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Site-specific evaluation of Cu, Zn, Fe and Mn availability in arable soils

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Abstract

Investigations were undertaken on an agricultural farm (52 ha) located at the Wielkopolska region, Western Poland. Soil samples (294) were collected at 0–30 cm depth from 6 fields after harvesting of winter triticale, winter wheat, winter barley, grass mixtures, winter oilseed rape and sugar beet. The following properties were determined: silt and clay, organic carbon (C_{org}), pH (in 0.01 moles $CaCl_2$ dm^{-3}), cation exchange capacity (CEC). Copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) were extracted by aqua regia test (total content) and 0.005 moles diethylene triamine pentaacetic acid (DTPA), pH 7.3 (active and potentially available forms). Potential availability and soil physical as well as chemical changes of these micronutrients were evaluated by using availability factors and thermodynamic parameters (Gibbs free energy change, ΔG°).

Data show that 83% of all tested soil samples were characterised by $C_{org} < 25$ g kg^{-1} . Moreover, the variability in pH was very high ($4.7 < pH_{CaCl_2} > 7.8$), *ca* 1/6 of investigated soils (16%) were acid, but on the other hand, 82% exhibited $pH > 5.5$. The mean CEC value amounted to 12.0 $cmol_{(+)}$ kg^{-1} , with 71% of soils representing $CEC < 12.0$ $cmol_{(+)}$ kg^{-1} . In fact, the range $12.0 \leq CEC \leq 25.0$ $cmol_{(+)}$ kg^{-1} , designating moderate buffering properties, shared *ca* 55%. The DTPA-based availability factor (AF) followed the order $Zn > Cu > Fe > Mn$, with respective indices $22.9 > 19.8 > 5.5 > 0.42$. Next, linear relationships established for the pairs C_{org} vs $DTPA_{Cu,Zn,Fe,Mn}$ resulted in the following correlation coefficients (r): C_{org} vs $DTPA_{Cu}$, $r = 0.67^{**}$; C_{org} vs $DTPA_{Zn}$, $r = 0.60^{**}$; C_{org} vs $DTPA_{Fe}$, $r = 0.56^*$; C_{org} vs $DTPA_{Mn}$, $r = 0.50^*$. It appeared that in the case of increasing or decreasing pH, the reactions of Cu, Mn and Fe in the soil solution should be similar, i.e. progressive unavailability or progressive availability, respectively.

Thermodynamic changes (ΔG° values) calculated for Zn, Cu, Fe and Mn were the basis for establishing the following operational ranges: $-5.0 \leq \Delta G^\circ$, readily available (for Zn); $-5.0 \geq \Delta G^\circ \geq -10.0$, moderately available (for Cu); $-10.0 \geq \Delta G^\circ \geq -15.0$, slightly available (for Fe); $\Delta G^\circ \leq -15.0$, hardly available (for Mn). The ΔG° -based values showed that micronutrient availability criteria should not be restricted to quantitative evaluation only.

Key words: arable soils, availability factor, diethylene triamine pentaacetic acid, Gibbs parameters, micronutrients.

Introduction

One of the major constraints for crop productivity in many countries of the world is the deficiency of micronutrients. The fact that about half of the world's population suffers from micronutrient shortage makes plant nutrition research indispensable (Cakmak, 2002; Alloway, 2008). Factors influencing the accumulation of micronutrients in plants are related to their concentrations in the soils which control their phytoavailability (Sienkiewicz et al., 2009; Tunçay et al., 2013). Intensive cropping often leads to nutrients' imbalance in soils and may affect nutritional status of plants (Kabata-Pendias, 2001). It is also known for agricultural species, that soil analysis does not always discriminate between responsive and non-responsive sites. Moreover, the levels of Cu, Zn, Fe and Mn in soil decreases with increasing pH, due to their adsorption/retention by soil particles (Brennan, 2005). Hence, high pH soils may also indicate a problem of low micronutrients availability, but acidic ones are

characterised most frequently by sufficient to excessive micronutrient supply. In acidic soils, fundamental chemical properties for plant nutrition (e.g., cation exchange and buffer capacity) are largely governed by organic matter content (Carter, 2002).

Chemical changes and fate of micronutrients are strictly related to the following three factors: i) soil buffering capacity mostly controlled by pH, clay and silt content and organic matter levels, ii) the total and available fractions of micronutrients, and finally iii) crop plants and their requirements. All these factors usually affect the potential capacity of soil to supply micronutrients (quantitatively) as well as the concentrations and activity of the latter ones (Uprety et al., 2009). The total amount of each micronutrient is distributed over pools in soils. Hence, the total micronutrient content does not provide an accurate estimate of the amount available to plant (Sharma et al., 2004). The plant-available micronutrient

in soils can be estimated by soil analysis, which provides the degree of efficiency or excess of plant nutrients. Of the many soil extractants, diethylene triamine pentaacetic acid (DTPA) is widely used for this purpose (Brennan, 2005). As such, the plant-available micronutrient in soils is just a function of the total content.

Several studies have pertinently focused on ranges of micronutrients in soils, where crop plant responses are none, weak or optimal (Cakmak, 2002; Grzebisz et al., 2008). Next, some reports have outlined the impact of buffering properties on availability parameters (Diatta et al., 2009), and the antagonistic relationship, as Cu-Zn antagonism has been suggested by Dangarwala (2001). Field investigations, integrating different plant species (i.e. differentiated cropping systems) and stressing intrinsic soil factors ruling micronutrients availability (for instance energetic changes), are still marginal.

Hence, the general aim of the current field study was to evaluate the effect of soil properties on Cu, Zn, Fe and Mn changes at different agrochemical sites. This approach was initiated due to the emergence of deficiency symptoms on the crop plants reported in the paper. The specific aim was to outline and suggest operational parameters to be considered when assessing the availability of the above reported micronutrients.

Materials and methods

Location and sampling characteristics. The sampling site is an agricultural farm (52 ha) located in the Wielkopolska region (17°18' E, 52°57' N), Western Poland. Soil samples (294) were collected using a 30-mm diameter core sampler from 6 arable fields at the 0–30 cm depth at post harvest, i.e. within the period from August to October 2010, due to different harvesting terms. The fields were formerly cropped with winter triticale (15 soil samples), winter wheat (102), winter barley (60), grass mixtures (15), winter oilseed rape (69) and sugar beet (33). These crop plants were decisive in scheduling the sampling depth. It was assumed that with such diversity of crop plants, the optimal depth should be 0–30 cm, due to the particular rooting systems of the plants. The next argument was that key soil physical and chemical processes controlling Cu, Zn, Fe and Mn availability operate mostly within this arable layer.

Physical and chemical analyses. 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. Silt and clay were determined by the Casagrande-Proszynski areometer procedure (Ryan et al., 2001), while organic carbon (C_{org}) – by the dichromate wet oxidation method (Pansu, Gautheyrou, 2003). Next soil reaction (i.e. pH) was assayed potentiometrically in a 0.010 mole $CaCl_2$ dm^{-3} suspension (weight:volume – 1:5) according to Ryan et al. (2001). The cation exchange capacity (CEC) of the soils was obtained by applying the ammonium acetate test, i.e. 1 mole CH_3COONH_4 dm^{-3} at pH 7.0 (weight:volume – 1:10) followed by the summation of exchangeable alkaline cations (Ca, Mg, K, Na) and exchangeable acidity (1 mole

KCl dm^{-3} test), according to Hazelton and Murphy (2007). Micronutrients, i.e. Cu, Zn, Fe and Mn were extracted by using the aqua regia test (ISO 11466:1995 EN) procedure. Briefly, an air-dried sediment sample (1.00 ± 0.001 g) was weighed into a glass beaker; 15 cm^3 of aqua regia (1:3 concentrated nitric acid and hydrochloric acid) were added, and the beaker heated under reflux for 2 h on a sand bath. Beaker contents were filtered through filter paper into a 15 cm^3 tube and filled to the mark with bidistilled water. Micronutrients soluble in aqua regia were determined by atomic absorption spectrometry (AAS) (Varian SpectrAA 250 plus, Germany) and considered as a total metal content. Next, active and potentially mobilisable micronutrient forms were extracted by the 0.005 moles diethylene triamine pentaacetic acid (DTPA) dm^{-3} , pH 7.3, test suggested by Sidhu and Sharma (2010). Ten grams of appropriate soils were mixed with 20 cm^3 of 0.005 moles dm^{-3} DTPA, pH 7.3 (weight:volume – 1:2) for two hours, the extraction proceeded as described above. Micronutrients in filtrates as well as other elements were determined as in the case of aqua regia. Relative standard deviations in both cases were calculated from pooled data for applied methods. In the precision test, the average relative standard deviations (%) of analyzed soil samples for all micronutrients ranged from 0.70% to 12.55%. The accuracy of chemical tests was determined using a reference material ERM-CC141 (Certified Reference Materials, 2013, Institute for Reference Materials and Measurements, Belgium).

Availability assessment of Cu, Zn, Fe and Mn.

Reactions of micronutrients with soil colloids affect directly their availability. Hence, the knowledge of interacting factors and/or mechanisms is helpful in evaluating any potential micronutrient supply as well as the possible emergence of deficiencies. The availability factor (AF) as suggested by Obrador et al. (2007) was applied for this purpose. It is expressed as follows:

$$AF = \frac{DTPA_{Cu, Zn, Fe, Mn} \times 100}{Total_{Cu, Zn, Fe, Mn}} \quad (1),$$

where AF – availability factor (%), $DTPA_{Cu, Zn, Fe, Mn}$ – amounts of DTPA-extractable micronutrients ($mg\ kg^{-1}$), $Total_{Cu, Zn, Fe, Mn}$ – aqua regia extractable micronutrients ($mg\ kg^{-1}$).

Exchange/adsorption processes were additionally evaluated throughout thermodynamic changes of Cu, Zn, Fe and Mn in investigated soils. Standard Gibbs free energy was calculated on the basis of equilibrium constant as suggested by Diatta et al. (2010) according to the relationship:

$$\Delta G^{\circ} = -RT \ln K_{R(Cu, Zn, Fe, Mn)} \quad (2),$$

$$K_{R(Cu, Zn, Fe, Mn)} = \frac{S_{(Cu, Zn, Fe, Mn)}}{C_{DTPA(Cu, Zn, Fe, Mn)}} \quad (3),$$

where ΔG° – Gibbs free energy ($kJ\ mole^{-1}$), R – universal gas constant ($8.314\ J\ mole^{-1}\ K^{-1}$), T – absolute temperature (273 K), $K_{R(Cu, Zn, Fe, Mn)}$ – Rawat equilibrium constant ($dm^3\ kg^{-1}$), $S_{(Cu, Zn, Fe, Mn)}$ – pool of Cu, Zn, Fe and Mn potentially retained by soils. This is the difference

between aqua regia and 0.005 moles dm^{-3} DTPA-extractable micronutrients (mg kg^{-1}), C-DTPA_(Cu, Zn, Fe, Mn) – concentrations of Cu, Zn, Fe and Mn in DTPA extracts (mg dm^{-3}).

All chemical analyses were duplicated under laboratory conditions (temperature set at 22°C). Graphs and calculations were made by using software *Excel*[®] *Sheet* and *STATISTICA*[®] ver. 8.0 facilities. Data with *, **, *** are statistically significant at the level of $P < 0.1$, 0.01 and 0.001, respectively.

Results and discussion

Physical and chemical properties of soils. The widespread need for micronutrients observed in recent years can be accounted for in three ways (Vijayakumar et al., 2011): i) naturally deficient in some soil types, ii) their deficiency has been brought out by crop removal and iii) low input along with crop residues or manure as well as the destruction of soil organic matter. Soils investigated in the current study exhibited a wide range of physical and chemical properties as reported in Table 1. Soil particles, such as silt and clay are generally considered to constitute the mineral part which strongly and efficiently controls micronutrients' availability. A relatively low or high content of silt and clay is then indicative among others of a potentially high or low availability, respectively. The range (150–730 g kg^{-1}) implies that both conditions were operating. The mean value and standard deviation ($360 \pm 150 \text{ g kg}^{-1}$) indicates that the studied soils may be considered as loamy in nature, therefore exhibiting good structural development and relatively high nutrient retention capacity (Schulten, Leinweber, 2000). It appeared from these dataset that 83% of all tested soil samples (i.e. 294) were characterised by $C_{\text{org}} < 25 \text{ g kg}^{-1}$, but 6% and 2% by $C_{\text{org}} > 100$ and 200 g kg^{-1} , respectively.

Table 1. Selected physical and chemical properties of investigated soils

Description (n = 294)	Silt and clay	Organic carbon (C_{org})	$\text{pH}_{\text{CaCl}_2}$	Cation exchange capacity (CEC) $\text{cmol}_{(+) } \text{kg}^{-1}$
	g kg^{-1}			
Min.	150	2.6	4.7	5.1
Max.	730	243.9	7.8	66.3
Mean	360	24.2	6.2	12.0
Standard deviation	150	37.6	0.8	13.8

According to Hazelton and Murphy (2007), a productive soil should have an organic carbon content of at least 23.2 g kg^{-1} . The predominance of soils with $C_{\text{org}} < 25 \text{ g kg}^{-1}$ implies that most of investigated sites were characterised by relatively low levels of organic carbon, which in turn favours availability processes to run easily. On the other hand, in organic soils ($C_{\text{org}} > 100 \text{ g kg}^{-1}$) the availability and fate of Cu, Zn, Fe and Mn

should be strongly controlled by organic carbon content. Soil reaction (pH) is of prime importance in controlling the availability of micronutrients, since it affects directly their solubility as well as activity in the soil environment (Diatta, 2008; Diatta et al., 2009). As can be seen from Table 1, the variability in pH was very high ($4.7 < \text{pH}_{\text{CaCl}_2} > 7.8$), with a mean value of 6.2. The reference pH value (in 0.010 mole $\text{CaCl}_2 \text{ dm}^{-3}$) for considering a soil as moderately acid is levelled at 5.5 (Hazelton, Murphy, 2007). Then, ca 1/6 (16%) of studied soils were acid, but on the other hand, 82% exhibited $\text{pH} > 5.5$, of which only 6% with $\text{pH} = 6.2$ (i.e. slightly acid). Next, nearly half (47%) of soils revealed a $\text{pH} > 6.2$, which may be indicative of a non-limiting parameter for micronutrient supply to crops. Buffering properties of soils are regulated by several physical as well as chemical properties, of which clay and silt content, organic matter level and pH play the key role. These also directly affect adsorption, desorption and exchange processes, responsible for micronutrients behaviour in soils. Ratings for CEC as suggested by Hazelton and Murphy (2007) were used for interpreting buffering capacity of soils (Table 2).

Table 2. Rating (according to Hazelton and Murphy, 2007) for cation exchange capacity (CEC)

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

Data provided in Table 1 stress the great heterogeneity of investigated fields covering an area of 52 ha. The mean CEC value amounted to 12.0 $\text{cmol}_{(+) } \text{kg}^{-1}$ ($5.1 \leq \text{CEC} \leq 66.3 \text{ cmol}_{(+) } \text{kg}^{-1}$), which apparently implies that buffering capacities were moderate to slightly low, since 71% of soils exhibited $\text{CEC} < 12.0 \text{ cmol}_{(+) } \text{kg}^{-1}$. In fact the range $12.0 \leq \text{CEC} \leq 25.0 \text{ cmol}_{(+) } \text{kg}^{-1}$, considered to represent moderate buffering properties shared ca 55%, but only 5% of soils were characterised by very high CEC $> 40 \text{ cmol}_{(+) } \text{kg}^{-1}$. This small group was identified with $\text{pH} > 6.2$ and simultaneously $C_{\text{org}} > 100 \text{ g kg}^{-1}$.

Potential availability and pH-based Cu, Zn, Fe, Mn behaviour in soils. The determination of micronutrients availability is usually performed throughout several chemical tests (Agbenin et al., 2002). The total content of micronutrients has less practical meaning in terms of availability. Data presented in Table 3 vary significantly as a proof of the heterogeneity of investigated sites. It should be mentioned that the maximal level differed from the minimal by a factor of ca 65, 34, 18, and 17 for Fe, Zn, Mn and Cu, respectively. On this basis, one may tentatively conclude that Fe and Zn will be potentially more available as compared to Mn and Cu.

Table 3. Total micronutrient content of investigated soils

Description (n = 294)	Cu	Zn	Fe	Mn
	mg kg ⁻¹			
Min.	1.08	2.75	72.3	18.6
Max.	17.83	93.02	4687.2	340.3
Mean	6.08	18.12	1089.5	121.6
Standard deviation	3.51	11.75	743.3	77.3

This assumption was verified by the data provided in Table 4, specifically for potentially available (DTPA) microelement pools, but AF, as suggested by Obrador et al. (2007) followed the order: Zn > Cu > Fe > Mn. It appeared from these AF-based values that Mn was the least, whereas Zn the most available. Interestingly, Fe availability levelled at *ca* 1/4 that of Cu, despite the relatively high values of DTPA_{Fe} as compared to DTPA_{Cu}. Values obtained by Obrador et al. (2007) showed that AF indices were much higher for Zn than Mn on acidic soils, i.e. on average 22.7% and 6.7%, respectively. Two aspects may be pointed out for elucidating the unexpected behaviour of these micronutrients for the current study: i) the prevalence of soils with relatively low organic carbon content (83% soil samples characterised by C_{org} < 25 g kg⁻¹), ii) 82% of soils exhibited pH > 5.5, but with nearly half (47%) revealing a pH > 6.2. Organic matter controls the affinity, attraction strength of micronutrients with mostly functional groups, whereas soil reaction, i.e. pH is involved in processes related to ionic activities in the solution.

Table 4. Potentially available (0.005 moles diethylene triamine pentaacetic acid (DTPA) dm⁻³) and availability factors (AF) for micronutrients of investigated soils

Description (n = 294)	Cu	Zn	Fe	Mn
	DTPA test (mg kg ⁻¹)			
Min.	0.02	0.22	0.30	0.02
Max.	1.32	5.80	183.6	1.96
Mean	0.41	1.13	35.9	0.39
Standard deviation	0.21	1.27	30.4	0.23
AF %				
Mean	19.8	22.9	5.5	0.42
Range	0.62–47.3	2.90–67.5	0.05–65.5	0.07–3.86

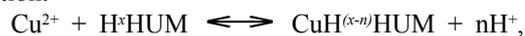
The electronegativity of these metals follows the order: Cu (1.90) > Fe (1.83) > Zn (1.65) > Mn (1.55), which implies that Cu and Fe should build up stronger and more stable bonds with soil colloids (particularly organic ones), as opposite to Zn and Mn (Islam, 2010). This assumption has been verified partly by data listed in Table 4, where AF values followed the order: Zn > Cu > Fe > Mn. Linear relationships established for the pairs C_{org} (independent variable) vs DTPA_{Cu,Zn,Fe,Mn} (dependent variable) resulted in the following correlation coefficients (*r*): C_{org} vs DTPA_{Cu}, *r* = 0.67**^{*}; C_{org} vs DTPA_{Zn}, *r* = 0.60**^{*}; C_{org} vs DTPA_{Fe}, *r* = 0.56*^{*}; C_{org} vs DTPA_{Mn}, *r* = 0.50*^{*}.

Positions occupied by Cu and Mn (based on *r* values) are fully in line with the electronegativity rank, except for Zn and Fe, being permuted. Iron chemistry is basically regulated by mineral soil colloids and pH, but in the case of zinc, organic colloids and pH. Zinc, Cu, Fe and Mn showed positive correlations with organic carbon but negative with pH.

In their studies on the availability of Zn, Cu, Fe, Mn in soils, Sidhu and Sharma (2010) have reported that the total content of these micronutrients increased with an increase in clay and silt and CEC, whereas the DTPA-extractable levels decreased with increasing pH and calcium carbonate content. Similar data have been reported by Mathur et al. (2006), who showed that DTPA_{Zn} correlated among others significantly and negatively with pH (*r* = -0.383), but positively with organic carbon (*r* = +0.738). In our study, the correlation coefficients for the pairs C_{org} vs Zn and Cu were the highest as compared to Fe and Mn.

The sensitivity of Cu, Zn, Fe and Mn to changes induced by pH is illustrated in Figures 1 and 2. Two groups of reactions may be identified: i) the linear group represented by Cu, Fe and Mn, ii) the third degree polynomial group with Zn. Such specific properties imply that Cu, Mn and Fe should behave similarly with increasing (progressive unavailability) or decreasing (progressive availability) pH. The recorded correlation coefficients for the pairs DTPA_{Cu,Fe,Mn} vs pH showed that active Mn (*r* = -0.74***^{*}) and Fe (*r* = -0.70***^{*}) forms were more sensitive to the raise in pH as compared to Cu (*r* = -0.50*^{*}), but on the other hand they shared *ca* 0.32, 3.3 and 16 % of the total content, respectively. This confirms the amphoteric characteristics of manganese and iron oxides, where pH plays a key role in their chemical behaviour, specifically related to the mineral phase of the soil.

The relatively high share of Cu (i.e. 16% of its total level) deserves due attention. This metal exhibits high affinity both to mineral as well as organic soil colloids. According to Römken and Dolfing (1998), at pH above 5.0, more than 99% of the total dissolved Cu concentration is bound to dissolved organic compounds, which by developing their net negative surface charge acted as efficient carriers participating in Cu solubility and mobility in soils. This assumption is supported by the reaction:



where HUM expresses the organic compound.

The average pH of investigated soils is 6.2; therefore, the dissolution of organic compounds is expected to be important. This process is strengthened due to the pH of the DTPA solution, established at 7.3. The joint effect of both soil and DTPA pH may have been responsible for the high extractability of Cu.

Mechanisms that control Zn solubility are still poorly understood. According to Kiekens (1995), the activity of Zn²⁺ in soils is directly proportional to the square of the proton activity; therefore, the solubility of Zn will decrease proportionally with increasing values of

soil pH, as illustrated in Figure 1. Investigations carried out by Catlett et al. (2002) have revealed that the activities of Zn were very low (in the range $10^{-7.9}$ – $10^{-10.9}$ moles) and inversely related to soil pH. Next, a direct identification of solid phases controlling Zn solubility was not obvious and tentatively explained by the possible formation of $ZnFe_2O_4$ (franklinite). Data listed in Tables 2 and 3 showed that the levels of Fe were high enough to create conditions enabling the potential build up of any Zn_xFe_y compounds. The relatively high share of available Zn (DTPA-extractable), i.e. 16% of its total content implied

that the formation of the above mentioned compound was less probable. Schwab and Lindsay (1983) plotted Fe^{2+} activity as a function of pH and pointed out that its activity was controlled by $FeCO_3$ (siderite) at pH below 8, and by $Fe_3(OH)_8$ (ferrosic hydroxide) at pH above 8. However, in the current study, the highest recorded pH was below the value at which ferrosic hydroxide should be formed. Therefore a mixture of $ZnFe_2O_4$ and $FeCO_3$ may have been partly controlling iron chemistry in the soil, but this view needs a detailed study.

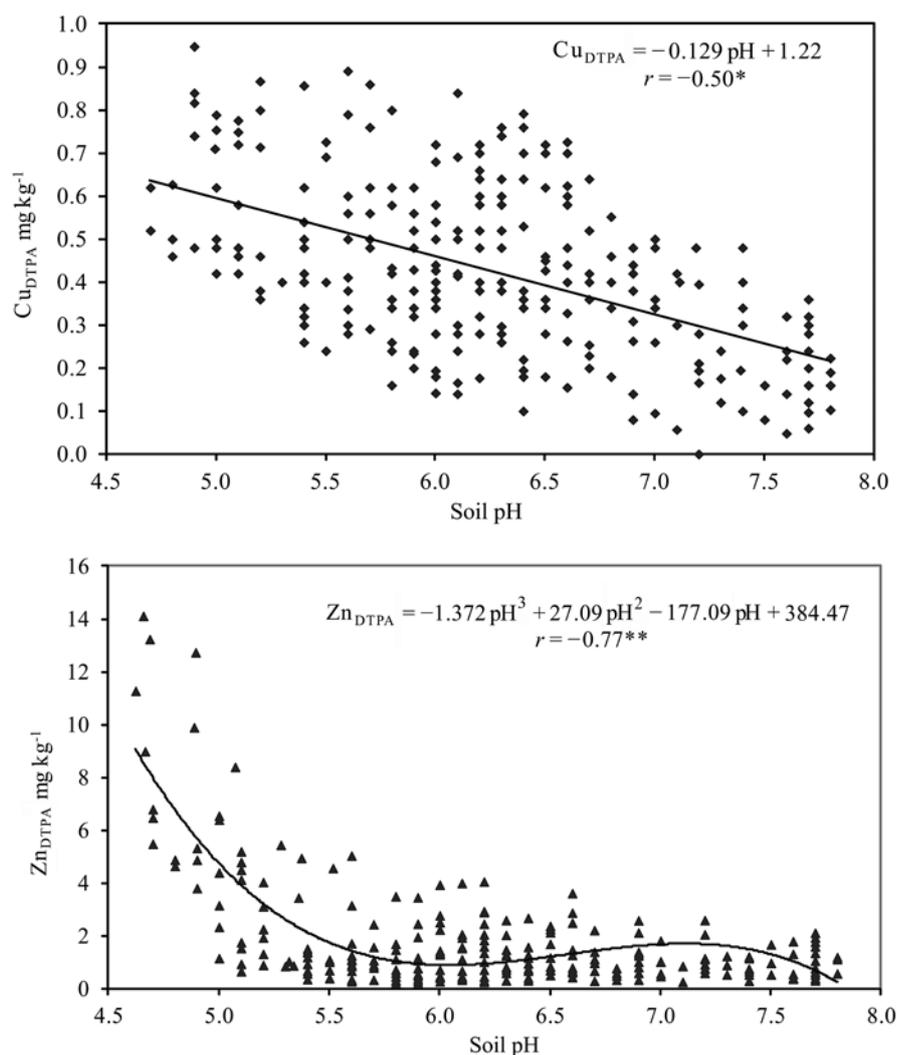


Figure 1. Changes in copper (Cu) and zinc (Zn) extractability as induced by soil pH

Gibbs free energy changes vs potential availability of micronutrients. While total ion concentration (i.e. sum of free and complexed ions) of the soil solution provides important information on the quantities of ions available for plant uptake and movement through soil profile, it is important that the reactions of particular chemical forms with the soil solid phase be known (Diatta, 2008). A useful and informative way of determining whether a soil phase controls the concentration of an element in the soil solution is to apply a thermodynamic approach to the availability of Cu, Zn, Fe and Mn (Table 5).

Physical and chemical reactions in soils operate thermodynamically, since they proceed throughout classic energy changes (Catlett et al., 2002). The spontaneity of these processes requires that the changes in the enthalpy bear a value below zero ($\Delta G^\circ < 0$). In other words, the lowest the ΔG° value, the strongest the micronutrient is retained by soil, i.e. the least its solubility and availability. Four main ranges may be operationally suggested: $-5.0 \leq \Delta G^\circ$ – readily available (for Zn), $-5.0 \geq \Delta G^\circ \geq -10.0$ – moderately available (for Cu), $-10.0 \geq \Delta G^\circ \geq -15.0$ – slightly available (for Fe), $\Delta G^\circ \leq -15.0$ – hardly available (for Mn). Data presented in Table 5

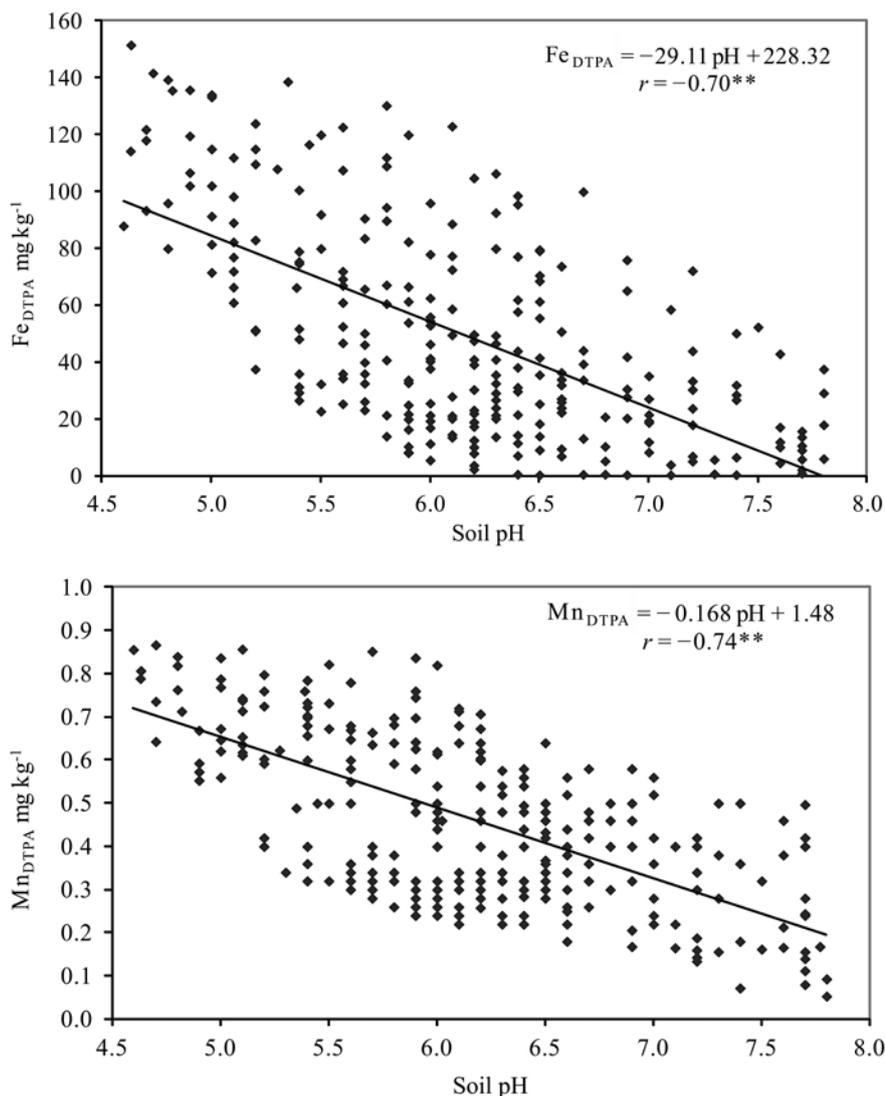


Figure 2. Changes in iron (Fe) and manganese (Mn) extractability as induced by soil pH

Table 5. Potential micronutrients availability expressed as Gibbs free energy changes (ΔG°) for six investigated arable fields

Field (No. of soil samples)	Crop plant	Cu	Zn	Fe	Mn
		ΔG° kJ mole ⁻¹			
1 (n = 102)	winter wheat	-6.28	-4.81	-9.73	-15.35
2 (n = 15)	winter triticale	-5.48	-5.08	-13.03	-16.06
3 (n = 60)	winter barley	-6.41	-4.64	-10.25	-15.62
4 (n = 69)	winter oilseed rape	-6.28	-5.43	-11.58	-13.89
5 (n = 33)	sugar beet	-6.22	-3.01	-12.14	-17.96
6 (n = 15)	grass mixtures	-7.24	-4.89	-10.44	-14.32
Mean for micronutrients		-6.32	-4.64	-11.19	-15.53
Standard deviation for means of micronutrients		0.56	0.84	1.27	1.44

revealed also additional site-specific (plant-specific) micronutrient availability. Thus the ΔG° -based values showed that Cu should be potentially more available for winter triticale but less for grass mixtures. In the case of Zn, its supply was higher (*ca* 2 times) from the sugar

beet site as compared to winter oilseed rape. Iron and manganese were found both to be slightly and hardly available; however, their shortage should be manifested typically for winter triticale and sugar beet, respectively. The slightly available range prevailed for Fe and Mn.

Conclusions

1. Investigated sites reflected sandy to loamy sand soils with wide ranges of soil characteristics varying from 4.7 to 7.8 for pH, 2.6 to 243.9 g kg⁻¹ C_{org} and cation exchange capacity (CEC) from 5.1 to 66.3 cmol₍₊₎ kg⁻¹. The latter ones are of prime importance in controlling the availability of micronutrients.

2. The total content of copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) varied significantly with a difference between the lowest and highest level characterised by a factor of *ca* 65, 34, 18, and 17 for Fe, Zn, Mn and Cu, respectively.

3. The DTPA-based availability factor (AF) followed the order Zn > Cu > Fe > Mn, with respective indices 22.9 > 19.8 > 5.5 > 0.42. Linear and polynomial relationships for pH vs DTPA_{Cu,Zn,Fe,Mn} revealed that in the case of increasing or decreasing pH, the reactions of Cu, Mn and Fe in the soil solution should be similarly, i.e. progressive unavailability or progressive availability, respectively.

4. Mean thermodynamic values (ΔG°) calculated for Cu, Zn, Fe and Mn amounted to -6.32, -4.64, -11.19 and -15.53 kJ mole⁻¹, respectively. This implies that Mn was the least available, contrarily to Zn characterised by a highest availability. The ΔG° -based values showed that micronutrients availability criteria should not be restricted to quantitative evaluation only.

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Vietovei būdingo Cu, Zn, Fe ir Mn pasisavinimo dirvožemyje vertinimas

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Santrauka

Eksperimentai buvo vykdyti 52 ha augalininkystės ūkyje, esančiame Vakarų Lenkijoje, Wielkopolska regione. Dirvožemio ėminiai (294) buvo paimti iš 0–30 cm sluoksnio šešiuose laukuose, nuėmus žieminius kvietrugius, žieminius kviečius, žieminius miežius, žolių mišinius, žieminius rapsus ir cukrinius runkelius. Tirtos šios savybės: dumblo bei molio ir organinės anglies (C_{org}) kiekis, $\text{pH}_{\text{CaCl}_2}$ ir katijonų mainų talpa (CEC). Bendrieji vario (Cu), cinko (Zn), geležies (Fe) ir mangano (Mn) kiekiai buvo nustatyti ekstrahuojant karališkuoju vandeniui (*aqua regia*), o aktyvios ir potencialiai pasisavinamos formos – dietilen-triamino pentaacto rūgštimi (DTPA). Potencialus pasisavinimas ir šių mikroelementų pokyčiai dirvožemyje vertinti atsižvelgiant į pasisavinimo veiksnį ir termodinaminį rodiklį (Gibso laisvosios energijos pokytį, ΔG°).

Tyrimų duomenys rodo, kad 83 % visų tirtų ėminių dirvožemyje C_{org} buvo mažiau nei 25 g kg^{-1} . Be to, buvo nustatyta labai didelė pH variacija ($4,7 < \text{pH}_{\text{CaCl}_2} > 7,8$): maždaug 16 % tirtų ėminių dirvožemis buvo rūgštus, o 82 % pH buvo didesnis nei 5,5. Vidutinė CEC vertė buvo 12,0 $\text{cmol}_{(+)}$ kg^{-1} , o 71 % dirvožemių CEC buvo mažesnė nei 12,0 $\text{cmol}_{(+)}$ kg^{-1} . 55 % dirvožemių buferingumas buvo vidutinis intervale: $12,0 \leq \text{CEC} \leq 25,0$ $\text{cmol}_{(+)}$ kg^{-1} . Taikant DTPA pasisavinimo geba pasiskirstė taip: $\text{Zn} > \text{Cu} > \text{Fe} > \text{Mn}$ (atitinkamai 22,9 > 19,8 > 5,5 > 0,42). Nustatyti tokie linijinės koreliacijos koeficientai (r): C_{org} vs DTPA_{Cu} , $r = 0,67^{**}$; C_{org} vs DTPA_{Zn} , $r = 0,60^{**}$; C_{org} vs DTPA_{Fe} , $r = 0,56^*$; C_{org} vs DTPA_{Mn} , $r = 0,50^*$.

Apskaičiavus Zn, Cu, Fe ir Mn termodinaminį pokytį (ΔG° vertes), nustatyti tokie intervalai: $-5,0 \leq \Delta G^\circ$ – lengvai pasisavinamas (Zn), $-5,0 \geq \Delta G^\circ \geq -10,0$ – vidutiniškai pasisavinamas (Cu), $-10,0 \geq \Delta G^\circ \geq -15,0$ – mažai pasisavinamas (Fe), $\Delta G^\circ \leq -15,0$ – beveik nepasisavinamas (Mn). ΔG° paremtos vertės parodė, kad mikroelementų pasisavinimo kriterijai neturėtų apsiriboti tik kiekybinio įvertinimu.

Reikšminiai žodžiai: dirvožemis, dietilen-triamino pentaacto rūgštis, Gibso rodikliai, mikroelementai, pasisavinimo veiksnys.