

The content of heavy metals in soils and plants around the waste landfill in Siechnice (Poland)

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Abstract. Metal concentrations (Cu, Zn, Pb, Ni, Cr) in soils and plants around the metallurgical waste landfill of Siechnice, Poland, have been determined. The soil samples were collected from the surface layer of 0-25 cm. The soils and plants were digested in HNO₃, 60%, using the Microwave Digestion System (Milestone Start D). The analysis of metals has been carried out through the Flame Atomic Absorption Spectroscopy (FAAS) method. The pH and the conductivity of the soil solutions were measured. The pollution index (Wn) and the bioaccumulation coefficient (WB) have been determined. The permissible content of Cu, Zn, Ni and Cr in soils were exceeded compared to the geochemical background in uncontaminated soils of Poland. Chromium concentrations have also been exceeded relative to the standard for soils, according to the Polish Ministry of Environment Regulation from September 1st, 2016. The assessment of the bioaccumulation coefficients of metals in plants (*Plantagolanceolata* L. and *Zea mays* L.) has shown significant bioaccumulation of copper and zinc compared to the permissible concentrations of undesirable substances in feed in agreement with the Polish Ministry of Agriculture and Rural Development Regulation from January 23rd, 2007.

1 Introduction

The main sources of heavy metals in the environment are the anthropogenic activities. Branches of significant impact are those from the industry: mining, metallurgy, energy, and also transport. In the beginning of operation of Siechnice ironworks produced carbide and welding electrodes. Since 1932, it had been producing ferrochromium [1]. Table 1 shows the emission of pollutants from the organized and unorganized sources released by the Siechnice ironworks during the last years of its operation. The waste landfill is a remnant of the closure of the plant in 1995. The heap of slags with admixture of metallic phase is located in the south-east of Wrocław, in the Siechnice municipality, by the provincial road no. 95 from Wrocław to Olawa. In the north-east direction, at a distance of approx. 300 meters from the landfills, are located the water-bearing areas of Wrocław. Moreover, in the vicinity there is mainly agricultural wasteland. The only exception is the farmland in the south side of the landfill, by the provincial road no. 95. Within the area there is a municipal sewage treatment plant, concrete plant and shipping companies.

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Table 1. Emission from the ironworks of Siechnice [1].

Metal	Emission [Mg/a]		Precipitation [Mg/km ² ·a]
	Organized	Unorganized	
Cr	95	126	0.02 – 4.5
Fe	9.5	12.6	0.01 – 2.3
As, Mn, Pb, Ni, V, Cu, Cd	43	3	0.005 – 0.12

The landfill is located on sandy soils and loam soils, similarly as the Wrocław water-bearing areas. They are quaternary formations, and the aquifer level consists of gravel and coarse, medium and fine sands. They are characterized by a high rate of infiltration. Groundwater is isolated by clays and poorly drained loams. This is a barrier against effluents that could penetrate deep into the soil together with the rainwater.

On an area of approx. 12 hectares lies approx. 2 million Mg of waste in the form of slag and dust caused by the production of ferrochromium (Tab. 2). In order to secure the landfill site against the elution of heavy metals into the soil, the waste has been stabilized with boron and calcium compounds - the works have been carried out since 1981 [1]. Since 2012 the exploitation of waste located on a heap is being carried out to recover the chromium.

Table 2. The composition of waste [1].

Component	Percentage of composition [%]
CaO	35 – 56
SiO ₂	16.6 – 41.3
Al ₂ O ₃	0.5 – 9.5
Cr ₂ O ₃	0.5 – 10.5
Fe ₂ O ₃	0.25 – 3.8
MgO	5.4 – 14.5
metallic ferrochromium	no data

The metallic pollutants from soils are accumulated in the trophic chain. Plants, depending on the species, show a typical threshold of heavy metal tolerance. The excess of metal results the inhibition of growth, disturbances of the photosynthesis process and deformation of the root system in plants [2, 3]. The English plantain (*Plantagolanceolata* L.) and maize (*Zea mays* L.) are able to accumulate metals in amounts exceeding their physiological needs, without harm to the organism. They were used in phytoextraction of metals from floatation tailings from the copper industry. *Plantagolanceolata* L. collects the elements in the stem and leaves. Study showed the presence of 53 mg Cu/kg of dry matter and 100 mg Zn/kg of dry matter in English plantain. In the process of phytoextraction of zinc and nickel *Zea mays* L. was used. Maize accumulates impurities mainly in the root, to a lesser extent in the stem and leaves. The content of zinc, which deforms the root system and inhibits the growth of corn, is 250 mg Zn/kg of dry matter. Toxic concentration of zinc in the soil for maize is 750 mg/kg of dry matter [4–6].

2 Materials and methods

In the summer season of 2016 14 environmental samples were collected from the area around the heap in Siechnice. In one location, three soil samples were collected each time within the distance of approx. 100–200 cm from each other. The soils were collected from the surface layer of 0–25 cm. The soil and plant samples no. 1 were collected at the border of Wrocław water-bearing areas (towards the north-east of the landfill of metallurgic waste). Samples of no. 2 came from the area in the east of the Siechnice heap, 4 meters from the water reservoir, between the eastern ring road of Wrocław and the Stawowa Street. The soil samples no. 3a, 3b and 3c were picked up from cropland close to the

landfill (the southern direction). Samples no. 3c were collected from the location closest to the heap. Soil and plant samples no. 3b were picked up from a place located in a greater distance from the landfill. Samples no. 3a were collected by the provincial road no. 95. Also, samples no. 4 came from a cultivated field located on the opposite side of the provincial road no. 95. Samples no. 5 came from the roadside of West Street, which is the access road for the landfill in Siechnice (west side of the landfill). Samples of maize (*Zea mays* L.) were collected from the farmland (3a, 3b, 3c), while English plantain samples (*Plantagolanceolata* L.) were collected from the remaining locations.

Each time three of the air-dried soil samples were sifted and averaged. Measurements of pH and electrical conductivity in the soil solutions with a stoichiometry ratio of 1:2.5 (m:v) were made according to PN-ISO 10390:1997. Prepared in accordance with PN-ISO 11465:1999, the soil and plant samples were digested (ca. 0.2 g of dry matter) in 8 ml of HNO₃, 60%. The microwave mineralization process was conducted with use of the Start D device (Milestone). Metal concentrations (Zn, Cu, Ni, Cr, Pb) have been determined through the FAAS method with use of the iCE 3500 Solaar Thermo device (Thermo Scientific) [PN-ISO 11047:2001]. Arithmetic mean and standard deviation were calculated with three replicates of the sample.

Chemical analyses have been carried out in the certified Laboratory of Toxicology and Environmental Research in the Faculty of Environmental Engineering at the Wrocław University of Science and Technology.

3 Results and discussion

3.1 The physicochemical parameters

Soil solutions no. 1, 2, 4 and 5 are alkaline (pH above 7.50 in 1 M KCl and 7.90 in H₂O). Soil samples no. 5 have the most alkaline character, pH of 8.52 in 1 M KCl, pH of 8.92 in H₂O. That may be due to the influence of metallurgical waste currently being transported from the heap in Siechnice. Other samples may also be contaminated with dust from the heap, because of the destruction of carbonate layer which protected the metallurgical waste against the migration of metals into the ground depth together with rainwater.

Soil samples from the cultivated field which is located in the immediate vicinity of the heap (3a, 3b, 3c) have slightly acidic character. In the 1 M KCl solution, the pH values ranged from 6.00 to 6.38, and were also below 7.00 in H₂O. The acidification of soils may be caused by the ongoing agrotechnical treatments and the fertilizing of soils.

The measurements of conductivity indicate slight and medium salinity of soils around the waste landfill in Siechnice, ranging from 13.23 to 40.26 mS/m (lower limit 25 mS/m [7]). The only exception is sample no. 3a with recorded EC value of 102.32 mS/m. Such high salinity of the soil can be a result of the decline of the land, causing the gravitational runoff of the rainwater with mineral compounds and their accumulation in the trough. In addition, the factor fostering the salinity is also sprinkling the provincial road no. 95 with salt in winter. The salinity of the soil sample no. 5 (40.26 mS/m) may result from the contamination of land during the exploitation of the heap and transport of the metallurgical waste from the heap in Siechnice. In this location, the pH of the soil was the highest. In the soil sample no. 4 from the cropland (31.60 mS/m) salinity may be the effect of the use of mineral fertilizers. The lowest value of the EC (14.20 mS/m) was observed in sample no. 2, collected from the greatest distance from the heap and roads.

3.2 Spectroscopy analyses

The concentration of chromium was exceeded at one measurement point with respect to an acceptable level of metal in soils resulting from the Polish Ministry of Environment Regulation from 1. September, 2016 [8] (Tab. 3, Fig. 1). By the landfill's exit road (sample no. 5) the concentration of chromium amounts to 276.49 mg/kg of dry matter. High content of chromium could be the result of the ongoing exploitation and disposal of excavated material from the heap, as well as the long-term works of the Siechnice ironworks. Also may be due to the proximity of roads, including a motorway bypass of Wrocław, used for transporting the waste from the heap in Siechnice. Exceeding of chromium in the soil may be a consequence of sliding of the excavated material from trucks on the road. In the immediate vicinity of the water-bearing area of Wrocław the concentration of chromium was 119.66 mg Cr/kg of dry matter (soil sample no. 4). Movement of the dust determined by the direction of winds blowing in this area from the south-west to the north-east direction.

Table 3. The content of heavy metals in soils.

No.	Cu [mg/kg]		Zn [mg/kg]		Pb [mg/kg]		Ni [mg/kg]		Cr [mg/kg]	
	x	s	x	s	x	s	x	s	x	s
1	23.05	0.58	77.25	1.31	17.5	0.92	5.35	0.20	119.66	1.54
2	3.15	0.77	19.35	1.16	b.o.	b.o.	3.11	0.57	47.84	0.68
3a	10.14	0.80	47.65	1.85	6.71	0.78	3.53	0.19	85.29	0.79
3b	7.59	0.25	47.36	1.04	9.45	0.57	2.75	0.77	104.44	2.97
3c	7.05	0.34	45.98	0.74	12.73	0.62	3.14	0.74	62.65	1.45
4	16.40	0.84	38.03	0.66	4.17	0.78	2.27	0.42	8.16	0.31
5	16.03	0.63	55.23	0.72	no	no	13.71	0.59	276.49	1.02

x - arithmetic mean; s - standard deviation for 3 measurements, no - below the limit of Pb quantification with FAAS method.

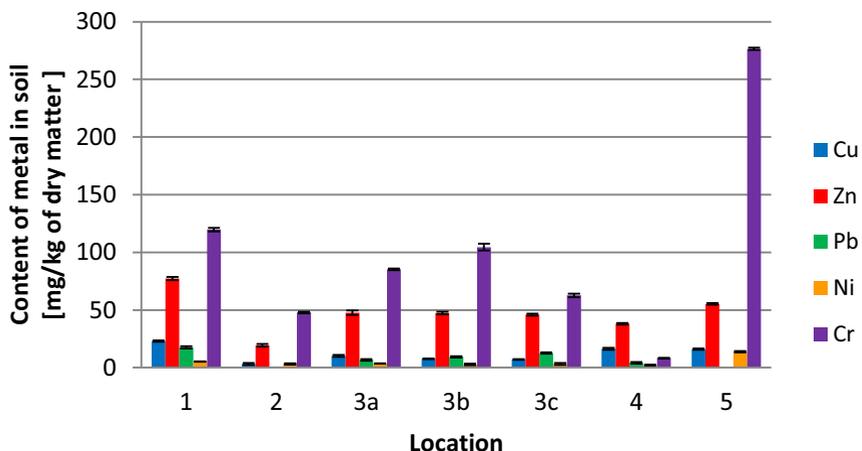


Fig. 1. The content of heavy metals in soils.

The concentration of other metals in soils are below the limit values set by the standard [8], but there are higher than the geochemical background in Poland. The average content of metals in the surface level of soils for the geochemical background of the whole Poland are, respectively: Cu - 6.5 mg/kg; Zn - 33 mg/kg; Pb - 18 mg/kg; Ni - 11 mg/kg; Cr - 40 mg/kg [9]. The increased concentrations of heavy metals in soil samples may be the

result of contamination of the area during operating period of the Siechnice ironworks and transferring of dust in the wind according to the isolines of the dust fall [1].

Copper in soil samples is within the range of 3.15 to 23.05 mg/kg of dry matter (Tab. 3). The lowest concentration was recorded at the measurement point no. 2, and the maximum content of zinc was observed in the sample no.1. Zinc is in the range of 19.35 to 77.25 mg/kg of dry matter. Similarly to the copper, the zinc content is lowest at the location no. 2, and the highest concentration is in the soil sample no.1. The lead concentration does not exceed the geochemical background in soil samples. The minimum content of lead is in the soil sample no. 4 (4.17 mg/kg of dry matter) and the highest concentrations were reported in location no. 1 (17.5 mg/kg of dry matter). Higher concentration of nickel compared to the geochemical background was observed only in sample no. 5 (13.71 mg/kg of dry matter). The minimum concentration of Ni is in sample no. 4 (2.27 mg/kg of dry matter). Low concentrations of heavy metals in location no. 4 are due to a remote location of sampling in the south-west of the landfill, on the opposite side of the road no. 95. The influence of dust moving with the wind in this direction is the smallest.

During the comparison of the results (Tab. 4) of acceptable concentration of heavy metals in forage plants [10], exceedings of the content of copper were observed, except for the seeds of maize (*Zea mays* L.). The English plantain (*Plantagolanceolata* L.) accumulates from 15.33 to 20.17 mg Cu/kg of dry matter in the tissues (limit for the forage plants: 10 mg Cu/kg of dry matter [10]). In the case of maize (*Zea mays* L.) the highest concentration of metal was observed in the root (from 19.64 to 21.4 mg Cu/kg of dry matter). The leaves of *Zea mays* L. accumulated from 16.63 to 20.09 mg Cu/kg of dry matter. The lowest concentration of the element was observed in the seed of maize (from 6.51 to 7.65 mg Cu/kg of dry matter), therefore it is possible to use the seeds in the animal feed.

Table 4. The content of metals in plants.

<i>Plantagolanceolata</i> L.	Cu [mg/kg]		Zn [mg/kg]	
	x	s	x	s
1	16.73	0.24	63.32	1.08
2	15.33	0.29	54.55	0.20
4	16.28	0.09	52.67	0.33
5	20.17	0.13	37.72	0.54
<i>Zea mays</i> L. - leaf				
3a	17.68	0.41	46.75	0.73
3b	19.64	0.30	32.96	0.22
3c	16.63	0.17	39.08	0.16
<i>Zea mays</i> L. - root				
3a	21.40	0.13	42.47	0.41
3b	20.09	0.61	100.56	1.37
3c	21.96	0.33	43.15	0.22
<i>Zea mays</i> L. - seed				
3a	6.51	0.02	5.50	0.13
3b	7.28	0.18	23.31	0.73
3c	7.65	0.23	13.35	0.17

x - arithmetic mean; s – standard deviation for 3 measurements.

The content of zinc in plants generally does not exceed the acceptable concentration of 100 mg Zn/kg of dry matter in the feed plants [10]. The only exception is the sample no. 3b,

where the root of maize (*Zea mays* L.) reported a slightly over-normative value – 100.56 mg Zn/kg of dry matter. Similarly to the case of copper, the lowest concentration of zinc was observed in the seeds of maize (from 5.50 to 23.31 mg Zn/kg of dry matter). The results show that the test plants can be used in the phytoremediation process of areas contaminated with zinc and copper. In *Plantagolanceolata* L. the accumulation of zinc is 2–3 times higher than copper. In maize a similar correlation was observed (2-fold higher accumulation of Zn). In the roots of *Zea mays* L. 4-fold higher concentration of zinc was observed.

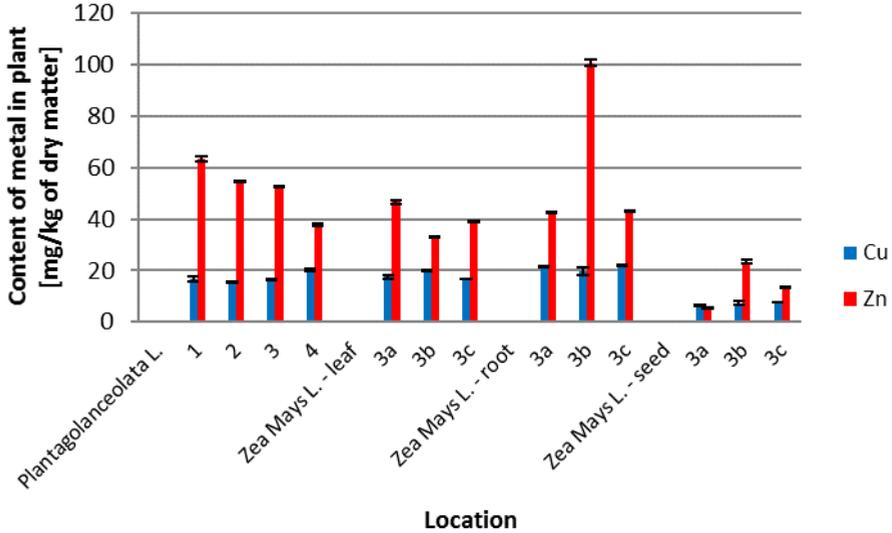


Fig. 2. The content of copper and zinc in plants.

3.3 Pollution index

The pollution index (W_n) is expressed as the ratio of metal in the soil to the geochemical background in uncontaminated soils of Poland. The calculated coefficients of the accumulation of metals in the soil are shown graphically in Figure 3.

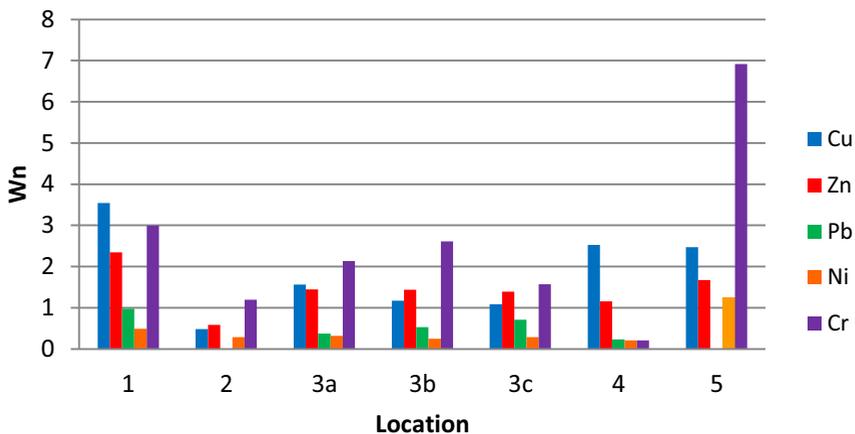


Fig. 3. The pollution indexes (W_n) of metals in soils.

The highest, almost 7-fold enrichment of the soil with chromium, relative to the average chromium content in the geochemical background in Polish [9], was observed in sample no. 5. Such high value of Wn 6.91 may indicate the influence of the waste from the landfill and the contamination of the soil. Other soil samples are also enriched with chromium (Wn 1.20 – 2.99). Only sample no. 4 is not enriched with this metal (Wn 0.2). Enrichment of the soil with copper and zinc was observed for the same soil samples. The maximum values of Wn for copper and zinc were in sample no. 1 and amounted of 3.55 and 2.34 for Cu and Zn respectively. The remaining samples were also enriched with copper and zinc. Wn indexes for copper were in the range of 1.08 – 2.52 and for zinc from 1.15 to 1.67. Only soil sample no. 2 was not enriched with copper (Wn 0.48) or zinc (Wn 0.59). Soil sample no. 5 was enriched with nickel and the pollution index is 1.25. None of the soils contained concentration of lead above the geochemical background.

3.3 Bioaccumulation coefficient

The bioaccumulation coefficient (WB) represents the ratio of the content of the metal in plant (its organs) in relation to the content of the metal in the soil. The parameter determines the ability of the plant to collect the components from the soil and also indicates the size and speed of metal movement from the soil solution to the aerial parts of plants. The calculated bioaccumulation coefficients of copper and zinc (WB) in maize (*Zea mays* L.) and English plantain (*Plantagolanceolata* L.) are shown graphically in Figure 4.

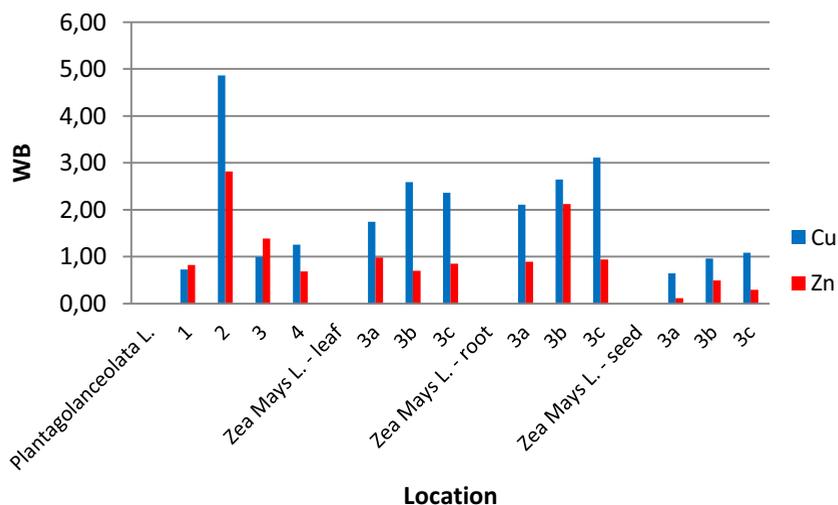


Fig. 4. The bioaccumulation coefficients of metals in *Plantagolanceolata* L. and *Zea mays* L.

The bioaccumulation coefficient values show that plants accumulate higher amounts of copper (WB 0.64–4.87) than zinc (WB 0.12–2.82). Some plants have accumulated metals in the tissues in quantities which could endanger the trophic chain. In sample no. 2 of the English plantain (*Plantagolanceolata* L.) the maximum value of WB for both copper and zinc, respectively 4.87 and 2.82 (Fig. 4), was recorded. High bioaccumulation coefficient values of copper were also observed in sample no. 5 (WB 1.26) and sample no. 4 (WB 0.99). A higher concentration of zinc in English plantain than in the soil was also recorded in sample no. 4 (WB 1.38).

During the analysis of the values of the bioaccumulation coefficients of copper and zinc in maize (*Zea mays* L.) it was observed that copper is essentially cumulated in biomass. The majority of the accumulation of copper takes place in the root of maize (WB 2.11–3.11) and

in its leaves (WB 1.74–2.59). In the seeds of maize the copper concentration (WB 1.09) is comparable to copper content in the soil. In the case of zinc, only in one sample no. 3b higher accumulation was noted in the roots of maize than in the soil (WB 2.12).

4 Conclusions

- Soils from the area around the landfill of metallurgical waste in Siechnice have alkaline character. Such pH limits the ability of the activation and migration of heavy metals contained in the soils deeper into the soil profile. The only exception is sample no. 3 from the cropland near the heap of metallurgical waste. The agrotechnical treatments and the fertilizing of the soil are the reasons for the slightly acidic character of soil no. 3. This creates a potential risk of migration of heavy metals into the soil profile.
- Essentially, the tested soils are of slight and medium salinity. The exception is sample no. 3a, of which the EC value was of 102.32 mS/m. Such high salinity may be due to the accumulation of mineral compounds, coming from the rainwater flowing of the neighborhood areas and also the provincial road no. 95, in the decline of land.
- Chromium has been exceeded in sample of soil no. 5 (276.49 mg Cr/kg of dry matter) compared with the Polish Ministry of the Environment Regulation from 2016, which may be a result of the ongoing works on the heap of metallurgic waste in Siechnice.
- In the six soil samples chromium, copper and zinc were in excess as compared to the geochemical background (Wn). In soil no. 5 exceeding of the concentration of chromium is nearly 7-fold and nickel was exceeded about 1.25-times. Exceeding of copper and zinc in soil no. 1 is approx. 3.5-fold and 2.3-fold, respectively. There were no exceedances of lead in the soil samples.
- In plants excess of the content of copper and zinc in the biomass was observed, in comparison to the limit concentrations of these metals in forage plants [10]. In sample no. 2 of the English plantain (*Plantagolanceolata* L) almost 5-fold higher concentration of copper and almost 3-times higher content of zinc were reported. The values of the bioaccumulation coefficient (WB) of copper in maize (*Zea mays* L.) are lower. Exceeding of metal in roots and leaves of the maize was approx. 3-fold. The content of zinc was exceeded above 2-times only in the roots of *Zea mays* L. in sample no. 2.

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