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INTERNATIONAL Agrophysics
www.international-agrophysics.org

Int. Agrophys., 2017, 31, 551-562
doi: 10.1515/intag-2016-0074

Relationship between assimilable-nutrient content and physicochemical properties of topsoil**

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Received February 28, 2017; accepted August 17, 2017

A b s t r a c t. In the years 2008-2011, an environmental study was conducted for Polish soils, focusing on the south-eastern Poland soils, as they exhibit significant acidification. This study aimed at assessing the current pH_{KCl} and the supply of basic macro- (P, K, Mg and $S\text{-}SO_4$) and microelements (B, Cu, Fe, Mn and Zn) in the collected soil samples, and also at determining their relationship with the soil agronomic category, humus content and pH class. Soil reaction and humus and macronutrient content were positively correlated with the amount of colloidal clay and particles < 0.02 mm. In the majority of cases, the macro-element content in the soil was positively correlated with soil pH and humus content. As for microelements, a usually significant and positive correlation was found between the soil agronomic category and the content of manganese, iron and zinc, whereas for the content of boron and copper, no such relationship was observed. A significant and positive correlation between soil reaction and the content of manganese, iron and boron was also found. Such correlations were not observed in relation to copper and zinc content. Statistical analysis indicated that the content of boron and manganese depended to the greatest extent on the investigated physicochemical properties.

K e y w o r d s: soil nutrients, soil reaction, macroelements, microelements, topsoil

INTRODUCTION

The soil cover in Poland was formed mostly after the latest glaciation period (Ber, 2005) and includes several soil types of which, according to the taxonomy of soil in Poland developed by the Polish Society of Soil Science (Polish Soil Classification, 2011), the brown earth and podzols are the most commonly reported soil types. Brown earth soils (brown soils and lessive soils) cover about 51.5% of the country's area and podzols (podzolic soils, podzols and rusty soils) cover about 26% of the area (Bednarek *et al.*, 2004). Albeluvisols soils, which are typical for this part of Europe, are also commonly found. When analysing the soil cover of Poland in relation to the soil cover of Central Europe, which lies almost entirely in the subboreal belt and, at a first glance, exhibits homogeneity (Jones *et al.*, 2005), one can easily notice that the area coverage of brown earth soils increases westwards, whereas the share of podzols increases eastwards and northwards (Niewiadomski and Tołoczko, 2014). As for soil cover towards the southern and south-eastern directions, mostly podzols, luvisols and albeluvisols soils can be found. Although Poland's soil cover shows a considerable productivity, inappropriate soil management, resulting in, for example, high acidification and a very low renewability index of organic matter resources in soil (Skłodowski and Bielska, 2009), makes it poorly rated when compared to the soil cover of Central Europe.

One of the basic agro-technical soil management treatments which has a remarkably high impact on yield and crop quality is the fertilisation of soil and plants (Antonkiewicz *et al.*, 2012). In order to properly identify plant fertilisation needs, the current supply of certain macroelements to the fertilised soils has to be known. These include such elements as phosphorus (Berg and Joern, 2006; Bünemann *et al.*, 2011; Fernandes *et al.*, 2000; Mc Dowell and Sharpley,

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**This paper was co-funded by the Polish National Centre for Research and Development as part of the LCAgri project, Contract No. BIOSTRATEG1/271322/3/NCBR/2015.

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2003), potassium (Brennan and Bell, 2013; Fotyma, 2007; Moody and Bell, 2006), magnesium (Tkaczyk *et al.*, 2016; Tyler and Olsson, 2001) and sulphate-sulphur (Gąsior and Alvarez, 2012; Szulc *et al.*, 2014), and microelements such as boron (Majidi *et al.*, 2010; Shaaban, 2010; Szulc and Rutkowska, 2013), copper (Rutkowska *et al.*, 2013; Su and Yang, 2008), iron (Mcgrath and Zhao, 2006), manganese (Antonkiewicz *et al.*, 2016) and zinc (Barczak *et al.*, 2009; Domańska, 2009; Rutkowska *et al.*, 2014a). This knowledge should be complemented by the equally important data on other physicochemical properties of the fertilised soils, such as pH_{KCl} or humus content (Aponte *et al.*, 2010; Lipiński and Bednarek, 1998). Another agro-technical treatment which should be considered as greatly influencing crop yield and quality is acidic-soil liming (Tkaczyk and Bednarek, 2011).

The knowledge of physicochemical soil parameters, among which micro- and macronutrients contents play a particularly important role, is fundamental to precision agriculture, since the technical and economic viability of regulating these parameters can vary. Soil physical characteristics can be improved by appropriate agro-technical treatments, *i.e.* proper cultivation, melioration and fertilisation (Lamorski *et al.*, 2013; Walczak *et al.*, 1997). Crop production modellers are also looking for representative data on micro- and macroelement content and their interactions with various properties of soils by employing increasingly sophisticated simulation models, including soil sub-models. Such models, despite phasic development, organ formation, biomass production, yield and quality formation, can consider soil-crop water relations and the nutrient (N, P, K) balance. Frequently, the enforced system is used in crop growth simulation models to assess individual and comprehensive management patterns, with a variety of environments and totally different genotypes included (Fronzek *et al.*, 2017; Pirttioja *et al.*, 2015; Ruiz-Ramos *et al.*, 2017). Spatio-temporal changes in climate dynamics are also often analysed and assessed (Baranowski *et al.*, 2015; Hoffmann *et al.*, 2017; Krzyszczak *et al.*, 2017). This provides valuable information on the impact of climate change on crop production and macro- and micronutrient content in the soil.

Notably, the use of mineral fertilisers in Poland, especially calcium fertilisers, has been very low in recent years. As a consequence, Poland arable soils exhibit significant acidification (Siebielec *et al.*, 2012). This is caused by both natural and anthropogenic factors, the main reason being, however, the insufficient usage of calcium fertilisers (Filipek and Skowrońska, 2013). This applies overwhelmingly to the soils of south-eastern Poland, especially when compared to other parts of the country.

Therefore, our study aimed to assess, for a representative set of soils typically found in south-eastern Poland, the reaction of soils and their basic-macro- (P, K, Mg, $S\text{-}SO_4$) and microelement (B, Cu, Fe, Mn, Zn) supply. The specific aim was to relate macro- and micronutrient contents to the agronomic categories, humus content and soil reaction.

MATERIALS AND METHODS

A number of environmental studies were conducted for soils in Poland over a period of four consecutive years, from 2008 to 2011. Our primary focus was on the soils of south-eastern Poland, since they exhibit significant acidification. First, soil sample collection locations were selected to cover the studied area uniformly. Then, the designated soil collection locations were matched with farms located on soils belonging to each of the agronomy categories, *i.e.* very light, light, medium or heavy (< 10, 11-20, 21-35, or >35% of the fraction with a diameter of < 0.02 mm, respectively). However, no soil collection locations were designated if a category of soil in a given area accounted for less than 10% of the area of land under agricultural use. The locations were additionally verified using GPS during sample collection. The samples were collected using the Egner soil probe sampler from a 0-20 cm layer and each sample was weighted approximately 500 g. In line with the IUNG-PIB recommendations, the number of repetitions for each area was determined based on livestock density. Accordingly, one repetition was made for areas with a livestock density of less than 40 livestock units (LSU)/100 ha agricultural land (AL), two repetitions for areas with 40-80 LSU/100 ha AL and three repetitions for areas with more than 80 LSU/100 ha AL. All of the chemical analyses were conducted in an accredited lab of the Regional Agrochemical Station in Lublin. Particle size distribution (PSD) in the collected soil samples was measured using the laser diffraction method (LDM). The pH in 1 mol KCl dm^{-3} and soil humus content were measured using the Tiurin method, and phosphorus and potassium contents were identified using the Egner-Riehm (DL) method. The atomic absorption spectrometry (AAS) method was employed to assay magnesium after the extraction of 0.0125 mol $CaCl_2$ dm^{-3} from soil. Sulphur levels in sulphates ($S\text{-}SO_4$) were determined using the nephelometric method. Assimilable forms of copper, iron, manganese and zinc were assayed using the AAS method after dissolution in 1 mol HCl. Boron was assayed using the colorimetric method with curcumin (A catalogue of methods, 2011). Macronutrients were assayed in 32 741 soil samples, while microelements were assayed in 2 194 samples. The results were assessed statistically using the one-way non-orthogonal analysis of variance classification with Tukey confidence intervals ($p=0.05$). The relationships between the content of analysed soil nutrients and particle size distribution, humus content and the reaction of the investigated soils were determined by calculating correlation coefficients. Subsequently, multiple regression equations were calculated on the basis of the correlation analysis to allow the estimation of micronutrient content in the soil.

RESULTS AND DISCUSSION

An analysis was conducted of soil reaction, humus content and macronutrient content in topsoil, divided into specific agronomic categories, in all soil samples (Table 1). The results indicate that a relationship between agronomic categories and soil reaction can be established, since very light soils are acidic, light and medium soils are slightly acidic, and heavy soils are neutral. We found that the pH_{KCl} of very light soils is significantly lower than the pH_{KCl} of light, medium and heavy soils. Also, it was evident that soil reaction is significantly higher for heavy soils compared to the other categories. Conversely, no statistically significant differences were found between the pH of light and medium soils. These results are in agreement with the results of previous studies (Filipek and Skowrońska, 2013; Lipiński and Bednarek, 1998; Tkaczyk and Bednarek, 2011). These studies indicated that soil reaction is an important characteristic of soil, as it has a significant impact on the availability of the assimilable forms of macro- and microelements. In his follow-up study, Lipiński (2000; 2005a) noticed a slow but steady improvement in the pH of Polish soils. He concluded that most strongly acidified soils can be found in eastern and central parts of the country. He also found that almost half the arable soils are in great need of liming. Tkaczyk and Bednarek (2011) established that 52.1% of arable soils in south-eastern Poland exhibited very acidic or acidic pH, with 22.8% being slightly acidic; soil liming was necessary for 47.2% of the examined area and recommended for 13.0% of the area. Optimum levels of pH and humus content in soil, combined with the availability of assimilable forms of macroelements in quantities adequate to meet crop fertilisation needs, are of crucial importance to achieving large high-quality yields (Antonkiewicz *et al.*, 2012; Sharpley, 1995).

The mean values of humus content in the analysed soils, as assigned to their agronomic categories, ranged from 1.46 to 2.41%. In very light, light and medium soils, the variability of humus content was statistically insignificant, whereas for heavy soils, it was significantly higher. Phosphorus content in the analysed soil samples varied from 6.1 to 1312.4 mg P kg^{-1}, while the mean values of phosphorus content in the analysed soils, as assigned to their agronomic categories, ranged from 67.7 to 109.2 mg P kg^{-1}. According to the Egner-Riehm limit values, phosphorus content in very light, light and medium soils was high, with only little variation between these categories. Conversely, phosphorus content in heavy soils was very high and differed statistically from the three mentioned categories. This result suggests some changes in phosphorus content distribution compared to what was found by Lipiński (2005b), who observed that soils with very low and low phosphorus content accounted for about 38% of agricultural land in Poland, and that most were located in eastern and south-eastern Poland.

The mean values of assimilable potassium content differed statistically in each category. According to the Egner-Riehm limit values, this content was moderate in very light soils and high in light, medium and heavy soils. This finding sheds new light on the previous studies by Lipiński (2005c), who claimed that nearly half the agricultural soils in Poland had very low or low potassium content, and also that it was the most deficient plant nutrient in agriculture. However, the percentage area of soils with very low and low amounts of potassium had been decreasing as of the early 1990s (Lipiński, 2000). The results presented in this paper suggest that this trend continues.

The mean values of magnesium content were average in very light and heavy soils, and high in light and medium soils. In medium and heavy soils, magnesium content was significantly higher than in very light and light soils. This finding confirms that there has been a steady improvement in magnesium content in the soils of south-eastern Poland. This is in disagreement with the study by Dudziak (1973), who observed that almost 70% of arable land in south-eastern Poland had an undersupply of assimilable forms of

Table 1. Mean, minimum and maximum (under the mean in brackets) values of soil reaction, humus content and the content of the essential nutrients in topsoil, depending on the agronomic category

Soil agronomic category	pH_{KCl}	Humus content (%)	P	K	Mg	$S\text{-}SO_4$
			(mg kg^{-1})			
Very light	5.24 b (3.78 ÷ 8.3)	1.47 a (0.1 ÷ 9.47)	67.7 a (10 ÷ 453.4)	82.2 a (19.1 ÷ 309.6)	28.5 a (6 ÷ 118)	4.81 b (0.01 ÷ 91.7)
Light	5.97 a (4 ÷ 8.42)	1.46 a (0.6 ÷ 7.61)	79.7 a (8.72 ÷ 545)	141.9 b (22.4 ÷ 655.7)	58.8 a (6 ÷ 170)	15.60 a (0.18 ÷ 225.1)
Medium	6.00 a (4 ÷ 8.78)	1.48 a (0.17 ÷ 8.25)	82.7 a (6.1 ÷ 654)	169.2 c (19.1 ÷ 1037.5)	90.2 b (7 ÷ 465)	14.70 a (1.49 ÷ 161.3)
Heavy	6.83 c (4 ÷ 7.83)	2.41 b (0.84 ÷ 3.97)	109.2 b (14.4 ÷ 1312.4)	223.2 d (41.5 ÷ 971.1)	97.0 b (10 ÷ 435)	16.92 a (2 ÷ 132.7)

a, b, c, d, e, f – means labelled with the same letter are not significantly different at the significance level $\alpha = 0.05$.

magnesium and that at least half of them should be fertilised with this macroelement. Czuba and Zaniuk (1968) reported that magnesium content is significantly correlated with the occurrence of colloidal clay and, to a slightly lesser extent, with organic carbon. Lipiński and Bednarek (1998) corroborated this finding. Our findings seem to be consistent with Lipiński (2005d), who reported that the supply of assimilable magnesium to soil had been improving, and that most of the soils deficient in this element – more than 40% of arable land – are located in the central-western and south-eastern parts of Poland (Greater Poland, Opole, Łódz, Mazovia and Lublin regions).

The abundance of sulphate sulphur varied substantially, from 0.01 to 225.1 mg $S\text{-}SO_4$ kg^{-1}, whereas the mean values of sulphate-sulphur content in the analysed soils, as assigned to their agronomic categories, ranged from 4.81 to 16.92 mg $S\text{-}SO_4$ kg^{-1}. In very light soils, this content was significantly lower than in the other categories. The content of this form of sulphur showed no statistical variation between light, medium and heavy soils. Similar conclusions were drawn by Lipiński (2000), who investigated the influence of certain factors which affected the occurrence of sulphate-sulphur in the arable soils of south-eastern Poland. Szulc *et al.* (2004), who examined the variations in the content of the various forms of sulphur in the soil profile under different tillage systems, found that a reduction in soil cultivation caused an increase not only in humus content, but also in the content of all the examined forms of sulphur, including $S\text{-}SO_4$. Conversely, Jakubus (2000) observed that organic matter significantly affected the content of total sulphur and organic sulphur, and, to a lesser extent, of sulphate-sulphur, in very light and light soils. Kozłowska-Strawska and Kaczor (2004) expanded this conclusion by observing that sulphur content in soil depends not only on the species of cultivated plants, but also on the employed form of sulphur fertilisation. Terelak *et al.* (1995), following extensive research, concluded that about 53% of Polish agricultural soils (in a 0-20 cm layer) were characterised by low (<15.0 mg kg^{-1}) $S\text{-}SO_4$ content, with only 5% exhibiting very high (>50.0 mg kg^{-1}) $S\text{-}SO_4$ content.

The assessment of pH_{KCl} and humus content, and phosphorus, potassium, magnesium and sulphur content in soil indicates that these quantities are strongly and positively dependent on the amount of the smallest fraction in a soil, *i.e.,* colloidal clay, and particles smaller than 0.02 mm. The reason is probably that as the amount of the smallest soil fractions increases, so does the cation-exchange capacity of an adsorption complex, resulting in an increased amount of exchangeable potassium and magnesium. The increase in the content of the assayed nutrients, including phosphorus and sulphur, in heavy soils was brought about by a higher amount of humus, and thus higher mineralisation rates of organic compounds. A further analysis of the impact of soil organic matter on the occurrence of macronutrients shows that the contents of macroelements are generally higher for soils with higher humus contents (Table 2 and Fig. 1). The mean values of phosphorus content increased steadily with increasing amounts of humus. However, the differences between classes I and II, III and IV, as well as IV and V were too small to be considered statistically significant. It should be noted here that the content of this nutrient in class III was demonstrated to have been statistically higher than in classes I and II, and lower than in class V. Potassium content ranged from 19.1 to 655.7 mg K kg^{-1}, whereas the mean values of potassium content in the analysed soils, as assigned to their agronomic categories, ranged from 94.2 to 194.2 mg K kg^{-1}, and increased steadily from class I to IV. However, the differences between classes I and II, III and V, as well as IV and V were statistically insignificant. We found that the mean values of magnesium content increased consistently from class II to V, but the differences in the

Table 2. Mean, minimum and maximum (under the mean in brackets) values of macroelement content in the soil, depending on humus content

Humus content class	P	K	Mg	$S\text{-}SO_4$
	(mg kg^{-1})			
I (0-0.5%)	39.9 a (6.54 ÷ 85.02)	94.2 a (19.1 ÷ 146.9)	58.6 a,b (6 ÷ 97)	0.03 a (0.01 ÷ 0.08)
II (0.51-1.00%)	67.7 a (11.77 ÷ 244.2)	119.9 a (19.1 ÷ 319.6)	46.4 a (6 ÷ 95)	3.27 a,b (0.01 ÷ 35.18)
III (1.01-1.50%)	97.3 b (9.59 ÷ 311.74)	155.4 b (19.1 ÷ 502.2)	62.6 a (6 ÷ 227)	9.14 c (0.02 ÷ 41.18)
IV (1.51-2.00%)	99.2 b,c (15.26 ÷ 381.5)	194.2 c (19.1 ÷ 655.7)	87.6 b,c (7 ÷ 435)	9.17 b,c (0.1 ÷ 49.51)
V (> 2.01%)	120.8 c (6.54 ÷ 453.4)	165.4 b,c (19.1 ÷ 560.3)	101.4 c (6 ÷ 465)	18.6 d (0.11 ÷ 91.69)

Explanations as in Table 1.

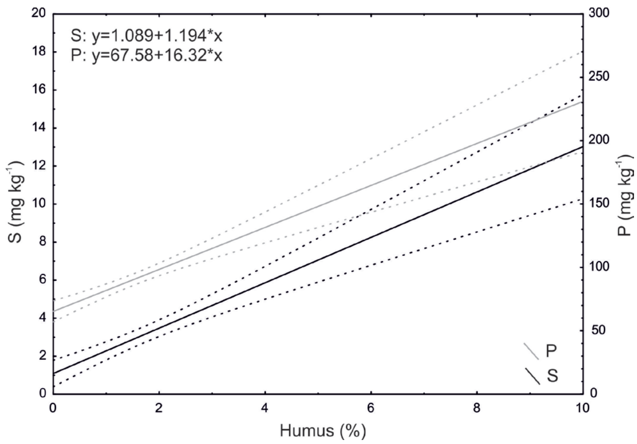

Fig. 1. Phosphorus and sulphur content, depending on humus content in the soil.

content of this element between classes I, II and III, I and IV, as well as IV and V were statistically insignificant. Also, the mean values of sulphate-sulphur content in soil grew consistently with increasing humus content (Fig. 1). However, no significant differences between classes I, II and IV, as well as III and IV were observed. In class V soils, $S\text{-}SO_4$ content was statistically higher than in the other soil classes. This evidently positive correlation between phosphorus, potassium, magnesium and sulphur content, and humus content are most probably attributable to the mineralisation of organic compounds, as well as to the release of those elements from the mineral compounds occurring in the soil (by acidolysis).

We found a clear and positive relationship between the content of assimilable forms of macronutrients and the soil reaction class (Table 3). Phosphorus content in topsoil was higher for neutral and alkaline soils than for acidic soils. However, in very acidic, acidic and slightly acidic soils, variations in the content of this nutrient were not significant. In neutral soils, it was significantly higher than in all the acidic classes of soil reaction and significantly lower than in alkaline soils. Also, the content of potassium increased consistently from very acidic to alkaline soils, but the content of this nutrient was significantly lower than in the other soil reaction classes only in very acidic soils. Potassium content did not vary statistically between acidic, slightly acidic, neutral and alkaline soils. The magnesium content-pH class relationship was also positive and significant, but not as unambiguous as for P and K. We found that Mg content did not vary significantly between very acidic and acidic soils, as well as slightly acidic, neutral and alkaline soils. Sulphate-sulphur content increased steadily, starting from very acidic soils up to alkaline soils. The lowest content of this element was found in very acidic soils and it differed statistically from the other reaction classes, but these differences were statistically insignificant between acidic and slightly acidic, as well as neutral and alkaline soils. The noticeable, positive and generally significant dependence of the assayed forms of macronutrients (P, K, Mg and $S\text{-}SO_4$) on the pH class should be emphasised here. The smallest content of the above-mentioned elements were observed in very acidic and acidic soils, the largest – in neutral and alkaline soils.

Not only soil reaction, humus content and macroelement availability in soils, but also optimum levels of soil micronutrients are of crucial importance to obtaining high-quality crop yields (Antonkiewicz, 2010; Antonkiewicz *et al.*, 2016; Rutkowska *et al.*, 2014b; Su and Yang, 2008). Micronutrient contents in topsoil, divided into specific agronomic categories, are presented in Table 4. The content of soluble boron in assayed soils ranged from 0.04 to 65.2 mg B kg^{-1}, whereas the mean values of boron content in the analysed soils, as assigned to their agronomic categories, ranged from 2.92 to 4.97 mg B kg^{-1}. In very light soils, it was lower compared to the other soil agronomic categories,

Table 3. Mean, minimum and maximum (under the mean in brackets) values of macronutrient content in the soil, depending on soil reaction

pH of the soil	P	K	Mg	$S\text{-}SO_4$
	(mg kg^{-1})			
Highly acidic	59.6 a (13.08 ÷ 275.6)	131.7 b (19.1 ÷ 485.6)	36.9 b (6 ÷ 510)	4.51 b (0.01 ÷ 35.18)
Acidic	68.5 a (6.54 ÷ 732.5)	168.7 a (19.1 ÷ 1560.4)	82.8 a,b (6 ÷ 720)	8.6b c (0.02 ÷ 52.12)
Slightly acidic	79.5 a (6.1 ÷ 1312.36)	175.4 a (19.1 ÷ 1386.1)	97.5 a (12 ÷ 770)	14.8 a,c (0.02 ÷ 124.5)
Neutral	115.9 b (15.27 ÷ 662.7)	190.0 a (19.1 ÷ 971.1)	87.6 a (9 ÷ 451)	18.5 a (0.25 ÷ 225.1)
Alkaline	154.4 c (13.08 ÷ 994.1)	190.5 a (27.4 ÷ 1037.5)	106.8 a (10 ÷ 884)	21.0 a (2.01 ÷ 132.7)

Explanations as in Table 1.

Table 4. Mean, minimum and maximum (under the mean in brackets) value of microelement content in the soil, depending on the agronomic category

Soil agronomic category	B	Cu	Fe	Mn	Zn
	(mg kg^{-1})				
Very light	2.92 a (0.18 ÷ 13.9)	1.47 a (0.3 ÷ 16.4)	671.2 b (159 ÷ 1805)	49.2 a (2.5 ÷ 243.4)	4.68 a (0.4 ÷ 54.4)
Light	4.97 a (0.12 ÷ 65.2)	10.3 a (0.3 ÷ 97.5)	1155.6 a (21 ÷ 5995)	147.2 b (11.6 ÷ 294.1)	7.54 a,b (0.8 ÷ 118.9)
Medium	3.93 a (0.04 ÷ 64.2)	6.51 a (0.3 ÷ 108.5)	1395.5 c (21 ÷ 6810)	178.9 c (9.35 ÷ 472.1)	10.08 b (0.97 ÷ 274.3)
Heavy	4.62 a (0.25 ÷ 24.4)	6.91 a (1.69 ÷ 57.4)	1053.8 a (122.7 ÷ 5840)	196.8 d (35.3 ÷ 530.4)	7.14 a,b (2.2 ÷ 71.1)

Explanations as in Table 1.

for which the amount of boron increased markedly. Still, no significant differences in boron content between agronomic categories were found. This suggests that some changes have occurred in the boron content relationship with the other soil components of south-eastern Poland mineral soils compared to the findings of a study by Myszka (1960). Myszka claimed that for soils typically found in the Lublin Upland, the amount of hot water-soluble boron depended mainly on particle size distribution (PSD) and humus content, but pH should be also taken into account when assessing boron content in soils. A similar conclusion can be found in Goldberg (1997), whereas Zembaczyński and Żmigrodzka (1968) found that for soils in the Zielona Góra Province, the content of soluble boron in soils depended more on the amount of organic carbon than on PSD or soil reaction. Dudziak (1973) observed that 35% of soils in the Lublin Province are characterised by low amounts of assimilable boron. Dudziak and Bednarek (1980) expanded this conclusion by claiming that the highest content of this element could be found in the arable-humic layer of Hrubieszów-Tomaszów chernozems and that, in most cases, certain physicochemical properties of these soils had no evident influence on this content. Kociałkowski and Cieśla (1968) found that considerable boron deficiencies occurred in the arable layer of Kuyavia Upland soils, which may have had an adverse impact on the quality and yield of sugar beets. In terms of soil type, the highest content of this element was observed for the chernozem soils, whereas the podzolic and brown earth soils had the lowest boron contents (Czuba *et al.*, 1968).

We noticed a substantial variation in the mean values of the content of copper dissolvable in a 1 mol HCl solution in the analysed soils, as assigned to their agronomic categories. This variation was particularly marked between very light and light soils, but statistical analysis did not find any significant differences in the content of this nutrient between the individual agronomic categories of soil. This finding is, to some extent, in agreement with previous studies. Indeed, Dudziak (1973) reported that 44% of arable soils in the Lublin region were characterised by low contents of this element. A close relationship between the content of soluble copper and the PSD of soil was also identified (Lipiński and Bednarek, 1998). Moreover, Terelak *et al.* (1995) found that about 99% of agricultural land in Poland showed natural (O^o) and slightly increased (I^o) contents of copper, allowing the production of high-quality animal fodders and consumable agricultural products. In terms of soil type, the highest levels of assimilable copper were found in alluvial soils, while the lowest – in podzolic soils (Czuba *et al.*, 1968).

The mean values of iron content were significantly higher in light and medium soils when compared to very light soils. There were no statistically significant differences in the content of this micronutrient between light and heavy soils.

The mean values of manganese content in the analysed soils, as assigned to their agronomic categories, increased significantly, starting from very light soils up to heavy soils. Similar results were obtained by previous studies. Czuba *et al.* (1968) found that the highest levels of active Mn can be observed for alluvial soils, and the lowest for the chernozem soils. Kociałkowski and Cieśla (1968) found that the arable layer of the Kuyavia Upland soils showed deficiencies in the assimilable form of manganese, whereas 22% of arable soils in the Lubelskie region showed low contents of this element (Dudziak, 1973). Although Piotrowska (1967) found no statistically significant correlations between Mn content and the amount of organic matter for the loess soils of the Sandomierz-Opatów highland, other researchers demonstrated that the content of this nutrient depended on particle size distribution in each particular pH class (Lipiński and Bednarek, 1998).

The mean values of soluble-zinc content were the lowest in very light soils. The soluble-zinc content in these soils was significantly lower than in the other agronomic categories. No significant differences in the content of this

Table 5. Mean, minimum and maximum (under the mean in brackets) values of micronutrient content in the soil, depending on humus content

Humus content class	B	Cu	Fe	Mn	Zn
			(mg kg^{-1})		
I (0-0.5%)	2.37 a (0.4 ÷ 4.8)	1.02 a (0.3 ÷ 1.9)	562.4 a (159 ÷ 849)	33.5 b (2.5 ÷ 86.4)	1.97 a (0.4 ÷ 6)
II (0.51-1.00%)	4.32 a (0.13 ÷ 9.5)	1.28 a (0.3 ÷ 3.2)	648.3 a (439 ÷ 1162)	67.4 b (2.5 ÷ 175.7)	3.92 a,b (0.4 ÷ 8.5)
III (1.01-1.50%)	3.55 a (0.18 ÷ 20.5)	2.90 a (0.3 ÷ 42.7)	970.7 b (21 ÷ 1948)	159.6 a (3.8 ÷ 453.4)	5.48 a,b (1.2 ÷ 15.35)
IV (1.51-2.00%)	4.49 a (0.36 ÷ 46.9)	6.42 b (0.5 ÷ 57.4)	1139.5 b,c (54 ÷ 2215)	167.5 a (12.6 ÷ 317.8)	8.74 b,c (1.6 ÷ 54.4)
V (> 2.01%)	9.16 b (0.58 ÷ 65.2)	4.69 a,b (0.9 ÷ 15.5)	1332.2 c (280 ÷ 5995)	160.3 a (6.7 ÷ 385.5)	13.4 c (1.7 ÷ 161)

Explanations as in Table 1.

element were observed in light, medium and heavy soils. The content of this element had been studied before, with slightly different conclusions. Dudziak (1973), for instance, concluded that 19% of arable soils in the Lublin region were characterised by low content of this nutrient. Barczak *et al.* (2009) reported that the content of assimilable Zn depended largely on soil type, the form of sulphur fertilisation and the mutual interactions between these factors. Soil type as an important factor behind the varying contents of zinc was also mentioned in a study by Domańska (2009). Conversely, Piotrowska (1967) observed that, despite the apparent accumulation of zinc in the humic horizons, the content of this nutrient showed no statistically significant correlation with the amount of organic matter for the loess soils of the Sandomierz-Opatów highlands.

To summarise, out of the assayed microelements, only manganese, iron and zinc contents depended significantly, and usually positively, on the soil agronomic category, whereas no statistically significant dependence of agronomic categories on the content of boron and copper was observed.

An assessment of the impact of soil organic matter on the occurrence of micronutrients showed that boron content did not depend significantly on humus content in the first four soil classes, while it was significantly higher in class V soils when compared to the other classes (Table 5). As for soluble copper in the assayed soils, no statistically significant differences in the content of this element were observed between class I, II, III, and V soils. The same applies to class IV and V soils.

A significant impact was found of humus content classes on the amount of iron, its content increasing with each class. However, no statistically significant differences were observed between classes I and II, III and IV, as well as IV and V. The content of soluble forms of manganese was higher from class I up to class IV of humus content, but no significant differences were found between classes I and II, as well as III, IV and V. A marked and steady increase in the content of zinc in relation to the amount of humus in soil was observed (Fig. 2). The lowest content of this microelement was observed for class I soils, and highest for V class soils, but no significant variation in Zn content between classes I, II and III, II, III and IV, as well as IV and V were identified.

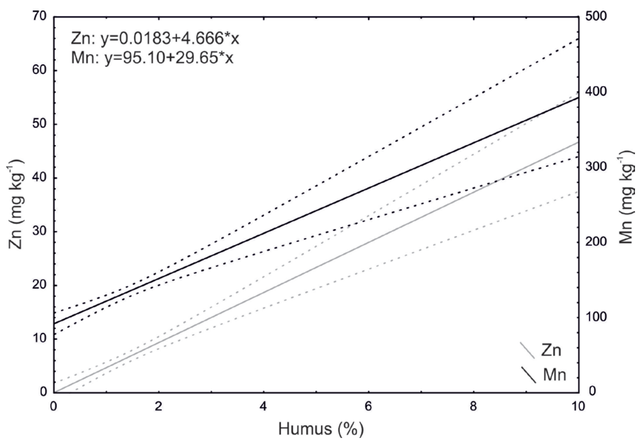

Fig. 2. Manganese and zinc, depending on humus content in the soil.

In conclusion, the analysis of the influence of soil humus on the content of soluble forms of micronutrients indicated that particularly evident and positive correlations could be observed for zinc, iron and manganese, whereas similar, although less pronounced, correlations were reported for copper and boron content.

Many studies have reported that the content of soluble forms of micronutrients depended significantly on soil reaction (Dudziak, 1973; Dudziak and Bednarek, 1980). The relationships between the content of microelements and pH in the assayed soils are presented in Table 6. More specifically, boron content depended significantly on soil pH, and

Table 6. Mean, minimum and maximum (under the mean in brackets) values of microelement content in the soil, depending on the pH

pH of the soil	B	Cu	Fe	Mn	Zn
	(mg kg^{-1})				
Highly acidic	3.22 a,b (0.09 ÷ 65.2)	4.65 a (0.3 ÷ 61.9)	910.7 a (159 ÷ 2335)	121.9 a (2.5 ÷ 317.8)	8.77 a (0.4 ÷ 274.3)
Acidic	3.18 a (0.04 ÷ 46.9)	7.63 a (0.3 ÷ 97.5)	1093.3 a (89 ÷ 6348)	139.0 a (3.7 ÷ 309.6)	8.48 a (0.97 ÷ 239)
Slightly acidic	3.79 a,b (0.2 ÷ 37.4)	4.69 a (0.6 ÷ 32.5)	1407.8 b (33.7 ÷ 6810)	158.4 c (5.91 ÷ 472.1)	7.54 a (1.5 ÷ 55)
Neutral	5.10 b,c (0.33 ÷ 64.2)	14.27 a (0.6 ÷ 47.7)	1409.0 b (58.4 ÷ 5870)	183.8 b (7.82 ÷ 453.4)	10.63 a (2.65 ÷ 161)
Alkaline	5.85 c (0.33 ÷ 46)	6.28 a (0.3 ÷ 108.5)	958.2 a (21 ÷ 3438)	191.8 b (13.6 ÷ 495.2)	10.05 a (0.8 ÷ 111)

Explanations as in Table 1.

it was the lowest in highly acidic and acid soils, whereas the highest content of this microelement was observed for neutral and alkaline soils. No significant differences in the content of this nutrient were observed between very acidic, acidic and slightly acidic soils, as well as between highly acidic and slightly acidic soils, and neutral, and alkaline soils. Furthermore, no significant impact of pH on copper content was found, whereas iron content increased noticeably, starting from very acidic soils, up to neutral soils. However, no significant differences in the content of Fe were found when compared to very acidic, acidic and alkaline, as well as to slightly acidic and neutral soils. The content of manganese gradually increased from very acidic soils up to alkaline soils, but no significant differences in the content of this element between highly acidic and acidic soils, as well as neutral and alkaline soils were identified. Also, no statistically significant influence of soil reaction on the content of Zn was observed. To summarise, a significant and positive influence was found of soil pH on the content of soluble forms of manganese, iron and boron. However, no such correlations were found for copper and zinc.

A calculation of the correlation coefficients R between humus content in soil, soil reaction and the contents of the assayed forms of macro and microelements (Table 7) showed a significant and positive correlation between the contents of humus, pH_{KCl} and all of the assayed nutrients (except for potassium and copper). Regrettably, the highest determination coefficient R^2 was only 18.7% and represented the relationship between zinc and humus content. A significant and positive correlation was observed for the relationship between pH_{KCl} and other indicators. Also, numerous significant and positive correlation coefficients were identified between assimilable forms of macro and microelements and the assayed-soil characteristics. Among other nutrients, phosphorus content depended significantly and positively on the majority of the assayed characteristics of soil. The highest determination coefficient illustrating these relationships was observed for P and Mg relationships, but it was only 26.6%. Furthermore, among the calculated characteristics, significant and positive correlations were observed between the content of potassium and soil reaction, potassium content and phosphorus content, magnesium content and sulphur content, magnesium content and humus content; magnesium content and pH_{KCl} content, and between magnesium content and the content of assimilable forms of phosphorus, potassium, sulphur and iron. Significant and positive correlations were also identified between the content of sulphate-sulphur and the majority of the assayed characteristics of the soil. The highest determination coefficient was obtained for the relationship between $S\text{-}SO_4$ and boron contents (33.8%), whereas a slightly lower determination coefficient was obtained for the $S\text{-}SO_4$ – humus content relationship (16.1%). Numerous significant and positive correlation coefficients were also observed between microelements. At 26%, the highest determination coefficient was obtained for the relationship between iron and manganese, while slightly lower coefficients were related to boron, zinc and copper relationships.

Multiple regression equations were calculated on the basis of the correlation analysis, allowing an estimation of the projected values of micronutrient contents in soil and the choice of the optimum subset of independent variables. The calculated multiple regression and determination coefficients showed that of the five assayed microelements, boron and manganese contents exhibited the most significant dependence on the physicochemical properties of soil (Table 8). However, it should be noted that the physicochemical properties determined the content of these nutrients in soil to an extent of less than 50%.

The study aimed to provide new insights into the present status of the soils in the area under study. A knowledge of the current pH_{KCl} of the soil and the supply of assimilable

Table 7. Nutrient content depending on certain physicochemical properties of soil (correlation coefficients, $\alpha = 0.05$)

Variable	Humus content	pH_{KCl}	P	K	Mg	$S\text{-}SO_4$	B	Cu	Fe	Mn	Zn
Humus content	–	0.288	0.274	*	0.187	0.401	0.151	*	0.312	0.279	0.432
pH_{KCl}	0.288	–	0.175	0.103	0.079	0.338	0.122	*	0.083	0.310	*
P	0.234	0.175	–	0.238	0.516	0.129	0.115	*	0.090	0.099	0.183
K	*	0.103	0.238	–	0.349	0.213	*	*	*	*	*
Mg	0.187	0.079	0.516	0.349	–	0.137	*	*	0.034	*	*
$S\text{-}SO_4$	0.401	0.338	0.129	0.213	0.137	–	0.581	0.283	0.228	0.252	*
B	0.151	0.122	0.115	*	*	0.581	–	*	0.154	0.405	*
Cu	*	*	*	*	*	0.293	*	–	0.080	0.066	0.143
Fe	0.312	0.083	0.090	*	0.084	0.228	0.154	0.080	–	0.510	0.127
Mn	0.276	0.310	0.099	*	*	0.252	0.405	0.066	0.510	–	0.084
Zn	0.432	*	0.183	*	*	*	*	0.143	0.127	0.084	–

*irrelevant dependence.

Table 8. Microelement content in the soil, depending on certain physicochemical properties of soil calculated using multiple regression equations

Microelement	R (regression coefficient)	R^2 (determination coefficient)	Multiple regression equation
B	0.696	0.485	$Y_B = 4.98 + 0.28_{S\text{-}SO_4} + 0.04_{Mn} - 0.03_{Cu} - 1.55_{pH} - 0.001_{Fe}$
Cu	0.414	0.171	$Y_{Cu} = 1.25 + 1.50_{S\text{-}SO_4} - 1.84_B + 0.75_{Zn} - 8.39_{humus}$
Fe	0.540	0.292	$Y_{Fe} = -100.55 + 6.42_{Mn} + 186.51_{humus}$
Mn	0.666	0.444	$Y_{Mn} = -15.4 + 0.03_{Fe} + 3.96_B + 21.3_{pH} - 0.80_{S\text{-}SO_4}$
Zn	0.521	0.271	$Y_{Zn} = -1.02 + 8.00_{humus} - 0.34_{S\text{-}SO_4} + 0.06_{Cu} + 0.36_B$

forms of essential macro (P, K, Mg, $S\text{-}SO_4$) and micronutrients (B, Cu, Fe, Mn, Zn) to the soil can help farmers to plan and manage reasonable fertilisation treatments using calcium, calcium-magnesium, mineral, natural and organic fertilisers at the farm level. This information can also prove useful in facilitating agricultural advisory services related to fertilization activities in the area under study. The insights about the relationships between soil components might be equally relevant, helping farmers to make decisions related to fertilisation and soil liming. The broad representativeness of our study in terms of the assayed soil samples and their diversity (different soil categories, humus content classes and soil reaction) makes it possible to use multiple regression equations for the areas with a wide range of soil conditions so as to help farmers to ensure a proper supply of nutrients for a healthy growth of crops, and to increase soil productivity using only a limited set of independent variables (to save time and consumables when planning and performing chemical analyses of soil samples).

CONCLUSIONS

1. The evaluation of humus content, pH_{KCl} and the supply of phosphorus, potassium, magnesium and sulphate sulphur to soils, taking into account the particle size distribution of these soils, indicated that the above factors depended on the amount of colloidal clay and particles with a diameter of < 0.02 mm. The obtained correlation was significant and positive.

2. Positive correlations were usually observed between humus content and phosphorus, potassium, magnesium and sulphate-sulphur contents in the soil.

3. Highly pronounced and generally significant correlations were identified between the content of the assayed forms of macronutrients (P, K, Mg and S-SO_4) and soil reaction class. The lowest content of these elements was observed for highly acidic and acidic soils, whereas the largest for neutral and alkaline soils.

4. Among the assayed forms of micronutrients (B, Cu, Fe, Mn, Zn), manganese, iron and zinc contents showed significant and positive relationship with the soil agronomic category, whereas no statistically significant relationship was observed with boron and copper contents.

5. Humus content in soil had a significant and positive impact on the content of assimilable forms of zinc, iron, manganese and, to a slightly lesser extent, on copper and boron content.

6. Significant and positive relationships were found between soil pH_{KCl} and the content of assimilable forms of manganese, iron and boron. However, no such relationships were observed for copper and zinc content.

7. Statistical analysis showed that out of the five assayed micronutrients (B, Cu, Fe, Mn, Zn), boron and manganese contents were highly influenced by the physicochemical properties of the soil. However, physicochemical properties determined the content of these microelements in soil to an extent of less than 50%. The broad representativeness of the assayed soil samples allows the application of multiple regression equations to estimate micronutrient contents in areas with varying soil conditions.

8. The identification of the current soil reaction, humus content and the supply of assimilable forms of macro- and micronutrients to the soil, as well as the determination of relationships between these factors and certain physicochemical properties of the soil, afford new opportunities to farmers, allowing them to estimate more precisely the fertilisation needs related to the plants cultivated in the area under study, and later, to balance the supply of certain macro- and micronutrients to the soil.

Conflict of interest: The Authors do not declare conflict of interest.

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