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THE IMPACT OF ZANGEZUR COPPER AND MOLYBDENUM COMBINE ACTIVITIES ON THE POLLUTION OF AGRICULTURAL LANDS AND CROPS BY TOXIC ELEMENTS

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The aim of the study was to assess the pollution of agricultural lands and crops with some potentially toxic trace elements conditioned by the activities of Zangezur Copper and Molybdenum Combine, as well as an assessment of the risk level of the studied crops for human health. The study was implemented in 2018. It was revealed that the soils of agricultural land in the surroundings of the combine were polluted by some trace elements, in particular by copper, but the content of Cu in crops growing in this area did not exceed the maximum permissible concentrations (MPC). The exceeding of MPC was registered in case of Cd, Ni, Zn and Cr. The highest excess of toxic elements in vegetables was observed in garlic and above-ground parts of red beet, and in an apple among fruits. In this regard, it is essential to implement the soil renewal and remediation activities in the studied area, in particular, phytoremediation, which is considered to be a harmless and cost-effective approach to remove toxic pollutants.

Keywords: Zangezur Copper and Molybdenum Combine, toxic elements, pollution, agricultural land, soil, crops.

Introduction. The agricultural lands are a major natural resource for human survival, as it is one of the main sources of agricultural production. Currently, trace metals are among the main pollutants of agricultural land. In fact, they are widely spread, highly toxic and persistent, as they remain in the environment for a long time (for example, through the food chain). Management practices play a crucial role in the amount and impact of these pollutants.

Altogether, the natural concentration of toxic metals in agricultural lands depends primarily on the mineral composition of the geological parent material [1, 2]. But certain sites may suffer from elevated concentrations of toxic metals due to atmospheric deposition associated with mining and smelting [3] and burning of fossil fuels [4].

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Recently, the increase in anthropogenic contamination has resulted in various degrees of toxic metal contamination of agricultural lands. Nowadays the mining industry is one of the main sources of anthropogenic pollution of the soil [5–10]. The increased prominence of toxic metal contamination on agricultural lands has attracted the attention of leading scientists in the field of soil science and ecology [11, 12]. Several recent reports showed that crops growing on soils with high concentrations of toxic metals accumulated these metals [13–15]. These toxic metals may have a high risk to human health. The pollution of agricultural lands and crops by trace metals causes concern, because of its impact on human health and on the possibility of long-term sustainability of food production in polluted sites [16]. This has led to a major share in worldwide concern towards the prevention of toxic metal accumulation on agricultural lands and in crops [17].

Pollution of agricultural lands with toxic metals as a result of mining at present is also one of the most severe ecological problems in Syunik Marz of Armenia [18]. Therefore, the objectives of this study were: 1) to investigate some toxic metal concentration in the topsoil and crops growing in these soils; 2) to estimate the level of risk of studied crops for human health.

Materials and Methods.

Studied Area. The studied area is situated in the south part of Armenia, near the Kajaran village. The studies were conducted in agricultural land (coordinates: N 39°09,486'; E 46°07,186'), located at a distance of about 1.5 *km* in western direction from Zangezur Copper and Molybdenum Combine. Studied area is situated at an altitude of 1941 *m* a.s.l. and belongs to the watershed of the Voghji River. The soils of the area belong to the type of decalcified mountain cambisols.

Soil and Crop Samples Collection. The sampling of soil and crops (or their edible parts) from the studied area was conducted in 2018. Soil samples were collected from a depth of 0–30 *cm* using a special sampling kit. The soil sampling from agricultural land was done by the envelope method: 5 samples in total, collected from the center point and the angles of a grid of 25 *m*×25 *m*, were mixed, and thereafter 3.5 *kg* of this composite sample were taken for the analyses.

Pretreatment of Soil and Crop Samples. After removing unwanted contents (stones, plant material, etc.), in laboratory, the samples were air-dried at room temperature (20–22°*C*), ground in a mortar to pass through a 1.0 *mm* mesh, and then were stored in an all-glass jar for physicochemical analysis. For the determination of toxic metal content, the soil samples were ground and passed through a 0.15 *mm* nylon mesh. From crops, 9 plant species were selected, from 7 of them, only usable parts (fruits or tubers) were sampled, for the remaining 2 species the whole plants were harvested. For each crop, ten different plants were gathered, and a mixed sample was prepared from them. After that, samples were thoroughly washed with running tap water, then twice with deionized water for deletion of any particles. Thereafter the fresh weights of plants (below-ground and above-ground parts) and of their usable parts were determined. The samples were dried in an oven at 70°*C* to reach the constant weight for dry weight determination, after which the samples were homogenized, passed through 0.15 *mm* sieve and stored in an all-glass jar for the toxic metal analysis.

Trace Metal Analysis. To determine the total trace metal content, the soil samples were digested in a mixture HNO_3+$HClO_4$+HF in the ratio 5:1:1 by volume

[19]. Crop samples were digested in a mixture of HNO_3 and $HClO_4$ in the ratio 4 : 1 by volume at 150°*C* for 200 *min* (0.1 *g* sample of crops in 10 *mL* of acid mixture) [20, 21]. Trace metals were measured by atomic absorption spectrometry (AAS; PG990, PG Instruments Ltd). Acetic acid was used to determine the bioavailable trace metals in the soil samples: 1 *g* of ground soil was placed in a 50-*mL* tube, mixed in a stepwise fashion with 40 *mL* of 0.11 *M* CH_3COOH, and the suspension was equilibrated for 16 *h* at 20–22°*C* [22]. After that, the mixture was filtered and the trace metals were measured in the filtrates using AAS.

Statistical Analysis. Trace metal concentrations in crop samples were assessed using three separate replicates. The statistical analysis was performed using SPSS software, Version 15.

Results and Discussion. There are different types of agricultural lands in the vicinity of processing plant and open mine of Zangezur Copper and Molybdenum Combine. In case of pollution of these areas by toxic trace metals, they may be included in food chains and penetrate the human body.

Considering the above, the sampling of soil, as well as the edible parts of some crops, was implemented in agricultural land in the environs of Kajaran village. The general physicochemical characteristics of the studied soil sample are presented in Tab. 1. A weak acidic reaction, high contents of carbon and humus were observed in the soil sample, which creates favorable conditions for the growth of majority of crops. While the moderately bad texture, as well as comparatively high bulk and relative densities observed in the soil sample, are conditioned by the big portion of heavy fractions in the soil.

Table 1

General physicochemical characteristics of studied soil sample

Physicochemical characteristics	Study results
pH	6.7
Humus content, %	5.28
Carbon, %	3.06
Texture	sandy loam
Texture classification	moderately bad
Bulk density, g/cm^3	1.57
Relative density, g/cm^3	2.54

Total contents and the contents of bioavailable forms of some high-risk toxic elements were determined in the soil sample from agricultural land (Tab. 2). The total content of copper was 3.82 times higher than that in soil samples from the background site located in the studied territory, while the total content of arsenic was higher only 1.09 times [10]. Such a high content of copper is directly conditioned by mining activities carried out in this area. It should be mentioned that the copper is the main metal extracting here.

The presence in soils of trace metals and other toxic elements can pose a significant threat to human health. As trace elements, some metals (e.g., iron, copper, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Excessive concentrations of toxic metals may induce serious metabolic changes and disturbance of metabolic processes, which, in turn, reduces the organism resistibility, brings to disturbance of allergic and somatic status and, finally, to dysfunction of the various organs and systems. The recently increased toxicity of trace metals, by affecting human beings, can cause damage or impairment of mental and central nervous function. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Repeated prolonged exposures to a number of metals and their compounds may also lead to origination of malignant tumors [23].

Table 2

The total contents and the contents of bioavailable forms of some trace elements in studied soil sample (mg/kg)

Element	Total	Bioavailable
Cr	27.93	0.085
Ni	31.29	0.014
Cu	275.31	0
Zn	142.50	0
As	28.36	0.017
Se	0.49	0.009
Cd	0.59	0.004
Sb	1.26	0.016
Pb	15.34	0

In this regard, the contents of toxic elements accumulated in the cultures grown in the research area were studied. The results of investigation of toxic elements in the edible parts (in wet and dry masses) of crops grown in the agricultural land under study are presented in Tabs. 3 and 4. The maximum permissible concentrations (MPC) of these elements in vegetables and fruits (wet mass) are given in Tab. 5.

Table 3

The total contents of some elements in edible parts of crops (wet mass, mg/kg)

Element	Garlic	Potato	Carrot	Red beet (above-ground)	Red beet (below ground)	Onion (above-ground)	Onion (below ground)	Apple	Straw-berry	Rasp-berry	Black-currant
Cr	0.75	0.48	0.27	0.45	0.28	0.23	0.16	0.57	0.19	0.34	0.34
Ni	0.39	0.27	0.21	0.35	0.25	0.14	0.77	0.15	0.06	0.27	0.14
Cu	1.67	1.84	1.05	4.29	4.16	0.87	0.46	0.75	4.84	1.72	1.37
Zn	9.36	3.81	5.25	10.29	7.93	0.92	1.70	0.94	7.91	5.31	2.35
As	0.18	0.13	0.09	0.10	0.07	0.10	0.04	0.16	0.03	0.09	0.07
Se	0.26	0.11	0.10	0.07	0.04	0.04	0.03	0.08	0.03	0.02	0.04
Cd	0.06	0.04	0.05	0.13	0.05	0.04	0.02	0.05	0.01	0.02	0.02
Sb	0.18	0.11	0.08	0.07	0.07	0.06	0.04	0.16	0.03	0.08	0.06
Pb	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.04

The study revealed that the contents of Cd exceeded MPC in garlic, potato, carrot, in below-ground and above-ground parts of red beet, in above-ground parts of onion and in apple. The maximal excess of MPC by 4.3 times was observed in above-ground parts of red beet. In case of Cu and As, the MPC excess was not registered in any agricultural crop. The content of Ni was higher than MPC only in below-ground parts of onion. In case of Pb and Se in all eleven samples studied, the MPC excess was not recorded, while the content of Zn slightly exceeded MPC by 1.03 times only in above-ground parts of red beet. The content of Cr exceeded the maximum permissible concentrations in all plants, except the below-ground parts of onion, in particular, in garlic – 3.75 times, in potato – 2.4 times, in carrot – 1.35 times, in above-ground parts of red beet – 2.25 times, in below-ground parts of red beet – 1.4 times, in above-ground parts of onion – 1.15 times, in apple – 5.7 times, in strawberry – 1.9 times, in raspberry and blackcurrant – 3.4 times. The content of Sb in all studied cultures was within acceptable bounds.

Table 4

The total contents of some elements in edible parts of crops (dry mass, mg/kg)

Element	Garlic	Potato	Carrot	Red beet (above-ground)	Red beet (below ground)	Onion (above-ground)	Onion (below ground)	Apple	Straw-berry	Rasp-berry	Black-currant
Cr	1.89	3.01	1.98	3.76	1.25	2.34	1.52	3.55	2.79	2.00	2.10
Ni	0.99	1.68	1.56	2.87	1.12	1.45	7.26	0.91	0.85	1.57	0.86
Cu	4.21	11.65	7.72	35.62	18.87	8.83	4.33	4.67	69.53	10.03	8.50
Zn	23.54	24.11	38.48	85.55	35.92	9.34	16.11	5.81	113.61	30.93	14.61
As	0.45	0.84	0.64	0.83	0.34	1.04	0.37	0.99	0.49	0.53	0.41
Se	0.65	0.72	0.71	0.55	0.18	0.39	0.25	0.47	0.44	0.14	0.23
Cd	0.16	0.23	0.36	1.07	0.21	0.45	0.14	0.28	0.14	0.14	0.12
Sb	0.45	0.69	0.55	0.54	0.31	0.63	0.34	0.98	0.49	0.48	0.38
Pb	0.00	0.00	0.00	0.30	0.01	0.00	0.00	0.00	0.00	0.00	0.27

Table 5

Maximum permissible concentrations (MPC) of some elements in wet mass of vegetables and fruits (mg/kg) [24]

Element	MPC in vegetables	MPC in fruits
Cd	0.03	0.03
Cu	10.0	10.0
As	0.2	0.2
Ni	0.5	0.5
Pb	0.5	0.4
Se	0.5	0.5
Zn	10.0	10.0
Cr	0.2	0.1
Sb	0.3	0.3

Conclusion. In the course of the research it was revealed that the soils of agricultural land situated *ca.* 1.5 *km* from the Zangezur Copper and Molybdenum Combine were polluted by some toxic trace metals, in particular by Cu. Notwithstanding that the content of Cu in crops growing in this area has not exceeded MPC, instead, the MPC excess was registered in case of Cd, Ni, Zn and Cr. Cd is the most harmful metal from the above elements, since it is found in large quantities in agricultural crops and is included in the list of extremely toxic trace metals.

The highest excess of toxic trace metals in vegetables was observed in garlic and above-ground parts of red beet, while in fruits the largest amounts were registered in apple, therefore, the cultivation of these agricultural crops in the studied territory and their usage is not advised. In this connection, great efforts should be made to devise effective methods of restoration of polluted agricultural lands, in particular, the phytoremediation as a socially accepted, cost-effective and ecofriendly method.

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