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CORRELATION BETWEEN HEAVY METALS IN SOIL AND *Lotus corniculatus* IN A STUDY ACHIEVED IN COPȘA MICĂ

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Abstract

Heavy metals pollution is a global issue in the whole word. All soils contain heavy metals, but their concentrations usually are very low. According to the literature, bird's-foot trefoil (Lotus corniculatus) is used as adsorbent of heavy metals from soil. The study was achieved in Copșa Mică area, known for a long time in the top of the most polluted cities in Europe, due to the emissions from two factories. In article it is described the correlation between total forms and DTPA extractable forms and concentrations in Lotus corniculatus plants of cadmium, lead, copper and zinc. In conclusion, cadmium was most easily absorbed of Lotus corniculatus, while lead was identified as having the lowest accumulation in Lotus corniculatus, so it can be used for the removal of some heavy metals from soil.

Key words*: soil, heavy metals, Lotus corniculatus, Copșa Mică.*

INTRODUCTION

Because of the human population rapid growth, heavy metal pollution issues are increasing everywhere in the whole world due to the industrialization and urbanization (Bae et al., 2016). One of the major problematic pollutants are heavy metals like cadmium, lead which represents a significant threat for public health. Heavy metals are a continual source of pollution and are not biodegradable (Borda & Sparks, 2008). An alternative, less expensive with high efficiency for removal of heavy metal from soil is phytoremediation. *Lotus corniculatus*, commonly known as bird's-foot trefoil, is a leguminous plant often studied for its role in soil remediation, especially in heavy metals soil pollution/contamination. This plant is known to tolerate various environmental stresses, including the presence of heavy metals in the soil, making it a research priority of phytoremediation studies (Moussa et al., 2012).
Lotus corniculatus absorbs heavy metals from the soil through its root system. Once absorbed, the metals are translocated to various parts of the plant, including the leaves and stems (Escaray et al., 2012). The plant can accumulate metals in different tissues, but it is not a hyperaccumulator. It may accumulate metals like copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) in moderate amounts, depending on soil conditions (Pichtel et al., 2000).
The main objective of this study is to evaluate the contamination/pollution degree with heavy metals of the meadows from Copșa Mică of analyzing total and mobile forms and the concentration of heavy metals in *Lotus coniculatus* which is a plant that can accumulate heavy metals.

MATERIALS AND METHODS

The research study has been achieved in Copșa Mică area. From the meadows situated in this area were collected 14 soil samples and 14 plant samples representing *Lotus corniculatus*, 6 samples are from Axente Sever, 1 sample from Valea Viilor, 1 from Copșa Mică, 4 from Târnava and 2 from Micăsasa. In Figure 1 is presented the location of the meadows in the study area in Copșa Mică. Soil samples were collected from surface (0-20 cm). The total concentration of cadmium, lead, zinc and copper were determined in the soil samples of acid digesting in a microwave digestion system, then dosing of atomic absorption spectrometry (Vrînceanu et al., 2022).

Figure 1. The location of the meadows in the study area in Copșa Mică (Google Earth)

The concentration of cadmium, lead, zinc and copper extractable in DTPA were determined in the soil samples of extraction method using diethylenetriaminepentaacetic acid, then dosing of atomic absorption spectrometry.

The plant samples were digested also with nitric acid in a microwave digestion system. The concentration of cadmium, lead, zinc and copper were measured of using atomic absorption spectrometry.

In Table 1 is presented the distance from the basket located in Copșa Mică of the meadows from the studied area

Table 1. The distance from the basket located in Copșa Mică of the meadows from the studied area

	Meadows code	Distance from the basket (m)
1	PP1AS	530
2	PP3AS	1160
3	PP10AS	2770
4	PP12AS	1900
5	PP15AS	2180
6	PP16VV	4010
7	PP19CM	2760
8	PP20TV	4510
9	PP22MS	4220
10	PP23MS	4459
11	PP34AS	5134
12	PP35TV	5180
13	PP36TV	3636
14	PP37TV	5368

RESULTS AND DISCUSSIONS

Lotus corniculatus may contribute to soil improvement beyond just metal uptake. As a plant, it fixes nitrogen, improving the nitrogen concentration of the soil. This can be especially beneficial in soils where heavy metal contamination has led to low nutrient levels (Moussa et al., 2022).

Table 2 presents the concentrations of total heavy metals (cadmium, lead, zinc and copper) in soil samples from the meadows in Copșa Mică area along with the reference values of the total cadmium, lead, zinc, copper concentrations in soil for sensitive use of land according with Order 756/1997 to evaluate the contamination / pollution degree.

As it can be observed, total cadmium concentration in soil varies between 0.38 and 48.29 $mg \cdot kg^{-1}$, with an average value of 8.65 $mg \cdot kg^{-1}$ and a coefficient of variation of 143.1% with the highest values registered near the basket from Copșa Mică. The intervention threshold is exceeded in 7 points from the studied area, 5 samples being collected from Axente Sever, 1 sample from Copșa Mică and 1 sample from Târnava. The alert threshold is exceeded in 2 points, 1 from Târnava and 1 from Micăsasa.

Table 2. The concentration of total heavy metals (cadmium, lead, zinc and copper) in soil samples from the meadows in Copșa Mică area and the reference values of the total cadmium, lead, zinc, copper concentrations in soil for sensitive use of land according with Order 756/1997

	Meadows code	Total Cd in soil (mg/kg DW*)	Total Pb in soil (mg/kg DW*)	Total Zn in soil (mg/kg DW*)	Total Cu in soil (mg/kg DW*)
1	PP1AS	48.29	955	2015	182
2	PP3AS	6.15	217	462	50
3	PP10AS	12.38	398	850	60
4	PP12AS	11.40	282	684	56
5	PP15AS	5.05	167	326	161
6	PP16VV	2.50	93	168	27
7	PP19CM	16.92	599	930	101
8	PP20TV	5.63	236	414	108
9	PP22MS	3.12	87	206	38
10	PP23MS	1.36	42	97	19
11	PP34AS	0.38	25	89	61
12	PP35TV	3.91	132	285	61
13	PP36TV	2.89	90	226	32
14	PP37TV	1.18	58	142	23
Minimum		0.38	25	89	19
Maximum		48.29	955	2015	182
Median		4.48	149.5	305.5	58.0
Geometric mean		4.42	151.0	330.5	55.8
Arithmetic mean		8.65	241.5	492.4	69.9
Standard deviation		12.38	258.8	515.3	50.5
Coefficient of variation		143.1%	107.2%	104.7%	72.2%
Normal values		1.0	20	100	20
Alert threshold		3.0	50	300	100
Intervention threshold		5.0	100	600	200

*DW - Dry Weight

Total lead concentration in soil varies between 25 and 955 mg·kg^{-1}, with an average value of 241.5 mg·kg^{-1} and a coefficient of variation of 107.2% and the highest values registered near the basket from Copșa Mică. The intervention threshold is exceeded in 8 points from the studied area, 5 samples being collected from Axente Sever, 1 sample from Copșa Mică and 2 samples from Târnava. The alert threshold is exceeded in 4 points, 2 from Târnava, 1 from Valea Viilor and 1 from Micăsasa.

Total zinc concentration in soil varies between 89 and 2015 mg·kg^{-1}, with an average value of 492.4 mg·kg^{-1} and a coefficient of variation of 104.7%. The intervention threshold is exceeded in 4 points from the studied area, 3 samples being collected from Axente Sever and 1 sample from Copșa Mică. The alert threshold is exceeded in 3 points, 2 from Axente Sever and 1 from Târnava.

Total copper concentration in soil varies between 19 and 182 mg·kg^{-1}, with an average value of 69.9 mg·kg^{-1} and a coefficient of variation of 72.2%. The intervention threshold is not exceeded for any sample. The intervention threshold and alert threshold in 4 points, 2 from Axente Sever, 1 from Copșa Mică and 1 from Târnava.

In Table 3 are presented the concentration of mobile forms of heavy metals, in soil samples from the meadows in Copșa Mică area.

The mobile concentration of cadmium varies between 0.23 mg·kg^{-1} and 33.5 mg·kg^{-1}, with an average value of 6.07 mg·kg^{-1} and a coefficient of variation of 141.7%. The mobile concentration of lead varies between 3.6 mg·kg^{-1} and 275.5 mg·kg^{-1}, with an average value of 88.9 mg·kg^{-1} and a coefficient of variation of 99.7%.

The mobile concentration of zinc varies between 7.1 mg·kg^{-1} and 336.3 mg·kg^{-1}, with an average value of 91.7 mg·kg^{-1} and a coefficient of variation of 119.0%.

The mobile concentration of copper varies between 1.59 mg·kg^{-1} and 23.41 mg·kg^{-1}, with an average value of 8.84 mg·kg^{-1} and a coefficient of variation of 68.9%. The highest concentration of mobile heavy metals are near the basket from Copșa Mică and are decreasing with the increasing of the distance from the pollution source.

Table 3. The concentration of heavy metals extractable form in DTPA (cadmium, lead, zinc and copper) in soil samples from the meadows in Copșa Mică area

	Meadows code	Cd_{DTPA} in soil (mg/kg DW*)	Pb_{DTPA} in soil (mg/kg DW*)	Zn_{DTPA} in soil (mg/kg DW*)	Cu_{DTPA} in soil (mg/kg DW*)
1	PP1AS	33.55	121.5	336.3	14.23
2	PP3AS	5.13	106.0	137.3	9.57
3	PP10AS	10.33	275.5	123.5	6.76
4	PP12AS	9.53	108.6	323.0	6.49
5	PP15AS	3.54	58.8	65.0	23.41
6	PP16VV	1.96	27.4	24.1	2.46
7	PP19CM	9.11	259.7	97.3	10.27
8	PP20TV	4.05	151.3	62.4	15.10
9	PP22MS	1.71	23.8	27.4	4.32
10	PP23MS	0.83	14.0	7.8	1.59
11	PP34AS	0.23	3.6	7.1	12.05
12	PP35TV	1.98	50.6	25.3	10.75
13	PP36TV	2.06	28.4	30.4	4.04
14	PP37TV	0.93	15.4	17.4	2.66
Minimum		0.23	3.6	7.1	1.59
Maximum		33.55	275.5	336.3	23.41
Median		2.80	55	46	8.17
Geometric mean		3.02	50.2	48.1	6.86
Arithmetic mean		6.07	88.9	91.7	8.84
Standard deviation		8.60	88.6	109.1	6.09
Coefficient of variation		141.7%	99.7%	119.0%	68.9%

*DW - Dry Weight

The concentration of heavy metals in *Lotus corniculatus* plant samples from the meadows in Copșa Mică area are presented in Table 4. The cadmium concentration in *Lotus corniculatus* plant varies between 0.10 mg· kg^{-1} and 2.5 mg·kg^{-1}, with an average value of 0.95 mg·kg^{-1} and a coefficient of variation of 83.2%.

Table 4. The concentration of heavy metals in *Lotus corniculatus* plant samples from the meadows in Copșa Mică area

	Meadows code	Cd_{plant} (mg/kg DW*)	Pb_{plant} (mg/kg DW*)	Zn_{plant} (mg/kg DW*)	Cu_{plant} (mg/kg DW*)
1	PP1AS	1.44	3.43	46	7.2
2	PP3AS	0.86	0.32	54	13.9
3	PP10AS	2.50	0.86	70	7.0
4	PP12AS	1.75	0.21	132	4.6
5	PP15AS	0.75	2.39	47	6.8
6	PP16VV	0.32	2.10	45	7.4
7	PP19CM	1.99	1.10	60	5.8
8	PP20TV	0.75	4.90	63	9.0
9	PP22MS	0.15	1.07	25	2.8
10	PP23MS	0.18	0.72	38	4.6
11	PP34AS	0.10	1.75	20	4.4
12	PP35TV	1.73	0.50	70	5.5
13	PP36TV	0.52	0.19	46	4.6
14	PP37TV	0.29	0.43	31	4.8
Minimum		0.10	0.19	20.0	2.80
Maximum		2.50	4.90	132.0	13.90
Median		0.75	0.97	46.5	5.65
Geometric mean		0.62	0.92	48.0	5.87
Arithmetic mean		0.95	1.43	53.4	6.31
Standard deviation		0.79	1.38	27.4	2.71
Coefficient of variation		83.2%	96.5%	51.3%	42.9%

*DW - Dry Weight

The lead concentration in *Lotus corniculatus* plant varies between 0.19 mg·kg^{-1} and 4.9 mg·kg^{-1}, with an average value of 1.43 mg· kg^{-1} and a coefficient of variation of 96.5%. The zinc concentration in *Lotus corniculatus* plant varies between 20 mg·kg^{-1} and 132 mg·kg^{-1}, with an average value of 53.4 mg· kg^{-1} and a coefficient of variation of 51.3%.

The copper concentration in *Lotus corniculatus* plant varies between 2.80 mg·kg^{-1} and 13.9 mg·kg^{-1}, with an average value of 6.31 mg·kg^{-1} and a coefficient of variation of 42.9%.

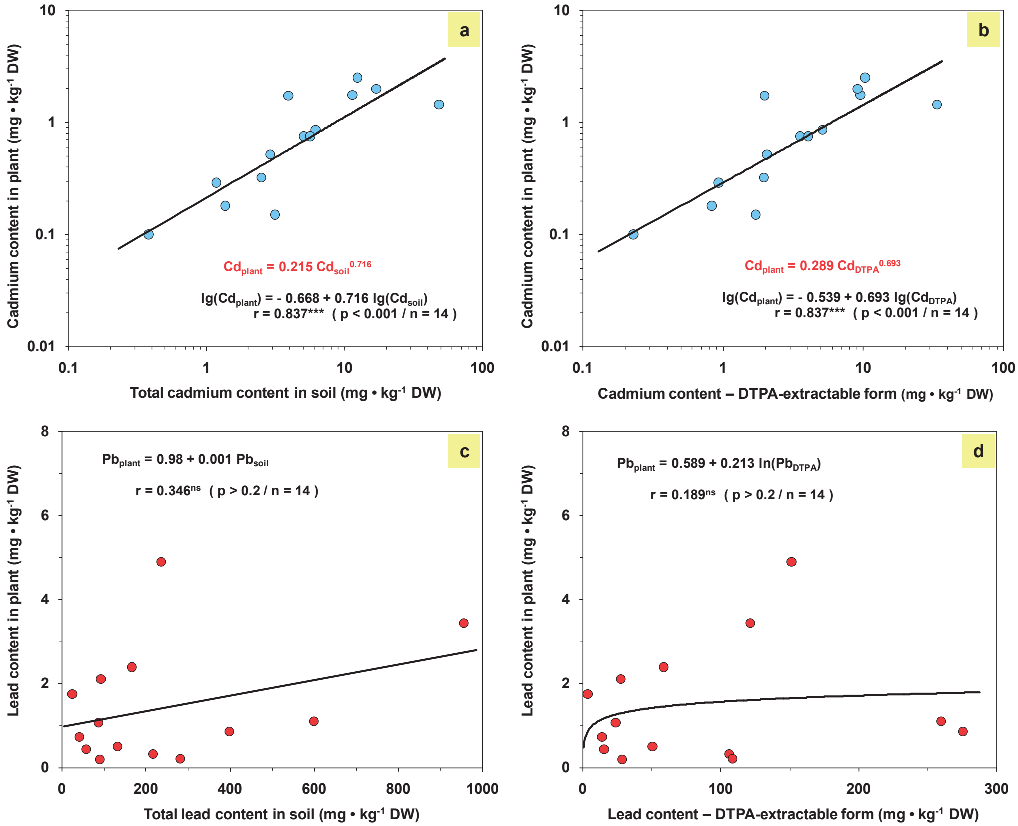

Figure 2. Regression curves that estimate the stochastic dependency between total cadmium concentration in soil (a), soil cadmium concentration – DTPA-extractable form (b), total lead concentration in soil (c), soil lead concentration – DTPA-extractable form (d) and cadmium/lead concentrations in *Lotus corniculatus* plants.

In Figure 2 are presented the regression curves that estimate the stochastic dependency between total cadmium concentration in soil (a), soil cadmium concentration – DTPA-extractable form (b), total lead concentration in soil (c), soil lead concentration – DTPA-extractable form (d) and cadmium/lead concentrations in *Lotus corniculatus* plants.

The value of the linear correlation coefficient between total cadmium concentration in soil and cadmium concentration in *Lotus corniculatus* plants is significant, r = 0.837*** (Figure 2a).

Also a significant linear correlation coefficient between cadmium concentration – DTPA-extractable form in soil and cadmium concentration in *Lotus corniculatus* plants have been found, r = 0.837*** (Figure 2b). In conclusion, this good correlation coefficient of cadmium proves that *Lotus corniculatus* can be a very good plant to remediate a moderate soil polluted with cadmium.

The regression curves that estimate the stochastic dependency between total lead concentration in soil and lead concentrations in *Lotus corniculatus* plants has a insignificant linear correlation coefficient with a value of r = 0.346^{ns} (Figure 2c).

Also a insignificant linear correlation coefficient between lead concentration –

DTPA-extractable form in soil and lead concentration in *Lotus corniculatus* plants have been found, r = 0.189^{ns} (Figure 2d). So, the low correlation coefficient of lead shows that *Lotus corniculatus* is not an efficient plant to remediate moderate soil polluted with lead.

CONCLUSIONS

In this study are presented the data regarding the accumulation of heavy metals (cadmium, lead, zinc and copper) in *Lotus cornicalatus* plants from the soil polluted which is known as a plant that can accumulate heavy metals. The highest correlation coefficient between total and mobile heavy metal and *Lotus corniculatus* was observed at cadmium (r = 0.837***). The translocation of heavy metals, especially of cadmium, in *Lotus corniculatus* plants is dangerous because of its ingestion of herbivores. It is important to note that the heavy metals that *Lotus corniculatus* plants accumulates may eventually enter the food chain.

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*** Ministry Order No. 756 from November 3, 1997 for approval of Regulation concerning environmental pollution assessment published.