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AVAILABLE AND POTENTIALLY AVAILABLE ZINC IN ARABLE BLACK EARTHS (GLEYIC CHERNOZEMS) UNDER CONVENTIONAL SOIL MANAGEMENT

Based on a seven step sequential extraction procedure, available and potentially available fractions of zinc in agricultural soils classified to black earths (gleyic chernozems) being under conventional soil management were separated. It was found that zinc is present mostly in non available fractions and the content of labile zinc is scant. The total contents of Zn ranged from 22.7 to 221.0 mg/kg. The exchangeable Zn was low accounting for less than 7% of the total in most soils. Zinc availability is restricted due to fixation of metal to soil components: iron oxides and organic matter. Zinc was also found in significant amounts in residual fraction, which refers to metal tightly bound in crystal lattice of primary minerals. The study shows that in majority of analyzed soils, available zinc is below the deficit limit. It is necessary to recognize the scale of the problem due to possible application of Zn fertilizer.

1. INTRODUCTION

During the past several decades metals contents in agricultural soils have increased. Application of mineral fertilizers, livestock manure, sewage sludge and pesticides are major source of the accumulated metals, including zinc. Industrial and urban dust transported to the agricultural land might also contaminate soils with heavy metals [1]. When the concentration of zinc in the soil solution is too high, phytotoxicity effects are observed. From the other hand, application of phosphorus fertilizers are known to induce Zn deficiency in plants, due to insufficient solubility of Zn compounds [2]. Zinc has a number of critical functions in biological systems, including protection of structural and functional integrity of biological membranes, detoxification of highly toxic oxygen-

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-free radicals and maintenance of protein synthesis [3, 4]. This is an essential micronutrient for plants serving as an enzyme catalyst. It activates such enzyme as alcohol dehydrogenase and controls element proportions in the plant cells [5]. Deficit of zinc leads to limitation of plant growth due to low tryptophan synthesis and the retardation of auxin. In recent years, zinc deficiency in human diet was reported as a serious problem [6]. There has been little consideration of the factors that modulate the bioavailability and mobility of zinc in very productive black earths (gleyic chernozems) from Kujawy, agricultural region in Poland.

The goal of this research was to quantify mobile and potentially mobile forms of zinc in plow layer of these soils. A sequential extraction method was applied for the assessment of actual and potential availability of zinc. Trace metals fractionation is a good tool to quantify how strongly trace metals are held in soils and conversely, how easily they might be released to solution.

2. MATERIALS AND METHODS

Ten soils selected to represent arable gleyic chernozems [7] from the Kujawy region were sampled from 0 to 30 cm deep (plough layer). The soils were formed from boulder loam and are under conventional tillage system for at least 70 years. For the past 5 years of treatment, no fertilizers other than N, P, K were applied. Weather conditions are typical of temperate climate with long term annual temperature averages: 9 °C and rainfall average 560 mm in the region. For the investigation, the following sites were selected (Fig. 1): Kruszwica (sample No. 1), Janikowo (No. 2), Ujma (No. 3), Zakrzewo (No. 4), Kruszyn (No. 5), Osięciny (No. 6), Nowa Wieś (No. 7), Radziejów (No. 8), Gnojno (No. 9), Wierzchosławice (No. 10). Soils were air dried and ground to pass through a 2 mm mesh. pH was measured in H_2O (pH_w) and 1 M KCl (pH_{KCl}) solution using a 1:2.5 w:v soil/solution ratio; organic C was determined by dichromate oxidation. The cation exchange capacity (CEC) was determined by extraction with $BaCl_2$ after removal of water soluble ions using a PU-9100X spectrometer by the atomic absorption and atomic emission techniques [8].

The concentration of total zinc in soils was determined after the digestion in a mixture of concentrated HF and $HClO_4$, according to Crock and Severson [9]. Plant available zinc was extracted with diethylenetriamine pentacetic acid-triethylenamine (DTPA-TEA) solution by the Lindsay and Norvell method [10].

The procedure of Miller et. al. [11] was adapted to fractionate Zn. Selective extractants with increasing strength of extraction were applied in a sequence to determine the following fractions of zinc: F_1 – water soluble and exchangeable, non-specifically adsorbed, extractable with 0.5 M $Ca(NO_3)_2$, F_2 – associated with carbonates – extractable with a mixture of 0.44 M CH_3COOH and 0.1 M $Ca(NO_3)_2$, F_3 – associated with Mn oxides, extractable with NH_2OH HCl, F_4 – bound to organic matter, separated by extraction with 0.1 M $K_4P_2O_7$, F_5 – associated with amorphous iron oxides, extractable with ammonium oxalate, F_6 – precipitated or coprecipitated with crystalline iron oxides, extracted with ammonium oxalate in the presence of ascorbic acid, F_7 – residual phase – fraction considered bound within the lattice of silicate minerals, calculated by the difference between total metal and the sum of extractable fractions. Analyses were done in triplicate, the presented data are mean values. The resultant solutions from sequential analysis and mineralization were analyzed by the flame atomic absorption spectrometry (AAS) using a Philips PU 9100 X spectrometer. The analytical accuracy of AAS was ascertained by a standard reference material (Till 3) of known composition.

Fig. 1. Investigated area: Kruszwica (sample No. 1), Janikowo (No. 2), Ujma (No. 3), Zakrzewo (No. 4), Kruszyn (No. 5), Osięciny (No. 6), No.wa Wieś (No. 7), Radziejów (No. 8), Gnojno (No. 9), Wierzchosławice (No. 10)

3. RESULTS AND DISCUSSION

The soils analyzed differed in the organic matter content ($C_{org.}$ 9.1–19.3 g/kg) and contained clay in the range 7–13 wt. % (Table 1). Cation exchange capacity (CEC) related to these components was in the range 68.0–206.6 mmol(+)/kg. Soils were neutral or slightly alkaline with pH_w from 7.05 to 7.85, except for the one sample with pH 6.31 and pH_{KCl} from 6.40 to 7.49 (Table 1).

Table 1

Selected physicochemical properties of soils

Sample No.	pH_w	pH_{KCl}	C_{org} [g/kg]	Clay [wt. %]	CEC [mmol(+)/kg]
1	7.60	6.68	15.8	14	135.4
2	7.81	7.32	9.1	10	68.0
3	7.85	7.30	16.0	10	148.4
4	7.92	7.49	19.3	10	206.6
5	7.56	7.48	10.7	13	108.7
6	7.58	7.28	16.8	8	130.0
7	7.45	6.80	14.4	9	142.9
8	6.31	5.61	11.1	8	73.1
9	7.05	6.40	13.6	7	85.4
10	7.56	6.85	15.7	10	121.7

Total zinc concentrations were in the range 22.7–216.0 mg/kg (Table 2). The mean value of zinc content was 33.8 mg/kg [12]. The background level for this metal in soils formed from glacial till of Vistula glaciation is 33.0 mg/kg [13, 14]. Thus, elevated levels of zinc were detected in several studied soils (samples No. 1, 3, 9, 10). However, it is below the directive limits of the European Union Council for concentration of metals in arable soils, which for zinc is 300 mg/kg [15]. The excess of zinc in soil can reduce crop yields and may represent a potential hazard to the food chain.

Table 2

Total contents, DTPA extractable zinc and fractions of zinc ($F_1 – F_7$) in studied soils [mg/kg]

Sample No.	Total	DTPA	F_1	F_2	F_3	F_4	F_5	F_6	F_7
1	83.8	1.19	2.7	8.5	1.5	14.4	4.4	11.2	41.1
2	35.4	0.89	0.5	2.3	1.3	2.6	2.5	6.9	19.3
3	81.3	3.05	4.6	17.7	2.1	18.3	4.9	5.6	28.1
4	22.7	1.67	0.3	1.9	0.7	3.0	2.4	6.5	7.9
5	26.4	0.91	0.2	1.6	1.2	2.2	0.6	8.4	12.2
6	25.9	1.87	0.6	2.3	0.9	3.6	3.8	5.7	9.0
7	29.5	1.11	0.3	1.6	0.8	2.8	2.7	7.6	13.7
8	28.6	3.11	2.0	3.7	1.3	2.5	4.0	7.2	7.9
9	216.0	8.02	12.5	32.1	3.6	27.2	9.7	12.5	124.4
10	55.3	1.46	1.2	4.5	1.4	4.2	3.3	9.8	30.9

Extraction with DTPA-TEA according to Lindsay and Norvell [10] gives good indicator of the amount of metal available to plants roots. Plant available zinc occurs as

Zn^{2+} and $ZnOH^{+}$, organically complexed Zn in solution and easily desorbed on the surface of soil colloids [16].

The content of Zn extracted with the DTPA ranged from 0.89 to 8.02 mg/kg (Table 2). Critical level of DTPA – extractable zinc was reported as 0.2–2.0 mg/kg [5]. Thus, in a majority of analyzed samples, the available Zn is below the deficit limit. Higher content of zinc was found in soils with slightly elevated level of this metal in our study. Factors affecting Zn availability to plants are total Zn content, pH, organic matter contents, contents of clay and calcium carbonate, redox conditions, concentrations of other trace elements and macronutrients, especially P, and climate [16]. Such a low content of zinc is caused by its removal through crop harvest and the lack of fertilization with microelements.

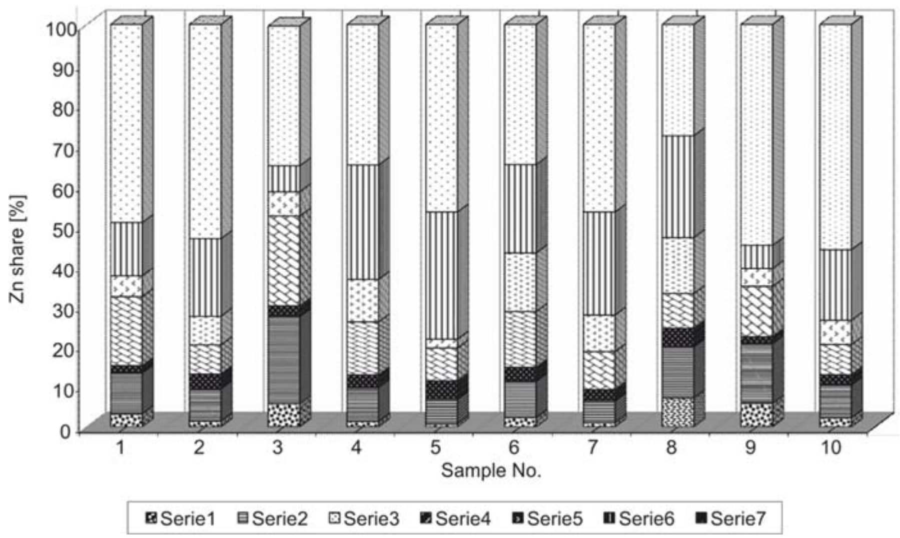

Fig. 2. Chemical partitioning of zinc in soils, expressed as percentage of the total contents

Although various investigations have determined plant available nutrients under various management systems, little information is available on interactive effects of agricultural management on forms and actual and potential availability of micronutrients [17, 18]. Selective chemical extraction allowed us to separate individual fractions of zinc (Table 2). The partitioning of metals in soils based upon the procedure of Miller et al. [11]. The sequential extraction technique partitions zinc into seven operationally defined fractions: water soluble and exchangeable, bound to carbonates, bound to Mn oxides, associated with soil organic matter, bound to amorphous iron oxides, bound to crystalline iron oxides and zinc in residual form. The results confirmed relatively low mobility of zinc and dominance of residual fraction (F_7) in the studied soils (Fig. 2). The residual fraction, which refers to zinc bound in crystal lattice of primary soil minerals accounts for approximately three fourth of the total Zn in the studied soils (Table 2). Metal in this fraction is relatively tightly bound and its release to solution is slow. Because the residual pool of zinc is unavailable, the other fractions, presumably more reactive, were called labile. The second abundant fraction was associated with crystalline iron oxides (F_6). Other authors reported that zinc is retained in soils mainly by iron oxides, particularly in soils with low contents of organic matter [19, 5]. Metals associated with Fe and Mn oxides are potentially labile and could be released under anoxic conditions upon decomposition of the oxides.

Between 7.3% and 22.5% of Zn was recovered as organically bound (Fig. 2). Organic matter has large influence on Zn availability. Usually, available Zn increases as the amount of soil organic matter increases [20]. Previous studies [21] has shown that organic matter forms complexes with Zn. Soil organic matter exerts a direct and indirect impact on the availability of Zn. Processes such as organic matter transformation, soil microbial activities and crop root activities release organic acids into the soil. This leads to a decline in the soil pH and accelerates the dissolution of non available micronutrients like zinc. Therefore, organic matter plays an important role in enhancing the availability of zinc [18].

The highest variation in Zn content exhibits carbonate fraction (F_2), which accounts from 1.6 mg/kg to 32.1 mg/kg. Zinc in the carbonate, specifically adsorbed fraction accounts for 5.4–21.8% of the total (Fig. 2) pH decrease will lead to release of zinc retained on a matrix by weak electrostatic interactions or coprecipitated with carbonate. The mobility of this fraction depends on soil pH and this pool of zinc is released into the solution below pH 5.0. Zinc bound to manganese oxides (F_3) was quite low, that is 0.7–3.6 mg/kg, which was equivalent to 1.7–4.5% of the total contents. Thus, this fraction is of little importance due to plant requirements in the studied soils. A very small amount of zinc occurred in the water soluble and exchangeable phase (0.7–7% of total). The exchangeable form (F_1), defined as the fraction bound to the surface of “active”, colloidal soil components is subject to desorption process and is readily available. In general, zinc availability in the studied soils is restricted due to fixation of metal to soil components, mainly iron oxides (F_5 and F_6) and organic matter (F_4).

Comparison of Zn contents in soils with elevated level of metal and soils with geochemical background value showed that the former one contained larger amounts of zinc potentially more labile: water soluble and exchangeable, associated to carbonates and bound to organic matter (Fig 2). Thus, low availability of Zn was observed in the most soils studied. Low plant available zinc concentrations in the studied soils is connected with micronutrient removal through crop harvest and the lack of microelements supplementation with microelement fertilizers.

4. CONCLUSIONS

Data from the studies indicate that the gleyic chernozems are not contaminated with zinc. Intensive agricultural use of these productive soils do not caused the accumulation of this metal. Under the existing conditions, labile Zn fractions are scant, particularly in soils with low – on the geochemical level – total metal contents. Thus, the investigated soils contain insufficient concentration of available zinc for the proper plant growth. Significant amounts of zinc were identified as potentially labile: bound to carbonates, organic matter and amorphous iron and crystalline iron oxides.

There is a need to continue the investigation on the type of Zn associations with these soil components, to recognize the scale of the problem and eventually apply zinc fertilization.

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