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Short Communication

Assessing Heavy Metal Content in Soils Surrounding Electroplating Plants

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Abstract

The aim of the present work was to establish the effect the Łódź electroplating plant on the content of chromium, zinc, and copper in soil. The soil samples for analysis were collected from the surface layer within the border of the city of Łódź. The following general properties of the agricultural soil used for the study were determined: pH, organic matter content, and mechanical analysis. The concentration of each of the metals was determined in soil extract or mineralizate by FAAS. The results indicate that the metals content in soil samples collected in the area of the city of Łódź depends on the type of processes carried out in the plating and from its location in the city.

Keywords: chromium, zinc, copper, galvanizing, electroplating plant, FAAS, urban soils

Introduction

There are various sources of environmental pollution by heavy metals. The most important of these are industrial plants, public transport, and agriculture. The largest amount of pollutants get into the soil and deposit on land through sewage route, with dust and solid and liquid waste generated by the industry such as metallurgy, production of alloys, and their processing [1]. Many plants (including electroplating) emit harmful gases and dust, which contaminate soil when deposited from polluted air [1, 2].

It is necessary to control the content of heavy metals, which have the capability to accumulate in, among other things, the soil and plants. Currently a lot of research is being conducted on the determination of metals pollution in soils of different areas such as highway surroundings [3], metal smelters [4], power plants [5, 6], garbage dumps [7], and metal foundries [1, 8].

The subject of this paper is examination of soil samples from eight sites adjacent to galvanizing plants in Łódź.

In galvanizing plants, waste results from wastewater treatment technology. Wastewater is generated in processes of surface preparation of metals for machining (degreasing, pickling) and in galvanic coating processes as a results of water exchange in scrubbers.

The electrolytic plating method develops metallic coatings on various materials. Application of a protective surface is primarily intended to increase resistance of the material against environmental influence, but often is also applied in order to modify physical properties of the surface. Frequently utilized galvanic treatment technologies are plating by zinc, tin, cadmium, copper, nickel, gold, chrome, and oxidation [9, 10].

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Experimental Procedures

Soil Sample Collection and Preparation

The soil samples for analysis were collected from the surface layer (0-20 cm) within the border of the city of Łódź in 2011 according to ISO standards [11]. The soil samples were collected outside the area of eight plants, on lawns in their direct vicinity (for each plant collecting five samples of soil). The samples were collected systematically and equal distances were maintained.

Table 1. The results of soils analysis.

Number of galvanizing plant	Soil pH in 1 mol/l KCl	Organic matter content %	Mechanical analysis [%]		
			Fractions:		
			Φ 1 ÷ 0.1	Φ 0.1 ÷ 0.02	Φ < 0.02
1	7.2	3.9	95.20	4.70	0.10
2	7.2	5.3	91.00	8.80	0.20
3	7.5	3.9	94.40	5.53	0.07
4	7.2	3.1	90.00	9.84	0.16
5	7.8	3.1	91.82	8.10	0.08
6	7.3	2.4	93.70	6.14	0.16
7	7.3	6.4	85.10	14.50	0.40
8	7.4	5.5	85.50	13.72	0.78

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 [12].

The following general properties of the agricultural soil used for the study were determined: pH, organic matter content, and mechanical analysis. Soil pH was determined in 1mol·L^{-1} KCl solution [13]. 25 mL of KCl solution were added to 5 mL of soil and stirred with a magnetic agitator for 2 hours at a rate of about 50 rev/min. Next, soil pH was measured using a Delta 350 (Mettler) pH-meter. For organic matter determination the dry soil was placed in a muffle furnace to follow the decrease in mass at 550ºC [14]. The mechanical analysis was carried out using stainless steel sieves (0.02, 0.1, 1.0 mm). The results of the analyses are given in Table 1.

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 (±0.001 g) were placed in plastic beakers and 50.0 ml of 1 mol/l HCl solution was added according to the standard [15]. Then the content of the beaker was stirred with a magnetic agitator for 1 hour at a rate of about 50 rev/min. The solution was then passed through a medium filter and the first part of the filtrate was rejected [15].

Total content of Zn, Cu, and Cr were determined in mineralizates prepared according to the ISO and the instructions recommended by the manufacturer of microwave equipment [16].

A mixture of concentrated HCl and HNO_3 acids (mixed in a 1:3 or 3:1 ratio) was poured on 0.5000 g weighed amounts of soil, with granularity below 2 mm. Next the samples were mineralized using a "Plazmatronika" mineralizer. When the process was finished the solution was transferred to a 25 ml measuring flask and diluted with distilled water.

The concentration of each of the metals was determined in soil extract or mineralizate by means of flame atomic absorption spectrophotometer (FAAS) in the reducing oxy-acetylene flame with the use of an appropriate lamp and wavelength specific for each metal element (Cr – 357.9 nm, Zn – 213.9 nm, and Cu – 324.7 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 5.00 μg/ml for Cr, from 0.00 to 6.00 μg/ml for Zn, and from 0.00 to 3.00 μg/ml for Cu. 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 results of total amounts of the metals in soil mineralizates are presented in Tables 2 and 3.

Method accuracy was confirmed by the analysis of certified reference material Light sand Soil with normal analyte levels 7001, certificate No. 0217-CM-7001-04. Recovery was 92% for Cr, 99% for Zn, and 96% for Cu.

Results and Discussion

Organic matter content in all soil samples indicates that these are the mineral soils. All analyzed soils belong to the granulometric group of loamy sand and are alkaline. Due to the pH and content of organic matter the metals present in the soils are strongly adsorbed, and thus less available to plants.

Total contents of Cu and Zn were similar regardless of the type of mixture used for soil mineralization (concentrated HCl and HNO_3 acids mixed in a 1:3 or 3:1 ratio). In the case of Cr, acids used to mineralization in a 1:3 ratio were a better mixture.

Total chromium content in the analyzed soil samples is from 59 to 311 mg/kg. According to the directive of the minister of the environment [17] the concentration of chromium in the built-up and urbanized areas should not

Table 2. Bioavailable forms of chromium, zinc, and copper in soils*.

Number of galvanizing plant	Bioavailable forms of metals [mg/kg]					
	Chromium	RSD %	Zinc	RSD %	Copper	RSD %
1.	4.10±0.13	5.1	35.9±3.3	3.1	3.85±0.29	4.8
2.	94.6±5.0	6.4	159±8	8.0	72.0±4.1	5.0
3.	4.98±0.18	4.9	54.5±2.8	5.0	5.99±0.5	5.8
4.	4.98±0.15	4.0	90.1±6.1	5.1	8.67±0.67	4.1
5.	3.20±0.32	6.1	25.4±2.8	3.2	3.73±0.41	6.0
6.	2.83±0.21	6.0	51.6±2.1	4.9	58.3±3.1	5.2
7.	24.3±1.8	4.0	78.3±5.8	7.1	35.1±3.5	6.2
8.	23.6±2.0	3.9	11.0±0.8	4.1	11.0±0.6	4.6

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

Table 3. The results of chromium, zinc, and copper determination in soils*.

Number of galvanizing plant	Total content of metal [mg/kg]											
	Chromium				Zinc				Copper			
	HNO_3:HCl 1:3	RSD %	HNO_3:HCl 3:1	RSD %	HNO_3:HCl 1:3	RSD %	HNO_3:HCl 3:1	RSD %	HNO_3:HCl 1:3	RSD %	HNO_3:HCl 3:1	RSD %
1	72.8±3.5	4.9	64.8±4.0	7.0	533±20	6.9	499±20	6.0	39.0±2.5	4.7	37.2±1.8	4.1
2	311±17	2.2	200±15	4.0	317±11	4.9	300±19	5.2	143±8	3.9	135±5	3.2
3	83.9±4.2	5.3	73.4±3.8	4.0	201±18	4.5	186±10	4.8	14.2±0.8	5.6	15.2±1.1	6.1
4	59.2±4.7	7.8	62.1±5.2	5.2	442±20	5.8	444±23	4.8	27.5±1.0	4.4	29.2±1.9	3.7
5	61.8±4.2	6.3	59.3±3.2	3.2	170±10	4.1	152±8	3.9	14.8±0.9	5.7	15.4±1.3	6.0
6	113±5	3.8	97.4±3.1	3.1	116±5	4.3	115±4	4.0	215±17	4.9	230±17	3.9
7	151±7	4.2	107±4	4.0	808±22	7..2	820±17	7.4	189±15	5.9	198±9.0	5.7
8	143±5	3.9	97.3±3.2	3.2	93.2±2.9	3.9	113±6	4.2	93.0±4.0	5.8	113±8	4.3

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

exceed 150 mg/kg in the surface soil layer. This level is exceeded only in electroplating No. 2, in which the process has metal chromium. The soil collected from this plant part to the total bioavailable form is about 30%, which may be indicative of anthropogenic origin chromium.

The content of bioavailable Zn in soil samples (Table 2) range from 11 to 159 mg/kg. According to the Polish Standard [15], bioavailable Zn content of over 20.5 mg/kg is considered to be high. Zinc content over that level was observed in 75% of the samples. According to the directive of the minister of the environment established in 2002 on quality standards for soil and land quality standards [17], the total zinc in built-up and urbanized areas should not exceed 300 mg/kg. This value was exceeded in 4 cases (Table 3). The maximum value of the zinc (808 mg/kg) was in the soil samples collected in electroplating plant No. 7, which deals with galvanizing. The plant is located in the city center. Electroplating building is surrounded by tall tenements from three directions, and a high traffic street closes the plant from the fourth direction. Therefore, the excessive zinc content in the soil taken from the site results from two factors – electroplating plant and road transportation.

Total copper content in the examined soil samples ranges from 15 to 230 mg/kg (Table 3). According to the Directive of the Minister of the Environment [17], the total copper in built-up and urbanized areas should not exceed 150 mg/kg. The highest concentration of this metal (230 mg/kg) was in the soil, collected adjacent to the plant for the production of copper and brass art jewelry.

The results indicate that the electroplating plants influence the surrounding soil pollution with heavy metals.

Previous papers [5, 6] investigated the effect of dust from a power plant in Łódź (Poland) 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 indicate that the main source of contamination with these metals are large industrial plants and heavy motor traffic. The power plant dust has no influence on soil content.

Another paper [18] investigated the impact of long-term electroplating industrial activities on heavy metal contamination in agricultural soils and potential health risks for local residents. Hazardous levels of Cu, Cr, and Ni were observed in water and paddy soils at sites near the plant. The soils showed a high risk for Ni and medium risk for Cu and Cr at certain sites. The contamination of these elements is related to the electroplating wastewater.

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