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

G. A. Gevorgyan, K. A. Ghazaryan, T. H. Derdzyan

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, heavy metal pollution of soil, health risks.

I. 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 countries of the world especially in developing countries [3].

G. A. Gevorgyan is with the Department of Ecology and Nature Protection of the Faculty of Biology of the Yerevan State University, the Republic of Armenia; the Scientific Center of Zoology and Hydroecology of the National Academy of Sciences of the Republic of Armenia (phone: 0037495101184; fax: 00374 10 554641; e-mail: gev_gor@mail.ru).

K. A. Ghazaryan is with the Department of Ecology and Nature Protection of the Faculty of Biology of the Yerevan State University, the Republic of Armenia (e-mail: kghazaryan@ysu.am).

T. H. Derdzyan is with the Department of Ecological Chemistry of the Faculty of Chemistry of the Yerevan State University, the Republic of Armenia (e-mail: derdzyan.t@gmail.com).

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 which are considered as dangerous pollutants causing 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.

II. 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).

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. The soil samples were transferred into well labeled polyethylene bags for storage and laboratory analyses.

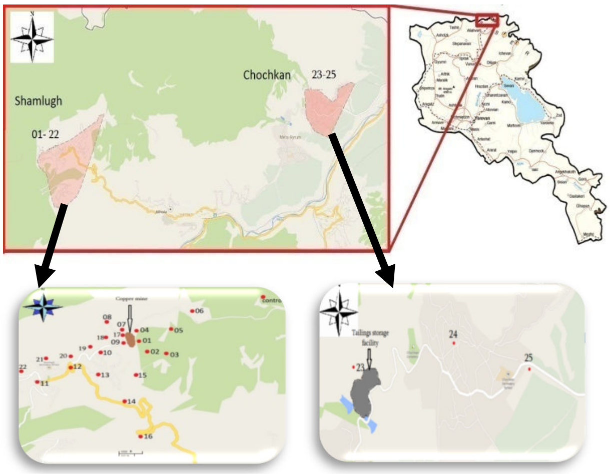

Fig. 1 The map of Armenia showing investigated territories and sampling sites in and near Shamlugh town

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 proportion of anthropogenic metal was determined by [11]:

$$\text{Anthropogenic metal} = (X - X_c)/X \times 100 \quad (1),$$

where X is metal concentration in the soil sample, X_c is metal concentration in the control sample.

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

$$EF = [(M_c/M_r)]s / [(M_c/M_r)]b \quad (2),$$

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 factors which are presented in Table I.

TABLE I
CONTAMINATION CATEGORIES ACCORDING TO THE ENRICHMENT FACTOR VALUES [11]

EF value	Contamination categories
< 2	deficiency to minimal enrichment
2-5	moderate enrichment
5-20	significant enrichment
20-40	very high enrichment
> 40	extremely high enrichment

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 (3)-(5):

$$ED_{ing} = \frac{C \times IR \times CF \times ED \times EF}{BW \times AT} \quad (3)$$

$$ED_{derm} = \frac{C \times ABS \times AF \times CF \times ED \times EF \times SA}{BW \times AT} \quad (4)$$

$$ED_{inh} = \frac{C \times ET \times ED \times EF}{PEF \times 24 \times AT} \quad (5)$$

The values and definitions of the parameters given in (3)-(5) are presented in Table II.

TABLE II
THE VALUES AND DEFINITIONS OF VARIABLES FOR HUMAN HEALTH RISK ASSESSMENT [12], [13]

Parameters	Unit	Definition	Value	
			Child	Adult
C	mg/kg	heavy metal concentration		
ABS	-	dermal absorption factor	0.03	0.001
AF	mg/cm^2	soil to skin adherence factor	0.2	0.07
BW	kg	average body weight	16	70
ED	year	exposure duration	6	30
EF	d/year	exposure frequency	350	350
ET	h/d	exposure time	24	24
IR	mg/d	soil ingestion rate for receptor	200	100
SA	cm^2/event	skin surface area available for exposure	2800	5700
AT	d	averaging time for non-carcinogens	EDx365	
CF	kg/mg	unit conversion factor	10^{-6}	
PEF	m^3/kg	soil-to-air particulate emission factor	1.36×10^9	

The non-carcinogenic hazard quotient (HQ) value (unitless) of individual heavy metals was calculated by (6):

$$HQ_{ing/derm/inh} = \frac{ED_{ing/derm/inh}}{Rfd_{ing/derm/inh}} \quad (6)$$

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 (Table III).

TABLE III
THE VALUES OF REFERENCE DOSES AND CONCENTRATION FOR THE ASSESSMENT OF HEALTH RISKS POSED BY DIFFERENT HEAVY METALS [12]-[14]

Heavy metals	RfD_{ing}	RfD_{derm}	RfD_{inh}
Cu	4.0×10^{-2}	4.00×10^{-2}	NA
Pb	3.5×10^{-3}	3.50×10^{-3}	NA
As	3.0×10^{-4}	2.85×10^{-4}	1.5×10^{-5}
Ni	2.0×10^{-2}	8.00×10^{-4}	9.0×10^{-5}
Zn	3.0×10^{-1}	3.0×10^{-1}	NA
Co	3.0×10^{-4}	3.0×10^{-4}	6.0×10^{-6}

NA = not available

According to (7), 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:

$$HI_m = \sum HQ = HQ_{ing} + HQ_{derm} + HQ_{inh} \quad (7)$$

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

$$THI = \sum_{i=0}^{n} HI_m \quad (8)$$

III. 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 Figs. 2–7.

Cu content in almost all investigated sites was higher than its concentration in the control site. High Cu concentrations were registered particularly in № 07, 09, 14, 16-18 observation sites where its content exceeded the maximum permissible concentration (MPC) (grade II of China soil environmental quality standard) for agricultural production (Fig. 4) [9]. This is explained by the fact that № 07, 09, 17 and 18 observation sites were very close to the copper mine, and № 14 and 16 sampling sites were near to the road through which ore was transferred from the mining area (Fig. 1).

Pb and As concentrations in almost all observation sites exceeded the background (control) level (Figs. 3 and 4).

The background (control) level of Ni, Zn and Co was lowly exceeded in most of soil samples (Figs. 5-7).

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 (Figs 2-7). 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 (Figs. 3, 4, 6, 7) [9], [10].

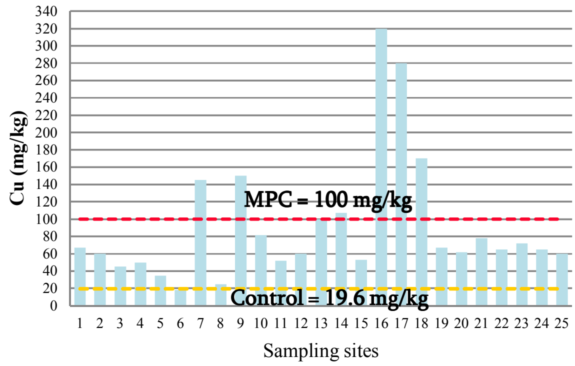

Fig. 2 Copper content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

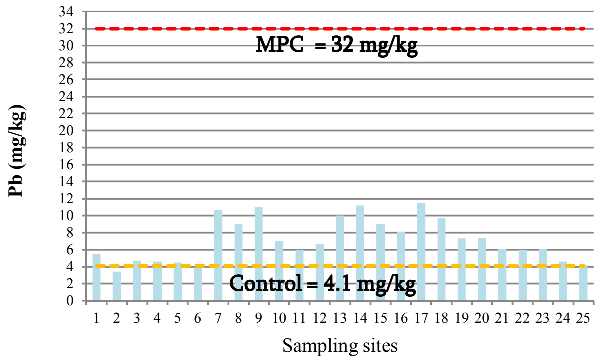

Fig. 3 Lead content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

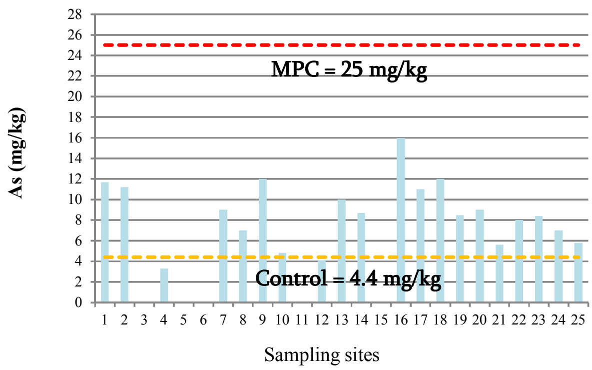

Fig. 4 Arsenic content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

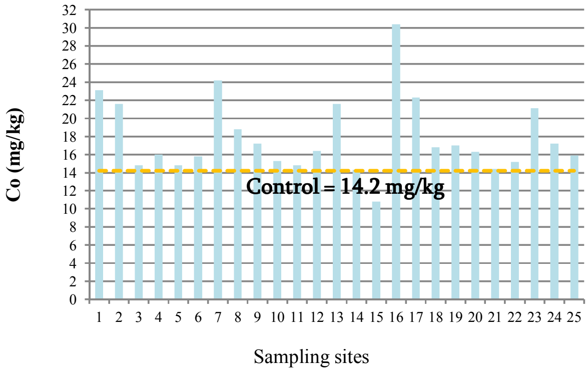

Fig. 5 Cobalt content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

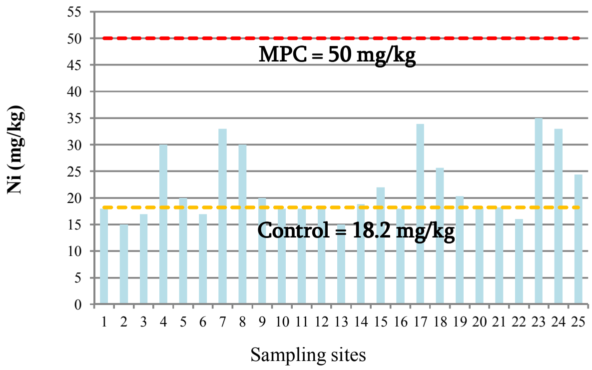

Fig. 6 Nickel content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

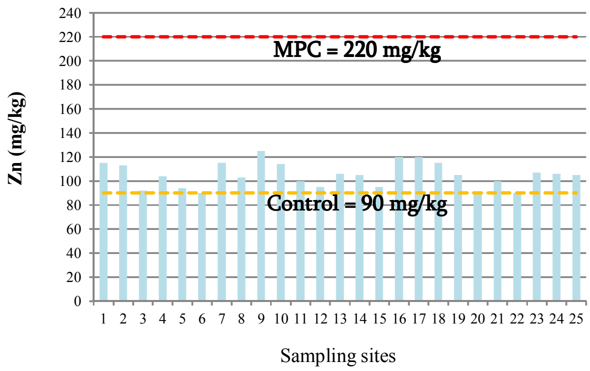

Fig. 7 Zinc content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

Considering the heavy metal content of the control (background) sample as representing lithogenic metal, the proportion of anthropogenic metal was determined which is presented in Figs. 8-13. Figures show that heavy metal concentrations in the soils were conditioned by both lithogenic and anthropogenic sources, but the content of Cu in almost all 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: Cu>Pb>As>Co>Ni>Zn (Figs. 8-13).

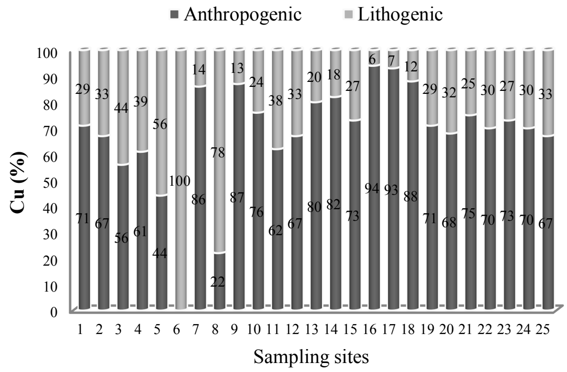

Fig. 8 The proportion of lithogenic and anthropogenic copper content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

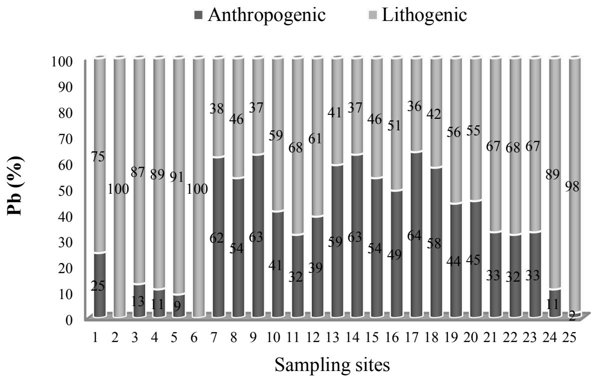

Fig. 9 The proportion of lithogenic and anthropogenic lead content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

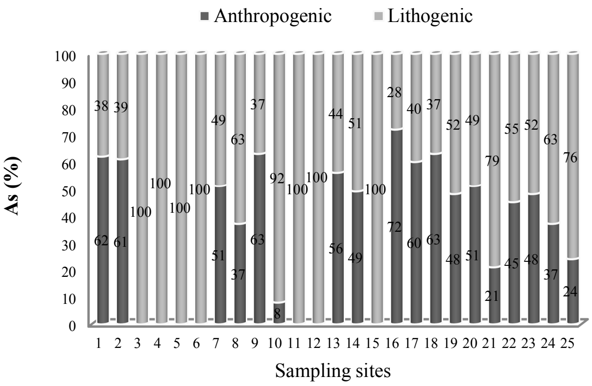

Fig. 10 The proportion of lithogenic and anthropogenic arsenic content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

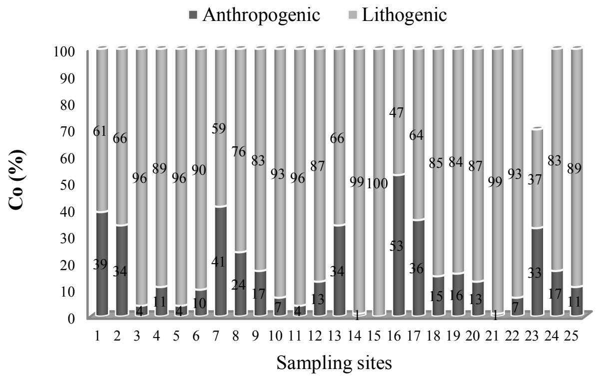

Fig. 11 The proportion of lithogenic and anthropogenic cobalt content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

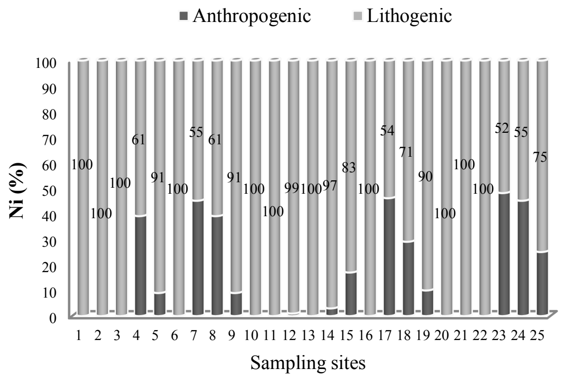

Fig. 12 The proportion of lithogenic and anthropogenic nickel content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

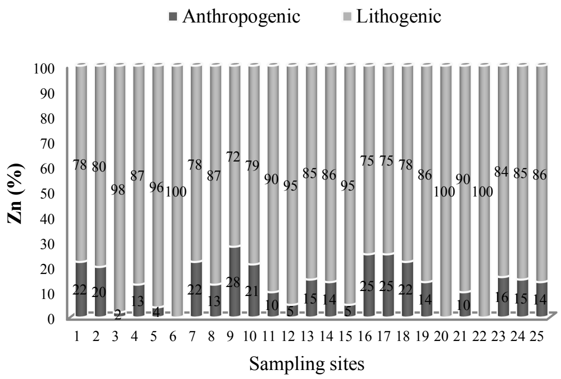

Fig. 13 The proportion of lithogenic and anthropogenic zinc content in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

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. IV). According to EF values, the enrichment degree of different heavy metals was in the order of Cu>Pb>As>Co>Ni (Tabs IV and V). High heavy metal enrichment degree in the soils was registered in the observation sites nearest the open mine and the ore transportation road (Fig. 1, Table V).

TABLE IV
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 № 01, 02, 07-09, 13, 14, 16-20, 22-25 observation sites were above the safe level (THI<1) for children living in the investigated territory (Fig. 14) [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 № 17-20 observation sites 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, 14).

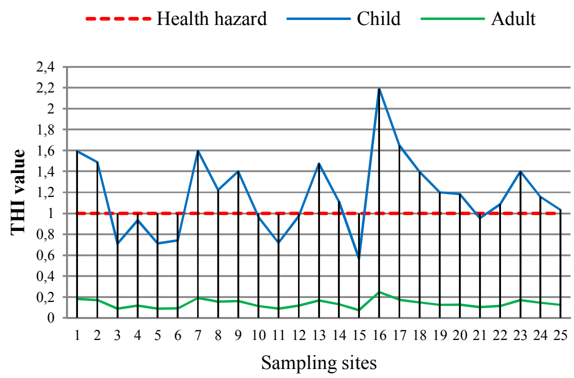

Fig. 14 The values of the total non-carcinogenic chronic hazard index (THI) of heavy metals in the soils around the Shamlugh copper mine and the Chochkan tailings storage facility

TABLE V
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	moderate	moderate	moderate	moderate	moderate		significant		significant	moderate	moderate	moderate	moderate	moderate	moderate	significant	significant	significant	moderate	moderate	moderate	moderate	moderate	moderate	moderate
Pb							moderate						moderate	moderate	moderate		moderate								
As	moderate	moderate														moderate		moderate		moderate					
Co																									
Ni																									

= deficiency to minimal enrichment noderate enrichment nificant enrichment

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 VI). 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 VI
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
Maxumum	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
Maxumum	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

IV. 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 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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