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HEAVY METALS ACCUMULATION IN SOME LEAFY VEGETABLES FROM PRIVATE GARDENS IN COPȘA MICĂ

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Many previous studies have reported high levels of metals (Cd, Pb, Zn) content in soils and vegetation from area affected by historical contamination in Copșa Mică area. Furthermore, some of them (Cd or Zn) can be slowly and consistently transferred from contaminated soils into food crops increasing toxic metals exposure to human beings in the long-term through the food chain. Leafy vegetables cultivated in kitchen gardens in contaminated areas often accumulate excessive amounts of heavy metals and pose a threat to human health. Therefore, this study attempts to quantify quality and safety of some leafy vegetables grown in individual gardens from contaminated area, Copșa Mică. The metals contents in leafy vegetables were positively correlated to total contents of metals in soil. Additionally, models were developed to predict the accumulation of Cd, Cu, Pb and Zn in different leafy vegetables (parsley, celery and lettuce) based on Cd, Cu, Pb and Zn content in soils. The results of this study are important to estimate the metals accumulation in vegetables from individual gardens, while also improving the safety of foodstuff produced in contaminated areas.

Key words: cadmium, accumulation, vegetables, Copșa Mică.

INTRODUCTION

Vegetables constitute an important part of the human diet and in recent years, their consumption is increasing gradually, particularly due to the increased awareness on the food value of vegetable. Sometimes, they contain toxic elements over a wide range of concentrations[1].

The accumulation of heavy metals from soils to vegetables has been studied extensively due to the close relation of vegetables to human health. Yusuf *et al*. (2006) quoted by Chao *et al*. (2007) studied the concentrations of Cd, Cu and Ni in five different edible vegetables from three industrial and three residential areas of Lagos City, Nigeria, and concluded that these heavy metals in industrial areas were much higher than those of the residential areas.

Heavy metals are one of the important types of contaminants that can be found on the surface and in the tissue of fresh vegetables. In order to protect public health, it is essential to keep contaminants at levels which are toxicologically acceptable, so Commission Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

Huang *et al*. (2021) analyzed the heavy metal contents in vegetables in a peri-urban area in southeast China and showed the hazard index caused by the intake of local heavy-metal-containing vegetables was significantly higher than 1, indicating significant adverse health effects on local residents.

Cadmium, lead and zinc are the main contaminants that posed a risk to the health of the population in the area affected by pollution from most important factory for processing non-ferrous ores – Copșa Mică, Romania. Despite of the historical heavy metals contamination, the individual gardens are still important for local communities. In Copșa Mică area, local community can cease to cultivate of highly contaminated fields to avoid the harmful effects of metals on human health but there are still a lot of individual gardens where owners continue to use them for vegetables production.

Ćwieląg-Drabek *et al*. (2020) considered that within such gardens, it would be desirable to abandon vegetable and fruit crops that may be harmful to consumers and use them only for recreational purposes.

Among heavy metals, Cd is highly toxic to plants and animals even at very low concentrations due to its non-essentiality in living organisms[5]. Due to highly mobility in soil, cadmium can be slowly and consistently transferred from contaminated soils into food crops increasing Cd exposure to human beings in the long-term through the food chain[6]. The high dose exposure to cadmium (Cd) by ingestion can cause severe stomach disease. Long-term exposure to low doses causes kidney disease, which damages the renal tubules and impedes the absorption of calcium (Ca), leading to brittle bones that are less resistant to breakage[7].

Therefore, the European Food Safety Authority adopted an opinion on cadmium in food and, in view of the toxic effects of cadmium the Authority established a tolerable weekly intake for cadmium of 2.5 µg/kg body weight. It also concluded that subgroups such as vegetarians, children, smokers and people living in highly contaminated areas may exceed the tolerable weekly intake by about 2-fold. As measure to achieve this target, the values limits for cadmium in some foodstuff were reduced according with Commission Regulation (EU) 2021/1323.

Data from previous studies indicates that vegetables could be classified according with their ability to accumulate heavy metals in edible parts, as follows:

leafy/stem vegetables > root vegetables > tubercles > fruiting vegetables/fruits.

Besides the vegetable species and cultivars, the metals uptake is also governed by the physico-chemical parameters of soils. The total metal content in soils is considered as a good predictor parameter on cadmium accumulation in vegetables.

Main leafy vegetables identified in studied area were lettuce, celery and parsley.

Therefore, this study attempts to quantify quality of some leafy vegetables grown in individual gardens from contaminated area, Copșa Mică.

The study will provide a theoretical reference for a safe production of leafy vegetables in contaminated areas.

MATERIALS AND METHODS

The present study was carried out during 2019–2021 in one of the critical areas in terms of heavy metal contamination, Copșa Mică. The studied area includes seven localities: Avente Sever, Agârbiciu, Soala, Micăsasa, Târnava, Copșa Mica and Bazna. This area presents the highest risk of interception of heavy metals through locally produced local food, due to the large abundance of agro-systems in the structure of local socio-ecological systems.

During this study were collected 55 soil samples, 55 parsley (*Petroselium crispum*), 45 celery (Apium graveolens) and 20 lettuce (*Latuca sativa*) samples from individual gardens located in contaminated area. Each soil sample was a mixture of 6 sub-samples that were collected from the surface soil (0–20cm). The corresponding leafy vegetables was a mixture of shoots and leaves from mature plants from each garden.

The soil samples were air-dried at room temperature and then crushed and sieved through 2 and 0.2 mm meshes, before storage and analysis.

The withered and decay tissues were removed from the leafy vegetables samples and then the edible parts were washed twice in tap water before being cut and frozen.

Soil pH was measured using the potentiometric method (1:2.5 w/v, soil: water). The soil organic carbon content (SOC) was determined on 0.2mm grounded soil samples using dichromate oxidation followed by titration with ferrous ammonium sulphate (Walkley and Black, 1934).

The available phosphorus and potassium in soil were extracted with ammonium acetate lactate (AL extractable) at pH 3.75 (Romanian Standard STAS 7184/19-82 based on the Egner–Riehm-Domingo method, Egner et al., 1960) and analysed by flame photometry (for potassium content) and UV/Vis spectrometry (for phosphorus content).

The pseudo-total concentration of Cd was determined only in the soil samples by atomic absorption spectrometry, after extraction by the aqua regia – microwave digestion method. Microwave digestion was performed using 10 mL of aqua regia (7.5 mL HCl and 2.5 mL HNO_3) at 140 °C for 30 min., method developed according to SR ISO 11466:1999. A certified soil reference material (ERM–CC141) was used to ensure the accuracy of the analytical data. The average recovery value of Cd in the reference soil was 85%.

The vegetable samples were digested with nitric acid in a microwave digestion system. The metal content was measured using atomic absorption spectrometry (Flame GBC 932AA or Graphite furnace GBC SavanatAAZ).

Means of data were compared by least significant difference tests at $p < 0.05$.

Linear regression analyses were performed using the statistical package STATISTICA CSS (Complete Statistical System by StatSoft, Tulsa, OK, USA).

RESULTS AND DISCUSSIONS

A summary of main soil chemical characteristics and metals contents are presented in Table 1. Soil pH ranged from slightly acid (pH 6.34) to slightly alkaline (pH 8.26) with mean pH value was 7.47.

Soil organic carbon (SOC) ranged from 1.47 to 3.92 % with average value 2.44%, nitrogen content in soil ranged from 0.16 to 0.60 % with average value 0.27%, levels of available phosphorus (PAL) ranged from 67 mg kg^{-1} to 744 mg kg^{-1} with average value 379 mg kg^{-1} and KAL contents ranged between 262 mg kg^{-1} and 1360 mg kg^{-1} with average content 615 mg kg^{-1}.

The chemical parameters of soils collected from private gardens included in this study are affected by the high anthropization level and the diversity of cultivation practices. The heterogeneity of the pH values is an effect of the different cultivation practices such as liming, organic fertilization or irrigation used in private gardens studied.

Also, the average contents for Cd, Cu, Pb and Zn exceeds the alert thresholds for sensitive use of land (according with Order 756/1997).

Total Cd in soils ranged from 0.10 to 35.8 mg kg^{-1} covering a range that has been classified as background levels to highly polluted soil. The same situation was noticed for Pb and Zn. The highest value for zinc content was obtained for a sample soil collected from a private garden located in Axente Sever (3168 mg kg^{-1}). This value exceeds the intervention threshold established for less sensitive use of land (1500 mg kg^{-1}).

The soil-plant transfer model is the most used model for predict metal in vegetables.

Therefore, in our study, the total metal content was used as variable to develop the stochastic models for estimating the metal content of leafy vegetables. The selection of this parameter was also based on the fact that it is the only indicator for which reference values are found in the regulations for assessing the degree of pollution (Order 756/1997).

Table 1

Summary of soil properties and metals contents in soil

Soil properties	Unit	Range of variation			Geometric mean	Median	Arithmetic mean
pH		6.34	–	8.26	7.46	7.58	7.47
Cd	mg/kg	0.10	–	35.81	2.77	4,92	6.03
Pb	mg/kg	19	–	952	117	133	171
Zn	mg/kg	124	–	1811	366	358	454
Cu	mg/kg	25	–	132	63	62	67
Mn	mg/kg	219	–	910	569	621	592
Organic C	%	1.47	–	3.92	2.37	2.35	2.44
Total N	%	0.16	–	0.60	0.26	0.26	0.27
Available P (PAL)	mg/kg	67	–	744	335	348	379
Available K (KAL)	mg/kg	262	–	1360	559	580	615

According to log-log diagram (Figure 1), the parsley (leaf) plant accumulated high amounts of cadmium, lead and zinc. The values of Cd, Pb and Zn contents in parsley were correlated with total metal content in soil by means of a power regression equation.

For cadmium, the value of linear correlation coefficient ($r = 0.373^{**}$), corresponding to linear form of the regression equation was significantly ($p<0.05$) indicating a good correlation between the cadmium content in parsley plant and the cadmium content in soil.

The high cadmium accumulation capacity of aromatic herbs, like parsley, was observed by other authors[9] (Säumel *et al*., 2012) in studies carried out in another contaminated areas. Also, for zinc, the value of linear correlation coefficient ($r = 0.389^{**}$), corresponding to linear form of the regression equation was significantly ($p<0.05$). A highly strong correlation was noticed for Pb content in parsley leaves and total Pb content in soil ($r = 0.556^{***}$).

For copper there is no significant correlation between copper content in parsley leaves and total Cu content in soil. The lower ability of parsley to accumulate copper was reported by Pruteanu *et al*., (2022). According to these authors, the values of the transfer coefficient for contaminated soils it decreases spinach > strawberries > carrots > parsley > radishes > blackcurrants > plums.

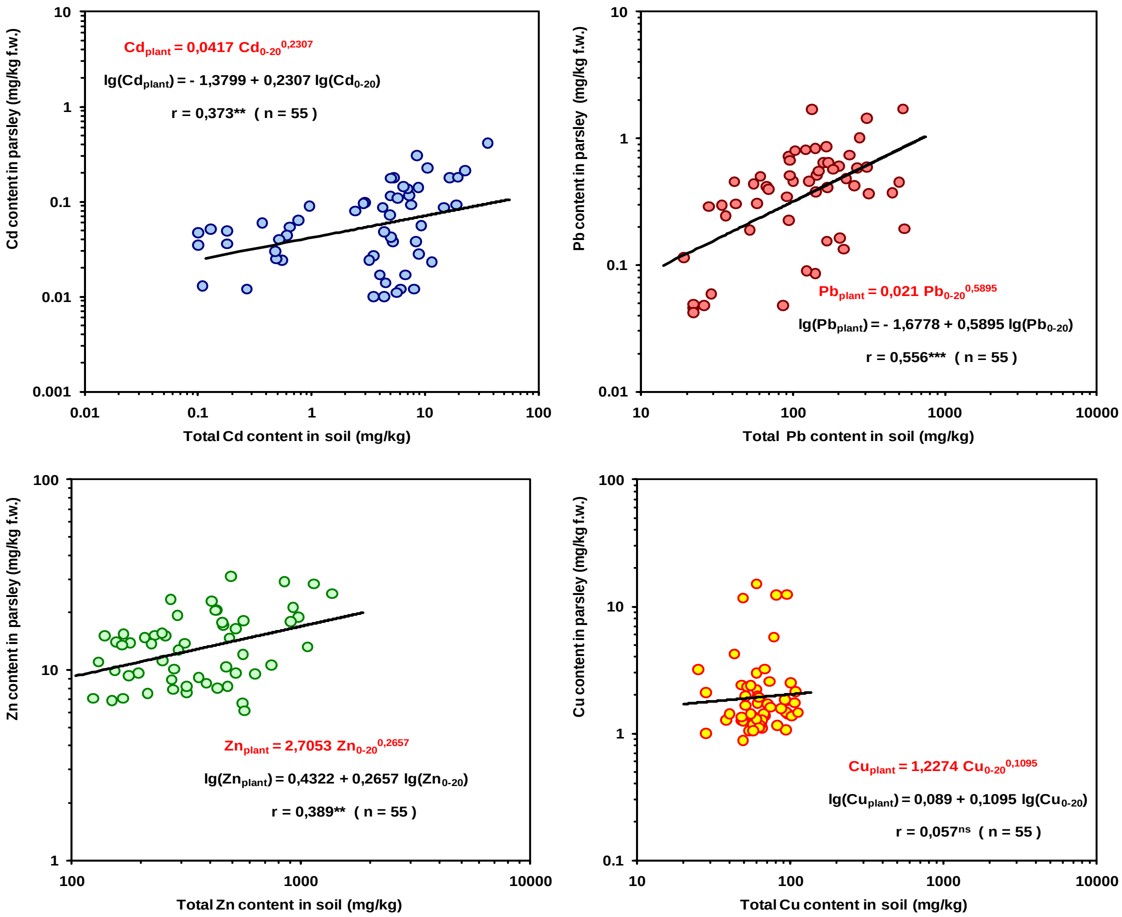

Figure 1. Log-log diagram for power regression curves that estimate the stochastic dependency between total metal content in soil and metal content in parsley (leaves).

Celery (*Apium graveolens* L.) ranks with one of the most important green vegetables which widely planted in the individual gardens from studied areas. In order to assess the quality of celery plants cultivated in individual gardens from studied area, 45 samples were collected. The Figure 2 presents the dependency of metals (Cd, Cu, Pb and Zn) in edible parts of celery (leaf) on total metal (Cd, Cu, Pb and Zn) content in soil.

The value of linear correlation coefficient ($r = 0.724^{***}$), corresponding to linear form of the regression equation was highly significant indicating a very strong correlation between the cadmium content in celery plant and the cadmium content in soil.

Also, Xiao *et al*. (2018) reported that total Cd in soil can be used to estimate soil-crop Cd transfer in celery plant. According to observation of Arsenov *et al*., (2021) celery showed strong phytoextraction ability (99.9 μg/g Cd of dry weight) with high potential to tolerate Cd due to the efficient antioxidative mechanisms.

Also, very strong correlations were noticed between the total lead and zinc contents in soil and their contents in the celery leaves ($r_{Pb} = 0.491^{***}$: $r_{Zn} = 0.628^{***}$).

The lead content values in celery plants collected during this study ranged between 0.011 mg kg^{-1} and 5.79 mg kg^{-1}. The highest value was reported for celery samples collected from an individual garden located in Copșa Mică.

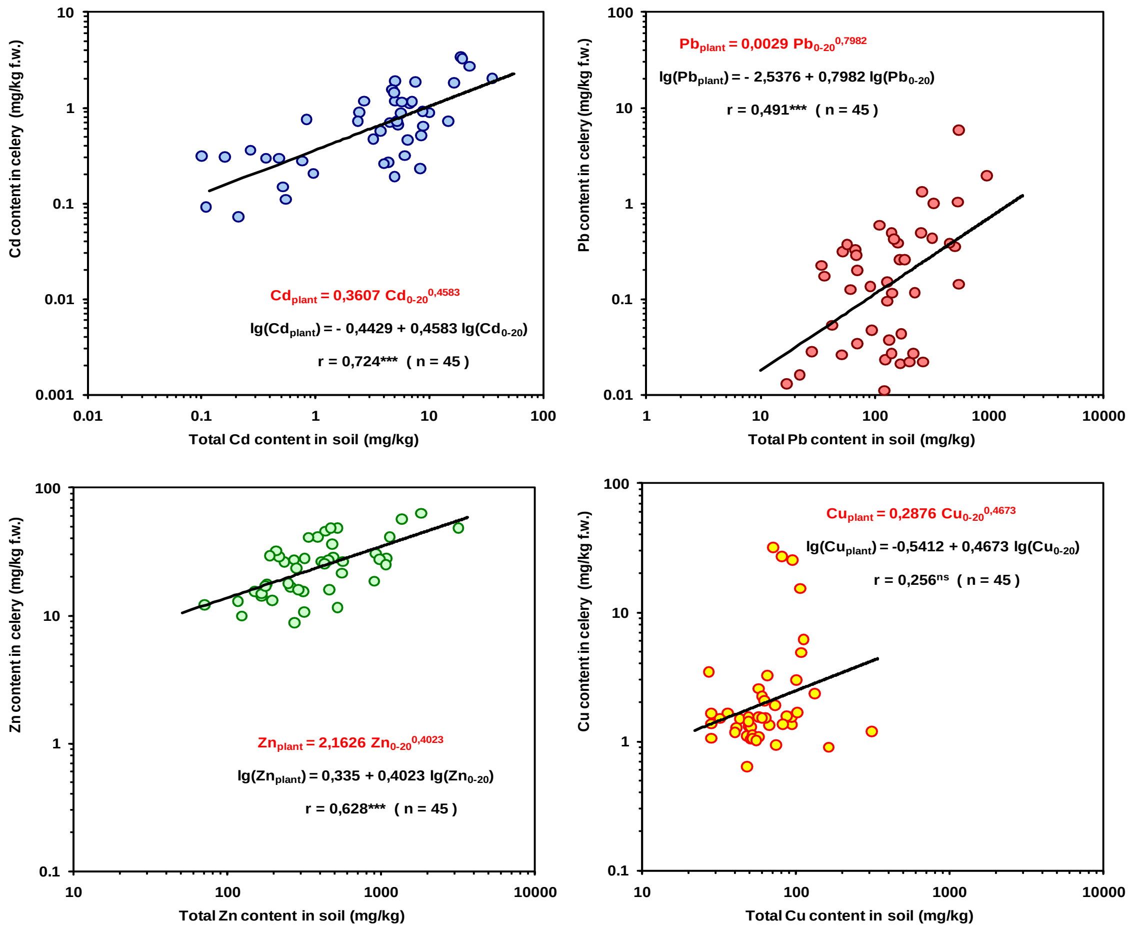

Figure 2. Log-log diagram for power regression curve that estimates the stochastic dependency between total cadmium content in soil and cadmium content in celery (leaves).

The dependency of metal (Cd, Cu, Pb and Zn) content in lettuce on total metal (Cd, Cu, Pb and Zn) content in soil is presented in Figure 3.

Bidar *et al*., (2020) noticed that, lettuce has high capacity of accumulating cadmium.

In our study, the values of cadmium content in lettuce ranged between 0.015 mg kg^{-1} and 1.820 mg kg^{-1}. According with EU Regulation 2021/1323, the maximum allowable value for cadmium for leafy vegetables is 0.10 mg kg^{-1}.

The value of linear correlation coefficient ($r = 0.754^{***}$), corresponding to linear form of the regression equation was highly significant indicating a very strong correlation between the cadmium content in lettuce leaves and the cadmium content in soil.

The value of linear correlation coefficient ($r = 0.660^{***}$), corresponding to linear form of the regression equation was highly significant indicating a very strong correlation between the zinc content in lettuce leaves and the zinc content in soil.

The observations of previous studies suggest that lettuce is among the plant species that tolerates high concentrations of Zn. Moreira *et al*., (2021) considered that despite the fact that Zn is an essential micronutrient, visual symptoms were detected for Zn content in soil as low as 300 mg kg^{-1}, although the effects were much more pronounced at 1200 mg kg^{-1}.

For Pb and Cu values of linear correlation coefficient corresponding to linear form of the regression equation was no significant indicating a weak correlation between the metal content in lettuce leaves and the metalcontent in soil.

The investigations relied on a large-scale field survey and the results indicated that all vegetables included in this study have high capacities to accumulate cadmium, lead and zinc in edible parts. There were many vegetables collected from studied area whose cadmium concentrations exceeded the threshold values (0.10 mg kg^{-1}). Considering this, leafy vegetables ability to accumulate cadmium, lead and zinc can be a problem when it comes to edible parts. In the point of view of toxicology and food safety, growing of leafy vegetables should be strictly regulated and distinguished based on the purpose of growing, and further vegetables usage.

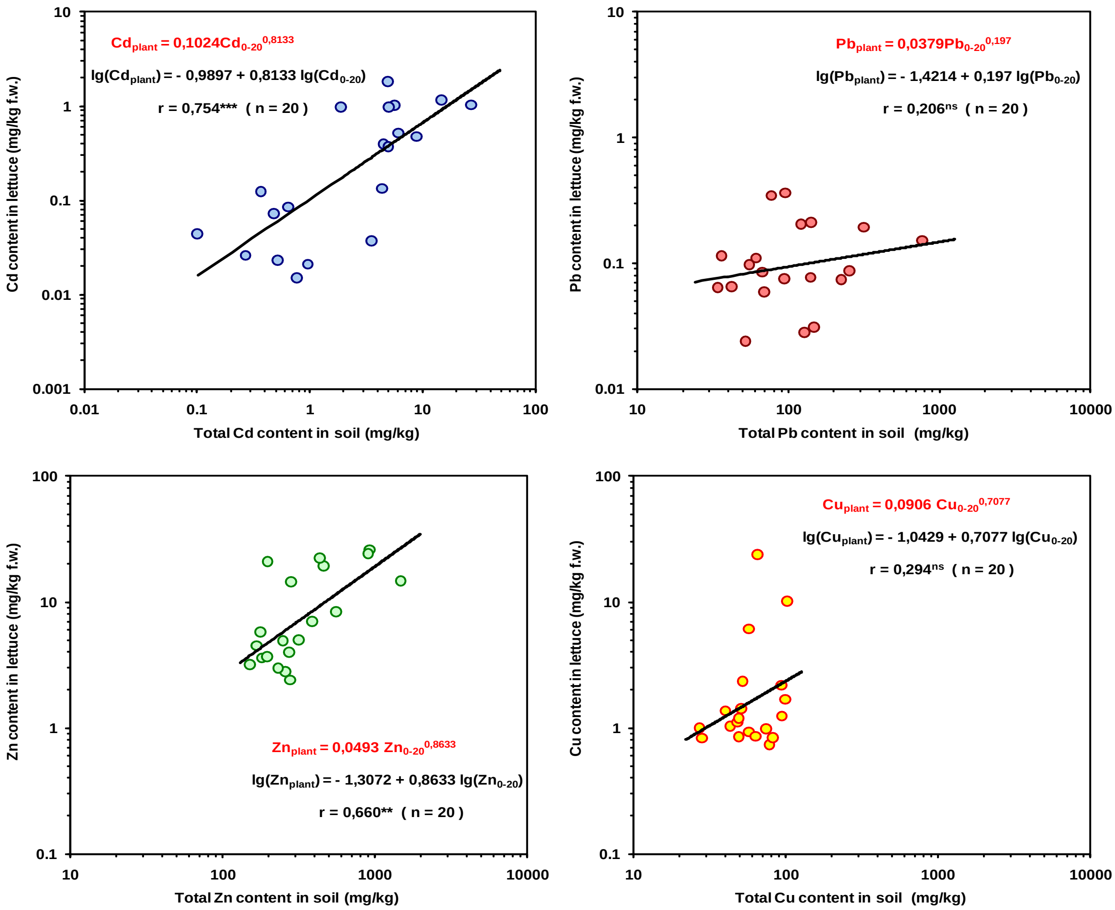

Figure 3. Log-log diagram for power regression curve that estimates the stochastic dependency between total cadmium content in soil and cadmium content in lettuce (leaves).

CONCLUSIONS

It is clearly evident from the findings of present study that most of the leafy vegetables are hyper accumulators of the non-essential heavy metals such as lead and cadmium. The diverse leafy vegetables species also showed marked differences in respect of metal uptake which could be emphasized for selection of vegetable crops for cultivation on metals contaminated soils depending on their metal uptake potential and their accumulation to edible part.

The consumption of self-produced vegetables from contaminated areas is of great concern because these products are not subject to control of the metal concentrations unlike commercial foodstuff production, which is constrained to regulatory threshold values established by EC.

Using the regression equations developed during this study, cadmium and zinc accumulation in parsley, celery and lettuce were quantitatively predicted by the measurement of total metal content in soil.

The results of our study can be used in all contaminated areas where individual gardens exist, to ensure a comprehensive understanding of where potential hazards exist and how to reduce the risk on human health.

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