The correlation of the values of plant-avalilable Pb and Cd in soil determined using different types of extragens

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Abstract: The plant-available amount of Pb and Cd in soil was determined by extraction using the solutions: 1) 0.5 M Na_2EDTA, pH 5.2; 2) 1 M KCl, pH 7.0; 3) 0.1 M KCl, 0.05 M Na_2EDTA, pH 6.2; 4) 2 % CH_3COOH, pH 2.5 and 5) 1 M CH_3COONH_4, pH 4.8. Chernozem and hydromorphic black soil types from the Middle Banat were used. It can be concluded that the values of the plant-available amounts of Pb and Cd in a soil depends on the stability constants of their complexes with ligands in the extraction solution. The conversion factors for the recalculation of the amounts of Pb and Cd obtained using the citted extractants have been calculated.

Keywords: lead, cadmium, soil, metal extraction.

INTRODUCTION

The plant-available amounts of metals in soil has been determined using various types of solutions for their extraction. The used types of solutions are based on experience. No information can be found in the literature about the connection between the composition of the extraction solution and the obtained values of the plant-available amounts of metals, specificially Pb and Cd in this case, as well as the possibility of the recalculation of the values of the plant-available metal amounts obtained using different extraction solutions. These solutions, which are used in practice, consist of least one but sometimes more substances which can form complexes with the metals.

EXPERIMENTAL

Atomic absorption spectrophotometer Varian-275 series and a pH-meter Radiometer-28 were used for the determination of the Pb(II) and Cd(II) concentrations and pH measurement, respectively.

The pH-values of the solutions were adjusted using NaOH and HCl solutions (0.1 M).

All chemicals were of p.a. quality.

For the experiments, the following solutions[1-3] are used: 1) 0.5 M Na_2EDTA, pH 5.2; 2) 1 M KCl, pH 7.0; 3) 0.1 M KCl, 0.05 M Na_2EDTA, pH 6.2; 4) 2 % CH_3COOH, pH 2.5; and 5) 1 M

CH_3COONH_4, pH 4.8. According to some authors, DTPA solutions can be used for the determination of the plant-available amount of Pb, while according to others for the determination of the total amount of Pb in the soil. For this reason DTPA solutions were not used in the work.[4,5]

Pb and Cd standard solutions were prepared in the corresponding extracton solution for each series of Pb and Cd measurements. The standard solution were used for the construction of calibration curves.

The soil was sampled in July 2001, after harvest. The types of soil used were chernozem (from the area of the village Mihajlovo) and hydromorphic black (from the area of the village Radojevo), Banat. 15 samples were taken from different parts of the area. Each sample of both types of soil were analysed individually. The sampling was carried out by a sonder (depth 0–30 cm). The samples were air-dried, ground and sieved in the laboratory.[6]

For the determination of the total Pb and Cd amounts, a definite quantity of air dried sample was measured and wet-ashed with HNO_3 and $HClO_4$ (conc.), using a standard procedure.[1] The Pb and Cd concentration in the filtrate were determined by atomic absorption spectroscopy.

For the determination of plant-available Pb and Cd amounts, the metals were extracted from 20 g of an air-dried sample using 50 cm^3 of the above cited extraction solutions. The contents of Pb and Cd in filtrate were determined by atomic absorption spectroscopy.[1-3]

The amounts of Pb and Cd (total and plant-available) in each sample were determined in triplicate and the mean value was used as the Pb or Cd amount in a sample.

All experiments were performed at room temperature.

RESULTS AND DISCUSSION

Using the corresponding values of the amounts of Pb and Cd in the 15 samples of chernozem and of hydromorphic black type of soil, the mean values of the total and the plant-available amounts of Pb and Cd in the soil for each extractanta, as well as the standard deviation were calculated (Table I). The statistical criterium for the elimination of extreme values was used.[7]

TABLE I. Mean values of the total, Pb(t) and Cd(t), and plant-available, Pb(x) and Cd(x), amounts in chernozem and hydromorphic black soil in mg/kg and standard deviation obtained using different extraction solutions[a]

Soil type	Pb(t)	Pb(1)	Pb(2)
Chernozem	10.8±0.99	3.32±0.44	0.38±0.14
Hydr. black	8.26±0.79	3.40±0.82	0.28±0.04
	Pb(3)	Pb(4)	Pb(5)
Chernozem	4.27±0.75	0.54±0.14	0.28±0.18
Hydr. black	4.11±0.57	0.30±0.08	0.33±0.09
	Cd(t)	Cd(1)	Cd(2)
Chernozem	0.93±0.05	0.20±0.02	0.32±0.01
Hydr. black	0.82±0.08	0.18±0.03	0.28±0.02
	Cd(3)	Cd(4)	Cd(5)
Chernozem	0.17±0.01	0.14±0.02	0.14±0.02
Hydr. black	0.17±0.02	0.12±0.03	0.11±0.03

[a] No. of extractant type cited above in the Experimental, is given in parenthesis

The results obtained can be explained by comparing the obtained values of the amounts of plant-available Pb and Cd, provided by extraction using various extractants, with the stability constant of the corresponding complexes (Table II).

TABLE II. Stability constants of Pb an Cd complexes[8,9]

Metal ion	Ligand	Stability constant			Temperature/°C	Ionic strength,
		mean	min.	max.		
Pb(II)	Chloride	$\beta_2 = 1.87$	1.48	2.36	18–25	0–4
	Acetate	$\beta_2 = 3.21$	2.59	3.99	20–30	0–2
	EDTA	$\beta_1 = 17.7$	16.8	18.4	20–25	0–1
Cd(II)	Chloride	$\beta_2 = 2.28$	1.6	2.74	0–45	0–3
	Acetate	$\beta_2 = 2.38$	2.19	2.7	25–30	0–3
	EDTA	$\beta_1 = 16.2$	15	16.6	20–25	0.1–0.2

In order to find the correlation between the amount of plant-available metal and the stability constant of complexes with ligands in the extraction solution, it is necessary to observe the soil-extraction solution system.

The first characteristics of the system is the very small total amount of the investigated metal M in relation to many other inorganic and organic compounds in the soil, as well as in relation to complexing substances in the extractants. Practically, the concentration of the other substances in this system are constant and independent of the formation of different types of metal ion complexes.

The second characteristics is the metal M equilibrium reactions in the system: soil - extraction solution. In this system two types of reaction exist. One is the dissolution of less soluble compounds of metal, MX_s, that exist in the solid phase and can be characterised by their solubility product, S:

$$S = [M] [X]^s \qquad (1)$$

Real soils are very complex systems and can have many less soluble compounds of the investigated metal (MX_s, MY_p, MR_q, ...). However, the concentration of the metal ion M in solution is determined by compounds having higher values of the solubility product S.

The second type of reactions in solution are the following:

a) formation of metal ion M complexes with components of the extraction solution, L_1, L_2, ...:

$$M + aL_1 \leftrightarrow ML_{1a} \qquad (2.1)$$

$$M + bL_2 \leftrightarrow ML_{2b} \qquad (2.2)$$

b) formation of complex compound with ligands Z, Q, P, ... dissolved from the soil by the extraction solution:

$$\text{M} + z\text{Z} \leftrightarrow \text{MZ}_z \tag{3.1}$$

$$\text{M} + q\text{Q} \leftrightarrow \text{MQ}_q \tag{3.2}$$

$$\text{M} + p\text{P} \leftrightarrow \text{MP}_p \tag{3.3}$$

The corresponding stability constants are:

$$\beta_{\text{L}_1} = [\text{ML}_{1a}]/[\text{M}]\,[\text{L}_1]^a \tag{4.1}$$

$$\beta_{\text{L}_2} = [\text{ML}_{2b}]/[\text{M}]\,[\text{L}_2]^b \tag{4.2}$$

$$....................$$
$$....................$$

$$\beta_{\text{Z}} = [\text{MZ}_z]/[\text{M}]\,[\text{Z}]^z \tag{5.1}$$

$$\beta_{\text{Q}} = [\text{MQ}_q]/[\text{M}]\,[\text{Q}]^q \tag{5.2}$$

$$\beta_{\text{P}} = [\text{MP}_p]/[\text{M}]\,[\text{P}]^p \tag{5.3}$$

If a less soluble compound MX_s exist in the solid phase, the concentration of the metal ion M in the extraction solution is determined by the solubility product of the compound. The corresponding concentration of ion M is the equilibrium concentration for all reactions in solution (4.1,.....5.1,....).

The total metal concentration in the extraction solution, *i.e.*, the amount of plant-available metal M_E is:

$$[\text{M}_\text{E}] = \text{M} + [\text{ML}_{1a}] + [\text{ML}_{2b}] + [\text{MZ}_z] + [\text{MQ}_q] + [\text{MP}_p] + ... \tag{6.1}$$

By the combination of expressions (4), (5) and (6), the following equation is obtained:

$$[\text{M}_\text{E}] = [\text{M}]\,(1 + \beta_{\text{L}_1}\,[\text{L}_1]^a + \beta_{\text{L}_2}\,[\text{L}_2]^b + \beta_{\text{Z}}\,[\text{Z}]^z + \beta_{\text{Q}}\,[\text{Q}]^q + ... \tag{6.2}$$

This the plant-available amount of metal M (total concentration of metal in the extraction solutions) is a function of the stability constants of the corresponding complexes in solution and the concentrations of the ligands.

The concentrations of the complexes $[\text{MZ}_z]$, $[\text{MQ}_q]$, $[\text{MP}_p]$, ..., *i.e.*, the complexes formed from metal and soluble soil components in the extraction solution, as well as the concentration of metal ion [M], are small compared with the concentration of metal complexes formed with components of the extraction solution, and are almost zero. This conclusion is based on the following data. The water present

in a soil extract metal compounds from the solid phase. This water forms natural waters, *i.e.*, lakes, rivers and groundwaters. The concentrations of Pb and Cd in these waters, minimal and maximal, according to the relevant literature data[10,11] are given in Table III. These concentrations are equilibrium concentrations in the soil – water system.

TABLE III. Concentrations of Pb and Cd in the extraction solutions and in different types of natural waters[10,11]

Element	Pb/(μg/dm^3)					Cd/(μg/dm^3)				
Extractant type[a]	1	2	3	4	5	1	2	3	4	5
Chernozem	1328	167	1879	238	123	80	128	68	56	56
Hydr. black	1360	123	1808	132	145	72	112	68	48	44

Element	Pb/(μg/dm^3) mini-mum-maximum	Cd/(μg/dm^3) mini-mum-maximum
River waters	0.001 – 0.030	0.0003 – 0.008
Lake waters	0.08 – 0.10	0.006 – 0.008
Groundwaters	0.005 – 20	0.002 – 3
Accumulation[11] lake[b]	9 – 18	1

[a] No. of extractant type cited above in the Experimental. [b] Formed from Raška river springwater

Using the data of the plant-available amounts of Pb and Cd (Table I), the volume of extractant and the quantity of soil used in experiments, the concentration of Pb and Cd in the extraction solutions were calculated (Table III). By comparing the obtained values with the concentrations of Pb and Cd in natural waters, it can be concluded that the concentrations in natural waters (rivers and lakes) in all cases are less than 1 % of concentrations in the extractant solutions, *i.e.*, less than the experimental error of the measurement. Only the maximal values of Pb and Cd concentrations in groundwaters are higher than 1 % of corresponding concentrations in the extractant solutions, but are less than the standard deviation. This is also true when the accumulation lake water is considered. In this case, from equation (6.2), the following equation is obtained:

$$[M_E] = [M]\beta_{L_1}[L_1]^a + [M]\beta_{L_2}[L_2]^b + k_1\beta_{L_1} + k_2\beta_{L_2} \qquad (6.3)$$

or, if only one complexing substance is present in the extraction solution:

$$[M_E] = [M]\beta_{L_1}[L_1]^a = k_1\beta_{L_1} \qquad (6.4)$$

From Eqs. (6.3) and (6.4), it can be concluded that the amount of plant-available metal $[M_E]$ is a function of the stability constant of the complex formed by the metal ions and complexing compounds in the extraction solution, as well as of the values of the constants k_1, k_2, ...

For the same type of soil and two types of extraction solutions, 1 and 2, according to Eq. (6.4), the correlation factor f_x for the conversion of plant-available amounts of metal $[M_{E_2}]$ into $[M_{E_1}]$ is:

$$[M_{E_1}] = [M_{E_2}] f_x = [M_{E_2}] (k_1 \beta_{L_1})/(k_2 \beta_{L_2}) \qquad (7.1)$$

Using Eq. (6.4), in the cases when extraction solutions containing more than one complexing compound were applied, an equation of the same type as (7.1) is obtained. Table IV shows the correlation factor calculated using data in Table I.

According to Eqs. (6.3) and (6.4), the plant-available amount of metal is a function of the stability constants of complexes, as well as of the ligand concentration. The ligand concentration depends, in corresponding cases, on the dissociation constant, the pH of solution and on the total ligand concentration. This is the reason why correlations of the plant-available amounts of metal and the stability constant are only approximate. By comparing the data in Table I, it can be seen that similar or lower values of plant-available Pb or Cd in extractants without Na_2EDTA is the consequence of the lower values of corresponding stability constants. The plant-available Pb amounts obtained using solutons with Na_2EDTA are very high as the consequence of the high value of the stability constant of the complex. Also the value of the plant-available amount of Pb obtained by using 0.1 KCl, 0.05 M Na_2EDTA solution, is higher than that obtained using a 0.5 M Na_2EDTA solution, which is in correlation with Eq. (6.4) – formation of two complexes. The very low values of plant-available amounts of Cd obtained using solutions with Na_2EDTA, similar to the cases when other solutions were used, can be the consequence of the adsorption of the formed complex CdEDTA on the solid phase, which has a very high stability constant (Table II).

TABLE IV. Correlation factors (f_c) for the recalculation of the plant-available Pb and Cd amounts in a soil, obtained using different extraction solutions

Correlation of solution types[a]	f_c/Chernozem		f_c/Hydromorphic black	
	Pb	Cd	Pb	Cd
1:2	8.74	0.62	12	0.64
1:4	6.20	1.43	11	1.50
1:5	11.9	1.43	10	1.64
2:4	0.70	2.29	0.93	2.23
2:5	1.40	2.29	0.85	2.54
4:5	1.95	1.00	0.91	1.09

[a] No. of extractant type cited above in the Experimental

From the values of the correlation factors in Table IV, it can be concluded that the correlation factors between two extraction solutions have relatively high values

when the components in the solutions form complexes with very differrent stability constants.

Also, in the case of Cd, the correlation factors obtained for the two types of soil, are very similar, but in the case of Pb the differences are greater.

The obtained values of the correlation factors can be used for recalculation of data obtained in practice using different extraction solution, due to the real comparison of the qualites of these soil.

ИЗВОД

УПОРЕЂИВАЊЕ ВРЕДНОСТИ БИЉЦИ ДОСТУПНОГ Pb и Cd У ЗЕМЉИШТУ ОДРЕЂЕНИХ КОРИШЋЕЊЕМ РАЗЛИЧИТИХ ВРСТА ЕКСТРАГЕНАСА

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Биљци доступан садржај Pb i Cd у земљишту одређен је коришћењем екстракционих раствора: 1) 0,5 M Na$_2$EDTA, pH 5,2; 2) 1 M KCl, pH 7.03; 3) 0,1 M KCl, 0.05 M Na$_2$EDTA, pH 6,2; 4) 2 % CH$_3$COOH, pH 2,5 и 5) 1 M CH$_3$COONH$_4$, pH 4.8. У експериментима коришћени типови земљишта били су чернозем и хидроморфно црно из средњег Баната. Закључено је да вредност биљци доступног Pb и Cd у земљишту зависи од константе стабилности њихових комплекса са лигандима из раствора за екстракцију. Одређени су фактори за прерачунавање садржаја Pb и Cd добијених коришћењем наведених раствора.

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