Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XII, 2023
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

RESEARCH ON THE HEAVY METALS CONTENT IN SOILS FROM VARVOR LOCALITY, DOLJ COUNTY

Gilda-Diana BUZATU, Ana Maria DODOCIOIU

University of Craiova, Faculty of Horticulture, 13 A.I. Cuza Street, Craiova, Romania

Corresponding author email: anadodocioiu@gmail.com

Abstract

In the current research, heavy metals content (Zn, Ni, Cd, Cu, Pb) was analysed in soil and corn cobs samples to determine if the soil and corn plants are polluted with these heavy metals, corroborated with the humus content, total nitrogen, mobile forms of phosphorus and potassium, soil reaction, clay, sand and silt. Soil samples were collected from 9 parcels located in the Varvor area. Varvor is situated in the SW of Dolj County, 18 km from Craiova, and positioned in the northeast part of the Desnatui Plain, on the border with the high Balacita Plain. Following the results, was found that all values obtained for these parameters are falling below the established normal values by Order 756/1997, for sensitive soils. Only concerning Cu content of the analysed soil samples, the limit value of 20 mg kg $^{-1}$ was exceeded for 6 of the 9 samples, the variation range being between 19.1-35.8 mg kg $^{-1}$. Heavy metals content in corn cobs were within the acceptable limits according to Codex Alimentarius, except for cadmium, which exceeded the limit value established by Commission Regulation no. 1881/2006.

***Key words**: chemical, heavy metals, physical, properties, soil.*

INTRODUCTION

Among the pollutants, heavy metals have a recognized toxic potential on all living organisms, each of these metals being dangerous outside a certain range of values.

Due to soil's ability to store heavy metals over the years, the soil can be considered a repository for them (Buzatu & Dodocioiu, 2015).

Sources of heavy metals can be both natural (lithogenetics, pedogenetics) and anthropogenic: fertilizers and amendments, manure, urban sludge, irrigation water, pesticides, non-ferrous industry, residues from coal combustion, vehicle emissions etc.

These can contribute to greater or lesser loading of the soil and, implicitly, of the plants with these chemical elements (Dodocioiu & Mocanu, 2009; Buzatu & Dodocioiu, 2017).

In Romanian soils are predominant the following heavy metals: manganese, copper, zinc, boron, molybdenum, lead, nickel, chromium and sometimes beryllium, vanadium, zirconium, scandium (Davidescu & Davidescu, 1988).

Most of the agricultural soils in our country are formed on sediments with a medium and fine texture, with reserves of trace elements inherited from the parent material. Naturally high levels in the soil can result from geological processes, but mostly result from agriculture and industrial activity.

Heavy metals are elements that exist in nature and that can create a complete biological cycle, i.e. from soil - plant - animal - man.

Among these heavy metals, copper, zinc and nickel are essential for plant growth, entering the active zone of some enzymes, thus being co-factors or co-enzymes (Sungur et al., 2014).

The absorption of nutrients by plants disturbs the balance in the soil solution, which leads to the passage of some elements from the adsorbed state into the soil solution. The organic matter in the soil, on one hand, retains a series of elements, and on the other hand, following the microbiological activity, it releases a series of elements, for this reason it could be considered a dynamic balance. The intensity of the absorption process of heavy metals from the soil into the plant differs depending on the soil and plant type, fertilizers, irrigation and the interaction between these factors (Milačič & Štupar, 1995; Banks et al., 2006).

Workplace and food are main routes of human exposure to the action of heavy metals. Higher plants are very sensitive to climate changes: zinc reduces biological activity in the soil, modifies its physicochemical properties, acts on microorganisms by disrupting the transformation process of organic matter in the soil and slows down physiological processes. In addition, cadmium (often present in phosphate fertilizers) produces the blocking of microbiological processes.

The toxic effect of heavy metals also manifests itself on the microorganisms in the soil, which further leads to the modification of the activity of all the microorganisms in the soil (Ashraf & Ali, 2007).

Cadmium and lead compete with minerals such as calcium, magnesium or iron for absorption but can also bind to structural proteins, enzymes and nucleic acids, so they can interfere with their functioning (Andrade et al., 2017).

In order to reduce the mobility of some heavy metals (i.e. cadmium) from the soil to cereals is considered the utilization of organic fertilizers and liming (Zhao et al., 2015).

Maize is considered the basic grain in animal and human food (Lu et al., 2015).

Because complete removal of heavy metals from grains can rarely, if ever, be achieved; prevention is more effective than treatment (Thielecke & Nugent, 2018).

Some heavy metals such as cadmium and lead have no physiological role in plants and as a result, they are considered not essential for plants growth (Singh, 2011). But others such as copper, nickel and zinc are considered essential for normal growth and metabolism of plants and have toxic effects when found in larger quantities than the plants need (Garrido et al., 2002; Rascio & Izzo, 2011).

Occurrence of cancer, cardiovascular, neurological and other diseases are some negative effects resulted after consuming vegetal products with heavy metals, as reported by different authors (Jarup, 2003; Baghaie & Fereydoni, 2019).

Considering the maintenance of human and animal health, it is necessary to monitor the content of heavy metals in plants and to consider Directive no. 86/278/CEE, regarding the use of sludge from sewage treatment plants as fertilizer in agriculture, and for crops known to have a content of these elements, they must be excluded from animal and human feed.

The main objectives of this research were: (1) to determine the physical and chemical characteristics of the analyzed soil; (2) to determine the content of heavy metals in soil and corn cobs; (3) to evaluate the relationship between the uptake of heavy metals by corn cobs and the content of heavy metals in soil.

MATERIALS AND METHODS

Experimental site

The study was carried out in Varvor locality on a stagnant, vertic, moderately pseudo-glazed, bathycalcaric preluvosol with loamy/clayey texture, generated by disaggregation-alteration material consisting of medium-fine and fine material stratifications, in the year 2021, the area where wheat and corn are cultivated. Varvor is situated in the SW of Dolj County, 18 km from Craiova, and positioned in the northeast part of the Desnatui Plain, on the border with the high Balacita Plain, temperate continental climate, with precipitation of 551.4 mm/year.

Soil and plant sampling

We collected 9 paired soil - corn samples. The soil samples were collected from 0-20 cm surface layer. Corn cobs samples (*Zea mays, Gramineae* family) were taken from the 9 plots from which soil samples were taken. All the samples were transported to the laboratory where they were analyzed. Soil samples were dried at the room temperature, grounded with an agate mortar and sieved.

Soil analysis

Soil diagnosis and inclusion in the soil classification system was carried out in accordance with the Romanian Soil Taxonomy System (SRTS, Florea & Munteanu, 2012).

Determination of the granulometry composition of the soil was achieved by treating the soil samples in order to obtain the dispersion according to the Kacinski method. The separation of the particle size fractions was carried out by sieving for particles smaller than 0.02 mm and by pipetting for particles with a diameter equal to or greater than 0.02 mm. The results were expressed in percentages compared to the material remaining after pre-treatment, the sum of the fractions being 100%.

The determination of the pH value was carried out by the potentiometric method, using a Mettler Toledo, MP 220 pH-meter, at a soil: water ratio of 1:2.5.

The humus content (%) was determined by wet oxidation according to the Walkley-Black method modified by Gogoasa.

The total N content (%) was determined by Kjeldahl method, using Raypa MBC-6 digester and Pro-Nitro-1, I.C.T. distillation unit.

The content of mobile P in the soil was determined according to the Egner-Riehm-Domingo method, colorimetrically with a Jasco V-530 UV VIS spectrophotometer.

The K content in the soil was determined according to the Egner-Riehm-Domingo method, using the flame photometer Jenway PFP-7.

Determination of heavy metals in the soil was carried out by weighing 3 g of soil and moistening it with 1 mL of deionized water, then the sample was mineralized using 21 mL of HCl and 7 mL of HNO_3, the solution obtained was then used to determine the content of heavy metals using iCE™ 3000 AAS Spectrometer Thermo Fisher Scientific.

Plant analyses

Determination of heavy metals in corn cobs was carried out by drying the corn cobs in an oven at 105°C, grounded with the knife mill Grindomix GM 200, Retsch, followed by the mineralization of plant samples (1 g of plant product) which is carried out using 5 mL of HNO_3 (65%) and 4 mL H_2O_2 (35%). The solution thus obtained is prepared for the determination of the metal content of plant samples with the help of the iCE™ 3000 AAS Spectrometer Thermo Fisher Scientific.

RESULTS AND DISCUSSIONS

Research was carried out on a preluvosol, stagnant, vertic, moderately pseudo-glazed, bathycalcaric with loamy/clayey texture, generated by disaggregation-alteration material consisting of medium-fine and fine material stratifications (Table 1).

A quantity of 30 t/ha sewage sludge was applied to this soil, its chemical composition being presented in Table 2.

Soil is characterized with low humus content, low to medium total nitrogen content, very high phosphorus content, high/very high mobile potassium content, loamy/clay texture, an imperfect global drainage and a strong compaction of the lower horizons.

The values obtained for the physicochemical characteristics of the soil were processed using the statistical package SPSS 17, the descriptive statistics including the minimum value, the maximum value, the average value and the standard deviation and are presented in Table 1.

Table 1. The physicochemical characteristics of the preluvosol from Varvor statistically interpreted

Physico-chemical characteristics of the soil	Minimum	Maximum	Mean	Std. Deviation
pH	5.28	5.91	5.50	0.21
Humus (%)	2.12	2.90	2.41	0.29
N total (%)	0.12	0.15	0.13	0.01
P mobile ($mg \cdot kg^{-1}$)	97	137	111.44	16.94
K mobile ($mg \cdot kg^{-1}$)	186	207	194	8.30
Clay (%)	35.70	49.80	43.70	5.70
Sand (%)	31	38.10	34.08	3.26
Silt (%)	19.2	26.2	23.33	3.03

Table 2. Characterization of sewage sludge

Parameter	Determined value
Humidity, %	263
pH	7.82
N total, %	4.80
P total, %	0.22
Ca, %	0.79
Mg, %	0.35
Cu ($mg \cdot kg^{-1}$)	167
Zn ($mg \cdot kg^{-1}$)	663
Pb ($mg \cdot kg^{-1}$)	62.3
Cd ($mg \cdot kg^{-1}$)	2.22
Co ($mg \cdot kg^{-1}$)	4.51
Ni ($mg \cdot kg^{-1}$)	94.8
Cr ($mg \cdot kg^{-1}$)	68.90

The soil has the following morphological characteristics:

- 0-20 cm - dark brown Ao horizon, loamy texture, subangular and small angular polyhedral structure, dry, gradual transition.
- 20-40 cm - A/By horizon, dark yellowish-brown colour, clayey texture, medium-large angular polyhedral structure, very plastic, very adhesive, moderately compacted, rare thin roots, dry, gradual transition.
- 40-74 cm - horizon Bt1w2, brown colour 20-25% stains in redox colours, clayey texture, polyhedral angular and large prismatic structure, shows clay films and oblique faces, very plastic, very adhesive, present cracks filled with very rare material that penetrate up to 80-90 cm deep, strongly compacted, gradual transition.
- 74-100 cm - Bt2w2, dark yellowish-brown colour by 25-30%, spots and dots in

oxidation-reduction colours, clay loamy texture, massive structure, strongly compacted.

According to the data presented in Table 1, the pH of the soil varied between 5.28 and 5.90, in these conditions the soil reaction was moderately acidic (pH=5.28) and weakly acidic (pH=5.91). In acidic, well-aerated soils, heavy metals are easily mobile and therefore accessible to plants (Król et al., 2020).

Humus content of the soil is between 2.12 and 2.90%, with a mean content of 2.41%, indicating a low supply state.

Regarding the total N content in the analysed samples, it varied between 0.12-0.15%, this indicating a low to medium supply state of the soil in this element.

The mobile phosphorus content varied between 97-137 mg·kg^{-1} P, with an average of 114.44 mg·kg^{-1} P. These values indicate a very good state of soil supply with phosphorus.

The potassium content recorded values between 186-207 mg·kg^{-1} K, with an average of 194 mg·kg^{-1} K, values between 186-200 mg·kg^{-1}K indicate a good state of soil supply in this element, and values that exceed 200 mg·kg^{-1} K indicate a very good supply of soil in this element.

The obtained concentrations of heavy metals in the stagnant preluvosol from Varvor locality were compared with the normal values of these metals in soils for sensitive use allowed by the legislation in force (Order 756/1997) and were processed with statistical package SPSS 17, descriptive statistics including maximum value, minimum value, arithmetic mean and standard deviation. All these data are presented in Table 3.

Table 3. Values of the content of heavy metal in the soils from Varvor (mg·kg^{-1})

Metal	Minimum	Maximum	Mean	Std. Deviation
Cd	0.07	0.27	0.13	0.06
Cu	19.1	35.8	22.95	5.67
Pb	10.0	17.7	13.21	2.59
Ni	13.6	15.5	14.51	0.66
Zn	43.1	68.1	57.88	7.02

The values of cadmium, nickel, zinc, lead concentrations are below the normal values mentioned in Order 756/1997 for soils with sensitive use, except for the values of the copper concentrations (Table 4).

The range of variation for the copper content of the analysed soils is between the minimum value of 19.1 mg·kg^{-1} and the maximum value of 35.80 mg·kg^{-1} (mean value of 22.95 mg·kg^{-1}), for 6 out of 9 samples, the normal value of 20 mg·kg^{-1} according to Order 756/1997 is exceeded but staying below the alert threshold of 100 mg·kg^{-1}. Copper is one of the microelements essential for plant nutrition, contents lower than 10 mg·kg^{-1} in soils determine the deficiency in this element in vegetation, while higher contents can be toxic.

Total copper content from the surface layer of different soil type varies between 4 and 49 mg·kg^{-1}, while the available copper content varies between 0.5 -5 mg·kg^{-1} (Radulov et al., 2011). Fulvic acids from organic matter show a preference for copper in the formation of complexes, showing a very strong affinity for the organic matter in the soil, forming very stable complexes and that is why it remains in the soil.

Regarding the heavy metal concentration values obtained for the soil samples, they had the following descending order: Zn>Cu>Pb>Ni>Cd, which is in correlation with the research of Lokeshwari and Chandrappa (2006), who concluded that zinc is a very mobile element and therefore the retention capacity of the soil is much lower.

Table 4. Reference values (mg·kg^{-1}) according to Order 756/1997 for sensitive soil

Metal	Normal values	Alert threshold	Intervention threshold
Cd	1	3	5
Cu	20	100	200
Pb	20	50	100
Ni	20	75	150
Zn	100	300	600

All the data obtained indicates that the application of biosolids shows the lack of pollution of the soil by the application of sludge, which suggests that these types of soils have the intrinsic possibility of limiting the effect of acidity on the balance of heavy metals.

The values obtained for content of heavy metals in corn cobs were processed using the statistical package SPSS 17, the descriptive statistics

including the minimum value, the maximum value, the average value and the standard deviation and are presented in Table 5.
Regarding the values of the heavy metals' concentrations obtained for corn grains samples, they had the following descending order: Zn>Cu>Ni>Pb>Cd, this being in correlation with research conducted by Sungur and his team (2014).

Table 5. The values of the content of heavy metal in corn cobs (mg·kg^{-1})

Metal	Minimum	Maximum	Mean	Std. Deviation	Maximum allowed limits *
Cd	0.03	0.15	0.08	0.04	0.20
Cu	1.23	4.39	2.49	1.31	50
Pb	0.12	0.16	0.12	0.01	0.30
Ni	0.12	0.79	0.49	0.25	67
Zn	9.21	15.31	14.41	1.96	100

* According to Codex Alimentarius Commission 2001

The highest values of heavy metal concentrations were recorded for zinc because it is more mobile and once embedded in biochemical compounds and in specific anatomical-physiological structures it can no longer be displaced from the corn cobs. This is followed by copper and then by nickel. The lowest concentrations of heavy metals were recorded for cadmium and lead.
In conclusion, it can be said that copper and zinc have much higher mobility compared to the other heavy metals analyzed.
Research has shown that when heavy metals (zinc, iron, nickel, copper, lead) are found in the soil, they will accumulate in all the vegetative organs of the plants that grow on this soil (Ibrahim, 2015).
Heavy metals content in corn were within the acceptable limits, according to Codex Alimentarius, 2001.
According to EU regulations, the maximum allowed concentrations for cadmium and lead are limited (***, Commission Regulation no. 1881/2006), the maximum allowed concentration in the case of cereals are 0.2 mg·kg^{-1} for lead and 0.10 mg·kg^{-1}for cadmium, these being much lower than those established by Codex Alimentarius. Regarding the other heavy metals studied, no maximum limits are established by Commission Regulation no. 1881/2006. According to this, in 3 of 9 corn cobs samples analyzed, the limit value for cadmium was exceeded and for lead, all the concentrations of the analyzed samples are below the limit.
All the copper concentration values do not indicate an excess of the normal content values, which is 3-15 mg·kg^{-1}, although for grains these concentrations can be even higher (Lațo et al. 2012).
The correlation coefficient (r) ranges from 0.68 - moderate correlation for copper, to 0.80-0.84 - strong correlation for lead, zinc, and to 0.90-0.91 strong-very strong for cadmium and nickel. This indicates that there is a direct correlation between the content of heavy metals in the soil and the content of metals accumulated in the corn cobs (Table 6).

Table 6. Correlation coefficients between total heavy metal content in soil and corn cobs

Metal mg·kg^{-1}	Correlation coefficient
Cd	0.90
Cu	0.68
Pb	0.80
Ni	0.91
Zn	0.84

CONCLUSIONS

Following the results, it can be concluded that all values obtained for cadmium, lead, nickel and zinc are falling below the established normal values by Order 756/1997, for sensitive soils. Only with regard to copper content of the analysed soil samples, the limit value of 20 mg kg $^{-1}$ was exceeded for 6 of the 9 samples, the variation range being between 19.1-35.8 mg kg^{1}. Analysis of the data obtained indicates that application of biosolids specifies the lack of pollution of the soil by the application of sludge, which suggests that these types of soils have the intrinsic possibility of limiting the effect of acidity on the balance of heavy metals.
Heavy metals content in corn cobs were within the acceptable limits according to Codex Alimentarius, except for cadmium, which exceeded the limit value established by Commission Regulation no. 1881/2006. There is a direct correlation between the content of heavy

metals in the soil and the content of metals accumulated in the corn cobs. Compared to the other analysed metals in corn cobs, the highest values were registered for zinc, copper and nickel and the minimum values were registered for lead and cadmium.

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