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CONTENT OF TOTAL ZINC AND ITS FRACTIONS IN SELECTED SOILS IN THE PROVINCE OF PODLASIE

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Abstract

The aim of this research was to determine the total content of zinc and its fractions in arable soils of the Province of Podlasie (*województwo podlaskie*) and to assess the correlation between the zinc content, its fractions and physicochemical properties of soils.

The research material consisted of samples taken from arable soils in 81 points of the province, with one point chosen in the majority of the districts. Each point was located on mineral soil used as arable land, without any external source of contamination like roads or industrial plants. Samples were taken after harvest, from the arable layer, determined to lie within the depth of 0-30cm. The samples were submitted to determinations of the basic physicochemical properties of soil. The content of total zinc was determined after mineralization in *aqua regia*, by the flame atomic absorption spectrometry method. The content of zinc fractions was determined by the BCR method. There were four fractions determined: exchangeable, bound with oxides and hydroxides, bound with organic matter and residual zinc.

The physicochemical properties of soils were highly differentiated except the grain-size composition. The content of total zinc was typical of arable uncontaminated soils and fluctuated in a wide range. The content and shares of zinc fractions in total zinc were as follows: for very light and light soil: organic>bound with oxides and hydroxides>exchangeable>residual; for medium-heavy soil: organic>exchangeable>bound with oxides and hydroxides>residual. Distribution of zinc in particular fractions was dependent to some degree on pH, content of organic matter and grain-size composition.

Key words: soils, zinc, properties, fraction.

ZAWARTOŚĆ CYNKU OGÓŁEM I JEGO FRAKCJI W WYBRANYCH GLEBACH WOJEWÓDZTWA PODLASKIEGO

Abstrakt

Celem pracy było określenie całkowitej zawartości cynku oraz jego frakcji w glebach uprawnych Podlasia użytkowanych jako grunty orne oraz określenie zależności między zawartością cynku, jego frakcji a własnościami fizykochemicznymi gleb.

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Materiał badawczy stanowiły próbki pobrane z gleb uprawnych w 81 punktach woj. podlaskiego. Wybrano po jednym punkcie w większości gmin tego województwa. Zlokalizowane były one na glebach mineralnych użytkowanych jako grunty orne, pozbawione zewnętrznych źródeł zanieczyszczeń, jak drogi czy zakłady przemysłowe. Próbki pobrano z warstwy uprawnej, określonej na głębokość 0-30 cm, po zbiorze roślin uprawnych. W próbkach oznaczono podstawowe właściwości fizykochemiczne gleb.

Oznaczono zawartość cynku ogólnego, po mineralizacji w wodzie królewskiej, metodą atomowej spektrometrii absorpcyjnej płomieniowej. W glebach oznaczono zawartość frakcji cynku metodą BCR. Oznaczono 4 frakcje, tj. dostępną, związaną z tlenkami i wodorotlenkami, związaną z substancją organiczną i rezydualną.

Stwierdzono, że właściwości fizykochemiczne badanych gleb były bardzo zróżnicowane, z wyjątkiem składu granulometrycznego. Zawartość cynku ogółem była typowa dla niezanieczyszczonych gleb uprawnych i mieściła się w szerokich granicach. Zawartość i udział frakcji cynku w ogólnej jego zawartości układały się w następujący szereg w przypadku gleb bardzo lekkich i lekkich: organiczna > związana z tlenkami i wodorotlenkami > wymienna> rezydualna, a w przypadku gleb średnich: organiczna> wymienna> związana z tlenkami i wodorotlenkami> rezydualna. Rozmieszczenie cynku w poszczególnych frakcjach zależało w pewnym stopniu od wartości pH, zawartości węgla organicznego oraz składu granulometrycznego gleb.

Słowa kluczowe: gleby, cynk, właściwości, frakcje.

INTRODUCTION

Zinc is an essential microelement in the nutrition of crops, especially maize, which covers increasingly larger acreage of farmland in Poland (Kabata-Pendias 2002, Spychaj-Fabisiak, Długosz 2006). The main source of zinc for plants is soil. The content of this microelement depends on the type of parent rock and soil texture. However, the content of the available form of zinc depends mainly on soil reaction, content of organic carbon, sorptive capacity, share of exchangeable cations in the sorptive complex, as well as organic and mineral fertilisation which supplies this microelement and factors which modify physicochemical properties of soils and thus the zinc availability (Dąbkowska-Naskręt, Różański 2009, Czekała, Jakubus 2000). The share of phytoavailable forms in the total zinc content is highly differentiated and depends on many factors. With the same total content, there could be different amounts of available forms of this metal, from low to very high, up to a toxic level (Czekała, Jakubus 2000).

In Poland, the total content of metals in soil, including zinc, serves to estimate soil contamination degrees (Kabata-Pendias 2002). Apart from the total content, the quantity of available form extracted in 1 mol dm^{-3} HCl is determined. Most often, the content of metals, including zinc - which is said to be available - is higher than that of the easily available fractions. There are several methods for determination of these fractions, but is seems that the BCR method can meet the expectations (Sutherland, Tack 2003).

The aim of this research was to determine the total content of zinc and its fractions in arable soils in the Province of Podlasie (*województwo podlaskie*),

which underlie arable land, and to assess the correlation between zinc content, its fractions and physicochemical properties of soils.

MATERIAL AND METHODS

The research material consisted of samples taken from arable soil in 81 points in the whole prrovince, with one point selected in almosst every district. Each point was located on mineral soil used as arable land, without any external source of contamination like roads or industrial plants. Samples were taken after harvest, from the arable layer, determined to lie within the depth of 0-30 cm. The following crops were grown: maize (14 points), grain (53 points), rape (2 points), buckwheat (2 points) and grass (the other points). The samples were submitted to the determinations of basic physicochemical properties: grain-size distribution by the Cassagrande's method with Pruszynski's modification, organic carbon content by the Tiurin's method, pH in 1 mol dm^{-3} KCl by potentiometry. The soils were assinged agronomical categories, and divided into three groups: very light, light and medium-heavy soil. Heavy soils were excluded because they does not occur in the Province of Podlasie. The soils were grouped acording to pH, agronomical category and content of organic carbon. This arrangement served as the background for the presetation of average percentages of zinc fractions in its total zinc content.

The content of total zinc was determined after mineralization in *aqua regia*, by the flame atomic absorption spectrometry method. Afterwards, the metal was determined in the fractions: exchangeable, bound with Fe and Mn oxides and with organic matter by the modified BCR method (Community Bureau of Reference, currently Standards, Measurement and Testing Programme). The extraction of exchangeable, water and light acids soluble part of zinc (1 stage, fraction I), bound with iron and manganese hydroxides (2 stage, fraction II) and bound with organic matter (3 stage, fraction III) was also performed. In the first stage, acetic acid was used (concentration 0.11 mol dm^{-3}); the second one used hydroxylamine hydrochloride (concentration 0.5 mol dm^{-3}), whereas at the third one involved hydrogen peroxide and ammonium acetate (concentration 1 mol dm^{-3}, pH=2). Zinc was determined by the flame technique on an atomic absorption spectrophotometer. The percentages of particular fractions in the total content of zinc were calculated. The correlation coefficients between physicochemical properties of soils and total zincc content and its fractions were calculated with the use of Statistica programme.

RESULTS AND DISCUSSION

Among very light and light soils, loamy sand and poorly loamy sand are most common, whilee sandy clays prevail among medium-heavy soils. The content of fine fraction in very light soils ranged from 4 to 10%, in light soils – from 11 to 20%, and in medium-heavy soils – there was approximately 22% of fine fraction on average, in the range of 20-28% (Table 1).

Table 1

Physicochemical properties of soils

Soils		Characteristics of soils			
		pH	C_{org} (g kg^{-1})	content of fine fraction (%)	total Zn (mg kg^{-1})
Very light $n = 10$	min-max	4.0-5.8	8-21	4-10	13.5-38.6
	$\bar{x}$	4.6	17	9	29.6
Light $n = 25$	min-max	4.2-6.9	10-22	11-20	19.4-52.5
	$\bar{x}$	5.2	18	16	33.5
Medium-heavy $n = 46$	min-max	4.1-7.8	7-42	21-28	14.5-58.8
	$\bar{x}$	6.1	24	22	35.1

The pH of very light soils was highly varied, from 4.0 to 5.8. The pH of light soils ranged from 4.2 to 6.9, but was higher in medium-heavy soils than in very light and light soils. The analyzed soils are characteristic for Podlasie, where most soils are light and acidic. The content of organic carbon in the soils was differentiated and ranged from 8.0 to 42.0 g kg^{-1}.

The content of total zinc in the first group soils was in a wide range, from 13.5 to 38.6 mg kg^{-1}. There was more of zinc in the second group of (light) soils: from 19.4 to 52.5 mg kg^{-1}. Medium-heavy soils contained from 14.5 to 58.8 mg kg^{-1} of total zinc (Table 1). This diversity corresponds to the relationship between total zinc and grain-size distribution in soils. The correlation coefficient between total zinc content and fine grain fraction was 0.29 (Table 2). Higher correlation coefficients between the total content of zinc and colloidal parts of soils are reported by Dąbkowska-Naskręt and Różański (2009). The total content of zinc in the analyzed soils is the same as

Table 2

Correlation coefficients between total zinc and its fractions in soils and properties of soils

Variable	Total Zn	Fraction I	Fraction II	Fraction III	Fraction IV
pH	0.12	0.01	0.18	0.02	0.29*
C org	0.1	-0.14	0.05	0.22*	0.12
Content of fine fraction	0.25*	-0.04	0.2	15	0.24*

* confidence level $p < 0.05$

the natural content of this element in soils of Poland (KABATA-PENDIAS 2002). The results of total zinc in the soils are similar to those obtained by SKORBIŁOWICZ et al. (2002), who demonstrated that total zinc fluctuated from 13.2 to 54.8 mg kg^{-1} in acid soils in Podlasie.

In the exained soils grouped by acidification, the percentage of particular zinc fractions as compared to total Zn was only slightly differentiated (Figure 1). The content of available zinc (fraction I) was the highest in strongly acidic soils, reaching about 30% of total Zn. The zinc content in this fraction was lower in weakly acidic and acidic soils, increasing in soils with

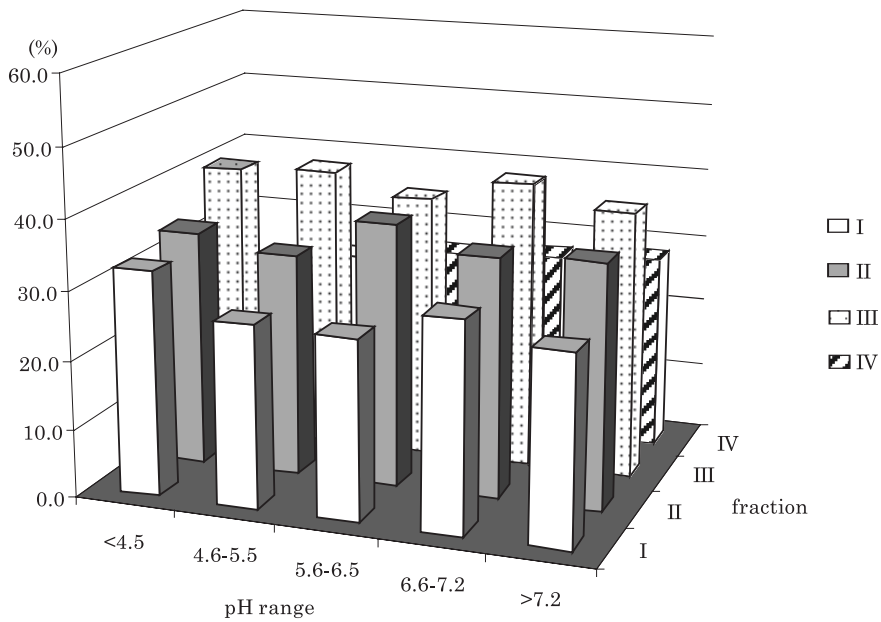

Fig. 1. Percentage of zinc fractions in total content in soils depending on pH

higher pH. Many authors (GE et al. 2000, KUCHARZEWSKI et al. 2004, KALEMBASA, PAKUŁA 2006) emphasize increased zinc solubility in more acidic soils. The current results show that the release of available zinc forms is not only pH dependent, especially in soils with pH higher than 6.6, where an increase in the content of the most soluble zinc form extracted with weak acetic acid was noted. A decrease in the content of exchangeable zinc, as argued by LORENZ et al. (1997), is connected with an increase in the share of zinc bound with organic matter due to the formation of complex organic-mineral anions, which are able to sustain high mobility of zinc in soils with elevated pH.

The share of zinc bound with organic matter (fraction III) in the analyzed soils was higher than in fraction I. An increase in the content of fraction III in soils with pH 4.6-5.5 and 5.6-6.5 was related to a decrese in the content of fraction I. In soils with different pH ranges, the relationships between fractions changed. The share of mobile fractions was decreasing, while the

share of more stabile fractions was increasing, which was especially evident in the case of acidic and light acidic soils. In soils with pH higher than 7.2, the share of the residual fraction higher by a few per cent than in soils with lower reaction. The supports the claim by Lorenz et al. (1997) that zinc is transferred in acidic soils from the residual fraction into soluble and potentially soluble fractions, while the reverse transfer occurs in soils with higher pH. This is implied by values of the correlation coefficient between pH and the residual fraction (stabile) – Table 2.

No significant influence of the grain composition of soils on zinc content in particular fractions was noted (Figure 2). Some tendency can be seen towards decreasing the content of exchangeable fraction while increasing the

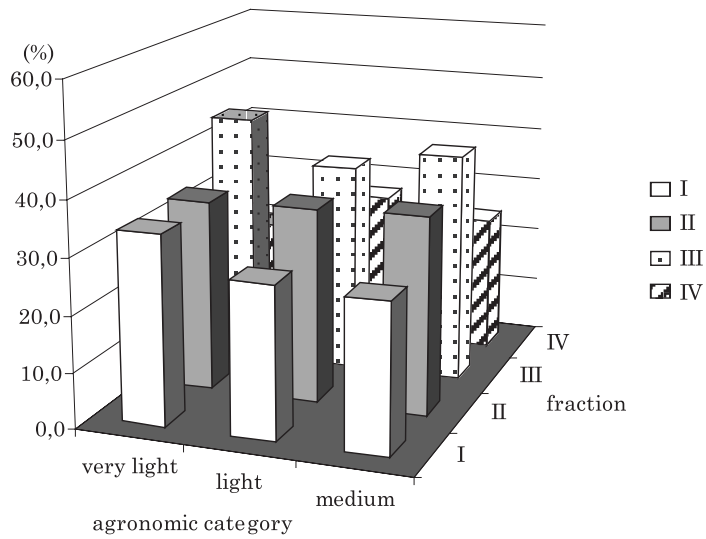

Fig. 2. Percentage of zinc fractions in total content in soils depending on the agronomical category

content of fine fraction. A higher agronomical category of soils was associated with a decreasing zinc mobility. The share of exchangeable fraction in light and medium-heavy soils was 10% lower than in very light soils. In very light soils, there was an evident transfer of most stabile fraction (residual) into fraction III with organic matter. In light and medium soils, the relationship between fractions was similar and can be described as follows: the highest share of zinc was in fraction with organic matter, the second mosst abundant was zinc bound with oxides and hydroxides of manganese and iron, followed by residual fraction and exchangeable fraction. Similar shares of zinc fractions were reported by Kabała and Singh (2006). In the current study, soils formed from sand had most zinc (40% on average) in the available fraction, follwoed by zinc in the fraction with organic matter (25%), and the leastzinc was found in the residual soil fraction.

The correlation coefficients for the first three zinc fractions and fine fraction were not significant. The significant relationship was observed only for the residual fraction and total content of zinc (Table 2).

The next factor affecting the solubility of zinc is the content of organic matter in soils (Lorenz 1997, Korzeniowska, Stanisławska-Glubiak 2004, Kucharzewski et al. 2004).

The share of exchangeable zinc in soils containing up to 30 g kg^{-1} of carbon was similar. The increase of carbon content above 30 g kg^{-1} caused the decreased zinc mobility in the analyzed soils (Figure 3). Oxides and hydroxides of manganese and iron (fraction II) had a higher share of bound zinc. The samples were characterized by a significant content of zinc bound with organic matter (fraction III). Most of zinc in this fraction, at the expense of the exchangeable fraction, was noted in soils with the content of carbon above 40 g kg^{-1}. The soils contained the least zinc in the residual fraction. Different results were obtained by Dąbkowska-Naskręt and Bartkowiak (2002), who studied soils with a similar grain-size composition and found most zinc in the residual fraction. Those soils were different from the ones analyzed in our research by the reaction (neutral and alkaline), which was probably the cause of differences in the share of zinc fractions.

Organic matter forms quite strong bonds with zinc, whicch resulted in a slight influence of the organic carbon content on exchangeable zinc (low correlation coefficients) – Table 2. Similar results were obtained by Mercik et al. (2004). According to these authors, the content of soluble zinc in sandy soils is increasing with a higher content of organic carbon, which can be seen

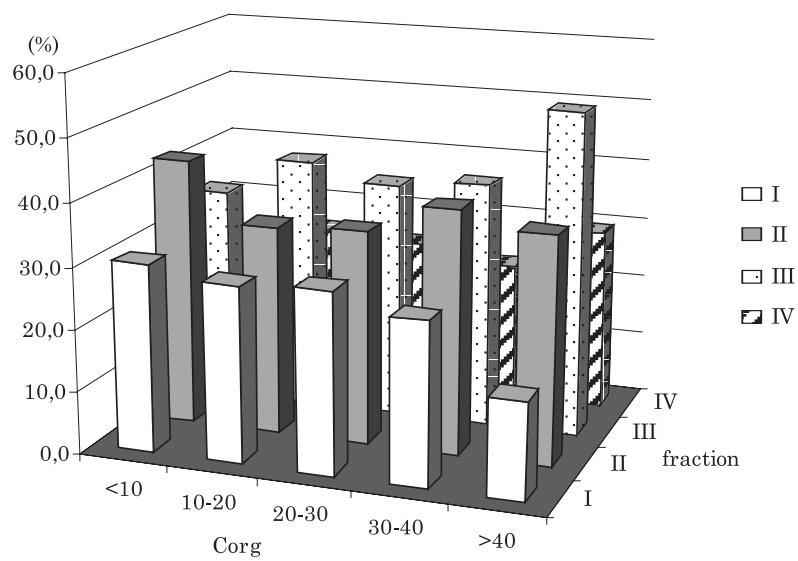

Fig. 3. Percentage of zinc fractions in total content in soils depending on the content of organic carbon (g kg^{-1})

in soils with the carbon content up to 40 g kg^{-1}. A strong relationship (correlation coefficient above 0,7) between zinc and organic matter was proven by Korzeniowska and Stanisławska-Glubiak (2004).

Some of the studied samples were characterized by a significant content of organic carbon, despite the lower share of fine fraction, which affected the binding of zinc in fraction III, and which indicates the correlation coefficient between C_{org} and fraction III as well. Ge et al. (2000) proved that zinc which is soluble in soils with neutral and alkaline reaction occurs mainly as organic complexe, whereas in acid soils is appears as exchangeable ions.

CONCLUSIONS

1. The content of total zinc was typical of arable uncontaminated soils and fluctuated in a wide range.

2. The content and shares of zinc fractions in total zinc were as follows: for very light and light soils: organic>bound with oxides and hydroxides>exchangeable>residual; for medium-heavy soil: organic>available>bound with oxides and >residual.

3. Distribution of zinc in particular fractions to some degree depended on pH and the content of organic matter; to a lesser degree, it was dependent on the grain-size composition of soil.

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