Soil micronutrient availability to crops affected by long-term inorganic and organic fertilizer applications

B. Rutkowska, W. Szulc, T. Sosulski, W. Stępień

Agricultural Chemistry Department, Warsaw University of Life Sciences-SGGW, Warsaw, Poland

ABSTRACT

The effects of mineral and organic fertilization on the contents of Fe, Cu, Zn, Mn, B and Mo in soil and in the soil solution as well as on availability of these elements for crops were investigated in the long-term field trial. The highest contents of Zn, Fe, Mn and Cu in soil and soil solution were observed in the treatment with the lowest pH (NPK). In this same combination the content of B and Mo was the lowest. The concentration of Zn, B and Fe in the soil solution significantly increased under farmyard manure application. Liming significantly decreased contents extractable by 1 mol/L HCl forms of Mn and Zn and significantly increase the content of Mo in the soil. Regardless of fertilization applied, microelement concentrations in the soil solution are sufficient for fulfilling nutritional needs of plants cultivated during the trial.

Keywords: microelements; plant; soil solution; long-term fertilization

Obtaining high yields with good quality relies upon appropriate provision of macro- and microelements into plants. Even though plant requirements for microelements are considerably lower when compared to those for macroelements, microelements are essential nutrients needed for proper plant growth and development. Deficiency of microelements in plants results firstly in decreasing plant resistance to harmful environmental factors, followed by declining yields and their quality (Alloway 2008).

Long-term mineral and organic fertilization can significantly modify soil properties such as pH, organic matter contents or else soil richness in available forms of macronutrients, which determine availability of micronutrients to plants (Li et al. 2007). Mineral fertilization, and especially nitrogen fertilization contributes to a decrease of soil pH and this enhances mobility of Cu, Fe, Mn and Zn (Fan et al. 2011). Several studies showed that phosphorus fertilization limits Zn availability for plants (Li et al. 2007, Fan et al. 2011). Systematic, long-term application of farmyard manure results in an increase of organic matter content in soil. Together with increased organic matter, an increase of Zn availability is observed, whereas Cu and Mn availability to plants is decreased (Singh et al. 2010, Fan et al. 2011).

The aim of this study was (1) to determine the effect of long-term fertilization on microelement contents in soil and in the soil solution as well as (2) to track relationships between plant nutritional requirements and microelement amounts in soil and the soil solution, when observed under the conditions of long-term fertilization.

MATERIAL AND METHODS

The study was carried out based on the permanent fertilization trial sited at the Experimental Station of the Faculty of Agriculture and Biology, Warsaw University of Life Sciences-SGGW, which is located in Skierniewice, Poland. The experiment

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was established in 1923, following randomized block design on Luvisols (FAO 2006) soil of the type of loamy sand with the following fractions in 0–30 cm layer: sand (> 0.05 mm) – 87%, silt (0.002–0.05 mm) – 5%, clay (< 0.02 mm) – 7%. The trial was carried out in five-field crop rotation (potatoes, spring barley, red clover, winter wheat, rye) and included the following fertilizer treatments: Ca, FYM (farmyard manure), NPK, CaNP, CaPK, CaNK, CaNPK, CaNPK + FYM. The following fertilization rates were applied: N – 90 kg/ha (ammonium nitrate), P – 26 kg/ha (triple superphosphate), K – 91 kg/ha (potassium chloride 50%). Liming was applied once in 5 years at a rate 1.43 t Ca/ha. FYM was applied at a rate 30 t/ha once in 5 years.

Soil samples were collected from the soil layer 0–30 cm after plant harvest in the years 2009–2011. In the samples, the following parameters were assessed:

– pH – by potentiometric method after extraction in 1 mol/L KCl (10 g of soil was suspended in 25 mL of KCl and left for 24 h to equilibrate), using a pH meter (Schott, Mainz, Germany) with a glass electrode;
– total organic carbon content – by dry combustion at high temperatures in a furnace with the collection and detection of evolved CO_2 with C-MAT 5500 apparatus (Ströhlein Instruments, Kaarst, Germany);
– soil total nitrogen content using the Kjeldahl method with Vapodest 50s apparatus (Gerhardt, Königswinter, Germany);
– the content of available phosphorus (PE-R) (PN-R-04023 1996) and the content of potassium in soil with the Egner-Riehm method – DL (PN-R-04022 1996); contents of available forms of B, Cu, Fe, Mn, Mo and Zn in soil after extraction in 1 mol/L HCl (10 g of soil was shaken with 100 mL HCl on a rotary shaker for 2 h at 120 rounds/min), with ICP-AES method (IRYS Advantage ThermoElementar, Cambridge, UK).

The soil solutions were obtained following the vacuum displacement method and using an oil vacuum pump (Dynavac OP4, Melbourne, Australia) (Wolt and Graveel 1986). The total concentration of B, Cu, Fe, Mn, Mo and Zn in the soil solutions was assessed with ICP-AES (inductively coupled plasma – atomic emission spectrometry) method.

In the trial the following crops were cultivated potatoes (cv. Hermes), spring barley (cv. Stratus), yellow lupin (cv. Dukat), winter wheat (cv. Symfonia), rye (cv. Dańkowskie Złote). The three plants from crop rotation (winter wheat, potatoes, lupine) were selected to the researches.

Plant material was dried out at 60°C using PREMED drier (Marki, Poland), then ground and milled with the use of a rotor mill ZM200 Retsch (Haan, Germany) and mineralized following the wet chemistry method using a mixture of acids HNO_3 and $HClO_4$ (Velp Scientifica, Usmate, Italy). Afterwards, the plant samples were utilized for determination of the total content of B, Cu, Fe, Mn, Mo, Zn with ICP-AES method. Based on the plant uptake of microelement quantities as well as the concentrations of these elements in the soil solution the value of solution recovery coefficient (SRC) was calculated following the formula below:

$$SRC = \frac{\text{nutrient uptake with plant yield (g/ha)}}{\text{nutrient quantity in soil solution (g/ha)}}$$

Numerical values of solution recovery coefficient provide information on how many times nutrient uptake is lower than nutrient quantity in the soil solution. At SRC values < 1, nutrient quantity in the soil solution is sufficient for plant nutritional needs. When SRC value is > 1, nutrient quantity in the soil solution is too low to cover plant nutritional needs.

The results were statistically analyzed with ANOVA using the Statistica PL software (Krakow, Poland).

RESULTS

Under the conditions of long-term fertilization, slightly acidic soil reaction was observed in the treatments where liming and FYM were applied. Only in NPK treatment a decrease of pH value was observed (Table 1). Long-term FYM application contributed to the accumulation of organic matter in soil. The lowest amounts of total N were observed in the control (Ca) and in the treatment without N fertilization (CaPK). The total N content in soil was increasing as a result of N fertilization and FYM applications. The content of available phosphorus and potassium in soil was the lowest in the control and in the treatments where P and K were not applied. Application of P and K as well as FYM resulted in a significant increase of available P and K forms in soil (Table 1). Similar effects of fertilization on soil properties changes were shown by Sosulski et al. (2011), Mercik and Stępień (2012).

Long-term fertilization influenced changes in micronutrients contents only to some extent. The highest contents of available forms of Cu, Fe, Mn and Zn were observed in soil with the lowest pH

Table 1. Properties of soil in long-term fertilization experiment (mean from 2009–2011)

Treatment	pH	C_{org}	N_{tot}	P available	K available
		(g/kg)		(mg/kg)	
Ca	6.40[b]	5.56[a]	0.52[a]	14.1[a]	51.5[a]
FYM	6.35[b]	11.0[c]	0.92[d]	74.3[cd]	91.1[b]
NPK	4.65[a]	5.84[a]	0.60[ab]	60.5[b]	86.5[b]
CaPK	6.35[b]	5.99[a]	0.49[a]	69.0[c]	128.1[c]
CaNP	6.50[b]	5.79[a]	0.62[b]	71.5[cd]	49.2[a]
CaNK	6.30[b]	6.02[ab]	0.61[b]	15.1[a]	101.1[bc]
CaNPK	6.20[b]	6.11[b]	0.63[bc]	67.2[c]	93.4[b]
CaNPK + FYM	6.25[b]	8.44[c]	0.79[c]	79.8[d]	179.2[d]

Values indicated with the same letter are not significantly different ($P \leq 0.05$)

(NPK). Liming significantly decreased the content of available forms of Mn and Zn in soil. Singh et al. (2010) showed that NPK fertilization significantly influenced the increase, and organic fertilization to reduce the mobility of Cu and Mn. In the case of zinc observed in this study, liming resulted in a decrease of its content, while FYM applications significantly increased the content of this element in soil in relation to the control object. Similar relationships were observed by Sienkiewicz et al. (2009). The contents of available boron and molybdenum forms in soil were the lowest in the treatment with exclusive mineral fertilization and they increased both at liming treatments and FYM applications (Table 2).

Fertilization significantly influenced changes in the concentration of microelements in the soil solution (Table 3). The lowest B and Mo concentration was found in the soil solution from the treatment with exclusive mineral fertilization (NPK). As a result of liming, an increase was observed of the concentration of both elements in CaNPK treatment. Application of FYM (CaNPK + FYM) caused further increase of B and Mo concentration when compared to both CaNPK and NPK treatments. Soil pH has a strong effect on the processes of adsorbing and releasing ions MnO_4^{2-} into the soil solution (Reddy et al. 1997). Availability of molybdenum for plants increases together with increasing soil pH (Smith et al. 1997). In acidic and neutral soils, boron mainly occurs as $B(OH)_3^0$ and this form is fixed onto soil solid particles only to a small extent. In the solution of soil with pH > 7, there rapidly increases the concentration of $B(OH)_4^-$ ions which compete with hydroxyl anions for adsorption sites on soil solid particles (Goldberg 1997).

Reddy et al. (1997) showed that in the soil solution, anions MoO_4^{2-} could form complex ions with humic and fulvic acids. This influences an increase of molybdenum availability for plants through restraint adsorption of ions MoO_4^{2-} on Fe, Mn and Al oxides, especially in acidic soils. The organic matter indicates high ability to adsorb

Table 2. The content of microelements extractable by 1 mol/L HCl in soil (mean from 2009–2011)

Treatment	B	Cu	Fe	Mn	Mo	Zn
	(mg/kg)					
Ca	0.53[ab]	3.03[a]	608.5[a]	111.2[ab]	0.023[ab]	4.77[a]
FYM	0.55[ab]	3.07[a]	597.3[a]	101.7[a]	0.034[b]	5.04[b]
NPK	0.49[a]	3.12[a]	654.9[a]	116.1[b]	0.019[a]	5.68[c]
CaPK	0.55[ab]	2.82[a]	576.9[a]	102.8[a]	0.022[ab]	4.87[a]
CaNP	0.50[a]	2.95[a]	580.5[a]	103.2[a]	0.020[a]	4.47[a]
CaNK	0.51[ab]	3.09[a]	629.9[a]	105.6[a]	0.033[b]	4.48[a]
CaNPK	0.55[ab]	2.99[a]	574.3[a]	108.5[a]	0.031[b]	4.48[a]
CaNPK + FYM	0.59[b]	2.89[a]	569.3[a]	104.1[a]	0.035[b]	4.90[a]

Values indicated with the same letter are not significantly different ($P \leq 0.05$)

Table 3. Microelement concentration in the soil solution (mean from 2009–2011)

Treatment	B	Cu	Fe	Mn	Mo	Zn
	(μmol/L)					
Ca	3.11[a]	0.40[a]	14.5[a]	15.6[a]	0.027[a]	2.08[a]
FYM	3.34[b]	0.41[a]	18.0[b]	15.0[a]	0.029[ab]	3.27[c]
NPK	2.88[a]	0.57[b]	18.4[b]	17.6[b]	0.025[a]	2.92[bc]
CaPK	3.24[ab]	0.40[a]	16.0[a]	15.7[a]	0.027[ab]	2.68[b]
CaNP	3.20[ab]	0.48[ab]	16.5[ab]	15.7[a]	0.029[ab]	2.22[a]
CaNK	3.19[ab]	0.49[ab]	16.9[ab]	15.7[a]	0.026[a]	2.67[b]
CaNPK	3.18[ab]	0.47[ab]	17.9[ab]	16.0[ab]	0.027[ab]	2.67[b]
CaNPK + FYM	3.39[b]	0.45[a]	18.0[b]	15.7[a]	0.030[b]	3.02[c]

Values indicated with the same letter are not significantly different ($P \leq 0.05$)

boron. Intensity of this process depends on soil pH and it reaches the maximum at soil pH = 9 (Gu and Lowe 1990, Yermiahu et al. 2001).

The highest concentrations of Cu, Fe, Mn and Zn were found in the solution of soil from the treatment with the lowest pH value (NPK). Liming (CaNPK) decreased the concentration of these elements in the soil solution. Long-term application of FYM (CaNPK + FYM) had an effect on a decrease of the concentrations of Cu and Mn as well an increase of Fe and Zn concentration in the soil solution when compared to CaNPK treatment (Table 3). Microelement mobility strongly depends upon soil pH, organic matter contents as well as the content of macroelements, including phosphorus. Fertilization with nitrogen as ammonium form results in soil acidification through nitrification of this ion. Together with increasing soil acidification, an increase is observed of the content of available Cu, Fe, Mn and Zn both in soil and the soil solution (Li et al. 2007, Rutkowska et al. 2009, Sienkiewicz et al. 2009).

Long-term fertilization with phosphorus (CaNP) decreased Zn concentration and increased Mo concentration in the soil solution, when compared to the treatment where P fertilization was not applied (CaNK) (Table 3).

In conditions of phosphorus fertilization precipitation of $Zn_3(PO_4)_2$ in the soil solution and decrease of Zn mobility is observed (Li et al. 2007, Fan et al. 2011). Phosphates compete with molybdates for adsorption sites on the surface of the solid soil layer. As a result of this process, desorption of MoO_4^{2-} into the soil solution is enhanced (Vistoso et al. 2009).

Long-term organic fertilization influences the content of available microelement forms in soil as well as in the soil solution. Together with increasing contents of organic matter in soil, mobility of Cu, Fe and Mn in the soil solution decreases. These elements show high affinity to organic matter and as a result they form stable bonds. The content of Zn in soil increases under the influence of organic matter, because this element forms labile organic-mineral complexes (Behera et al. 2011).

Table 4. Yields of plants in long-term field experiment (t of dry matter/ha) (mean from 2009–2011)

Treatment	Winter wheat		Potatoes		Yellow lupine	
	grain	straw	tubers	stalk	seeds	straw
Ca	2.79[a]	3.07[a]	3.00[a]	1.34[a]	0.83[a]	1.04[a]
FYM	3.54[b]	3.89[bc]	3.47[a]	1.54[ab]	1.11[bc]	1.39[bc]
NPK	3.35[b]	3.69[bc]	4.02[ab]	1.79[c]	1.16[bc]	1.45[c]
CaPK	3.25[b]	3.36[b]	3.23[a]	1.44[a]	1.10[bc]	1.38[bc]
CaNP	3.30[b]	3.63[b]	3.62[a]	1.61[b]	1.07[b]	1.34[bc]
CaNK	3.37[b]	3.71[bc]	4.04[ab]	1.80[c]	0.99[b]	1.24[b]
CaNPK	3.56[b]	3.92[bc]	4.32[b]	1.92[cd]	1.13[bc]	1.41[bc]
CaNPK + FYM	3.59[b]	3.95[c]	4.50[b]	2.00[d]	1.18[c]	1.48[c]

Values indicated with the same letter are not significantly different ($P \leq 0.05$)

Based on the plant uptake of microelement quantities (Table 4) as well as the concentrations of these elements in the soil solution calculated the value of solution recovery coefficient was calculated. Regardless of fertilization applied, microelement amounts in the soil solution were sufficient for covering nutritional needs of plants cultivated in the study, which is confirmed by SRC < 1 values obtained. Only in the case of potatoes, SRC values for B and Cu in several treatments were slightly higher than 1, which suggests that these nutrients' quantities in the soil solution were too low to cover nutritional needs of potatoes (Table 5).

In the present study, in the previous ones carried out within long-term trials, and also in those concerning the area of whole Poland, it was found that microelement quantities observed in the soil solution are sufficient for covering plant needs (Rutkowska et al. 2006).

Long-term fertilization affected amounts of Cu, Fe, Zn, Mn, B, and Mo in soil and the soil solution through the effects on physical and chemical soil properties. In the treatment with exclusive mineral fertilization, characterized by the highest soil acidification, the highest amounts of Fe, Mn, Zn and Cu were found in soil and the soil solution. Liming contrarily decreased the content of these elements in soil and the soil solution. Farmyard manure applications limited the content of Mn and Cu as well as they increased Zn mobility. The lowest amounts of B and Mo were observed in soil and the soil solution in the treatment with exclusive mineral fertilization. Liming and FYM applications caused an increase of B and Mo contents in soil

Table 5. Relationship between microelement uptake by plants and the content of these elements in the soil solution (solution recovery coefficient) (mean from 2009–2011)

Treatment	B	Cu	Fe	Mn	Mo	Zn
Winter wheat						
Ca	0.30^{a}	0.68^{ab}	0.29^{a}	0.20^{a}	0.58^{a}	0.91^{b}
FYM	0.33^{a}	0.76^{b}	0.29^{a}	0.22^{a}	0.65^{ab}	0.80^{a}
NPK	0.35^{a}	0.66^{a}	0.30^{a}	0.23^{ab}	0.64^{ab}	1.00^{b}
CaPK	0.36^{ab}	0.66^{a}	0.30^{a}	0.24^{ab}	0.73^{b}	0.85^{ab}
CaNP	0.38^{b}	0.77^{b}	0.30^{a}	0.25^{b}	0.74^{bc}	0.90^{b}
CaNK	0.39^{b}	0.57^{a}	0.27^{a}	0.21^{a}	0.77^{c}	0.77^{a}
CaNPK	0.36^{ab}	0.74^{b}	0.30^{a}	0.25^{b}	0.69^{b}	0.80^{a}
CaNPK + FYM	0.36^{ab}	0.83^{b}	0.29^{a}	0.26^{b}	0.70^{b}	0.73^{a}
Potatoes						
Ca	0.75^{a}	0.95^{a}	0.36^{a}	0.28^{a}	0.43^{a}	0.78^{b}
FYM	0.77^{a}	1.00^{ab}	0.35^{a}	0.30^{a}	0.46^{a}	0.65^{a}
NPK	0.87^{b}	0.94^{a}	0.38^{ab}	0.33^{ab}	0.48^{ab}	0.88^{c}
CaPK	0.98^{bc}	1.03^{ab}	0.41^{b}	0.37^{b}	0.60^{b}	0.82^{b}
CaNP	1.05^{c}	1.21^{c}	0.41^{b}	0.40^{b}	0.61^{b}	0.88^{c}
CaNK	1.08^{c}	0.89^{a}	0.38^{ab}	0.33^{ab}	0.63^{b}	0.75^{ab}
CaNPK	1.03^{c}	1.21^{c}	0.43^{b}	0.40^{b}	0.59^{b}	0.81^{bc}
CaNPK + FYM	0.80^{a}	1.05^{b}	0.33^{a}	0.33^{ab}	0.47^{a}	0.58^{a}
Yellow lupine						
Ca	0.53^{a}	0.42^{a}	0.20^{a}	0.35^{a}	0.53^{a}	0.61^{ab}
FYM	0.68^{b}	0.55^{b}	0.24^{b}	0.46^{b}	0.71^{b}	0.62^{ab}
NPK	0.67^{b}	0.45^{ab}	0.23^{ab}	0.45^{b}	0.64^{ab}	0.73^{b}
CaPK	0.62^{ab}	0.41^{a}	0.21^{a}	0.41^{a}	0.66^{b}	0.56^{a}
CaNP	0.71^{bc}	0.51^{b}	0.22^{a}	0.47^{b}	0.72^{bc}	0.64^{b}
CaNK	0.81^{c}	0.41^{a}	0.22^{ab}	0.43^{ab}	0.82^{c}	0.60^{a}
CaNPK	0.70^{bc}	0.51^{b}	0.23^{a}	0.48^{b}	0.70^{b}	0.59^{a}
CaNPK + FYM	0.66^{b}	0.54^{b}	0.22^{a}	0.48^{b}	0.68^{b}	0.52^{a}

Values indicated with the same letter are not significantly different ($P \leq 0.05$)

and the soil solution. Microelement quantities determined in the soil solution are sufficient to cover plant nutritional needs.

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Corresponding author:

Dr. hab. Beata Rutkowska, Warsaw University of Life Sciences-SGGW, Agricultural Chemistry Department, Nowoursynowska 159, 02 776 Warsaw, Poland
phone: + 22 5932 628, e-mail: beata_rutkowska@sggw.pl