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

DISTRIBUŢIA ŞI MOBILITATEA CROMULUI ÎN SOLURILE CULTIVATE CU LEGUME. (I) CULTURI TRADIŢIONALE

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Abstract. *Research bring a series of new data concerning the speciation and distribution processes and risk potential of chrome in soil cultivated with vegetables. A number of 16 samples of soils cultivated with vegetables (tomatoes, cucumbers, pepper, cauliflower and celery), in the open field and plastic tunnels, using traditional technologies (was used for thi experiment). Soil samples were taken from 0-20 cm depth interval of the row and the interval between rows. The experimental results have indicates that the studied soils are not contaminated and have a high supply level of chrome. Towards to chemical-mineralogical components of soils, the chrome has a heterogeneous distribution, and the speciation and distribution inter-phases equilibriums are very sensitive to the variation of physic-chemical conditions. The risk potential of chrome is very low, due to the reduced mobility and biodisponibility of speciation forms and due to high probability of reducing Cr(IV) to Cr (III), in the conditions of studied soils.*

Key words: chrome, chemical speciation, vegetables cultures.

Rezumat. *Studiile aduc o serie de date noi referitoare la procesele de speciaţie şi de distribuţie, respectiv potenţialul de risc a cromului în solurile cultivate cu legume. 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 din intervalul de adâncime 0-20 cm de pe rândul de plante şi de pe intervalul dintre rânduri. Datele experimentale au arătat că solurile studiate nu sunt contaminate şi au un nivel ridicat de aprovizionare cu crom. În raport cu componenţii chimico-mineralogici ai solurilor, cromul prezintă o distribuţie heterogenă, iar echilibrele de speciaţie şi distribuţie interfazică sunt foarte sensibile la variaţiile condiţiilor fizico-chimice. Potenţialul de risc a cromului este foarte mic, datorită mobilităţii şi biodisponibilităţii reduse a formelor de speciaţie şi probabilităţii ridicate de reducere a Cr(IV) la Cr(III) în condiţiile solurilor studiate.*

Cuvinte cheie: crom, speciaţie chimică, culturi legumicole

INTRODUCTION

The chrome is a common trace element for most of soil types, with an important role in pedogenetic processes, plants nutrition and animal metabolism. The chrome content in soils varied in relatively large limits, as a function of type of soil and the utilization way of these. Worldwide is considered that the normal values of the chrome content for agricultural soils are between 10 and 150 μg.g^{-1} (average: 40 μg.g^{-1}) (Adriano, 2001). In Romania, according to The Order of Water, Forest and Environmental Protection Ministry no 756/1997, the normal chrome content in agricultural soils is 30μg·g^{-1}. The maxim admissible contents of chrome in agricultural soils, accepted by most of the countries from the European Union, are 100 μg.g^{-1} for Cr(III) and 4 μg.g^{-1} for Cr(VI). In case of soils cultivated with vegetables, for the countries from European Union, was proposed that the limit values of Cr(VI) in soil to be < 1 μg.g^{-1} (Kabata-Pendias, 2007). The chrome content in vegetables varied between 0.16 and 0.5 μg.g^{-1} (average: 0.09 μg.g^{-1}), values which situated the vegetables, in the category of agricultural products with the high chrome contents. According to the data from literature can be mentioned that even the soils have, generally, high chrome contents, in agricultural products the chrome content is low (Davidescu, 1992).

The chrome distribution in soils is realized as species derivate from two oxidation states, which are thermodynamically stable: (i) Cr(III) with reduced mobility and toxic potential (similarly with Al and Fe), and (ii) Cr(VI) very mobile and with a high toxic potential, even at low concentrations (Katz, 1993). The toxicity of Cr(VI) (specially his mutagen and canceries effects) is by 10 – 100 times higher than Cr(III) (Lewis, 1982). The behaviour of chrome in soils is characteristic for each oxidation state, being determined by the influence of environment on the equilibrium between Cr(III) and Cr(VI), and by the interaction mechanisms of the species derivate from these oxidation states with the mineral and organic components of soils (Pantsar-Kallio, 2001; Stewart, 2003).

The data from literature regarding the distribution and mobility of chrome in soils cultivated with vegetables are mostly contradictories and insufficient for the formulation of some generalities. Ours studies bring a series of new data, concerning to the speciation and inter-phases distribution processes, the mobility, biodisponibility and risk potential of chrome, in soils cultivated with vegetables.

MATERIAL AND METHOD

For experiments have used 16 samples of soil cultivated with vegetables ((tomatoes, cucumbers, pepper, cauliflower and celery) in the field and solariums, using traditional technologies (table 1). Soil samples were taken from 0-20 cm depth (A horizon), on the plant row and the interval between rows, in August 2009, from AS Maxim Tg. Frumos Ranch. The drawing of samples, the sampling, the determination of pH and redox potential were performed according with usual methodology for soil analysis (Bulgariu, 2005; Bulgariu, 2007).

The determination of chrome was done on average samples, in the following way: (**i**) the total chrome – by flame atomic absorption spectrometry (Vario 6 Fl, with mono-element lamp), after samples weathering with HNO_3 conc. + $HClO_4$ conc. mixture; (**ii**) Cr(VI) – by UV-VIS molecular absorption spectrometry (Rayleigh V/9200 Spectrophotometer) with diphenil-carbazide, after extractive weathering with chorhidrate of hydroxylamine and 2 % HNO_3; (**iii**) Cr(III) – by X-ray fluorescence spectrometry (Epsilon 5 XRF Spectrometer) on parallel samples; (**iv**) mobile and fix fraction of chrome – have been separated from soil by sequential solid/liquid extraction in seven steps (table 3); in extracts the total chrome was determined by flame atomic absorption spectrometry (Bulgariu, 2007;Ure, 1993). The results presented in this paper represent the arithmetic mean of three determinations made on the same sample. Supplementary information about the speciation and occurrence forms have been obtained from microscopic analysis, X-ray diffraction, IR and Raman spectrometry, performed on soil samples.

Table 1

The soil samples used for the experiments

No. sample	Details	Loc.	pH		E_h[(3)]; mV
			$pH(H_2O)$[(1)]	pH(KCl)[(2)]	
TFMax.1	Solar / cucumbers	Interval	6.83	6.05	591.61
TFMax.2	Solar / cucumbers	Row	6.91	6.07	587.08
TFMax.3	Solar / tomatoes-Izmir	Interval	7.19	6.31	619.55
TFMax.4	Solar / tomatoes-Izmir	Row	7.23	6.28	603.71
TFMax.5	Field / cauliflower-Fremont	Interval	7.11	6.54	573.67
TFMax.6	Field / cauliflower-Fremont	Row	7.16	6.65	584.03
TFMax.7	Field / celery -Mentor	Interval	6.98	6.35	463.88
TFMax.8	Field / celery -Mentor	Row	6.95	6.26	461.27
TFMax.9	Solar / cucumbers-Merengue	Interval	6.73	5.92	589.18
TFMax.10	Solar / cucumbers - Merengue	Row	6.89	6.10	596.77
TFMax.11	Solar / pepper	Interval	6.57	5.76	620.48
TFMax.12	Solar / pepper	Row	6.63	5.81	622.04
TFMax.13	Solar / tomatoes -Venice	Interval	7.31	6.19	569.34
TFMax.14	Solar / tomatoes -Venice	Row	7.24	6.26	576.69
TFMax.15	Solar / tomatoes -Balett	Interval	7.15	6.28	580.60
TFMax.16	Solar / tomatoes -Balett	Row	7.22	6.16	587.28

(1)pH determined in distilled water, (2)pH determined in 0.1 M KCl solution (3)Redox potential – potentiometric method, suspension procedure: 10 g soil / 50 mL solution; grain size < 0.01 mm; contact time: 30 min. Loc. – location (Borlan, 1981; Bulgariu, 2005).

RESULTS AND DISCUSSIONS

In studied soils, the total chrome content, Cr(T), varied between 47.53 and 81.39 $\mu g.g^{-1}$, values higher that the normal content of chrome in soils (40 $\mu g.g^{-1}$), but lower than the value of alert threshold for sensitive soils (100 $\mu g.g^{-1}$) (table 2).The Cr(III) content varied between 46.32 and 79.55 $\mu g.g^{-1}$ and represent 94.35–98.46 % from Cr(T). The content of Cr(VI) varied between 1.20 and 3.16 $\mu g.g^{-1}$ and represent 1.52–5.62 % from Cr(T). For all soil samples the content of Cr(VI) is lower than the value of alert threshold for sensitive soils.

The results presented in table 2 show that: (**i**) the content of Cr(T) is higher in case of vegetables crops from field (76.35–81.39 $\mu g.g^{-1}$), than in case of the crops from plastic tunnels (47.53–72.29 $\mu g.g^{-1}$); (**ii**) in function of cultivated vegetables type, the content of Cr(T) in soil follows the order: tomatoes (47.53–59.19 $\mu g.g^{-1}$) < cucumbers (60.87–69.29 $\mu g.g^{-1}$) < pepper (68.71-72.29 $\mu g.g^{-1}$) < celery (76.35-80.11 $\mu g.g^{-1}$) < cauliflower (79.04-81.39 $\mu g.g^{-1}$); (**iii**) with the exception of soil samples 7 and 8 (the cauliflower culture in field), the content of Cr(T) from soil samples on the row is higher that those on the interval – the differences of these varied between 2.35 and 6.59 $\mu g.g^{-1}$ (average: 4.41 $\mu g.g^{-1}$);

(**iv**) the content of Cr(VI) is lower in case of crops from field (1.22–1.83 µg.g^{-1}) than in case of cultures from solariums (1.20–3.16 µg.g^{-1}); (**v**) in function of cultivated vegetables type, the content of Cr(VI) in soil follows the order: tomatoes – Izmir (2.96–3.16 µg.g^{-1}) > pepper (2.76–2.85 µg.g^{-1}) > cucumbers (1.80–2.04 µg.g^{-1}) > cauliflower (1.68–1.83 µg.g^{-1}) > tomatoes – Venice (1.20–1.83 µg.g^{-1}) > tomatoes – Balett (1.60–1.64 µg.g^{-1}) > celery (1.22–1.25 µg.g^{-1}); (**vi**) the contents of Cr(T), Cr(III) and Cr(VI) do not have significant correlations with the main chemical-mineralogical components of studied soils.

Table 2

The contents of chrome from studied soil samples

sample			Cr(T); µg.g^{-1}	Cr(III)		Cr(VI)	
No.	Details	Loc.(2)		µg.g^{-1}	%(1)	µg.g^{-1}	%(1)
TFMax.1	Solar / cucumbers	Interval	60.87	59.06	97.02	1.8	2.95
TFMax.2	Solar/ cucumbers	Row	64.22	62.17	96.80	2.04	3.17
TFMax.3	Solar / tomatoes	Interval	52.60	49.63	94.35	2.96	5.62
TFMax.4	Solar / tomatoes	Row	59.19	56.02	94.64	3.16	5.33
TFMax.5	Field / cauliflower	Interval	79.04	77.35	97.86	1.68	2.12
TFMax.6	Field / cauliflower	Row	81.39	79.55	97.73	1.83	2.24
TFMax.7	Field / celery	Interval	80.11	78.88	98.46	1.22	1.52
TFMax.8	Field / celery	Row	76.35	75.09	98.34	1.25	1.63
TFMax.9	Solar/ cucumbers	Interval	65.70	63.81	97.12	1.88	2.86
TFMax.10	Solar/ cucumbers	Row	69.29	67.38	97.24	1.9	2.74
TFMax.11	Solar / pepper	Interval	68.51	66.17	96.58	2.76	4.02
TFMax.12	Solar / pepper	Row	72.29	69.99	96.81	2.85	3.94
TFMax.13	Solar / tomatoes	Interval	47.53	46.32	97.45	1.2	2.52
TFMax.14	Solar / tomatoes	Row	52.85	51.01	96.51	1.83	3.46
TFMax.15	Solar / tomatoes	Interval	50.37	48.76	96.80	1.6	3.17
TFMax.16	Solar / tomatoes	Row	56.29	54.64	97.06	1.64	2.91

(1)% from total content of chrome. (2)Loc. – location. Drawing place of soil samples.

The experimental results from table 3 indicate that: (**i**) the weight of mobile fractions (with high biodisponibility) of chrome (F.1 and F.2 fractions) is relatively reduced (5.04–23.52 % from Cr(T), average: 10.02 %), and lower than the weight of fix fractions (residual, inaccessible for plants; F.7 fraction; 10.11–27.15 % from Cr(T), average: 20.45 %), and respectively lower than the weight of pseudo-mobile fractions (from which the chrome can be only partial mobilized in conditions of studied soils, F.3, F.4, F.5 and F.6 fractions; 61.65–82.15 % from Cr(T), average: 75.91 %); (**ii**) in case of crops from the field, the weight of mobile fraction of chrome (5.0–9.11 % from Cr(T)) is lower than in case of cultures from solariums (5.21–23.52 % from Cr(T)); (**iii**) the contents of chrome in mobile fractions in case of soil samples from the row (3.04–10.56 µg.g^{-1}) are lower than those from the intervals between rows (5.29–16.11 µg.g^{-1}); (**iv**) in function of cultivated vegetables type, the relative content of chrome in mobile forms, follow the order: pepper (10.56–16.11 µg.g^{-1}) > cucumbers (4.16–10.03 µg.g^{-1}) > celery (3.84–7.29 µg.g^{-1}) > cauliflower (4.95–6.63 µg.g^{-1}) > tomatoes (3.04–5.94 µg.g^{-1}); (**v**) Cr(VI) is mostly distributed (> 90 % from total content of Cr(VI)), in the F.2, F.3 and F.7 fractions, predominantly as species with relatively reduced mobility (biodisponibility).

Table 3

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

No.	Details	F.1	F.2	F.3	F.4	F.5	F.6	F.7
TFMax.1	Solar / cucumbers (I)	3.87	5.24	3.07	5.08	15.49	18.19	9.95
TFMax.2	Solar / cucumbers (R)	1.89	2.26	2.30	10.12	14.07	16.95	16.35
TFMax.3	Solar / tomatoes (I)	1.67	3.88	1.70	5.46	15.44	16.67	7.70
TFMax.4	Solar / tomatoes (R)	1.21	1.86	0.54	9.25	16.04	15.89	14.31
TFMax.5	Field / cauliflower (I)	1.48	5.14	7.41	7.44	27.41	17.41	12.68
TFMax.6	Field / cauliflower (R)	1.01	3.93	5.47	9.17	25.11	14.92	20.90
TFMax.7	Field / celery (I)	2.53	4.75	5.96	10.46	23.33	16.90	16.07
TFMax.8	Field / celery (R)	1.06	2.78	4.23	11.70	17.01	17.59	21.84
TFMax.9	Solar / cucumbers (I)	3.08	6.95	4.06	8.41	21.31	15.26	6.64
TFMax.10	Solar / cucumbers (R)	1.39	3.02	3.22	13.21	18.64	13.65	15.85
TFMax.11	Solar / pepper (I)	5.93	10.17	1.95	10.16	15.11	15.39	9.70
TFMax.12	Solar / pepper (R)	3.85	6.71	1.22	15.44	14.94	13.29	16.85
TFMax.13	Solar / tomatoes (I)	1.44	3.84	2.20	4.69	14.78	14.13	6.58
TFMax.14	Solar / tomatoes (R)	1.02	2.02	0.56	9.23	13.17	12.87	13.91
TFMax.15	Solar / tomatoes (I)	1.99	3.94	2.00	5.56	14.23	13.22	9.30
TFMax.16	Solar / tomatoes (R)	1.21	2.22	1.04	9.32	13.90	12.97	15.28

(I) – soil samples from the interval between rows. (R) – soil sampled 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).

CONCLUSIONS

In relation to the contents of Cr (T), Cr (III) and Cr (VI) determined experimentally, the studied soils are not contaminated and have high levels of chromium supply. In relation to chemical and mineralogical components of studied soils, chromium all have a heterogeneous distribution, atypical compared with other micronutrients. This behaviour of chrome in soils cultivate with vegetables is determined by: (i) relatively reduced mobility of chrome; (ii) in the inter-phases distribution processes and in the adsorption processes by plants, the chrome interact antagonist with most of the essential macro- and micro-elements; (iii) the high sensitivity of speciation and distribution equilibriums of chrome at relatively reduced variation of physic-chemical conditions. The risk potential of chrome is very low, due to reduced mobility and biodisponibility of his speciation forms, and to the high reduction probability of Cr(VI) to Cr(III), in the conditions of studied soils.

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