ACCUMULATION OF HEAVY METALS IN *VICIA SPP*. SPECIES HARVESTED FROM THE PERMANENT MEADOWS IN THE COPȘA MICĂ AREA, SIBIU COUNTY

Vera CARABULEA[1], Dumitru-Marian MOTELICĂ[1], Nicoleta Olimpia VRÎNCEANU[1], Bogdan Ștefan OPREA[1], Georgiana PLOPEANU[1], Mihaela COSTEA[1], Florența JAFRI[1]

National Research and Development Institute for Soil Science, Agrochemistry and Environment, 61 Marasti Blvd, District 1, 011464, Bucharest, Romania, E-mail: carabulea_vera@yahoo.com

Coressponding author: oprea.bogdan95@yahoo.com

Abstract

Copșa Mică is one of the most famous historically polluted areas in the country. This paper shows the accumulation of heavy metals (Cd, Pb, Zn and Cu) from soil in vetch plants (Vicia spp.) from permanent meadows in Copșa Mică area, Sibiu County. The estimation of the results is based on a set of data (n=14) collected from permanent grasslands located at different distances from the pollution source. The value of the linear correlation coefficient between the total cadmium content and the mobile cadmium content in the soil and in the plant is statistically significantly different from zero indicating a close correlation between the variables. In addition, at total lead content, simple power regressions were found to be the best for estimating the accumulation of these elements in pea plants. And for total zinc and copper, the value of the linear correlation coefficient is not significantly different from zero, indicating that the estimation of zinc and copper accumulation cannot be described by simple power regressions. The results of this study are important for estimating the accumulation of heavy metals in the vegetation of permanent grasslands, which are consumed by livestock in the area.

Key words**: **heavy metals; pollution, soil, Vicia spp.

INTRODUCTION

Soil pollution with heavy metals is a global problem that should attract the attention of scientists in the field, because it is the substrate that provides food for humans and animals, and can influence the quality of food, which has a direct impact on human health (Cui et al., 2004, Alle, 2019; Borozan et al., 2021, Tkachuk, 2020).

Tkachuk (2020) presents the notion of heavy metal is, because this group includes copper, zinc and other elements that have a positive biological effect, but when they accumulate beyond the limit, they can be toxic and block biochemical processes in living organisms.

Cadmium is a non-essential element for plants and is one of the most toxic pollutants of human activities (Ahmad et al., 2015; Rizwan et al., 2016; Hernandez et al., 2015 cited by Zhang et al., 2020). Excess Cd in soil inhibits plant growth and development, reduces crop yield and quality, and is deposited in edible parts (Ahmad et al., 2015).

Copșa Mică in Sibiu County is one of the industrial areas, the most known with a high level of pollution. The main sources of pollution in the area under study are due to the industrial activities of two economic agents: S.C. SOMETRA S.A. and S.C. CARBOSIN S.A. (Vrîncenu, N. et al., 2009; Vlad, I. et al., 2023). Studies have shown that there is still a high level of metals in the soil, despite the fact that the company ceased its activity. (Hoaghia M. et al., 2022). In Romania, the Copsa Mica industrial region is considered one of the most

polluted areas in the country, due to the intense non-metallurgical activities carried out in the past. The genus *Vicia* L., from the *Leguminosae* family, nitrogen-fixing (Sierra et al, 2008), annual, climbing, rarely erect plants. Leaves pinnate, with terminal rachis usually in a whorl. Leaflets numerous, stipules entire or occasionally toothed. Flowers solitary, axillary, twin or in racemes. Calyx with 5 lobes or teeth, erect or curved. Pods oblong to linear, compressed, glabrous or hairy. The seeds are usually globose, compressed or angular (Flora of Romania, Vol. V). The genus *Vicia* includes over 200 species known worldwide (Ibañez et al, 2020). Most of it is found in the mediterranean and the temperate zone in the northern hemisphere (Rahmati et al., 2012).

MATERIALS AND METHODS

The present paper presents a study carried out in 2023, regarding the accumulation of heavy metals (Cd, Cu, Pb and Zn) in vetch plants (*Vicia spp.*) from permanent meadows in correlation with the polluted soil in the Copșa Mică area. The historically recognized area, with a high degree of pollution due to the two SC SOMETRA SA and CARBOSIM industrial platforms.

The estimation of the accumulation of heavy metals in vetch plants (*Vicia spp.*) was carried out on the basis of a set of soil and plant samples, from the vegetation of permanent meadows within the communes: Copșa Mică, Axente Sever, Târnava, Micăsasa and Valea Viilor.

The collection points were positioned with the help of GPS, establishing the coordinates, altitude and distance from the basket for each point. Soil samples were collected using the agrochemical probe at the depth of 0–20 cm (by homogenizing 13 subsamples), then they were dried at room temperature, mortared and passed through a 0.2 mm sieve. From these samples, the content of heavy metals (Cd, Pb, Zn and Cu) was determined by atomic absorption spectrometry, after extraction by the aqua regia - microwave digestion method.

Plant samples were identified and harvested from permanent grasslands, then dried, chopped and ground. Plant samples were treated with nitric acid in a microwave digestion system. Total heavy metal content was determined using atomic absorption spectrometry (Flame GBC 932AA or graphite furnace GBC SavanatAAZ).

Microsoft Excel 2010 was used for statistical data processing.

RESULTS AND DISCUSSIONS

Table 1 shows the total contents of heavy metals, at the depth of 0–20 cm, from the permanent meadows in the Copșa Mică area.

The values of the total cadmium content in the soil, at the depth of 0–20 cm, vary between 2.50 $mg \cdot kg^{-1}$ (minimum value) and 17.74 $mg \cdot kg^{-1}$ (maximum value), with a standard deviation of 4.92 $mg \cdot kg^{-1}$ and a coefficient of variation of 68.7%. Total soil lead content ranges from 86 $mg \cdot kg^{-1}$ to 692 $mg \cdot kg^{-1}$ with a standard deviation of 186.7 $mg \cdot kg^{-1}$ and a coefficient of variation of 78.7%. Zinc has values between 168 $mg \cdot kg^{-1}$ and 993 $mg \cdot kg^{-1}$, with a standard deviation of 253.4 mg·kg-1 and a coefficient of variation of 58.3%, and copper between 22 $mg \cdot kg^{-1}$ and 161 $mg \cdot kg^{-1}$, with a standard deviation of 27.2 $mg \cdot kg^{-1}$ and coefficient of variation of 68.5%.

According to Order 756/1997 on soil pollution, the arithmetic mean values of the cadmium content (7.16 $mg \cdot kg^{-1}$), at the depth of 0–20 cm, exceed the alert threshold for less sensitive uses, and as regards the content of lead (237.1 $mg \cdot kg^{-1}$) and zinc (632.8 $mg \cdot kg^{-1}$) exceed the intervention threshold for sensitive uses. The average values of the copper content

(71.1 mg·kg^{-1}) fall within the alert threshold for sensitive use types.

Table 2 shows the values of the statistical parameters that characterize the variability of the content of heavy metals in the soil – the forms extractable with DTPA, where are the minimum and maximum values, as well as the geometric and arithmetic mean concentrations. The mobile cadmium content varies between 1.96 mg·kg^{-1} (minimum value) and 15.44 mg·kg^{-1} (maximum value), with an arithmetic mean of 5.16 mg·kg^{-1} and a coefficient of variation of 77.3 %. Lead ranges from 23 mg·kg^{-1} to 301 mg·kg^{-1} with an arithmetic mean of 92.6 mg·kg^{-1}, standard deviation of 86.4 mg·kg^{-1} and coefficient of variation of 93.3 %. The zinc content values range from 24 mg·kg^{-1} to 340 mg·kg^{-1} with an average of 112.4 mg·kg^{-1}, with a standard deviation of 91.3 mg·kg^{-1} and a coefficient of variation of 81.2 %, and copper has values between 2.46 mg·kg^{-1} and 23.41 mg·kg^{-1} with an average of 6.93 mg·kg^{-1} and the coefficient of variation of 66.9 %.

One of the plants identified in the Copșa Mică area is *Vicia spp.* Fabaceae (Legume family). The heavy metal content found in *Vicia spp.* plants from permanent grasslands is shown in Table 3.

The cadmium content in *Vicia spp.* plants varied between 0.03 mg·kg^{-1} and 4.90 mg·kg^{-1}, the arithmetic mean value being 1.85 mg·kg^{-1} and the coefficient of variation of 89.7 %. The lead content values ranged from 0.40 mg·kg^{-1} to 7.24 mg·kg^{-1}, with an arithmetic mean of 2.92 mg·kg^{-1}, a standard deviation of 2.24 mg·kg^{-1} and a of variation of 76.7 %. The zinc content was between 23.0 mg·kg^{-1} and 179.0 mg·kg^{-1}, with the arithmetic mean – 103.7 mg·kg^{-1} and the coefficient of variation 46.0 %, and copper from 4.10 mg·kg^{-1} to 12.30 mg·kg^{-1} and the coefficient of variation 35.1 %.

Logarithmic plots for power-type regression curves estimating the stochastic dependence between total soil heavy metal content, soil heavy metal content – DTPA extractable form and Vicia spp. plants are shown in Figure 1 and Figure 2.

The value of the linear correlation coefficient obtained for the dependence between the total cadmium content in the soil and Vicia spp. plants (Figure 1a) and the mobile cadmium content in the soil and in the plant (Figure 1b) is significantly different from zero indicating a close correlation between the two variables, the value of the linear correlation coefficient being r=0.625* and respectively r = 0.577* for extractable forms.

For lead, the value of the linear correlation coefficient is distinctly significant for total forms of heavy metals in soil r=0.758** (Figure 1c) and for mobile forms r=0.508^{ns} (Figure 1d).

The power regression curves estimating the stochastic dependence between total soil and plant zinc content (Figure 2a) is insignificant (r=0.531^{ns}). The dependence of mobile zinc content in soil and plant zinc content (Figure 2b) shows a strong correlation between the two variables and a distinctly significant linear correlation index (r=0.761**), which proved to be a good estimate of the accumulation in plants of *Vicia spp*.

Table 1. Values of statistical parameters that characterize the central tendency and the variability of the total cadmium, lead, zinc, copper contents in soil (n=14)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
				mg/kg DW			
Cd_{soil}	2,50	17,74	6,07	5,94	7,16	4,92	68,7%
Pb_{soil}	86	692	192,0	189,3	237,1	186,7	78,7%
Zn_{soil}	168	993	365,5	378,5	434,4	253,4	58,3%
Cu_{soil}	22	161	44,5	47,9	57,2	39,2	68,5%

Table 2. Values of statistical parameters that characterize the central tendency and the variability of the cadmium, lead, zinc, copper contents in soil – DTPA-extractable forms (n=14)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
				mg/kg DW			
Cd_{DTPA}	1,96	15,44	3,77	4,10	5,16	3,99	77,3%
Pb_{DTPA}	23	301	62	66,5	92,6	86,4	93,3%
Zn_{DTPA}	24	340	81	83,1	112,4	91,3	81,2%
Cu_{DTPA}	2,46	23,41	6,93	6,65	7,94	5,31	66,9%

Table 3. Values of statistical parameters that characterize the central tendency and the variability of the cadmium, lead, zinc, copper contents in the *Vicia spp*. plants (n=14)

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
				mg/kg DW			
Cd_{plant}	0,03	4,90	1,23	0,94	1,85	1,66	89,7%
Pb_{plant}	0,40	7,24	2,36	2,07	2,92	2,24	76,7%
Zn_{plant}	23,0	179,0	102,0	91,2	103,7	47,7	46,0%
Cu_{plant}	4,10	12,30	6,35	6,91	7,29	2,56	35,1%

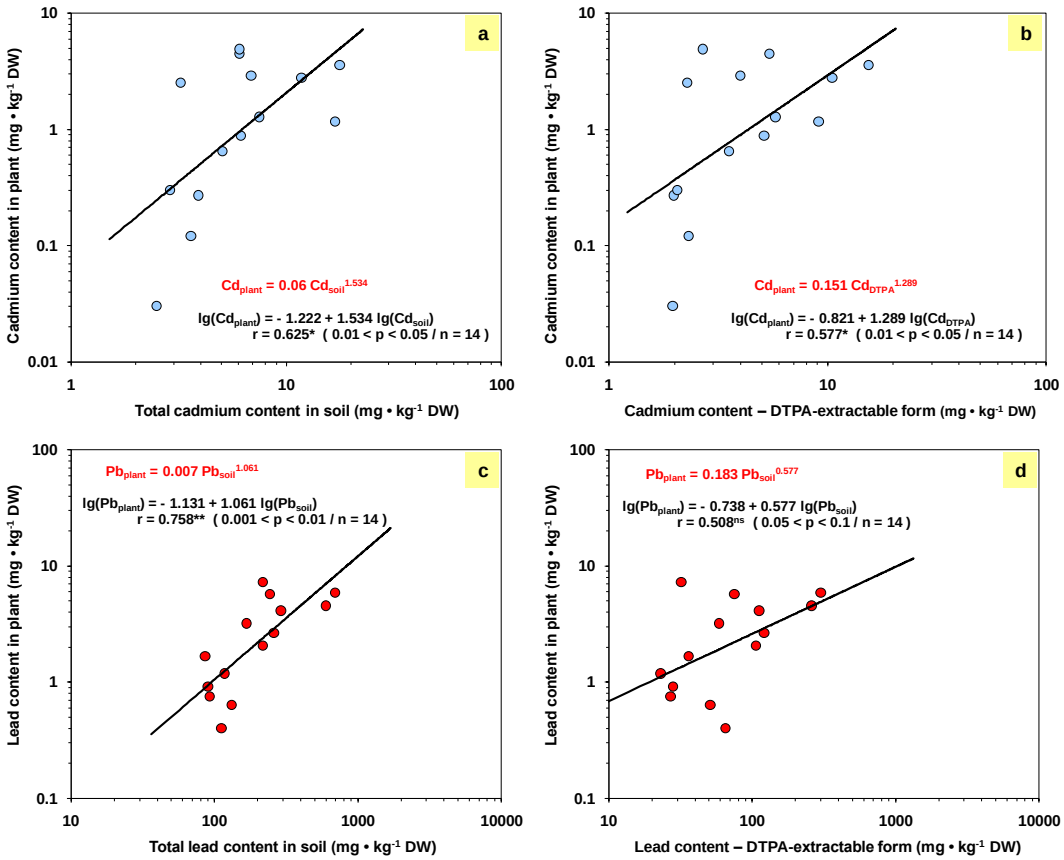

Figure 1. Log-log diagrams for power regression curves that estimate the stochastic dependency between total cadmium content in soil (a), soil cadmium content – DTPA-extractable form (b), total lead content in soil (c), soil lead content – DTPA-extractable form (d) and cadmium/lead contents in *Vicia spp.* plants.

For both total copper and extractable copper, the value of the linear correlation coefficient is insignificant ($r = 0.272^{ns}$ and $r=0.363^{ns}$), which shows that the estimation of copper accumulation in pea plants cannot be described by equations of the type of simple power (Figure 2c and Figure 2d).

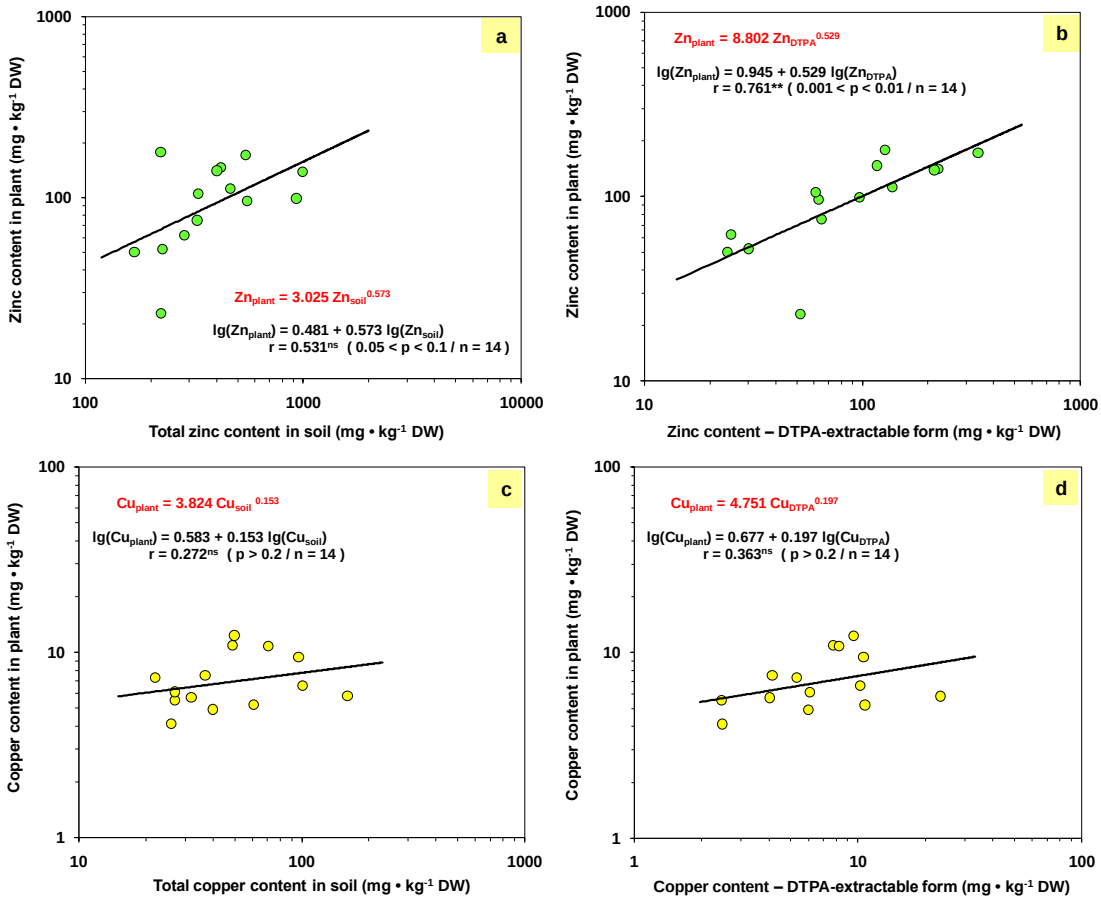

Figure 2. Log-log diagrams for power regression curves that estimate the stochastic dependency between total zinc content in soil (a), soil zinc content – DTPA-extractable form (b), total copper content in soil (c), soil copper content – DTPA-extractable form (d) and zinc/copper contents in *Vicia spp.* plants.

CONCLUSIONS

This study shows the accumulation potential of heavy metals (Cd, Pb, Zn and Cu) from polluted soils in *Vicia spp.* from permanent grasslands. *Vicia spp.* is one of the common plants in permanent grasslands in the study area. The results show a statistically significant difference different from zero, showing a close correlation between total and mobile cadmium content in soil and plants of *Vicia spp*. Simple power regressions performed best for plant accumulation of total lead and mobile zinc, distinctly significant correlations.

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