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ASSESSMENT OF POSSIBLE ZINC ACCUMULATION IN SOILS IN THE ZONE OF POTENTIAL ZINC-WORKS INFLUENCE

OCENA MOŻLIWOŚCI AKUMULACJI CYNKU W GLEBACH W STREFIE POTENCJALNEGO ODDZIAŁYWANIA CYNKOWNI

Abstract: The work aimed at determining the susceptibility to zinc accumulation of soils exposed to potential influence of zinc-works. Estimation of soil zinc binding ability was conducted by a modified method suggested by H.P. Blume and G. Brummer, according to which soils are divided into 5 classes differing with heavy metal accumulation ability depending on their physicochemical properties. The most important parameter of this division is soil pH, whereas the content of organic matter and < 0.02 mm particles fraction content in soil play an auxiliary role. Conducted assessment of zinc binding ability in soils revealed that in the area of potential influence of zinc-works, soils with low zinc accumulation ability have the biggest share. Among all analysed soils, 68 % of samples collected from the 0–10 cm layer and 58 % from the 40–50 cm layer reveal low or medium zinc binding abilities. Such high percentage of soils with these disadvantageous properties is mainly due to the fact that in these areas there is the highest number of acid soils with granular size distribution of loose sands. In case when the zinc-works starts operation, there is a serious potential of introducing excessive zinc amounts to food chain.

Keywords: soil, zinc, accumulation of zinc, pH, grain size distribution

The natural environment is constantly exposed to the effect of industrial emission, which to a considerable degree contributes to pollution of soil and other elements of the environment. Zinc is a component of many compounds emitted to the environment. Elevated zinc concentration in the environment is often connected with motorization, however industry also has its share in zinc emission [1]. Zinc compounds, such as: $ZnCl_2$, ZnO, zinc dust and ash are the main components of pollution created by zinc-works. Excessive industrial emission of zinc may contribute to a serious soil pollution with this metal. In some areas zinc pollution is considerable, which results among others in this metal accumulation in the close to the surface arable soil levels.

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The highest content of zinc occur in the areas where its ores are excavated and processed [1]. Zinc is one of more mobile metals in soil and its bioavailability is high due to very good solubility of its compounds. Higher plants take up zinc proportionately to its concentration in soil, therefore soil pollution with this metal may pose a hazard of its increased amount in food chain [2–4]. Apart from anthropogenic factor, zinc concentration in soil is also affected by a number its properties like: the kind of parent rock, grain size composition, soil pH or organic matter content [5].

Many authors have demonstrated that increase in soil acidity has a decisive influence on zinc solubility and therefore on its accumulative abilities in soil [3, 6]. It has been shown that in soil with neutral pH or slightly alkaline reaction zinc undergoes chemisorption on metal oxides and aluminosilicates and largely occurs in the form of organic complexes, so-called stable, hardly bioavailable zinc forms [7]. In case of slightly acid and acid soils, zinc is hardly complexed by organic substance, becomes mobile and is present in the soil solution as free ions, so-called labile zinc forms [8]. Other authors reported that a high solubility of zinc falls on soil pH below 4.5, whereas its strong binding in soil occurs when pH exceeds the value of 7 [9, 10]. The research aimed at determining possible zinc accumulation in soils in the zone of potential zinc-works influence.

Materials and methods

Field research was conducted in July 2010 in Trzcianka district, the area of potential influence of newly constructed zinc-works where production did not start until the end of 2011. In compliance with the Environmental Decision [11], planned yearly volume of production conducted by means of zinc flame spraying will be between 25 000 and 40 000 Mg of steel, at the maximum productivity reaching 10 Mg $\cdot$ h^{-1}.Trzcianka district is situated in the north-eastern part of Wielkopolska region, on the border of Pojezierze Waleckie and Pradolina Notecka, in the czarnkowsko-trzcianecki county. It is the area of high natural and tourist values, of which 50 % is covered by forests, whereas its western and central parts are interspersed with numerous lakes. The eastern part of the district, about 10 km from the zinc-works is a part of the Natura 2000 area [11].

The sampling places were planned so as to make possible estimating the extent and range of the zinc-works under construction influence on the natural environment. Square net was chosen as the method of sample collection in the immediate vicinity of the investment. Soil samples for analyses were collected from two layers (0–10 and 40–50 cm) in 19 points (Fig. 1) distanced from the centre of the zinc-works area by a 0.5, 1 and 5 km to the north, east, south and west and from the points situated at the distance of 0.7 and 1.4 km in the indirect directions of the first degree (NE, SE, SW, and NW). The sample collection points were localised using Garmin GPSap62s satellite receiver.

Basic physicochemical properties were assessed in the collected soil material: grain size distribution (Casagrande's method in Proszynski's modification), pH (by potentiometer in 1 mol $\cdot$ dm^{-3} KCl suspension) and organic matter content (by Tiurin's method).

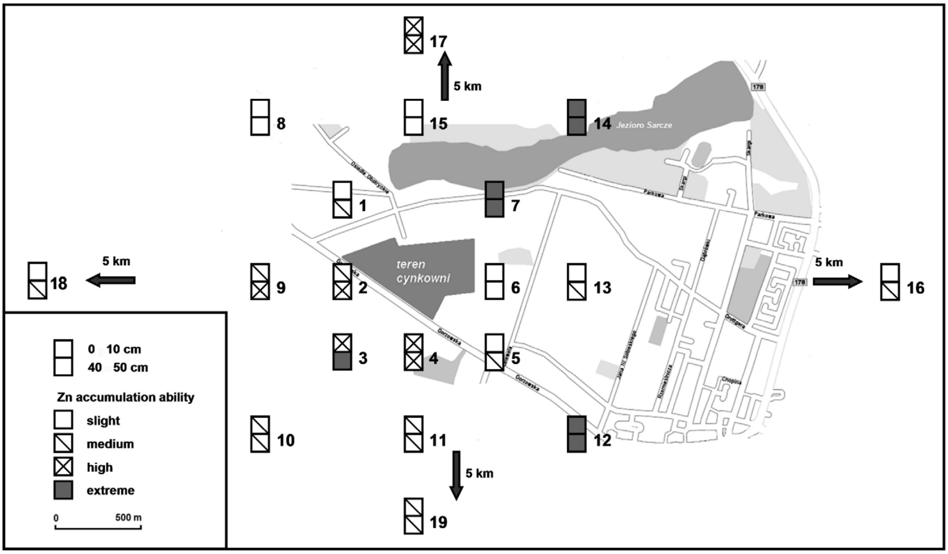

Fig. 1. Distribution of sampling sites and the ability to accumulate zinc in the topsoil (0–10 cm) and subsoil (40–50 cm)

In order to determine total zinc content, the soil material was dissolved in the mixtures of HNO_3 and $HClO_3$ acids (3 : 2). Zinc content in the obtained filtrates was assessed using ICP-OES method on Optima 2300 DV apparatus (Perkin Elmer).

Soil capability for zinc binding was assessed using the technique suggested by Blume and Brummer [12] and Gambus et al [7]. The assessment considers three basic physicochemical soil properties: pH (KCl), organic matter content and granular size composition. These parameters allow to classify a soil to a scale from 0 to 5. Class 0 denotes lack of zinc binding possibility, whereas class 5 comprises soils with a very high capability of this metal accumulation. The way of assigning a soil to a determined class was presented in Table 1.

Table 1

Influence of soil properties on its zinc accumulation ability (Zn acc)

pH_{KCl}	Zn acc	Content of organic matter [%]	Zn acc	Content of fraction < 0.0 [%]	Zn acc
2.5 3	0 1	0–2	0	< 20	0
3.5 4	1.5 2	2–8	0	20–35	0.5
4.5 5	2.5 3	8–15	0.5	35–50	0.5
5.5 > 6	4 5	> 15	0.5	> 50	1

The determining parameter is soil pH, while an adequate content of organic matter and floatable particles may correct the class number by 0.5 or one unit.

The results were verified statistically using Statistica 10 packet.

Results and discussion

Selected properties of analysed soils were presented in Table 2. In the vicinity of the zinc-works, soils with acid pH prevailed in the in the 0–10 cm layer (47 %), soils with slightly acid pH constituted (32 %). Neutral or very acid soils constituted 11 %. In the 40–50 cm layer, slightly acid soils prevailed (42 %), acid ones made up (32 %) and neutral ones (16 %). Very acid soil made up only 5 %. Analysis of grain size composition revealed that 79 % of soils from the 0–10 cm layer and 74 % from the 40–50 cm layer were very light soils, whereas the other 11 % and 16 % were light soils (Table 2).

Table 2

Selected physico-chemical properties of soils from the area of galvanizing plant

No. of sample	pH_{KCl}		Fraction < 0.02 [%]		Organic matter [g · kg^{-1} d.m.]		Zn [mg · kg^{-1} d.m.]	
	0–10 cm	40–50 cm	0–10 cm	40–50 cm	0–10 cm	40–50 cm	0–10 cm	40–50 cm
1	4.82	5.40	8	6	10.5	12.5	36.1	20.4
2	5.45	5.80	9	7	34.6	38.5	25.1	111.6
3	5.86	6.05	11	4	19.2	28.3	50.8	163.4
4	5.85	5.96	10	4	12.2	16.4	25.1	19.0
5	4.69	5.29	6	11	12.2	11.1	46.1	84.3
6	4.06	4.22	7	6	6.9	16.2	19.3	47.4
7	6.89	6.95	15	13	28.7	5.5	29.7	96.8
8	4.23	4.98	7	5	5.3	4.5	20.2	19.7
9	5.16	5.54	5	5	34.8	33.2	27.8	36.3
10	5.23	5.30	7	4	33.5	32.0	50.6	39.4
11	5.25	5.45	5	3	15.4	15.9	43.6	32.0
12	6.54	6.98	15	10	6.0	5.6	248.1	228.0
13	4.96	5.08	12	16	14.5	15.6	27.6	209.7
14	6.42	6.65	8	10	20.5	18.9	25.0	22.8
15	4.29	4.39	5	5	25.7	24.5	17.6	14.6
16	4.45	4.66	8	13	33.0	28.9	55.2	31.0
17	5.94	6.00	6	4	42.2	27.8	40.7	60.6
18	4.97	5.23	9	15	9.7	8.7	39.0	27.8
19	5.21	5.23	3	7	14.5	13.2	17.7	20.5
Minimum	4.06	4.22	3	3	5.3	4.5	17.4	14.6
Maximum	6.89	4.98	15	16	42.2	33.2	248.1	228.0
Mean	5.28	5.53	8	8	19.7	17.5	44.6	57.5
Median	5.21	5.40	8	6	15.4	16.1	29.7	36.3
VC [%]	15	14	40	53	58	55	89	82

Organic matter content in the soil samples from both analysed layers was similarly diversified. Its average content in the top layers was higher than the content noted in the subsoil, respectively 19.7 and 17.5 $g \cdot kg^{-1}$ d.m. (Table 2).

Among the analysed physicochemical parameters, zinc content proved the most diversified. The research revealed highly varied concentrations of this metal in soil collected in the vicinity of zinc-works V = 89 % (0–10cm) and 82 % (40–50 cm). Mean content of zinc in the topsoil of the studied soils was 44.6 mg (median 29.7 mg) and fluctuated from 17.4 to 248.1 $mg \cdot kg^{-1}$ d.m. In the deeper layer, *ie* 40–50 cm zinc content ranged from 14.6 to 228 mg, at average content 57.5 $mg \cdot kg^{-1}$ d.m. (median 36.3 mg). Such big difference between arithmetic means and values of medians results from the fact that among the studied samples were single soils with definitely higher content of zinc than the others. Large quantities of this element were assessed particularly in the soil from point 12 (Fig. 1), situated in the strongly urbanized area in the immediate vicinity of industrial plants and communication routes (Table 2). Similarly, a relatively high concentrations of zinc in the subsoil samples from points 3 and 13 is probably due to human activities. It is also worth mentioning that in almost a half of studied soils, higher zinc content were registered in the 40–50 cm layer in relation to its content in the topsoil, which might have been caused by the grain size composition of the analysed soils, low pH and considerable mobility of the metal.

Classification of zinc accumulation ability in soils in the zinc-works neighbourhood was presented in Fig. 1 and Table 3.The assessment of zinc binding in soil in the 0–10 cm level indicates a prevalence in the area of soils with low zinc binding ability (42 %). Soil with medium zinc binding ability constituted 26 %, whereas those with high and very high ability, respectively 16 % each. The main reason of this state is prevalence of light and very light soils with acid pH in this area. In the 40–50 cm layer, soil with medium zinc binding ability predominated (43 %), the next were soils with high and very high ability (21 %) and those with low ability (16 %) (Table 3).

Table 3

Classification of zinc accumulation ability in soils from the area of galvanizing plant

Zn accumulation ability	Soil class	Soils			
		0–10 cm		40–50 cm	
		number	% share	number	% share
Slight	2	8	42	3	16
Medium	3	5	26	8	42
High	4	3	16	4	21
Extreme	5	3	16	4	21

Spatial distribution of individual classes of zinc binding ability in the studied soils indicates a certain dependence on the metal distribution in the topsoil. In the immediate vicinity of the zinc-works (points 1–7), in the 0–10 cm level soils with low zinc binding ability prevail (43 % of samples), which at the same time are soils with low total content of this metal (Fig. 1, Table 2). In the 40–50cm layer in the same points soils with very high, high and medium zinc accumulation ability constituted, respectively 29 % each and those with low ability 14 %. At the same time, soil in this layer revealed a higher zinc content than soil in the 0–10 cm layer (Fig. 1, Table 2).

Zinc is an element commonly occurring in the earth's crust, its mean content in soils fluctuates from 30 to 125 mg · kg^{-1} [2]. High concentration of zinc in soil negatively affects its properties. Zinc content over 100 mg · kg^{-1} d.m. of soil hinders nitrification processes, whereas concentrations over 1000 · kg^{-1} d.m. of soil negatively affect a majority of microbiological processes [1]. Research conducted by other authors [5] revealed that zinc toxic effect on plants, depending on their species and soil properties, appears at the concentrations of between 100 and 500 mg · kg^{-1}. Among the analysed 19 soils only one sample from the 0–10 cm layer and 4 from the 40–50 cm layer contained more than 100 mg Zn · kg^{-1} d.m. According to the assessment suggested by the researchers from IUNG-PIB in Puławy, which distinguished a 6-degree soil classification with respect to heavy metal content, considering the soil reaction and grain size distribution, 3 % of the analysed soils revealed natural (0 degree) Zn content, 37 % elevated concentrations (degree I), 34 % a weak pollution (degree II), 16 % medium pollution (degree III) and 11 % showed strong pollution (degree IV) [13]. On the other hand, according to the Decree of the Minister of the Natural Environment of 9 September 2002 on the soil standards and earth quality standards [14] the analysed soils were not polluted with zinc.

Conclusions

1. Assessment of zinc binding ability in soils in the 0–10 cm layer in the area of potential influence of zinc-works indicates a prevalence in the region of soils with low zinc binding ability with simultaneous low total content of this metal.

2. Due to prevalence in the area of potential zinc-works influence of acid and very acid soils characterised with low abilities to mobilise heavy metals, once the production starts in the zinc-works, there is a high probability of excessive amounts of zinc penetrating the food chain.

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OCENA MOŻLIWOŚCI AKUMULACJI CYNKU W GLEBACH W STREFIE POTENCJALNEGO ODDZIAŁYWANIA CYNKOWNI

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Abstrakt: Celem pracy było określenie podatności na akumulację cynku gleb narażonych na potencjalne oddziaływanie cynkowni. Oszacowanie zdolności gleb do wiązania cynku przeprowadzono zmodyfikowaną metodą zaproponowaną przez Blume i Brümmera, zgodnie z którą gleby dzieli się na 5 klas różniących się zdolnością akumulowania metali ciężkich w zależności od ich właściwości fizyczno-chemicznych. Najważniejszym parametrem tego podziału jest odczyn gleby, zaś pomocniczą rolę odgrywają zawartość materii organicznej i frakcji o średnicy cząstek < 0,02 mm w glebie. Przeprowadzona ocena zdolności wiązania cynku w glebach wykazała, że na terenie potencjalnego oddziaływania cynkowni największy udział mają gleb o małej zdolności akumulowania cynku. Spośród wszystkich przeanalizowanych gleb aż 68 % próbek pobranych z warstwy 0–10 cm i 58 % z poziomu 40–50 cm charakteryzuje się małymi lub średnimi możliwościami wiązania cynku. Tak duży odsetek gleb właśnie o tak niekorzystnych właściwościach jest spowodowany głównie tym, że na badanym obszarze najwięcej jest gleb kwaśnych o składzie granulometrycznym piasków luźnych. W przypadku uruchomienia produkcji cynkowni istnieje duże prawdopodobieństwo wprowadzenia nadmiernych ilości cynku do łańcucha troficznego.

Słowa kluczowe: gleba, cynk, akumulacja cynku, pH, skład granulometryczny