ACCUMULATION OF SOME HEAVY METALS IN CARROT ROOTS SAMPLED FROM HOUSEHOLDS IN COPSA MICA

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Abstract

Heavy metals can affect the vegetables and can accumulate in vegetables and thereby indirectly can affect human health. Due to various factors including the disposal of municipal and industrial wastes, application of fertilizers, atmospheric deposition and discharge of wastewater on land, has resulted in increase in the concentration of heavy metals in the soil. Soil normally contains a low concentration of heavy metals such as copper (Cu) and zinc (Zn), which are the essential micronutrients for the optimum growth of the plants. Heavy metals like cadmium (Cd) and lead (Pb) are usually not found in agricultural soil and are toxic to plants. The paper presents a case study achieved in Copsa Mica. As a result of a historical pollution (over 60 years) and a present pollution, the Copsa Mica area is an affected area by atmospheric pollution, characterized by inadequate ambient air quality, surface water pollution, soil pollution, qualitative degradation of vegetable products and possible risk to the health of animals and people in the area. There were sampled carrots roots from 51 households. Obtained data were used to estimate the bioaccumulation of some heavy metals (Cd, Cu, Pb and Zn) in carrot roots. The highest correlations between soil and plant total metal content were obtained for cadmium and lead. It is noted the increased tendency of accumulation of cadmium (r=0.761) in carrot roots compared to lead (r=0.660). In the case of copper and zinc, the correlation established between the two variables is not very strong, thus for zinc r=0.439, while for copper the value was obtained r=0.151.

Key words: accumulation, heavy metals, carrot roots, Copsa Mica

Soil normally contains a low concentration of heavy metals such as copper (Cu) and zinc (Zn), which are the essential micronutrients for the optimum growth of the plants. Metals like cadmium (Cd) and lead (Pb) are usually not found in agricultural soil and are toxic to plants (Tucker R. et al, 2003; Alghobar M.A., Suresha S., 2017).

Gan et al, 2017, achieved a case study that suggested one efficient strategy for clean agricultural production and food safety in high natural background area, to breed vegetable varieties with low heavy metal accumulation and to enlarge planting scale of these varieties.

Sfinchez-Camazano M. et al, 1994, have determined the Pb and Cd contents of soils and vegetables from 16 urban gardens of Salamanca (Spain). Pb and Cd occur at pollution levels in the surveyed gardens. The total and soluble Pb levels were found to be related to the traffic density. The Cd levels appear to be more closely related to the distance from roadways, as well as to the age of the garden and the flow of visitors.

Conventionally-, organically- and selfgrown carrots available across the Czech market were characterized based on their elemental, nitrate

and dry matter content (218 samples, parameters) in order to assess the quality of the carrots and address the question whether organic also means better. The results were compared with information describing the elemental composition of carrots published previously, recommended intakes, legislative daily and limits contaminants in food. Significant differences in the amounts of Na, K, S, Al, Mn, Ni, As and Cd were observed between conventional and organic carrots. Krejcová et al, 2016 concluded that carrots are an excellent source of potassium.

Results obtained by Chaoua et al (2018) revealed high risks indexes, heavy metal contaminated food crops in studied area, and consequently, a great health risk to the local human and animal populations. Thus, preventive measures must be taken to reduce heavy metal pollution of irrigation water and soils to protect both, human and animal health in Marrakech and Morocco.

Verma P. et al (2007) developed a model that can be used for predicting metal accumulation in different vegetables under dynamic field conditions using appropriate water extraction and metal uptake functions. The governing equations

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developed in the mathematical model were solved using finite difference techniques to obtain the cadmium accumulation in radish, carrot, spinach and cabbage.

Hou S. et al (2018) have achieved a pot experiment to investigate the effects of Cd and Cu mixtures to growth and nutrients (sugar, carotene or vitamin C) of carrot under greenhouse cultivation condition. The metals contents in plants increased obviously with Cd and Cu contamination in soil. The biomass production and nutrients declined with Cd and Cu contents increasing. Cd (20 mg kg⁻¹) treatment caused maximum reduction of sugar content (45.29%) in carrot root. The results of multivariate regression analysis indicated that combination of Cd and Cu exerts negative effects to carrot, and both growth and nutrients negatively correlated were with concentrations. It is concluded that the Cd and Cu mixtures caused toxic damage to vegetable plants as Cd and Cu gradient concentrations increased.

Qirui A. et al (2020), examined the effects of mixtures of cadmium and copper on physiological measures and expression of growth-related genes in carrot under greenhouse cultivation. A cluster analysis showed that in the additions with mixtures of Cd and Cu, the plant phenotype was affected first, and then with increases in the added concentration, the expression of genes was also affected. In summary, in the additions with mixtures of Cd and Cu, plants were damaged as Cd and Cu concentrations increased.

Beccaloni E. *et al*, achieved a study by collecting data on thirty-five different vegetables and fruits from a total of 255 samples. Sampling areas were represented by small and medium vegetable family gardens. Spices and herbs showed the highest concentrations; the highest median concentrations for other food have been found in leafy vegetables for Cd (0.147 mg/kg), in fruits for Pb (0.294 mg/kg), in pulses for Zn (13.03 mg/kg).

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Nabulo G. and Oryem-Origa H., concluded that the lowest Pb and Zn concentrations were found in the fruit compared to the leaves of the same crops. Leaves of roadside vegetables were therefore considered a potential source of heavy metal contamination to farmers and consumers in urban areas. It is recommended that leafy

vegetables should be grown 30 m from roads in high-traffic, urban areas.

MATERIAL AND METHOD

The present study was carried out during 2019- 2021 in one of the critical areas in terms of heavy metal contamination, Copşa Mică. The studied area includes seven localities: Avente Sever, Agârbiciu, Soala, Micăsasa, Târnava, Copşa Mica and Bazna. This area presents the highest risk of interception of heavy metals through locally produced local food, due to the large abundance of agrosystems in the structure of local socioecological systems (Vrînceanu N.O. *et al*, 2022).

During this study were collected 51 soil samples, 51 carrots (*Daucus carota*), samples from individual gardens located in contaminated area. Each soil sample was a mixture of 6 sub-samples that were collected from the surface soil (0-20 cm).

The soil samples were air-dried at room temperature and then crushed and sieved through 2 and 0.2 mm meshes, before storage and analysis.

The heavy metals concentration of Pb, Cd, Zn and Cu was determined in the soil samples by atomic absorption spectrometry.

The vegetable samples were digested with nitric acid in a microwave digestion system. The metal content was measured using atomic absorption spectrometry (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

Root vegetables are favorite vegetables of the locals and very often grown in individual households. Their cultivation in households in areas affected by contamination with heavy metals can represent a risk for the health of the consumer, therefore it is important to estimate metal contents using various stochastic models that take into account both the degree of soil contamination and the plant species.

The studied area includes seven localities and 51 samples have been collected. From Avente Sever were collected 12 samples, from Agârbiciu 5 samples, from Soala 3 samples, from Micăsasa 18 samples, from Târnava 3 samples, from Copșa Mica 6 samples and from Bazna 4 samples.

In *table 1* are presented the values of statistical parameters that characterize the central tendency and the variability of the total cadmium, lead, zinc, copper contents in soil surface layer 0-20 cm.

The average contents for Cd, Cu, Pb and Zn exceeds the alert thresholds for sensitive use of land according with Order 756/1997. In *table 2* are presented the reference values of the total cadmium, lead, zinc, copper contents in soil for sensitive and less sensitive use of land.

In case of Cadmium were registered values that exceed the intervention thresholds in all the samples collected from Copsa Mica, 9 samples from 18 collected from Micăsasa, 7 samples from 12 collected from Avente Sever and 2 samples from 3 collected from Târnava. Also, were registered values that exceed the alert thresholds in 5 samples from 12 collected from Avente Sever, in 6 samples from 18 collected from Micăsasa and in one sample from 3 collected from Târnava. Normal values were registered in all samples collected from Agârbiciu, Bazna and Soala, also for 3 samples from 18 collected from Micăsasa.

Lead registered normal values in all the samples collected from Bazna and one sample from 3 collected from Soala. The alert threshold was exceeded in all the samples collected from Agârbiciu, in 6 samples from 18 collected from

Micăsasa, in one sample from 12 collected from Avente Sever and in 2 samples from 3 collected from Soala. The intervention threshold was exceeded in all the samples collected from Copsa Mica and Târnava, in 11 samples from 12 collected from Avente Sever and 12 samples from 18 collected from Micăsasa.

Zinc values exceeded the intervention thresholds in all the samples collected from Copsa Mica, one sample from 18 collected from Micăsasa and 3 samples from 12 collected from Avente Sever. Also, were registered values that exceed the alert thresholds in all the samples collected from Târnava, 7 samples from 12 collected from Avente Sever and 11 samples from 18 collected from Micăsasa. Normal values were registered in all samples collected from Agârbiciu, Bazna and Soala, also for 6 samples from 18 collected from Micăsasa and 2 samples from 12 collected from Avente Sever.

Copper have registered normal values excepting 3 samples from 12 collected from Avente Sever and one sample from 6 collected from Copsa Mica.

Table 1
Values of statistical parameters that characterize the central tendency and the variability
of the total cadmium, lead, zinc, copper contents in soil (layer 0-20 cm)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
Cd _{soil}	0.10	27.11	4.81	3.11	5.97	5.69	95.3%
Pbsoil	22	770	140	126.3	172.5	145.1	84.1%
Znsoil	117	1472	358	369.9	453.6	307.8	67.9%
Cu _{soil}	27	163	62	62.7	66.7	24.4	36.6%

Table 2
The reference values of the total cadmium, lead, zinc, copper contents in soil for sensitive and less sensitive use of land according with Order 756/1997

Element	Normal values	Alert	thresholds	Intervention thresholds		
		Sensitive use of land	Less sensitive use of land	Sensitive use of land	Less sensitive use of land	
Cd _{soil}	1	3	5	5	10	
Pb _{soil}	20	50	250	100	1000	
Zn _{soil}	100	300	700	600	1500	
Cu _{soil}	20	100	250	200	500	

In *table 3* are presented the values of statistical parameters that characterize the central tendency and the variability of the cadmium, lead, zinc, copper contents in the carrot roots.

The cadmium content values in carrot roots collected during this study ranged between 0.008

mg kg⁻¹ and 0.730 mg kg⁻¹. The average contents for Cd exceed the alert thresholds contents in plant. According with EU Regulation 2021/1323, the maximum allowable value for cadmium for leafy vegetables is 0.10 mg kg⁻¹, except aromatic herbs. For aromatic herbs the maximum allowable

limits are 0.20 mg kg⁻¹ Cd reported to fresh material. The values obtained exceed the maximum allowable in all samples collected from Târnava, in 8 samples from 12 collected from Avente Sever, 5 samples from 6 collected from Copsa Mica, 10 samples from 18 collected from Micăsasa.

The lead content values in carrot roots collected during this study ranged between 0.010 mg kg⁻¹ and 0.348 mg kg⁻¹. The average contents for Pb do not exceed the alert thresholds contents in plant. According with CE Regulation 1881/2006, the maximum allowable value for lead in vegetables, leaf vegetables is 0.10 mg kg⁻¹ wet

weight. In all the samples collected from Copsa Mica and Avente Sever, except one, in 6 samples collected from Micăsasa, in one sample from 5 collected from Agârbiciu and in one sample from 3 collected from Târnava the values obtained exceed the maximum allowable value for lead.

The zinc content values in carrot roots collected during this study ranged between 1.1 mg kg⁻¹ and 11.7 mg kg⁻¹. The copper content values in carrot roots collected during this study ranged between 0.27 mg kg⁻¹ and 1.19 mg kg⁻¹. All the values registered for zinc and copper in carrot roots are normal values.

Table 3

Values of statistical parameters that characterize the central tendency and the variability
of the cadmium, lead, zinc, copper contents in the carrot roots

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
Cdcarrot	0.008	0.730	0.101	0.091	0.148	0.152	102.7%
Pbcarrot	0.010	0.348	0.097	0.075	0.103	0.076	73.8%
Zn _{carrot}	1.1	11.7	3.20	3.37	3.68	1.71	46.5%
Cucarrot	0.27	1.19	0.52	0.54	0.57	0.215	37.7%

According to log-log diagram (figure 1), the carrots plant accumulated high amounts of cadmium. The values of cadmium contents in carrots were correlated with total cadmium content in soil by means of a power regression equation.

For cadmium, the value of linear correlation coefficient (r = 0.761**), corresponding to linear form of the regression equation was highly significantly (p < 0.05) indicating a good correlation between the cadmium content in soil.

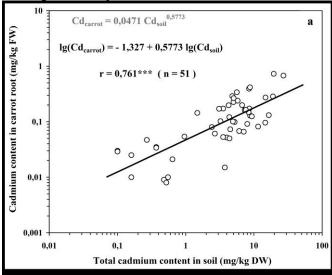


Figure 1 Log-log diagrams for power regression curves that estimate the stochastic dependency between the total cadmium contents in soil (layer 0-20 cm) and the cadmium contents in the carrot root

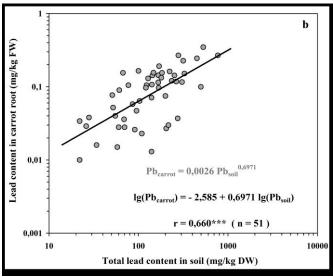


Figure 2 Log-log diagrams for power regression curves that estimate the stochastic dependency between the total lead contents in soil (layer 0-20 cm) and the lead contents in the carrot root

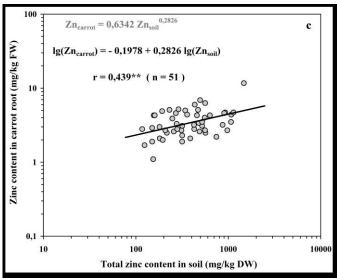


Figure 3 Log-log diagrams for power regression curves that estimate the stochastic dependency between the total zinc contents in soil (layer 0-20 cm) and the zinc contents in the carrot root

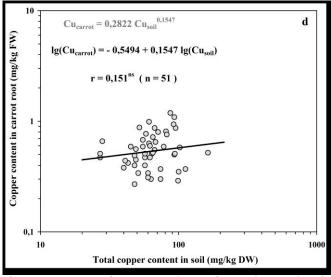


Figure 4 Log-log diagrams for power regression curves that estimate the stochastic dependency between the total copper contents in soil (layer 0-20 cm) and the copper contents in the carrot root

The value of linear correlation coefficient ($r = 0.660^{***}$), corresponding to linear form of the regression equation was highly significant indicating a very strong correlation between the lead content in carrot roots and the lead content in soil (figure 2). According to log-log diagram (figure 3), the the total zinc contents in soil (layer 0-20 cm) and the zinc contents in the carrot root have a significant correlation with a coefficient by 0.439. Figure 4 presents the correlation between the total copper contents in soil (layer 0-20 cm) and the copper contents in the carrot root. The value of linear correlation coefficient is $r = 0.151^{ns}$) and has no significant correlation.

CONCLUSIONS

The highest soil contamination cadmium, lead and zinc was found in Copsa Mica, Avente Sever and Micăsasa. The contamination of arable layer of soil is the reason for contamination of locally cultivated vegetables with cadmium and lead much more above the maximum permissible concentration. The highest correlations between soil and plant total metal content were obtained for cadmium and lead. It is noted the increased tendency of accumulation of cadmium (r=0.761) in carrot roots compared to lead (r=0.660). In the case of copper and zinc, the correlation established between the two variables is not very strong, thus for zinc r=0.439, while for copper the value was obtained r=0.151. The results can be used to estimate the health risk of consumption of vegetables cultivated.

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REFERENCES

- Alghobar M.A., Suresha S., 2017 Evaluation of metal accumulation in soil and tomatoes irrigated with sewage water from Mysore city, Karnataka, India, Journal of the Saudi Society of Agricultural Sciences, 16(1):49-59.
- Beccaloni E., Vanni F., Beccaloni M., Carere M., 2013
 Concentrations of arsenic, cadmium, lead and zinc in homegrown vegetables and fruits:
 Estimated intake by population in an

- industrialized area of Sardinia, Italy, Microchemical Journal, 107:190-195.
- Chaoua S., Boussa S., El Gharmali A., Boumezzough A., 2020 Impact of irrigation with wastewater on accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco, Journal of the Saudi Society of Agricultural Sciences, 19(8):548-550.
- Gan Y., Wang L., Yang G., Dai J., Wang R., Wang W., 2017 - Multiple factors impact the contents of heavy metals in vegetables in high natural background area of China, Chemosphere, 184:1388-1395.
- Hou S., Zheng N., Tang L., Ji X., 2018 Effects of cadmium and copper mixtures to carrot and pakchoi under greenhouse cultivation condition, Ecotoxicology and Environmental Safety, 159:172-181.
- Krejcová A., Návesník J., Jicínská J., Cernohorsky T., 2016 An elemental analysis of conventionally, organically and self-grown carrots, Food Chemistry, 192:242-249.
- Nabulo G., Oryem-Origa H., 2006 Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda, Environmental Research, 101:42–52.
- Qirui A., Xiaolan H., Zheng N., Hou S., Sun S., Wang S., Penyang L., Xiaoqian L., Xue S. 2020 Physiological and genetic effects of cadmium and copper mixtures on carrot under greenhouse cultivation, Ecotoxicology and Environmental Safety, 206, 111363.
- Sana C., Boussa S., El Gharmali A., Boumezzough A.
 2020 Impact of irrigation with wastewater on
 accumulation of heavy metals in soil and crops in
 the region of Marrakech in Morocco, Journal of
 the Saudi Society of Agricultural Sciences,
 19(8):548-550
- Sfinchez-Camazano M., Sfinchez-Martin M.J., Lorenzo L.F., 1994 - Lead and cadmium in soils and vegetables from urban gardens of Salamanca (Spain), The Science of the Total Environment, 146/147:163-168.
- Tucker R., Hardy D.H., Stokes C.E., 2003 Heavy Metals in North Carolina Soils, Occurrence and Significance, N.C. Department of Agriculture and Consumer Services, Agronomic division, Raleigh, Available from: <www.ncagr.com/agronomi/>.
- Verma P., George K. V., H. Singh V., Singh R.N., 2007
 Modeling cadmium accumulation in radish, carrot, spinach and cabbage, Applied Mathematical Modelling 31, 1652–1661.
- Vrinceanu N.O., D.M. Motelica, Costea M., Oprea B., Plopeanu G., Carabulea V., Tanase V., Preda M., 2022 - Cadmium accumulation in some leafy vegetables from provate gardens in Copsa Mica, Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XI, Online ISSN 2393-5138, ISSN-L 2285-6064 392-397.
- ***COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
- ***COMMISSION REGULATION (EU) 2021/1323 of 10
 August 2021 amending Regulation (EC) No
 1881/2006 as regards maximum levels of
 cadmium in certain foodstuffs.