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HUMAN HEALTH RISK ASSESSMENT OF HEAVY METAL POLLUTION IN SOILS AROUND KAPAN MINING AREA, ARMENIA

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ABSTRACT

Non-carcinogenic and carcinogenic health risks of heavy metal pollution in the soils around the Kapan mining area, Armenia were investigated. The results of the study showed that the content of heavy metals (Cr, Mn, Ni, Cu, Zn, As, Mo, Cd, Pb) in the soils sampled in June, 2013 may have posed non-carcinogenic and even carcinogenic risks to population, mainly children living in this territory. Cr was the main element causing human health risks in the area.

Key words: *mining industry, heavy metals, soil, human health risks*

INTRODUCTION

Due to the continuous industrialization in many parts of the world, pollutants are emitted into the terrestrial environment and pose a great threat to human health [16]. Heavy metals are a common occurrence in the environment and have resulted in human exposure for the entire history of mankind [11]. Soil is a dynamic, natural body occurring on the surface of the earth [2]. Soil contamination with heavy metals has severely increased over the last few decades, mainly from industrial wastes and human activities. Soil pollution with heavy metals is a result of both natural processes such as weathering of minerals, and anthropogenic activities, related to industries, fossil fuel burning, emissions from vehicles, mining, agriculture and metallurgical processes and their waste disposal [13]. The degree of soil metal contamination can pose hidden danger to human health via many different ways (e.g. oral ingestion, dermal contact and inhalation pathways) [12]. Once absorbed by the body, heavy metals continue to accumulate in vital organs like brain, liver, bones and kidneys, for years or decades causing serious health consequences [11].

Mining and metallurgical industries are highly developed in the Republic of Armenia and have been the driving force behind economic development in some territories of the country, particularly in Syunik and Lori Marzes (administrative districts) since the last decades of the twentieth century [3, 6, 8, 9]. The insufficient management of mining discharges in these areas has become a serious threat to the environment [1, 3–9]. Kapan region in Syunik Marz is considered as one of metallurgical industrial centers in Armenia. Mining activities in this territory are mainly expressed by heavy metal pollution of the environment [4, 6–9].

Therefore, the investigation of the heavy metal pollution in the soils and related human health risks in this territory is required. The aim of the present study was to assess human health risks of the heavy metal pollution in the soils around Kapan mining area, Armenia.

MATERIAL AND METHODS

The soils around the Kapan mining area located in the southeastern part of Armenia were investigated in June, 2013. The soils in these areas belong to the type of mountain cambisol. 12 observation sites were selected around the Kapan copper-molybdenum combine (Nos. 1–6) and the Geghanush tailing dump (Nos. 7–12). A control site was selected 4 *km* away from the Kapan copper-molybdenum combine.

The soil samples were obtained from a depth of 0–20 cm and transferred into the well labeled polyethylene bags for storage and laboratory analysis. The collected samples were air-dried at room temperature. 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 soil samples were digested by the Aqua Regia (HCl–HNO_3, 3:1) digestion method [20]. The digested soil samples were analyzed for heavy metals (Cr, Mn, Ni, Cu, Zn, As, Mo, Cd, Pb) by using ELAN9000 inductively coupled plasma mass spectrometer (ICP-MS).

Health risks associated with heavy metals in soil were examined based on the risk assessment methodology adopted from the U.S. Department of Energy and the U.S. Environmental Protection Agency (equations (1)–(13)) [15, 18]. The non-carcinogenic chronic daily exposure doses (DED_{nc}) through oral ingestion (mg/kg/d), dermal absorption (mg/kg/d) and inhalation (mg/m^3) were calculated using equations (1)–(3):

$$DED_{ing-nc} = \frac{C \times IngR \times ED \times EF \times CF}{BW \times AT_{nc}} \qquad (1)$$

$$DED_{derm-nc} = \frac{C \times ABS \times AF \times ED \times EF \times SA \times CF}{BW \times AT_{nc}} \qquad (2)$$

$$DED_{inh-nc} = \frac{C \times ET \times ED \times EF}{PEF \times 24 \times AT_{nc}} \qquad (3)$$

where C is measured heavy metal concentration (mg/kg), IngR is the soil ingestion rate for receptor (mg/d), CF is the unit conversion factor (kg/mg), ED is the exposure duration (year), EF is the exposure frequency (d/year), ABS is the dermal absorption factor (unit less), AF is the soil to skin adherence factor (mg/cm^2), SA is the skin surface area available for exposure (cm^2), ET is the exposure time (h/d), BW is the average body weight (kg), AT_{nc} is the averaging time for non-carcinogens (d), PEF is the soil-to-air particulate emission factor (m^3/kg) [15, 18].
The non-carcinogenic hazard quotient (HQ_{nc}) value (unit less) of individual heavy metals was calculated by equation (4):

$$HQ_{nc} = \frac{DED_{nc}}{RfD/RfC} \qquad (4)$$

...where RfD is the reference dose (mg/kg/d) through oral ingestion and dermal absorption, RfC is the reference concentration (mg/m^3) through inhalation [10, 15, 18].
The individual metal non-carcinogenic hazard index (HI_{nc}) value was calculated by equation (5):

$$HI_{nc} = \sum HQ_{nc} = HQ_{ing-nc} + HQ_{derm-nc} + HQ_{inh-nc} \qquad (5)$$

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

$$THI_{nc} = \sum_{i=0}^{n} HI_{nc} \qquad (6)$$

The carcinogenic daily exposure doses (DED_{ca}) for Cr, Ni, As, Pb, Cd were used to assess carcinogenic health risks. DED_{ca} through oral ingestion (mg/kg/d), dermal absorption (mg/kg/d) and inhalation (mcg/m^3) were calculated using equations (7)–(11):

$$DED_{ing-ca} = \frac{C \times IR \times EF \times CF}{AT_{ca}} \qquad (7)$$

$$IR = \frac{ED_{child} \times IngR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times IngR_{adult}}{BW_{adult}} \qquad (8)$$

$$DED_{derm-ca} = \frac{C \times ABS \times EF \times DFS \times CF}{AT_{ca}} \qquad (9)$$

$$DFS = \frac{ED_{child} \times SA_{child} \times AF_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times SA_{adult} \times AF_{child}}{BW_{adult}} \qquad (10)$$

$$DED_{inh-ca} = \frac{C \times ET \times ED \times EF}{PEF \times 24 \times AT_{ca}} \times 10^3 \qquad (11)$$

where IR is soil ingestion rate-age adjusted (mg x year/kg/d), DFS is soil dermal contact factor-age adjusted (mg x year/kg/d), AT_{ca} is averaging time for carcinogens (d) [17, 18].
The individual metal non-carcinogenic hazard index (HI_{ca}) value was calculated by the equation (12):

$$HI_{ca} = DED_{ca} x\ CSF/IUR \qquad (12)$$

where CSF is the oral and dermal cancer slope factor $(mg/kg/d)^{-1}$, IUR is the inhalation unit risk $(mcg/m^3)^{-1}$ [10, 12, 18].
The total carcinogenic hazard index (THI_{ca}) value was calculated by the following equation:

$$THI_{ca} = \sum_{i=0}^{n} HI_{ca} = HI_{ca-ing} + HI_{ca-derm} + HI_{ca-inh} \qquad (13)$$

RESULTS AND DISCUSSION

The results of the investigation of heavy metal contents in the soils around the Kapan mining area are given in *Table 1*. The study results showed that heavy metal concentrations in the soils were conditioned by both lithogenic and anthropogenic sources as the concentrations of different heavy metals in all the investigated observation sites excedeed the background (control) level. The highest level of anthropogenic metal was especially registered in case of Cu and Mo which is explained by the high concentrations of these metals in the ore of the Kapan copper-molybdenum combine (*Table 1*).

Table 1. Some heavy metal contents (*mg/kg*) in the soils around the Kapan copper-molybdenum combine and the Geghanush tailing dump.

Parameters	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb
	Soils around Kapan copper-molybdenum combine								
Minimum	17.54	813.23	26.40	32.57	65.98	6.86	0.25	0.23	4.02
Maximum	99.45	1557.61	118.52	72.76	127.13	22.49	1.14	0.52	22.43
Mean	52.48	1122.41	67.35	51.21	96.82	12.60	0.65	0.33	12.48
Standard deviation	31.14	263.08	34.26	15.47	24.76	5.81	0.33	0.12	6.43
	Soils around Geghanush tailing dump								
Minimum	18.57	854.38	20.52	37.84	56.15	2.74	0.12	0.12	2.64
Maximum	47.43	161.15	56.05	100.42	97.67	7.77	0.53	0.23	7.13
Mean	35.95	1365.37	39.01	66.67	78.43	5.21	0.33	0.18	4.77
Standard deviation	11.93	293.11	14.50	22.79	15.64	2.09	0.14	0.042	2.02
Control	23.20	527.70	26.40	8.97	75.50	7.48	0.18	0.24	10.26

The heavy metal pollution in soil can increase human health risks through different exposure pathways. In this study, non-carcinogenic and carcinogenic health risks posed by oral ingestion, dermal contact and the inhalation of particulates were investigated. The results of the study showed that the THI_{nc} values in all the observation sites were above the safe level ($THI_{nc}<1$) for children living in the investigated territory (*Fig. 1*). Children are particularly more sensitive 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 [6]. The cancer risk levels posed by Cr, Ni, As, Pb, Cd were mostly in the acceptable range (10^{-6}–10^{-4}), however, in some cases, the THI_{ca} value was very close to and even above the safe level (*Fig. 2*) [19]. Such heavy metal pollution degree in the soils around the Kapan copper-molybdenum combine and the Geghanush tailing dump may pose non-carcinogenic and even carcinogenic health hazards affecting the activities of different tissues, organs and organ systems such as respiratory and gastrointestinal tracts, central nervous and cardiovascular systems, blood, skin, etc. [10, 14].

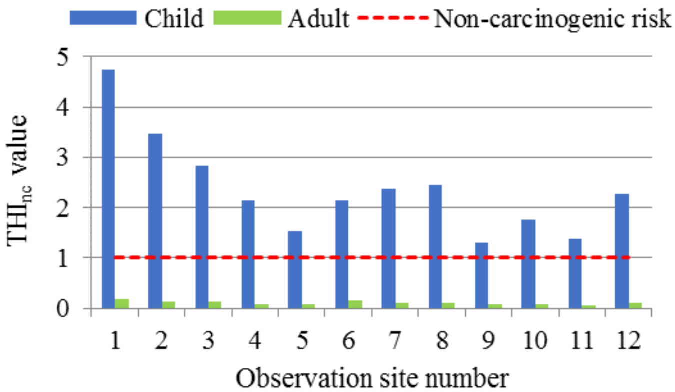

Fig. 1. Values of the total non-carcinogenic chronic hazard index (THI_{nc}) of heavy metals in the soils around the Kapan copper-molybdenum combine and the Geghanush tailing dump.

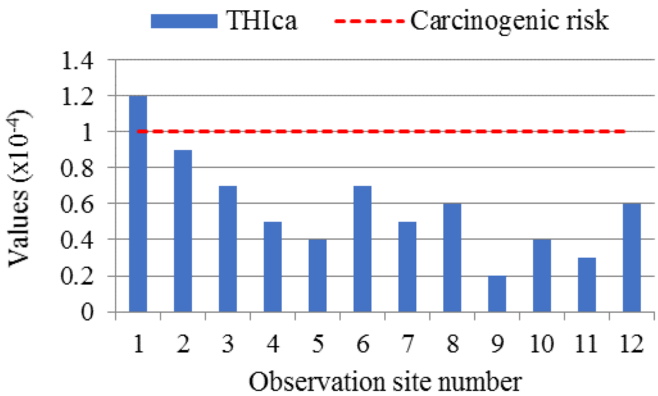

Fig. 2. Values of the total carcinogenic hazard index (THI_{ca}) of heavy metals in the soils around the Kapan copper-molybdenum combine and the Geghanush tailing dump.

According to the individual metal non-carcinogenic hazard index (HI_{nc}) values, health hazard of individual heavy metals was in the order of Cr>As>Mn>Ni>Pb>Cu>Cd>Zn>Mo (soils around the Kapan copper-molybdenum combine) and Cr>Mn>As>Ni>Cu>Pb>Cd>Zn>Mo (soils around the Geghanush tailing dump) (*Tables 2* and *3*). The investigated heavy metals can be ranked by individual metal carcinogenic risk levels as follows: Cr>As>Pb>Ni>Cd (Table 4). Cu and Mo were the main anthropogenic heavy metals in the investigated soils, nevertheless the highest human health risks were posed by Cr which is explained by the fact that different heavy metals don't have the same toxicity levels and penetration characteristics and may cause health effects at different pollution degrees. Such pollution degree of Cr in soil may cause non-carcinogenic hazards to children (*Tables 1–4*) [5, 6].

Table 2. Individual metal non-carcinogenic hazard index (HI_{nc}) values in the soils around the Kapan copper-molybdenum combine.

Parameters	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb
	Individual metal HI_{nc} value for child								
Minimum	0.5579	0.2422	0.0525	0.0113	0.0030	0.3185	0.0007	0.0128	0.0159
Maximum	3.1632	0.4610	0.2358	0.0252	0.0059	1.0446	0.0032	0.0290	0.0888
Mean	1.6690	0.3334	0.1340	0.0177	0.0045	0.5850	0.0018	0.0184	0.0494
Standard deviation	0.9904	0.0774	0.0681	0.0054	0.0011	0.2700	0.0009	0.0069	0.0255
	Individual metal HI_{nc} value for adult								
Minimum	0.0107	0.0206	0.0021	0.0011	0.0003	0.0318	0.0001	0.0004	0.0016
Maximum	0.0602	0.0365	0.0096	0.0025	0.0006	0.1050	0.0003	0.0009	0.0089
Mean	0.0313	0.0277	0.0055	0.0018	0.0004	0.0583	0.0002	0.0005	0.0049
Standard deviation	0.0189	0.0057	0.0028	0.0005	0.0001	0.0276	0.0001	0.0002	0.0025

Table 3. Individual metal non-carcinogenic hazard index (HI_{nc}) values in the soils around the Geghanush tailing dump.

Parameters	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb
	Individual metal HI_{nc} value for child								
Minimum	0.5906	0.2539	0.0408	0.0131	0.0026	0.1272	0.0003	0.0067	0.0105
Maximum	1.5086	0.4762	0.1115	0.0348	0.0045	0.3608	0.0015	0.0128	0.0282
Mean	1.1434	0.4049	0.0776	0.0231	0.0036	0.2419	0.0009	0.0098	0.0189
Standard deviation	0.3794	0.0860	0.0289	0.0079	0.0007	0.0970	0.0004	0.0024	0.0080
	Individual metal HI_{nc} value for adult								
Minimum	0.0110	0.0214	0.0016	0.0013	0.0003	0.0128	0.0000	0.0002	0.0010
Maximum	0.0297	0.0373	0.0047	0.0035	0.0004	0.0371	0.0001	0.0004	0.0028
Mean	0.0222	0.0328	0.0032	0.0023	0.0004	0.0243	0.0001	0.0003	0.0019
Standard deviation	0.0074	0.0065	0.0013	0.0008	0.0001	0.0099	0.0000	0.0001	0.0008

Table 4. Individual metal carcinogenic hazard index (HI_{ca}) values in the soils around the Kapan copper-molybdenum combine and the Geghanush tailing dump.

Parameters	Cr	As	Pb	Cd	Ni
	Soils around Kapan copper-molybdenum combine				
Minimum	1.5E-05	1.6E-05	5.2E-08	1.2E-10	2.0E-09
Maximum	8.5E-05	5.1E-05	2.9E-07	2.8E-10	9.1E-09
Mean	4.5E-05	2.9E-05	1.6E-07	1.8E-10	5.1E-09
Standard deviation	2.7E-05	1.3E-05	8.3E-08	6.5E-10	2.6E-09
	Soils around Geghanush tailing dump				
Minimum	1.6E-05	6.3E-06	3.4E-08	6.4E-11	1.6E-09
Maximum	4.1E-05	1.8E-05	9.2E-08	1.2E-10	4.3E-09
Mean	3.1E-05	1.2E-05	6.2E-08	9.3E-11	3.0E-09
Standard deviation	1.0E-05	4.8E-06	2.6E-08	2.2E-11	1.1E-09

CONCLUSIONS

Generally, it's possible to state that the operation of Kapan copper-molybdenum combine caused significant soil pollution with heavy metals which may have posed non-carcinogenic and even carcinogenic risks to population, mainly children living in this territory. The highest human health risks were posed especially by Cr the content of which in the soils may have caused non-carcinogenic health hazards. To mitigate such health risks, policy makers need to implement strict regulation on mining and industry on containment and discharge of waste and byproducts and to organize soil recultivation works.

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