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GEOAVAILABILITY AND PHYTOCONCENTRATION OF ZN: FACING THE CRITICAL VALUE CHALLENGE (POLAND)

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Abstract

The verification of the concept "Facing the *critical value* challenge" has been performed on 9 arable fields of an agricultural farm (52 ha) located in the village Kujawki (Golancz District, Wielkopolska Region, Poland). In total, 99 soil samples were collected at the depth 0-20 cm from 9 fields. Basic properties were determined, i.e., soil particle distribution, organic carbon, pH (in 0.01 moles $CaCl_2$ dm^{-3}), cation exchange capacity (CEC). Moreover, Cu, Zn, Fe and Mn were extracted by 6 moles HCl dm^{-3} (pseudo total forms) and 0.005 moles DTPA, pH 7.3 (active and potentially mobile forms). Plant material (99 samples) was collected from winter triticale, winter wheat, winter barley, grass mixtures, winter oilseed rape and sugar beet at respective growth stages, dried, ground and analysed for Zn. The elaboration of soil (Zn_{-DTPA}) and plant (Zn_{-Plant}) critical values proceeded in two steps, i) tabular interpretation of data through adjustment to critical values in literature, ii) graphical readaptation of the C-Shaped, i.e. Piper-Steenbjerg curve.

The results revealed that the amounts of Zn_{-DTPA} varied in a wide range, from 0.80 to 4.30 mg kg^{-1}, but its overall share in total Zn fluctuated from 2.0 to 7.9%. This implies that the geoavailability of zinc compounds seems to be relatively high. The relationship established for the pairs Zn_{-Total} *versus* Zn_{-DTPA} ($Y_{Zn-DTPA} = 0.092_{Zn-Total} - 2.00$; $R^2 = 0.63$) yielded a significantly high coefficient of determination as a proof of the importance of Zn_{-Total} in controlling the Zn_{-DTPA} pool. The *critical* Zn_{-DTPA} *range* varied from 0.80 to 1.43 mg kg^{-1} with a mean value of *ca* 1.08 mg kg^{-1}, reflecting 67% of all investigated sites.

The readapted C-Shaped, i.e. Piper-Steenbjerg curve (Zn_{-Plant} *versus* Zn_{-DTPA}) allowed establishing a *critical* Zn_{-Plant} content at 15.3-39.7 mg kg^{-1} for the investigated crop plants. The mean critical value reached 33.3 mg kg^{-1} and divided plants into two groups, i) *experiencing deficiency*: winter wheat, winter oilseed rape, sugar beet and grass mixtures and ii) *not experiencing deficiency*: winter triticale, winter barley and winter wheat. These fin-

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dings give a new insight into the urgent need for elaborating critical values for a wide range of crop plants in use in Poland.

Key words: zinc, geoavailability, phytoconcentration, DTPA, Piper-Steenbjerg curve, critical value, crop plants.

GEODOSTĘPNOŚĆ I FITOKONCENTRACJA ZN: WYZWANIE W STOSUNKU DO WARTOŚCI KRYTYCZNEJ (POLSKA)

Abstrakt

Weryfikację koncepcji „Wyzwanie w stosunku do wartości krytycznej" przeprowadzono na 9 polach uprawnych gospodarstwa rolnego (52 ha) zlokalizowanego w miejscowości Kujawki (gmina Gołańcz, woj. wielkopolskie, Poland). Pobrano 99 próbek gleb z głębokości 0-20 cm i oznaczono następujące właściwości: skład granulometryczny, węgiel organiczny, pH (w 0,01 mola $CaCl_2$ dm^{-3}), kationową pojemność wymienną (CEC). Ponadto Cu, Zn, Fe i Mn ekstrahowano roztworem 6 moli HCl dm^{-3} (formy pseudocałkowite) oraz 0,005 mola DTPA, pH 7.3 (formy aktywne i potencjalnie ruchliwe). Materiał roślinny, tj. pszenżyto ozime, pszenicę ozimą, jęczmień ozimy, mieszankę traw, rzepak ozimy i buraki cukrowe (99 próbek) pobrano w odpowiednich stadiach wzrostu roślin. Po wysuszeniu i zmieleniu oznaczono zawartość Zn. Wartości krytyczne dla gleby (Zn_{-DTPA}) i roślin ($Zn_{-Roślina}$) opracowano dwustopniowo, stosując a) tabelaryczną interpretację danych przez dopasowanie do literaturowych wartości krytycznych, b) graficzne zaadaptowanie krzywej C-Shaped, tzn. Piper-Steenbjerga.

Wykazano, że ilości Zn_{-DTPA} wahały się w szerokim zakresie (0,80-4,30 mg kg^{-1}), lecz ogólny procentowy udział w całkowitej zawartości wyniósł od 2,0 do 7,9%, co wskazuje na to, że geodostępność związków cynku jest względnie wysoka. Wysoki współczynnik korelacji dla zależności między Zn_{-Total} a Zn_{-DTPA} ($Y_{Zn\text{-}DTPA}$ = $0{,}092_{Zn\text{-}Total}$ – 2,00; R^2 = 0,63) był dowodem na ważną rolę Zn_{-Total} w kontrolowaniu stężenia Zn_{-DTPA}. Krytyczny zakres Zn_{-DTPA} wynosił 0,80-1,43 mg kg^{-1}, a wartość średnia ok. 1.08 mg kg^{-1}, co odzwierciedla 67% badanych pól uprawnych.

Zaadaptowana krzywa C-Shaped, czyli Piper-Steenbjerga, w formie $Zn_{-Roślina}$ - Zn_{-DTPA} umożliwiła opracowanie wartości krytycznych Zn_{-Plant} mieszczących się w zakresie 15,3--39,7 mg kg^{-1} dla roślin. Średnia wartość krytyczna wynosiła 33,3 mg kg^{-1}, na podstawie której podzielono rośliny na dwie grupy: a) z niedoborem: pszenica ozima, rzepak ozimy, burak cukrowy i mieszanka traw, b) bez niedoboru: pszenżyto ozime, pszenica ozima i jęczmień ozimy. Te wyniki ujawniają nową pilną potrzebę opracowania wartości krytycznych dla wielu roślin uprawianych w Polsce.

Słowa kluczowe: cynk, geodostępność, fitokoncentracja, DTPA, krzywa Piper--Steenbjerg'a, wartość krytyczna, rośliny uprawne.

INTRODUCTION

The sustainable productivity of soil depends mainly on its ability to supply essential nutrients (including Zn) to growing plants (DIATTA, KOCIALKOWSKI 1998). Physical and chemical changes of Zn in soils are regulated by soil-specific precipitation, complexation and adsorption reactions. Soil Zn occurs in three principal fractions: (i) water-soluble Zn (including Zn^{2+} and soluble organic fractions); (ii) adsorbed and exchangeable Zn in the colloidal fraction (associated with clay particles, humic compounds and Al and Fe hydroxides); and (iii) insoluble Zn complexes and minerals (LINDSAY 1979, BARROW, 1993, ALLOWAY 2004).

The mean total Zn content of the lithosphere is estimated to be 80 mg kg^{-1} and a common range for soils is 10-300 mg kg^{-1}, mean 50 mg kg^{-1} (WEDEPOHL 1972). On the other hand, KABATA-PENDIAS, PENDIAS (1995) reported that most of surface soils are characterized by Zn levels within the range 17-125 mg kg^{-1}. It should be mentioned that the total Zn content is seldom used as a test for evaluating both its geoavailability and further phytoconcentration. According to BARBER (1995), concentrations of water-soluble Zn in the bulk soil solution are generally very low on farmlands and usually fluctuate between $4 \cdot 10^{-10}$ and $4 \cdot 10^{-6}$ moles. However, in calcareous soils, Zn^{2+} may be as low as 10^{-11}-10^{-9} moles, which can severely retard crops' growth (HACISALIHOGLU, KOCHIAN 2003). Next, the exchangeable Zn fraction typically ranges from 0.1 to 2 mg kg^{-1}, but insoluble Zn is estimated as > 90% and is practically unavailable for biotic assimilation.

Zinc in the soil solution where pH is below 6.5 may occur as Zn^{2+}, ZnCl, $ZnOH^{+}$, complexed with organic matter or associated with colloidal particles. The extent of zinc speciation depends on stability constants of the species formed, ionic strength, pH and the type and relative concentrations of cations and anions in the solution (LINDSAY 1972b). This may be roughly formulated as:

$$K = \frac{(M_a\ L_b)^{ax-by}}{(M^{x+})^a\ (L^{y-})^b} \quad \text{from the equation: } aM^{x+} + bL^{y-} = M_a L_b{}^{ax-by},$$

where:

K – stability constant,
M – Zn ions,
L – ligands,
a – moles of Zn,
b – moles of ligand molecules.

Theoretical approaches on Zn geoavailability have been subjected to experimental measurements, which allowed formulating equilibrium constants (MA, LINDSAY 1990, 1993, CATLETT et al. 2002), exhibiting the solubility of Zn as directly proportional to the square of protons' activity as follows: Soil-Zn + 2 $H^{+} \Leftrightarrow Zn^{2+}$, then their results generated a log K^o for this equation of 5.8. The transformation of this equilibrium reaction gives a log $(Zn^{2+}) \Leftrightarrow 5.8 - 2$ pH, implying that the solubility and therefore Zn geoavailability increase with a decreasing soil pH.

It is well known that an optimum plant growth and crop yield depend not only on the total amount of nutrients present in soil at a particular time but also on their availability (Domańska 2009, Kumar, Babel 2011). Several attempts undertaken over the last century (Mazé 1915, Sommer, Lipman 1926) to evaluate the Zn phytoconcentration as induced or regulated by geochemical processes have faced the challenge of great heterogeneity of soils and unlimited diversity (species, varieties) of plants. The essentiality of Zn forces soil scientists and plant breeders to work out ranges which will be helpful for nutritional remediative interventions. For the purposes of phytoconcentration, the establishment of *critical ranges/values* (or levels) appears to be worth endeavor.

In most crops, *typical* Zn concentration in leaves required for adequate growth approximates 15-20 mg Zn kg^{-1} DW (Marschner 1995). Because plants vary in their requirements for Zn, even among cultivars, it is difficult to set a single critical value. According to Brennan et al. (1993), plants with Zn contents below 20 mg kg^{-1} in dry tissue can be suspected of Zn deficiency, but the *normal ranges* are usually 25 to 150 mg kg^{-1} in dry plant tissues.

For years, the long-term process of standardization of zinc fluxes in the soil–root–shoot continuum has been promoting the application of DTPA (diethylene triamine pentaacetic acid) as a geochemical test for establishing Zn critical values. Next, remarkable achievements in research on the potential of plants to accumulate Zn have been made (Broadley et al. 2007), but linking this process to the DTPA extractable Zn is still scantily highlighted in Polish agricultural conditions.

The aim of the current study was to verify the concept of Zn geoavailability and phytoconcentration under field conditions. The specific purposes concerned the establishment of critical DTPA based Zn values and the respective critical Zn concentrations in winter Triticale, winter wheat, winter barley, grass mixture, winter oilseed rape and sugar beet.

MATERIAL AND METHODS

Location and sampling characteristics

Soil sampling and chemical analyses

Soil samples were collected at the depth 0-20 cm from an agricultural farm (52 ha) located in the village Kujawki (District of Gołańcz; Wielkopolska Region, 17°18»E; 52°57»N, Poland). The soil sampling took place in June and July 2010. The sampling sites consisted of 9 arable fields, where 99 soil samples were gathered under the following cropped fields: 5 soil samples (under winter triticale), 35 (winter wheat), 20 (winter barley), 5 (grass mixture), 23 (winter oilseed rape) and 11 (sugar beet).

The collected soil samples were first air-dried at room temperature, crushed to pass a 2.0 mm screen and stored in plastic bags before chemical analyses. Soil particle distribution was determined by the Casagrande-Proszyński areometer procedure, while organic carbon ($C_{org.}$) by the Tiurin's method (Nelson, Sommers 1986). Next, soil reaction (i.e., pH) was assayed potentiometrically in a 0.010 mole $CaCl_2$ dm^{-3} suspension according to Polish Standard (1994).

The cation exchange capacity (CEC) of the soils was determined with the ammonium acetate test, i.e., 1 mole CH_3COONH_4 dm^{-3} at pH 7.0, followed by the summation of exchangeable alkaline cations (Ca, Mg, K, Na) and exchangeable acidity (1 mole KCl dm^{-3} test), according to Thomas (1982). Zinc was extracted by using 6 moles HCl dm^{-3} and the recovered amounts designated as pseudo-total (Gupta et al. 1996). Briefly, 20 cm^3 of 6 moles HCl dm^{-3} were added to 2 grams of soil (in polyethylene tubes) and the mixture was placed in a low speed shaker (112 rpm) for 1 hour before filtering. Next, the active and mobilisable Zn forms were extracted by the 0.005 moles DTPA dm^{-3}, pH 7.3 (Diethylene triamine pentaacetic acid) test suggested by Lindsay and Norvell (1978) and later Liang and Karamanos (1993). Ten grams of soil were mixed with 20 cm^3 of 0.005 moles DTPA dm^{-3}, pH 7.3 for two hours; the extraction proceeded as described above. Zinc concentrations in filtrates as well as other elements were determined by the FAAS method (Flame Atomic Absorption Spectrometry, Varian Spectra 55B). All chemical analyses were performed in duplications.

Plant sampling and chemical analyses

Plant samples were collected from 6 crop plants, i.e., winter triticale, winter wheat, winter barley, grass mixture, winter oilseed rape and sugar beet, grown on 9 arable fields. The following growth stages were considered:

1) winter triticale (cv. Fredro), winter wheat (cv. Tonacja), winter barley (cv. Matilda) at BBCH29;
2) grass mixture (with 75% of *Lolium multiflorum*) at 25-30 cm height;
3) winter oilseed rape (cv. Cabriolet) at spring regrowth;
4) sugar beet (cv. Raketa) at 6-7 leaves (well developped).

The sampled plant material (in total 99) was dried at 60°C for 3 days in a dryer (SLW 100 ECO). After drying, plant samples were ground in a blender 8010EG; model HGBTWTG4. Adequate portions of the plant mass (0.15 g) were weighted out on an analytical balance (Sartorius A 200S) and digested in 2.5 cm^3 concentrated nitric acid in a MARS 5 apparatus (Microwave Accelerated Reaction System) manufactured by the CEM Corporation. Zinc concentrations in the digests were determined by FAAS (Flame Atomic Absorption Spectrometry, Varian Spectra 55B). All chemical analyses were performed in duplications. Statistical evaluations were performed by using the Statgraphics® software and graphs elaborated with Excel® sheet facilities.

RESULTS AND DISCUSSION

Characteristics of investigated fields (sites)

One of the most common constraints to agricultural plant production is the soil heterogeneity, which implicitly regulates the availability of mineral elements and further shapes spatial biomass distribution (Kiepul, Gediga 2009, Diatta et al. 2012). The same problem appeared on the investigated agricultural fields, where 6 plant species were grown (Table 1). Selected physical and chemical soil parameters revealed markedly high heterogeneity, for example the clay content within the broad range of 317-471 g kg^{-1} and particularly varied levels of organic carbon ($C_{org.}$) fluctuating from 12.7 to 171.1 g kg^{-1}. The analyzed soils may be considered as mostly loamy in nature, which generally manifests in good structural development and relatively high nutrient retention capacity (Dimoyiannis et al. 1998, Schulten, Leinweber 2000).

Table 1

Selected physical and chemical parameters of 9 investigated arable fields, (mean values)

Field/Site (No. of soil samples)	Type of crop plant	Clay (< 0.02 mm)	Organic carbon (Corg)	pH $CaCl_2$	CEC
		(g kg^{-1})			(cmol(+) kg^{-1})
A (n = 5)	winter triticale	341	21.3	5.4	4.4
B (n = 11)	winter wheat	448	16.2	5.8	4.6
C (n = 10)	winter barley	350	13.7	6.1	9.4
D (n = 10)	winter barley	318	12.7	6.7	16.7
E (n = 5)	grass mixtures	430	171.1	7.6	20.9
F (n = 23)	winter oilseed rape	325	33.7	6.0	11.0
G (n = 16)	winter wheat	317	12.9	6.5	15.4
H (n = 11)	sugar beet	384	14.0	6.2	9.9
I (n = 8)	winter wheat	471	17.6	6.1	10.7

The order of soils according to organic carbon suggested by Sequi and De Nobili (2000), that is C_{org} < 5.8 g kg^{-1} (very low); 5.8-10.4 g kg^{-1} (low), 11-14.5 g kg^{-1} (moderate), C_{org} > 14.5 g kg^{-1} (high), translated into three operational groups distinguishable from the data reported in Table 1. These include sites C, D, G, H characterised by C_{org} in the moderate range; A, B, F, I representing the high range and site E with an extremely high C_{org}

level. This means that the investigated fields possess good properties, which should directly help to manage the chemistry of most elements, including Zn, as demonstrated by LINDSAY (1972b) on the basis of soil organic ligands toward zinc ions.

Setting up a good plant stand depends intrinsically on soil reaction (i.e. pH), since pH regulates the solubility as well as the retrogradation of minerals (SKWIERAWSKA et al. 2012). It is most important to keep soil pH on a slightly acid level, which for the 0.01 moles $CaCl_2$ dm^{-3} test is *ca* 6.0-6.5. Most of the investigated sites corresponded to this state, since 6 out of 9 sites had pH between 6.0 and 6.7, except site E characterised by pH of 7.6, (i.e. slightly alkaline). This soil characteristic along with the content of clay and organic carbon are essential factors building and stabilizing buffering capacities, roughly expressed as the cation exchange capacity (CEC).

Ratings for the CEC as suggested METSON (1961) and HAZELTON and MURPHY (2007) – Table 2 show that three prevalent ranges: 6-12 $cmol_{(+)}$ kg^{-1} (sites: C, F, H, T); 12-25 $cmol_{(+)}$ kg^{-1} (sites: D, E, G) and finally 25-40 $cmol_{(+)}$ kg^{-1} (sites: A, B), corresponding to the low, moderate and high CEC, respectively. It should be mentioned that the first two ranges comprised *ca* 78% of all values, which implies that Zn is not strongly retained by soils and should be more easily released (supplied) for biological assimilation. Next, in terms of exchange processes, this may be related to the reduction of the number of negative charges on soil colloids reducing the adsorption of Zn on exchange sites. These geochemical conditions will favor zinc transfer from bulk soils to the *phytosink*, i.e., plants.

Table 2

Rating for the cation exchange capacity (CEC)

Rating	CEC (cmol(+) kg^{-1})
Very low	< 6
Low	6 - 12
Moderate	12 - 25
High	25 - 40
Very high	> 40

Zinc geoavailability versus DTPA critical values

The geoavailability of Zn is controlled by several factors, hence the relative difficulty in elaborating average values (mainly chemical tests), which reasonably express the actual state. Several attempts have been undertaken to outline a “universal” chemical test, but the multitude of soil factors on one hand, and plant heterogeneity (species, varieties) on the other hand substantially dispersed the final target. However, since the 1970s, the use of the DTPA test (Lindsay, Norvell 1978) has been progressing and the achievements, i.e. establishment of some critical values, are more convincing (Sharma et al. 2004, Brennan 2005, Alloway 2008).

The data listed in Table 3 (total and potentially available) show the variation of mean Zn_{-DTPA} values accordingly to the total content and investigated sites. The amounts of Zn_{-DTPA} varied in a wide range, from 0.80 to 4.30 mg kg^{-1}, but the overall share in total Zn fluctuates from 2.0 (site H) to 7.9% (site C), which implies that the geoavailability of zinc compounds seems to be relatively high. The relationship established for the pairs Zn_{-Total} *versus* Zn_{-DTPA} ($Y_{Zn\text{-}DTPA} = 0.092_{Zn\text{-}Total} - 2.00$; $R^2 = 0.63$) yielded a significantly high coefficient of determination as a proof of the importance of the Zn_{-Total} in controlling the Zn_{-DTPA} pool. The values obtained by Ibrahim et al., (2011) fell within a range of 2.62-7.02 mg kg^{-1} (mean = 4.65) slightly narrower than observed in the case of data reported by Kirmani et al. (2001), i.e. 0.47-6.50 (mean = 1.98).

Table 3

Total, potentially available and Zn content in 9 investigated arable fields and plants, respectively, (mean values)

Field/Site (No. of soil samples)	Type of crop plant	Total[a]	Potentially available[b]	Plant[c]
		Zn (mg kg^{-1})		
A (n = 5)	winter triticale	48.6	1.50	43.0
B (n = 11)	winter wheat	39.5	1.15	39.7
C (n = 10)	winter barley	54.2	4.30	39.4
D (n = 10)	winter barley	36.5	1.24	38.7
E (n = 5)	grass mixtures	19.5	1.03	15.3
F (n = 23)	winter oilseed rape	33.1	1.43	22.7
G (n = 16)	winter wheat	54.8	3.20	44.0
H (n = 11)	sugar beet	41.7	0.82	32.6
I (n = 8)	winter wheat	26.0	0.80	24.5

a – 6 moles HCl dm^{-3}, *b* – 0.005 moles DTPA dm^{-3},
c – concentration in green biomass

One of the challenging aspect in evaluating the potential availability of Zn is the elaboration of the *critical value* for a given site or agricultural field. This is necessary for practical purposes, for instance, predicting possible deficiency. Critical values listed in Table 4 revealed that the reported data vary quite similarly within the suggested ratings, irrespective of the significantly different soil conditions and crop plants (see footnote referen-

Table 4

Critical values[a, b, c, d] (DTPA-based) for interpreting the levels of Zn in agricultural soils (mg kg^{-1})

Parameter/Reference	Rating		
	low	medium	high
Zn[a]; Zn[b]	< 0.8	0.8 - 2.0	> 2.0
Zn[c]; Zn[d]	< 0.6	0.6 - 1.2	1.2 - 2.4
Pakistan[e]	< 0.5	0.5 - 1.0	> 1.0
Brazil[e]	< 0.5	0.6 - 1.2	> 1.2
Canada[e]	< 0.5	0.5 - 1.0	> 1.0
USA[e]	< 0.5	0.6 - 1.0	> 1.0

[a]Lindsay, Norvell 1978; [b]Ibrahim et al. 2011; [c]Takkar, Mann 1975; [d]Kirmani et al. 2011; [e]Lhendup, Duxbury 2008

ces). In the current study, an attempt has been made to propose critical Zn_{DTPA} values as illustrated in the Figure 1. Notably, the optimal critical range varied from 0.80 to 1.43 mg kg^{-1} with the mean value of *ca* 1.08 mg kg^{-1}, reflecting 67% of all investigated sites. The said amount should be rated generally as a medium one, but in overall the investigated sites present a medium-high status. According to Brennan et al. (2009), the critical Zn_{DTPA} for several investigated crop plants fluctuated within the range

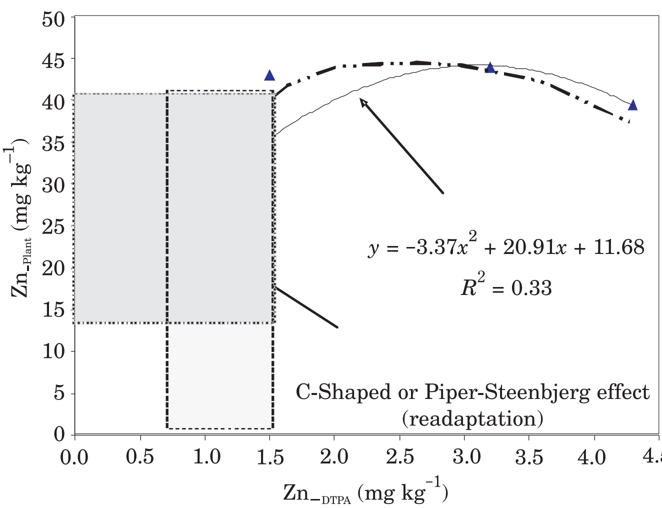

Fig. 1. Graphical readaptation of the C-Shaped or Piper-Steenbjerg curve for elaborating Zn_{-DTPA} and Zn_{-Plan} critical values

0.10-1.00 mg kg^{-1}, but ALLOWAY (2004) has reported a range of 0.45-0.67 mg kg^{-1} as adequate for wheat in India, adding that these values depended on the region and soil characteristics. The same applied to the critical value (0.68 mg kg^{-1}) for dryland in Iran (FEIZIASL et al. 2009). For fields subjected cropped with soybean and wheat in India, BARMAN et al. (1998) suggested a critical operational Zn_{-DTPA} value of 1.5 mg kg^{-1}, specifically for soils with a high silt and clay content. The latter value is high enough, but significantly lower than the ones elaborated for ginger (*Zingiber officinale* Rosc.) soils, i.e. 2.10-4.53 mg kg^{-1}, mean = 2.95 (SRINIVASAN et al. 2009). It should be mentioned that with such high Zn concentration, most cropped plants suffered biomass loss, probably, due to their response to the toxic effect of the metal.

Most studies dealing with the elaboration of critical Zn_{-DTPA} values have been performed in geographical zones in which soils are frequently slightly alkaline to alkaline. Under such conditions, zinc geochemistry is mainly controlled by the occurrence of anionic ions, which in turn are not the basic form taken up by plants. The geochemical approach suggested by MA and LINDSAY (1990, 1993) and CATLETT et al. (2002) fully elucidates this state in terms of the direct pH impact over Zn solution activity, i.e. log $(Zn^{2+}) \Leftrightarrow 5.8 - 2$ pH. Therefore, the higher the solution pH, the lower the Zn^{2+} activity and *vice-versa*. This may confirm the critical ranges reported by ALLOWAY (2004) or BRENNAN et al. (2009) and also the value equal 0.40 mg kg^{-1} obtained by CAKMAK (2004) for calcareous soils in Anatolia (Turkey). This approach demonstrates that soil pH seems to play a crucial role, but additional factors such as clay and silt levels should not be omitted.

Phytoconcentrations: elaboration of critical Zn values

Modern agricultural practices appear to have increased the extent and severity of zinc deficiency due to i) inadequate soil pH, particularly alkaline conditions, ii) increasingly growing biomass yield, which induces Zn mining from soil reserves. These characteristics have a direct impact on Zn uptake and its subsequent accumulation in plant organs. Zinc concentrations in six crop plants (Table 3), i.e. winter triticale, winter wheat, winter barley, grass mixture, winter oilseed rape and sugar beet, vary within a wide range of 15.3-44.0 mg kg^{-1}, with the lowest and highest levels found for grass mixtures and winter wheat, respectively. The linear relationship obtained from the pairs Zn_{-Total} *versus* Zn_{-Plant} ($Y_{Zn\text{-}Plant} = 0.80_{Zn\text{-}Total} + 0.93$; $R^2 = 0.67$) makes it clear that 67% of Zn taken up by tested crop plants should be strictly linked to its total content in soils. This is supported by the relationship reported earlier (i.e., $Y_{Zn\text{-}DTPA} = 0.092_{Zn\text{-}Total} - 2.00$; $R^2 = 0.63$) indicating that the Zn-DTPA pool should potentially reflect Zn accumulated in plants.

As shown in Figure 1, the concentrations below the lower critical level (15.3 mg kg^{-1}) will indicate potential deficiency and the need for remedial action (such as the use of zinc fertilizers or foliar sprays). Values between the lower and upper critical concentrations (15.3-39.7 mg kg^{-1}) will indicate an appropriate zinc status and no need for corrective action, while those above the upper critical value (39.7 mg kg^{-1}) will express a high zinc status reflecting the possibility of toxicity toward susceptible crops. Therefore, the 2^{nd} polynomial relationship characterized by a relatively low coefficient of determination (R^2 = 0.33) visibly displays the *plateau-generated* Zn-DTPA levels higher than 1.5 mg kg^{-1}.

The C-Shaped or Piper-Steenbjerg effect (hand-fitted curve for zinc, readapted), illustrated in Figure 1, deserves due attention. In fact, this curve reflects the relationship between the Zn concentration in plant tissue and the respective yield/biomass build-up (PIPER 1942, STEENBERG 1951, ALLOWAY 2004, BRENNAN 2005). The lower portions of the growth response curve can show an increase in growth with a decline in zinc concentration and can cause problems in the interpretation of plant analyses (IFA 1992). Some authors have suggested that problems with the C-shaped response curve can be minimized by analyzing whole shoot samples (as performed in the current study), but others still consider whole shoots to be unsuitable (ROSELL, ULRICH 1964, GENC et al. 2002). Nevertheless, in many parts of the world, when farmers collect samples for plant analysis, it is often whole shoots of young plants which are sampled (ALLOWAY 2004).

For the purpose of this study, the Piper-Steenbjerg approach has been readapted in order to illustrate the relationship for the pairs Zn_{-Plant} *versus* Zn_{-DTPA}, hence critical values of Zn were obtained for the investigated crop plants. This approach seems advisable, since it links the direct flow of Zn from labile Zn pools and its expected sink (i.e., plants), irrespective of the soil type and plant characteristics (species, varieties). Next, it uncovers a possibility of simultaneously elaborating targeted critical values for physiologically different crop plants.

Elaborated critical plant values versus interpretative standards

A rule of the thumb states that one of the biggest challenges is confronting empirical data with existing standards. In fact, interpretation standards are frequently discrepant as a result of the extensive heterogeneity of plant materials (Table 5). Two levels may be operationally considered for critical values established in this study: a *deficiency* and a *sufficiency* status, which tend to overlap according to ranges suggested by authors (footnote). The calculated mean critical value (data in Figure 1) is equal to 33.3 mg kg^{-1}, a value reflecting generally a sufficient rather than a deficient level. The investigated crop plants may be divided into two basic sites (Figure 2).

Table 5

Critical values[a, b, c, d] for interpreting the levels of Zn in crop plants (mg kg^{-1})

Parameter/Reference	Status		
	deficiency	sufficiency	excess
	(mg kg^{-1})		
Zn[a]	10 - 20	27 - 100	100 - 400
Zn[b]	15	10 - 100	-
Zn[c]	< 15 - 30	15 - 70	> 70
Zn[d]	reference plant - 50		

[a]Kabata-Pendias, Pendias 1995; [b]Pais, Jones Jr. 1997; [c]Cakmak, Marschner 1987; [d]Markert 1994

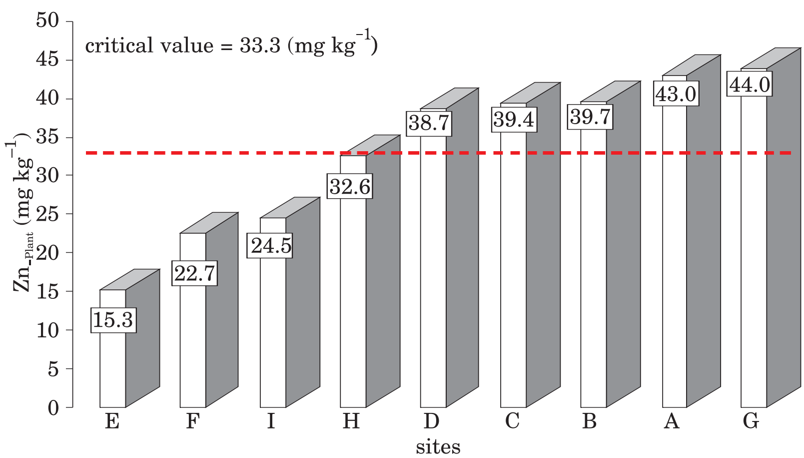

Fig. 2. The Zn_{-Plant} critical value delimitation of investigated sites into experiencing deficiency (Zn_{-Plant} < 33.3 mg kg^{-1}) and not experiencing deficiency (Zn_{-Plant} > 33.3 mg kg^{-1})

Sites where plants may experience deficiency, i.e. Zn_{-Plant} < 33.3 mg kg^{-1}:

E – winter wheat,
F – winter oilseed rape,
I – sugar beet,
H – grass mixtures;

Sites where plants do not experience deficiency, i.e. Zn_{-Plant} > 33.3 mg kg^{-1}:

D – winter Triticale,
C – winter wheat,
B – winter barley,

A – winter barley,

G – winter wheat.

These sets are highly interesting for the following reasons: the deficiency group consists of crop plants characterised by high vegetative biomass (except winter wheat), whereas the sufficiency group is made of crops with moderate yields of vegetative biomass. These findings shed new light on the urgency with which we need to elaborate critical values for a wide range of crops to use in Poland and possibly in other countries. The case of zinc reported in this paper seems encouraging.

CONCLUSIONS

1. The nine investigated fields have presented substantially diverse soil properties, but provided growth conditions which seemed favorable to growing crops, except for two sites characterized by pH_{CaCl_2} ca 5.5 and CEC ca 4.5 $cmol_{(+)}$ kg^{-1}.

2. The amounts of Zn_{-DTPA} varied from 0.80 to 4.30 mg kg^{-1}, i.e., 2.0 to 7.9% of total Zn. These percentages imply that the geoavailability of zinc compounds was relatively high. The mean critical Zn_{-DTPA} value amounted to 1.08 mg kg^{-1} (range: 0.80-1.43 mg kg^{-1}), reflecting 67% of all investigated sites.

3. On the basis of the readapted C-Shaped, i.e. Piper-Steenbjerg curve, the critical Zn_{-Plant} content for the investigated crop plants was determined at 15.3-39.7 mg kg^{-1} with the mean value of 33.3 mg kg^{-1}.

4. The mean critical Zn_{-Plant} divided plants into two groups: i) experiencing deficiency: winter wheat, winter oilseed rape, sugar beet and grass mixtures and ii) not experiencing deficiency: winter triticale, winter barley and winter wheat. There is a need to elaborate critical values for most crops cultivated in Poland.

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