HEAVY METALS ACCUMULATION IN SOIL AND CELERY ROOT (*APIUM GRAVEOLENS* L.) HARVESTED FROM THE POLLUTED AREAS IN SIBIU COUNTY, CENTRAL ROMANIA

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Abstract

Heavy metals are harmful environmental contaminants that are mostly the result of human activities. Vegetable roots may easily absorb heavy metals, which can then accumulate up to high levels in the edible sections. The celery root is a vegetable that is frequently cultivated in individual gardens and its production in polluted soil might provide a risk to the consumer's health, not necessarily due to the amount ingested but rather due to the cumulative effect of long-term usage.

The present study is aimed to estimate the bioaccumulation of heavy metals (cadmium, lead, copper, and zinc) from the soil in the celery root, harvested from 26 households located in the polluted areas (Axente Sever, Agârbiciu, Bazna, Copșa Mică, Micăsasa, Șoala, and Târnava). Total soil (0-20 cm) and celery root heavy metals contents varied as follows: for Cd (soil = 0.10 mg/kg – 14.80 mg/kg; celery root = 0.058 mg/kg – 1.254 mg/kg); for Pb (soil = 28 mg/kg – 326 mg/kg; celery root = 0.022 mg/kg – 0.620 mg/kg); for Cu (soil = 25 mg/kg – 163 mg/kg; celery root = 0.60 mg/kg – 2.51 mg/kg); for Zn (soil = 117 mg/kg – 1076 mg/kg; celery root = 3.1 mg/kg – 11.7 mg/kg). The highest values of correlation coefficients were obtained for the regression curves established for the estimation of Cd, Pb, and Zn accumulation in celery root (r = 0.788 for Cd, r = 0.796 for Pb, and r = 0.656 for Zn). In the case of copper, the linear correlation coefficient is relatively low (r = 0.092).

***Key words**: accumulation, celery root, heavy metals, pollution*

INTRODUCTION

Increased levels of heavy metals in the soil may inhibit crop development, affecting food security both quantitatively and qualitatively. Food chain contamination might be dangerous for ecosystems and people's health (Lee et al., 2006;Luo et al., 2007). Celery root (celeriac) (*Apium graveolens* var. *Rapaceum*), belongs to the family *Apiaceae*, genus *Apium*. It may be used in cooked or raw salads, frequently as a flavoring in stews, and soups, as well as mashed or baked. Sometimes celery roots are prepared for canning, freezing, or dehydrating. They have around 88% water, various proteins, lipids, carbohydrates, microelements, vitamins (C, thiamine, riboflavin, B6), and phytochemicals in the form of phenolic compounds (Lim, 2015; Popova et al., 2014). The diversity of environmental contaminants has significantly increased as a result of the industrial revolution, economic globalization, and diverse human activities (Toth et al., 2016). Because of their specific toxicity, bioaccumulation, persistence, and non-biodegradability, heavy metals pose a threat to the ecosystem, a risk to soil pollution, plant toxicity, and the quality of natural resources (Wang et al., 2015). Through their root systems, plants absorb heavy metals from contaminated soils and water as well as through aerial parts exposed to the air from polluted areas (Deribachew et al., 2015). According to Heidarieh et al. (2013), Taghizadeh et al. (2017) plant species quickly absorb heavy metals such as Cd, Cr, and Pb through their root systems, which are then considerably accumulated and amplified in their edible portions. Heavy metals are not biodegradable, they can remain for a very long time in both aquatic and terrestrial ecosystems (Nouri et al., 2011). Heavy metal concentrations in plants are directly proportional to soil concentrations (Sun et al., 2013). It is crucial to evaluate the bioavailability of Cd in soil in order to prevent the contamination of the food chain (Cornu et al., 2009). Therefore, in the early phases of heavy metals contamination, plant species are thought to be useful bio-indicators. The level of metal in the environment where plants develop throughout time is measured by the quantity of metallic components in plants (Ahmed et al., 2012).

Vegetables are a significant source of proteins, vitamins, minerals, fiber, and micronutrients that are necessary for good health as well as the prevention and treatment of many illnesses. Vegetables may contain varying levels of heavy metals (Radwan & Salama 2006). Heavy metals contamination of vegetables has been claimed to have significantly increased in recent years, posing a severe threat to modern society's health (Pan, Wu & Jiang, 2016). One of the main causes of environmental contamination comes from the atmospheric emissions of industries (Addo et al., 2012). Four different elements: cadmium, lead, zinc, and copper were studied by Radwan et al. (2006) in various fruits and vegetables. The findings revealed that lead and cadmium levels were greatest in leafy crops like lettuce and spinach (Radwan & Salama 2006). According to Suciu et al. (2008) cited by Dumitru et al. (2014) processing of mining was the biggest environmental hazard in the Copşa Mică, central Romania. The most contaminated district in Sibiu county, Copşa Mică, located on the Târnava Mare river, was designated an environmental disaster area. The primary source of the pollution was the non-ferrous metallurgical firm S.C. Sometra S.A. Other economic agents' emissions from Mediaş city's industrial platform (S.C. Emailul, S.C. Vitrometan, S.C. Geromed) contributed to pollution in this area. This study aims to estimate the bioaccumulation of heavy metals (cadmium, lead, copper, zinc) in celery roots under different scenarios in correlation to soil content.

MATERIALS AND METHODS

For this study, celery root (*Apium graveolens* L.) and soil samples were collected from 26 households located in the Copșa Mică area, Sibiu county during 2021-2022. In this area, the pollution level is very high, especially at the ground level, due to gas emissions from factories that have been operating in the past (since the 1930s) for about 60 years. Soil samples were taken from the top layer (0-20 cm), then air-dried at room temperature and ground for analysis. Heavy metals content from soil samples was determined using atomic absorption spectrometry, after the extraction by the aqua regia - microwave digestion method. Celery root samples were cleaned twice in tap water, chopped and frozen. The samples were treated with nitric acid in a microwave digestion system. To determine the content of heavy metals the atomic absorption spectrometry was used (Flame GBC 932AA or Graphite furnace GBC SavanatAAZ). Microsoft Excel 2002 was used for the statistical processing and graphical representation of data.

RESULTS AND DISCUSSIONS

The content of heavy metals in the soil (Table 1) ranged for Cd between 0.1 mg/kg^{-1} and 14.8 mg/kg^{-1}, Pb had values from 28 mg/kg^{-1} to 326 mg/kg^{-1}, Zn ranged between 117 mg/kg^{-1} and 1076 mg/kg^{-1} and Cu had values from 25 mg/kg^{-1} to 163 mg/kg^{-1}. The concentration of heavy metals in soil had the following pattern: Zn>Pb>Cu>Cd. The lowest value of the arithmetic mean was registered by cadmium (4.31 mg/kg^{-1}), while lead had the highest value (383.0 mg/kg^{-1}). The geometric mean of the total heavy metals in soil ranged from 1.82 mg/kg^{-1} for cadmium and 323.5 mg/kg^{-1} for zinc. At the same time, zinc obtained the highest value (238.2 mg/kg^{-1}) in terms of standard deviation, while the lowest value was recorded by cadmium (3.95 mg/kg^{-1}). The lowest value regarding the coefficient of variation of the content of heavy metals in the soil was obtained by copper (48.1%) and the highest was recorded by cadmium (91.6%).

Table 1. Values of statistical parameters that characterize the central tendency and the variability of the total cadmium, lead, zinc and copper contents in soil (n=26)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
	- - - - - - - -	- - - - - - - -	- - - - - - - -	mg/kg DW	- - - - - - - -	- - - - - - - -	- - - - - - - -
Cd_{soil}	0.1	14.8	4.45	1.82	4.31	3.95	91.6%
Pb_{soil}	28	326	118.5	100.9	131.2	92.5	70.5%
Zn_{soil}	117	1076	317	323.5	383.0	238.2	62.2%
Cu_{soil}	25	163	58.5	58.8	65.3	31.4	48.1%

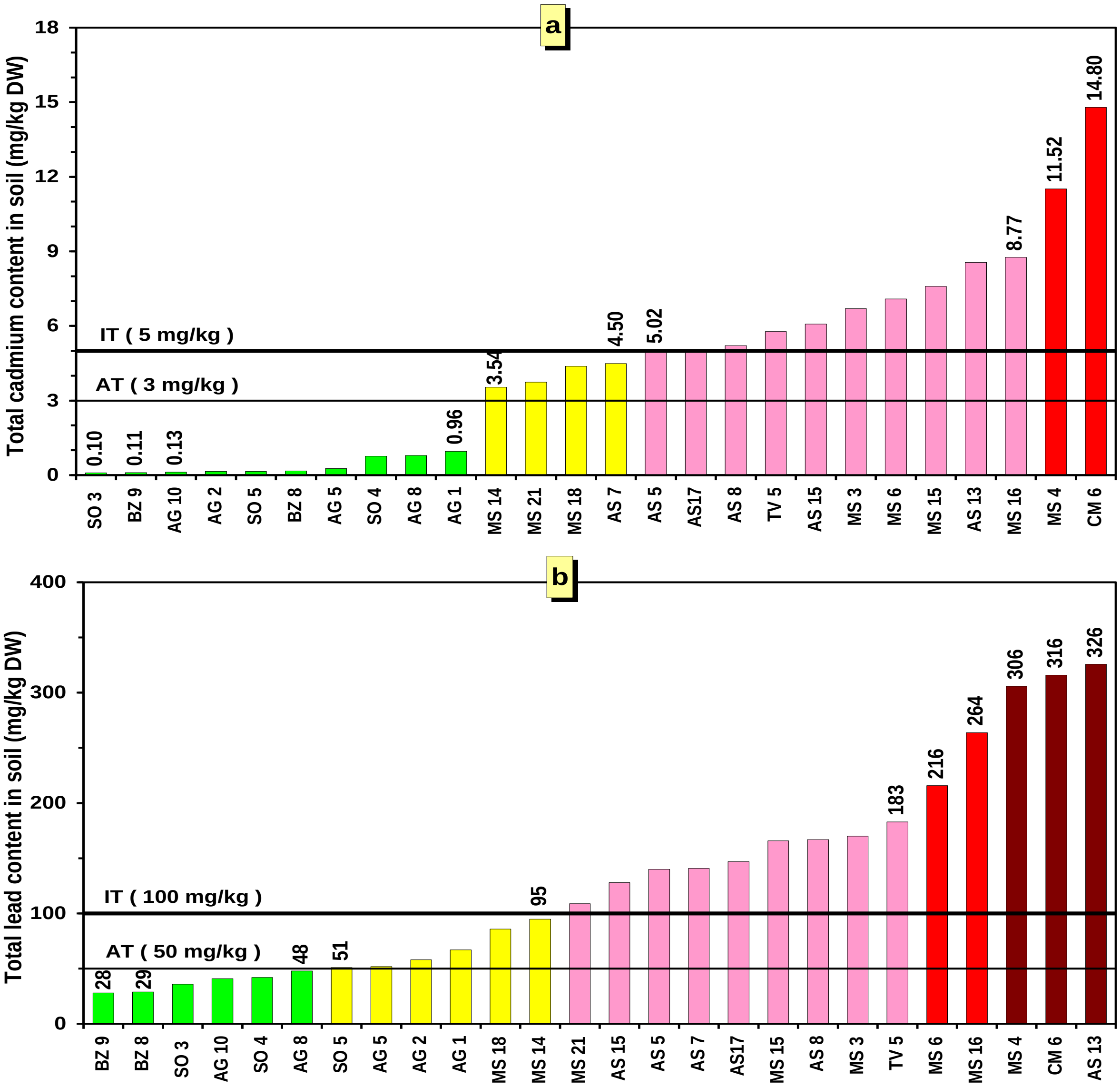
DW - Dry Weight

Table 2. Values of statistical parameters that characterize the central tendency and the variability of the cadmium, lead, zinc, and copper contents in the celery roots (n=26)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
	- - - - - - - -	- - - - - - - -	- - - - - - - -	mg/kg FW	- - - - - - - -	- - - - - - - -	- - - - - - - -
Cd_{celery}	0.058	1.254	0.311	0.362	0.463	0.321	69.3%
Pb_{celery}	0.022	0.620	0.105	0.117	0.163	0.138	84.7%
Zn_{celery}	3.1	11.7	6.95	6.72	7.03	2.06	29.3%
Cu_{celery}	0.60	2.51	1.41	1.27	1.35	0.45	33.3%

FW - Fresh Weight

The concentration of heavy metals in celery root (Table 2) had the following pattern: Zn>Cu>Cd>Pb, slightly different from the one found in the soil. Nevertheless, zinc was the heavy metal with the highest quantity found in celery root (*A. graveolens*) samples, ranging from 3.1 mg/kg^{-1} to 11.7 mg/kg^{-1}. The second highest heavy metal by content was copper (Cu), with values from 0.60 mg/kg^{-1} to 2.51 mg/kg^{-1}. Lead (Pb) and cadmium (Cd) contents measured from 0.022 mg/kg^{-1} and 0.620 mg/kg^{-1}, and from 0.058 mg/kg^{-1} to 1.254 mg/kg^{-1}, respectively. The geometric mean of the heavy metals content in celery root ranged from 0.117 mg/kg^{-1} for lead (Pb) and 6.72 mg/kg^{-1} for zinc (Zn). The values registered for cadmium and copper in terms of the geometric mean were 0.362 mg/kg^{-1} and 1.27 mg/kg^{-1}, respectively. The lowest value for the arithmetic mean was obtained by lead (0.163 mg/kg^{-1}), while zinc recorded the highest value (7.03 mg/kg^{-1}), cadmium had a value of 0.463 mg/kg^{-1} and copper 1.35 mg/kg^{-1}. The standard deviation values regarding the content of heavy metals in celery root varied from 0.138 mg/kg^{-1} for lead to 2.06 mg/kg^{-1} for zinc. In terms of the coefficient of variation, it was observed that the highest value was obtained by lead (84.7 %), followed by cadmium with a value of 69.3 %, and then by copper (33.3 %), while zinc obtained the lowest (29.3 %).



IT - Intervention **T**hreshold for sensitive use of land* **DW - D**ry **W**eight

AT - **A**lert **T**hreshold for sensitive use of land*

* **Ministry Order 756/1997**

Notes: **AS** - Axente Sever, **AG** - Agârbiciu, **SO** - Şoala (villages of Axente Sever commune)
BZ - Bazna, **MS** - Micăsasa, **TV** - Târnava (communes in Sibiu County)
CM - Copşa Mică (town in Sibiu County)

Figure 1**.** Cadmium and lead contents in soil (layer 0-20 cm).

Analyzing Figure 1a, the total cadmium content (mg/kg d.w.) in the soil (0-20 cm layer), it can be observed that the contents varied from 0.10 mg/kg^{-1} SO 3 to 0.96 mg/kg^{-1} AG 1, these being both below the alert and intervention thresholds for sensitive land use. The samples collected from households MS 14, MS 21, MS 18, and AS 7 had values between 3.54 mg/kg^{-1} and 4.50 mg/kg^{-1} which fell below the intervention threshold but exceeded the alert threshold. The highest contents which exceeded both the alert and intervention thresholds had values between 5.02 mg/kg^{-1} for AS 5 and 14.08 mg/kg $^{-1}$ CM 6 (Ministry Order 756/1997). Based on data in Figure 1b, the total lead content (mg/kg) in the soil (0-20 cm layer), varied from 28 mg/kg^{-1} for BZ 9 to 48 mg/kg^{-1} for AG 8, both values were below the alert and the intervention thresholds for sensitive land use. The samples collected from 6 households had values between 51 mg/kg^{-1} and 95 mg/kg^{-1} ,below the intervention threshold but exceeding the alert threshold.

The highest contents that exceeded both the alert and intervention thresholds according to Ministry Order 756/1997, had values between 109 mg/kg^{-1} for MS 21 and 326 mg/kg^{-1} AS 13.

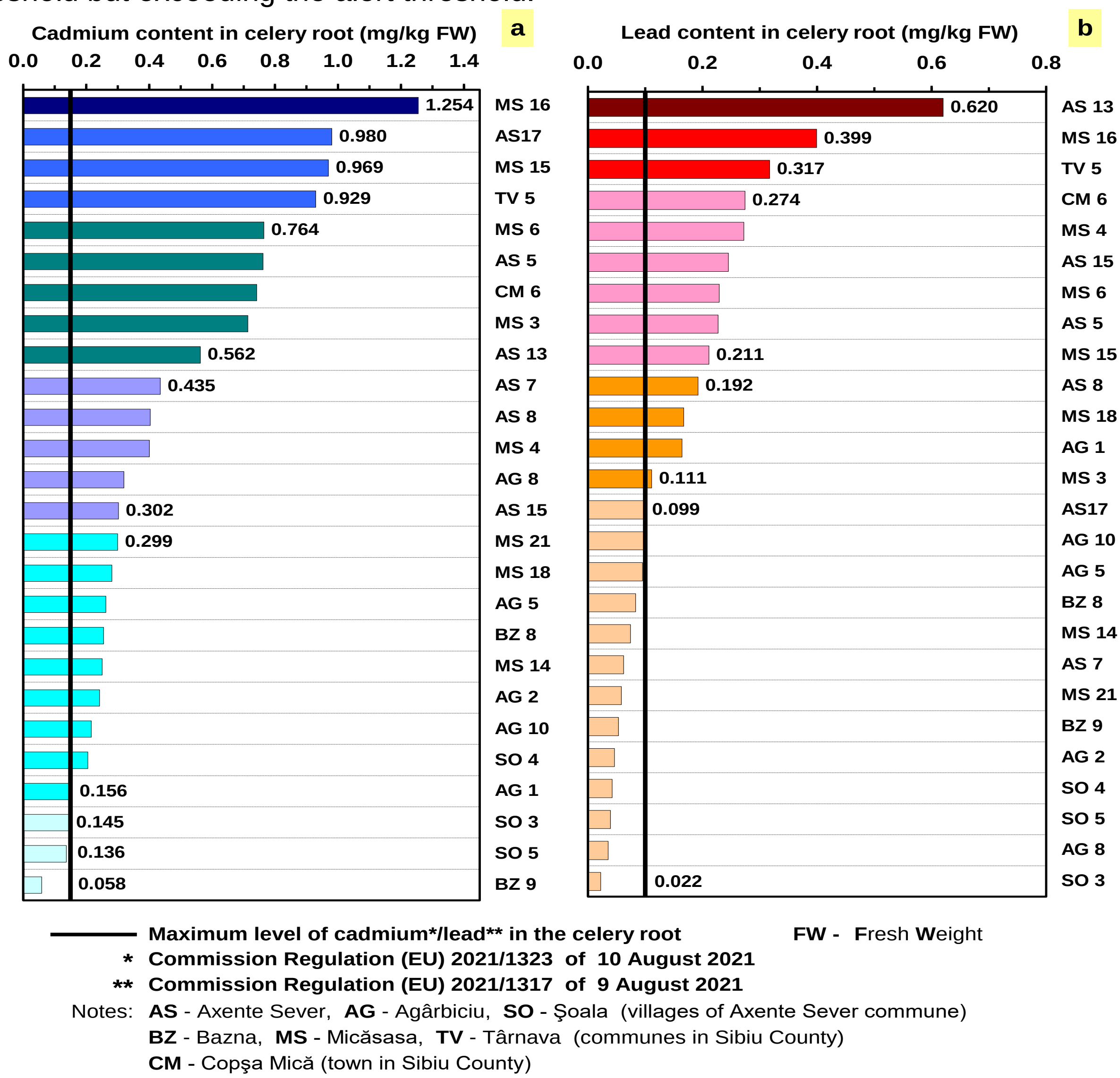


Figure 2. Cadmium and lead contents in the celery roots harvested from the Copşa Mică area.

Figure 2a shows values of the cadmium content in the celery root. For 23 households Cd content exceeds the maximum limit allowed in the European Union (0.15 mg/kg^{-1} f.w.) according to Commission Regulation (EU) 2021/1323. The highest value of cadmium content (1.254 mg/kg^{-1}) was recorded for the celery root harvested from Micăsasa (MS16), and the lowest content (0.156 mg/kg^{-1}) was obtained by the sample from Agârbiciu (AG 1). The lowest value (0.058 mg/kg^{-1}) within the limit established by Commission Regulation (EU) 2021/1323 was obtained for the sample collected from Bazna (BZ 9), samples collected from the Șoala (SO 3; SO 5) also recorded values below the allowed limit with values of 0.136 mg/kg^{-1} and 0.145 mg/kg^{-1}, respectively. This element has a high capacity for absorption by the plant and transmission to the edible sections. Additionally, cadmium has a strong capacity to get through the root's cell membrane. The danger of cadmium in the food chain has grown due to each of these causes (Sharifi et al., 2010). Following the content of lead in celery root (Figure 2b), it can be seen that the maximum value allowed (0.10 mg/kg^{-1} f.w.) by Commission Regulation in the European Union 2021/1317 was exceeded in half of the households analyzed. The lowest value was recorded by MS 3 (0.111 mg/kg^{-1}), while the celery root harvested from Axente Sever (AS 13) had the highest lead content (0.620 mg/kg^{-1}). The other half that fell within the maximum allowed limits varied from 0.022 mg/kg^{-1} in the case of SO 3 to 0.099 mg/kg^{-1} for AS 17.

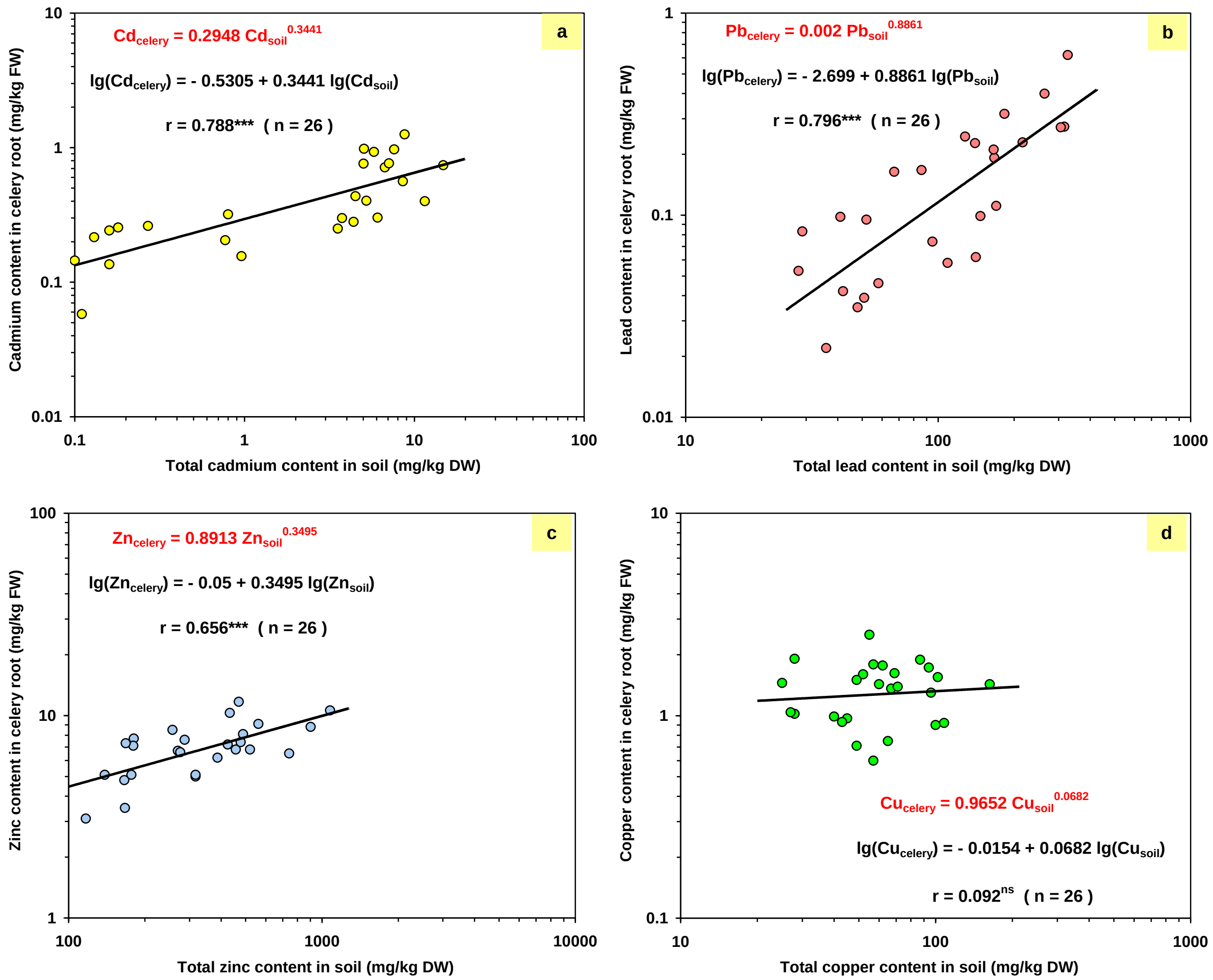


Figure 3. Log-log diagrams for power regression curves that estimate the stochastic dependency between the total cadmium, lead, zinc, copper contents in soil (layer 0-20 cm) and the cadmium, lead, zinc, copper contents in the celery root.

Figure 3, shows logarithmic plots for power regression curves that estimate the stochastic relationship between the total amounts of cadmium, lead, zinc, and copper in the soil and the amounts of those metals in celery root. The highest value of the correlation coefficient (Figure 2b) was obtained for the regression curve established for the estimation of lead bioaccumulation (r = 0.796). The second highest value of the correlation coefficient (Figure 2a) was obtained for cadmium (r = 0.788). The regression curve established to estimate the bioaccumulation of zinc in celery root (Figure 2c) recorded a value of r = 0.565, while for copper (Figure 2d) the value obtained was insignificant (r = 0.092).

CONCLUSIONS

Celery roots and soil were examined in this research to determine their heavy metal content. Metal in celery root was concentrated in the following order: Zn>Cu>Cd>Pb. The concentration of heavy metals in the soil had the following pattern: Zn>Pb>Cu>Cd. Zinc had the highest value in both celery root and soil samples (celery root = 11.7 mg/kg^{-1}, soil = 1076 mg/kg^{-1}). The lowest content in the celery root was recorded by lead (0.022 mg/kg^{-1}), and in the soil, cadmium had the lowest value (0.1 mg/kg^{-1}). Celery root from this region may provide a health risk to consumers since Cd and Pb levels are above levels regulated by the EU Commission Regulation.

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REFERENCES

Addo, M. A., Darko, E. O., Gordon, C., Nyarko, B. J. B., Gbadago, J. K., Nyarko, E., Affum, H., & Botwe, B. O. (2012). Evaluation of heavy metals contamination of soil and vegetation in the vicinity of a cement factory in the Volta Region, Ghana

Ahmed, W., Ahmed, A., Ahmad, A., Randhawa, M. A., Ahmad, R., & Khalid, N. (2012). Heavy metal contamination in vegetables grown in Rawalpindi, Pakistan. Journal of the Chemical Society of Pakistan, 34(4).

Commission Regulation (EU) 2021/1317 of 9 August 2021 amending Regulation (EC) No 1881/2006 as regards maximum levels of lead in certain foodstuffs (Text with EEA relevance) (OJ L 286 10.08.2021, p. 1, ELI. Available online: http://data.europa.eu/eli/reg/2021/1317/oj (accessed on 22 September 2022).

Commission Regulation (EU) 2021/1323 of 10 August 2021 amending Regulation (EC) No 1881/2006 as regards maximum levels of cadmium in certain foodstuffs (Text with EEA relevance) (OJ L 288 11.08.2021, p. 13, ELI. Available online: http://data.europa.eu/eli/reg/2021/1323/oj (accessed on 22 September 2022).

Cornu, J. Y., Parat, C., Schneider, A., Authier, L., Dauthieu, M., Sappin-Didier, V., & Denaix, L. (2009). Cadmium speciation assessed by voltammetry, ion exchange and geochemical calculation in soil solutions collected after soil rewetting. Chemosphere, 76(4), 502-508.

Deribachew, B., Amde, M., Nigussie-Dechassa, R., & Taddese, A. M. (2015). Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implications in Eastern Ethiopia. African Journal of Food, Agriculture, Nutrition and Development, 15(3), 10013-10032.

Dumitru, M., Motelică, D. M., Vrînceanu, N., Dumitru, S., & Vrînceanu, A. G. (2014). Effects of long-term industrial pollution on heavy metals accumulation in soils and maize crops on Târnava Mare river bottomland. Acta Metallomica–MEEMB, 11(1), 35-42.

Heidarieh, M., Maragheh, M. G., Shamami, M. A., Behgar, M., Ziaei, F., & Akbari, Z. (2013). Evaluate of heavy metal concentration in shrimp (Penaeus semisulcatus) and crab (Portunus pelagicus) with INAA method. SpringerPlus, 2(1), 1-5.

Lee, C. S. L., Li, X., Shi, W., Cheung, S. C. N., & Thornton, I. (2006). Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Science of the Total Environment, 356(1-3), 45-61.

Lim, T. K. (2015). Edible medicinal and non medicinal plants: modified stems, roots. bulbs 10.1007/978-94-017-9511-1, 9 Springer, Dordrecht.

Luo, W., Lu, Y., Giesy, J. P., Wang, T., Shi, Y., Wang, G., & Xing, Y. (2007). Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China. Environmental geochemistry and health, 29(6), 459-471.

Ministry Order No. 756 from November 3, 1997 for approval of Regulation concerning environmental pollution assessment, published in Official Monitor No. 303/6 November 1997.

Nouri, J., Lorestani, B., Yousefi, N., Khorasani, N., Hasani, A. H., Seif, F., & Cheraghi, M. (2011). Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead–zinc mine (Hamedan, Iran). Environmental Earth Sciences, 62(3), 639-644.

Pan, X. D., Wu, P. G., & Jiang, X. G. (2016). Levels and potential health risk of heavy metals in marketed vegetables in Zhejiang, China. Scientific reports, 6(1), 1-7.

Popova, M., Stoyanova, A., Valyovska-Popova, N., Bankova, V., & Peev, D. (2014). A new coumarin and total phenolic and flavonoids content of Bulgarian celeriac. Bulgarian Chemical Communications, 64, 88-93.

Radwan, M. A., & Salama, A. K. (2006). Market basket survey for some heavy metals in Egyptian fruits and vegetables. Food and chemical toxicology, 44(8), 1273-1278.

Sharifi, M., Afyuni, M., & Khoshgoftarmanesh, A. H. (2011). Effects of Animal Manure, Sewage Sludge, and Cadmium Chloride on Cadmium Uptake of Corn Shoots. Journal of Water and Wastewater; Ab va Fazilab (in persian), 21(4), 98-103.

Sun, C., Liu, J., Wang, Y., Sun, L., & Yu, H. (2013). Multivariate and geostatistical analyses of the spatial distribution and sources of heavy metals in agricultural soil in Dehui, Northeast China. Chemosphere, 92(5), 517-523.

Taghizadeh, S. F., Davarynejad, G., Asili, J., Nemati, S. H., Rezaee, R., Goumenou, M., & Karimi, G. (2017). Health risk assessment of heavy metals via dietary intake of five pistachio (Pistacia vera L.) cultivars collected from different geographical sites of Iran. Food and chemical toxicology, 107, 99-107.

Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. J. E. I. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. Environment international, 88, 299-309.

Wang, S., Wang, Y., Zhang, R., Wang, W., Xu, D., Guo, J., & Yu, K. (2015). Historical levels of heavy metals reconstructed from sedimentary record in the Hejiang River, located in a typical mining region of Southern China. Science of the Total Environment, 532, 645-654.