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Spectrophotometric Determination of Cadmium (II) in Soil of Allotment Gardens in Łódź

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Abstract

Cadmium was determined in the soil of six allotment gardens of Lodz, situated in areas with different traffic patters (the centre of the city and its suburbs). It was determined in the form of cadmium (II) dithizonate by the extraction-spectrophotometric method.

Keywords: cadmium(II), dithizone, soil

Introduction

Although in nature cadmium occurs in trace amounts and constitutes only 0.00005% of the crust of the earth, it has been listed by UNEP/WHO as substance dangerous to the environment, because along with such metals as lead, mercury, copper, zinc, chromium, tin and silver it poses a risk of disturbing the balance in ecosystems [1, 2]. One characteristic feature of cadmium is its high stability in environment. It is accumulated in soil and living organisms [3, 4, 5, 6]. It is easily absorbed by plants, both through their root systems and by leaves, usually in proportion to its concentration in the environment. Acid reaction of soil increases its mobility and availability [7].

Cadmium poses a particular risk to the health of humans and animals because it is easily absorbed, it remains in tissues for a relatively long time and is accumulated in vital organs, especially in kidneys and liver [8]. Its biological half-life is 10-30 years [7]. It is not found in the organisms of children, its total amount varies from 30 to 40 mg in 45-year old people and increases up to the age of 60, when it begins to decrease [9]. A lethal dose of cadmium is 2 mg per 1 kg of body weight and is much lower than that of other toxic metals [1].

In the lithosphere cadmium appears mainly in the form of sulphides and its presence is connected with the deposits of zinc and copper. Therefore, emissions of zinc and copper works contribute the highest proportion of industrial cadmium pollution, accounting for 60% of all anthropogenic sources of pollution with cadmium [7, 10]. The amount of cadmium in the environment may also be increased locally by incineration of solid waste. These processes cause pollution of soil and underground and surface water. The content of cadmium in soil increases as a result of the application of the artificial fertilizers. Its amount is 0.1-17.0 mg per kg in phosphatic fertilizers and 0.5-8.0 mg per kg in nitrogenous fertilizers [11]. Literature data [12] show that in the world, the mean content of cadmium in soil varies from 0.2 to 1.0 mg per kg of soil, whereas in Poland it is 0.2-0.3 mg per kg soil. Availability of cadmium to plants depends not only on its content in the soil, but also on its form, the strength by which it is bound with the soil components and the kind of plant. Investigations show that contamination of fruit by harmful metals, including cadmium, is considerably lower than of other agricultural products, especially grain and root vegetables [13, 14]. Cadmium content in plants generally increases proportionally with its content in soil **[15].**

The extent of cadmium pollution of soil in the area of the city of Lodz is not high [16]. Using the six-degree pollution scale recommended by IUNG in Putawy, over 60% of soils may be classified as free from pollution with cadmium. Increased amounts of cadmium (second degree of pollution - low level of soil pollution) occur in about 0.5% if the city area, mainly in its central part.

Cadmium has not been determined in the soils of the allotment gardens in Lodz or the plants grown in the gardens.

Experimental

Reagents and Apparatus
- Concentrated chloric (VII) acid (Riedel-de-Haen AG)
- Hydrochloric acid 0.1 mole/1
- Concentrated nitric (V) acid
- Stock standard solution of cadmium 0.1 mg/ml; 0.1000 g of metallic cadmium was dissolved in 20 ml of nitric (V) acid (1:1) and diluted with water in a 11 flask up to the mark
- Working standard solution of cadmium 0.001 mg/ml; 10 ml of stock standard solution were diluted with water in a 11 flask up to the mark. The solution was prepared on the day when calibration curves were plot ted
- Dithizone solution; 80 mg (extraction solution I) and 8 mg (extraction solution II) of dithizone were dissol ved in 11 chloroform
- Potassium cyanide: 1% and 0.05% solutions in 40% NaOH solution
- Hydroxylamine hydrochloride; 20 g of $NH_2OH \cdot HC1$ were dissolved in 100 ml of water
- Tartaric acid 2% water solution
- Chloroform
- Thymol blue 0.1% water solution
- Spectrophotometer SPECORD M-40
- Spectrophotometer SPECOL 11
- Microwave mineralizer Uni Clever BM-12

NB.: All chemicals used were analytical grade and were used without further purification.

Soil Sampling and Mineralization

Soil samples were collected in accordance with the standard [17] in the following allotment gardens:
1. "Rena-Kord" (Smugowa Street, in the vicinity of PKS coach station),
2. "Sielanka" (between Sienkiewicza Street and Kilihskiego Street),
3. "Uniontex"(in the area of Rydza-Smiglego Ave., Milionowa Street, Prz^dzalniana Street and Tymienieckiego Street),
4. "Poltex" (Wlokniarzy Ave., Drewnowska Street and the railway line),
5. "Nowe Rokicie" Wtokniarzy Ave., Obywatelska Street and the railway line) and
6. "Stoki" (Pomorska Street).

The gardens selected for the study were situated in areas with different traffic levels, in the centre of the city ("Sielanka") and in its suburbs ("Stoki"). They also differed in size (from the very big "Uniontex" gardens with the surface area of 32.1 ha to the very small "Sielanka" gardens of 1.3 ha). In the large gardens soil samples were collected in several places, at different distances from the streets with different intensities of road traffic.

The samples were mineralized in a microwave mineralizer, using chloric (VII) acid.

In the obtained solutions cadmium was determined spectrophotometrically, by the dithizone-cyanide method.

Principle of the Method [18]

In the basic medium dithizone (diphenylthiocarbazone, H_2Dz) and cadmium (II) ions form pink cadmium dithizonate $Cd(HDz)_2$, soluble in $CHC1_3$ and $CC1_4$. The spectrophotometric method of determination of trace amounts of cadmium involves extraction of the complex of cadmium (II) with dithizonate from the basic medium containing cyanides by means of chloroform, in the presence of sodium-potassium tartrate. Under these conditions cadmium is separated from Pb(II), Zn(II), Sn(II) and Bi(III). Tartaric acid (pH~3) is used to decompose dithizonate after extraction. Cadmium (II) dithizonate is extracted again from the slightly basic medium (pH~9) using chloroform, with the addition of cyanides, whose amount is 10 times lower than in the course of the first extraction. Under these conditions only $Cd(HDz)_2$ passes to chloroform. Absorbance of the pink solution is measured at λ = 520 nm. ($\zeta = 8.8 \cdot 10^4$)

Determination

Twenty millilitres of the solution obtained after mineralization of the soil sample were measured into a separatory funnel, 10 ml of redistilled water were added and pH was established (within the range of 1.5-2.5) by means of 20% solution of NaOH against thymol blue as indicator. Next, 1 ml of sodium-potassium tartrate, 5 ml of 1% potassium cyanide in 40% solution of NaOH and 1 ml of hydroxylamine hydrochloride were added in succession. Fifteen millilitres of dithizone solution (extraction solution I) in chloroform were added to the mixture and shaken for 1 minute. After separation, the chloroform layer was tapped to another separatory funnel containing 25 ml of refrigerated tartaric acid. Extraction solution I was added again to the solution remaining in the first separatory funnel and after shaking for 1 minute both chloroform extracts were mixed. Next, they were shaken for 2 minutes with a solution of tartaric acid. Chloroform with excess of dithizone was rejected. After 5 ml of chloroform were added the solution was shaken again for 1 minute, the layers were separated and the chloroform layer was removed. Then, 0.25 ml of hydroxylamine hydrochloride, 15 ml of dithizone solution in chloroform (extraction solution II) and 5 ml of 0.5% potassium cyanide solution in 40% NaOH were added to the tartaric acid solution containing the extracted cadmium and the mixture was shaken for 1 minute. After separation of phases, the pink chloroform layer was transferred to a 25 ml measuring cylinder. Extraction was repeated using 5 ml of dithizone solution (extraction solution II), the extract was transferred to a cylinder and chloroform was added to 25 ml. Absorbance of the obtained solution was measured by means of spectrophotometer against blank test as reference. Optical pathlength of the cells was 5 cm. The content of cadmium in the solutions obtained after mineralization of the soil

samples was read from the previously plotted calibration curve and calculations were made to find the content of cadmium in 1 kg of dry soil mass.

The calibration curve was plotted for cadmium content in the examined samples ranging from 0.0 to 6.0 µg. For this purpose 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 6.0 ml of the standard solution of cadmium were measured to separatory funnels and redistilled water was added to 25.0 ml. Further procedure was the same as that used for determination of cadmium. The calibration curve is presented in Fig. 1.

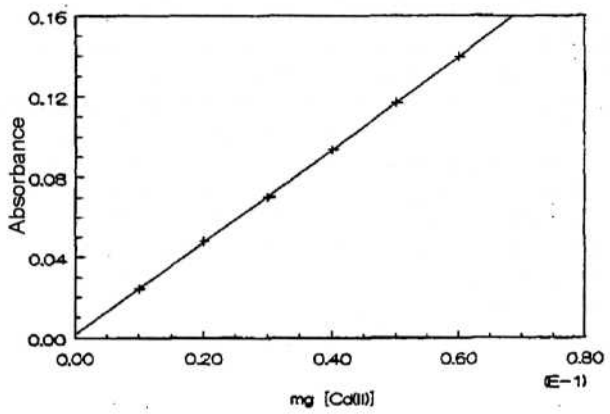

Fig. 1. The calibration curve for determination of cadmium(II) dithizonate by the extraction-spectrophotometric method.

Results

Mean results of determination of cadmium in the soil of the largest of the gardens, i.e. "Uniontex" are presented in Table 1 and Fig 2. The samples were collected from a 10 cm layer of soil in many places in the garden, at different distances from the arterial road with heavy traffic (Smiglego-Rydza Ave.) and other streets with considerably less traffic. The data in Table 1 show that the content of cadmium is not high in any of the places where samples were collected. The soil of the examined allotment garden is in category 0-1, i.e. between the categories of soils free from cadmium pollution and soils with elev-

Fig. 2. Situation of alloment gardens "Uniontex" with section numbers.

Table 1. Mean values of cadmium [mg/kg s.m.j content found in the soil of "Uniontex" allotment gardens.

Section number*	Part of section				Section number*	Part of section	
	a	b	c	d		a	b
1	0.43	0.41	0.58	0.49	10	0.39	0.58
2	0.60	0.58	0.68	0.62	11	0.62	0.85
3	0.77	0.78	0.77	0.83	12	0.70	0.85
4	0.39	0.40	0.40	0.47	13	0.83	
5	0.57	0.49	0.65	0.39	14	0.81	
6	0.74	0.76	0.91	0.91	15	0.83	
7	0.40	0.39	0.42	0.59	16	0.73	
8	0.57	0.64	0.54	0.69	17	0.76	
9	0.69	0.74	0.90	0.87	18	0.59	

* - Sections from 1 to 9 about area 3 hectare divided in four parts (a, b, c, d). Sections from 10 to 12 about area 1 hectare divided in two parts (a, b). Sections from 13 to 18 were about a half hectare area

ated content of cadmium (0.4-0.9 mg per kg of dry mass). However, it is evident that the content of cadmium grows as the distance between the place of sample collection and the road with heavy traffic, i.e. Rydza-Smigtego Ave. decreases. Mean content of cadmium in the samples collected in the area between streets of medium and heavy traffic are higher than those from the area enclosed by Rydza Smiglego Ave., much less busy Milionowa Street and Tymienieckiego Street and another allotment garden. Samples of 10 cm layers of soil were also collected in the "Poltex" gardens. The content of cadmium was between 0.46 and 0.58 mg per kg of dry mass. In the other allotment gardens samples were collected at depths of 5 cm and 20 cm. The determination results are presented in Table 2. Considerable spread of the values of cadmium content is observed in the soil of the "Nowe Rokicie" gardens, enclosed by Obywatelska Street (heavy traffic), Wlokniarzy Ave. (heavy traffic), a railway line and other allotment gardens. In the 5 cm layer of soil the content of cadmium varies from 0.29 to 0.95 mg per kg of dry mass, and in the 20 cm layer it is between 0.17 and 0.83 mg per kg of dry mass.

Table 2. Mean values of cadmium [mg/kg s.m.] content found in the soil of different allotment gardens in Lodz.

Depth of sample collection	"Sielanka"	"Rena - Kord"	"Stoki"	"Nowe Rokicie"	"Poltex"
0 – 5 cm	0.61 – 0.80	0.86 – 0.94	0.22 – 0.45	0.29 – 0.95	0.55 – 0.71
0 – 20 cm	0.49 – 0.62	0.78 – 0.81	0.16 – 0.27	0.17 – 0.83	0.46 – 0.58

The investigation shows that the content of cadmium does not exceed the value of 1.0 mg per kg of dry mass in any of the above-mentioned gardens, so the soils of the allotment gardens in Lodz are within category 0-1 in the

six-degree pollution scale, i.e. between normal and elevated content of cadmium. The soil of "Stoki" garden, situated in the suburbs, is free from pollution with cadmium.

In all of the gardens under study the pollution of soil with cadmium increases as the distance from busy roads becomes shorter. In layers of soil closer to the surface the content of cadmium is always higher than in the deeper layers. In gardens of smaller area the spread of cadmium content values at their different points is clearly higher than in larger ones.

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