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ENVIRONMENTAL RISKS OF HEAVY METAL POLLUTION OF THE SOILS AROUND KAJARAN TOWN, ARMENIA

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The present study was aimed in assessing the heavy metal pollution of the soils around Kajaran Town, Armenia and related environmental risks. The investigations showed that the soils around the mining complex near Kajaran Town were highly polluted with heavy metals (Mo, Cu, Pb, As, Zn, Ni) and this was conditioned by Zangezur copper and molybdenum combine activity. Such heavy metal pollution degree in the soils may pose risks to agricultural production and the health of population especially children in this territory.

***Keywords*:** Kajaran Town, metallurgical industry, heavy metal pollution, soil, environmental risks.

Introduction. Soil is a basic environmental component constituting ecosystem and the most important material basis of human being survival and development, but at the same time, it is perhaps the most endangered part of our environment, open to influence from a variety of different pollutants arising from human activities (industrial, agricultural activities, etc.) [1].

Heavy metals are a dangerous group of soil pollutants. Heavy metal contamination of the natural environment is a worldwide problem, because they can't be naturally degraded like organic pollutants and are able to accumulate in the different parts of food chain [2].

Heavy metal pollution of soil can be dangerous for humans. Some of today's most prevalent illnesses are increasingly blamed on toxic environmental contaminants: heavy metals/metalloids that become pollutants as a result of previous industrial, mining or other activities, synthetic chemical wastes carelessly dumped in waterways or landfills, products of combustion spewed into the air, pesticide residues and chemical additives in the food we eat [3].

Mining and smelting operations are important causes of heavy metal contamination in the environment due to activities such as mineral excavation, ore transportation, smelting and refining and the disposal of tailings and wastewater around mines [4, 5]. Metallurgical industry is developed in the Republic of Armenia. Since the last decades of the twentieth century, mining and beneficiation of a variety of minerals have been the driving force behind economic development,

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particularly in Lori and Syunik Marzes (administrative districts) of the Republic of Armenia [6]. Kajaran Region in Syunik Marz is considered as one of metallurgical industrial centers in Armenia. Human activities in this territory are mainly expressed by heavy metal pollution of the environment [7].

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

Materials and Methods. The soils around Zangezur copper and molybdenum combine were studied in May, 2014. 29 observation sites were selected around the mining complex near Kajaran Town.

The coordinates of sampling sites were recorded by GPS.

4 soil samples were taken from each observation site, and the mean heavy metal concentration of 4 samples was considered for each observation site. 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 soil 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 [8]. The digested soil samples were analyzed for heavy metals (Mo, Cu, Pb, As, Zn, Ni) 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, China and UK soil quality standards for agricultural production were used to assess heavy metal pollution degree in the soils [9–11].

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

$$\mathrm{ED}_{\mathrm{ing}} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{CF} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{BW} \times \mathrm{AT}}, \quad (1)$$

$$\mathrm{ED}_{\mathrm{derm}} = \frac{\mathrm{C} \times \mathrm{ABS} \times \mathrm{AF} \times \mathrm{CF} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{SA}}{\mathrm{BW} \times \mathrm{AT}}, \quad (2)$$

$$\mathrm{ED}_{\mathrm{inh}} = \frac{\mathrm{C} \times \mathrm{ET} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{PEF} \times 24 \times \mathrm{AT}}, \quad (3)$$

where C is measured heavy metal concentration, *mg*/*kg*; IR is soil ingestion rate for receptor, *mg* per day; CF is unit conversion factor, *kg*/*mg*; ED is exposure duration, year; EF is exposure frequency, day/year; ABS is dermal absorption factor, unitless; AF is soil to skin adherence factor, *mg*/cm^2; SA is skin surface area available for exposure, cm^2/event; ET is exposure time, *h*/day; BW is average body weight, *kg*; AT is averaging time for non-carcinogens, day; PEF is soil-to-air particulate emission factor, m^3/*kg* [12, 13].

The values and definitions of the parameters given in the Eqs. (1)–(3) were taken into consideration according to [12, 13].

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

$$HQ_{ing/derm/inh} = \frac{ED_{ing/derm/inh}}{RfD/RfC_{ing/derm/inh}}, \quad (4)$$

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

The individual metal hazard index (HI_m) value was calculated by the equation

$$HI_m = \sum HQ = HQ_{ing} + HQ_{derm} + HQ_{inh}. \quad (5)$$

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

$$THI = \sum_{i=0}^{n} HI_m. \quad (6)$$

Result and Discussion. The concentrations (*mg*/*kg*) of some heavy metals in the soils around Zangezur copper and molybdenum combine are presented in Fig. 1.

The exceeding of maximum permissible concentration (MPC) of potentially toxic elements in the soils was observed in case of all the investigated heavy metals, which indicated the anthropogenic pressure on the soils around Zangezur copper and molybdenum combine [9–11]. The investigated heavy metals can be ranked by anthropogenic pollution degree as follows: Mo > Cu > Pb > As > Zn > Ni. The contents of Cu and Mo in all the investigated sites exceeded the MPC for agricultural production and were mostly conditioned by anthropogenic factor especially metallurgical industrial activity [9, 11] (Fig. 1, a–f). This is explained by high concentrations of these metals in the ore of Zangezur copper and molybdenum combine.

The heavy metal pollution of soil 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 [15]. The investigation of health risks posed by the aforementioned exposure pathways showed that the total non-carcinogenic chronic hazard index (THI) values in all observation sites were above the safe level (THI<1) for children living in the investigated territory (Fig. 2). 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 [15].

According to the individual metal non-carcinogenic hazard index (HI_m) values, health hazard of individual heavy metals was in the order of Mo > As > Cu > Pb > Ni > Zn (Tab. 1).

Molybdenum, copper and lead were the main anthropogenic heavy metals in the investigated soils but the highest health risks after molybdenum were posed by arsenic, the pollution degree of which in the soils was comparatively low (see Fig. 1, a–c, e; Tab. 1). This 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.

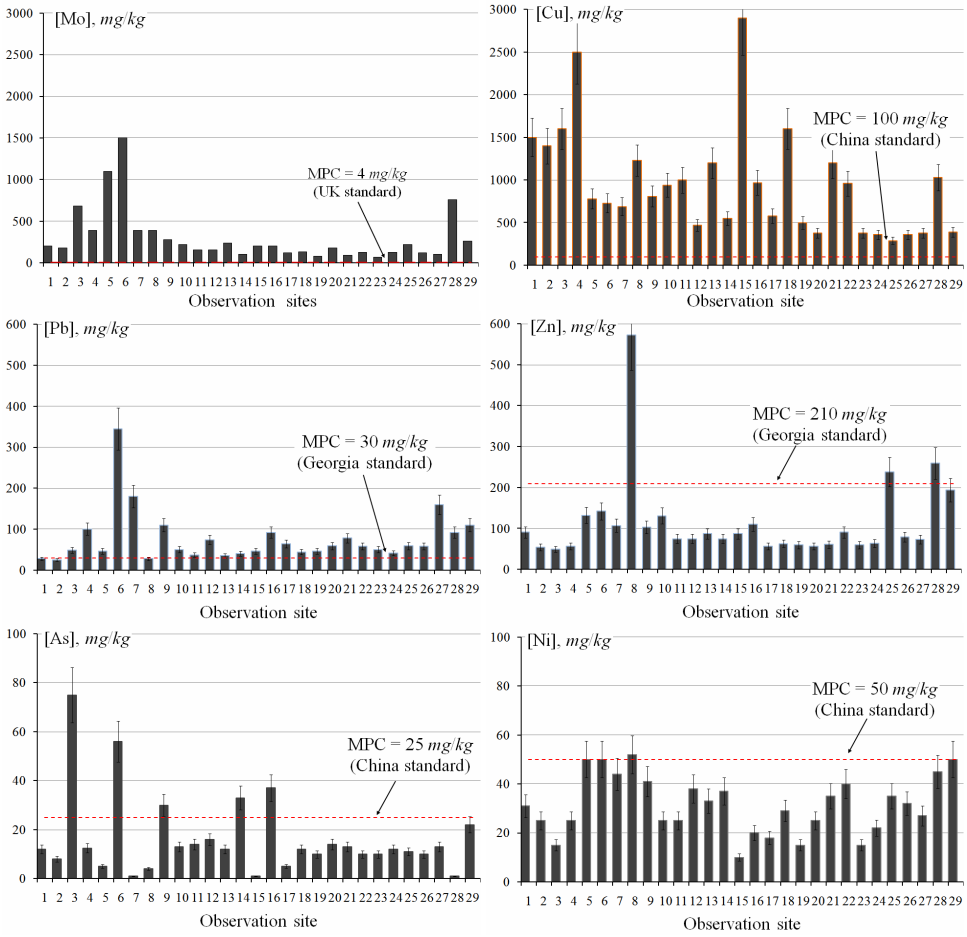

Fig. 1. Average measured concentration, maximum permissible concentration for heavy metal content in the soils around Zangezur copper and molybdenum combine.

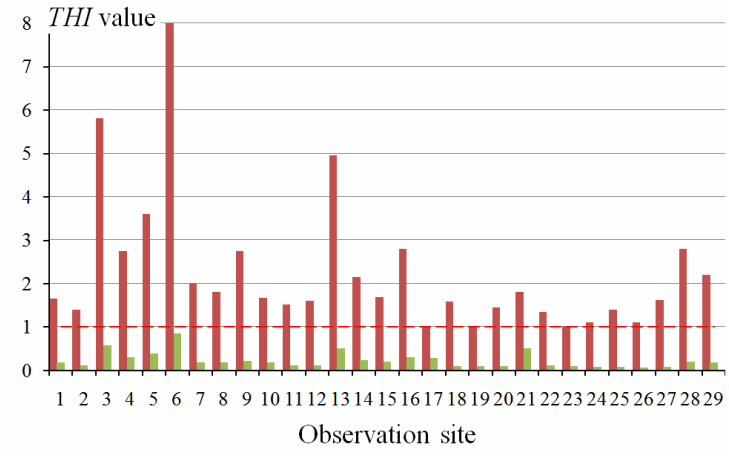

Fig. 2. The values of the total non-carcinogenic chronic hazard index (THI) of heavy metals in the soils around Zangezur copper and molybdenum combine.

Table 1

Individual metal non-carcinogenic hazard index values in the soils around Zangezur copper and molybdenum combine

Parameters	Mo	As	Cu	Pb	Ni	Zn
	HI_m for child					
Minimum	0.1688	0.0369	0.0943	0.0928	0.0186	0.0021
Maximum	3.8980	3.2702	3.6262	1.2820	0.1039	0.0302
Mean	0.7843	0.7087	0.4310	0.2823	0.0589	0.0078
Standard deviation	0.8451	0.7104	0.6506	0.2369	0.0232	0.0089
	HI_m for adult					
Minimum	0.0179	0.0034	0.0100	0.0098	0.0008	0.0002
Maximum	0.4126	0.3454	0.4111	0.2515	0.0215	0.0026
Mean	0.0830	0.0742	0.0583	0.0376	0.0039	0.0006
standard deviation	0.0895	0.0759	0.1001	0.0482	0.0045	0.0005

Thus, heavy metal pollution degree in the soils around Zangezur copper and molybdenum combine was unallowable for agricultural production and may have posed children health hazards affecting the activities of different organ systems (Tab. 2).

Table 2

Primary target organs of heavy metal poisoning through oral ingestion, dermal contact and inhalation [14, 16]

Heavy metals	Mo	As	Cu	Pb	Ni	Zn
Primary target organs	blood	skin, respiratory tract	gastrointestinal tract	cardiovascular system	weight	blood

Conclusion. In general, it is possible to state that the operation of Zangezur copper and molybdenum combine has caused significant pollution of the soils with heavy metals (Mo, Cu, Pb, As, Zn, Ni). Heavy metal pollution degree in the soils around the mining complex may have posed risks to agricultural production and the health of population especially children in this territory. High environmental risks were posed especially by molybdenum, arsenic, copper and lead. Thus, it is required to implement recultivation works in this territory for environmental safety.

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