Short Communication

# Assessing Heavy Metal Content in Soils Surrounding a Power Plant

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#### **Abstract**

The aim of the present work was to establish the effect of dust from the EC3 power plant in Łódź on the content of heavy metals in the 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 sources of soil contamination with these metals are primarily large industrial plants and heavy motor traffic. The power plant dust has no influence on soil content.

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

### Introduction

The present work continues investigations of dust released from Łódź's power plant and how it influences the content of bioavailable heavy metals in soil in the city area [1]. Contamination of the soil over the natural level by Pb, Zn, Cr, and Co could be one of the indicators of anthropogenic environmental pollution. Fast development of industry, continuously increasing population, and intensification of road traffic are regarded as the foremost causes of ecosystem pollution in urban areas [2]. Two types of pollution sources can be distinguished: spot-like (human activity related) and of surface origin (of both natural and anthropogenic sources) [3]. Heavy metal elements present in the soil is one of the most important signs of environmental pollution. They are transferred to the soil in the form of atmospheric dust [4-6]. In the city of Łódź, as in the most Polish cities, power plants produce electrical energy and hot water by incineration of coal. This results in the release of various pollutants, e.g. heavy metals, that in turn contaminate soil through dust fall. Emission of dust and gas by-products in modern plants (or adapted ones) is reduced greatly due to filtration and further conversion into nontoxic products.

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Nevertheless, some part of pollutants is still released into the atmosphere as volatile ash, soot, and metal dust.

#### **Experimental Procedures**

Soil Sample Collection and Preparation

Soil samples for analysis were collected from the surface layer (0-20 cm) within the border of the city of Łódź in 2007 along two axes: north-south and east-west, which intersect at the power plant site. 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, 41% of the wind in Łódź comes from the west and 34% from the east [7].

Therefore, a decision was made to collect samples more frequently along the latter axis (27 collections) than along the north-south axis (11 collections). The soil samples referred to as EC3 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. The prepared soil samples were stored in plastic containers and used for further analyses [8].

## Preparation of Soil Extracts and Mineralizates

Soil extracts in which the bioavailable elements were determined were prepared in the following way: the weighed portions of previously prepared soil with granulation below 2 mm and mass of about 5 g ( $\pm 0.001$  g) were placed in plastic beakers and 50.0 ml of 1 mol/l HCl solution was added according to the standard [9]. 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 and the first part of the filtrate was rejected [9].

In order to determine total content of the metals, mineralization of soil for a few select samples was conducted using a Plazmatronika mineralizer. We determined that organic carbon content was below 20% (5-8%), so there was no need for an additional quantity of acid to oxidative degradation of samples in a mineralizer [10]. A concentrated HClO<sub>4</sub> or a mixture of concentrated HNO<sub>3</sub> and HClO<sub>4</sub> acids (mixed in a 1:2 ratio) were used to mineralize weighed portions of soil with granulation below 0.1 mm of

mass of about 0.5 g. When the process was finished the solution was transferred to a 25 ml measuring flask and diluted with distilled water [10].

## Principles and Determination Procedure for Select Elements by FAAS Method [11]

The concentration of each metal was determined in soil extract or mineralizate by means of flame atomic absorption spectrophotometry (FAAS) in a reducing oxy-acetylene flame using an appropriate lamp and wavelength specific for each metal element (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 to 20.00 μg/ml for Fe, and from 0.00 to 5.00 µg/ml for Cr. All the solutions were diluted with 1 mol/l HCl solution. Lanthanum solution (5% LaCl<sub>3</sub>) 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.



Fig. 1. Sample collection sites.

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	26.1±1.1	108	
Zinc	108±3.5	107±2.0	99	
Cobalt	9.15±0.47	8.91±0.64	97	
Chromium	71.9±5.9	66.4±5.7	92	

<sup>\*</sup>n = 5; p = 95%, n - number of samples, <math>p - confidence level.

#### **Results and Discussion**

Due to the considerable number of time-consuming mineralization procedures, evaluation of total metal content in the soil was conducted only for selected samples. Nevertheless, determination of bioavailable heavy metals was carried out for all soil samples. As there are no Polish standards for several of the bioavailable elements evaluated in this work, total content of metals was used as a benchmark for determining soil contamination. Thus, for randomly selected soil samples (showing significant variation in bioavailable element contents in extracts) total metal content was assessed. Based on the results (Table 2), the proportion of bioavailable metals was estimated.

Based on the number of evaluated soil samples, it was found that better results of mineralization process were achieved by using a mixture of HClO<sub>4</sub> and HNO<sub>3</sub> acids instead of only HClO<sub>4</sub>.

The amounts of the heavy metals (extract in 1 mol/l HCl) in the analyzed soil samples, depending on the site of sample collection, are presented in Figs. 2-4 (the east-west axis) and in Table 3 (the north-south axis).

The content of bioavailable Zn in soil samples (Fig. 3 and Table 3) ranges from 0.40 to 407 mg/kg. According to the Polish Standard [9], bioavailable Zn content of over 20.5 mg/kg is considered to be high. Zinc content over that level was observed in 64% of the samples collected on the north-south axis and 59% of the samples from the sites along the east-west axis. According to the 2002 Directive of the Minister of the Environment on quality standards for soil and land quality [12], total zinc in built-up and urbanized areas should not exceed 300 mg/kg, in which bioavailable zinc is about 80 mg/kg (Table 2). This value was exceeded in 26% of the samples collected along the east-west axis and in 45% of those taken along the north-south axis. These areas should be considered contaminated with zinc.

The content of bioavailable Fe in the examined soil samples is from 197 to 5,128 mg/kg (Fig. 2 and Table 3). According to Polish Standards [13], bioavailable Fe content exceeding 3,800 mg/kg is high and this occurs in 9% of the samples taken along the north-south axis and in no samples from the sites situated along the east-west axis.

The content of bioavailable Pb in soil samples (Fig. 3 and Table 3) is from 3.00 to 173 mg/kg. Since there is no Polish Standard for the allowed content of bioavailable lead,

it was necessary to assess the degree of contamination with this element on the basis of its total content. The results given in Table 2 indicate that bioavailable lead constitutes from 30 to 40% of total lead. A direct relationship was observed between total lead content and the proportion of its bioavailable forms. This is in accordance with results reported previously [1]. According to the ministry directive, total lead concentration in built-up and urbanized areas should not exceed 100 mg/kg in the surface layer of the soil [12]. This level was exceeded in 22% of the samples taken along the east-west axis and in 36% of those collected along the north-south axis.

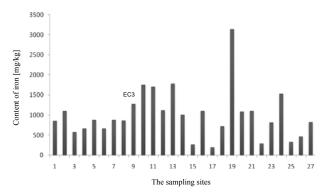


Fig. 2. Content of bioavailable iron (extract of 1 mol/l HCl) on the east-west axis of the EC3 power plant.

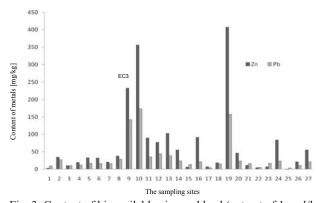


Fig. 3. Content of bioavailable zinc and lead (extract of 1 mol/l HCl) on the east-west axis of the EC3 power plant.

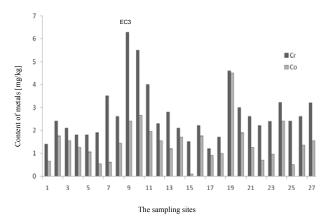


Fig. 4. Content of bioavailable chromium and cobalt (extract of 1 mol/l HCl) on the east-west axis of the EC3 power plant.

Table 2. Comparison of bioavailable and total forms of Pb, Zn, Co, Cr, and Fe content in select soil samples.

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Coext	Co		41	13	17	17
balt	Mineralizate	HClO <sub>4</sub>	15.1	19.3	24.2	34.9
Content of kobalt [mg/kg]	Miner	HNO <sub>3</sub> + HCIO <sub>4</sub>	18.5	21.9	26.3	38.7
Ю		Ext. HCl	2.66	2.90	4.50	02.9
Дe	Fe ext.	total %	5	13	6	13
		HClO₄	20,502	33,665	14,744	21,580
Content of iron [mg/kg]	Mineralizate	HNO <sub>3</sub> + HCIO <sub>4</sub>	1,179 24,458 20,502	39,334	19,445 14,744	3,149 24,014 21,580
Co		Ext. HCl	1,179	5,129	1,758	3,149
Cr	Cr	10tal	3	6	9	5
nium	Mineralizate	HClO <sub>4</sub>	52.9	41.7	64.6	51.1
Content of chromium [mg/kg]		HNO <sub>3</sub> + HCIO <sub>4</sub>	75.9	9.62	7.76	69.4
Conte		Ext. HCl	2.30	7.10	5.50	3.40
uZ	Zn total	%	23	27	27	27
nc	Mineralizate	HClO <sub>4</sub>	601	1,185	1,244	1,490 1,290
Content of zinc [mg/kg]	Miner	HNO <sub>3</sub> + HCIO <sub>4</sub>	647	1,349	1,300	1,490
Co		Ext. HCl	150	369	356	407
дd	Pb total	%	36	40	40	26
ad		HClO₄	387	409	390	112
Content of lead [mg/kg]	Mineralizate	HNO <sub>3</sub> + HCIO <sub>4</sub>	425	434	448	122
ŭ		Ext. HCl	152	173	157	31.6

Table 3. Statistical analysis for the content of bioavailable metals (extract 1 mol/l HCl) on the north-south axis of the EC 3 power plant.

		RSD	[%]	5.12	4.89	5.99	8.83	6.34	6.13	5.90	3.23	7.09	5.20	4.18	
9	3	Confidence intervals	[mg/kg]	1.35±0.12	1.10±0.11	1.65±0.19	2.40±0.25	2.20±0.38	3.00±0.42	6.10±0.45	$0.50\pm0.01$	0.55±0.06	0.30±0.02	2.95±0.15	
		RSD	[%]	10.8	7.13	8.05	5.02	6.13	9.80	12.0	6.13	6.25	7.04	11.1	
AH AH	21	Confidence intervals	[mg/kg]	1012±53	739±38	998±49	1280±80	690±33	1179±61	5128±257	688±43	720±56	585±22	2585±355	
		RSD	[%]	5.10	6.15	4.57	4.75	4.02	8.23	4.00	5.49	4.80	9.02	4.12	
ئ	5	Confidence intervals	[mg/kg]	1.60±0.14	2.20±0.33	2.80±0.16	6.29±0.37	1.90±0.28	2.30±0.11	7.10±0.49	2.20±0.15	1.79±0.11	1.90±0.13	3.70±0.18	
		RSD	[%]	4.32	8.9	6.34	6.62	7.3	3.74	1.9	6.30	11	5.28	4.17	
Zn	Zur	Confidence intervals	[mg/kg]	9.30±0.50	15.9±0.7	39.5±3.1	233±19	46.3±2.8	150±7	369±15	171±10	9.45±0.55	1.90±0.13	167±3	
	Pb	RSD	[%]	2.25	7.91	9.30	10.2	6.35	8.72	9.18	4.03	4.91	10.2	6.34	
- Yd		Confidence intervals	[mg/kg]	9.00±0.25	12.8±0.5	31.6±3.6	142±8.0	24.3±0.8	49.5±2.1	152±11	26.1±2.9	11.8±0.7	4.32±0.55	62.8±3.0	
		No.		1.	2	3	4 *	5	9	7	∞	6	10	11	

\*n = 5; p = 95%, n - number of sample, p - confidence level. \*\* The sampling site which is located close to EC3.

The content of bioavailable Cr in the examined samples ranges from 1.20 to 7.10 mg/kg (Fig. 4 and Table 3), which calculated as total chromium (Table 2) is from 18.5 to 109 mg/kg. According to the ministry directive, the concentration of chromium in the built-up and urbanized areas should not exceed 150 mg/kg in the surface soil layer [12]. This level is not exceeded in any of the areas included in the study.

The content of bioavailable Co in the soil samples is from 0.10 to 6.10 mg/kg (Fig. 4 and Table 2), which calculated as total cobalt is about 0.70 to 41.0 mg/kg (Table 2). Natural content of this element may vary within a wide range from 0.1 to 34 mg/kg, according to Kabata-Pendias [14]. According to the ministry directive, 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 [12]. This level is exceeded in one sample collected on the east-west axis (3% of all samples), and in one sample collected on the north-south axis (9% of all samples).

The results indicate that the EC3 power plant is not the principal source of heavy metals in Łódź area soils. There is no increase in their concentration according to the Łódź "wind rose," which suggests the direction of the dust emission from the power plant. Higher accumulation of the metals was not observed in the close vicinity of the EC3 power plant. There is, however, an apparent impact of major communication arteries on the urban environment. Metal contents were found to be relatively high along transportation routes, which is in agreement with previously conducted studies on another power plant [1].

This is consistent with reports in literature that indicate that the most important factor influencing the accumulation of heavy metals in soils is road transport [15-17]. Metal content in surface soil decreases with increasing distances from highways [18-20].

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