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Letters to Editor

Spectrophotometric Determination of Lead in the Soil of Allotment Gardens in Łódź

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Abstract

This work presents the results of determination of lead in the soils of six allotment gardens located in different parts of the city (in the centre and on the outskirts). Lead was determined spectrophotometrically in the form of pink lead(II) ditizonate.

Keywords: lead(II), ditizone, soil.

Introduction

Lead is considered one of the environmentally hazardous elements because, along with cadmium, mercury, copper, zinc and chromium it poses a particularly high risk of disturbing the chemical balance in the ecosystem [1]. The content of lead in the soil is directly related to its granularity and mineral composition, as well as the origin of its parent rock. The natural content of lead in the soils formed of sands does not normally exceed 16 mg per kg of soil, and in more packed soils it is usually within the range of 13 to 60 mg per kg of soil [2, 3,4, 5]. Due to low solubility of minerals containing lead, it is less mobile in the environment than other elements such as zinc or cadmium. However, if the contamination is severe, lead easily finds its way to the food-chain. The factors contributing to the excessive intake of lead and other heavy metals are: acidity of soil, low content of humus and its low sorption capacity. The results reported by IUNG in Pulawy suggest that in Poland normal content of lead in the soil does not exceed 20 mg per kg of soil. The mean content of lead in cultivated land in Poland is 13.8 mg per kg of soil, the range of variation from 0.1 to 1723 mg per kg of soil. Analysis of soils in Poland has demonstrated that over 97% of soils used for agricultural purposes exhibit normal content of this element [6]. However, the development of industry and motorization and increasing use of communal and industrial waste water for liming and fertilizing soil as well as long-lasting use of some pesticides may lead to excessive concentrations of lead, cadmium, zinc, copper or mercury in the soil [7]. It has been discovered that there is a correlation between content of heavy metals in soils and in vegetables grown on them [8, 9, 10]. There is evidence that the content of lead, cadmium or zinc in the vegetables grown using environmentally safe methods may be up to 60% lower than in those grown in a traditional way [11]. This shows to what extent the presence and amount of these elements in plants depend on contamination of the soil where they are grown.

This is also of great importance to human health, as lead belongs to toxic elements which can acumulate in the human organism (the maximum daily dose of lead which does not lead to accumulation is 0.50 mg [12]). Excessive amounts of this element cause disorders in the metabolism of other microelements, e.g. iron (which may be manifested as anaemia), copper or zinc (which has a negative effect on the function of heart and kidneys) [13].

The extent of lead contamination in the area of Łódź agglomeration (212 km^2) is not high. According to the six-degree scale recommended by IUNG in Pulawy [2], more than 60% of the soils can be classified as free from

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contamination by this element, 20% belong to soils with increased content of lead, and the rest are slightly contaminated. The highest concentration of lead is observed in soils of the central part of the city, which account for about 10% of its area (2nd degree of contamination according to IUNG scale).

So far there have been no investigations on the content of lead in the soils of the allotment gardens in Lodz. Since some of them are situated in the centre of the city and close to roads with heavy traffic, it seems prudent to determine lead in the soils of these gardens. The present work is a part of the investigation of the content of heavy metals in the soils of the allotment gardens in Łódź [15, 16].

Experimental

Reagents and Apparatus

- Concentrated chloric(VII) acid Riedel-de-Haen AG)
- Stock standard solution of lead(II), concentration lmg/cm^3 was prepared in the following way: 1.5980g $Pb(NO_3)_2$ dried at 110°C, was diluted with water in a 1 dm^3 flask, 1 cm^3 of contentrated nitric(V) acid was added.
- Working standard solution of lead(II), concentra tion 0.01 mg Pb^{2+}/cm^3: 10 cm^3 of stock standard solution was diluted with water in a 1 dm^3 flask. The solution was prepared the same day the calibration lines were plotted.
- Dithizone solution; 50 mg (exctraction solution I) and l0mg (extraction solution (II) of dithizone were dis solved in 1 dm^3 chloroform.
- Ammonia solution of potassium cyanide: 20 g po tassium cyanide were dissolved in 580 cm^3 25% NH_4OH solution and diluted with water in a 1 dm^3 flask.
- 10% sodium tartrate solution.
- 25% ammonia
- Nitric(V) acid (1+99)
- Hydroksylamine hydrochloride; 20 g of NH_2 -HC1 was dissolved in 100 cm^3 of water.
- Spectrophotometer SPECOL 11
- Microwave mineralizer Uni Clever BM-12

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

Soil Sampling and Mineralization

The soil samples were collected in six allotment gardens in Łódź: "Uniontex" (In the area of Rydza-Smigłego St. Milionowa St., Przedzalniana St. and Tymienieckiego St.), "Sielanka" (between Sienkiewicza St. and Kilinskiego St.) "Rena-Kord" (Smugowa St., next to the bus station), "Poltex" (Wlokniarzy Ave., Obywatelska St., railroad), and "Stoki" (Pomorska St.) The gardens selected for the study are located in different parts of the city. Two of them („Sielanka" and "Rena-Kord") are in the city centre, while "Stoki" is situated on the outskirts, far from busy streets. The selection of the gardens allowed an examination of the effect of the intensity of the traffic on the content of lead in the soil. The surface area of the gardens is also varied (from 1.3 ha in "Sielanka" to 32.1 ha in "Uniontex").

The primary soil samples were collected according to a standard procedure [17] by means of a soil rod at two depths: 5 and 20 cm. Final samples were prepared according to standard procedure [18]. Prior to mineralization the soil was brought to the state of "air dryness" by leaving the samples for two weeks in a dry and well-ventilated place. The samples (about 1.0 g) were mineralized in a microwave mineralizer using chloric(VII) acid. The hot solution was filtered into 50 ml measuring flasks and water was added to the mark. Lead content was determined in thus prepared samples by the dithizone-cyanide method.

Principle of the Method [18, 19]

In a slightly alkaline medium ditizone (diphenylthiocarbazone, H_2Dz) forms with lead(II) ions a red-pink lead(II) ditizonate - $Pb(HDz)_2$, soluble in chloroform and other non-polar solvents. The 7-10 pH range is optimal for the extraction of this complex. The spectrophotometric method of determining microgram amounts of lead consists in the extraction of lead(II) ditizonate in the slightly alkaline medium by means of chloroform. The basic masking agents are cyanides which form stable complexes with Ag, Hg, Cu, Zn, Cd, Ni and Co, thus preventing their reaction with ditizone. If a tartrate or citrate is introduced into the solution before lead is extracted, the precipitation of readily hydrolyzing metals is prevented. The addition of hydroxylamine provides a reducing medium, which is advisable because ditizone is easily oxidized. The absorbance of the coloured lead(II) ditizonate is measured at λ = 520nm (molar absorption ratio $\zeta = 6.86 \cdot 10^4$).

Determination

Ten millilitres of the solution obtained after mineralization of the soil samples were placed in a separatory funnel, then 10 ml of 10% sodium citrate solution and 2 ml of 25% ammonia were added (pH of the solution was 8 - 9). From this mixture metals were extracted by adding consecutively 5 ml portions of extraction solution I until ditizone became green after extraction. Time per extraction was 1 minute. The chloroform extracts collected in the other separatory funnel were acidified by adding 25 ml of nitric acid (V) (1 + 99) and after shaking for 1 minute the chloroform layer was removed. Five millilitres of 20% hydroxylamine, 5 ml of ammonia solution of potassium cyanide and 10 ml of the extraction solution were added to the water layer remaining in the separatory funnel. The mixture was shaken for 1 minute. After separating the layers the chloroform extract was collected to a 25 ml measuring cylinder and the remaining part was shaken again in the separatory funnel with 10 ml of extraction solution II. Next, both chloroform extracts were mixed and chloroform was added to obtain 25 ml. The absorbance of the solution was measured by means of a spectrophotometer against blank test as reference. 5 cm absorption cells were used. The previously plotted cali-

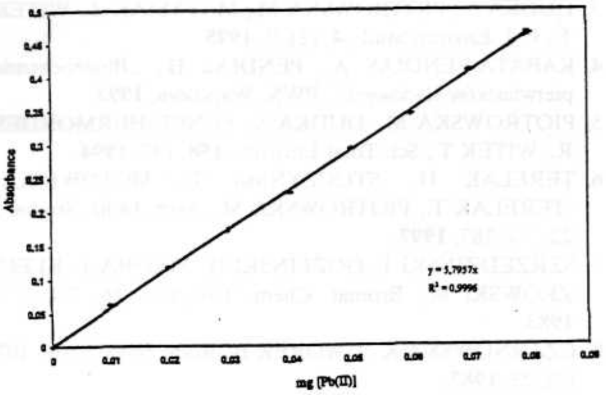

Fig. 1. The calibration curve for determination of Pb(II) dithiyonate using the extraction-spectrophotometric method.

bration curve was used to read the content of lead in the mineralizate solutions and to calculate the content of metal per kg of dry mass of soil. The determination for every sample collection site was done twice or three times. The differences between the obtained results did not exceed ±5%.

The calibration curve was plotted for the content of lead from 0.00 to 0.08 mg. For this purpose from 0.0 to 8.0ml of working solution of lead(II) was measured into the separatory funnels, water was added to 10.0 ml and the same procedure as in the case of the determination of lead was used. In the examined range of lead concentration the dependence between absorbance and the concentration was rectilinear (Fig. 1).

Results

Tables 1 and 2 list the content of lead in the soil of the selected allotment gardens in Łódź. The largest garden, "Uniontex" was treated separately. Due to its large size, the results for all sample collection sites are presented. In this garden samples were collected at one depth: 1-10 cm. The results are presented in Table 1. They show that the content of lead does not indicate contamination with this element in any of the collection sites. According to the guidelines of IUNG the soil in this garden should be considered as free from pollution and having a normal level of lead (from 40 to 51 mg per kg of dry mass). It seemed interesting to compare the level of lead in the samples of soil from the part of the garden situated along the busy arterial road (Rydza-Smigłego Ave.) with the soil from the inner part of the garden, which is less exposed to pollution. It is evident that the content of lead increases in the samples collected near the road and is lower in the samples collected in the inner area and the parts next to another allotment garden and the park. The differences amount to 20%.

Table 1. Mean values of Pb(II) [mg/kg d.m.] 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	44.15	40.02	41.27	41.71	10	49.93	50.95
2	41.23	40.38	42.07	40.07	11	48.71	51.23
3	41.02	42.17	39.71	42.07	12	49.81	50.18
4	40.15	41.02	40.27	42.71	13	50.55	
5	45.18	44.95	48.71	48.50	14	50.58	
6	48.64	47.25	46.07	45.35	15	49.18	
7	44.23	50.36	48.25	47.18	16	44.95	
8	44.87	47.21	45.13	50.58	17	45.72	
9	46.25	47.18	49.95	50.01	18	46.70	

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

In "Poltex" garden the samples were also collected at one depth (0-10 cm). The results are presented in Table 2. According to IUNG recommendations, the soil shows 0 - I degree of the content of lead, between normal and increased level of the metal. The content of lead is particularly high near the railroad.

In all the other allotment gardens the samples were collected at two depths: 0-5 cm and 0-20 cm. The results are given in Table 2. They indicate that the highest amounts of lead are present in the soil of "Rena-Kord" garden (75-90 mg per kg of dry mass), situated close to the centre of the city and the bus station. In all the soil samples the content of lead is increased.

High scattering of the results is observed in the determination of lead in the soil of "Nowe Rokicie" garden. In the layer of 0-5 cm it varies from 55 to 92 mg per kg of dry mass of soil, while in the layer of 0-20 cm it is from 44 to 86 mg per kg of dry mass of soil. It is connected with

Table 2. Mean values of Pb(II) [mg/kg d.m.] content found in the soil of dfferent gardens in Łódź.

Depth of sample collection	"Sielanka"	"Rena--Kord"	"Stoki"	"Nowe Rokicie"	"Poltex"
0 – 5 cm	60.06 – 69.77	75.32 – 89.40	36.65 – 40.06	55.47 – 91.11	–
0 – 20 cm	56.16 – 65.79	64.52 – 81.53	35.13 – 35.80	43.78 – 85.384	4.23 – 76.68

the size of the garden and its location between two busy streets, the railroad and other allotment gardens.

The lowest amounts of lead are observed in "Stoki" garden (from 36 to 40 mg per kg of dry mass of soil), which results from its location at the outskirts and far from busy roads.

Analysis of the results shows that the content of lead. in the soil of allotment gardens in Lodz does not exceed 100 mg per kg of dry mass of soil. In the six-degree IUNG scale of contamination they are placed between 0 and I degree, a normal and increased content of lead. In all the gardens, as a rule, the level of lead in the soil depends on the intensity of traffic in the area. In the 0-5 cm layer of soil the content of lead was always higher than in the 0-20 cm layer, which suggests that the increase in its amount in the soil is related to its concentration in the atmosphere.

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