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DISTRIBUTION COEFFICIENTS OF METALS IN SOIL AND PLANTS AS INDICATORS OF PHYSICAL – CHEMICAL PROPERTIES OF SOIL

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ABSTRACT
Relation of concentration of metals in soil and plants can present very important indicator of physical – chemical properties of soil and plants, because it could be the base for estimating the level of metal content in plants and contamination, as well as the mobility of ionic metal forms at phases.
Experimental work includes metal's intake by vegetables from both contaminated and non-contaminated soil, and determined concentrations are used for calculation of distribution coefficients in soil and plants for some elements such as zinc, cadmium, lead and copper. Experiments have been performed in laboratory conditions and distribution coefficients obtained in this work present indicator of level of plant contamination and physical – chemical changes at equilibrium phases.
Obtained results showed that the soil conditions dictate the intake of ionic forms of heavy metals by vegetable root, and the intake is mostly dependent on physical – chemical properties of soil such as pH; CEC; electrical conductivity, and other.
Key words: distribution coefficients, soil, metal

1. INTRODUCTION
Plants can adsorb a part of heavy metals from soil, thus participating in the metal’s cycle in the nature. The transport of ionic parts of heavy metals from soil solution to the root of plant depends on various factors such as natural compounds in roots, diameter of ionic forms of heavy metals, plant affinity to heavy metals, etc. The natural compounds in the root plants are ionic transporters, which transport ionic forms of heavy metals to other parts of plant, such as leafs, berries, etc.
The transporters have potential kinetic parameters, such as transport capacity (V_{max}), activity to ionic forms of heavy metals causing that plants have selective capacity to heavy metals [3]. It is also important to emphasize that the adsorption of heavy metals from plants depend on their binding in the soil, because if they are dissolved in the soil solution (active – mobile metals form), then they can be adsorbed by plants [6]. Adsorption can be active (metabolic) and passive (non-metabolic). Active adsorption is performed by the metabolic energy and it runs against chemical gradient of heavy metals concentration in solution. Thus, metals such as cadmium, zinc, copper and lead are adsorbed [4] by plants and present the indicators of contamination, or their relation in soil and plant, which is called distribution coefficient. The term indicator refers to the use of an organism (plant), or part thereof, to obtain quantitative information on the quality of its environment [1]. Accumulative indication involves the selection of a species that accumulates the pollutant, in this case, heavy metals, to be monitored, and to measure the concentrations of this substance in the organism when exposed to various environmental levels [2]. Evidence of accumulation, in turn, may have potential biological consequences for a species. Indicators should be sedentary or resident to the area of interest, intensively investigated, easy to identify and sample, abundant, long-lived, available for sampling all year, have a wide geographical distribution, and be relatively tolerant to pollutants[8].

2. MATERIALS AND METHODS

The growing of vegetables was perfomed in the laboratory conditions in order to avoid contamination of vegevetables and soil from the environment. In the period of three months, vegetables, lettuce, carrot and cucumbers, were growing in the laboratory and only desitillated water was added into soil. After the period of three months, samples of above mentioned vegetables, were prepared and analysed for the determination of heavy metal contents. The pH value of the soil sample was 7,45, which was adjusted about 6 in order to provide the acid soil conditions. The reduction of pH was achieved by the addition of appropriate amount of aluminum sulphate. The higher content of heavy metals, lead, copper, zinc and cadmium was provided by the addition of their appropriate solutions into the soil. In the prepared soil samples, cucumbers, lettuce and carrots were grown. Samples of vegetables were washed by distillated water and then dried at 105 °C about one hour. The gram of each sample was burned at 550 °C, lasting one hour. After burning, samples were solved in supra-pure HNO_3 and taken into vessel of 25 ml by filling with re-destilited water to the top. Soil analyses were performed by standard methods, and determination of heavy metal content (Pb, Zn, Cd and Cu) was performed by differential pulse anodic stripping voltammetry, DPASV.

Analyses of lead were performed in 0,1 M KNO_3, with the following instrumental parameters:

- Working Electrode (WRK): HMDE
- Referent Electrode (REF): Ag/AgCl (1 M KCl), E = 0.22 V

and equipment:

- Electrochemical Cell, Princeton Applied Research (EG & G) model 303A with Working (HMDE), Referent (Ag/AgCl) and Supporting (Pt-wire) Electrode.
- Potenciostat/Galvanostat, PAR, model 263 A.
- Computer P II with software Model 270/250 Research Electrochemistry Software, version 4.3.

After determination of the content of heavy metals in vegetables and soil, the distribution coefficients were calculated as followes:

Distribution Coefficient = the content of heavy metal in plant/content of heavy metal in soil

3. RESULTS AND DISCUSSION

Table 1. Distribution coefficients for heavy metals for letuce and soil for laboratory conditions

Metals content	pH	Metal	I	II	III	IV	V	VI
Natural metal's content	pH=6	Copper	0,41	0,10	0,22	0,08	0,43	0,10
		Lead	0,53	0,07	0,14	0,06	0,45	0,11
		Zinc	0,09	0,01	0,04	0,07	0,16	0,05
		Cadmium	0,02	0,005	0,21	0,19	0,05	0,004
	pH=7,5	Copper	0,05	0,04	0,26	0,26	0,21	0,11
		Lead	0,19	0,09	0,09	0,40	0,32	0,53
		Zinc	0,04	0,06	0,10	0,12	0,04	0,10
		Cadmium	0,006	0,003	0,007	0,06	0,008	0,25
Increased metal content	pH=6	Copper	0,062	0,023	0,055	0,067	0,055	0,017
		Lead	0,089	0,030	0,103	0,068	0,126	0,123
		Zinc	0,027	0,014	0,017	0,017	0,024	0,013
		Cadmium	0,036	0,024	0,042	0,017	0,127	0,012
	pH=7,5	Copper	0,054	0,019	0,049	0,049	0,029	0,010
		Lead	0,064	0,016	0,070	0,104	0,105	0,060
		Zinc	0,011	0,007	0,013	0,25	0,034	0,009
		Cadmium	0,027	0,024	0,026	0,011	0,154	0,07

In the laboratory, the heavy metal intake, was the highest for the lead, 0,53, slightly acid soil, experiment I. On the other hand, the lowest value of distribution coefficient was with cadmium, 0,003, slightly alkaline conditions, experiment II. Considering the increased metals concentration in soil, the highest distribution coefficient was observed with cadmium, 0,127, experiment V, slightly acid conditions, but the lowest with zinc, 0,007, alkaline conditions, and experiment II. With slightly acid soil conditions, natural metal content, pH = 6, the highest value of distribution coefficients was determined for lead, lettuce, experiment I, but the lowest was with cadmium, experiment VI, 0,004. The highest value of distribution coefficient was with natural metal's content and slightly acid conditions is with lead, 0,53, experiment VI, but the lowest 0,003. Considering the results of distribution coefficients in soil, with increased heavy metal content and pH = 6, maximum value was for cadmium, 0,127, experiment V, but minimal 0,012, experiment VI, and cadmium as well. The distribution coefficients with slightly alkaline conditions and increased metals content, were the highest for cadmium, 0,154, experiment V, but the lowest for zinc, 0,07.

Table 2.Distribution coefficients for heavy metals for cucumbers and soil for laboratory conditions

		Metal	I	II	III	IV	V	VI
Natural metal's content	pH=6	Copper	0,18	0,06	0,16	0,17	0,13	0,04
		Lead	0,21	0,25	0,55	0,06	0,76	0,13
		Zinc	0,11	0,10	0,06	0,14	0,10	0,04
		Cadmium	0,01	0,25	0,01	0,11	0,007	0,003
	pH=7,5	Copper	0,37	0,09	0,09	0,34	0,21	0,14
		Lead	0,44	0,61	0,09	0,22	0,32	0,20
		Zinc	0,10	0,05	0,04	0,11	0,04	0,11
		Cadmium	0,16	0,21	0,008	0,009	0,008	0,003
Increased metal content	pH=6	Copper	0,025	0,009	0,016	0,010	0,008	0,008
		Lead	0,031	0,044	0,031	0,033	0,056	0,022
		Zinc	0,013	0,010	0,028	0,007	0,009	0,009
		Cadmium	0,091	0,244	0,127	0,037	0,381	0,020
	pH=7,5	Copper	0,055	0,014	0,015	0,049	0,022	0,006
		Lead	0,077	0,035	0,016	0,055	0,031	0,051
		Zinc	0,012	0,003	0,008	0,005	0,005	0,004
		Cadmium	0,168	0,068	0,031	0,104	0,216	0,039

The distribution coefficient for cucumbers with slightly acid and alkaline soil conditions was the highest for lead, 0,76, experiment V, and the lowest with cadmium, 0,0007, experiment V. It is also important to emphasize that lead had the highest value of distribution coefficient, 0,61, experiment II, with natural content of metals in soil, and slightly alkaline conditions. The results of distribution coefficients with increased metals content and pH = 6, showed the highest value for cadmium, 0,381, experiment V, and the lowest zinc, 0,007, experiment IV. The highest value of distribution coefficient, slightly alkaline and increased metals content, was determined in the experiment V, for cadmium 0,216. On the other hand, minimum value of distribution coefficient for cucumbers in alkaline soil conditions was calculated for zinc, 0,003.

Table 3. Distribution coefficients for heavy metals for carrot and soil for laboratory conditions

Metals content	pH	Metal	I	II	III	IV	V	VI
Natural metal's content	pH=6	Copper	0,28	0,12	0,24	0,26	0,10	0,24
		Lead	0,30	0,04	0,17	0,32	0,45	0,13
		Zinc	0,07	0,03	0,04	0,13	0,08	0,12
		Cadmium	0,004	0,02	0,01	0,07	0,004	0,22
	pH=7,5	Copper	0,21	0,19	0,07	0,16	0,29	0,29
		Lead	0,24	0,09	0,14	0,03	0,30	0,16
		Zinc	0,05	0,04	0,02	0,06	0,09	0,19
		Cadmium	0,001	0,007	0,008	0,004	0,002	0,17
Increased metal content	pH=6	Copper	0,077	0,039	0,108	0,057	0,094	0,011
		Lead	0,064	0,026	0,061	0,083	0,025	0,162
		Zinc	0,007	0,014	0,015	0,011	0,036	0,012
		Cadmium	0,250	0,006	0,192	0,399	0,239	0,039
	pH=7,5	Copper	0,050	0,029	0,085	0,030	0,051	0,006
		Lead	0,031	0,035	0,016	0,060	0,003	0,118
		Zinc	0,005	0,017	0,017	0,002	0,022	0,009
		Cadmium	0,126	0,001	0,256	0,326	0,124	0,029

Results in Table 3., present the distribution coefficients from soil to carrot, with pH = 6 and pH = 7,5, natural and increased metal content in soil. According to the results in Table 3., lead had the highest value for distribution coefficient, experiment V, 0,45, but cadmium had the lowes value, 0,004, slightly acid conditions and natural metals content in soil. With pH = 7,5 and natural metals content, carrot in experiment V, took the most of lead, where distribution coefficient was determined as 0,3. In the soil conditions, e.g. natural metals content and slightly acid conditions, the lowest distribution coefficient was determined for cadmium, 0,001, experiment I. In soil conditions with increased metal content and slightly acid conditions, with carrot samples, the highest value was determined for cadmium, experiment IV, 0,399. It is also important to emphasize that the lowest value was also for cadmium, experiment II, 0,006. Results showed that the distribution coeffcients were the highest for camium in soil alkaline conditions and with increased metals level, 0,326, experiment III.

4. CONCLUSIONS

1. Distribution coefficients are indicators of heavy metal's contamination, both soil and plants, particularly vegetables;
2. In some sampales, values of distribution cefficients were higher, particulrly for lead and cadmium, and it can indicate the presence a higher concetrations of those metals in plants, as well as in soil.
3. Distribution coefficients for zinc and copper are within limits given by the literature, therefore they can be used as indicators of contamination of plants, particularly vegetables, by heavy metals;
4. When considering the content of heavy metals in soil and plants, their limits must be taken into consideration, because maximum allowed concentrations of heavy metals given by regualtions are much less for cadmium and lead, than for copper and zinc. The difference between maximum allowed concetrations given by regualtions, eg. much less values for cadmium and lead cause a very high distribution coefficents.

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