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VARIABILITY OF ZINC CONTENT IN CULTIVATED LUVISOLS OF THE PAŁUKI REGION (CENTRAL POLAND)

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Abstract

Zinc is an essential microelement that is required for the proper growth and development of crops, and its content in the soil varies. Due to the physiological functions it performs in living organisms, zinc is considered an essential element in the nutrition of plants and animals. The total forms of trace elements do not fully reflect the possibilities of their absorption. They provide only approximate ranges of the soil's abundance in a given ingredient. Plants can obtain microelements only from bioavailable forms.The content of available forms of elements in soils is one of the important determinants of plant yield. Zinc deficiency is a serious problem in agricultural soils around the world because it results in reduced crop yields. The aim of the study was to assess the content of total and available forms of zinc in the surface horizons of arable Luvisols in the Pałuki region, that has been intensively used for agriculture.

Basic physical and chemical soil properties were determined using methods commonly applied by soil science laboratories. The content of total zinc forms was determined using the Crock and Severson method. Forms bioavailable to plants were identified using the Lindsay and Norvell method. The content of both forms of zinc was determined by atomic adsorption spectroscopy (AAS).

In the analysed samples of arable land, low contents of total and available forms of zinc were recorded. The correlation analysis that was

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carried out confirmed that the content of these forms in the soil is significantly influenced by reaction. Due to the low levels of zinc forms found in the studied agricultural soils, It is necessary to monitor the amounts of this trace element.

Keywords: zinc, total and DTPA-extractable forms, arable soils, Luvisols

INTRODUCTION

Soil provides plants with the macro and microelements necessary for proper life and development. The lack of any element disturbs plant development cycles. Zinc is an important micronutrient for plants because it is involved in many key cellular functions, such as metabolic and physiological processes, enzyme activation and ion homeostasis (Yang et al. 2020, Alsafran et al. 2022). Due to the physiological functions it performs in living organisms, zinc is considered an essential element in the nutrition of plants and animals (Allowey 2004, 2009). The content of trace elements, including Zn, in the soils of the Earth's crust depends on their abundance in the parent rock, weathering and soil-forming processes, and grain-size composition. Human activity affects these content levels, especially in the uppermost soil layers, which in turn affects the chemical composition of plants and the quality of our food (Tripathi et al. 2015, Li et al. 2019). The Zn content in soils varies greatly. The zinc occurs in easily soluble compounds, which favours its migration, especially when the soil is acidic (Terelak et al. 2000, Van Oort et al. 2006). Mobile forms of zinc, which determine the availability of the element to plants, should be expected to differ in amount between genetic horizons of different types. Zinc is easily taken up from the soil by plants, both in the form of cations and organic chelates. Even insoluble compounds can be a source of Zn for the plant. However, the amounts of Zn contained in the soil may be insufficient for the proper development of plants. Therefore, zinc deficiency is a serious problem in agricultural soils worldwide because it reduces the yields and nutritional quality of crop produce (Zeng et al. 2021). It is estimated that approximately 50% of the world's cereal-growing soils are deficient in bioavailable forms of this element. Zn deficiency is one of the most serious limitations in the cultivation of cereals, especially wheat (Korzeniowska 2009). In agricultural soils, microelements are introduced by the application of certain fertilisers or materials that improve soil properties. The content of available forms of elements in soils is one of the important determinants of plant yield. The content of these forms depends on, among other things, soil pH, sorption capacity, organic matter, content and mineral fertilisation (Barczak et al. 2009, Barman et al. 2018).

The research objective was to assess the content of total and available forms of zinc in the surface horizons of arable Luvisols in the Pałuki region. The obtained results will provide actual information on the status of zinc content in soils, that have been intensively used for agriculture for decades.

MATERIALS AND METHODS

Pałuki is an ethnographic region in the north-eastern part of the Greater Poland region. It lies in the historical Kalisz region, on the southern and western banks of the Noteć River. Pałuki is mostly located in the Chodzież Lake District. The southernmost parts lie in the Gniezno Lake District, and the northern ones in the Toruń–Eberswalde Ice-marginal Streamway (Fig. 1) (Solon et al. 2018). Luvisols dominate in this area (Bartkowiak et al. 2015). Fifty-three soil samples from two sites (Posługowo and Świątkowo) were selected for the study. The research material consisted of samples of arable soil taken from the arable horizon (0–30 cm). Representative soil samples with a disturbed structure were taken from the surface horizons using the square method with an Egner stick. The overall sample consisted of five single samples. The analysed soils were formed from tills and have been cultivated conventionally for at least 70 years in rotation, with cereals predominating. The weather conditions are typical of a temperate climate with a long-term average annual temperature of 9°C and an average rainfall of 560 mm in the region.

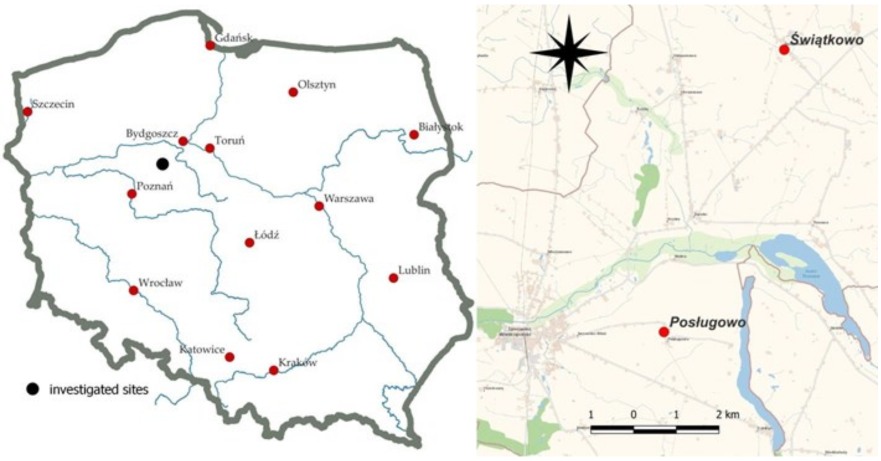

Figure 1. Location of the research area.

The following physicochemical properties were determined in soil samples dried and sieved through a 2-mm mesh: grain size by laser method using the Mastersizer 2000 particle analyser; reaction in H_2O and KCl by potentiometric method (PN-ISO 10390, 1997); organic carbon content by Tiurin method (PN-ISO 14235, 2003). The content of total zinc forms after soil mineralisation in solutions of hydrofluoric acid (HF) and chloric acid (VII) was determined by the method of Crock and Severson (1980). To assess the current and potential availability of zinc, the method of Lindsay and Norvell (1978) was used, employing a DTPA solution (diethyltriaminepentaacetic acid). The content of total and available forms of zinc was determined by atomic adsorption spectroscopy (AAS) on a Solaar 4 spectrophotometer.

Moreover, as suggested by Obrador et al. (2007) the bioavailability index (AF) was calculated according to the formula (1):

$$AF = \frac{DTPA\ Zn \cdot 100}{Total\ Zn} \tag{1}$$

where:
AF – bioavailability index (%),
DTPA Zn – amount of Zn extracted with DTPA ($mg \cdot kg^{-1}$),
Total Zn – total Zn content ($mg \cdot kg^{-1}$).

Measures of location (arithmetic mean and median), measures of variance (standard deviation [SD], coefficient of variation [CV%]), and measures of asymmetry and tailedness (skewness and kurtosis) were calculated for the population of obtained results. The results of the analyses of the examined characteristics were also subjected to simple correlation analysis ($p<0.05$) to determine the degree of dependency between individual characteristics. The work also uses multidimensional statistical method - principal component analysis (PCA). All determinations were made in three replicates, and the results are presented herein as arithmetic means. The statistical analysis was done in Statistica 13 Pl software.

RESULTS AND DISCUSSION

The analysed soils had a highly homogeneous granulometric composition, as evidenced by the low coefficient of variation (Table 1). All soil samples were classified into one granulometric group: loams. Most samples had a grain size typical of the granulometric subgroup ”sandy loam” (United States Department of Agriculture 2006). By contrast, the arable horizon was dominated by sand and silt fractions. The lowest was the clay fraction, which ranged from 1.99 to 9.83%.

Table 1. Statistical parameters of the analyzed soil properties: Sand, Silt, Clay [%]; C_{org} [g·kg^{-1}]; Total Zn, DTPA Zn [mg·kg^{-1}]; AF [%].

Parameters	Sand	Silt	Clay	pH H_2O	H KCl	Corg	T Zn	DTPA Zn	AF
Min	44.03	22.57	1.99	4.93	4.01	3.1	14.7	0.57	2.09
Max	74.25	46.15	9.83	7.31	6.58	19.5	88.0	33.0	37.50
Mean	59.52	35.07	5.42	5.82	5.01	6.08	31.15	2.35	6.56
Median	60.95	34.49	4.69	5.36	4.50	5.30	24.96	1.41	5.56
SD	6.96	5.43	1.82	0.73	0.83	3.20	13.64	4.39	5.02
CV [%]	11.70	15.49	33.65	12.54	16.50	52.55	43.80	186.89	76.48
Skewness	-0.17	0.10	0.44	-0.24	-0.52	5.90	8.53	39.06	25.14
Kurtosis	0.39	-0.45	0.46	0.82	0.81	2.37	2.80	6.16	4.58

T Zn – Total Zn; DTPA Zn - DTPA-extractable forms of Zn; AF – Available Factor; SD - standard deviation; CV - coefficient of variation

Soil reaction is a chemical feature that changes dynamically. It is conditioned by processes occurring in the soil profile and by external factors. In the tested soil samples, no major differences were found in active or exchangeable acidity. The coefficient of variation for active acidity was in the low variability class, amounting to a CV of 12.54%, whereas exchangeable acidity was in the medium variability class and amounted to 16.50% (Table 1). The determined active acidity (pH H_2O in the range of 4.93 – 7.31) and hydrolytic acidity (pH KCl in the range of 4.01 – 6.58) established that the reaction of the analysed soils ranged from acidic to neutral. A significant proportion of the samples was slightly acidic with an average of pH 5.82 for active acidity and pH 5.01 for exchangeable acidity. Most soil reaction results were below the arithmetic means, as indicated by the median value being lower than the mean (5.36 and 4.5).

The organic carbon content in the tested samples ranged from 3.10 to 19.5 g·kg^{-1}, with an average of 6.08 g·kg^{-1} and a standard deviation of 3.2 g·kg^{-1}. The coefficient of variation was >30%, indicating a wide variation in organic carbon content in the soil material. In the distribution analysis, the median showed that most of the results were below the mean (Table 1). According to the European criterion for assessing organic carbon content in soils that was developed based on the European Soil Database (ESB), these values were low or very low (Gonet 2007). The lowness of the content of organic carbon may have been caused by intensive agricultural cultivation in the study area. Haynes (2005) and Kobierski et al. (2015) report that the determinants of organic carbon content in the soil include factors determined by cultivation methods, including the amount of post-harvest residues left by farming equipment. Intensive agricultural production combined with simplified crop rotation or monoculture may therefore reduce the amount of organic residues and, consequently, decrease the content of organic matter in soils. However, the variation in the organic carbon content depends primarily on the type of soil (Kwiatkowska-Malina 2018).

In the study area, the average total zinc content was 31.15 mg·kg^{-1} and ranged from 14.7 to 88.0 mg·kg^{-1} (Table 1). The calculated coefficient of variation (43.8%) indicates the high variability of the results. On the other hand, the median being below the mean indicates that most of the analysed soil samples contained less total zinc than the arithmetic mean. To determine the sidedness and symmetry of the distribution of the results, the skewness (asymmetry coefficient) was calculated. The positive skewness value (8.53) indicates right-sided asymmetry. However, a positive kurtosis result (the measure of tailedness) of 2.80 means that the number of extreme outliers in the data exceeds that of a normal distribution. The total content of zinc in the study area was close to the average for Polish soils, which is 32.4 $mg \cdot kg^{-1}$ (Terelak et al. 2000, Koncewicz-Baran and Gondek 2010). Lower amounts of total zinc were obtained by Jaworska and Dąbkowska-Naskręt (2012) in arable soils near Głogów and by Bartkowiak et al. (2014) and Glińska-Lewczuk et al. (2014) in alluvial soils. The literature states that the content of total forms of microelements, including zinc, depends on, among other things: soil grain size, organic matter content and pH (Baran et al. 2008, Kabata-Pendias 2011). The amount of total zinc in the soil also depends on land use and intensity of cultivation (Kobierski et al. 2011, Skwaryło-Bednarz et al. 2014). The correlation analysis that was carried out confirmed the relationship between the content of total zinc forms and the content of sand and silt fractions, reaction and organic carbon. A significant positive relationship was found between total zinc and active acidity ($r = 0.604$; $p<0.05$), exchangeable acidity ($r = 0.621$; $p<0.05$) and organic carbon ($r = 0.441$; $p<0.05$) (Table 2). The interaction between total forms of zinc in the soil and certain soil properties was also assessed using the value of the determination coefficient (R^2) and a regression equation (Table 2). Based on the calculated coefficient of determination, it was found that exchangeable acidity has a 38.6% and 19.4% influence on total contents of Zn and organic carbon, respectively. The linear regression equation shows that an increase of 1 pH unit in the soil increased the total zinc content by 12.06 $mg \cdot kg^{-1}$. At the same time, it increased organic carbon by 1.45 $mg \cdot kg^{-1}$. Badora (2002) reports that, at pH 5.8, zinc binds to humic acids up to 60% of its cationic concentration, while at lower pH values its sorption almost disappears. Kabata-Pendias (2011) confirms that, under acidic conditions, organic matter is the primary adsorbent of metals. In addition to organic matter, granulometric composition also has a significant impact on the binding of zinc in soils, and the two combine to shape the soil's sorption properties. In this study, the content of total zinc forms was found to correlate significantly negatively with sand fraction ($r = -0.505$; $p<0.05$) and significantly positively with silt fraction ($r = 0.536$; $p<0.05$).

Table 2. Coefficient of linear correlation between parameters soil.

Variables		Equation	r	R^2
Dependent (Y)	**Independent (X)**			
Sand	**T Zn**	y= 67.7852 - 0.2185x	-0.505	0.255
Silt	**T Zn**	y= 28.2172 + 0.1858x	0.536	0.287
pH H_2O	**T Zn**	y= 4.8591 + 0.0245x	0.604	0.364
pH KCl	**T Zn**	y= -27.905 + 12.0607x	0.621	0.386
C_{org}	**T Zn**	y= 17.3122 + 1.4555x	0.441	0.194
pH KCl	**DTPA Zn**	y= -11.442 + 2.8916x	0.431	0.186
C_{org}	**DTPA Zn**	y= -1.2711 + 0.5564x	0.387	0.150
T Zn	**DTPA Zn**	y= -4.9836 + 0.2476x	0.716	0.513

The total forms of trace elements do not fully reflect the possibilities of their absorption. They provide only approximate ranges of the soil's abundance in a given ingredient. Plants can obtain microelements only from bioavailable forms. Studies on the range of the two forms of microelements in the soil are reflected in the practical fertilisation and nutrition of plants (Chojnicki and Kowalska 2009). The content of zinc extracted with DTPA ranged from 0.57 to 33.0 mg·kg^{-1} (Table 1). The average content of available zinc forms in the study area was 2.35 mg·kg^{-1}, with a very high variability of 186.89% and a standard deviation of 4.39 mg·kg^{-1}. The distribution analysis showed that, in most of the analysed samples, the content of DTPA-extracted zinc was below the mean. Barczak et al. (2009) report that the average content of available forms of zinc in Polish soils is 27.2 mg·kg^{-1}. The tested soils are therefore very low in bio-available zinc. However, this content is higher than the content defined as deficient for plants, i.e. 0.8 mg·kg^{-1} (Lindsay and Norvell 1978). The optimal level of Zn in the soil obviously also depends on the method used to determine zinc. The highest zinc content relates to 1 mol HCl dm^{-3}, and the lowest to DTPA, which results from the difference in amounts of Zn extracted by these methods (Korzeniowska and Stanisławska-Glubiak 2004). The low amounts of available forms of zinc may be due to zinc depletion in the soil and the type of soil. Chernozems and Phaeozems have higher contents of available forms than Luvisols and Podzols (Kabata-Pendias 2011). The literature states that, in Poland, Zn deficiency is not the most important micronutrient problem. It is estimated that 13–14% of the country's soils are low in available forms of zinc (Korzeniowska 2009).

The percentage ratio of bioavailable zinc to total zinc element (bioavailability coefficient AF) ranged from 2.09 to 37.50%, with a mean of 6.56% and a high coefficient of variation. In most samples, AF did not exceed the arithmetic mean threshold, as evidenced by the median being below the mean (Table 1). The content of bioavailable zinc forms is influenced by soil processes and its total content in the soil. However, the most important elements shaping the content and bioavailability are organic matter and soil reaction. The reaction of soils is, together with the soil humic content, of the greatest importance to the bioavailability of micro- and macroelements. Under acidic soil conditions, the availability and mobility of elements increases. Plants grown in acidic conditions, with a pH below 6, rarely suffer from zinc deficiency, because its availability increases significantly in such conditions (Cuske et al. 2013, Ahmad et al. 2012, Rutkowska et al. 2014). The correlation analysis showed a significant positive correlation between the content of available forms of zinc and pH in KCl ($r = 0.431$ $p<0.05$), the content of Corg ($r = 0.387$; $p<0.05$) and the content of total forms ($r = 0.716$; $p <0.05$) (Table 2). Based on the calculated coefficient of determination, it was found that the total forms of this element had the greatest impact on the content of available forms ($R^2 = 0.513$). The uptake of zinc from the soil is closely related to the zinc content in the soil, which in turn is largely dependent on pH. The linear regression equation shows that an increase of 1 pH unit in the soil increased the total zinc content by 2.89 $mg{\cdot}kg^{-1}$.

Principal component analysis (PCA) made it possible to reduce the eight-dimensional space to two components (factors), confirming their significance. It allowed two basic components to be identified (PC1 and PC2) that explained 78.62% of the total change in variance (Table 3). Factor 1 (PC1) accounted for 49.76% of all component variables and showed a high correlation with sand content (0.813), silt content (-0.821), active acidity (-0.765), exchangeable acidity (-0.762) and total zinc content (0.823). Factor 2 (PC2), which explained 28.86% of the total variance, was associated with the fractions of sand (0.729), silt (0.715) and clay (-0.711). Figure 2 shows that seven of the eight analysed parameters were grouped on one side of the factor axis. The longest vector of the primary variable indicates its greatest contribution in the composition of the primary component (sand). After analysing the distribution of basic soil properties and the amounts of zinc forms extracted from the soil on the plot of factor coordinates, it can be concluded that zinc content was most strongly associated with the pH of the soil.

Table 3. Factor loadings for the first two components of the analyzed soil properties.

Parameters	Component 1 (PC1)	Component 2 (PC2)
Sand	0.813*	-0.519
Silt	-0.821*	0.416
Clay	-0.586	0.729*
pH H_2O	-0.765*	-0.359
pH KCl	-0.762*	-0.402
C_{org}	-0.233	-0.711*
T Zn	-0.823*	-0.222
DTPA Zn	-0.634	-0.410
Variation (%)	49.76	28.86

* *statistically significant*

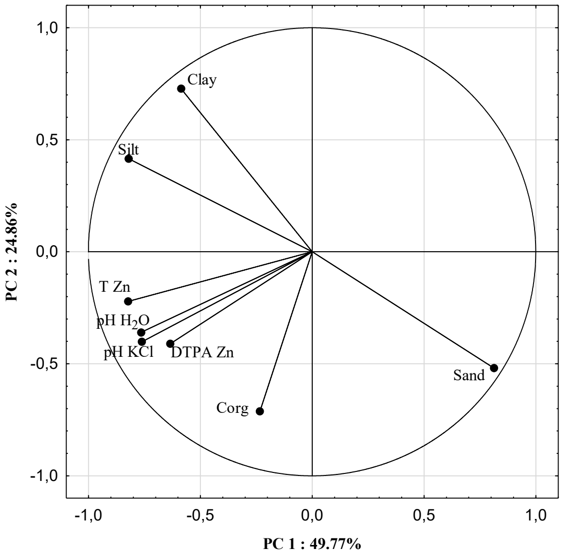

Figure 2. Configuration of variables in the system of the first two axes PC1 and PC2 of principal components.

CONCLUSIONS

Of all micronutrients, zinc deficiencies most severely limit the production of food of plant origin and are a common problem in agricultural soils. This is because this element is essential for plants, perform a number of important physiological functions in their metabolism. Low contents of total and available forms of zinc were recorded in the analysed samples of arable land. The total contents were at geochemical background levels, and the share of available forms did not exceed 10% in most of the analysed samples. The tested soils contain concentrations of available zinc, that are insufficient for proper plant growth. The availability of zinc to plants is influenced by those soil factors that control the amounts of zinc in the solution. These include, among others: total zinc content in the soil, pH, organic matter content. The correlation analysis confirmed a relationship between the content of total forms and the content of sand and silt fractions, soil reaction and organic carbon. Intensive agricultural use of these soils and their acidic reaction may have contributed to zinc depletion. Due to the lowness of the zinc content found in the tested agricultural soils, there is a need to monitor its amount, because crops will suffer from a deficiency of this microelement and will require it to be supplemented through fertilisation.

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