TRANSLOCATION OF SOME HEAVY METALS FROM THE SOIL IN ROOT VEGETABLES IN THE PLAIN AREA OF BANAT

Antoanela COZMA, Casiana MIHUȚ, V. D. MIRCOV, A. OKROS, Florina RADU, B. COZMA, L. NIȚĂ, Laura ȘMULEAC

[1] ***Banat's University of Agricultural Sciences and Veterinary Medicine "King Michael I of Romania" Timisoara, Romania***

Corresponding author:cozma@usab-tm.ro

Abstract. *The purpose of this paper was to determine the distribution of some heavy metals from the soil in root vegetables, cultivated in a plain area of Banat: Cenad place, area considered unpolluted with such metals. The physico-chemical properties of the soils and surface waters, also the climatic factors specific to this area, allows ecological production and encourages the cultivation of vegetables with a normal content of heavy metals. The concentrations in Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn from the soil (total and mobile forms) and from some root vegetables (total concentration) were determined: carrot, parsley, celery and potatoes. The obtained results of the heavy metals determination, made by atomic absorption spectrometry in acetylene-air flame method (FAAS), shows that their distribution in soil and vegetables is non-uniform, depending on the nature of the metal and also vegetables. The analysis of heavy metals contents from carrots, parsley, celery and potatoes show that the vegetables contain significant amounts of essential mineral elements and insignificant contents of toxic or potentially toxic metals. Translocation of heavy metals from soil to the plant is conditioned by a series of factors, among which the most important are the nature of the heavy metal, the physicochemical soil properties, the mineral needs of the plant. Considering the accessible concentrations (mobile forms) of heavy metals in the soil and the average heavy metal concentrations in the vegetables (average values for the four analyzed vegetables) it can be stated that fraction of metal translocated from soil to vegetables has the following values (%) : 13.79 (Fe), 3.82 (Mn), 91.99 (Zn), 24.73 (Cu), 70.83 (Co), 62.32 (Ni), 76.32 (Cr), 2.98 (Pb) and <15 (Cd). For a healthy nutrition it is very important to know these contents. The concentrations of heavy metals in the soil samples and in the analyzed vegetables are below the toxicity limits provided by the legislation. Therefore, vegetables grown in this area do not present a risk of contamination with heavy metals.*

Keywords*: heavy metals, soil, root vegetables, FAAS*

INTRODUCTION

The presence of heavy metals in the soil is the result of two processes: genetic inheritance from rocks and parent materials on which soils were formed and evolved (geogenic origin) and anthropogenic impact caused by agricultural and industrial technologies (ALI H. ET ALL, 2019, GOGOAȘĂ ET ALL., 2009, MIHUȚ, C., 2012). Banat soils present large loads of heavy metals, but up in the moment, no areas declared polluted have been identified (GOGOAȘĂ ET ALL., 2010). This is due to the lack of major industrial pollutants, as well as the favorable storage conditions of these chemical elements in soils (high content in clay and organic matter, high total cation exchange capacity, basicity, etc.). Any most important heavy metals addition to the already existing geogenicall background, through agro-pedo-amelioration activities or other industrial activities (various anthropogenic factors) can destroy the fragile balance, thus causing the appearance of pollution with one or more heavy metals (GOGOAȘĂ, I., 2005). From soil and water, heavy metals can reach the plant-animal-human food chain, causing the most serious diseases. In the absence of important industrial pollutants, toxic, abiotic diseases of heavy metals in plant products grown in Cenad area may result from the geochemical load of the soil, from the water used for irrigation or as a result of improper agro-pedo-amelioration works (JOLLY ET ALL., 2013; SARDAR K. ET ALL., 2013).

The increase of their concentration in vegetables, over certain limits considered optimal, determines toxic effects on the consumers of such products (GUERRA F. ET ALL., 2012). In fresh vegetables, heavy metals can accumulate in significant quantities, being absorbed directly from soils rich in such elements and/or taken from the polluted atmosphere, or as a result of inadequate foliar treatments (ZHOU H. ET ALL, 2016). The accessibility of the metallic microelements for plants depends on the soil reaction, the content of organic matter, mineral colloids, soil moisture and microbiological activity (RĂDULESCU, C. ET ALL., 2013; GOGOAȘĂ ET ALL,2010).

For the prevention of the soils, water and plant products pollution with heavy metals, it is recommended to periodically evaluate the distribution of such heavy metals in the soil-water-plant system and perform specific agro-improvement works.

MATERIAL AND METHODS

The researched area is located in the low Plain of Banat, the western corner, represented by the area around Cenad village. To perform the proposed experiment, soil and vegetable samples were collected, which after conditioning were tests to analysis of heavy metals. The soil samples were cleaned of vegetable crops, dried and grounded.

The plant samples were cleaned of soil residues by washing with distilled water, then dried by buffering with filter paper. For the chemical analysis, edible part of each vegetable were taken into account. Determination of total heavy metals content from soil was performed using the method of extraction in aqua regales by atomic absorption spectrometry in air-acetylene flame (SR ISO:11047 Soil quality).

The mobile forms of the heavy metals have been extracted in the solution of EDTA - ammonium acetate performed according to a method described by Lăcătușu et all., adapted to the specific working conditions (LĂCĂTUȘU ET ALL, 1998). The dosage of heavy metals in the vegetables was carried out by atomic absorption spectrometry. The method is based on measurement by atomic absorption spectrometry, of the heavy metals concentration from the acid extract obtained from the ash of the plant sample (MIHALI, C. ET ALL, 2012).

RESULTS AND DISCUSSIONS

The experimental results for the analysis of soil samples, total and mobile forms are presented in table 1.

Table 1

Concentration of heavy metals - total and mobile forms in soil samples from the Cenad area

Specification	Heavy metal (mean values), ppm								
	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Total forms, ppm	24250	653	76.54	36.2	22.1	27.1	44.2	18.6	2.01
Mobile forms, ppm	41.7	42.2	3.87	3.64	0.48	0.69	0.38	2.35	0.20
Transfer fraction, %	0.17	6.46	5.06	10.06	2.17	2.55	0.86	12.63	1.00

From data presented in table 1 can be seen that the distribution of the analyzed heavy metals is non-uniform. There are very high values of Fe content (24250 ppm) and high values of Mn content (653 ppm) compared to other elements, determined in lower concentrations (Zn, Cr, Ni, Cu, Co and Pb). Extreme values are recorded at Fe (24250 ppm, macroelement for soil), which is present in the highest concentration and Cd (microelement with pronounced toxic character), present only at a concentration of 2.01 ppm.

The distribution of heavy metals (total forms) in the analyzed soil samples shows the following decreasing trend: Fe> Mn> Zn> Cr> Cu> Ni> Co> Pb> Cd. Comparing the experimental obtained results (table 1) with the reference values of the concentrations of heavy metals in the soil (table 2) it can be sattled that the soil of the researched area falls into the category of soils with normal heavy metal contents. However, we note higher contents of Cd (2.01 ppm), Cr (44.2 ppm), Cu (36.2ppm), Ni (27.1ppm) and Pb (18.6ppm) values characteristic of this area, which is below the step of alert limit.

Table 2

Standard appreciation values for the concentrations of heavy metals in soil

Specification	Element (mg/kg dry matter)							
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Normal values	1	15	30	20	900	20	20	100
Threshold attention	3	30	100	100	1500	75	50	300
Intervention threshold	5	50	300	200	2500	150	100	600

The concentration of heavy metals in the mobile forms generally highlights the degree of their accumulation from soil to plants (WITTER, E., 1996). The distribution of mobile heavy metal forms is shown in Table 3. In this case, also a non-uniform distribution is observed, but less pronounced than in the case of total forms. The highest and very close concentrations were determined for Fe (41.7ppm) and Mn (42.2ppm). In lower concentrations, Zn, Cu and Pb were identified, with significantly close contents, ranging between 2.35-3.87 ppm. The lowest concentrations, were determined for Ni (0.69 ppm), Co (0.48 ppm), Cr (0.38 ppm) and Cd (0.20 ppm). Comparing the concentrations of heavy metals in total and mobile forms, it can be seen that only a part of the metal content can be accessible to the plants. In case of this experiment, the total heavy metal fractions that can be accessible for vegetables plants (transfer fraction) have the following values (%): 0.17 (Fe), 6.46 (Mn), 5.06 (Zn), 10.06 (Cu), 2.17 (Co), 2.55 (Ni), (0.86) Cr, 12.73 (Pb) and 1.00 (Cd).

Comparing the experimental values of the toxic or potentially toxic heavy metals content, with the recommended values from the literature (table 3) we find in this case that there were no exceedances of the maximum allowed toxicity limits (GOGOAȘĂ I., 2005).

Table 3

Maximum accepted limits in soil for some heavy metals,
mobile forms (EDTA - CH3COONH4 at pH = 7)

Specification	Element (mg/kg dry matter)			
	Cd	Cu	Pb	Zn
Maximum accepted limit	1.00	8.00	18.00	43.00

From all present of the above, Cenad village area does not present obvious risk of contamination with toxic or potentially toxic heavy metals, for the vegetables cultivated on these lands. The experimental results obtained in the analysis of heavy metals from vegetables grown on the soils of the researched area: carrot, parsley, celery and potatoes are presented in table 4.

Table 4

Heavy metals concentration (average values) in vegetables grown on soils in the Cenad area

Vegetable	Element (mg/kg fresh edible)								
	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Carrot	5.07	1.24	2.31	0.49	0.32	0.24	0.37	0.05	<0.03
Parsley	7.82	2.36	6.21	1.41	0.42	0.72	0.45	0.04	<0.03
Celery	4.21	1.52	3.31	0.76	0.28	0.36	0.26	0.06	<0.03
Potatoes	5.75	1.57	2.41	0.95	0.32	0.38	0.08	0.14	<0.03
Average values	5.71	1.67	3.56	0.90	0.34	0.43	0.29	0.07	<0.03

From data presented in table 4 it can be seen that the distribution of heavy metals in vegetables grown in this area is uneven, the concentration levels depending not only on the nature of the heavy metal, but also on the variety of vegetable product analyzed. By analyzing the mean concentrations of metals in mobile form (accessible) and the average concentrations of metals in vegetables (table 4), it can be seen that only a part of accessible metals accumulates in vegetables, such as: 13.79% of Fe, 3.82% of Mn, 91.99% of Zn, 24.73% of Cu, 70.83% of Co, 62.32% of Ni, 76.32% of Cr, 2.98 of Pb and 15% of Cd. This proves that the translocation of heavy metals from soil to the plant is conditioned by a series of factors, among which the most important are the nature of the heavy metal, the physicochemical soil properties, the mineral needs of the plant, etc (IOVI et all, 2000; MIHALI, C. ET ALL, 2012).

It can be observed that parsley is the vegetable which the highest amounts of heavy metals is accumulate. Smaller quantities (half that of parsley), approximately equal concentrates in carrots, celery and potatoes.

Iron, an essential bioelement for the body, is the best represented of all the analyzed heavy metals, its concentration limits being between 4.21 mg / kg celery and 7.82 mg / kg in parsley. Parsley is the richest in iron (7.82 mg / kg), followed by potatoes (5.75 ppm), carrots (5.07 pp) and celery (4.21 ppm).

Manganese was determined in significantly lower concentrations than iron, its content levels having values between 1.24 ppm, in carrots and 2.36 ppm, in parsley. The rest of the analyzed vegetables contain smaller amounts of manganese but relatively close, between 1.24-1.57 mg / kg.

Zinc, an essential microelement, over certain concentrations level can become toxic (GOGOAȘĂ, I. ET ALL, 2010). 10 mg / kg - for potatoes and 15 mg / kg for the rest of the analyzed vegetables was determined in concentrations between 2.31 mg / kg (in carrots) and 6.21 mg / kg (in parsley), below the maximum limit allowed by law. Parsley is the vegetable richest in zinc (6.21 mg / kg). Lower values between 2.31 - 4.72 ppm were identified in the root of carrots (2.31 ppm), potatoes (2.41 ppm) and celery (3.31 ppm).

Copper, essential trace element, above certain concentration limits may present toxicity (3 mg/kg - for potatoes and 5 mg/kg - for the rest of the vegetables analyzed) was determined in concentrations lower than iron, manganese and zinc, its concentration being in the range of 0.49 mg / kg (in carrots) and 1.41 mg / kg (in parsley), below the maximum allowed limit.

Cobalt was determined in slightly lower concentrations than copper, but in relatively close concentrations between 0.28 and 0.42 mg / kg.

Nickel was determined in low concentrations, the values of nickel content in the analyzed vegetables not exceeding 1 ppm (0.24 - 0.72 mg / kg). Under these conditions, the highest values are reported in parsley (0.72 ppm) and in potatoes (0.38ppm) and celery (0.36ppm).

Chrome has been identified in much lower concentrations than the heavy metals presented so far, the chromium content in the analyzed vegetables being below 0.5 ppm. Chromium concentration limits are between 0.08 ppm - in potatoes and 0.45 ppm - in parsley root.

Lead is a metal with a pronounced toxic character, maximum allowed limits by law being 0.3 ppm - for potatoes and 0.5 ppm - for other vegetables. It was identified in very low concentrations, in the range of 0.04 ppm (parsley) to 0.14 mg/kg (potato), below the maximum permissible limit. **Cadmium** is the most pronounced toxic character of all the analyzed heavy metals. The maximum allowed limits of Cd in the analyzed vegetables are very small: 0.1 mg/kg - in potatoes and 0.2 mg / kg for the rest of the vegetables. In all analyzed vegetables it was identified in very low concentrations (at the detection limit of the spectrometer), between 0.02 - 0.11 ppm, under the maximum admitted limits by law.

CONCLUSIONS

The heavy metals concentrations - total forms determined in the soil of the researched area is uneven depending on the nature of the analyzed metal and has values between 24250 ppm (Fe) - 2.01 ppm Cd. The distribution of heavy metals (total forms) in the analyzed soil samples shows the following decreasing trend: Fe (24250 ppm) > Mn (653 ppm)> Zn (76.54 ppm) > Cr (44.2ppm) > Cu (36.2ppm) > Ni (27.1 ppm) > Co (22.1 ppm)> Pb (18.6 ppm) > Cd (2.01 ppm).

The heavy metal concentration - mobile forms in the researched soil is much lower than the total concentration and shows the following decreasing trend: Mn (42.2 ppm) > Fe (41.7pppm) > Zn (3.87 ppm) > Cu (3.64 ppm) > Pb (2.35 ppm) > Ni (0.69 ppm) > Co (0.48 ppm) > Cr (0.38 ppm) > Cd (0.20).

Comparing the heavy metals concentrations - total and mobile forms, it can be observed that only a part of the content of the total concentration of a metal can be accessible to plants. In this experiment, the fractions from total metal concentrations, potentially accessible for vegetables, show the following values (%): 0.17 (Fe), 6.46 (Mn), 5.06 (Zn), 10.06 (Cu), 2.17 (Co), 2.55 (Ni), (0.86) Cr, 12.73 (Pb) and 1.00) Cd.

The heavy metal concentrations - total and mobile forms in the soil of the researched area do not present a risk of contamination with heavy metals, which is also confirmed by the heavy metal concentrations in the root vegetables grown on these soils.

The results obtained from the analysis of heavy metals from carrots, parsley, celery and potatoes show that these vegetables contain significant amounts of essential mineral elements and insignificant contents of toxic or potentially toxic metals.

Taking into account the accessible concentrations (mobile forms) of heavy metals in the soil and the average heavy metal concentrations in the vegetables (average values for the four analyzed vegetables) it can be stated that fraction of metal translocated from soil to vegetables has the following values (%): 13.79 (Fe), 3.82 (Mn), 91.99 (Zn), 24.73 (Cu), 70.83 (Co), 62.32 (Ni), 76.32 (Cr), 2 , 98 (Pb) and <15 (Cd).

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