SOIL SCIENCE ANNUAL
2020, 71(3), 205–214

https://doi.org/10.37501/soilsa/126079

New limit values of micronutrient deficiency in soil determined using 1 M HCl extractant for wheat and rapeseed

Jolanta Korzeniowska[1]*, Ewa Stanisławska-Glubiak[1], Wojciech Lipiński[2]

[1] Institute of Soil Science and Plant Cultivation-National Research Institute in Pulawy, Department of Weed Science and Tillage Systems in Wroclaw, Orzechowa 61, 50-540 Wroclaw, Poland
[2] National Agrochemical Station in Warsaw, Zolkiewskiego 17, 05-075 Warszawa-Wesola, Poland

* prof. J. Korzeniowska, j.korzeniowska@iung.wroclaw.pl, ORCID iD: https://orcid.org/0000-0003-3701-9576

Received: 01.05.2020
Accepted: 05.08.2020
Associated editor: J. Antonkiewicz

Keywords

Microelements
Soil, shortage
Criteria of assessment
Extractant

Abstract

The aim of the study was to revise the limit values for the assessment of the microelement concentration in the soil determined with 1 M HCl. Unlike the values used so far to determine low, medium and high concentrations, the new values indicate only the low concentration limit below which fertilisation is necessary. Moreover, the new values are differentiated according to the plant species, which is related to the different sensitivity of the plants to microelement deficit. These values were prepared for wheat and rapeseed on the basis of a large data collection of 3865 pairs of soil-plant samples taken from production fields located in 16 voivodeships of Poland. The concentration of micronutrients was determined in all soil and plant samples. In addition, pH, texture, and the content of organic carbon and available phosphorus were determined in soil samples. Moreover, grain and seed yield after wheat and rapeseed harvest was estimated for all fields. Two independent calculation methods were applied in order to increase the reliability of the developed values. One of them was the method of regression equations, using the micronutrient bioaccumulation coefficient, its critical concentration in the plant and relevant soil features. The equations were constructed using the Stagraphics program. For each micronutrient, 8 models were tested in search for the equation with the highest determination coefficient r^2. To verify the values calculated in this way, the "high yield method" was used, which involved determining the smallest concentration of a micronutrient in the soil at which a high yield could be achieved.

1. Introduction

Soil micronutrient deficits can significantly reduce crop yields (Cakmak et al., 1996; Karamanos et al., 2003; Imtiaz et al., 2010). Therefore, insufficient amounts of micronutrients should be supplemented by fertilizing. The decision on fertilisation should always be preceded by an assessment of the microelement content in the soil. This assessment is carried out in two steps: determination of the amount of micronutrients in the soil, and then the comparison of this amount with the relevant limit values. Determination of the total concentration of microelement in the soil is not sufficient as plants can take up only the so-called available forms. To determine these forms, various extractants are used, which simulate the possibility of plant uptaking micronutrients from soil. (McLaughlin et al., 2000; Menzis et al., 2007; Korzeniowska and Stanisławska, 2013).

In Poland, since 1986, agro-chemical laboratories (OSChR) have used using the extraction method based on 1 M HCl with the appropriate limit values to assess the concentration of microelements in the soil (Gembarzewski and Korzeniowska, 1990; Fertilizer Recommendations, 1990; Gembarzewski and Korzeniowska, 1996). The 1 M HCl solution is also successfully used for microelements extraction in Estonia (Loide et al., 2005) and Latvia (Cekstere and Osvalde, 2013). In recent years, the Institute of Soil Science and Plant Cultivation in Pulawy, Poland has conducted research on the replacement of 1 M HCl with Mehlich 3 solution, which also enables the extraction of P, K and Mg from the soil (Mehlich, 1994; Kęsik et al., 2015). Simultaneous extraction of macro and microelements would result in a significant reduction of analysis costs. The lower price of soil analyses enables farmers to perform them more often, which results in proper selection of fertilizer rates. However, the study did not show definitely better effect of Mehlich 3 solution than 1 M HCl. In general, both extractants gave similar results, with a slight advantage for 1 M HCl (Kantek and Korzeniowska, 2013; Korzeniowska and Stanislawska-Glubiak, 2015). The high correlation between the two extractants was also confirmed by Gediga et al. (2015) and Korzeniowska et al. (2016). This required development of limit values for Mehlich 3 extractant for Polish conditions (Korzeniowska et al., 2019; Stanislawska-Glubiak et al., 2019) and updating the "old values" for 1 M HCl that were used for 30 years in OSChR laboratories.

The best method of developing soil micronutrient deficit criteria would be to conduct strict field experiments to assess the response of plants to micronutrient fertilisation. In such case, it would be necessary to set up at least several dozen experiments across Poland under different soil and climatic conditions that modify the availability of microelements for plants. For organisational and financial reasons, such a method is difficult to implement. Therefore, a method based on a large collection of soil and plant samples taken from production fields representing the whole area of Poland, was adopted.

It was decided that the new limit values for 1 M HCl should take into account the different sensitivity of plants to microelements deficit. The old values are differentiated only according to selected soil features and do not take into account different plant needs. Moreover, it was decided to develop single-level values, as opposed to three-level old values, which defined low, medium and high concentrations. The new values define only low microelement concentration in the soil, below which fertilization of plants is recommended.

2. Materials and methods

The new limit values were developed on the basis of the large sample collections of soil and plants that were growing on this soil. Two collections were made: 1921 pairs of soil-plant samples taken in 2016 from wheat fields (Collection 1991) and 1944 pairs of samples taken in 2017 year from rapeseed fields (Collection 1994). All the samples were collected by accredited OSChR samplers from 16 Polish voivodeships, usually one soil-plant pair from each "gmina", the smallest administration unit (Tab. 1).

Samples from wheat fields were taken from 1 m^2 and rapeseed from 4 m^2. Each soil sample was created by mixing 5 samples taken with a soil sampler to the depth of 20 cm. At the same time as the soil samples, the corresponding plant samples were taken: whole wheat shoots were cut 2 cm above the ground at the beginning of the stem formation (BBCH 30/31), and rapeseed 5 cm above the ground in the period from the beginning of the main stem elongation to the appearance of the first internode (BBCH 30/31). Each sample of wheat consisted of a minimum of 80 and rapeseed of 20 shoots. After the harvest, farmers reported wheat and rapeseed yields for each field from which soil and plant samples were taken. In the case of wheat, the yield was obtained only for 1760 fields.

B, Cu, Fe, Mn and Zn concentration were determined in all soil samples. Microelements from the soil were extracted with 1 M HCl solution and then determined using ICP technique. During extraction, the ratio of soil to solution was 1 : 10, and shaking time on the rotary stirrer was 60 min at 40 rpm. Moreover, pH, organic carbon concentration (Corg), phosphorus concentration by Mehlich 3 (PM3), and texture were determined in soil samples. Microelements were also determined in plant samples. All chemical analyses were performed in accredited agro-chemical laboratories. Detailed methodology of analyses is given by Korzeniowska et al. (2019) and Stanisławska-Glubiak et al. (2019).

Table 1
Number of soil-plant samples taken in 16 voivodeships

Lp.	Voivodeship	Area in km^2	Wheat	Rapeseed
1	Opolskie	9 412	92	94
2	Świętokrzyskie	11 711	63	72
3	Śląskie	12 333	94	100
4	Lubuskie	13 988	93	89
5	Małopolskie	15 183	129	113
6	Podkarpackie	17 846	110	119
7	Kujawsko-pomorskie	17 972	118	90
8	Łódzkie	18 219	137	154
9	Pomorskie	18 310	124	139
10	Dolnośląskie	19 947	115	109
11	Podlaskie	20 187	67	70
12	Zachodniopomorskie	22 892	135	129
13	Warmińsko-mazurskie	24 173	140	195
14	Lubelskie	25 122	133	127
15	Wielkopolskie	29 826	182	186
16	Mazowieckie	35 558	189	158
	Sum		1921	1944

3. Results

3.1. Characteristic of soil and plant samples

Soil samples collected from wheat and rapeseed fields were very similar in terms of pH, texture, and Corg concentration. However, rapeseed was cultivated on, more acidic soils with a lower content of organic matter, but richer in phosphorus (Tab. 2). Soils from rapeseed fields also contained less microelements except for boron, which was slightly higher than on wheat fields (Tab. 3).

The content of microelements in wheat and rapeseed plants was arranged in a similar order, with the exception of boron. Both plants had the highest concentration of Fe, followed by Mn and Zn. Subsequently, wheat contained similar amounts of Cu and B, while in rapeseed the B concentration was up to 6 times higher than Cu concentration (Tab. 4). This suggests that rapeseed needs much more boron compared to wheat.

3.2. Yield description

The average yield of wheat grains was 5.6 t ha^{-1} and ranged from 1.0 to 10.6 t ha^{-1}, while of rapeseed 3.6 t ha^{-1} with fluctuations from 1.2 to 6.0 t ha^{-1}. In the case of wheat, the most frequent yields were in the range of 5.0 to 6.9 t ha^{-1} and involved 45% of fields (Tab. 5). The yields ≥ 7.0 t ha^{-1} were obtained for 33% of fields. In the case of rapeseed, the most frequent yields were in the range 3.0–4.9 t ha^{-1} (83% of fields). Yields above 4.9 t ha^{-1} were very rare, occurring only in 2% of the fields.

Table 2
Characteristic of soil samples

Soil feature	Wheat (n=1921)			Rapeseed (n=1944)		
	mean	SE	range	mean	SE	range
pH in KCl	6.2	0.21	3.7–8.2	6.1	0.02	3.8–8.2
Sand 2.00–0.05 mm, %	53.1	0.52	1.0–92.3	58.0	0.47	3.0–94.9
Silt 0.05–0.002 mm, %	43.2	0.49	7.6–99.8	38.4	0.43	5.1–89.0
Clay < 0.002 mm, %	3.7	0.05	0.1–46.5	3.6	0.05	0.0–14.5
Fraction < 0.02 mm, %	24.7	0.27	3.9–70.4	23.7	0.27	2.6–72.0
Corg %	1.3	0.01	0.05–9.80	1.25	0.01	0.29–4.78
PM3 mg 100 g^{-1}	172	0.26	12–1150	175	0.29	4–1290

Explanation: SE – standard error

Table 3
The concentration of microelements in soil samples determined by the 1 M HCl method in mg kg^{-1}

Micronutrient	Wheat (n=1921)			Rapeseed (n=1944)		
	mean	SE	range	mean	SE	range
B	1.25	0.02	0.04–6.78	1.35	0.03	0.02–8.66
Cu	4.19	0.06	0.30–22.5	3.90	0.06	0.5–21.7
Fe	1462	23.56	217–11039	1272	20.12	182–7966
Mn	179.8	1.99	11.9–648.8	173.7	1.91	13.0–677.5
Zn	12.8	0.24	1.2–132.9	11.8	0.21	0.8–74.0

Explanation: SE – standard error

Table 4
The concentration of microelements in plant samples in mg kg^{-1} d.m.

Micronutrient	Wheat (n=1921)			Rapeseed (n=1944)		
	mean	SE	range	mean	SE	range
B	4.22	0.07	0.12–24.50	39.5	0.50	7.6–172.0
Cu	5.29	0.07	0.60–33.20	6.30	0.06	1.89–34.40
Fe	121.8	2.01	12.5–699.0	169.7	2.48	22.5–987.9
Mn	42.6	0.61	3.75–171.0	57.9	0.79	10.7–292.0
Zn	27.1	0.27	3.0–117.0	54.0	0.35	7.8–173.0

Explanation: SE – standard error

Table 5
Frequency of yield distribution

Wheat grain			Rapeseed seeds		
Yield t ha^{-1}	Number of fields	Contribution of fields %	Yield t ha^{-1}	Number of fields	Contribution of fields %
≤ 3.9	126	7	≤ 1.9	24	1
4.0–4.9	255	14	2.0–2.9	264	14
5.0–5.9	374	21	3.0–3.9	901	46
6.0–6.9	427	24	4.0–4.9	714	37
7.0–7.9	308	17	5.0–5.9	40	2
8.0–8.9	205	12	≥6.0	1	0
≥ 9.0	65	4	Sum	1944	100
Sum	1760	100			

3.3. Relationship between limit values and soil features

The availability of micronutrients for plants depends on various soil factors, which should be taken into account when constructing the limit values. Most often, the literature reports a large influence of pH, soil texture and organic carbon concentration on the uptake of micronutrients by plants (Kabata-Pendias and Mukherjee, 2007). The uptake is also affected by other factors such as redox potential, nutrient interactions, and air-water conditions. However, limit values can only be linked to soil features that can be easily determined. Therefore, among many factors affecting the availability of microelements to plants, pH, soil texture, organic carbon concentration (Corg) and phosphorus concentrations (P_{M3}), which can interact with certain microelements, were included in the study.

The bioaccumulation factor (Mi_P/Mi_S) was used to determine which of the soil features has the greatest impact on the uptake of a given micronutrient, and should be included in the limit values. Mi_P/Mi_S is the quotient of the plant micronutrient (Mi_P) and the soil micronutrient (Mi_S), which shows the phytoavailability of this micronutrient. Calculation of the correlation between Mi_P/Mi_S and various soil features for microelements showed which of the features had the greatest impact on their availability for plants (Tab. 6, 7). Generally, an increase in pH, soil density and Corg content resulted in a decrease in the availability of microelements for plants, while the phosphorus con-

Table 6
Pearson correlation coefficient for bioaccumulation factor (Mi_P/Mi_S) and soil features for wheat (n=1921)

Mi_P/Mi_S[1]	pH	Silt 0,05–0,002 mm	Fraction < 0,02 mm	Clay < 0,002 mm	Corg	P_{M3}
B_P/B_S	–0,19***	0,09***	–0,20***	–0,17***	–0,16***	ns
Cu_P/Cu_S	–0,19***	–0,19***	–0,20***	–0,16***	–0,20***	ns
Fe_P/Fe_S	0.053*	–0.10***	–0.06**	–0.05*	–0.16***	–0.05*
Mn_P/Mn_S	–0.38***	–0.15***	–0.16***	–0.13***	–0.18***	–0.06*
Zn_P/Zn_S	–0.31***	–0.18***	–0.18***	–0.13***	–0.21***	–0.12***

Explanation: [1] Soil concentration in 1 M HCl; *, **, *** – significant level p < 0.05; 0.01; 0.001 respectively; ns – non-significant

Table 7
Pearson correlation coefficient for bioaccumulation factor (Mi_P/Mi_S) and soil features for rapeseed (n=1944)

Mi_P/Mi_S[1]	pH	Silt 0,05–0,002 mm	Fraction < 0,02 mm	Clay < 0,002 mm	Corg	P_{M3}
B_P/B_S	–0,14***	–0.15***	–0.17***	–0.14***	–0.16***	ni
Cu_P/Cu_S	–0.17***	–0.26***	–0.28***	–0.25***	–0.26***	ni
Fe_P/Fe_S	0.05*	–0.24***	–0.25***	–0.22***	–0.16***	ni
Mn_P/Mn_S	–0.31***	–0.33***	–0.33***	–0.30***	–0.19***	0,04*
Zn_P/Zn_S	–0.23***	–0.17***	–0.17***	–0.16***	–0.20***	–0,14***

Explanation: [1] Soil concentration in 1 M HCl; *, **, *** – significant level p < 0.05; 0.01; 0.001 respectively; ns – non-significant centration in the soil was less important (Tab. 6, 7). Differences in the impact of soil features on the availability of microelements for wheat and rapeseed were observed. In general, higher correlation coefficients were obtained for rapeseed than for wheat, which suggests a greater effect of pH, texture and Corg on microelement uptake by rapeseed than by wheat.

To sum up, in the case of wheat, the biggest negative impact on the availability of B exerted a < 0.02 mm fraction; on the availability of Cu – a < 0.02 mm fraction and Corg; on the availability of Fe – Corg; and on the availability of Mn and Zn – pH. In the case of rapeseed, the biggest negative impact on the availability of B, Cu and Fe had a < 0.02 mm fraction, on the availability of Mn – silt and a < 0.02 mm fraction, and on the availability of Zn – pH.

3.4. Calculation of limit values using regression equations

Limit values were calculated on the basis of regression equations describing the relationship between the Mi_p/Mi_S bioaccumulation factor (dependent variable) and specific soil features (independent variable). The regression equations were constructed using the Statgraphics program. For each micronutrient, 8 equation models were tested in search of the equation with the highest coefficient of determination r^2, such as linear, exponential, reciprocal, logarithmic, multiplicative and square-root. For example, the equations describing the relationship between Mn_p /Mn_S and pH for wheat were presented (Tab. 8).

Limit values were calculated on the basis of the selected equation with the highest r^2 coefficient. For Mn and wheat, it was equation number 8 (Tab. 8). After appropriate transformation of this equation and putting the critical Mn concentration in the plant as P_{Mn} (Tab. 9), the concentration of Mn in the soil was calculated (Mn_S). The detailed methods of calculation of the values and critical concentrations in the plant, were described in Korzeniowska et al. (2019) and Stanisławska-Glubiak et al. (2019).

Soil features, which were included in the equations as independent variables for each microelements, were selected on the basis of correlation coefficients describing the relationship between these features and the Mi_p/Mi_S bioaccumulation factor (Tab. 6, 7). For wheat, equations for B were constructed with fraction <0.02 mm; for Cu with fraction < 0.02 mm or Corg; for Fe with Corg; and for Mn and Zn with pH. The same procedure was applied in the case of rapeseed, but for Cu, apart from the < 0.02 mm fraction, Corg was also tested, while for Mn, apart from the < 0.02 mm fraction and silt, pH was also tested. This was due to the well-known strong impact of Corg on Cu uptake and of pH on Mn uptake (Kabata-Pendias and Mukherjee, 2007).

Table 8
Regression equations describing the relation of manganese bioaccumulation coefficient (Mn_p/Mn_S) and pH for wheat (n=1921)

No	Model	Equation	r^2 %
1	Linear	Mn_p/Mn_S = 1.01 – 0.12*pH	14.7***
2	Exponential	Mn_p/Mn_S = exp(0.50 – 0.33*pH)	17.4***
3	Reciprocal-Y	Mn_p/Mn_S = 1/(–3.79 + 1.57*pH)	9.4***
4	Reciprocal-X	Mn_p/Mn_S = –0.40 + 4.16/pH	16.9***
5	Logarithmic	Mn_p/Mn_S = 1.58 – 0.71*ln(pH)	15.9***
6	Multiplicative	Mn_p/Mn_S = exp(2.02 – 1.96*ln(pH))	18.3***
7	Square root-X	Mn_p/Mn_S = 1.72 – 0.58*sqrt(pH)	15.3***
8	Square root-Y	Mn_p/Mn_S = (1.06 – 0.09*pH)^2	**18.4*** **

Explanation: r^2 – determination coefficient; *** – significant level p < 0,001

Table 9
Critical concentration in plant acc. Korzeniowska i Stanislawska-Glubiak in mg kg^{-1}

Element	Wheat	Rapeseed
B	2.7	25
Cu	4.0	4.8
Fe	80	105
Mn	25	37
Zn	20	43

Explanation: the whole plant in BBCH 30/31 phase

Table 10
Selected regression equations for calculating threshold values

Element	Model	Equation	r^2 %
Wheat (n=1921)			
B	Exponential	B_p/B_S = exp(1.83 – 0.02*cz spl)	8.4***
Cu	Multiplicative	Cu_p/Cu_S = exp(0.37 – 0.47*ln(Corg))	8.6***
Fe	Logarithmic	Fe_p/Fe_S = 0.12 – 0.04*ln(Corg)	3,0***
Mn	Square root-Y	Mn_p/Mn_S = (1.06 – 0.09*pH)^2	18.4***
Zn	Square root-Y	Zn_p/Zn_S = (2.96 – 0.21*pH)^2	11,4***
Rapeseed (n=1944)			
B	Exponential	B_p/B_S = exp(4.14 – 0.02*cz spl)	8,3***
Cu	Reciprocal-Y	Cu_p/Cu_S = 1/(0.23 + 0.34*Corg)	17.4***
Fe	Square root-Y	Fe_p/Fe_S = (0.50 – 0.005*cz spl)^2	11.4***
Mn	Reciprocal-X	Mn_p/Mn_S = –0.47 + 5.29/pH	11.6***
Zn	Multiplicative	Zn_p/Zn_S = 43.89*pH^ – 1.16	6.7***

Explanation: r^2 – determination coefficient; *** – significant level p < 0,001

The selected equations with the highest coefficients of determination, on the basis of which limit values were calculated, are presented in Table 10. Unfortunately, despite high significance (p < 0.001), the coefficients of determination of the equations (r^2) were at a very low level. This undermined the reliability of the calculated values, and required verification.

3.5. Calculation of limit values using the high yield method

The method called "high yield method" was used to verify the limit values calculated by the regression equations. The basis of this method was the assumption that the searched limit value will be the lowest concentration of micronutrient in the soil at which high yields can be achieved. At first, a group of observations with high yields was separated from Collection 1921 (wheat) and Collection 1944 (rapeseed). High yields for wheat were set at ≥ 7.0 t ha^{-1}, and for rapeseed ≥ 4.0 t ha^{-1}. The separated groups consisted of 578 observations for wheat and 755 for rapeseed. Subsequently, first quintiles (QU1) of individual microelement concentration in soil were calculated for the separated groups. QU1 were taken as limit values. Details of the "high yield method" was described by Korzeniowska et al. (2019) and Stanisławska-Glubiak et al. (2019).

3.6. Final revision of limit values

The comparison of the values calculated by the regression equation method and the high yield method showed their very high similarity, which confirmed the reliability of the first method. When the values calculated by both methods overlapped or were very close to each other, the final values were determined by their averaging. When the differences between the limit values for both methods were bigger, the final correction was made on the basis of the assessment of microelement deficits in large collections of soil samples using both variants of the values. While establishing the final level of limit values, the difference between values for wheat and rapeseed was also considered. The different sensitivity of both species to microelements (e.g. B) should be reflected in the value level. The values calculated by both methods were also compared with those previously developed for Mehlich 3 extractant (Korzeniowska

Table 11
New limits values for low concentration of micronutrients in soil determined by 1 M HCl method for wheat in mg kg^{-1}

Element	Soil feature	Low concentration mg kg^{-1}
B	Fraction < 0.02 mm (%)	
	≤ 20	< 0.40
	21–35	< 0.70
	≥ 36	< 0.90
Cu	Corg (%)	
	≤ 1.0	< 2.2
	1.1–1.5	< 3.0
	1.6–2.0	< 3.4
	≥ 2.1	< 4.2
Fe	Corg (%)	
	≤ 1.0	< 700
	1.1–1.5	< 800
	1.6–2.0	< 900
	≥ 2.1	< 1000
Mn	pH	
	≤ 5.5	< 60
	5.6–6.5	< 100
	6.6–7.2	< 130
	≥ 7.3	< 150
Zn	pH	
	≤ 5.5	< 4.5
	5.6–6.5	< 6.0
	6.–7.2	< 7.5
	≥ 7.3	< 8.5

Explanation: Corg – organic carbon

Table 12
New limits values for low concentration of micronutrients in soil determined by 1 M HCl method for rapeseed in mg kg^{-1}

Element	Soil feature	Low concentration mg kg^{-1}
B	Fraction < 0.02 mm (%)	
	≤ 20	< 0.60
	21–35	< 1.00
	≥ 36	< 1.50
Cu	Corg (%)	
	≤ 1.0	< 1.8
	1.1–1.5	< 2.5
	1.6–2.0	< 3.0
	≥ 2.1	< 4.0
Fe	Fraction < 0.02 mm (%)	
	≤ 20	< 550
	21–35	< 750
	≥ 36	< 1200
Mn	pH	
	≤ 5.5	< 50
	5.6–6.5	< 90
	6.6–7.2	< 120
	≥ 7.3	< 140
Zn	pH	
	≤ 5.5	< 4.0
	5.6–6.5	< 5.5
	6.6–7.2	< 7.0
	≥ 7.3	< 8.0

Explanation: Corg – organic carbon

et al., 2019; Stanisławska-Glubiak et al., 2019). It was checked whether the evaluation made using limit values for 1 M HCl and Mehlich 3 given similar results. The final new limit values for 1 M HCl for wheat and rapeseed are presented in Tables 11 and 12.

4. Discussion

The limit values used so far in agrochemical laboratories to assess the concentration of microelements in the soil for 1 M HCl are three-level and define low, medium and high concentration (Fertiliser Recommendations, 1990). These values depend on one soil feature, with the exception of Mn and Mo for which 2 soil features are included. In order to show the complexity of these values, the values for Mn are given as an example (Tab. 13).

Comparing the limit values used so far (old) with those currently developed (new), it can be seen that soil features to which they are linked, are not the same (Table 14).

For B, the new values depend on fraction < 0.02 mm, while the old ones on pH. Both soil pH and soil texture are mentioned in the literature as the features affecting the availability of this element (Kabata-Pendias and Pendias, 1999; Zerrari et al., 1999). Also, the soil organic matter concentration modifies the availability of B for plants (Krishnasamyl et al., 1997). In our study, the correlation coefficients between the phytoavailability of B and the soil features mentioned above were at a similar level, but the highest was found for the fraction < 0.02 mm, which had a negative effect on the availability of this element (Tab. 6, 7). Under the soil-climatic conditions of Poland, B deficit may occur mainly in sandy acid soils with a low concentration of organic matter, due to the possibility of B leaching deep into the soil profile. On the other hand, in soils with high adsorption and retention capacity (e.g. soils with high pH, rich in clay minerals and iron or aluminium oxides), the total B concentration is higher than in sandy soils, but at the same time it may be poorly available to plants.

According to the old limit values (Fertilizer Recommendations, 1990), the low B concentration ranged from 0.8 to 2.2 mg kg^{-1} and, according to the new values, from 0.4 to 1.5 mg kg^{-1} (Tab. 14). Moreover, the new values take into account the species sensitivity to B deficit. Rapeseed is much more sensitive in demand for B than wheat (Katyal and Randhawa, 1983). The low B concentration in the soil for wheat was determined at 0.4–0.9 mg kg^{-1}, while for the more demanding rapeseed at 0.6–1.5 mg kg^{-1} level.

Table 13
Old limit values for concentration of Mn in soil determined by 1 M HCl method in mg kg^{-1}

Assessment of content	pH in 1 M KCl															
	do 4.5				4.6–5.0				5.1–5.5				od 5.6			
	Fraction < 0.02 mm															
	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
Low	< 9	< 13	< 16	< 18	< 12	< 21	< 28	< 40	< 15	< 30	< 50	< 75	< 17	< 40	< 85	< 110
Medium	9–90	13–130	16–160	18–180	12–125	21–210	28–280	40–390	15–150	30–310	50–510	75–750	17–170	40–400	85–830	110–1100
High	> 90	> 130	> 160	> 180	> 125	> 210	> 280	> 390	> 150	> 310	> 510	> 750	> 170	> 400	> 830	> 1100

Explanation: I ≤10, II 11–20, III 21–35, IV ≥ 36

Table 14
Comparison of old and new limit values for 1 M HCl

Element	Old values		New values	
	range (mg kg^{-1})	soil feature	range (mg kg^{-1})	soil feature
B	0.8–2.2	pH	wheat 0.4– 0.9 rapeseed 0.6–1.5	fraction < 0.02 mm fraction < 0.02 mm
Cu	0.9–5.0	fraction < 0.02 mm	wheat 2.2 – 4.2 rapeseed 1.8–4.0	Corg Corg
Fe	700	all mineral soil	wheat 700–1000 rapeseed 550–1200	Corg fraction < 0.02 mm
Mn	9–110	pH + fraction < 0.02 mm	wheat 60–150 rapeseed 50–140	pH pH
Mo	0.18–0.02	P_2O_5 + pH	–	–
Zn	0.7–11.5	fraction <0.02 mm	wheat 4.5–8.5 rapeseed 4.0–8.0	pH pH

The old limit values for Cu are dependent on soil fraction < 0.02 mm, while the new values include Corg. The phytoavailability of copper in our study was equally dependent on both these features (Tables 6, 7). Corg was selected because of many literature reports on high impact of organic matter on Cu mobility in soil (Inaba and Takenaka, 2005; Wang et al., 2009; Wu et al., 2010; Bravin et al., 2012; Antonkiewicz et al., 2019). The low Cu concentration in the soil, according to the old limit values was in the range of 0.9–5.0 mg kg^{-1}. The new values cover the range of 1.8–4.2 mg kg^{-1}, while for wheat they are more restrictive than for rapeseed (2.2–4.2 mg kg^{-1}). This is due to the higher sensitivity of wheat species to Cu deficit compared to rapeseed (Katyal and Randhawa, 1983).

There are big differences between the old and new limit values for Fe. According to the old values, the low concentration limit for all soils, regardless of their physicochemical properties, is 700 mg kg^{-1}. The new values depend on the Corg for wheat and on the soil fraction < 0.02 mm for rapeseed, and generally range from 550–1200 mg kg^{-1}.

Manganese concentration was estimated with old values in connection with soil pH and soil fraction < 0.02 mm. The low concentration of this element ranged from 9–110 mg kg^{-1} (Tab. 13, 14). The new values are only pH-dependent, with the low Mn concentration being set at a similar level for both plant species and range between 50–150 mg kg^{-1}. The range of low Mn concentration in the soil according to the new values is generally higher than according to the old ones, especially its lower value (50 mg kg^{-1} against 9 mg kg^{-1}). This may be due to the fact that the phytoavailability of Mn decreases with the increase of soil pH, and the new values were determined on the basis of a collection of samples taken from fields whose average pH was 6.2.

The evaluation of the Zn concentration with the old values was dependent on soil fraction < 0.02 mm, while the new values include soil pH. For this microelement there is a fairly large difference between old and new values. According to the old values, the low concentration is in the range of 0.7–11.5 mg kg^{-1}, while according to the new ones, it is in the range of 4.0–8.5 mg kg^{-1}, with a very similar range for both wheat and rapeseed. The lower values of this ranges differ considerably between the old and new values.

Using the new limit values, the percentage of soils showing micronutrient deficiencies was assessed compared to the assessment carried out with the old values. The amount of soils with a microelement shortage for wheat and rapeseed was estimated in a combined collection of 3865 soil samples (1921+1944), which can be considered to represent the soil conditions of Poland (Table 15).

The biggest difference between the old and new values was found in the B deficiency assessment. According to the evaluation carried out with the old values, the deficit of this element was as high as 66% of soils. Using the new values, 21% of deficient soils were found for wheat and 39% for rapeseed. Taking into account the high sensitivity of rapeseed and small wheat to B deficit, it seems that the assessment carried out with the new values is credible. For Cu, a low soil content according to the old values was found in 20% of the soils, while the deficits estimated according to the new criteria were varied depending on the plant species. For wheat, 33% of soils showed low Cu deficit and for rapeseed only 22%, which is justified by the greater sensitivity of wheat than rapeseed. The percentage of soils with low Fe concentration estimated by both methods is similar. According to the old values, this percentage was 17%, while according to the new ones, the average for both plant species was 18%. A relatively large difference can be seen in the assessment of Mn. On the basis of old limit values, only 1% of soils showed low Mn concentration, while according to the new values as much as 17% of soils showed too low Mn concentration for wheat and 13% of soils for rapeseed. It seems that in the collection of soils with an average pH 6.2, the assessment with the new values is more reliable. Zinc deficit determined in 12% of soils with old values increased after their estimation with the new values to 21% for wheat, and to 17% for rapeseed.

5. Summary

The idea of the new limit values for method with 1 M HCl was to simplify the interpretation of the results of soil analysis for farmers as much as possible. Therefore, in contrast of the old three-level values, only one value was established to determine the low concentration limit below which microelement fertilisation is necessary. In addition, only one soil feature, specific to a given micronutrient, was selected, according to which the threshold values was differentiated.

In general, the new values for the assessment of soil microelement deficit fit into the strategy of precision farming. The recommendations for fertilization with micronutrients based on the old limit values did not depend on the cultivated plant species. In many cases, especially for plants with low micronutri-

Table 15
Assessment of soil micronutrients deficiency in the collection of 3865 soil samples according to old and new limit values for 1 M HCl

Kind of limit values	B	Cu	Fe	Mn	Zn
	Samples with deficiency (%)				
Old values	66	20	17	1	12
New values for wheat	21	33	21	17	21
New values for rapeseed	39	22	15	13	17

ents needs, this fertilization may not be necessary and generated additional costs. A diagnosis based on the new values, adapted to the crop species, is much more precise and eliminates such problems.

References

Antonkiewicz, J., Kołodziej, B., Bielińska, E.J., Gleń-Karolczyk, K., 2019. Research on the uptake and use of trace elements from municipal sewage sludge by multiflora rose and Virginia fanpetals. Journal of Elementology 24, 3, 987–1005. https://doi.org/10.5601/jelem.2018.23.4.1757

Bravin, M.N., Garnier, C., Lenoble, V., Gérard, F., Dudal, Y., Hinsinger, P., 2012. Root-induced changes in pH and dissolved organic matter binding capacity affect copper dynamic speciation in the rhizosphere. Geochimica et Cosmochimica Acta 84, 256–268. https://doi.org/10.1016/j.gca.2012.01.031

Cekstere, G., Osvalde, A., 2013. A study of chemical characteristics of soil in relation to street trees status in Riga (Latvia). Urban Forestry and Urban Greening 12(1), 69–78. https://doi.org/10.1016/j.ufug.2012.09.004

Cakmak, I., Yilmaz, A., Kalayci, M., Ekiz, H., Torun, B., Erenoglu, B., Braun, H.J., 1996. Zinc deficiency as a critical problem in wheat production in Central Anatolia. Plant and Soil 180, 165–172.

Fertilizer recommendations. Part I. Limit values for macro and microelements assessment in the soils/Zalecenia nawozowe. Cz. I. Liczby graniczne do wyceny w glebach makro- i mikroelementów. IUNG Puławy 1990.

Gediga, K., Spiak, Z., Piszcz, U., Bielecki, K., 2015. Suitability of different soil extractants for determination of available Cu and Mn contents in Polish soils. Communications in Soil Science and Plant Analysis 46, 81–93. https://doi.org/10.1080/00103624.2014.988579

Gembarzewski, H., Korzeniowska, J., 1990. Simultaneous extraction of B, Cu, Fe, Mn, Mo and Zn from mineral soils, and an estimation of the results. Agribiological Research-Zeitschrift fur Agrarbiologie Agrikulturchemie Okologie 43(2), 115–127.

Gembarzewski, H., Korzeniowska, J., 1996. Selection of method of micronutrients extraction from soil and elaboration of threshold values by use of multiple regression equations/Wybór metody ekstrakcji mikroelementów z gleby i opracowanie liczb granicznych przy użyciu regresji wielokrotnej. Zeszyty Problemowe Postępów Nauk Rolniczych 434, 353–364.

Imtiaz, M., Rashid, A., Khan, P., Memon, M.Y., Aslam, M., 2010. The role of micronutrients in crop production and human health. Pakistan Journal of Botany 42(4), 2565–78.

Inaba, S., Takenaka, C., 2005. Effects of dissolved organic matter on toxicity and bioavailability of copper for lettuce sprouts. Environment International 31(4), 603–608. https://doi.org/10.1016/j.envint.2004.10.017

Kabata-Pendias, A., Mukherjee, A.B., 2007. Trace elements from soil to human. Springer Science & Business Media.

Kabata-Pendias, A., Pendias, H., 1999. Biogeochemistry of trace elements/Biogeochemia pierwiastków śladowych. PWN Warszawa.

Kantek, K., Korzeniowska, J., 2013. The usefulness of Mehlich 3 and 1 M HCl extractant to assess copper deficiency in soil for environmental monitoring purpose/Przydatność ekstrahentów Mehlich 3 i 1 M HCl do oceny niedoborów miedzi w glebie pod kątem monitoringu środowiska. Ochrona Środowiska i Zasobów Naturalnych 24(3), 1–5. https://doi.org/10.2478/oszn-2013-0024

14. Karamanos, R.E., Goh, T.B., Harapiak, J.T., 2003. Determining wheat response to copper in prairie soils. Canadian Journal of Soil Science 83(2), 213–221.

Katyal, J.C., Randhawa, N.S., 1983. Micronutrient. FAO Fertilizer and Plant Nutrition Bulletin.

Kęsik, K., Jadczyszyn, T., Lipiński, W., Jurga, B., 2015. Adaptation of the Mehlich 3 procedure for routine determination of phosphorus, potassium and magnesium in soil/Adaptacja testu Mehlicha 3 do rutynowych oznaczeń zawartości fosforu, potasu i magnezu w glebie. Przemysł Chemiczny 94(6), 973–976. https://doi.org/10.15199/62.2015.6.22

Korzeniowska, J., Stanislawska-Glubiak, E., 2013. A comparison of the suitability of several methods to estimate the bioavailability of elements in soils to plants. Fresenius Environmental Bulletin 22(4), 943–948.

Korzeniowska, J., Stanisławska-Glubiak, E., 2015. Comparison of 1 M HCl and Mehlich 3 for assessment of the micronutrient status of polish soils in the context of winter wheat nutritional demands. Communications in Soil Science and Plant Analysis 46(10), 1263–1277. https://doi.org/10.1080/00103624.2015.1033537

Korzeniowska, J., Stanisławska-Glubiak, E., Lipiński, W., 2016. Comparison of the extraction results of micronutrients from the soil by the 1 M HCl and Mehlich 3/ Porównanie wyników ekstrakcji mikroelementów z gleby roztworem 1 M HCl i Mehlich 3. Zeszyty Naukowe Uniwersytetu Przyrodniczego we Wrocławiu: Rolnictwo 619, 59–68.

Korzeniowska, J., Stanisławska-Glubiak, E., Lipiński, W., 2019. Development of the limit values of micronutrient deficiency in soil determined using Mehlich 3 extractant for Polish soil conditions. Part I. Wheat /Opracowanie liczb granicznych niedoboru mikroelementów w glebie oznaczanych przy użyciu ekstrahenta Mehlich 3 dla polskich warunków glebowych. Część I. Pszenica. Soil Science Annual 70(4), 314–323. https://doi.org/10.2478/ssa-2019-0028

Krishnasamyl, R., Jaisankarl, J., Suresh, M., 1997. Characterization of boron adsorption in soils of Tamil Nadu (S. India). [In]: Bell, R.W., Rerkasem, B (Eds.). Boron in Soils and Plants, 255–259.

Loide, V., Nõges, M., Rebane, J., 2005. Assessment of the agrochemical properties of the soil using the extraction solution Mehlich 3 in Estonia. Agronomy Research 3(1), 73–80.

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., Cook N., 2000. Soil testing for heavy metals. Communications in Soil Science and Plant Analysis 3, 11661–1700. https://doi.org/10.1080/0010362000937053124.
Mehlich, A., 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Communications in Soil Science and Plant Analysis 15(12), 1409–1416.

Menzies, N.W., Donn, M.J., Kopittke, P.M., 2007. Evaluation of extractants for estimation of the phytoavailable trace metals in soils. Environmental Pollution 145(1), 121–130. https://doi.org/10.1016/j.envpol.2006.03.021

Stanisławska-Glubiak, E., Korzeniowska, J., Lipiński, W., 2019. Development of the limit values of micronutrient deficiency in soil determined using Mehlich 3 extractant for Polish soil conditions. Part II. Rapeseed /Opracowanie liczb granicznych niedoboru mikroelementów w glebie oznaczanych przy użyciu ekstrahenta Mehlich 3 dla polskich warunków glebowych. Część II. Rzepak. Soil Science Annual 70(4), 324–330. https://doi.org/10.2478/ssa-2019-0029

Wang, X., Chen, X., Liu, S., Ge, X., 2010. Effect of molecular weight of dissolved organic matter on toxicity and bioavailability of copper to lettuce. Journal of Environmental Sciences 22(12), 1960–1965. https://doi.org/10.1016/S1001-0742(09)60346-6

Wu, C., Luo, Y., Zhang, L., 2010. Variability of copper availability in paddy fields in relation to selected soil properties in southeast China. Geoderma 156(3–4), 200–206. https://doi.org/10.1016/j.geoderma.2010.02.018

Zerrari, N., Moustaoui, D., Verloo, M., 1999. The various forms of soil boron: Importance, effect of soil characteristics and plant availability. Agrochimica 43(2), 77–88.

Nowe liczby graniczne niedoboru mikroelementów w glebie oznaczanych przy użyciu 1 M HCl dla pszenicy i rzepaku

Słowa kluczowe

Mikroelementy
Gleba
Niedobór
Kryteria oceny
Ekstrahent

Streszczenie

Celem pracy była nowelizacja liczb granicznych do oceny zawartości B, Cu, Fe, Mn i Zn w glebie oznaczanych przy użyciu 1 M HCl. W odróżnieniu od liczb dotychczas stosowanych, określających zawartość niską, średnią i wysoką, nowe liczby wskazują tylko granicę zawartości niskiej, poniżej której konieczne jest nawożenie danym mikroelementem. Ponadto nowe liczby są zróżnicowane w zależności od gatunku rośliny, co jest związane z różną wrażliwością roślin na deficyt mikroelementów. Liczby te opracowano dla pszenicy i rzepaku na podstawie dużego zbioru danych uzyskanych z kolekcji 3865 par próbek gleba-roślina, pobranych z pól produkcyjnych zlokalizowanych w 16 województwach kraju. W próbkach roślinnych oznaczono zawartość mikroelementów, a w próbkach glebowych oprócz mikroelementów również pH, skład granulometryczny oraz zawartość węgla organicznego i przyswajalnego fosforu. Dodatkowo dla wszystkich pól oszacowano plon ziarna pszenicy i nasion rzepaku. Zastosowano dwie niezależne metody obliczeń w celu zwiększenia wiarygodności opracowanych liczb. Jedną z nich była metoda równań regresji, wykorzystująca współczynnik bioakumulacji mikroelementu, jego zawartość krytyczną w roślinie oraz odpowiednie cechy gleby. Równania regresji konstruowano przy pomocy programu Stagraphics. Dla każdego mikroelementu testowano 8 modeli w poszukiwaniu równania o najwyższym współczynniku determinacji r^2. Do weryfikacji tak wyliczonych liczb użyto metody „wysokich plonów", która polegała na wyznaczeniu najmniejszej zawartości mikroelementu w glebie, przy której można osiągnąć wysoki plon.