# RESEARCH ON THE ACCUMULATION AND TRANSFER OF HEAVY METALS FROM THE SOIL TO BERRIES (BLUEBERRIES - *Vaccinium myrtillus L.* and RASPBERRIES - *Rubus idaeus*) / *CERCETĂRI PRIVIND ACUMULAREA ŞI TRANSFERUL METALELOR GRELE DIN SOL ÎN FRUCTE DE PĂDURE (AFINE - Vaccinium myrtillus L. ȘI ZMEURĂ - Rubus idaeus)*

**Mihaela NIȚU, Augustina PRUTEANU*), Iuliana GĂGEANU**
National Institute of Research – Development for Machines and Installations Designed
for Agriculture and Food Industry – INMA Bucharest / Romania
*E-mail: pruteanu_augustina@yahoo.com*
*DOI: https://doi.org/10.35633/inmateh-68-71*

***Keywords:*** *heavy metals, berries, contamination, pollution*

## ABSTRACT

*The current study has investigated the accumulation and transfer coefficient for three heavy metals (Cu, Pb, Zn) found in the contaminated soil with three concentrations (c1=1.5%, c2=3.0%, c3=4.5%, c4=6.0%), obtained by mixing the three metals, in blueberry and raspberry fruits. The pots in which the shrubs were planted were loaded with fertile soil which was mixed and homogenized in turn with each of the three solutions of different concentrations. The highest accumulation in blueberry fruits was recorded for zinc, then copper and the lowest for lead, while for raspberries the highest results was recorded for zinc, then lead and the lowest for copper. The findings are valid for all four concentrations used. The transfer coefficient decreases as the concentration of heavy metals increases, thus for high heavy metal concentrations, the values of the transfer coefficient are very low, and for small heavy metal concentrations in the soil, the values for the transfer coefficient are higher. From the assessment of accumulation and transfer of heavy metals to berries (blueberries and raspberry) grown in the contaminated soil, it was concluded that all concentrations of the copper, lead and zinc mix have shown a low risk for human consumption.*

## REZUMAT

*În acest studiu, s-a investigat acumularea si coeficientul de transfer a trei metale grele (Cu, Pb, Zn) din solul contaminat cu patru concentrații ($c_1$=1.5%, $c_2$=3.0%, $c_3$=4.5%, $c_4$=6.0%) obținute prin amestec din cele trei metale, in fructul de afin si zmeur. Ghivecele în care au fost plantați arbuștii au fost încărcate cu pământ fertil care a fost amestecat și omogenizat pe rând cu fiecare dintre cele trei soluții de concentrații diferite. Cea mai mare acumulare in fructele de afin a fost observată pentru zinc, apoi cupru si cea mai mica pentru plumb, iar in fructele de zmeur pentru zinc, cupru si cea mai mica pentru plumb. Constatările sunt valabile pentru toate cele patru concentrații folosite. Coeficientul de transfer scade pe măsură ce concentrația de metale crește, astfel încât la concentrații mari de metale valorile coeficientului de transfer sunt foarte mici, iar la concentrații mici de metale în sol valorile coeficientului de transfer sunt mai mari. Evaluarea acumulării ți transferului metalelor în fructul fructelor crescute în sol contaminat a concluzionat că toate concentrațiile în amestec de cupru, plumb și zinc au prezentat un risc scăzut pentru consumul uman.*

## INTRODUCTION

Environmental pollution, implicitly that of agricultural soils, with heavy metals is a current topic that concerns humanity. Toxic metals in the soil come from different sources, such as: household waste landfills, agricultural sources, industrial emissions, urban emissions and bedrock. The accumulation of heavy metals in the soil causes the pollution of agricultural soils, with consequences on the quality of fruits and vegetables as well as on human health *(Jolly et al., 2013; Huang et al., 2014, Pruteanu et al., 2019)*.

Fruits and vegetables are often consumed because they are an important source of food, being rich in bioactive compounds (tannins, anthocyanins, antioxidants), vitamins, minerals, proteins, carbohydrates and fibres necessary for human health *(Huang et al., 2014)*. They accumulate heavy metals in both edible and non-edible parts *(Cherfi et al., 2014)*. Heavy metals are necessary for the efficient functioning of biological systems, as long as their concentration in fruits and vegetables is balanced, in order not to produce a series of metabolic disorders *(Fawad et al., 2017)*. In this sense, heavy metal concentrations and nutritional intake from fruits and vegetables are important for maintaining human health *(Balčiauskas et al., 2022)*.

The soil-to-plant transfer factor is an important component due to human exposure to metals through the food chain. The accumulation of metals from soil, water or air in the vegetative organs of plants depends on the properties of metals and the exposure time of metals, absorption rates in different plant tissues and transfer between tissues, plant growth and metabolism parameters, metal partition coefficients between the compartments of the soil-plant system. The transfer factor differs depending on the type of metal, the plant species, but also on the type of soil *(Jolly et al., 2013, Cardei et al., 2021)*.

In the paper written by *Qihang et al., (2021),* the authors studied the geochemical characteristics of heavy metals in blueberries and soil for the Majiang area of Guizhou, China. As methods they used field survey, sampling and indoor analysis, and as benchmarks they relied on national standards for soil pollution risk control on agricultural land. The results showed that the content of heavy metals exceeds the standards only in the lower layer of the soil, without substantially affecting blueberry growth. In fruits, the content of heavy metals did not exceed the concentrations in the standard, which proved that the fruit was safe for consumption.

Also, in the research of *Rusinek et al., (2008)*, the content of heavy metals (Pb, Cd, Cu, Zn, Fe, Mn) was analysed in areas not exposed to pollution (Skierbieszów Landscape Park) and in polluted areas (Rejowiec Cement Factory) for blueberries, raspberries and wild strawberries harvested in the Lublin region. The results showed that, among the berries studied, blueberry had the lowest content of Pb, Zn, Fe, Mn, wild strawberries had a high content of Pb, Zn and Mn, and the content of cadmium was high for all the berries analysed.

*Wieczorek et al., (2010)*, analysed the concentrations of heavy metals (Pb and Cd) in berries (blackberry, raspberry, blueberry, wild strawberry) and wild-harvested hazelnuts as well as in fruit (blackberry, raspberries, blueberries) and hazelnuts harvested from plants grown in orchards in North Eastern Poland. In addition, Pb, Cd concentrations were determined in surface soil samples from the sites where the fruits were collected. It was found that the highest acceptable concentrations based on Polish standards for Pb and Cd were not exceeded in the berries. In wild berries, Pb was undetectable, and in those from orchards, Pb had values of 290 µg/kg. The concentration of Cd varied between 6 and 49 µg/kg wet weight for wild fruits and values up to 72 µg/kg wet weight for orchard fruits. For the soil samples, Pb and Cd had values between 3.2 - 14.9 mg/kg. *Zeiner et al., (2018),* analysed the content of Al, Cd, Cr, Ni and Pb in cranberries, blueberries and rosehips harvested from an unpolluted area in Croatia. The results showed that Cd and Cr were not detected in the samples, and Ni concentrations were mainly lower than 25 mg/kg, in a range comparable to the data from the specialized literature. The consumption of these berries in terms of Cd, Cr and Ni does not present any danger to health, while rosehips contain Pb and Al above the limit allowed in the fruits.

In another paper, the concentrations of 13 elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) were determined for several samples of cultivated and wild blueberry fruits. The authors analysed the total metal content after mineralization using plasma optical emission spectrometry. The results showed that high concentrations of Ca, Na, Mg, Mn and Zn were found in wild blueberries. Also, the concentrations of Cu, Cr, Fe and Ni were found to the same extent, both in wild and cultivated plants. Very high concentrations of Fe and Cd were identified in cultivated blueberries. The efficiency of metal extraction varied depending on their form (fresh or dried) for both blueberry types - wild or cultivated *(Dróżdż et al., 2018).*

In order to determine the transfer of heavy metals from soil to fruits, *Roba et al., (2016)* studied the concentration of four heavy metals (Zn, Cu, Pb, Cd) in raspberries, gooseberries and black currants grown in the gardens of the Ferneziu district residents from Baia Mare mining area (Romania). Due to the different absorption capacity of heavy metals, the concentrations varied for the analysed fruits as follows: Zn > Cu > Pb > Cd. *Lere, B. K. et al., (2021),* focused on the levels of heavy metals in water, soil, fruits and vegetables from three farms located in Nigeria. Water, soil, fruit and vegetable samples were randomly collected, processed and analysed for heavy metals. The concentration of heavy metals in soil was found to be the highest for Fe (57.30–63.51) mg/kg and the lowest was observed for Cu (0.45–1.45) mg/kg. High levels of Pb (0.02–0.03) mg/l, Cd (0.07–0.1) mg/l and Fe (3.23–3.42) mg/l were determined in the irrigation water. In fruits and vegetables, average metal concentration showed significant variation, with Fe having the highest concentration (7.82 mg/kg) in most farm samples. The health risk assessment of heavy metals in fruit and vegetable samples indicated that all metals were within the hazard limit of less than 1, except for Cd.

In their work, *Cui, Y.-J. et al., (2004)* measured the contamination levels of soils and vegetables with cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu), as well as the factors of transfer (TF) from soil to vegetable plants but also the risk of these heavy metals for health. The results of the research showed that both the soils and the vegetables in two villages in China, one located at 1500 m and another 500 m away from a smeltery were heavily contaminated, compared to another village located 50 km away from the smeltery. The intake of lead and cadmium from vegetables represented a high risk for the health of local residents (1.44 - 13.5 for Pb) and (3.87 - 7.42 for Cd).

The paper presents the transfer coefficient and the accumulation from the soil in berries (blueberries and raspberries) for the mixture obtained from three heavy metals (Cu, Pb, Zn), at different concentrations (c1 = 1.5%, c2 = 3.0%, c3 = 4.5%, c4 = 6.0%).

## MATERIALS AND METHODS

Raspberry (*Rubus idaeus*) and blueberry (*Vaccinium myrtillus L.*) fruits were chosen for this study, because they are rich in antioxidants. Raspberries belong to the *Rosaceae* family and are a bushy, perennial shrub with creeping shoots and straight stems. The fruit, called raspberry, is red, has a sour taste and a pleasant smell. Raspberries can be consumed fresh or industrially processed. The bioactive compound that can be extracted from raspberries is xylitol, beneficial for the prevention of dental caries *(Ardelean et al., 2008)*. Blueberries belong to the *Ericaceae* family and are a bushy, branchy subshrub with a long-branched stem. The fruit called blueberry is a blue, round berry with a pleasant sweet and sour taste *(Ardelean et al., 2008)*.

Blueberry and raspberry cuttings were planted in pots with soil contaminated using mixtures of heavy metals (copper, zinc and lead) in different concentrations, in order to identify the concentrations of heavy metals absorbed during plant growth.

Ten kg of soil was homogenized with 500 ml of heavy metal mixture (Cu, Zn, Pb) for each concentration of 1.5%, 3.0%, 4.5% and 6.0%. The solutions with the following concentrations 1.5, 3.0, 4.5 and 6.0 % were individually prepared in the laboratory. Copper sulphate, lead acetate and zinc sulphate were used as reagents, and distilled water as solvent. To obtain the mixtures of solutions with Cu, Pb, Zn for each of the concentrations of 1.5, 3.0, 4.5 and 6.0% that were individually prepared, equal parts were taken from each solution, element and concentration, and mixed until reaching homogeneity. Heavy metal loading was performed only when the shrubs were planted, without additional loading until harvest.

The control sample was obtained by planting berry shrubs using uncontaminated soil. The soil moisture was maintained at constant levels during the experiments by watering the berry shrubs.

The physico-chemical properties of the soil used in the experiments were: moisture 15%, pH 5.8; phosphorus 0.4%, potassium 0.8%, nitrogen 1.8%.

The experiments were carried out in a specially arranged and controlled space, between March and July 2020. The fruits subjected to the analysis were harvested when they were fully ripe. Images during the experiments are presented in Figure. 1.

**a**

**b**

**Fig. 1 - Aspects during the research on blueberries (a) and raspberries (b)**

The determination of Cu, Pb, Zn from the contaminated soil and from the studied berries was carried out by spectrophotometry (flame atomic absorption).

The transfer coefficient assesses the degree of bioavailability of metals from soil to plants and is a valid function of soil and plant properties. The coefficient was calculated as a ratio between the concentration of a metal (Cu, Pb, Zn) in the fruit and the concentration of the metal in the soil *(Bassey et al., 2014)*.

Based on dry weight, metal concentration in soil and plants was calculated. Thus, the transfer factor (tf) was calculated according to the formula below:

$$tf = \frac{C_{plant}}{C_{soil}} \tag{1}$$

where: $C_{plant}$ and $C_{soil}$ represent metal concentration (with Cu, Pb, Zn) in plants and soil *(Jolly et al., 2013)*.

Values of the transfer factor lower than 0.1 show that the plant does not accumulate metals in its tissues; however, values of the transfer factor above 0.2 show that the plant accumulates metals, requiring careful monitoring of the environment *(Khan et al., 2009; Sponza et al., 2002)*.

## RESULTS

Figure 2 shows the results regarding the content of heavy metals (Cu, Pb, Zn) in soil samples contaminated with mixed solutions of different concentrations (1.5%, 3.0%, 4.5%, 6.0%), as well as in uncontaminated soil.

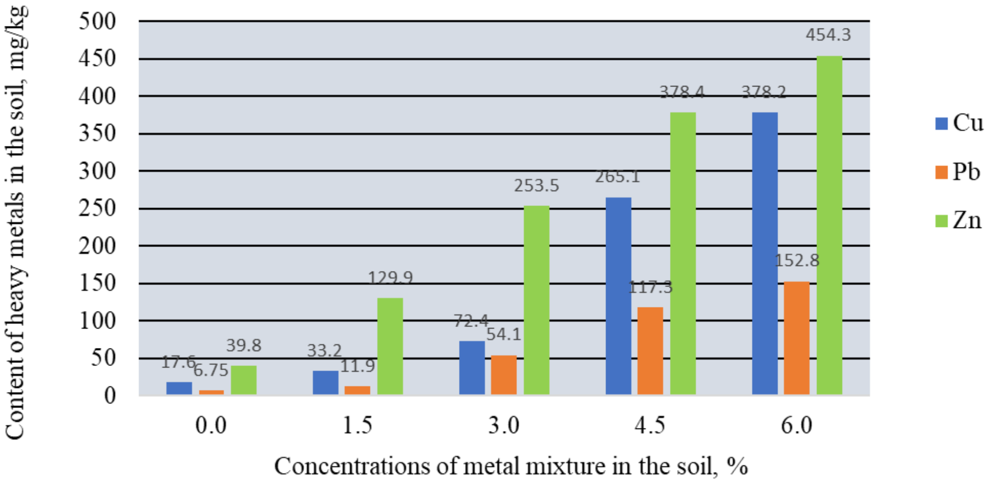


**Fig. 2 - The content of heavy metals in the soil**

It can be observed that, for all three heavy metals, their concentration in the soil increases progressively, depending on the increase in the concentration of the solutions, the highest concentrations being found for Zn.

Figures 3 and 4 show the results regarding the content of heavy metals (Cu, Pb, Zn) found in the raspberry and blueberry samples for different concentrations (1.5%, 3.0%, 4.5%, 6.0%), as well as in the control sample.

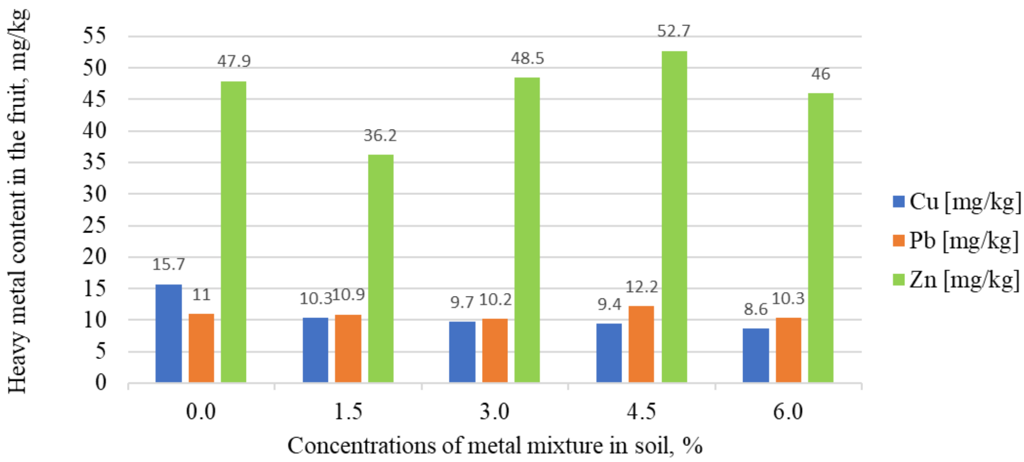


**Fig. 3 - The content of heavy metals in raspberry**

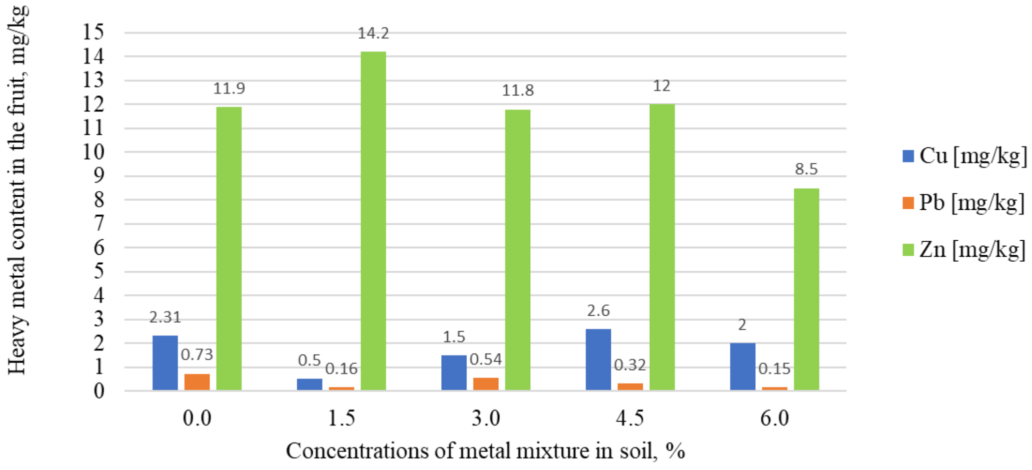


**Fig. 4 - The content of heavy metals in blueberries**

Analysing figures 3 and 4 for the different concentrations of metals in the soil and their transfer in the studied fruits, it was found that:

a. for raspberries:

- as the concentration of Cu in the soil increases, it decreases in the fruit;
- for Pb, at low concentrations in the soil, the accumulation in the fruit increases progressively, and at the maximum concentration in the soil (6%), it is lower;
- Zn has the highest concentrations in the fruit. For concentrations of 1.5% (36.2 mg/kg), 3% (48.5 mg/kg) and 4.5% (52.7 mg/kg), the Zn content increases gradually, and for the concentration of 6% (46 mg/kg) in the soil, it decreases in the fruit;
- in the control sample, with uncontaminated soil, all three studied metals are present in the fruit.

b. for blueberries:

- in the case of Cu, the content is progressively increasing in fruits for the first three concentrations, while at the maximum concentration of 6% in the soil, the Cu content decreases in the fruit;
- in the case of Pb, values are low, with a value of 0.54 mg/kg for a concentration of 3%;
- Zn has the highest concentrations in the fruit. The content in fruits varies as follows: a concentration of 1.5% translated into 14.2 mg/kg, 3% to 11.8 mg / kg, 4.5% to 12 mg/kg and the concentration of 6% to 8.5 mg/kg;
- for the control sample, all 3 metals were detected in blueberries and raspberries, and the Zn concentration has higher values that could endanger health.

Also, for all the metals studied, at a concentration of 3%, values close to those of the control sample were found.

The transfer factor (tf) values of heavy metals from soil to fruit are graphically shown in Figures 5 and 6.

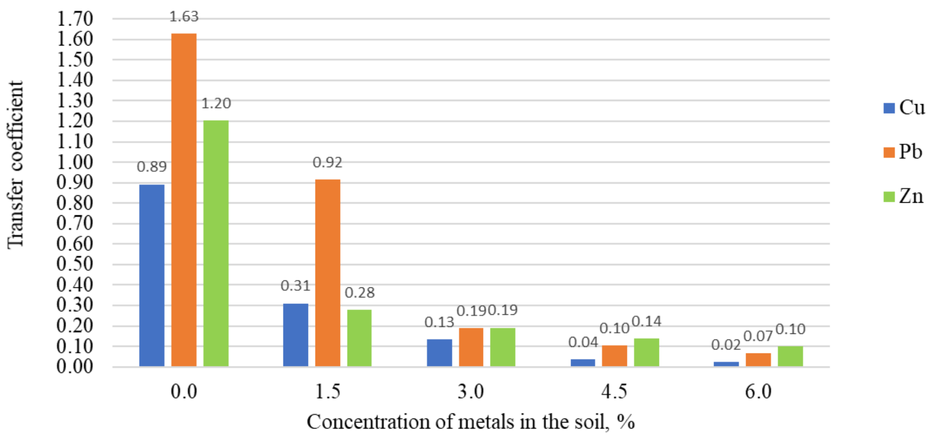


**Fig. 5 - The transfer coefficient of heavy metals in raspberries**

Analysing Figure 5, the results of the raspberry transfer factor show that:

- for the control sample it has values close to 1 in the case of copper and zinc and values greater than 1.5 for lead;

- for the concentration of the metal mixture of 1.5% in the soil, values of the transfer factor of 0.3 were found for copper and zinc, the transfer coefficient for lead tending towards 1 (0.92);

- for the other concentrations of heavy metal mixture in the soil (3%, 4.5%, 6%), the values of the transfer factor are very low for all metals, tending to 0 (tf = 0.02 for Cu at the concentration of 6% in the soil).

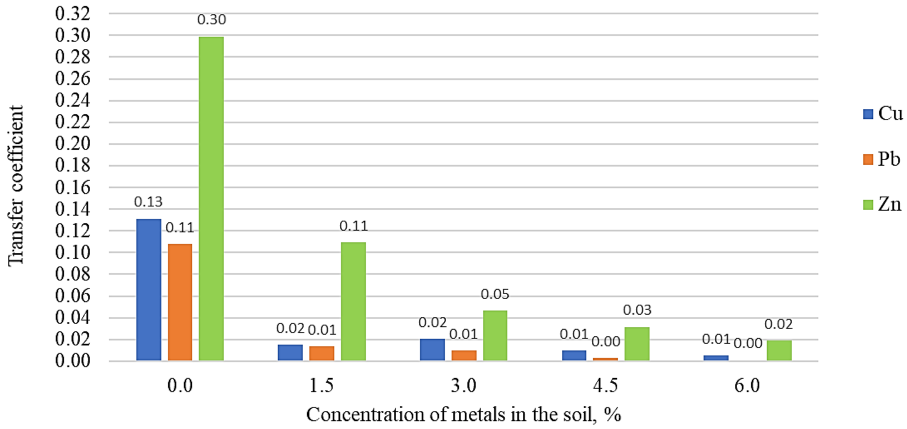


**Fig. 6 - The transfer coefficient of heavy metals in blueberries**

Analysing Figure 6, the results of the transfer coefficient in blueberries, show the following:

- for the control sample the values of the transfer factor are below 0.3 for all three metals;

- for all other concentrations of the mixture of heavy metals in the soil, the values of the transfer factor are very small (for concentrations of 4.5% and 6%, for Pb, the tf value = 0).

Therefore, it can be considered that for the berries studied, the higher the initial concentration of heavy metals in the soil, the weaker the bioaccumulation.

## CONCLUSIONS

For the berries studied, an increase tendency in the amount of heavy metal accumulated in the fruit can be observed, along with the increase in the concentration of the heavy metal mixture in the soil.

The accumulation of heavy metals in berries has revealed that the order of accumulation of metals in fruits is Zn>Pb>Cu for raspberry and Zn>Cu>Pb for blueberries. The highest accumulation among the studied metals is that of zinc for both berries. Lead is below the limit of the control sample, for both berries, this meaning that with the high concentrations the absorption capacity of the heavy metal in the soil decreases, which could lead to explanations related to the possibility that the plants develop protection mechanisms.

Considering the two berries grown applying various concentrations of metal mixture in the soil, a decrease tendency in the transfer coefficient of each heavy metal from the soil to the plant is noticed as the concentration of the mixture increases from 1.5% to 6.0%. Therefore, the bioaccumulation capacity of metals in fruits is small, but the accumulation of metals may have occurred at the level of the other vegetative parts of the shrubs (root, stem, branches and leaves).

Taking into account that forest fruits are rich in antioxidants and are highly appreciated by consumers, the bioaccumulation of heavy metals in fruits is an important aspect that was investigated in this work to evaluate the impact of soil contamination on fruits and can be further explored to develop mathematical models and finding some patterns for the accumulation of heavy metals in the soil and in plants/fruits.

## ACKNOWLEDGEMENT

The work has been funded by the Sectoral Programme MADR – ADER 2019-2022, ADER 25.4.1. Technology for obtaining biofertilisers and/or bioinsecticides for ecological production systems, Ctr. no. ADER 25.4.1/24.09.2020 and MRID, Programme 1 - Development of the national research-development system, 1.2 - Institutional performance - Projects for financing excellence in RDI, Ctr. no. 1PFE/30.12.2021.

## REFERENCES

[1] Ardelean, A., Mohan, Gh. (2008). *Medicinal Flora of Romania*. All Publishing, Bucharest.

[2] Balčiauskas, L., Ežerinskis, Ž., Stirkė, V., Balčiauskienė, L., Garbaras, A., Remeikis, V. (2022). The elemental composition of small mammals in a commercial orchard–meadow system. *Chemosphere, Volume 296*, 134 – 148. https://doi.org/10.1016/j.chemosphere.2022.134048

[3] Bassey, F.I., Iwegbue, C.M.A., Obi-Iyeke, G.E., Tesi, G.O., Rotu, A.R., Gobe, O.A., Tsafe, A.I. (2014). Heavy metals in soils and tomatoes grown in urban fringe environment in Asaba, Delta State, Nigeria. *Nigerian Journal of Basic and Applied Science, 22*, 27-31. https://doi.org/10.4314/njbas.v22i1.5

[4] Cârdei P., Tudora C., Vlăduț V., Pruteanu A., Găgeanu I., Cujbescu D., Bordean D*, Ungureanu N*, Cristea O. (2021). Mathematical model to simulate the transfer of heavy metals from soil to plant, *Sustainability 2021, vol. 13(11), 6157*, DOI: 10.3390/su13116157

[5] Cherfi, A., Abdoun, S., Gaci, O. (2014). Food survey: levels and potential health risks of chromium, lead, zinc and copper content in fruits and vegetables consumed in Algeria. *Food Chem Toxicol,* 70, 48–53. https://doi.org/10.1016/j.fct.2014.04.044

[6] Cui, Y.-J., Zhu, Y.-G., Zhai, R.-H., Chen, D.-Y., Huang, Y.-Z., Qiu, Y., Liang, J.-Z. (2004). Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Environment International* Volume 30, Issue 6, 785-791. https://doi.org/10.1016/j.envint.2004.01.003

[7] Dróżdż, P., Šėžienė, V., Pyrzynska, K. (2018). Mineral Composition of Wild and Cultivated Blueberries. *Biological Trace Element Research*, 173–177. https://doi.org/10.1007/s12011-017-1033-z

[8] Fawad, A., Hidayat, U., Ikhtiar, K. (2017). Heavy metals accumulation in vegetables irrigated with industrial influents and possible impact of such vegetables on human health. *Sarhad Journal of Agriculture, Volume 33, Issue 3*, 489-502. http://dx.doi.org/10.17582/journal.sja/2017/33.3.489.500

[9] Huang, Z., Pan, X.-D., Wu, P.-G., Han, J.-L., Chen, Q. (2014). Heavy metals in vegetables and the health risk to population in Zhejiang, China. *Food Control,* 36, 248-252. https://doi.org/10.1016/j.foodcont.2013.08.036

[10] Jolly, Y. N., Islam, A., Akbar S. (2013). Transfer of metals from soil to vegetables and possible health risk assessment. *Springer Plus,* 2, 385–391. https://doi.org/10.1186/2193-1801-2-385

[11] Khan, S., Farooq, R., Shahbaz, S., Khan, M.A., Sadique, M. (2009). Health risk assessment of heavy metals for population via consumption of vegetables. *World Applied Sciences Journal,* 6(12), 1602-1606.

[12] Lere, B. K., Basira, I., Abdulkadir, S., Tahir, S. M., Ari, H. A., Ugya, Y. A. (2021). Health risk assessment of heavy metals in irrigated fruits and vegetables cultivated in selected farms around Kaduna metropolis, Nigeria. *Egyptian Journal of Basic and Applied Sciences,* Vol.8, Issue 1, 317-329. https://doi.org/10.1080/2314808X.2021.1992956

[13] Nedelescu, M., Baconi, D., Neagoe, A., Iordache, V., Constantinescu, P., Ciobanu, A. M., Vardavas, I. A., Stan, M., Vinceti, M., Tsatsakis, M. A. (2017). Environmental metal contamination and health impact assessment in two industrial regions of Romania. *Science of the Total Environment,* 580, 984–995.

[14] Pruteanu A., Bordean D-M., Vlăduţ V. (2019). Accumulation of heavy metals in vegetables grown on contaminated soils, Proceedings of the 47th International Symposium on Agricultural Engineering "Actual Tasks on Agricultural Engineering", pp. 135-146, 2019, ISSN 1333-2651, Opatija - Croaţia

[15] Roba, C., Roşu, C., Piştea, I., Ozunu, Al., Baciu, C. (2016). Heavy metal content in vegetables and fruits cultivated in Baia Mare mining area (Romania) and health risk assessment. *Environ Sci Pollut,* 23, 6062–6073. https://doi.org/10.1007/s11356-015-4799-6

[16] Rusinek, E., Sembratowicz, I., Ognik, K. (2008). Content of selected metals in forest fruits depending on the harvest site. *Roczniki Panstwowego Zakladu Higieny,* 59(2), 155-161.

[17] Qihang, L. Chaofeng, L., Heng, W., Xiao W., Yuansheng, L., Ruidong, Y., Xuefeng W (2021). Geochemical Characteristics of Heavy Metals in Soil and Blueberries of the Core Majiang Blueberry Production Area. *Bulletin of Environmental Contamination and Toxicology*, 57–64. https://doi.org/10.1007/s00128-020-03007-4

[18] Sponza, D., Karaoglu, N. (2002). Environmental geochemistry and pollution studies of Aliaga metal industry district. *Environment International,* 27, 541-553. https://doi.org/10.1016/S0160-4120(01)00108-8

[19] Wieczorek, J., Pietrzak, M., Osowski, A., Wieczorek, Z. (2010). Determination of lead, cadmium, and persistent organic pollutants in wild and orchard-farm-grown fruit in northeastern Poland. *Journal of Toxicology and Environmental Health, Part A,* Vol.73, 1236-1243. https://doi.org/10.1080/15287394.2010.492009

[20] Zeiner, M., Cindri´ I. J. (2018). Harmful Elements (Al, Cd, Cr, Ni, and Pb) in Wild Berries and Fruits Collected in Croatia. *Toxics,* 6(2), 318-328. https://doi.org/10.3390/toxics6020031