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ASSESSMENT OF ECOLOGICAL AND AGRICULTURAL RISKS OF HEAVY METAL POLLUTION OF SOILS IN THE VICINITY OF KAPAN CITY, ARMENIA

G. A. GEVORGYAN [1*], K. A. GHAZARYAN [2], H. S. MOVSESYAN [2**]

[1] *Scientific Center of Zoology and Hydroecology of NAS RA*
[2] *Chair of Ecology and Nature Protection of YSU, Armenia*

Ecological and agricultural risks of heavy metal pollution of soils in risky areas around Kapan City (RA) were investigated. Soil samples were collected in June 2013 and analyzed for Cr, Mn, Ni, Cu, Zn, As, Mo, Cd, Pb, Co, Hg by the mass spectrometric method. The investigations showed that the soils around Kapan copper-molybdenum combine and Geghanush tailing dump were significantly polluted with heavy metals, which may have posed serious risks not only to soil biological health, but also to agricultural production.

Keywords: mining activity, heavy metals, soil, ecological and agricultural risks.

Introduction. Soil is the key part of the Earth system as it controls the hydrological, erosional, biological and geochemical cycles. The soil system also offers goods, services, and resources to Humankind [1, 2]. Soil pollution is defined as a phenomenon characterized by the loss of structural and biological properties by the soil layers as a result of numerous human and natural factors [3]. Heavy metal pollution of soil has become a critical environmental concern due to its potential adverse ecological effects. Heavy metals occur naturally at low concentrations in soils. However, they are considered as soil contaminants due to their widespread occurrence, as well as their acute and chronic toxicity. These metals are extremely persistent in the environment. They are non-biodegradable, non-thermodegradable and thus readily accumulate to toxic levels [4]. Soil contamination by heavy metals can lead to changes in soil characteristics and limit productive and environmental functions [5]. Since heavy metals do not break down, they might affect the biosphere for a long time [4]. Polluted soils are no longer appropriate for agricultural production, because they are unable to produce healthy food [5]. In recent years, with the development of global economy, both type and content of heavy metals in soil caused by human activities have gradually increased, resulting in the deterioration of the environment [6].

Mining and smelting operations are important causes of heavy metal contamination in the environment due to activities such as mineral excavation, ore transportation, smelting, refining and the disposal of tailings and wastewater

* E-mail: gev_gor@mail.ru ** E-mail: hasmikmov@ysu.am

around mines. Mining and metallurgical industries are highly developed in the RA, particularly in Syunik Marz and Lori Marz. Kapan Region (Syunik Marz, South-Eastern part of RA), where Kapan and Zangezur copper-molybdenum combines are operating, is considered as the main metallurgical industrial centre in Armenia. Human activities in this territory are mainly expressed by heavy metal emission into the environment [7]. Therefore, for conserving the soil resources and ensuring environmental safety in this territory, the investigation of heavy metal pollution in soils and of related environmental risks is urgently required.

The aim of the article was to investigate and assess the ecological and agricultural risks of heavy metal pollution of soils in risky areas around Kapan City.

Materials and Methods. The soils in the vicinity of Kapan City were investigated in June 2013. The investigated soils belong to the type of mountain cambisol. Observation sites were selected around Kapan copper-molybdenum combine (KCMC) (№№ 1–6) and Geghanush tailing dump (GTD) (№№ 7–12). A control site was selected 4 *km* away from KCMC.

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 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 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, 3:1) digestion method [8]. The digested soil samples were analyzed for heavy metals (Cr, Mn, Ni, Cu, Zn, As, Mo, Cd, Pb, Co, Hg) by using ELAN 9000 inductively coupled plasma mass spectrometer (ICP–MS) [9].

The ecological risks of heavy metals in the soils were assessed according to the Potential ecological risk index (PERI) method [6], calculated as follows:

$$C_r^i = C_s^i / C_n^i, \qquad E_r^i = C_r^i T_r^i, \qquad \mathrm{RI} = \sum E_r^i, \tag{1}$$

where C_r^i, C_s^i, C_n^i are the pollution factor; the measured concentration and the background concentration of a single element in soil, respectively; E_r^i is the PERI of a single element; T_r^i is the toxic response factor for a single element; RI is the comprehensive PERI. The classification of RI categories according to the PERI values is presented in Tab. 1 [10].

Table 1

The adjusted grading standard of potential ecological risk of heavy metals in soil

E_r^i	Pollution degree	RI	Risk level	Risk degree
$E_r^i < 30$	slight	RI < 40	A	slight
$30 \le E_r^i < 60$	medium	40 ≤ RI < 80	B	medium
$60 \le E_r^i < 120$	strong	80 ≤ RI < 160	C	strong
$120 \le E_r^i < 240$	very strong	160 ≤ RI < 320	D	very strong
$E_r^i \ge 240$	extremely strong	RI ≥ 320	–	

Individual heavy metal pollution degree for agricultural production on soil (Pollution index (PI)) was assessed by the following equation: PI=C_i/S_i, where C_i is the measured concentration of heavy metal *i* in soil; S_i is the maximum permissible concentration of heavy metal *i* for agricultural production in soil [11, 12].

The PI of each metal 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) [11].

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

$$\mathrm{NIPI} = \sqrt{\mathrm{PI}_{avg}^2 \mathrm{PI}_{\max}^2 / 2}, \tag{2}$$

where PI_{avg} is the average value of the single pollution indices of all heavy metals; $\mathrm{PI}_{\max}$ is the maximum value of the single pollution indices of all heavy metals [11, 13]. NIPI is classified by 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) [11].

Results and Discussion. The results of the study of heavy metals content in the investigated areas showed that the concentrations of different heavy metals in all the investigated observation sites exceeded the background (control) level, which indicated that heavy metal concentrations in the soils were conditioned by both natural and anthropogenic sources (Tab. 2). The main source of the heavy metal pollution of the soils in this area is KCMC activity.

Table 2

Heavy metal concentrations (mg/kg) in the soils around KCMC (№№ 1–6) and GTD (№№ 7–12)

Sampling site	Cr	Mn	Ni	Cu	Zn	As	Mo	Cd	Pb	Co	Hg
№№ 1–6	17.5–99.5	813.2–1557.6	26.4–118.5	32.6–72.8	66.0–127.1	6.9–22.5	0.3–1.1	0.2–0.5	4.0–22.4	11.7–28.1	0.1–0.3
№№ 7–12	18.6–47.4	854.4–1611.5	20.5–56.1	37.8–100.4	56.2–97.7	2.7–7.8	0.1–0.5	0.1–0.2	2.6–7.1	17.0–30.1	0.1–0.2
Control	43.2	527.7	26.4	9.0	75.5	7.5	0.2	0.2	10.3	10.3	0.1

Table 3

Individual and integrated metal potential ecological risk index values in the soils

Sampling site	E_r(Cr)	E_r(Mn)	E_r(Ni)	E_r(Cu)	E_r(Zn)	E_r(As)	E_r(Mo)	E_r(Cd)	E_r(Pb)	E_r(Co)	RI
KCMC	0.81–4.60	1.54–2.95	5.00–22.45	18.15–40.56	0.87–1.68	9.17–30.07	1.39–6.33	28.75–65.00	1.96–10.93	5.10–12.30	86.31–171.41
GTD	0.86–2.20	1.62–3.05	3.89–10.62	21.09–55.98	0.74–1.29	3.66–10.39	0.67–2.94	15.00–28.75	1.29–3.47	7.45–13.17	60.95–108.35

For assessing the biological health risks of heavy metal pollution in the investigated soils, the PERI values, which represent the sensitivity of various biological communities to harmful elements and illustrate the potential ecological risk, were applied (Tab. 3) [14]. According to them, the soils were significantly polluted with heavy metals (see the pollution degree in Tab. 4). All of this may have caused soil's biological health risks, the levels of which are illustrated in Tab. 5. The highest health risks to biological communities in the soils around KCMC may have been posed by Cd (slight-strong) and around GTD by Cu (mainly medium) (Tab. 5).

According to the values, individual metal pollution degree and related potential health risks to biological communities were in the order of Cd> >Cu>As>Ni>Co>Pb>Mo>Cr>Mn>Zn (soils around KCMC) and Cu>Cd>Co> >Ni>As>Mn>Pb>Mo>Cr>Zn (soils around GTD) (Tab. 3).

Table 4

Individual and integrated metal pollution degree and potential ecological risk levels for the biological health of the soils

Sampling site		E_r(Cr)	E_r(Mn)	E_r(Ni)	E_r(Cu)	E_r(Zn)	E_r(As)	E_r(Mo)	E_r(Cd)	E_r(Pb)	E_r(Co)	RI
Kapan copper-molybdenum combine	1	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**B**	**A**	**A**	**D**
	2	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**B**	**A**	**A**	**C**
	3	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**B**	**A**	**A**	**C**
	4	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**B**	**A**	**A**	**C**
	5	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**
	6	**A**	**A**	**A**	**A**	**A**	**B**	**A**	**C**	**A**	**A**	**C**
Geghanush tailing dump	7	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**
	8	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**
	9	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**
	10	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**
	11	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**B**
	12	**A**	**A**	**A**	**B**	**A**	**A**	**A**	**A**	**A**	**A**	**C**

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

Table 5

Individual and integrated heavy metal pollution degree for agricultural production of the soils

Sampling site		PI_{Cr}	PI_{Mn}	PI_{Ni}	PI_{Cu}	PI_{Zn}	PI_{As}	PI_{Mo}	PI_{Cd}	PI_{Pb}	PI_{Hg}	NIPI
Kapan copper-molybdenum combine	1											
	2											
	3											
	4											
	5											
	6											
Geghanush tailing dump	7											
	8											
	9											
	10											
	11											
	12											

Level of pollution: – non-pollution, – warning, – low, – moderate level.

Table 6

PI and NIPI values for agricultural production of the soils

Sampling site	PI_{Cr}	PI_{Mn}	PI_{Ni}	PI_{Cu}	PI_{Zn}	PI_{As}	PI_{Mo}	PI_{Cd}	PI_{Pb}	PI_{Hg}	NIPI
KCMC	0.19–1.11	0.54–1.04	0.33–1.48	0.25–0.55	0.30–0.58	0.69–2.25	0.00–0.01	0.12–0.26	0.06–0.35	0.10–0.15	0.62–1.67
GTD	0.21–0.53	0.57–1.07	0.26–0.70	0.29–0.76	0.26–0.44	0.27–0.78	0.00–0.00	0.08–0.12	0.04–0.11	0.06–0.10	0.47–0.82

The results of the study showed that heavy metal pollution degree in the investigated soils may have adversely affected not only soil biological health, but also agricultural production (Tabs. 4, 5). The highest risks to agricultural production of the soils around KCMC may have been posed by As and around GTD by Mn (Tab. 5). The investigated heavy metals can be ranked by individual metal pollution degree for agricultural production as follows: As>Ni>Mn>Cr>Zn>Cu>Pb>Cd>Hg>Mo in the soils around KCMC and Mn>As>Ni >Cr>Cu>Zn>Cd >Hg>Pb>Mo in the soils around GTD (Tab. 6). It is necessary to mention that some heavy metals pollution degree (for example, Cu and Cd levels), being the major stressor of soil's biological communities wasn't dangerous for agricultural production (Tabs. 4, 5). All of this indicates that individual heavy metal pollution degree in soil should be estimated for each of vulnerable components individually, which will enable to precisely understand all the related environmental risks.

Conclusion. In general, it is possible to state that KCMC activity caused significant heavy metal pollution in the soils. Such a heavy metal pollution degree not only may have posed serious soil's biological health risks, but also may have been dangerous for agricultural production. To mitigate such environmental risks, responsible authorities need to develop and implement a new policy of mining operation, which will take into consideration not only economic benefits, but also environmental security.

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