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COPPER ABSORPTION STATUS OF AGRICULTURAL PLANT SPECIES AND THEIR PHYTOREMEDIATION POTENTIAL

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The aim of the present study was to determine the contents of copper in agricultural soils situated on Darazam recultivated tailing dump and in crops growing on these soils, to evaluate the risk level of studied plants for human health and to find out their phytoremediation potential. Results of the study show that in coriander (aerial part) and in garlic (aerial and underground parts) as well as in the leaves of horseradish (fresh mass) the exceeding of maximum permissible concentration of copper content was observed. The lowest contents of copper were registered in the beans of common bean as well as in the berries of red currant and raspberry therefore these plants may be used as foodstuff. Maize has the greatest phytoremediation potential from all studied plants so it is reasonable to use this species for the reclamation of the area under the study.

Keywords**:** Zangezur Copper and Molybdenum Combine, agricultural plants, copper accumulation, health risks, phytoremediation potential.

Introduction. Soil as an important part of the natural ecosystem plays a significant role in elemental cycling. It has great functions as a filter, buffer, storage, and transformation compartment sustaining a relationship between the abiotic and biotic components of ecosystems [1]. One of the most important functions of soil is its productivity, which has a fundamental role for the survival of human population [2].

The problem of continuous environmental contamination is of global concern and hence the pollution of agricultural lands with heavy metals is a critical challenge for the scientists. Commonly, the concentration of heavy metals in agricultural soils is low and depends on the geological parent material composition, but due to their accumulative behavior and high toxicity, they have a potential hazardous influence not only on agricultural plants but also on human health [3, 4]. The quality of agricultural lands is directly connected to human health and ecological safety [5]. Contamination of soils by heavy metals is mainly related to anthropogenic sources, which include various human activities such as mining and

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smelting operations. Stated ecological problem is common to most of the mining regions in the world [6–12]. Nowadays the pollution of agricultural lands with heavy metals through mining and smelting industrial establishments is one of the most severe ecological problems in Armenia. Although some heavy metals (Cu, Zn and etc.) are important for plant nutrition, plants growing in the close vicinity of industrial areas or on the territories of recultivated tailing dumps display high concentration of these metals and the decrease of crop yields. Contaminating food chains they also have considerable health risks to human [13, 14].

In this connection the aim of our research was to investigate some physico-chemical properties of the topsoil, Cu concentration in agricultural plants growing on these soils as well as to estimate the risk level of studied plants for human health and to find out their phytoremediation potential. These aspects are very important in assessment of the impact of mining industry on human health and environment.

Materials and Methods.

1. *Study Area.* The studies were conducted in agricultural ground areas situated on the Darazam recultivated tailing dump. The study area is situated in the South part of Armenia, in South-East direction from the Kajaran City. This tailing dump was exploited formerly by the Zangezur Copper and Molybdenum Combine and was mothballed and recultivated after the filling. The Darazam recultivated tailing dump is situated on 1754 *m* above sea level and belongs to the watershed of the Voghji River. The soils of study area belong to mountain cambisol.

2. *Sample Collection.* The sampling of soil (sample Q-DA-05) and agricultural plants from the territory of the Darazam recultivated tailing dump was done in 2016. The coordinates of the sampling site were as follows N 39°08' 76.7"; E 46°10' 80.2". For the determination of soil pollution degree by copper the reference soil sample was collected in the site located at a distance of around 0.5 *km* from the Geghi water reservoir down the river (Q-CONT, N 39°13' 01.7"; E 46°13' 96.1"). Soil samples were collected from depth of 0–30 *cm*. The sampling in sites was performed by the method of envelope: 5 samples collected from the angles and the center point of a grid measuring 30×30 (*m*) were mixed and 3.5 *kg* of this composite sample were taken thereafter for the analyses. After the removal of unwanted content (stones, plant material, etc.) in laboratory the samples were air-dried at room temperature (20–22°*C*), grounded in a mortar to pass a 1.0 *mm* mesh and then were stored in an all-glass jar for analysis of their properties.

Thirteen agricultural plant species were selected for investigation, only the usable parts (leaves, fruits or tubers) in 5 species were selected, the rest of species were harvested entirely. For each species 10 different plants were gathered and the sample was prepared from their mixture. The samples were washed in laboratory with deionized water. The aerial and underground parts of the whole plants were separated, after that the fresh weights of plants (aerial and underground parts) and of their usable parts were determined. The samples were oven-dried thereafter at 70°*C* to reach the constant weight for dry weight determination, after that the plants were homogenized, passed through 0.15 *mm* sieve and stored in an all-glass jar for the copper analysis.

3. *Pretreatment and Heavy Metal Analysis of Soil and Plant Samples.* Soil samples were grounded in a mortar to pass a 0.42 *mm* nylon mesh. For determination of total copper content soil samples were digested with HNO_3+$HClO_4$+HF

(5:1:1, v:v:v) [15], while for the analysis of bioavailable Cu CH_3COOH was used. 1*g* soil was placed in 50 *mL* tubes, mixed in a stepwise fashion with 40 *mL* 0.11 *M* CH_3COOH, and the suspensions were equilibrated for 16 *h* at room temperature [16].

Plant samples for heavy metal analysis were digested by mixture of HNO_3 and $HClO_4$ (4:1, v:v) in closed vessels at 150°*C* for 200 *min* (0.1 *g* roots or shoots of plants by 10 *mL* mixture of acids) [17, 18].

Heavy metals were determined by atomic absorption spectrometry method (AAS) using atomic-absorption Spectrometer PG990 (PG Instruments LTD).

4. *The Assessment of the Ability of Plants to Accumulate Copper.* For the assessment of the ability of plants to accumulate Cu two indices were used: the bioconcentration factor of root (BCF_{root}) and translocation factor (TF) [19, 20].

BCF_{root} may be used to assess the copper accumulation capacity of root. BCF of root was calculated by following equation [21]: $BCF_{root}=Cu_{root}/Cu_{soil}$, where Cu_{root} is the copper concentration in the underground part of harvested plant and Cu_{soil} is the bioavailable copper concentration in the soil.

The TF was calculated using the following equation: $TF=Cu_{shoot}/Cu_{root}$, where Cu_{shoot} is the copper concentration in the aerial part of harvested plant.

5. *Statistical Analysis.* The statistical analysis was performed using SPSS software, version 15.

Results and Discussion.

1. *Some Physicochemical Properties of Studied Soil Samples.* The results of physicochemical studies of soil samples from the Darazam recultivated tailing dump (Q-DA-05) and reference site (Q-CONT) are shown in Tab. 1. According to data given in Table, pH of soil sample Q-DA-05 (8.2) is more alkaline compared with the pH of control sample Q-CONT (7.8). This fact can be explained by the differences in humus contents in these sites. As is generally known the high content of humus causes the decrease of pH value of the medium.

Humus content in soil sample Q-CONT is approximately 3.4 times higher than in sample Q-DA-05. Such big difference in humus contents may be conditioned both by agricultural activities implementing in the area of Q-DA-05 (the ploughing promotes increase of soil aeration and mineralization of organic compounds) and by comparatively higher concentration of pollutants, in particular of copper, that inhibits the biological activity of soil and so on. The content of sand in soil sample Q-DA-05 is lower while the contents of silt and clay are higher than in soil sample Q-CONT.

Considering the fact that in the ore processed at the Zangezur Copper and Molybdenum Combine Cu contains in the greatest quantities compared to other studied heavy metals, the total and bioavailable Cu contents were determined in soil samples. Tab. 1 shows, that almost no differences were registered in contents of bioavailable copper in soil samples from two studied sites while the total copper content was about 2.2 times higher in the site Q-DA-05. This fact is directly conditioned by the current activities of the Zangezur Copper and Molybdenum Combine (due to copper-rich dust distributed from open mine and processing plant) as well as by relatively high content of Cu in tailing dump exposed to reclamation by this time. Meanwhile the insignificant difference in bioavailable Cu contents in soil samples could be explained by agricultural activities in the Darazam recultivated tailing dump, as far as some part of bioavailable copper is removed from the soil during the harvesting while a part of it is washed out during the irrigation of farmland.

Table 1

Some physicochemical characteristics of studied soil samples (mean ± SE)

Sampling site	Q-DA-05	Q-CONT
pH	8.2 ± 0.2	7.8 ± 0.1
Humus content, %	1.93 ± 0.28	6.48 ± 0.38
Sand, %	15 ± 3	31 ± 4
Silt, %	50 ± 4	39 ± 4
Clay, %	35 ± 3	30 ± 3
$Cu_{bioavailable}$, *mg/kg*	3.28 ± 0.8	3.2 ± 0.5
Cu_{total}, *mg/kg*	155.5 ± 29.2	71.6 ± 11.0

2. *Copper Accumulation by Agricultural Plants.* The results of investigation of copper contents in aerial and underground parts of agricultural plants (in fresh and dry mass) are shown in Tab. 2. In fresh shoot mass the highest concentrations of Cu were observed in garlic (13.7 *mg*/*kg*) and coriander (12.2 *mg*/*kg*), whereas in dry shoot mass the highest contents were registered in onion (59 *mg*/*kg*), garlic (52 *mg*/*kg*) and spinach (51 *mg*/*kg*). Actually in dry and fresh mass the highest contents of Cu were observed in different plants and this fact is conditioned by different content of water in these crops. In particular the most significant difference was observed in the case of onion, namely in fresh mass the content of Cu was the lowest while in dry mass of this plant the content of Cu was the highest compared to other crops. In fresh and dry root masses the greatest contents of Cu were found in maize (36.4 and 85 *mg*/*kg* respectively) and lettuce (32.5 and 92.6 *mg*/*kg* respectively).

Table 2

Copper concentration in aerial and underground parts of agricultural plants (mg/kg)

Plant species	Cu_{shoot}, fresh weight	Cu_{root}, fresh weight	Cu_{shoot}, dry weight	Cu_{root}, dry weight
Maize (*Zea mays*)	9.9	36.4	43.0	85.0
Topinambour (*Helianthus tuberosus*)	6.4	7.6	34.0	46.5
Coriander (*Coriandrum sativum*)	12.2	14.7	47.5	37.5
Dill (*Anethum graveolens*)	9.0	22.9	45.0	40.0
Onion (*Allium cepa* L.)	5.1	9.6	59.0	61.8
Garlic (*Allium sativum*)	13.7	16.2	52.0	45.0
Spinach (*Spinacia oleracea*)	9.1	19.1	51.0	47.0
Lettuce (*Lactuca sativa*)	8.4	32.5	46.9	92.6

The highest contents of Cu in fresh and dry masses of edible parts of agricultural plants (Tab. 3) were observed in leaves of horseradish, used as pickles (16.2 and 45.9 *mg*/*kg* respectively). The lowest contents of Cu in fresh mass were registered in berries of red currant (3.2 *mg*/*kg*) and of raspberry (3.5 *mg*/*kg*) whereas in dry mass the lowest content of Cu was observed in berries of raspberry (31.5 *mg*/*kg*).

Maximum permissible concentration (MPC) of Cu in fresh mass of agricultural products is 10 *mg*/*kg* [22]. Study results show that from agricultural plants used as foodstuff the exceeding of MPC was observed in coriander (1.22 times in above-ground parts), in garlic (1.37 times in above-ground parts and 1.62 times in underground parts) and in leaves of horseradish (1.62 times).

Table 3

Copper concentration in edible parts of agricultural plants (mg/kg)

Plant species	Fresh weight	Dry weight
Potato (tuber) (*Solanum tuberosum*)	7.5	32.5
Red currant (berry) (*Ribes rubrum*)	3.2	33.5
Raspberry (berry) (*Rubus idaeus* L.)	3.5	31.5
Common bean (bean) (*Phaseolus vulgaris* L.)	4.6	43.3
Horseradish (leaf) (*Armoracia rusticana*)	16.2	45.9

3. *Phytoremediation Potential of Agricultural Plants.* For the improvement of the condition of agricultural ground areas the most important factor is the phytoextraction ability of agricultural crops since Cu, reaching dangerous concentrations, through this process is being removed from the soil whereby the further transfer of Cu into the food chains and subsequently to human is prevented.

The assessment of phytoremediation potential of agricultural plants was performed using bioconcentration factor of root (BCF_{root}) and translocation factor (TF) (Tab. 4). Allowing for the fact that BCF_{root} value of maize is rather high and it forms a strong rootage as well as the circumstance that meanwhile the TF value is low, this plant species is advisable to use for phytoremediation purposes. Specifically its aerial parts may be used in agricultural purposes (Cu contents do not exceed maximum permissible concentrations there), while the underground parts should be removed from the site. High BCF_{root} value is also observed in lettuce, but its rootage is not such strong and this circumstance decreases its phytoremediation potential.

The highest TF values were observed in coriander and garlic. This fact indicates that mentioned agricultural plants accumulate large quantities of copper in their aerial parts, which restricts their usage as foodstuff.

Table 4

BCF_{root} and TF of agricultural plants grown on the territory of the Darazam recultivated tailing dump

Plant species	BCF_{root}	TF
Maize (*Zea mays*)	25.91	0.51
Topinambour (*Helianthus tuberosus*)	14.18	0.73
Coriander (*Coriandrum sativum*)	11.43	1.27
Dill (*Anethum graveolens*)	12.20	1.13
Onion (*Allium cepa* L.)	18.84	0.95
Garlic (*Allium sativum*)	13.72	1.16
Spinach (*Spinacia oleracea*)	14.33	1.09
Lettuce (*Lactuca sativa*)	28.23	0.51

Conclusion. The study of pollution level of soils by copper in agricultural areas situated on the Darazam recultivated tailing dump as well as of ability of crops growing on these soils to accumulate copper was performed. Study results indicate that the content of total copper in the soil exceeds its background value about 2.2 times and that this has resulted in high contents of copper in agricultural plants grown in this area. In particular, in coriander (aerial parts), in garlic (aerial and underground parts) as well as in leaves of horseradish the exceeding of maximum permissible concentrations of copper was observed. Consequently the use of these plants as foodstuff is harmful, because they can have toxic influence on human organisms. At the same time very low concentrations of copper were registered in beans of common bean, as well as in berries of red currant and raspberry (fresh mass), therefore, these plants may be used as food.

Taking into consideration the total mass of crops, their growth intensity and copper accumulation ability it could be concluded that maize has the greatest phytoremediation potential from all studied plants, and this plant species may be used for recultivation of soils in agricultural territories situated on the Darazam recultivated tailing dump. These activities should be accompanied surely by the process of monitoring and it is obligatory to implement them under the strict control so as to prevent the secondary pollution and to reduce the possible threats to human health.

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R E F E R E N C E S

1. **Kabata-Pendias A., Sadurski W.** Trace Elements and Compounds in Soil. In Book: Elements and Their Compounds in the Environment. V. I (eds. Merian E., Anke M., Ihnat M., Stoeppler M.). K GAa, Weinheim: Wiley–VCH Verlag GmbH & Co, 2004, 1773 p.
2. **Kabata-Pendias A., Pendias H.** Trace Elements in Soils and Plants (3rd ed.). Boca Raton: CRC Press, 2001, 413 p.
3. **De Temmerman L., Vanongeval L., Boon W., Hoenig M.** Heavy Metal Content of Arable Soil in Northern Belgium. // Water Air Soil Pollut., 2003, v. 148, p. 61–76.
4. **Wang Z.H., Lin Q., Li C.H., Huang H.H., Yang M.L., Gan J.L.** et al. The Concentration Distribution and Assessment of Cu, Pb, Zn and Cd in Surface Sediments from Pearl River Estuary. // Res. Environ. Sci., 2004, v. 17, № 4, p. 5–9.
5. **Zhao Q., Sun B., Zhang T.** Soil Quality and Sustainable Environment: the Definition and Evaluation Methods of Soil Quality. // Soils, 1997, v. 3, p. 113–120.
6. **Krishna A.K., Govil P.K.** Heavy Metal Distribution and Contamination in Soils of Thane-Belapur Industrial Development Area, Western Indian. // Environ. Geol., 2005, v. 47, p. 1054–1061.
7. **Li M.S., Luo Y.P., Su Z.Y.** Heavy Metal Concentrations in Soils and Plant Accumulation in a Restored Manganese Mineland in Guangxi, South China. // Environ. Pollut., 2007, v. 147, p. 168–175.
8. **Wang X.S., Qin Y.** Accumulation and Sources of Heavy Metals in Urban Topsoils: a Case Study From the City of Xuzhou, China. // Environ. Geol., 2005, v. 48, p. 101–107.
9. **Thornton I.** Impacts of Mining on the Environment, Some Local, Regional and Global Issues. // Appl. Geochem., 1996, v. 11, p. 355–361.
10. **Steinnes E.** Metal Contamination of the Natural Environmental in Norway from Long Range Atmospheric Transport. // Water Air Soil Pollut., 2001, v. 1, p. 449–460.
11. **Ettler J., Rohovec J., Navratil T., Mihaljavic M.** Mercury Distribution in Soil Profiles Polluted by Lead Smelting. // Bull. Environ. Contam. Toxicol., 2007, v. 78, p. 13–17.

12. **Kachenko A.G., Singh B.** Heavy Metals Contamination in Vegetables Grown in Urban and Metal Smelter Contaminated Sites in Australia. // Water Air Soil Pollut., 2006, v. 169, p. 101–123.
13. **Obrador A., Rico M.I., Mingot J.I., Alvarej J.M.** Metal Mobility and Potential Bioavailability in Organic Matter-Rich Soil-Sludge Mixtures: Effect of Soil Type and Contact Time. // Sci. Total Environ., 1997, v. 206, p. 117–126.
14. **Wu X., Li L., Pan G.** Soil Pollution of Cu, Zn, Pb and Cd in Different City Zones of Nanjing. // J. Environ Sci., 2003, v. 24, № 3, p. 105–111.
15. **Baker D.E., Amacher M.C.** Nickel, Copper, Zinc, and Cadmium. In Book: Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties, Agronomy Monograph 9, (2nd ed. Page A.L., Miller R.H., Keeney D.R. eds.). Wisconsin, Madison: Agronomy Society of America and Soil Science Society of America, 1982, p. 323–336.
16. **Qingsong H.E., Yue R., Ibrahim M., Maha A., Waseem H., Fangui Z.** Assessment of Trace and Heavy Metal Distribution by Four Sequential Extraction Procedures in a Contaminated Soil. // Soil & Water Res., 2013, v. 8, № 2, p. 71–76.
17. **Zemberyova M., Bartekova J., Hagarova I.** The Utilization of Modified BCR Three-Step Sequential Extraction Procedure for the Fractionation of Cd, Cr, Cu, Ni, Pb and Zn in Soil Reference Materials of Different Origins. // Talanta, 2006, v. 70, p. 973–978.
18. **Qu J., Yuan X., Cong Q., Wang S.** Determination of Total Mass and Morphology Analysis of Heavy Metal in Soil with Potassium Biphthalate-Sodium Hydroxide by ICP-AES. // Spectrosc. Spectral Anal., 2008, v. 28, p. 2674–2678 (in Chinese).
19. **Mertens J., Luyssaert S., Verheyen K.** Use and Abuse of Trace Metal Concentrations in Plant Tissue for Biomonitoring and Phytoextraction. // Environ. Pollut., 2005, v. 138, p. 1–4.
20. **Wang H.Q., Lu S.J., Li H., Yao Z.H.** EDTA-Enhanced Phytoremediation of Lead Contaminated Soil by Bidens Maximowicziana. // J. Environ. Sci., 2007, v. 19, p. 1496–1499.
21. **Marchiol L., Fellet G., Boscutti F., Montella C., Mozzi R., Guarino C.** Gentle Remediation at the Former “Pertusola Sud” Zinc Smelter: Evaluation of Native Species for Phytoremediation Purposes. // Ecol. Eng., 2005 or 2013, v. 53, p. 343–353.
22. Database for Conducting a Full-Fledged Environmental Impact Assessment. Socio-Ecological Association. Yer., 2002, 228 p. (in Russian).