

ACCUMULATION OF HEAVY METALS IN *DACTYLIS GLOMERATA* L. PLANTS IN CORRELATION WITH SOIL IN PERMANENT MEADOWS IN THE COPȘA MICĂ AREA OF ROMANIA

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Abstract

This study aims to estimate the accumulation of heavy metals (Cd, Pb, Zn and Cu) from soil in Dactylis glomerata L. plants from permanent meadows in the polluted area of Copșa Mică, Romania. The estimation of heavy metal accumulation in Dactylis glomerata L. plants was carried out based on a data set collected from permanent meadows used for grazing and hay production. The logarithmic power-type regression plots estimating the stochastic dependence between the total cadmium content in the aerial part of Dactylis glomerata L. plants and soil is statistically significant, and for Cu, Pb and Zn they are less significant. The variation of the total metal content (Cd, Cu, Pb and Zn) determined in the soil samples in the 0–20 cm layer according to the distance from the pollution source is statistically significant. The results of this study are important for the estimation of heavy metal (Cd, Cu, Pb and Zn) accumulation in Dactylis glomerata L. plants from permanent grasslands, which are consumed by animals.

Key words: heavy metals, pollution, soil, *Dactylis glomerata* L.

INTRODUCTION

Soil pollution with heavy metals is an increasingly discussed problem all over the world because, in addition to high toxicity, they persist for a long time in the soil altering the ecosystem (Anaman et al., 2022; Patra, 2022; Senila et al., 2022; Chaplygin et al., 2020; Cai et al., 2015). High concentrations of heavy metals in soil are largely due to anthropogenic sources that heavily affect the soil, resulting in a high level of toxicity (Gupta et al., 2021). The main sources of soil pollution are metal processing and mining industries, burning of fossil fuels, exhaust gases from traffic, etc. (Bartha, 2021; Massa et al., 2010; Popa, 2005; Remon et al., 2005). Smelting activities are considered to produce polluting wastes and account for 40–70% of the heavy metals around those areas (Anaman et al., 2022).

Some heavy metals (Zn, Cu), which are essential micronutrients for plants, when in high concentrations become toxic, and others such as Cd, Pb are also dangerous in low concentrations.

These metals can accumulate in plant parts used in human and animal nutrition, which become toxic to living organisms (Pietrelli et al., 2022; Sabir et al., 2022; Castro-Bedriñana et al., 2021; Kachou et al., 2011).

The translocation of zinc and copper from soil to above-ground parts of plants are not surprising, as they are essential nutrients for many physiological processes, including photosynthesis and growth hormone production; therefore, plants tend to translocate them into leaves (Murtic, 2021; Roschztardt et al., 2019).

Studies by Gawryluk et al. (2020) show that grass species can be considered accumulators of Cu and Zn because the levels of these elements in the aboveground biomass of plants were higher than in the analysed soil (0–20 cm layer) and they are not high bioaccumulators of Pb.

The high content of cadmium in the soil has harmful effects on both organisms in the soil, as well as on the vegetation, which leads to the limitation of the growth of roots and shoots, can prevent breathing, photosynthesis, water

absorption and other (Quezada-Hinojosa et al., 2015).

Simple correlations between total metal content (Cd, Pb and Zn) and plant showed that the increasing content of heavy metals causes stress and death of metal-sensitive plants and the appearance of those tolerant to metals (Woch et al., 2016).

Studies are showing that the uptake and bioaccumulation of heavy metals in plants it depends, among other factors, on the plant species (Sharma & Dubey, 2005).

Dactylis glomerata L. is a perennial species with high fodder value, fast growing in spring, and resistant to drought, and low temperatures, but also to frequent mowing and pests, which makes it a common species in meadows and pastures (Malinowska et al., 2023; Nefed'eva et al., 2020).

Piertelli et al. (2022) showed that the accumulation of heavy metals (Cd, Cu, Ni, Pb, Zn) in *Dactylis glomerata* L. plants has a higher proportion in urban than in rural environments and higher accumulations in roots and basal leaves than in leaves, stems and flowers in both environments. The exception is chromium, which accumulates more in flowers than the other metals.

The most well-known areas polluted with heavy metals in Romania, over large areas, are located near the former metallurgical plants near Copșa Mică - Sibiu County, Zlatna - Alba County, Baia Mare-Maramureș County and Neferal-Acumulatorul near Bucharest (Sur et al., 2017; Manea et al., 2015; Gamenț et al., 2010; Vrînceanu et al., 2010).

Our study refers to the Copșa Mică area, where the main activity was the non-ferrous metallurgy of the two industrial platforms: S.C. SOMETRA S.A. with a profile of non-ferrous and ferrous metals and CARBOSIN S.A. with chemical profile (Vrînceanu et al., 2009). Even though metallurgical activities have been stopped, the soil remains loaded with heavy metals and local communities continue their agricultural activities.

From the studies carried out by Bartha et al. (2021), the soil pollution index according to the degree of pollution in the Copșa Mică area shows that 20% of the investigated soils have maximum pollution, 46% in the category of very strong pollution, 7% - strong pollution, 7% -

medium pollution, 7% - low pollution and 13% fall into the minimal pollution category.

MATERIALS AND METHODS

The present paper presents a study carried out in 2023, regarding the accumulation of heavy metals (Cd, Pb, Zn and Cu) in *Dactylis glomerata* L. plants in correlation with the polluted soil from the permanent meadows in the Copșa Mică area. This area is recognized with a high degree of historical pollution.

The estimation of the accumulation of heavy metals in *Dactylis glomerata* L. plants was carried out based on a set of data collected from permanent meadows in Copșa Mică, Axente Sever, Târnava, Micăsasa and Valea Viilor (Figure 1).



Figure 1. View from the field, Copșa Mică area

The soil samples were collected using the agrochemical probe at a 0-20 cm depth (by homogenizing 13 subsamples), then 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 in the field, then oven-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

The accumulation of the total heavy metal content in the 0-20 cm soil layer, from the permanent meadows in the Copsa Mică area, is presented in Table 1.

The values of the total cadmium content in the soil, at the depth of 0-20 cm, varied between 2.50 mg·kg⁻¹ and 48.29 mg·kg⁻¹, with a standard deviation of 11.77 mg·kg⁻¹ and a coefficient of variation of 104%. Total lead content ranges from 87 mg·kg⁻¹ to 955 mg·kg⁻¹ with a standard deviation of 256.9 mg·kg⁻¹ and a coefficient of variation of 76.3%. Zinc has values between 168 mg·kg⁻¹ and 2015 mg·kg⁻¹, with a standard deviation of 486.45 mg·kg⁻¹ and a coefficient of variation of 76.9%, and copper between 22 mg·kg⁻¹ and 182 mg·kg⁻¹, with a standard deviation of 49.88 mg·kg⁻¹ and 70.2%.

According to Order 756/1997 on soil pollution, the arithmetic mean values (11.32 mg·kg⁻¹) of the cadmium content exceed the intervention threshold for the use of several sensitive, and regarding the lead content (336.7 mg·kg⁻¹) and zinc (632.8 mg·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 characterizing the variability of the content of Cd, Pb, Zn and Cu in the soil - the extractable forms with DTPA, where are the minimum and maximum values, as well as the arithmetic mean concentrations. The extractable cadmium content varied between 1.71 mg·kg⁻¹ and 33.55 mg·kg⁻¹, with an arithmetic mean of 8.14 mg·kg⁻¹ and a coefficient of variation of 102.2%. Lead ranges between 23 mg·kg⁻¹ and 301 mg·kg⁻¹ with an arithmetic mean of 129.3 mg/kg, standard deviation of 93.7 mg·kg⁻¹, and coefficient of variation of 72.5%. Zinc content values range from 24 mg·kg⁻¹ to 336 mg·kg⁻¹ with a mean of 131.4 mg·kg⁻¹ with a standard deviation of 106 mg·kg⁻¹ and a coefficient of variation of 80.7%, and copper between 2.46 mg·kg⁻¹ and 23.4 mg·kg⁻¹ with a mean of 8.22 mg·kg⁻¹ and the coefficient of variation of 70.8%.

The average concentration of total and extractable forms in the 0-20 cm soil layer increases in the following order: Cd<Cu<Pb<Zn.

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 ⁻¹ DW							
Cd _{soil}	2.50	48.29	8.43	7.99	11.32	11.77	104.0%
Pb _{soil}	87	955	271.0	258.7	336.7	256.9	76.3%
Zn _{soil}	168	2015	552.5	496.4	632.8	486.5	76.9%
Cu _{soil}	22	182	57.5	57.8	71.1	49.9	70.2%

DW - Dry Weight

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 ⁻¹ DW							
Cd _{DTPA}	1.71	33.55	6.29	5.66	8.14	8.32	102.2%
Pb _{DTPA}	23	301	115	95.3	129.3	93.7	72.5%
Zn _{DTPA}	24	336	87	96.2	131.4	106.0	80.7%
Cu _{DTPA}	2.46	23.41	6.30	6.71	8.22	5.82	70.8%

DW - Dry Weight

Dactylis glomerata L. is one of the most common grasses in the Gramineae family found in the study area. The heavy metal content found in *Dactylis glomerata* L. plants from permanent grasslands is shown in Table 3.

The cadmium content of the plants ranged from 0.05 mg·kg⁻¹ to 1.21 mg·kg⁻¹, the mean value was 0.51 mg·kg⁻¹ and the coefficient of variation of 78.4%. Quezada-Hinojosa shows that *Dactylis glomerata* L. is a plant known for its

pastoral value and accumulates higher levels of cadmium in roots than in shoots. In the shoots, it

accumulates cadmium concentrations up to 0.8 mg·kg⁻¹, which does not pose a major risk.

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

Variable	Minimum	Maximum	Median	Geometric mean	Arithmetic mean	Standard deviation	Coefficient of variation
Cd _{plant}	0.05	1.21	0.41	0.33	0.51	0.40	78.4%
Pb _{plant}	0.15	4.38	1.15	0.78	1.27	1.22	96.1%
Zn _{plant}	34.7	122.4	60.3	58.7	63.4	25.9	40.9%
Cu _{plant}	2.80	5.30	4.01	3.99	4.07	0.83	20.4%

DW - Dry Weight

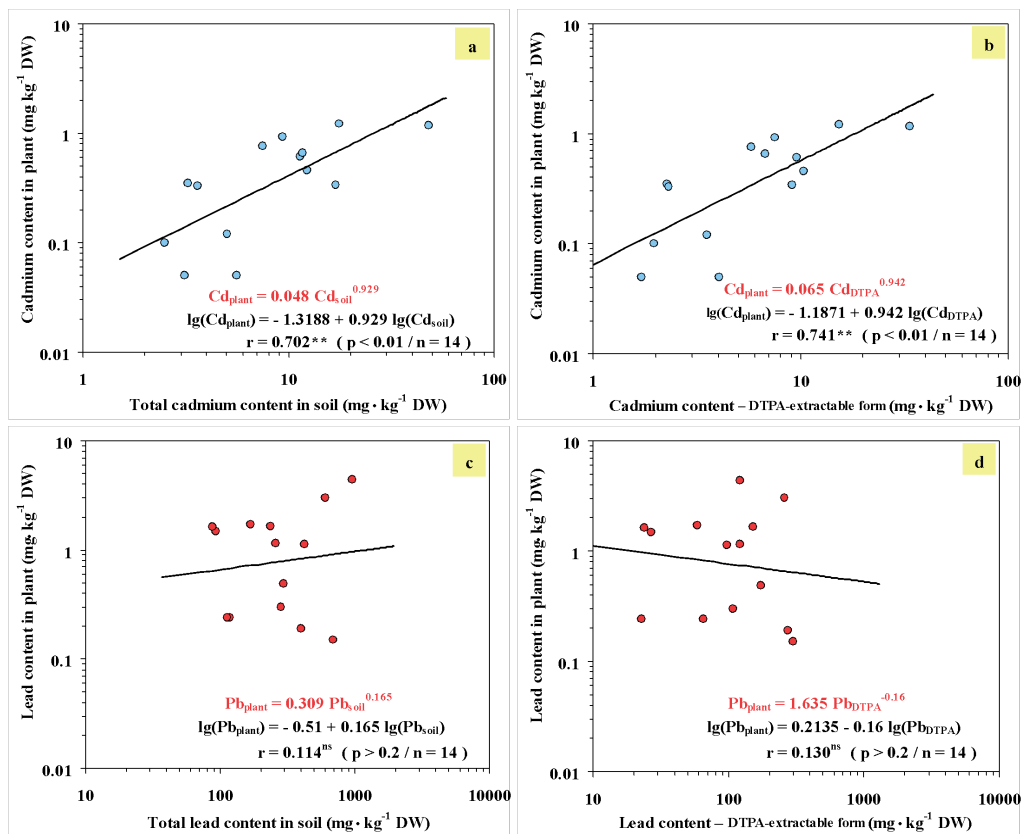


Figure 2. Log-log diagrams for power regression curves that estimate the stochastic dependency between total cadmium content in soil (a), soil cadmium content - DTPA-extractable form (b), total lead content in soil (c), soil lead content - DTPA-extractable form (d) and cadmium/lead contents in *Dactylis glomerata* L. plants

Lead values were between 0.15 mg·kg⁻¹ and 4.38 mg·kg⁻¹, with a standard deviation of 1.22 mg·kg⁻¹ and a coefficient of variation of 96.1%. The zinc content was between 34.7 mg·kg⁻¹ and 122.4 mg·kg⁻¹, with the arithmetic mean - 63.4 mg·kg⁻¹, and the copper between 2.80 mg·kg⁻¹ and 5.30 mg·kg⁻¹.

Logarithmic plots for power-type regression curves, estimating the stochastic dependence between total soil heavy metal content (Cd, Pb, Zn, and Cu), soil heavy metal content - extractable form DTPA from *Dactylis glomerata* L. plants are shown in Figure 2 and Figure 3.

The value of the linear correlation coefficient obtained for the dependence between the total cadmium content in the soil and the plant (Figure 2a) and the extractable cadmium content in the soil and the cadmium content in the plant (Figure 2b) is distinctly significantly different from zero indicating a close correlation between the two variables, the value of the linear correlation coefficient ($r = 0.702^{**}$) and respectively ($r = 0.741^{**}$) for extractable forms.

For lead, the value of the linear correlation coefficient is not significantly different from zero, for total forms $r = 0.114^{ns}$ (Figure 2c) and for extractable forms $r = 0.130^{ns}$ (Figure 2d), which indicates that the estimation of glomer lead accumulation in plants of *Dactylis glomerata* L. cannot be described by simple power regressions.

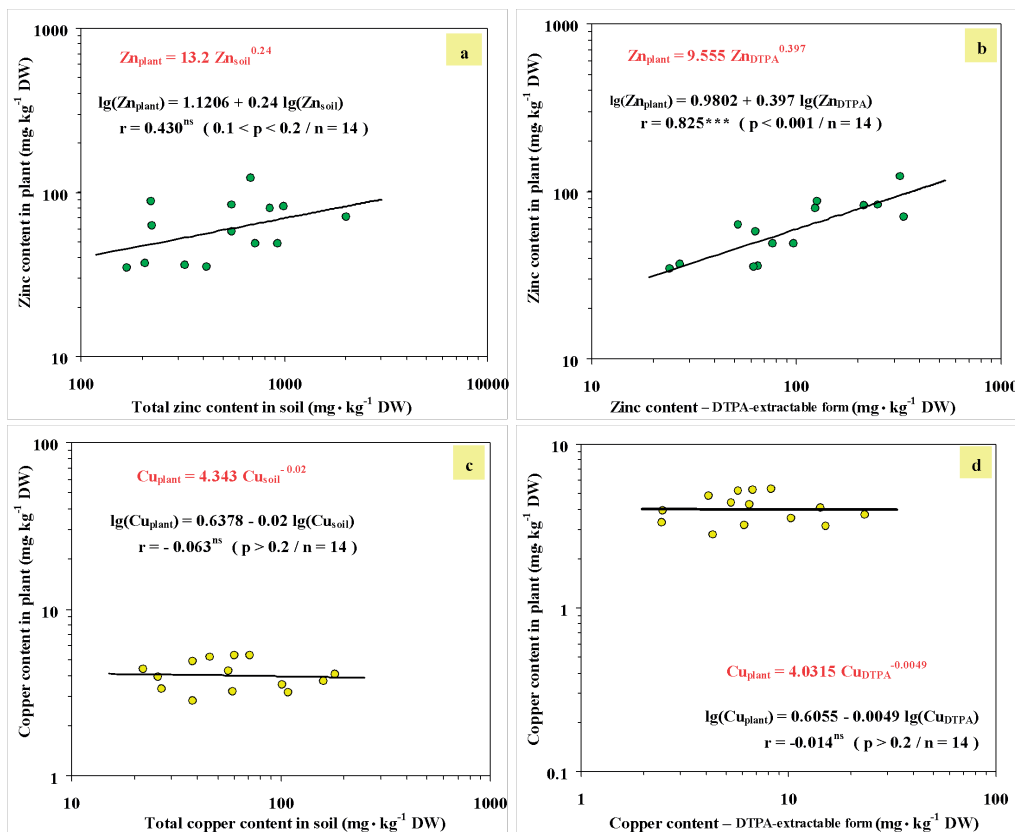


Figure 3. Log-log diagrams for power regression curves that estimate the stochastic dependency between total zinc content in soil (a), soil zinc content - DTPA-extractable form (b), total copper content in soil (c), soil copper content - DTPA-extractable form (d) and zinc/copper contents in *Dactylis glomerata* L. plants

The power regression curves estimating the stochastic dependence between the total zinc content of the soil (0-20 cm layer) and the aerial part of the *Dactylis glomerata* L. plant (Figure 3a) is insignificant ($r = 0.430^{ns}$). The dependence between the extractable zinc content in the soil and the total zinc content in the plant (Figure 3b) shows a strong correlation between the two variables and a distinctly significant linear

correlation index ($r = 0.825^{***}$), which proved to be the better estimation of bioaccumulation in *Dactylis glomerata* L. plants.

For both total copper and extractable copper, the linear correlation coefficient value is $r = -0.063^{ns}$ and $r = -0.014^{ns}$, which shows that the estimation of copper accumulation in *Dactylis glomerata* L. plants cannot be described by equations simple power type (Figure 3c and Figure 3d).

The copper content of the aerial part of the plant is not a good indicator of copper toxicity due to the immobilization of this element in plant roots (Vrinceanu et al., 2010).

Figure 4 shows the logarithmic plots for the power-type regression curves that estimate the variations in the total content of heavy metals

(Cd, Pb, Zn, and Cu) in the soil as a function of the distance from the pollution source - S.C. SOMETRA S.A. The linear correlation index between the total soil cadmium content and the distance from the pollution source is very significant ($r = -0.823^{***}$).

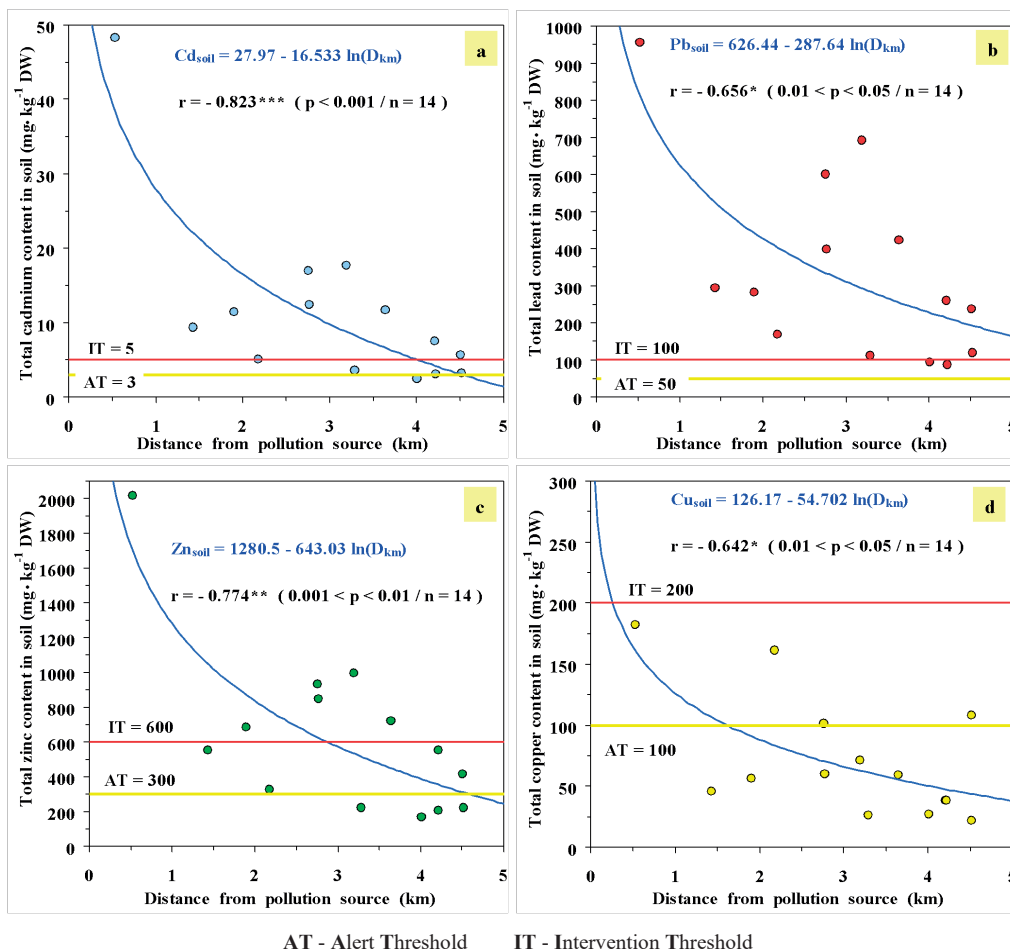


Figure 4. Total cadmium (a), lead (b), zinc(c) and copper(d) contents in soil as functions of the distance from the pollution source - S.C. SOMETRA S.A. (Coșșa Mică, 0-20 cm layer)

The values of the cadmium content of soil are greater than the alert threshold for sensitive uses (3 mg·kg⁻¹) and fall below this limit at distances of 4 km. The highest value of the total cadmium content in the soil was found in samples collected approximately 0.5 km from the pollution source (Figure 4a).

In Figure 4b, between total soil lead content and distance from the pollution source, the linear

correlation index is significant ($r = -0.656^*$). The values of lead content in the soil are above the alert threshold for sensitive uses (50 mg·kg⁻¹) and are increasing above the intervention threshold for sensitive uses (100 mg·kg⁻¹).

In the study by Jankowski et al. (2019), the largest amounts of Pb (13.52 mg·kg⁻¹) and Cd (0.333 mg·kg⁻¹) were found in the soil at a distance of 5 m from roadworthy lead and

cadmium content varied significantly and were dependent both the plant species (*Dactylis glomerata* L., *Arrhenatherum elatius* and *Alopecurus pratensis*) and the distance from the road. *Dactylis glomerata* L. accumulated the lowest content ($3.246 \text{ mg}\cdot\text{kg}^{-1}$) of lead and the greatest amount of cadmium ($0.286 \text{ mg}\cdot\text{kg}^{-1}$), and the highest concentrations were in plants growing at a distance of 5 m from the road, while at distances greater than 10 and 15 m, the concentrations decreased systematically.

The linear correlation index for zinc is distinctly significant ($r = -0.774^{**}$), with values below the alert threshold between 3 and 5 km and less than 50%, above the intervention threshold (Figure 4c).

Copper content values from the soil are lower than the intervention threshold for sensitive use ($200 \text{ mg}\cdot\text{kg}^{-1}$) over the entire studied area. Variance estimated by power regression equations indicates that total copper values in the 0-20 cm layer fall below the alert threshold at greater distances of 1 km from the pollution source. About 80% of the copper content values are below the alert threshold for sensitive uses. The values of the linear correlation coefficient ($r = -0.642^*$) are significant (Figure 4d).

CONCLUSIONS

The current study shows the potential for the accumulation of heavy metals from polluted soils in *Dactylis glomerata* L. plants from permanent meadows.

The results showed that the value of the linear correlation coefficient obtained for the dependence between the total and extractable content of cadmium plants from the soil and *Dactylis glomerata* L. is significantly significant and shows a close correlation between the two variables. The dependence between the content of extractable zinc in the soil and the content of zinc in the plant shows a strong correlation between the two variables.

In addition, the linear correlation coefficient values are not significant for lead and copper.

The index of linear correlation between total soil cadmium content and distance from the pollution source is strongly significant, for zinc distinctly significant, and for lead and copper significant.

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