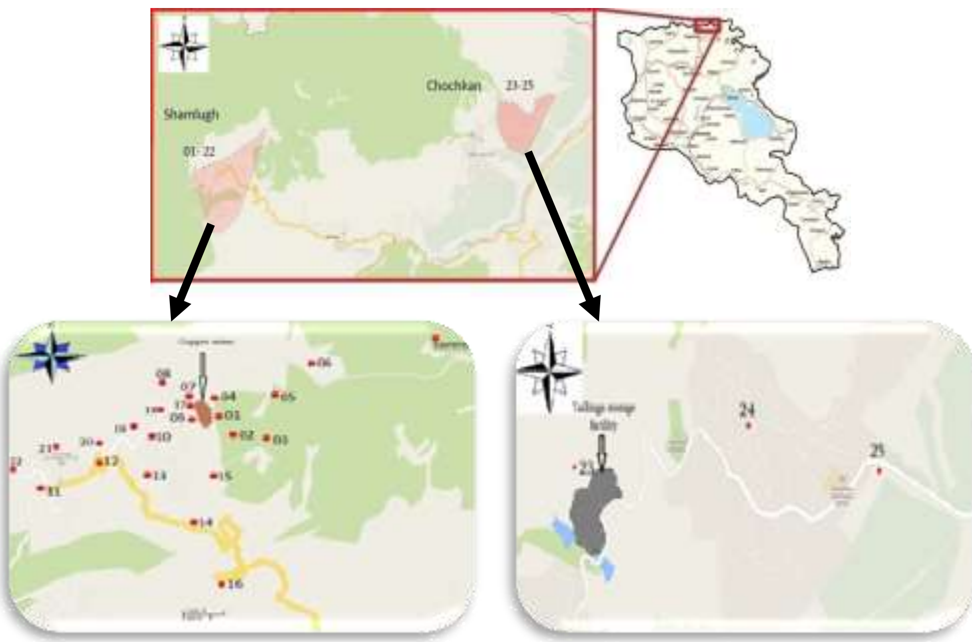

Fig. 1: The map of Armenia showing investigated territories and sampling sites in and near Shamlugh town.

The coordinates of sampling sites were recorded by a GPS.

4 soil samples were taken from each observation site from 3 locations near Shamlugh town (surroundings of the Shamlugh copper mine and the Chochkan active tailings storage; control site) (Fig. 1). The soil samples were obtained from a depth of 0-20 cm and transferred into well labeled polyethylene bags for storage and laboratory analysis.

The 4 soil samples collected from each observation site were mixed into each other prior to treatment and analysis.

The soil samples were oven dried at 70°C for 48 h. The dried samples were grounded into powder by a laboratory mortar and pestle, sieved with 1 mm mesh sieve and stored in an air tight container prior to analysis. The digestion of the soil samples was done by a technique described in [8].

The digested soil samples were analyzed for heavy metals by using "PG990" atomic absorption spectrophotometer (PG Instruments LTD, UK).

The standard guidelines for heavy metal content in soil haven't been developed in Armenia, therefore, the Georgia and China soil quality standards for agricultural production were used to assess heavy metal pollution level in the soils [9, 10].

The enrichment factor (EF) calculation is a common approach to estimate anthropogenic impact on soils. EF was calculated as follows [11]:

$$EF = [(M_c/M_r)]s / [(M_c/M_r)]b \qquad (1),$$

where M_c is the content of examined element, M_r is the content of reference element, s is the sample, and b is the background. A reference element is often used as a conservative element. The most common reference elements are Zn, Mn, Al, Fe, etc [11]. In this study, Zn was used as a reference element as it mainly originated from natural lithogenic sources.

Five contamination categories are recognized on the basis of the enrichment factor: <2=deficiency to minimal enrichment; 2-5=moderate enrichment; 5-20=significant enrichment; 20-40=very high enrichment; >40=extremely high enrichment [11].

Health risks associated with the heavy metal pollution of soil were studied via ingestion, dermal and inhalation routes to recipients based on the USDOE and USEPA risk assessment methodology [12, 13]. The non-carcinogenic chronic daily exposure doses through oral ingestion (mg/kg/d), dermal absorption (mg/kg/d) and inhalation (mg/m^3) were calculated using equations (2), (3) and (4):

$$ED_{ing} = \frac{C \times IR \times CF \times ED \times EF}{BW \times AT} \qquad (2),$$

$$ED_{derm} = \frac{C \times ABS \times AF \times CF \times ED \times EF \times SA}{BW \times AT} \qquad (3),$$

$$ED_{inh} = \frac{C \times ET \times ED \times EF}{PEF \times 24 \times AT} \qquad (4).$$

The values and definitions of the parameters given in equations (2), (3) and (4) were taken into consideration according to [12, 13].

The non-carcinogenic hazard quotient (HQ) value (unitless) of individual heavy metals was calculated by equation (5):

$$HQ_{ing/derm/inh} = \frac{ED_{ing/derm/inh}}{RfD/RfC_{ing/derm/inh}} \qquad (5),$$

where RfD_{ing}, RfD_{derm} are reference doses (mg/kg/d) through oral ingestion and dermal absorption respectively, RfC_{inh} is a reference concentration (mg/m^3) through inhalation [12-14].

According to equation (6), the sum of the HQs of different exposure pathways, expressed as the individual metal hazard index (HI_m), was used to assess non-carcinogenic effects posed by each metal:

$$HI_m = \sum HQ = HQ_{ing} + HQ_{derm} + HQ_{inh} \qquad (6).$$

Non-carcinogenic health risks posed by all metals, expressed as the total hazard index (THI), were assessed by the following equation:

$$THI = \sum_{i=0}^{n} HI_m \qquad (7).$$

3. Results and Discussion

The concentrations (mg/kg) of some heavy metals in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility are presented in Table I.

Cu content in almost all the investigated sites was higher than its concentration in the control site. High Cu concentrations were registered particularly in the observation sites № 07, 09, 14, 16-18 where its content exceeded the maximum permissible concentration (MPC) (grade II of China soil environmental quality standard) for agricultural production (Tab. I) [9]. This is explained by the fact that № 07, 09, 17 and 18 observation sites were very close to the copper mine, and the sampling sites № 14 and 16 were near to the road through which ore was transferred from the mining area (Tab. I, Fig. 1).

Pb and As concentrations in almost all the observation sites exceeded the background (control) level.

The background (control) level of Ni, Zn and Co was lowly exceeded in most of the soil samples (Tab. I).

Cu, Pb, As, Ni, Zn and Co contents in the investigated soils decreased with increasing distance from the open mine, the active tailings storage facility and the ore transportation road (Tab. I, Fig. 1). Although Pb, As, Ni and Zn concentrations in the investigated soils were mainly higher than their contents in the control site, however, they were bellow the MPC (grade II of China soil environmental quality standard and Georgia soil quality standard) for agricultural production (Tab. I) [9, 10].

Considering the heavy metal content of the control (background) sample as representing lithogenic metal, it’s possible to state that heavy metal concentrations in the soils were conditioned by both lithogenic and anthropogenic sources, but the content of Cu in almost all the investigated sites were mostly conditioned by anthropogenic factor especially metallurgical industrial activity. The contents of Ni, Zn and Co in the investigated soils were mostly formed by natural factor. The investigated heavy metals can be ranked by anthropogenic pollution degree as follows: Cu>Pb>As>Co>Ni>Zn (Tab. I).

TABLE I: Heavy Metal Concentrations (mg/kg) in the Soils Around the Shamlugh Copper Mine and the Chochkan Tailings Storage Facility

Number of sampling sites	Cu	Pb	As	Ni	Zn	Co
01	67.0	5.5	11.7	18.0	115	23.1
02	60.0	3.4	11.2	15.0	113	21.6
03	45.0	4.7	0.0	17.0	92	14.8
04	50.0	4.6	3.3	30.0	104	16.0
05	35.0	4.5	0.0	20.0	94	14.8
06	18.0	3.9	0.0	17.0	90	15.8
07	145.0	10.7	9.0	33.0	115	24.2
08	25.0	9.0	7.0	30.0	103	18.8
09	150.0	11.0	12.0	20.0	125	17.2
10	81.3	7.0	4.8	18.0	114	15.3
11	52.0	6.0	0.0	18.0	100	14.8
12	60.0	6.7	4.1	18.3	95	16.4
13	100.0	10.0	10	15.0	106	21.6
14	107.0	11.2	8.7	18.8	105	14.3
15	53.0	9.0	0.0	22.0	95	10.8
16	320.0	8.1	16.0	18.0	120	30.4
17	280.0	11.5	11.0	33.9	120	22.3
18	170.0	9.7	12.0	25.7	115	16.8
19	67.0	7.3	8.5	20.3	105	17.0
20	62.0	7.4	9.0	18.1	90	16.3
21	78.0	6.1	5.6	18.2	100	14.4
22	65.0	6.0	8.0	16.0	90	15.2
23	72.0	6.1	8.4	35.0	107	21.1
24	65.0	4.6	7.0	33.0	106	17.2
25	60.0	4.2	5.8	24.4	105	15.9
Control	19.6	4.1	4.4	18.2	90	14.2
MPC	100.0***	32.0**	25.0***	50.0***	220**	NA*

*Not available

**Georgia soil quality standard

***China soil environmental quality standard

Heavy metal enrichment degree in the soils was assessed by the enrichment factor (EF). The highest heavy metal enrichment degree in the soils was registered in case of copper. The soils were lowly enriched with nickel and cobalt (Tab. II). According to the EF values, the enrichment degree of different heavy metals was in the order of Cu>Pb>As>Co>Ni (Tabs II and III). High heavy metal enrichment degree in the soils was registered in the observation sites nearest the open mine and the ore transportation road (Tab. III, Fig. 1).

TABLE II: The Enrichment Factor Values in the Soils Around the Shamlugh Copper Mine and the Chochkan Tailings Storage Facility

Parameters	**Enrichment factor values**				
	Cu	**Pb**	**As**	**Ni**	**Co**
Minimum	0.9	0.7	0.0	0.7	0.7
Maximum	12.2	2.3	2.7	1.6	1.6
Mean	3.9	1.5	1.3	1.1	1.1
Standard deviation	2.7	0.5	0.8	0.3	0.2

Soil polluted with heavy metals can increase human health risks not only through soil-food chain but also different exposure pathways such as oral ingestion, dermal contact and the inhalation of particulates [7]. The investigation of health risks posed by oral ingestion, dermal contact and the inhalation of particulates showed that the total non-carcinogenic chronic hazard index (THI) values in the observation sites № 01, 02, 07-09, 13, 14, 16-20, 22-25 were above the safe level (THI<1) for children living in the investigated territory (Fig. 2) [15]. Children are particularly more susceptible to the exposure to toxic metals in soil than adults because they may absorb much more heavy metals from soil during their outdoor play activities [16]. The highest THI value was registered in the observation site (№ 16) nearest the ore transportation road but the highest health risks to humans especially children were posed from the observation sites № 17-20 as they were situated in Shamlugh town. The THI values for adult and child decreased with increasing distance from the open mine, the active tailings storage facility and the ore transportation road (Figs 1, 2).

TABLE III. Heavy Metal Enrichment Degree in the Soils Around the Shamlugh Copper Mine and the Chochkan Tailings Storage Facility According to the EF Values

Heavy metals	**Sample number**																								
	01	**02**	**03**	**04**	**05**	**06**	**07**	**08**	**09**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Cu																									
Pb																									
As																									
Co																									
Ni																									

= deficiency to minimal enrichment   oderate enrichment   ificant enrichment

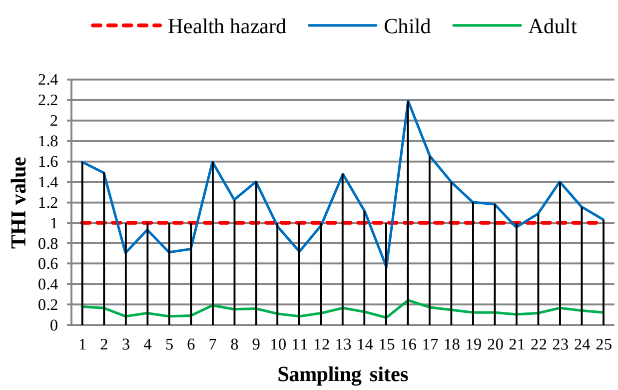

Fig. 2: The values of the total non-carcinogenic chronic hazard index (THI) of heavy metals in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility.

According to the individual metal non-carcinogenic hazard index (HI_m) values, health hazard of individual heavy metals was in the order of Co>As>Ni>Cu>Pb>Zn. Although the soils were lowly enriched with cobalt, however, the highest health hazards were posed by this metal as it had the highest HI_m values in the investigated soils, and lead was the second anthropogenic metal after copper, but the lowest health risks after zinc were posed by this metal (Table IV). This is explained by the toxicity level and penetration characteristics of individual heavy metals as some metals, that have high toxicity and penetration capacity, may cause health effects even at low concentrations, but others having lower toxicity and penetration capacity may pose health risks at higher pollution degrees. All of this indicates that the determination of individual heavy metal pollution degree in soil is not sufficient to assess related human health hazards precisely as in this case, the toxicity level and penetration capacity of metal are also important and should be taken into consideration.

TABLE IV. The Individual Metal Non-carcinogenic Hazard Index Values in the Soils Around the Shamlugh Copper Mine and the Chochkan Tailings Storage Facility

Parameters	Cu	Pb	As	Co	Ni	Zn
	Individual metal hazard index value for child					
Minimum	0.0060	0.0127	0.0000	0.4706	0.0280	0.0039
Maximum	0.1041	0.0427	0.6973	1.3186	0.0653	0.0054
Mean	0.0297	0.0265	0.3017	0.7747	0.0412	0.0045
Standard deviation	0.0237	0.0094	0.1962	0.1813	0.0121	0.0004
	Individual metal hazard index value for adult					
Minimum	0.0006	0.0014	0.0000	0.0505	0.0013	0.0004
Maximum	0.0110	0.0045	0.0741	0.1431	0.0273	0.0006
Mean	0.0035	0.0028	0.0321	0.0840	0.0136	0.0005
Standard deviation	0.0027	0.0010	0.0208	0.0197	0.0081	0.0001

4. Conclusions

The soils around the mining area near Shamlugh town were polluted with heavy metals (Cu, Pb, As, Co, Ni, Zn) due to copper mining activity. The main anthropogenic sources of the heavy metal pollution of the soils were the Shamlugh copper mine, the Chochkan tailings storage facility and the trucks transferring ore from the mining area. The soils were highly polluted particularly with copper, the degree of which in some observation sites was unallowable for agricultural production. The heavy metal pollution of some places, including almost all the observation sites in Shamlugh town, may have posed health risks to humans especially children living in this territory. Despite the high copper pollution of the soils, the highest health risks were posed by cobalt, the enrichment degree of which in the soils was comparatively low. This is explained by the fact that heavy metals have different toxicity levels and penetration characteristics.

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