Հայաստանի Գիտությունների Ազգային Ակադեմիա
Национальная Академия Наук Армении
National Academy of Sciences of Armenia

Հայաստանի Կենսաբանական Հանդես
Биологический Журнал Армении
Biological Journal of Armenia

•Փորձարարական և տեսական հոդվածներ •Экспериментальные и теоретические статьи•
•Experimental and theoretical articles•

Biolog. Journal of Armenia, 4 (70), 2018

POTENTIALLY TOXIC ELEMENTS CONTENT IN SOILS IN THE VICINITY OF SHAMLUGH COPPER MINING AREA (ARMENIA): ECOLOGICAL, AGRICULTURAL AND HEALTH RISK ASSESSMENT

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Ecological, agricultural and health risks of the soil pollution by potentially toxic elements (PTEs) (Cu, Pb, As, Ni, Zn, Co) in the vicinity of Shamlugh copper mining area located in the north-east of Armenia were investigated. The results of the study showed that the content of PTEs in the soils sampled in September 2014 may have posed serious risks to soil biological communities, human health as well as agricultural production, in case of soil used for agricultural purpose.

Soil – mining – potentially toxic elements – pollution – risks

Ուսումնասիրվել են Հայաստանի հյուսիս-արևելքում տեղակայված Շամլուղի պղնձարդյունաբերական տարածքի հարակից հողերի պոտենցիալ թունավոր տարրերով (ՊԹՏ) (Cu, Pb, As, Ni, Zn, Co) աղտոտվածության էկոլոգիական, գյուղատնտեսական և առողջական ռիսկերը: Հետազոտության արդյունքները ցույց են տվել, որ 2014 թ. սեպտեմբերին հավաքած հողանմուշներում ՊԹՏ պարունակությունը կարող էր առաջացնել լուրջ ռիսկեր հողի կենսահամակեցությունների, մարդու առողջության, ինչպես նաև գյուղատնտեսական նպատակով հողօգտագործման դեպքում գյուղատնտեսական արտադրության համար:

Հող – հանքարդյունաբերություն – պոտենցիալ թունավոր տարրեր – աղտոտում – ռիսկեր

Исследовано загрязнение потенциально токсичными элементами (ПТЭ) (Cu, Pb, As, Ni, Zn, Co) почв в окрестности Шамлугских медно-добывающих территорий, расположенных на северо-востоке Армении и его экологические, сельскохозяйственные риски, а также угрозы для здоровья. Исследования показали, что содержание ПТЭ в почвах, отобранных в сентябре 2014 г., может представлять серьезные риски для биологических сообществ почвы, здоровья человека, а также сельскохозяйственного производства в случае использования почвы в сельскохозяйственных целях.

Почва – добывающая промышленность – потенциально токсичные элементы – загрязнение – риски

Soil is an important natural resource to sustain life on earth because of its diverse functions that it plays in nature. It is the ultimate recipient of any waste that we throw or dispose as waste product in the environment [18]. Soil pollutants have an adverse effect on the physical, chemical and biological properties of the soil and reduce its productivity [12]. Soil pollution with such potentially toxic elements (PTEs) as heavy metals is a significant environmental problem worldwide and in particular hotspots often occur around mining facilities [7, 14]. Accumulation of heavy metals in soil can degrade soil quality, reduce crop yield and the quality of agricultural products, and thus negatively affect the health of human, animals and the ecosystem [7]. They are non-biodegradable, non thermo-degradable and thus readily accumulate to toxic levels [3]. Heavy metal toxicity has an inhibitory effect on plants growth, enzymatic activity, stomata functions, photosynthesis activity, microbial activity and the accumulation of other nutrient elements and also damages the root system [13].

Armenia is a country rich with polymetallic ores. There are 670 construction material and aggregate mineral mines in Armenia, among which 270 are inactive mines (including 8 metal mines) and 400 active mines (including 22 metal mines) [17]. Mining and metallurgical industries are mainly concentrated in the southern (Syunik Marz) and northern (Lori Marz) parts of Armenia. Giving priority to economic development, the possible environmental effects of metallurgical industrial activities in these areas have been ignored or little attention has been paid. The insufficient management of discharges induced by mining activities has become a serious threat to the environment and human health [4]. The aim of the present study was to assess the ecological, agricultural and health risks of PTEs pollution in soils near Shamlugh copper mining area (ShCMA) in Lori Marz.

Materials and methods. Soils in the vicinity of ShCMA located in the north-east of Armenia were investigated. 6 observation sites were selected near Shamlugh copper mine (ShCM) (№№ 1-3), Chochkan tailing dump (ChTD) (№ 4) and ore transportation road (OTR) (№№ 5 and 6). A control site (№ 7) was selected about 4 km away from ShCM. The soil samples were collected from a depth of 0-20 cm in September 2014. They were stored in well labeled polyethylene bags for further 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 (conc. HCl and conc. HNO_3 in ratio of 3:1) digestion method [21]. The digested soil samples were analyzed for PTEs (Cu, Pb, As, Ni, Zn, Co) using an atomic absorption spectrophotometer (PG990).

The ecological risks of PTEs in the soils were assessed according to the Potential ecological risk index (PERI) method proposed by Hakanson (1980). PERI was calculated based on the following equations [5]:

$$C_r^i = C_s^i / C_n^i, \qquad (1)$$

$$E_r^i = C_r^i * T_r^i, \qquad (2)$$

$$RI = \sum E_r^i, \qquad (3)$$

where C^i_r is the pollution factor of a single element in soil; C^i_s is the measured concentration of a single element in soil; C^i_n is the background concentration of a single element in soil; E^i_r is PERI of a single element; T^i_r is the toxic response factor for a single element; RI is the comprehensive PERI [2, 5]. The classification of potential ecological risk categories according to the PERI values is presented in tab. 1 [5].

Table 1. The adjusted grading standard of potential ecological risk of PTEs in soil

E^i_r	Pollution degree	RI	Risk level	Risk degree
$E^i_r<30$	Slight	RI<40	A	Slight
$30\le E^i_r<60$	Medium	40≤RI<80	B	Medium
$60\le E^i_r<120$	Strong	80≤RI<160	C	Strong
$120\le E^i_r<240$	Very strong	160≤RI<320	D	Very strong
$E^i_r\ge 240$	Extremely strong	RI≥320	-	

Individual PTE pollution degree for agricultural production on soil was assessed by the following equation [9]:

$$PI = C_i/S_i , \qquad (4)$$

where PI is the pollution index of each element in soil; C_i is the measured concentration of element i in soil; S_i is the maximum permissible concentration of element i for agricultural production on soil [1, 9]. The PI of each element is classified into five pollution categories: non-pollution (PI<1), low level of pollution (1≤PI<2), moderate level of pollution (2≤PI<3), strong level of pollution (3≤PI<5), very strong level of pollution (PI≥5) [9].

Integrated PTE pollution degree for agricultural production on soil was evaluated by the Nemerow integrated pollution index (NIPI):

$$NIPI = \sqrt{\frac{PI_{avg}^2 + PI_{max}^2}{2}} , \qquad (5)$$

where PI_{avg} is the average value of the single pollution indices of all elements; PI_{max} is the maximum value of the single pollution indices of all elements [9, 16]. NIPI is classified into the following pollution categories: non-pollution (NIPI≤0.7), warning line of pollution (0.7<NIPI≤1), low level of pollution (1<NIPI≤2), moderate level of pollution (2<NIPI≤3), high level of pollution (NIPI>3) [9].

Carcinogenic health risks associated with PTEs 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 (6)–(12)) [15, 20]. The carcinogenic chronic daily exposure doses (DED) through oral ingestion (mg/kg/d), dermal absorption (mg/kg/d) and inhalation (mcg/m^3) were calculated using equations (6)–(10):

$$DED_{ing} = \frac{C \times IR \times EF \times CF}{AT_{CA}} , \qquad (6)$$

$$IR = \frac{ED_{child} \times IngR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times IngR_{adult}}{BW_{adult}} , \qquad (7)$$

$$DED_{derm} = \frac{C \times ABS \times EF \times DFS \times CF}{AT} , \qquad (8)$$

$$DFS = \frac{ED_{child} \times SA_{child} \times AF_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times SA_{adult} \times AF_{child}}{BW_{adult}} , \qquad (9)$$

$$DED_{inh} = \frac{C \times ET \times ED \times EF}{PEF \times 24 \times AT} \times 10^3 , \qquad (10)$$

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 is averaging time for carcinogens (d) [19, 20]. The individual element non-carcinogenic hazard index (HI) value was calculated by equation (11):

$$HI = DED \text{ x } CSF/IUR, \qquad (11)$$

where CSF is the oral and dermal cancer slope factor $(mg/kg/d)^{-1}$; IUR is the inhalation unit risk $(mcg/m^3)^{-1}$ [6, 10, 11, 20]. The total carcinogenic hazard index (THI) value was calculated by the following equation:

$$THI = \sum_{i=0}^{n} HI = HI_{ing} + HI_{derm} + HI_{inh} . \qquad (12)$$

Results and Discussion. The results of the study showed that PTEs content in the soils near ShCM, ChTD and OTR was noticeably higher than that in the control site located about 4 km away from ShCM which indicated that PTE concentrations in the soils were formed not only by natural factors but also under anthropogenic influence (fig. 1). The main anthropogenic source of PTE pollution in the area is supposed to be Shamlugh copper mining activity.

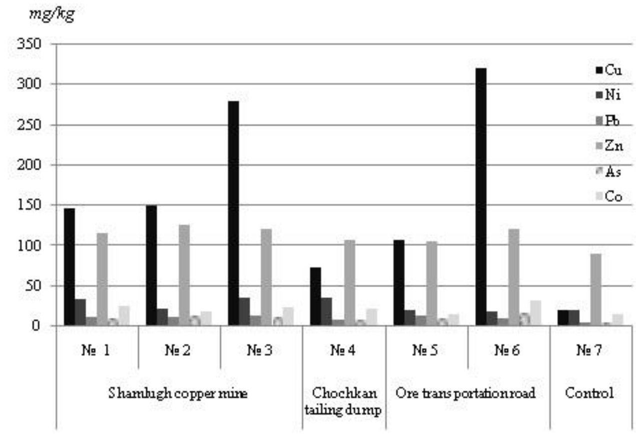

Fig. 1. Some PTE concentrations in the soils near ShCMA

PERI representing the sensitivity of biological communities to toxic substances and illustrating potential ecological risks is also introduced to assess the contamination degree of PTEs in the soils [8]. The index values (E_r and RI) showed that the soils in the vicinity of ShCMA were significantly polluted with PTEs which may have caused the medium-strong level of soil's biological health risks. The highest ecological risks may have been posed by Cu which is explained by high concentration of this element in the ore of ShCM. Potential ecological risks of individual elements were in the order of E_r(Cu)≥E_r(As)≥E_r(Pb, Ni, Co, Zn,) (tab. 2).

Table 2. Individual and integrated element pollution degree for the biological health of the soils near ShCMA

Sampling site		E_r(Cu)	E_r(As)	E_r(Pb)	E_r(Ni)	E_r(Zn)	E_r(Co)	RI
ShCM	№ 1	**B**	**A**	**A**	**A**	**A**	**A**	**C**
	№ 2	**B**	**A**	**A**	**A**	**A**	**A**	**C**
	№ 3	**C**	**A**	**A**	**A**	**A**	**A**	**C**
ChTD	№ 4	**A**	**A**	**A**	**A**	**A**	**A**	**B**
OTR	№ 5	**A**	**A**	**A**	**A**	**A**	**A**	**B**
	№ 6	**C**	**B**	**A**	**A**	**A**	**A**	**C**

A – slight; **B** – medium; **C** – strong.

The results of the study showed that PTE pollution degree in the investigated soils may have adverse effects not only on the biological health of the soil but also on the agricultural production, in case of soil used for agricultural purpose. The highest agricultural risks may have been posed by Cu and Co. Individual element pollution degree of different PTEs was in the order of $PI_{Cu} \geq PI_{Co} \geq PI_{As} \geq PI_{Zn, Ni, Pb}$ (soils near ShCM) and $PI_{Co} \geq PI_{Cu} \geq PI_{As} \geq PI_{Zn, Ni, Pb}$ (soils near ChTD and OTR) (tab. 3).

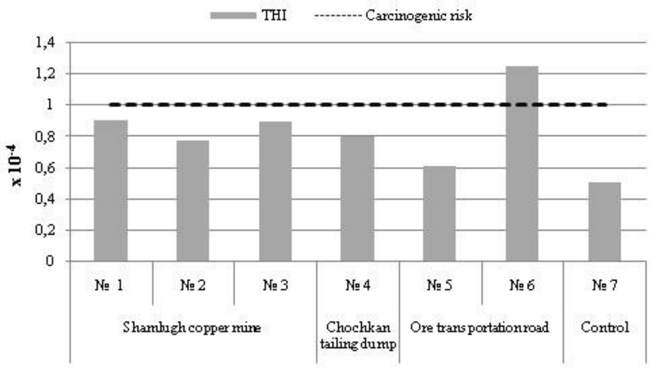

Fig. 2. Values of THI of PTEs in the soils near ShCMA

Generally, it can be stated that the Shamlugh copper mining activity caused significant PTE pollution in the soils which may not only have posed serious health risks to soil's biological communities and humans but also may have been dangerous for agricultural production, in case of soil used for agricultural purpose. Cu, Co and As were the main anthropogenic stressors in the investigated soils.

Acknowledgements

This work was supported by a research grant from the Armenian National Science and Education Fund (ANSEF) based in New York, USA (research project № plant-4928).

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Received on 12.06.2018