GEOMATICS AND ENVIRONMENTAL ENGINEERING • Volume 10 • Number 2 • 2016

http://dx.doi.org/10.7494/geom.2016.10.2.77

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The Content of Selected Heavy Metals of the Sediment and Soil Overburden Overlying Alkaline Sodium Waste on the Basis of the Settling Tanks of the Former "Solvay" Krakow Soda Works

1. Introduction

Heavy metals, although present in soils in small amounts, are one of the most important elements determining fertile or toxic properties of habitats [10]. Their behaviour in soils depends largely on different soil properties. One of the elementary factors in the mobility, concentration and distribution of heavy metals is soil pH [5, 9, 12]. An increase of soil pH causing the decreases of solubility of most of heavy metals. Their concentration is lower in alkaline soil solutions and their mobility decrease according to order: Cd > Ni > Zn > Mn > Cu > Pb [1, 12]. However, as it is noticed by Adamczyk-Szabela et al. [1], increase of soil pH not in all cases reduces the quantity of bioavailable heavy metals.

This subject was taken due to the lack of comprehensive research and data regarding the levels of heavy metals in alkaline soda sediments and formations overlying such waste material. As a part of the research, samples from the sediment ponds on the former "Solvay" Krakow Soda Works were analysed for the presence of selected elements from the group of heavy metals.

2. Characteristics of the Studied Area and Sample Collecting Method

Settlement tanks are located in the Małopolska voivodship in the south-western part of Kraków, in the valley of the Wilga River. They consist of three complexes comprising 25 sediment ponds. The total area of the storage site attributable to settlement ponds is about 80 hectares. Field studies were carried out on the settlement tanks of no. 21 to no. 25 located in the complex of sediment ponds no. 2 on the terrain of the former "Solvay" Krakow Soda Works (Fig. 1).

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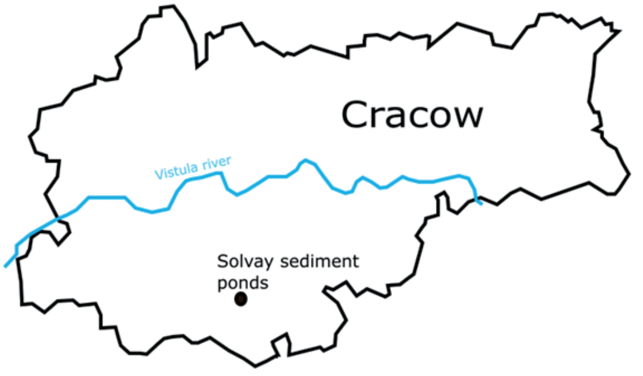

Fig. 1. Location of the studied area

In order to examine the content of trace elements 64 samples of soil that came from 40 open pits were analysed. The number of the samples from the pits was dependent on the thickness of the overburden layer. For the thickness not exceeding 15 cm one sample of the soil was collected but when the overburden layer was thicker than 15 cm two samples were collected. The first one came from the top 0–10 cm thick layer of the soil (hereinafter referred to as the TOP level), and the second – from 5 cm thick layer of soil located directly on the stored waste (hereinafter referred to as the BOT level).

The stored sediment was analysed in every 10 cm by taking samples from borehole from depth up to 120 cm, as well as description of the sediment by other authors [4] were taken into account.

The analyses described in this article were done by the soil laboratory at the Faculty of Mining Surveying and Environmental Engineering by following methodology:

- pH in 1 mol/dm^3 KCl by the potentiometric method,
- EC by the conductometric method,
- $CaCO_3$ content by Scheibler method,
- total Na, Mg, K, Ca, Fe and Cr, Mn, Ni, Cu, Zn, Sr, Cd, Pb (ASA method after mineralisation in a mixture of perchloric and nitric acids in a ratio of 4:1).

3. General Characteristics of the Stored Sediment

The technological processes of the Krakow Soda Works were mainly based on the Solvay process, a main end product of which was sodium carbonate, and the caustification method by which sodium hydroxide was obtained. In the case of the sodium production, both ash and caustic, the waste constituted a serious problem. It is estimated that approximately 5 million tons of waste was stored on the settling tanks of the "Solvay" Krakow Soda Works [15, 17].

Within the mass of waste accumulated on the settling tanks two compounds dominated, i.e. calcium carbonate ($CaCO_3$) and calcium oxide (CaO), and compounds such as SiO_2, R_2O_3, MgO, $CaSO_4$, Na_2O, $CaCl_2$, Na_2CO_3, NaCl as admixtures, and others [4], as well as heavy metals coming from rapidly corroding technological lines and pipelines [2, 11, 13].

In order to describe the basic physical and chemical parameters, the deposited sediment was subject to laboratory analysis. The sediment is characterised by a high pH (highest pH measurements in KCl are 12). The lowest values of pH equal to 7.6 came from the surface layers. For the specific electrolytic conductivity the highest values were observed in the surface layer. EC average value is 1.759 mS/cm (the minimum value of 0.245 mS/cm, the maximum value of 3.060 mS/cm). Carbonate content varies between 71.9–95.8% and increases in samples according to the depth of the deposition.

Table 1. Basic statistics of the selected parameters in the sediment

Parameter	Unit	Average	Minimum	Maximum	Standard deviation
KCl pH	–	11.1	7.6	12.0	1.1
EC	mS/cm	1.759	0.245	3.1	0.8
Carbonates	%	83.6	71.9	95.8	8.6
Total Na	mg/kg	2011.0	282.5	4110.0	1453.1
Total K	mg/kg	9097.5	4998.8	11924.0	2036.1
Total Mg	mg/kg	184.4	34.0	702.0	201.8
Total Ca	mg/kg	393625.0	370500.0	425000.0	20252.8
Total Fe	mg/kg	3007.9	1406.0	5214.0	1068.1

An element present in the sediment in the highest quantities is calcium -with tended content to increase with depth of sampling. Its average in the sediment was close to 400 000 mg/kg. Very little differences between the lowest and the highest value were recorded (Tab. 1).

4. Total Content of Pb, Cd, Sr, Zn, Cu, Ni, Mn, Cr in the Sediment Stored on the Settling Tanks of "Solvay" Krakow Soda Works

The sample analyses of the sediment waste did not exceed acceptable standards quantities for soil [16]. All the trace elements were characterized by a very unequal vertical distribution (Fig. 2), with the largest differences between the samples from maximum and minimum values levels in the case of lead and chromium. Next in order were: strontium, zinc and nickel.

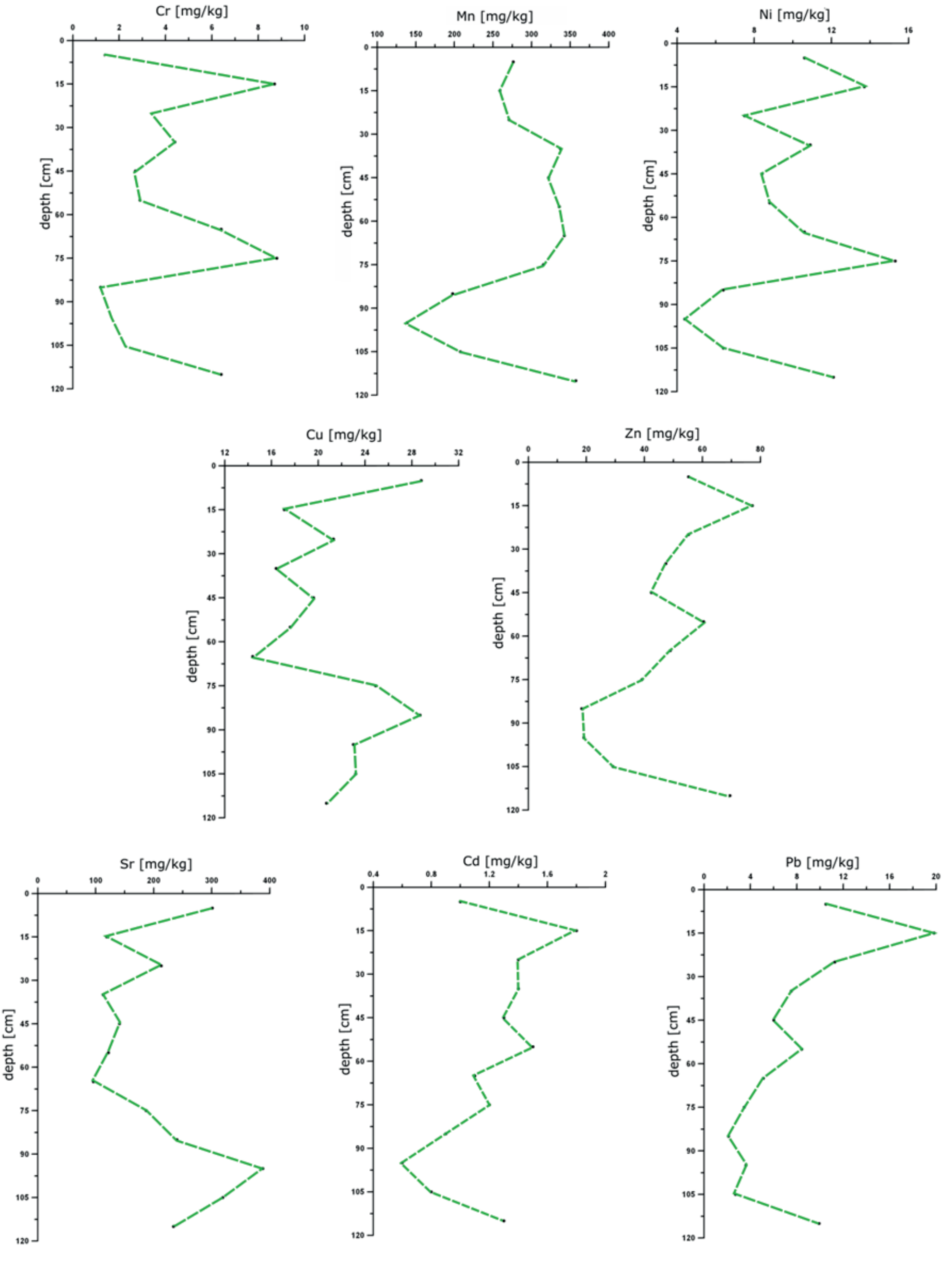

Fig. 2. Vertical distribution of the content of selected trace elements in the sediment

Taking into account the content of individual elements, manganese and strontium were present in the samples of the sediment in the largest quantities, which average amounts were respectively 280.00 mg/kg and 206.08 mg/kg (Tab. 2).

Table 2. Basic statistics of the content of selected heavy metals in the sediment

Parameter	Unit	Average	Minimum	Maximum	Standard deviation
Total Cr	mg/kg	4.19	1.20	8.80	2.74
Total Mn	mg/kg	280.00	138.85	357.35	68.59
Total Ni	mg/kg	9.59	4.40	15.30	3.21
Total Cu	mg/kg	21.31	14.40	28.80	4.64
Total Zn	mg/kg	46.83	18.40	77.20	18.42
Total Sr	mg/kg	206.08	96.00	388.00	93.84
Total Cd	mg/kg	1.19	0.60	1.80	0.33
Total Pb	mg/kg	7.53	2.10	19.83	4.99

Charts of vertical distribution of content of individual trace elements in the sediment enabled observation of the occurrence of certain relationships between some elements (Fig. 2). There is noticed a strong positive correlation between copper and strontium 0.71 and it is also the only significant relationship which exists between copper and any other heavy metal. Strontium additionally exhibits a strong negative correlation with Mn (correlation coefficient value −0.75) and Cd (0.79). In the case of other heavy metals, weaker or stronger positive correlations occur between them. Among heavy metals it was chromium which was characterized by the greatest variability, showing, positive correlations with cadmium.

Correlations of heavy metals with other measured physical and chemical parameters of the sediment were also noted. In the case of carbonates such correlations occurred with: Cu (0.80), Sr (0.77) and Cd (−0.69). Between the specific electrolytic conductivity positive correlations with cadmium (0.76) and negative with Cu (−0.71) and Sr (−0.75) were reported.

The occurrence of both a positive and negative strong correlation also concerned the content of macroelements, including sodium, which showed the largest number of relationships related to heavy metals, such as (correlation coefficient −0.78): Cu (0.90), Zn (−0.69), Sr (0.89), and Cd (−0.80).

5. Total Content of Pb, Cd, Sr, Zn, Cu, Ni, Mn and Cr in the Layer of Soil Overburden

The analysis of the content of heavy metals in the samples of soil material of the overburden layer showed that only in the case of cadmium could be spoken of its natural or near-natural content [7, 6, 18]. Maximum concentrations of this element reached only the level of 0.95 mg/kg (Tab. 3) that would allow for compliance with the Standards [16] even if the test area would be classified as the "A" group. For the other, concentrations of the content of the element in the soil material ranged on average value.

Table 3. Basic statistics of content of selected heavy metals in the soil samples from the overburden layer

Parameter	Unit	Average	Minimum	Maximum	Standard deviation
Total Cr	mg/kg	44.94	28.06	74.40	11.84
Total Mn	mg/kg	1136.89	518.00	2088.00	322.47
Total Ni	mg/kg	66.54	19.75	117.20	17.97
Total Cu	mg/kg	50.59	20.00	218.40	26.22
Total Zn	mg/kg	115.68	74.93	243.00	31.75
Total Sr	mg/kg	67.71	22.86	163.00	24.22
Total Cd	mg/kg	0.41	0.05	0.95	0.20
Total Pb	mg/kg	48.27	24.65	234.45	34.83

An average content of elements as chromium, cadmium and lead were 44.94 mg/kg, 0.41 mg/kg and 48.27 mg/kg respectively (Tab. 3). In those cases were at the level required by the standards [16] for the "A" group areas. Other elements averages values not exceed the standards [16] for the "B" group areas in 0–30 cm depth (Figs 3–5)

Copper and zinc content ranged from very low to very high, particularly in the bottom layer (BOT). Some of the samples from BOT were characterized by a concentration of the element Cu, Ni, Pb at the level much higher than the allowed concentration given by the Standards [16], even for the "B" group areas – as it is shown in Figures 3 and 4.

Copper, zinc, nickel and also manganese higher concentration were noticed – especially in BOT level. This group of heavy metals has similar chemical characteristic, their reactions in the soil are very similar as well as dependence on pH value [2].

Mean levels of strontium in the soil samples (Tab. 3) were also higher than the average values of typical Polish clay soils [8, 14]. However, the concentration shall be considered as a standard when dealing with the industrial area where the strontium content in the soils locally may be much higher [14].

Analysing the mean concentration of trace metals in both TOP and BOT levels, it appears that in virtually all cases, these values are slightly different from each other, whereas only in the case of chromium it was observed that it is slightly higher in the top level and in the case of the other elements higher mean amount of individual metals was observed in the bottom level (Figs 3–5).

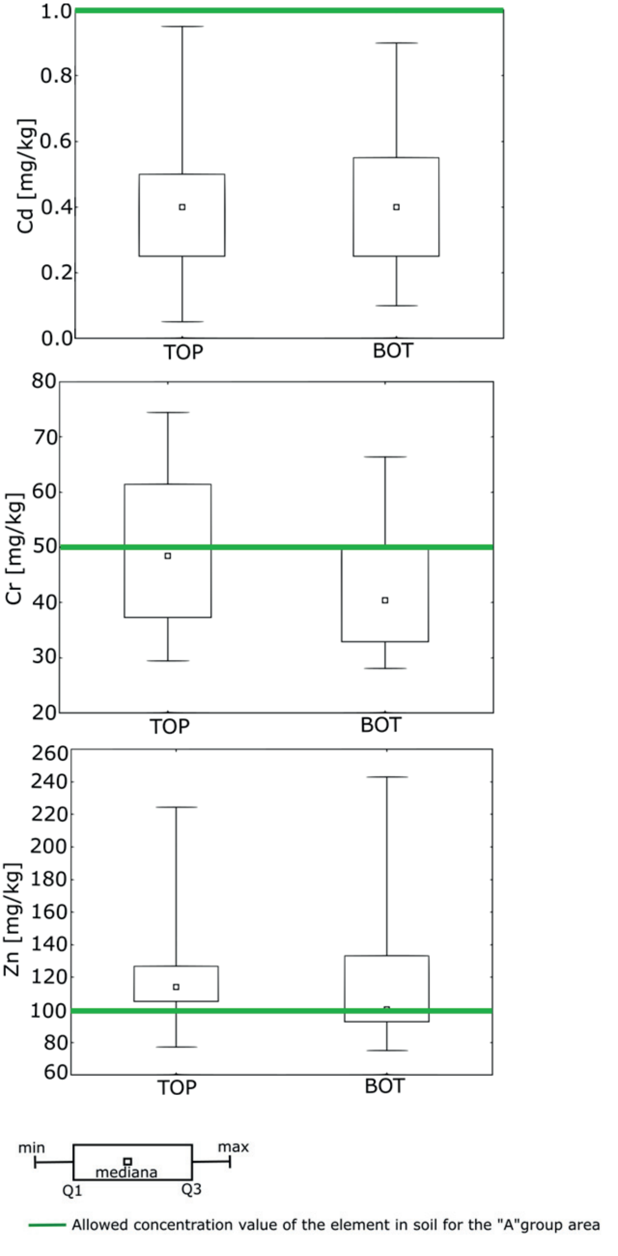

Fig. 3. Distribution of selected statistics of the content of some elements in the soil samples from the TOP and BOT levels of the overburden layer

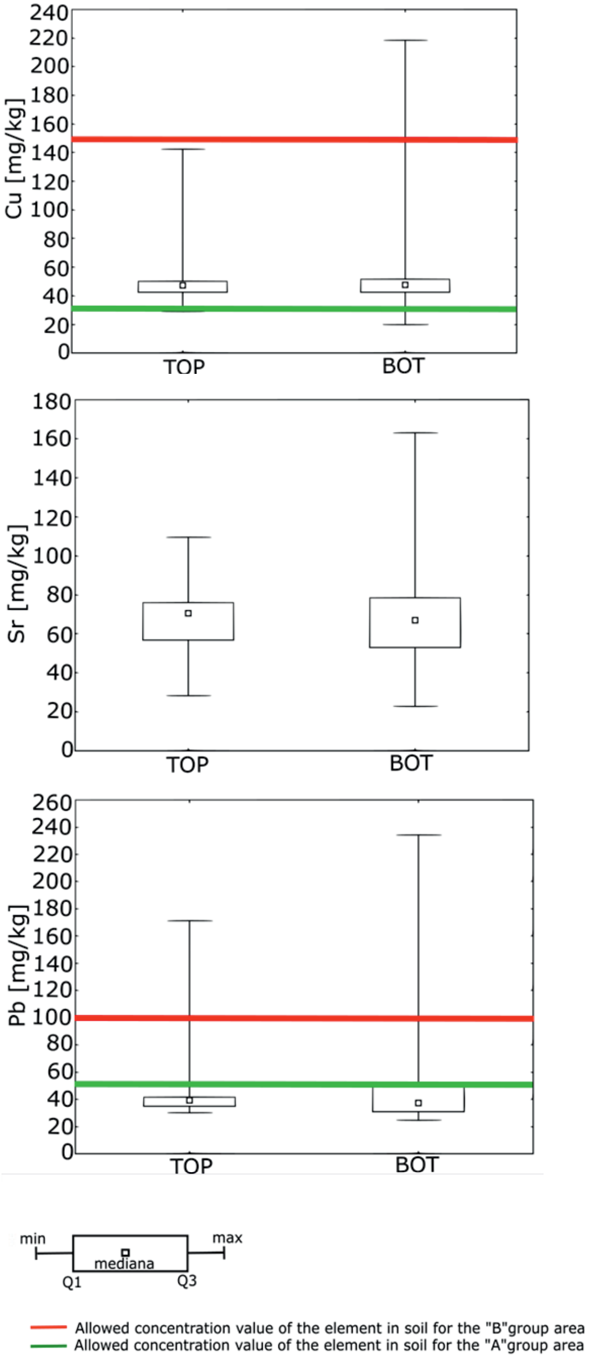

Fig. 4. Distribution of selected statistics of content of some trace elements in the soil samples from the TOP and BOT levels of the overburden layer

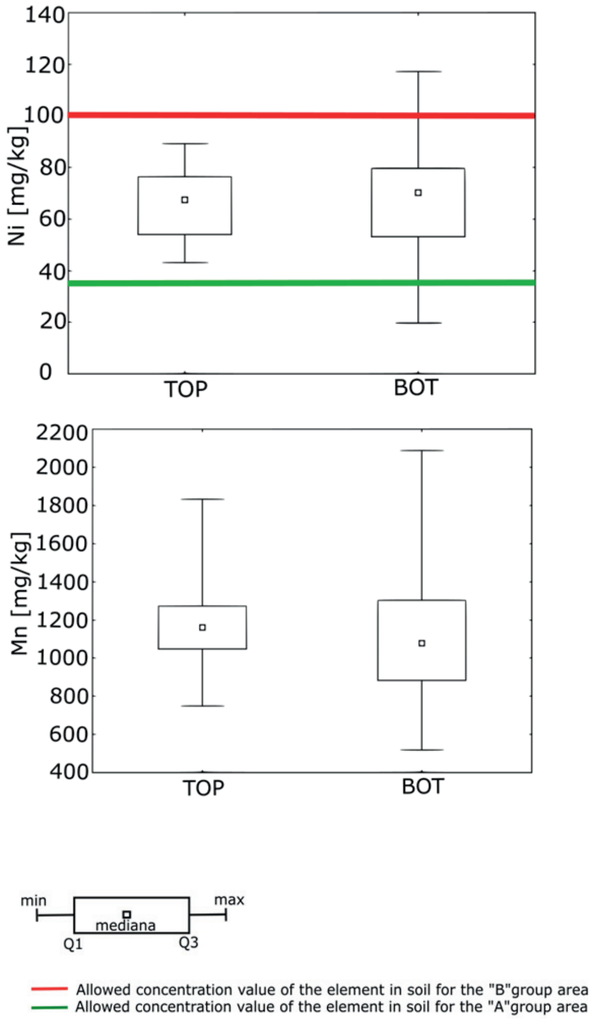

Fig. 5. Distribution of selected statistics of content of some trace elements in the soil samples from the TOP and BOT levels of the overburden layer

Statistical tests (significance level 0.05) showed that only in the case of a single element – zinc – the differences between the levels were statistically significant.

Among all the analysed elements a strong correlation was only observed between Zn and Sr (coefficient of correlation 0.73) (Fig. 6).

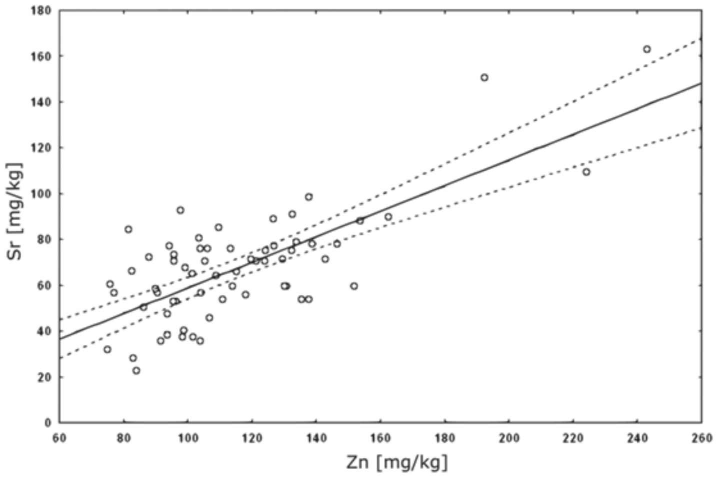

Fig. 6. Scatter chart of the spread of Sr and Zn with confidence intervals

6. Summary

The object of the research was to evaluate the content of heavy metals in the soil overburden covering the sodium industry waste. The analysis was based on the measurement of the total content of a given metals both in the sediment and in the overburden layer (ASA method after mineralisation in a mixture of perchloric and nitric acids in a ratio of 4:1). Determination of chemical and physical forms of those metals would complement the research with the information about possible interactions of these elements.

The article led to the following conclusions:

1. The highest average concentration of measured elements in the sediment was observed in the case of strontium and manganium.
2. The strongest correlation among heavy metals in the sediment was observed between cadmium and zinc.
3. Numerous correlations between the total sodium content and the concentration of selected heavy metals in the sediment were shown.
4. A higher concentration of all trace elements (except chromium) was observed in the bottom layer of the overburden, i.e. remaining in direct contact with the waste material.

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