THE DISTRIBUTION AND MOBILITY OF CADMIUM IN SOILS CULTIVATED WITH VEGETABLES. (I) TRADITIONAL CROPS

DISTRIBUŢIA ŞI MOBILITATEA CADMIULUI ÎN SOLURI CULTIVATE CU LEGUME. (I) CULTURI TRADIŢIONALE

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Abstract*. A number of 16 samples of soils cultivated with vegetables (tomato, cucumber, pepper, cauliflower and celery) using traditional technologies, in open filed and plastic tunnels, was used for this experiment. Soil samples were taken from a depth of 0-20 cm from the plant row and the interval between the rows. In studied soils, the total cadmium content varied between 1.28–2.61 $\mu g.g^{-1}$. The average cadmium content in mobile fractions is 0.4717 $\mu g.g^{-1}$ (24.72 % from Cd(T)), in fractions with medium mobility is 1.2808 $\mu g.g^{-1}$ (6.05 % from Cd(T)), and in fix fraction is 0.1561 $\mu g.g^{-1}$ (7.98 % from Cd(T)), respectively. The experimental results indicates that in studied soils are not polluted with cadmium, but the risk potential is significant, due to the high weight of mobile fractions from total cadmium content. According to the obtained results, 24.72 % is directly accessible to the plants (major risk potential) and 67.05 % is indirectly accessible to the plants (latent risk potential).*
Key words: cadmium, chemical speciation, vegetables cultures.

Rezumat*. Pentru studii s-au utilizat 16 probe de sol cultivat cu legume (tomate, castraveţi, ardei iute, conopidă şi ţelină), după tehnologii tradiţionale, în câmp şi în solarii. Probele de sol au fost prelevate de la adâncimea de 0-20 cm, de pe rândul de plante şi de pe intervalul dintre rânduri. În solurile studiate, conţinutul total de cadmiu variază între 1,28–2,61 $\mu g.g^{-1}$. Conţinutul mediu de cadmiu în fracţiunile mobile este 0,4717 $\mu g.g^{-1}$ (24,72 % din Cd(T)), în fracţiunile cu mobilitate medie este 1,2808 $\mu g.g^{-1}$ (67,05 % din Cd(T)), iar în fracţiunile fixe este 0,1561 $\mu g.g^{-1}$ (7,98 % din Cd(T)). Datele experimentale indică faptul că solurile studiate nu sunt poluate cu cadmiu, însă potenţialul de risc a cadmiului este semnificativ, datorită ponderii ridicate a fracţiunilor mobile: din conţinutul total de cadmiu, în medie, 24,72 % este direct accesibil plantelor (potenţial major de risc), iar 67,05 % este indirect accesibil plantelor (potenţial latent de risc).*
Cuvinte cheie: cadmiu, speciaţie chimică, culturi legumicole

INTRODUCTION

The problems regarding the distribution and biodisponibility of cadmium in soils cultivated with vegetables has an important place in agrochemical studies, due to high toxicity and major perturbations that this heavy metal may caused in mineral and biologic systems from soils (Alloway, 1990, Bulgariu, 2006, Pedias, 1992, Ross, 1994). Cadmium is one of the most toxic heavy metal (being included in A.I toxicity class, is very mobile and has a high biodisponibility, in the conditions of most soils types (Adriano, 2001; Bourg, 1995). In soil-plant-water systems, the cadmium has a remarkable tendency for concentration in soil solution, colloids and organic matter (as chemical species with high mobility), and progressive bioaccumulation in plants and animal organisms. Under these conditions, the cadmium can manifest, simultaneous, both toxic effects on the biological systems, and some high harmful effects on the dynamics of nutritive and microelements, organic matter or of biochemical processes from soils. The toxic effects are conditioned by different limits of cadmium concentration, but the harmful effects are restricted, not only by cadmium concentration, but also by type and content of speciation forms of this element (Bulgariu, 2007, Kabata-Pendias, 1992).

In agricultural soils, the normal content of cadmium varied between 0.01 and 2.00 $\mu g.g^{-1}$ (average: 0.35 $\mu g.g^{-1}$), and the maxim admissible concentration of cadmium in such soils is < 1 $\mu g.g^{-1}$, value accepted as reference in most of the countries. In Romania, according to The Order of Water, Forest and Environmental Protection Ministry no 756/1997, it has been establish the following limits for cadmium: normal content 1 $\mu g.g^{-1}$, alert threshold 3 $\mu g.g^{-1}$ and intervention threshold 5 $\mu g.g^{-1}$. For the countries from European Union, it was proposed, as limit value of cadmium in agricultural soils, especially for those cultivated with vegetables, to be < 0.1 $\mu g.g^{-1}$. The cadmium content in vegetables varied between 0.016 and 0.130 $\mu g.g^{-1}$ (average: 0.028 $\mu g.g^{-1}$), and these are higher than in case of other agricultural products (Adriano, 2001).

In soils cultivated with vegetables, the speciation, migration and inter-phases distribution processes of cadmium have a particular character, due mostly to the frequent modification, more or less severe, of the lithology and of the chemical-mineralogical characteristics of these soils. In consequence, the mobility, biodisponibility and risk potential of cadmium, in soils cultivated with vegetables are difficult to estimated, and the experimental data have not always a convergent character.

MATERIAL AND METHOD

For experiments a number of 16 samples of soil cultivated with vegetables (tomatoes, cucumbers, pepper, cauliflower and celery) in the field and plastic tunnels using traditional technologies (table 1) was used. Soil samples were taken from 0-20 cm depth (A horizon), from the plants row and the interval between rows, in August 2009, from AS Maxim Tg. Frumos Ranch. The determination of total cadmium content was done on average samples (triplicate) by flame atomic absorption spectrometry (Vario 6 FL Spectrometer, with mono-element lamp), after the soil samples weathering with HNO_3 conc. + $HClO_4$ conc. mixture (Dean). The fix and mobile cadmium fractions (table 1) have been separated from soil samples by sequential solid/liquid extraction in seven steps (Bulgariu, 2008, Sahuquillo,2003), in aqueous two-phase PEG 2000 – inorganic salt systems (Bulgariu,2005). From obtained extracts, the cadmium was determined by flame atomic absorption spectrometry.

The internal control of analytical data was performed on parallel samples by X-ray fluorescence spectrometry (Epsilon 5 XRF Spectrometer). The results presented in this paper the arithmetic mean of three determinations made on the same sample. Supplementary information about the speciation and occurrence forms of cadmium in studied soils have been obtained by microscopy, IR and Raman spectrometry, performed on soils samples, after marking cadmium with p,p'-dinitro-Sym-diphenylcarbazide (Bulgariu, 2007).

RESULTS AND DISCUSSIONS

Total cadmium. In studied soils, the total cadmium content, Cd(T), varied between 1.28 and 2.61 $\mu g.g^{-1}$, and these values are higher than the normal content of cadmium in soils, and lower than the value of alert threshold for sensitive soils (table 1). The cadmium content from soils is higher in case of crops from solariums (1.63–2.97 $\mu g.g^{-1}$) than in case of crops from the field (1.28–1.68 $\mu g.g^{-1}$). In function of types of vegetables, the total cadmium content in soils follows the order: tomatoes – Balett (2.16–2.97 $\mu g.g^{-1}$) > tomatoes-Venice (1.95–2.61 $\mu g.g^{-1}$) > tomatoes – Izmir (1.73–2.15 $\mu g.g^{-1}$) > cucumbers (1.63–2.17 $\mu g.g^{-1}$) > cauliflower (1.41–1.68 $\mu g.g^{-1}$) > celery (1.28–1.35 $\mu g.g^{-1}$). In case of crops from plastic tunnels, the content of cadmium from soils samples on the row is higher than for the samples of the interval between the rows – the difference between these being by 1.63–2.97 $\mu g.g^{-1}$ (average: 0.46 $\mu g.g^{-1}$). In case of crops from the field, the content of cadmium from the samples on the row is lower than for the samples from the interval between the rows – the difference between these being by 1.28–1.68 $\mu g.g^{-1}$ (average: 0.17 $\mu g.g^{-1}$). The cadmium content do not presents significant correlations with the main chemical-mineralogical components, pH, redox potential or soluble salts content of studied soils.

Mobile fractions of cadmium. The cadmium concentration in mobile fractions (with high biodisponibility, F.1 and F.2 fractions) varied between 0.2094 and 0.7323 $\mu g.g^{-1}$ (average: 0.4717 $\mu g.g^{-1}$), and the weight of these fraction at total cadmium content is 16.35–31.73 % from Cd (T) (average: 24.72 %). The data presented in table 1 indicate that the weight of mobile fractions at total cadmium content is higher than the residual fractions (inaccessible for plants, F.7 fraction), but is lower than the “pseudo-mobile” fractions. This observation is in good agreement with literature data and shows that the total amount of cadmium existing in the studied soils, on average only 24.72% is direct accessible to the plants, and this value determined the effective risk potential of cadmium for vegetables crops.

In case of crops from the field, the cadmium concentration from mobile fractions (0.2094–0.4246 $\mu g.g^{-1}$, average: 0.3244 $\mu g.g^{-1}$; 16.35–25.27 % from Cd(T), average: 22.46 %) is lower than in case of cultures from plastic tunnels (0.4092–0.7323 $\mu g.g^{-1}$, average: 0.5208 $\mu g.g^{-1}$; 17.46 % from Cd(T), average: 25.47 %). The concentration of cadmium from soil samples on the row (0.2094–0.7323 $\mu g.g^{-1}$, average: 0.4628 $\mu g.g^{-1}$; 16.35–27.89 % from Cd(T), average: 22.17 %) is lower than in case of soil samples on the interval between the rows (0.3668–0.6350 $\mu g.g^{-1}$, average: 0.4806 $\mu g.g^{-1}$; 21.53–31.73 % from Cd(T), average: 27.27 %).

In function of cultivated vegetables type, the concentration of mobile cadmium in studied soils follows the order: celery (0.2094–0.3668 μg.g^{-1}; 16.35–27.17 % from Cd(T)) < cauliflower (0.2971–0.4246 μg.g^{-1}; 21.07–25.27 % from Cd(T)) < pepper (0.3850–0.5132 μg.g^{-1}; 22.78–27.89 % from Cd(T)) < cucumbers (0.4092–0.5320 μg.g^{-1}; 21.53–31.73 % from Cd(T)) < tomatoes – Venice (0.4559–0.5734 μg.g^{-1}; 17.46– 9.40 % from Cd(T)) < tomatoes – Izmir (0.4821–0.5340 μg.g^{-1}; 22.42–30.86 % from Cd(T) < tomatoes – Balett (0.6350–0.7323 μg.g^{-1}; 24.65–29.39 % from Cd(T)).

Fractions with medium mobility (pseudo-mobile; with latent mobility) of cadmium. The concentration of cadmium in pseudo-mobile fractions (from which cadmium can be only partial mobilized in the conditions of studied soils; F.3, F.4, F.5 and F.6 fractions) varied between 0.9029 and 1.9608 μg.g^{-1} (average: 1.2808 μg.g^{-1}), and the weight of these fractions at the total cadmium content is 59.74–76.11 % from Cd(T) (average: 67.05 %). These results indicate that the total amount of cadmium existing in the studied soils, on average only 67.05 % is indirectly accessible to the plants (only in certain conditions), and this value determined the latent risk potential of cadmium for the vegetables cultures. The higher part from pseudo-mobile cadmium is bonded by organic matrix (F.6 fraction; 26.28–39.21 % from Cd(T), average: 35.14 %) and by the organic-mineral complexes (F.4 fraction; 15.08–23.29 % from Cd(T), average: 18.52 %) – table 1. In case of cultures from the field, the cadmium concentration in the pseudo-mobile fractions (0.9029–1.1322 μg.g^{-1}, average: 0.9982 μg.g^{-1}; 66.88–76.11 % from Cd(T), average: 70.03 %) is lower than in case of cultures from solariums (0.9817–1.9608 μg.g^{-1}, average: 1.3750 μg.g^{-1}; 59.74-71.91 % from Cd(T), average: 66.06 %). The concentration of pseudo-mobile cadmium from soil samples on the row (0.9743–1.9608 μg.g^{-1}, average: 1.4171 μg.g^{-1}; 62.46–76.11 % from Cd(T), average: 69.01 %) is higher than in case of soil samples from the intervals between the rows (0.9029–1.3723 μg.g^{-1}, average: 1.1444 μg.g^{-1}; 59.74–70.71 % from Cd(T), average: 65.10 %). In function of cultivated vegetables type, the concentration of pseudo-mobile cadmium follows the order: celery (0.9029–0.9743 μg.g^{-1}; 66.88–76.11 % from Cd(T)) < cauliflower (0.9835–1.1322 μg.g^{-1}; 67.39–69.75 % from Cd(T)) < pepper (1.1951–1.1493 μg.g^{-1}; 62.46–70.71 % from Cd(T)) < cucumbers (0.9817–1.4409 μg.g^{-1}; 60.22–68.66 % from Cd(T)) < tomatoes – Izmir (1.1017–1.5461 μg.g^{-1}; 63.68–71.91 % from Cd(T) < tomatoes – Venice (1.1651–1.8848 μg.g^{-1}; 59.74–70.81 % from Cd(T)) < tomatoes – Balett (1.3723–1.9608 μg.g^{-1}; 63.53–66.02 % from Cd(T)).

CONCLUSIONS

In studied soils, the total cadmium content varied between 1.28 and 2.61 μg.g^{-1}, and these values are higher than the normal content of cadmium in soils, but lower than the value of alert threshold for sensitive soils.

Table 1

The cadmium contents (µg.g^{-1}) of fix and mobile fractions in studied soils

No.	Details	Loc.[1]	Cd(T)	F.1	F.2	F.3	F.4	F.5	F.6	F.7
TFMax.1	Solar / cucumbers	Interval	1.90	0.1324	0.2768	0.0701	0.3290	0.1871	0.7185	**0.1848**
TFMax.2	Solar / cucumbers	Row	2.17	0.1553	0.3767	< LD*	0.4346	0.2241	0.7822	**0.1942**
TFMax.3	Solar / tomatoes -Izmir	Interval	1.73	0.2017	0.3323	0.0754	0.3219	0.1088	0.5956	**0.0892**
TFMax.4	Solar / tomatoes -Izmir	Row	2.15	0.1876	0.2945	0.1348	0.4762	0.1055	0.8296	**0.1154**
TFMax.5	Field / cauliflower -Fremont	Interval	1.68	0.1547	0.2699	0.1206	0.2929	0.1034	0.6153	**0.1164**
TFMax.6	Field / cauliflower -Fremont	Row	1.41	0.0892	0.2079	0.0912	0.2243	0.1229	0.5451	**0.1276**
TFMax.7	Field / celery-Mentor	Interval	1.35	0.1063	0.2605	0.1236	0.2037	0.0579	0.5177	**0.0766**
TFMax.8	Field / celery-Mentor	Row	1.28	0.0756	0.1338	0.0633	0.2982	0.1108	0.5020	**0.0911**
TFMax.9	Solar / cucumbers -Merengue	Interval	1.63	0.2166	0.3007	0.0857	0.2563	0.0828	0.5569	**0.1248**
TFMax.10	Solar / cucumbers -Merengue	Row	2.09	0.2217	0.2587	0.1897	0.4510	0.1329	0.6604	**0.1703**
TFMax.11	Solar / pepper	Interval	1.69	0.1103	0.2747	0.1451	0.3199	0.0866	0.6435	**0.1076**
TFMax.12	Solar / pepper	Row	1.84	0.1486	0.3646	0.1722	0.4060	0.0874	0.4837	**0.1768**
TFMax.13	Solar / tomatoes-Venice	Interval	1.95	0.2687	0.3047	0.0854	0.3355	0.1474	0.5968	**0.2043**
TFMax.14	Solar / tomatoes -Venice	Row	2.61	0.2067	0.2492	0.2513	0.4084	0.2202	0.9685	**0.2946**
TFMax.15	Solar / tomatoes -Balett	Interval	2.16	0.2607	0.3743	0.1185	0.3514	0.2188	0.6836	**0.1531**
TFMax.16	**Solar / tomatoes -Balett**	**Row**	**2.97**	**0.3145**	**0.4178**	**0.2129**	**0.5666**	**0.1983**	**0.9830**	**0.2714**

[1]Location. Place of sampling: interval – samples of the interval between the rows, row – samples on the row. **F.1** - soluble fraction in water (extractant: H_2O). **F.2** – easy extractable fraction (extractant: CH_3COONH_4 1.0 M, pH=7). **F.3** – fraction sensitive to the acidification processes; bonded by carbonates (extractant: CH_3COONa 1.0 M, pH=5; CH_3COOH). **F.4** – fraction sensitive to the complexation; bonded by non-silicates mineral phases (extractant: CH_3COONa -CH_3COOH / EDTA 10^{-2} M). **F.5** – easy reducible fraction; bonded by Fe and/ or Mn oxides (extractant: $(NH_4)_2C_2O_4$ / $H_2C_2O_4$). **F.6** – oxidisable fraction; bonded by organic matter and / or sulphurs (extractant: $K_4P_2O_7$). **F.7** – fraction bonded by matrix and silicates / aluminosilicates mineral phases; fix fraction, residual (extractant: $HClO_4$+HNO_3). LD- detection limit of atomic Absorption Spectrometer. Cd(T) – total cadmium content.

The average cadmium content in mobile fractions is 0.4717 µg.g^{-1} (24.72 % from Cd(T)), in the fractions with medium mobility is 1.2808 µg.g^{-1} (67.05 % from Cd(T)), and in fix fractions is 0.1561 µg.g^{-1} (7.98 % from Cd(T)). The higher part of cadmium with latent mobility is bonded by organic matter (26.28–39.21 % from Cd(T)) and by organic-mineral complexes (15.08–23.29 % from Cd(T)).

The experimental results indicate that the studied soils are not polluted with cadmium, but the risk potential of this is significant due to the high weight of mobile fractions: from total cadmium content, an average of 24.72 % is directly accessible to the plants (major risk potential), and 67.05 % is indirectly accessible to the plants (latent risk potential).

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