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ACCUMULATION OF ZINC IN SOIL IN METAL INDUSTRY AREA

AKUMULACJA CYNKU W GLEBACH TERENU ZAKŁADU PRZEMYSŁU METALOWEGO

Abstract: The metal industry area in Zielona Góra was tested, which has been functioning continuously since 1876. In the samples taken in the years 2009 and 2010 the chemical and physico-chemical properties of the soils were identified. Zinc was found in amounts between 321–3290 mg · kg^{-1}, with an average of 1340 mg · kg^{-1}. It clearly shows an anthropogenic rise in comparison to the other parts of the urban area under research – from 11 to 110 times. These values are also higher in comparison to the average content of zinc found in soils in Poland – 30 mg · kg^{-1}. Different contents of zinc were found on the premises of the plant, which depended on the location of a particular place in the relation to the production halls and other elements of the plant's infrastructure.

Keywords: zinc, soil, metal industry

Introduction

Industrial activity is one of the most important factors increasing the content of trace metals in the natural environment. A particularly high content of heavy metals is observed in soils exposed to a long-term risk of anthropopressure.

Zinc is one of the most mobile metals in the soil, affecting its overall content and different forms. Zinc undergoes soil sorption, which depends on the pH. At the pH of 5.5 it is bound by humic acids, whereas at a lower pH the sorption of this element almost completely disappears. In soils enriched with iron and manganese it is strongly absorbed on the surface of their oxides and hydroxides. Its concentration in ferruginous soil concretions nodules may reach the level of 2500 mg · kg^{-1}, and in manganese concretions 5500 mg · kg^{-1} [1].

The bioavailability of zinc in soil depends on its form, which is affected by the pH, temperature and oxidation-reduction potential and on soil sorption, solid phase capacity to exchange cations, competition with the other ions and the composition and quality of

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the soil solution [1–4]. Zinc is a trace element necessary for the development of plants, animals and humans, but in high concentrations causes a serious threat to the biosphere [5–7]. A content of about 100 mg · kg^{-1} of zinc in the soil may limit processes of nitrification and the presence of about 1000 mg · kg^{-1} causes harm to a majority of microbiological processes [8]. A reduction in the toxicity of zinc can be achieved by the treatment of the soil with lime, the addition of phosphate or sulfur compounds. Also, hydrated oxides of iron and manganese tend to hinder the process of zinc absorption by plants, which is equivalent to decreasing phytotoxicity [1]. In subject literature the negative effect of zinc on the populations of soil invertebrates is extensively described [9–14].

The main source of zinc in urban industrial and communication areas is human activity. Higher concentrations are observed in the soil near places of mining activities, foundries and steel mills, pipelines, industrial establishments and near busy thoroughfares – from emissions [15, 16]. The phenomenon of zinc accumulation in soils in the areas described is caused by the sedimentation of dust from the air.

The main source of industrial emissions of zinc into the environment are steel mills and foundries of metal and its alloys, created by the metallurgical industry. The main industrial sectors using zinc include the metal industry (used as an anti-corrosion agent and to the galvanization) and tinctorial industry. A major source of pollution are combustion processes of coal, but on the global scale they are approximately 10 % of the total emissions of this metal [1].

The aim of this study was to analyze the content of zinc in the soils of industrial area as an indicator of the long-term pressure of industrial activities on the natural environment.

Materials and methods

Description of the research object

The research object is the metal industry area located in Zielona Góra, which occupies about 11.5 acres, located in Sulechowska Street. Industrial activities in that area started in 1876. The activities involved the production of agricultural machinery, steel structures of industrial halls, bridges and railway stations. In 1886, the construction of railway freight and passenger carriages, tanks, mail carriages, refrigerated carriages, etc. During the Second World War the factory produced vehicles and equipment for the army. It produced armored trains, cannon parts, military vehicles, submarine hulls, aircraft parts. After 1945 it produced rolling stock, freight carriages and locomotives, but also steel structures [17, 18]. Currently the site produces rolling stock and steel structures. Currently in the industrial area rolling stock and steel structures are produced, part of the area is a repository of files and magazines.

The area under research is located a short distance from the city center, it is surrounded by residential buildings and single and multifamily ones to the north there is an area of greenery.

The area of industrial plant under construction was subjected to leveling. This kind of work still continues, traditionally with the use of waste materials, although in smaller quantities than before.

Research methods

Soil samples were taken from the metal industry area described in the years 2009 and 2010. Samples were collected in accordance with the provisions of the standards ISO 10381-1:2008, ISO 10381-2:2007 and ISO 10381-5, specifying how samples should be obtained for laboratory tests.

The industrial area was divided into 10 sub-surfaces from which aggregate samples with a disturbed structure were collected. Within each test area dozens of individual samples were collected to receive a bulk sample weighing about 1 kg. The places of soil sampling are shown in Fig. 1.

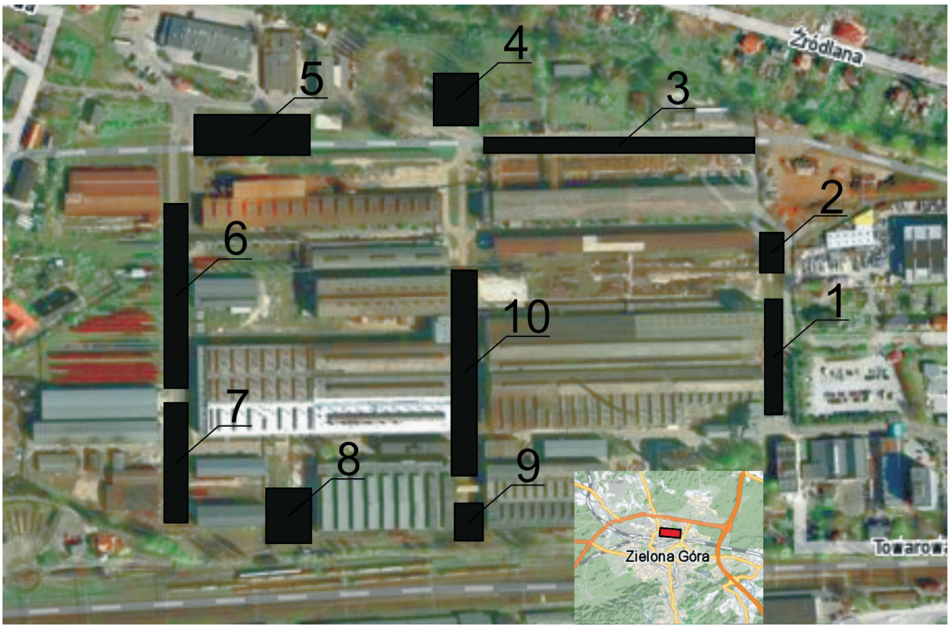

Fig. 1. Location of sampling points in the industrial area (photo: Fruzińska 2011 on undercoat Zumi.pl)

The samples collected were dried and sieved through a sieve with a diameter of 2 mm. The following tests were performed on the resulting material:

– determination of zinc in the soil in a subtotal form – atomic absorption spectrometry (AAS FL) after ignition of samples in a muffle furnace at 550 ^{o}C to constant mass and dissolving the residue after ignition in a mixture of hot concentrated acids HCl: HNO_3 relative 3 : 1 (aqua regia) according to the standard PN-ISO 11466:2002.

While previous studies performed:

– analysis of mechanical composition – areometric method by Casagrande in the modification of Proszynski, according to the standard ISO 11277:2009,

– indication of pH – according to the standard ISO 10390:2005, in water and 1-molar KCl,

– determination of manganese and iron in the soil in a subtotal form – atomic absorption spectrometry (AAS FL) after ignition of samples in a muffle furnace at 550 ^{o}C to constant mass and dissolving the residue after ignition in a mixture of hot concentrated acids HCl: HNO_3 relative 3:1 (aqua regia) according to the standard PN-ISO 11466:2002,

The analytical results underwent the Pearson correlation analysis. Correlation calculations were carried out by means of Statistica StatSoft 10 software.

Results and discussion

The content of zinc in the soils from the area under research compared with their pH, granulometric composition and the content of manganese and iron is shown in Table 1.

Table 1

The content of zinc, manganese, iron as well pH and sand content in the analyzed soil samples

Field number	Sampling series	Zinc content in soils [$mg \cdot kg^{-1}$]	Manganese content in soils [$mg \cdot kg^{-1}$]	Iron content in soils [$mg \cdot kg^{-1}$]	pH-H_2O	Sand content 2–0.05 [%]
1	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	1360	1670	57900	7.1	95
2	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	409	162	7887	7.1	95
3	a	444	469	27700	8.0	94
	b	421	443	26600	7.4	93
4	a	364	311	10600	7.9	93
	b	435	319	14100	7.3	96
5	a	412	360	18000	7.8	92
	b	321	328	15200	7.2	93
6	a	644	774	30300	8.2	92
	b	511	510	17000	7.2	96
7	a	3290	651	47200	8.0	89
	b	2910	731	55500	7.1	91
8	a	2980	1160	57000	8.0	92
	b	2440	1690	57520	7.2	91
9	a	1660	917	54800	7.7	86
	b	2420	1200	51700	7.3	94
10	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	1800	750	48900	7.5	94
Basic statistics						
Mean		1340	732	35171	7.5	93
Minimum		321	162	7887	7.1	86
Maximum		3290	1690	57900	8.2	96
Standard deviation		1090	462	19148	0.4	3

n.d. – no determined; a – samples taken in June 2009; b – samples taken in June 2010.

The concentration of zinc in the soils from the industrial area was high and ranged from 321 mg · kg^{-1} (in the sample 5b) to 3290 mg · kg^{-1} (in the sample 7a). The average content of zinc in uncontaminated sandy soils in Poland is 30 mg · kg^{-1} [1]. Therefore, the content of zinc in the soils from the area uner research is from 10.7 to 109.6 times greater than the index. This illustrates the intensity of the transformation of this area.

The results obtained in terms of the content of zinc divided the area under research into two sectors. Values above 1000 mg · kg^{-1} were characteristic of the areas directly adjacent to the production halls. These are the places identified as 1, 7, 9 and 10. In these areas there is an overhead railway line to transport elements manufactured between different halls in the technological cycle. Also, a high content was characteristic of area No. 8 – car park. A high concentration of zinc in the soil taken for testing from this area may be due to the content of zinc in the waste materials used for leveling the ground. In areas designated as 2, 3, 4, 5, 6 a lower content of zinc may be due to the less intensive use of these places during manufacturing operations.

The maximum concentration in sample No. 7a – 3290 mg · kg^{-1} significantly exceeded the permissible content of zinc in industrial soils, which is defined in the Directive of the Minister for the Environment on standards for the quality of soil of 9 September 2002. It specifies the permissible value of zinc in the industrial soils of group C – industrials areas, the premises of mines and communications areas at the depth of 0–2 m below the surface at the level of 1000 mg · kg^{-1}.

The content of zinc in soils is influenced by many forms of human activities, and its sources may have overlapping interactions areas. While examining the industrial area situated among the buildings and surrounded by busy roads it should be remembered that the presence of zinc in the soils of such areas may be the result of not only industrial activities but also intensive traffic, railway traffic and fossil fuel combustion.

Table 2 summarizes the results for zinc in the soils of the area under research compared with other locations in Zielona Gora [19].

Table 2

The average content of zinc in the soils under research compared with the content of zinc in the soils of the town of Zielona Gora [19]

Designation	Zn [mg · kg^{-1}]	pH-H_2O	Mechanical composition
Centrum[a]	143	6.5	gravelly sand
Os. Piastowskie[b]	127	7.1	gravelly sand
Makrownętrzne Gęśnika[c]	375	7.2	gravelly sand
Dolina Zielona[d]	30	7.7	gravelly sand
This study Mean ± S.D.[*]	1340 ± 1090	7.5 ± 0.4	gravelly sand

[*] – S.D. – standard deviation; [a] – Zielona Gora, a park in the city center, post brown regosol (0–30 cm); [b] – Zielona Gora, a housing estate green area, anthropogenic soil with an undeveloped profile (0–20 cm); [c] – Zielona Gora, a house garden, near Zrodlana Street, hortisol (0–40 cm); [d] – Zielona Gora, a pile of shoveled soil material, anthropogenic soil with an undeveloped profile (0–20 cm).

A comparison of the results of the research indicates a significant concentration of this element in the soils of the industrial area. Among the areas analyzed two are located in the vicinity of the area under research. The first of them – the "Zielona Dolina" estate (situated east of the area under research), is characterized by the presence of zinc in the soils at the level of 30 mg · kg^{-1} – comparable with the content in uncontaminated sandy soils. The second, "Makrownetrze Gesnika", situated north the factory premises was characterized by a relatively high content of zinc – 375 mg · kg^{-1}. The reasons for this phenomenon are not quite clear, due to the different historical forms of using those grounds, including the intensively fertilized allotments. The other two samples, taken at the Centre and the Piaskowskie estate, were characterized by an intermediate content of zinc, but similar to values reported in subject literature [20–22].

The researched showed that in the soils of the industrial area there are significant amounts of zinc, and the level of this element varies significantly from the content in the soils in Zielona Gora located both near and further away from the plant.

In order to compare the results of the research on zinc to the results obtained elswhere in the world it is necessary to pay attention to the specific conditions prevailing in each industrial area, often not to be found anywhere else.

Table 3

The zinc content in soils of industrial and urban areas of the world

City	Zn [mg · kg^{-1}] Mean ± S.D.	Comments
Industrial areas		
Hyderabad	812 ± 1360	[23]
Kosaya Gora	276 ± 44	[24]
Hangzhou	346 ± 314	[25]
This study	**1340 ± 1090**	
Urban areas		
London	183	[21]
Glasgow	207	[20]
Hongkong	168 ± 75	[22]
Bangkok	118 ± 185	[26]
Hamburg	516 ± 680	[27]
Manila	440 ± 618	[28]

This is due to the kind of industry, raw materials used for production, technologies, climate conditions, duration of industrial activities in areas under research, and other local conditions. Even in areas that are occupied only by metal and metallurgic industry establishments, a very different zinc content in soils can be observed. In comparison with the results of tests for this group of plants, the soil in the area under research shows a much higher concentration of zinc, comparable to the value of the Balanagar industrial area, near the city of Hyderabad in India – 1340 ± 1090 mgZn · kg^{-1} in the soils of the area under research to 812 ± 1360 mgZn · kg^{-1} in the soils around the Balanagar industrial area. In addition the difference between the average values may be due to the reasons mentioned above, the choice of sampling sites.

A significant difference between the content of zinc in soils in areas of the metal industry and urban areas can be seen. These points clearly to the industry as an important local source of soil enrichment in zinc.

For the analysis of the relationship between concentrations of trace metals and the percentage content of sand the Pearson correlation is used and the results are presented in the following figures. The results obtained indicate a significant positive correlation between Zn-Fe and Zn-Mn. The correlation coefficient Zn-Fe was 0.8518 and Zn-Mn was 0.6099. A positive correlation between zinc and manganese and iron indicates the origin of these elements from a common source, from industrial pollution. The presence of iron and manganese in large quantities in soils with an alkaline pH and their high positive correlation as confirmation of their anthropogenic origin is also reflected in the results of other researches [29, 30].

Statistical calculations demonstrated that there was a significant negative correlation between the content of zinc and the granulometric composition of soils. A correlation coefficient of Zn-Sand was –0.4906. It indicates a decreasing amount of zinc with an increasing percentage of sand in the soil.

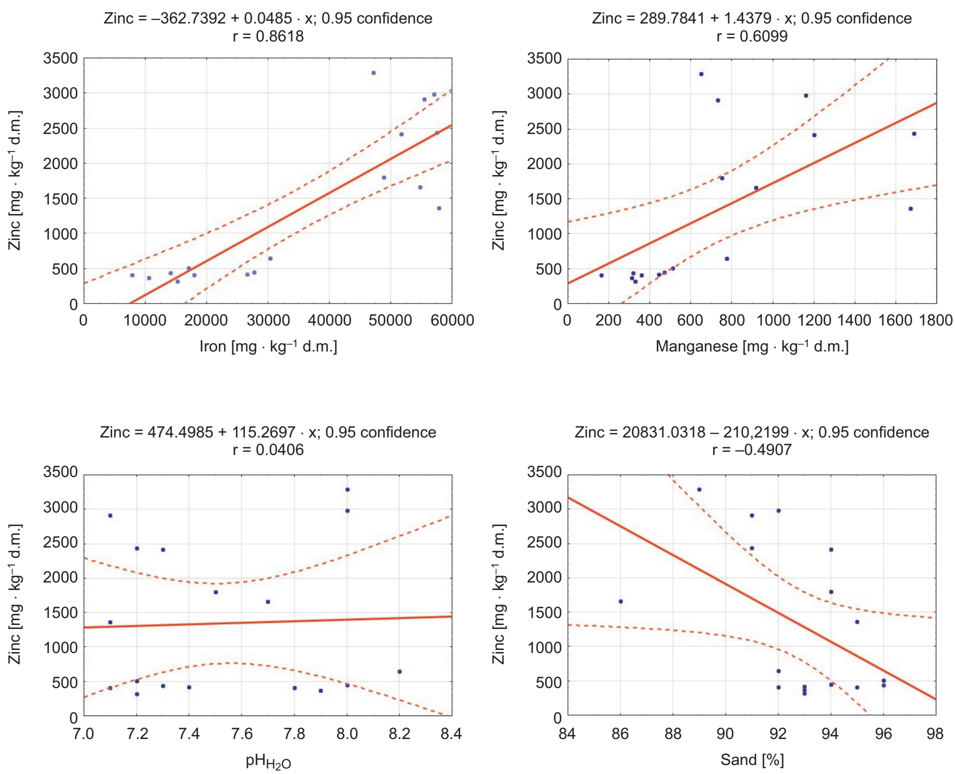

Fig. 2. Scatterplot of Zn-Fe, Zn-Mn, Zn-pH-H_2O and Zn-Sand

A statistical analysis showed no significant correlation between the pH of the soils and the content of zinc. This is due to fact that the zinc in the test samples appeared in different concentrations, and the pH differed slightly. The pH of the test samples according to data from subject literature has an influence on the sorption of zinc [1, 31]. However, in the soil situation under research this correlation cannot be confirmed.

The high accumulation of zinc compounds in industrial areas surrounded by urban areas (including residential areas) may pose a risk of migration of this element to the soil outside the industrial area. This can occur when pollution is carried by wind and by migration into the depths of soils profiles – into groundwater. Potential environmental risks posed by a higher content of zinc in the soil should be controlled through the constant monitoring of the soil, water and plants in the selected locations.

Conclusion

1. The content of zinc in soils of the industrial area was very high and exceeded the content of zinc in urban soils in Zielona Gora, the world's urban areas and some industrial areas.
2. The concentration of zinc in soils depended on the location of sampling.
3. The zinc content in soils was strongly positively correlated with the content of iron, manganese, negatively with the percentage content of sand. The research did not indicate the concentration of zinc from the pH of the soils.
4. The high concentration of zinc in the soils under research was caused by the activity of the metal industry.

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AKUMULACJA CYNKU W GLEBACH TERENU ZAKŁADU PRZEMYSŁU METALOWEGO

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Abstrakt: Badaniom poddano obszar przemysłu metalowego w Zielonej Górze, stale funkcjonujący od roku 1876. W próbkach pobranych w latach 2009 i 2010 określono właściwości chemiczne i fizyczno-chemiczne. Stwierdzono obecność cynku w granicach 321–3290 mg · kg^{-1} ze średnią 1340 mg · kg^{-1}. Wskazuje to wyraźne antropogenne podwyższenie względem innych terenów badanego ośrodka miejskiego – od 11 do 110 razy. Jest to także wartość wyższa w odniesieniu do średniej zawartości cynku, spotykanej w glebach Polski – zawartość 30 mg · kg^{-1}. Odnotowano zróżnicowanie zawartości cynku na terenie zakładu, co jest zależne od ulokowania względem hal produkcyjnych i innych elementów infrastruktury zakładu.

Słowa kluczowe: cynk, gleba, przemysł metalowy