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Letter to Editor

Assessing Heavy Metal Content in Soils Surrounding the Łódź EC4 Power Plant, Poland

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Abstract

The aim of the present work was to establish the effect of dust from the EC4 power plant in Łódź on the content of heavy metals in soil. The results of determination of Pb, Zn, Cr, Co and Fe in the soil samples collected in the area of the city of Łódź presented in the work indicate that the main source of contamination with these metals are large industrial plants and heavy motor traffic. Power plant dust has no influence on the content of elements in the soil.

Keywords: FAAS, lead, chromium, zinc, cobalt, iron, urban soils

Introduction

The present study on the contamination of soil in Łódź by heavy metals, continues the previous studies carried out in cooperation with the Łódź Municipality Department of Environmental Protection. Studies on the content of heavy metals in soil result from general interest in the status of the natural environment of large agglomerations and is an attempt to assess the degree of its degradation. The elevation of the content of these elements in the soil can be treated as one of the indicators of human influence on the environment. In large urban areas the most important origins of emission of heavy metals are industrial plants and motor transport [1-6]. Soil is usually examined with respect to the content of lead, cadmium, zinc, copper or mercury, since these metals belong to the group of elements which pose a particularly high risk to chemical equilibrium in the ecosystem [7-9]. The natural content of metals in the soil is directly related to the mineralogic and granulometric composition and the origin of the matrix soil and its range is very wide.

The content of lead in the soil varies from 13 to 60 mg/kg. The mean content of this element in arable land in Poland is not high (13.8 mg/kg), but the range of concentrations is wide and may be from 0.1 to 1723 mg/kg [8, 10-13].

The content of chromium in soils is low – from 7 to 150 mg/kg. It is assumed that the natural content of chromium in the surface layer of soil in Poland (0 – 20 cm) is from 2.0 to 81.0 mg/kg [14-15].

The content of zinc in soil varies from 7 to 360 mg/kg. Its assumed mean content is from 30 to 85 mg/kg. According to the Directive of the Minister of the Environment the content of zinc in urbanized areas in the surface layer of soil should not exceed 300 mg/kg [16], and according to the Polish Standard the content of bioavailable zinc of over 51 mg/kg in heavy mineral soils is considered high [17].

The level of cobalt in the soil varies within a wide range from 0.1 to 100 mg/kg. According to the catalogue of Environmental Protection, its natural content in the Polish soils varies from 1.0 to 18 mg/kg [18], and according to the Directive of the Minister of the Environment its content in urbanized areas should not be higher than 20 mg/kg in the surface layer of the soil.

The content of iron in soil is high, ranging from a fraction to several percent. Total iron in Polish soils is from

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2000 to 48000 mg/kg, and its deficiency may result from low solubility of its compounds in water [19-21].

The content of the above-mentioned metals was previously examined in the soil of allotment gardens in Łódź, situated in different parts of the city [22-27]. The purpose of the study is to assess the effects of the emission of dust from the power plant on the content of selected elements of the soil of the Łódź agglomeration.

Experimental Procedures

Soil Sample Collection and Preparation

The soil samples for analysis were collected from the surface layer (0-20 cm) within the limits of the city of Łódź in 2004 along two axes: north-south and east-west, which intersect at the site of the power plant. The selection of the directions of the axes and the number of samples collected on each axis were determined by the Łódź "wind rose." According to the information provided by the weather station Łódź–Lublinek, 41% of the wind in Łódź comes from the western section and 34% from the eastern section [28]. Therefore a decision was made to collect samples more frequently along the latter axis (30 collections) than along the north-south axis (14 collections). The soil samples referred to as EC4 were collected outside the area of the plant on lawns in its direct vicinity. The directions of the axis are shown in Fig. 1. The samples were collected systematically and equal distances were maintained. The samples were usually collected in lawns in the direct vicinity of streets or parks.

Soil samples were collected by means of a soil sampler. Pebbles and visible plant parts were removed. The samples were dried for two weeks in an airy place to bring them to an "air-dry state." Then the soil was ground in a porcelain mortar and sifted through screens with 2 or 0.1 mm mesh diameter. Thus prepared soil samples were stored in plastic containers and used for further analyses [29].

Fig. 1. Directions of sample collection sites.

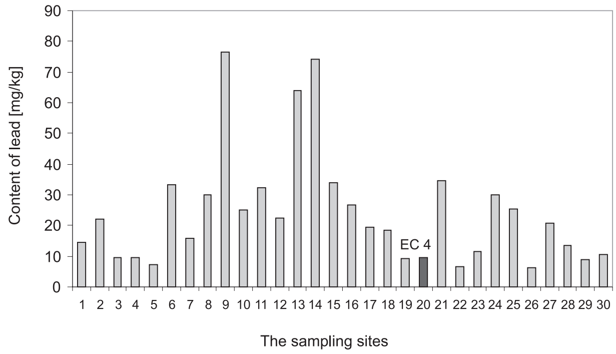

Fig. 2. The content of lead (extract of 1M HCl) on the axis east-west of the EC 4 power plant.

Preparation of Soil Extracts and Mineralizates

Soil extracts in which the selected elements were determined were prepared in the following way: the weighed portions of previously prepared soil with granulation below 2 mm and mass about 5 g (± 0.001 g) were placed in plastic beakers and 50.0 ml of 1 mol/l HCl solution was added. Then the content of the beaker was stirred with a magnetic agitator for 1 hour at a rate of about 40 rev/min. The solution was then passed through a medium filter as the first part of the filtrate was rejected [17].

In order to determine total content of the metals, the soil was mineralized in a "Plazmatronika" mineralizer in the medium of a mixture of concentrated HNO_3 and $HClO_4$. A mixture of 6 ml of HNO_3 and 3 ml of $HClO_4$ was poured onto the weighed soil portions with granulation below 0.1 mm of a mass of about 0.4500 g and mineralized. When the process was finished the solution was transferred to a 25 ml measuring flask and diluted with distilled water up to the mark [30]. The content of total organic carbon was previously determined in the samples. As it did not exceed 5-8%, it was not necessary to incinerate them [31].

Principles and Procedure of Determination of the Selected eElements by FAAS Method [18]

The concentration of each of the metals was determined in soil extract or mineralizate by means of atomic absorption spectrophotometer (AAS) in the reducing oxy-acetylene flame with the use of an appropriate lamp and wavelength (Cr – 357.9 nm; Fe – 248.3 nm; Pb – 217.0 nm; Co – 240.7 nm and Zn – 213.9 nm). Prior to each series of measurements a calibration line was created for each of the elements. The concentration range was different for each element and was from 0.00 to 10 μg/ml for Pb, from 0.00 to 4.00 μg/ml for Zn, from 0.00 to 2.50 μg/ml for Co, from 0.00 do 20.00 μg/ml for Fe and from 0.00 to 5.00 μg/ml for Cr. All the solutions were diluted with 1 M HCl solution.

Lanthanum solution (5% $LaCl_3$) in amounts necessary to keep its final concentration at the level of 1% was introduced only in the case of Cr determination.

The accuracy of the method was confirmed by the analysis of certified reference material Light sand Soil with normal analyte levels 7001, certificate No. 0217-CM-7001-04. The results of the determination of lead, cobalt, zinc, iron and chromium on the certified reference material are presented in Table 1.

Results and Discussion

The amounts of the heavy metals (extract in 1 M HCl) in the analyzed soil samples depending on the site of sample collection are presented in Figs. 2-5 (the east-west axis) and in Table 2 (the north-south axis). The contents of Pb (Fig. 2 and Table 2) range from 6.35 to 76.42 mg/kg. As there is no Polish Standard for the allowed content of lead, it is possible to assess the degree of contamination with this element only on the basis of its total content. Thus for randomly selected soil samples (showing big differences in the content of metals in extracts and mineralizates) total lead was additionally determined and on this basis the proportion of lead in 1M HCl extract was estimated (Table 3). The results indicate that the higher the level of total lead in the soil, the greater the proportion of its bioavailable form. It is from 14 to 30%. The distribution of lead content in the examined soil samples presented in the diagrams indicates that lead pollution of the sites situated along the east-west axis is more severe. The power plant is situated in the eastern part of the city and the north-south axis runs across the peripheral areas of Łódź. The east-west axis runs partly across the center of the city and some of the sites where samples were collected are situated close to busy roads. Motor traffic is one of the main sources of lead contamination [32, 33]. According to the Directive of the Minister of the Environment total lead concentration in built-up and urbanized areas should not exceed 100 mg/kg in the surface layer of the soil. This level was exceeded in 47% of the samples taken along the east-west axis and in 14% of those collected along the north-south axis.

The content of Zn in 1 M HCl extract (Fig. 3 and Table 2) is from 1.80 to 438.48 mg/kg. According to the Polish Standard, Zn content of over 20.5 mg/kg is considered to be high and is observed in 63% of the samples collected on the east-west axis and 14% of the samples from the sites along the north-south axis. According to the Directive of the Minister of the Environment passed in 2002 the content of zinc in built-up and urbanized areas should not exceed 300 mg/kg, which calculated as zinc in 1 M HCl extract is about 60 mg/kg (Table 3). This value was exceeded only in the soil samples collected along the east-west axis (33%) which runs through the center of the city and is in line with the Łódź wind rose, which is more exposed to the effects of the power plant dust emission.

The content of Cr (extract of 1 M HCl) in the examined samples range from 1.90 to 10.40 mg/kg (Fig. 4 and Table 2), which calculated as total chromium (Table 3) is from 42 to 62 mg/kg. Since the mean and most commonly observed levels of this element in Polish soils [18] range from 22 to 51 mg/kg, a slight Cr excess was observed only along the east-west axis (17%). According to the Directive of the Minister of the Environment the concentration of chromium in the built-up and urbanized areas should not exceed 150 mg/kg in the surface soil layer. This level is not exceeded in any of the areas included in the study.

Table 1. Comparison of the determined and certified values of lead, zinc, cobalt and chromium*.

Metals	Certified value [mg/kg]	Found [mg/kg]	Recovery [%]
Lead	24.1 ± 1.7	27.5 ± 1.9	114
Zinc	108 ± 3.5	106.9 ± 2.2	99
Cobalt	9.15 ± 0.47	8.51 ± 0.51	93
Chromium	71.9 ± 5.9	65.4 ± 5.5	91

*n = 5; p = 95%, n- number of sample, p – confidence level

The content of Fe (extract of 1 M HCl) in the examined soil samples is from 300 to 5530 mg/kg (Fig. 5 and Table 2), which calculated as total Fe is from 9125 to 36317 mg/kg (Table 3). According to the Polish Standards [34] Fe content exceeding 3800 mg/kg is high and occurs in 2% of the samples taken along the east-west axis and in no samples from the sites situated along the north-south axis.

The content of Co (extract of 1 M HCl) in the soil samples is from 0.25 to 7.68 mg/kg (Fig. 4 and Table 2), which calculated as total cobalt is about 4 to 43 mg/kg (Table 3). Natural content of this element may vary within a wide range from 0.1 to 34 mg/kg according to Kabata – Pendias [8] or from 1.4 to 18.8 mg/kg according to Ostrowska [18]. On the basis of this information it can be assumed that the content below 2 mg/kg of Co (extract of 1 M HCl) is a natural level of this metal in the soil. According to the Directive of the Minister of the Environment, the concentration of total cobalt in the surface layer of the soil in the built-up and urbanized areas should not exceed 20 mg/kg. This level is exceeded in four samples collected on the east-west axis,

Table 2. Statistical analysis for the content of metals (extract 1 M HCl) on the the axis north-south of the EC 4 power plant*.

No	Content of metal [mg/kg]									
	Pb		Zn		Cr		Fe		Co	
	Confidence intervals [mg/kg]	Relative standard deviations [%]	Confidence intervals [mg/kg]	Relative standard deviations [%]	Confidence intervals [mg/kg]	Relative standard deviations [%]	Confidence intervals [mg/kg]	Relative standard deviations [%]	Confidence intervals [mg/kg]	Relative standard deviations [%]
1.	12.9 ± 0.4	4.12	16.90± 0.9	4.12	2.10 ± 0.17	6.63	768 ± 38	3.93	0.70 ± 0.054	6.23
2.	8.90 ± 0.57	4.05	5.23 ± 0.26	4.05	2.00 ± 0.14	5.96	691 ± 30	3.50	0.70 ± 0.053	6.14
3.	19.4 ± 0.8	3.44	10.8 ± 0.6	4.31	2.40 ± 0.12	4.12	884 ± 36	3.27	0.97 ± 0.055	4.60
4.	7.03 ± 0.34	3.87	1.80 ± 0.13	5.87	1.90 ± 0.15	6.34	723 ± 27	3.03	0.30 ± 0.017	6.31
5.	34.9 ± 1.8	4.23	30.7 ± 1.7	4.69	3.39 ± 0.22	5.23	2366 ± 123	4.20	1.95 ± 0.083	6.74
6.	13.2 ± 1.0	6.18	6.41 ± 0.27	3.97	2.38 ± 0.16	5.26	883 ± 39	3.55	0.65 ± 0.056	6.31
7.	15.8 ± 1.3	6.53	18.3 ± 0.9	4.27	2.40 ± 0.15	4.97	859 ± 39	3.68	0.80 ± 0.049	4.63
8.	8.63 ± 0.46	5.38	1.95 ± 0.97	5.36	2.41 ± 0.15	5.13	415 ± 16	3.06	0.25 ± 0.02	6.30
9.	11.7 ± 0.7	4.69	19.5 ± 0.8	4.92	2.59 ± 0.17	4.93	698 ± 33	3.79	0.85 ± 0.048	5.63
10. EC 4	**9.53 ± 0.21**	**2.94**	**9.18 ± 0.47**	**4.97**	**2.59 ± 0.13**	**5.07**	**707 ± 22**	**2.54**	**0.80 ± 0.057**	**5.93**
11.	7.61 ± 0.54	5.75	4.20 ± 0.13	5.49	2.60 ± 0.17	5.36	377 ± 18	3.90	0.95 ± 0.049	5.12
12.	10.4 ± 0.6	3.92	12.3 ± 0.5	2.40	2.40 ± 0.19	5.26	641 ± 21	2.62	0.50 ± 0.049	6.27
13.	14.5 ± 0.9	5.97	11.2 ± 0.6	2.39	2.39 ± 0.13	4.95	982 ± 61	5.00	0.95 ± 0.053	5.37
14.	21.9 ± 1.0	3.77	40.1 ± 2.3	4.77	3.61 ± 0.26	5.91	2122 ± 92	3.50	3.20 ± 0.23	5.80

*n = 5; p = 95%, n- number of sample, p – confidence leve

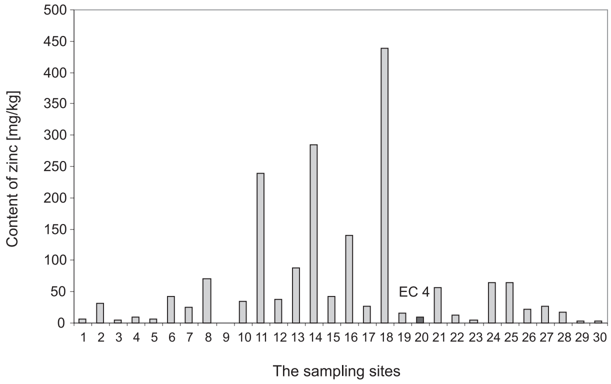

Fig. 3. The content of zinc (extract of 1M HCl) on the axis east-west of the EC 4 power plant.

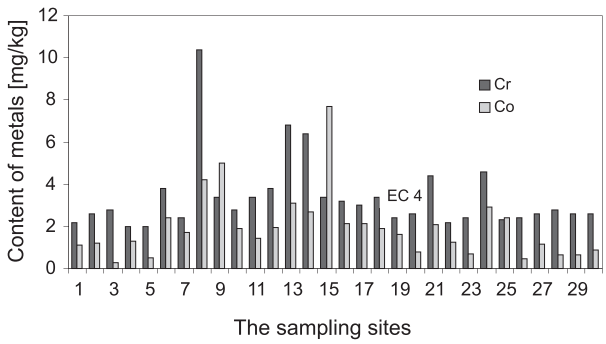

Fig. 4. The content of chromium and cobalt (extract of 1M HCl) on the axis east-west of the EC 4 power plant.

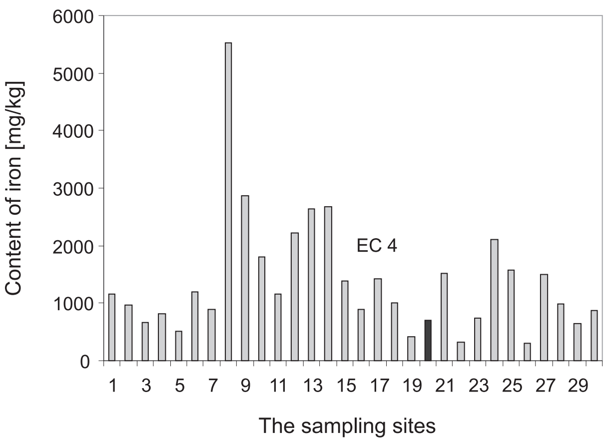

Fig. 5. The content of iron (extract of 1M HCl) on the axis east-west of the EC 4 power plant.

which accounts for 13% of all samples and in one sample collected on the north-south axis (7% of all samples).

The City of Łódź Atlas [35] informs us that the level of soil contamination with lead, zinc and copper in its area is low or medium. There is no data on cobalt or iron contamination. According to the Atlas of urban soil contamination in Poland [36], the level of Pb, Cu and Zn content

Table 3. Comparison of extracts of 1M HCl and total Pb, Zn, Co, Cr and Fe content in selected soil samples.

No.	Content of lead [mg/kg]		$\frac{Pb_{ext.}}{Pb_{total}}$ [%]	Content of zinc [mg/kg]		$\frac{Zn_{ext.}}{Zn_{total}}$ [%]	Content of cobalt [mg/kg]		$\frac{Co_{ext.}}{Co_{total}}$ [%]	Content of chromium [mg/kg]		$\frac{Cr_{ext.}}{Cr_{total}}$ [%]	Content of iron [mg/kg]		$\frac{Fe_{ext.}}{Fe_{total}}$ [%]
	Extract of 1 M HCl	Mineral. HNO_3 + $HClO_4$			Mineral. HNO_3 + $HClO_4$		Extract of 1 M HCl	Mineral. HNO_3 + $HClO_4$		Extract of 1 M HCl	Mineral. HNO_3 + $HClO_4$		Extract of 1 M HCl	Mineral. HNO_3 + $HClO_4$	
1.	76	262	29	439	1390	31	7.7	43	18	10	61	17	294	9,130	3
2.	63	222	29	285	927	31	5.0	30	17	6.8	49	13	707	15,690	4
3.	34	129	27	139	556	25	4.2	24	17	6.4	49	12	1190	20,500	6
4.	30	112	27	98	462	21	2.9	19	15	4.6	42	10	2120	21,580	10
5.	22	133	17	65	337	19	1.9	15	13	3.4	51	7	2370	22,090	11
6.	9.4	62	15	31	153	20	1.2	11	10	3.4	49	7	2870	28,960	10
7.	6.4	45	14	6.4	31	20	0.3	4.2	7.2	2.3	52	4	5530	36,320	15

in Łódź is clearly increased, especially in the center of the city and around big industrial plants. This is in agreement with our results, which also are in agreement with findings concerning the contents of these metals reported in our previous works [22-27]. These results indicate that power plant dust has no influence on the content of the elements in the soil. Higher accumulation of the metals is observed near major roads, which suggests that traffic is the main source of soil pollution in Łódź.

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