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CHANGES OF SOIL ABUNDANCE IN MICROELEMENTS  
IN LONG-TERM FERTILIZER EXPERIMENT (CZARNY POTOK)

*Received April 28, 2006*

*Abstract.* In the presented investigations contents of selected microelements were determined in soil and meadow sward of static fertilizer experiment at Czarny Potok near Krynica. The experiment set up in 1968 on the natural mountain meadow comprises 8 fertilizer objects. The studies presented in the work concern 36th year of the experiment. B, Mn, Zn, Fe, Cu and Co were determined in the 0-10 cm soil. Soil microelement forms soluble in 1 mol HCl dm<sup>-3</sup> and acidification indices were assessed. Long-term mineral fertilization had a significant effect on the contents of microelements in the soil of the permanent meadow and these changes were multidirectional. Diversification in the contents of microelements resulted from unilateral fertilization with phosphorus, acidifying effect of fertilizers and from liming which blocked solubility of microelements in the soil. The contents of most microelements in the soil of mountain meadow fertilized with mineral fertilizers for many years were considered as medium with the exception of boron which content oscillated between the low and medium. This justifies the necessity of boron fertilization.

Problems of microelement content in soil become an important factor in farm economy therefore intensive fertilization of grasslands must be associated with their better protection against excessive degrading [7]. The protection enables avoidance of phenomena negative from both agricultural and ecological perspective, because nutrients, which are not taken up by plants may be for example transferred into the soil profile with rainwater [5] or accumulate in the topsoil.

Soil reaction is one of the main factors affecting microelement phyto-availability [1]. Beside soil class, soil reaction became the main factor allowing to classify soil into microelement abundance class on the basis of its content extracted by 1 mol HCl dm<sup>-3</sup>. The assessment is not widely popular due to weak soil-plant relationships, but currently it has been the only quantified method.

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## MATERIALS AND METHODS

In the presented investigations concentrations of selected microelements were determined in the soil and meadow sward of static fertilizer experiment at Czarny Potok near Krynica (Table 1) [4]. The experimental soil belongs to acid brown soils with granular composition of light loam. The experiment set up in 1968 on a natural mountain meadow, comprises 8 treatments in two series (0Ca and +Ca): 1 – PK; 2 – 90 kg N<sub>s</sub> ha<sup>-1</sup> + PK; 3 – 180 kg N<sub>s</sub> ha<sup>-1</sup> + PK; 4 – 90 kg N<sub>m</sub> ha<sup>-1</sup> + PK; 5 – 180 kg N<sub>m</sub> ha<sup>-1</sup> + PK; 6 – 90 kg N<sub>s</sub> ha<sup>-1</sup>; 7 – P; 8 – no fertilization applied (s – ammonium nitrate, m – urea, K – 150 kg K<sub>2</sub>O ha<sup>-1</sup>, P – 90 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>). In 1985 the experimental design was modified and liming was applied (+Ca) on a half of each treatment. The measure was repeated in 1995. In 1994 a single regenerative treatment was applied with 10 kg Cu and 8 kg Mg ha<sup>-1</sup> as sulphates.

TABLE 1. BASIC INFORMATION ABOUT THE ECOSYSTEM OF THE EXPERIMENT

Feature	
Year of outset	1968
Location	20°54" E; 49°24" N; Beskid Sądecki 700 m a.s.l.; 7°
Initial botanical status	<i>Nardus stricta</i> ; <i>Festuca rubra</i>
Initial species number	39
Air temperature * (°C)	5,8/12,0
Rainfall * (mm)	853/568
Edaphic conditions	Dystric Cambisols (FAO) AhA (0-20 cm), ABbr (21-46 cm); BbrC (47-75 cm), % fraction 1-0.1 mm – 40; 0.1-0.02 mm – 37; <0.02 mm – 23
Initial soil reaction	pH KCl – 4.1
Plot area	42 m <sup>2</sup> (from 1985 ½ 42 m <sup>2</sup> )

\* year / growing period.

The research presented in the work relates to the 3rd and 37th year of the experiment. Following the second cut harvesting in Autumn 2004 soil samples were collected from the 0-10 cm layer and B, Mn, Zn, Fe, Cu and Co were assessed in them using ICP technique. Assessed were soil forms of microelements soluble in 1 mol HCl dm<sup>-3</sup> (according to Polish Standard [6]) and acidification indices were assessed.

## RESULTS AND DISCUSSION

As a result of long-term fertilization the soil reaction (Table 2) became significantly diversified on individual treatments, particularly due to nitrogen fertilizer. In the ninth year of the experiment after liming notable differences in soil reaction on individual treatments persisted. Soil reaction in the limed series revealed lesser diversification in comparison with 0Ca series, particularly when the absolute values of hydrogen ions share in acidification were considered.

The soil contents of manganese soluble in 1 mol HCl dm<sup>-3</sup> (Table 2) ranged between 95.8 and 156.4 mg Mn kg<sup>-1</sup>, however higher values were registered for +Ca series. In the 0Ca series the content of soil soluble manganese was significantly different between treatments receiving different nitrogen doses against PK treatment. The differences testify a considerable impact of acidification caused by intensive nitrogen fertilization and soil depletion of this element as a result of its removal with plant yield and point to a possible limiting these losses through liming. In both series only the application of unilateral P and PK fertilization caused that the soluble manganese content remained on the same level. Soil manganese content on all treatments of both series ranged widely within the medium soil abundance in this element.

Zinc content interval in the soil classified to medium soil category extended between 4.6 and 20.5 mg Zn kg<sup>-1</sup>. In both experimental series the lowest value for this element was registered on treatments receiving 180kg N ha<sup>-1</sup> as ammonium nitrate against PK background. In the 0Ca series zinc content in soil fertilized unilaterally with P and PK differed significantly from the content noted on the other treatments (Table 2). It might be caused by formation of zinc phosphates, from which microelement availability to plants is limited [1,2]. In the +Ca series at the lowest pH on unilaterally N-fertilized treatment, the highest content of this element were detected, whereas at the highest pH (5.59) on the treatment receiving 180 kg N as ammonium nitrate against PK background, the lowest quantities of this element were registered – 6.59 mg Zn kg<sup>-1</sup>. It confirms the significant effect of soil reaction and quantity of removed element on the degree of its mobilization from total forms and in consequence protection of the microelement resources in soil.

Copper content in soils of both series ranged between 4.92 and 10.54 mg Cu kg<sup>-1</sup>, which classified soils from individual treatments to the category with medium and high Cu content. In this case the diversification among treatments may be affected by 10 kg Cu ha<sup>-1</sup> applied ten years earlier as sulphate. In the studies conducted by Woźniak [7] higher content of copper (12.1 to 32.3 mg kg<sup>-1</sup> d.m.) were registered in acid brown soils. In the experiment discussed, the highest copper content in both series were noted in treatments unilaterally fertilized by P. Like for zinc, it might have resulted from copper phosphates formation and decreased leaching of this element into the soil profile due to the higher soil reaction [3].

TABLE 2. ACIDIFICATION INDEX AND CONTENTS (mg kg<sup>-1</sup> D.M. SOIL) OF MICRO-ELEMENTS SOLUBLE IN 1 M HCl dm<sup>-3</sup> AND IN 0Ca AND +Ca SERIES

Fertilization objects	pH KCl	Zn	Cu	Mn	Co	B	Fe
Mean value for the objects in 1970	4.1 +/-0.1 1*	12.35 +/-1.18	4.45 +/-0.19	370 +/-26.1	1.43 +/-0.14	0.92 +/-0.08	1195 +/-124
0Ca							
PK	4.2 ab**	11.12 h	7.34 ab	149.4 de	0.58 fg	0.804 ab	1778 de
90 kg N <sub>s</sub> ha <sup>-1</sup> + PK	4.5 cd	8.81 defg	8.74 bc	136.6 cde	0.29 abc	0.774 a	1700 cd
180 kg N <sub>s</sub> ha <sup>-1</sup> + PK	4.0 a	8.85 cd	7.43 ab	115.2 ab	0.31bcd	0.983 cde	1832 e
90 kg N <sub>m</sub> ha <sup>-1</sup> + PK	4.5 cd	9.90 efgh	6.32 a	133.8 cde	0.32 bcd	0.876 abc	1830 de
180 kg N <sub>m</sub> ha <sup>-1</sup> + PK	4.1 ab	9.13 bcdef	7.94 bc	95.8 a	0.21 ab	0.898 abcd	1594 cd
90 kg N <sub>s</sub> ha <sup>-1</sup>	4.3 bc	9.58 cdef	7.32 ab	119.8 ab	0.14 a	0.962 cde	1576 abc
P	4.6 D	11.3 lh	10.54 d	141.2 cde	0.28 abc	1.004 de	1552 bcd
'0'– no fertilization	4.7 d	8.95 cde	7.05 ab	139.5 cde	0.36 bcde	0.975 cde	1450 abc
+Ca							
PK	5.5 fgh	8.42 bcd	7.54 ab	155.2 e	0.52 efg	0.990 cde	1612 abcd
90 kg N <sub>s</sub> ha <sup>-1</sup> + PK	5.3 efg	7.94 abc	4.92 a	141.0 cde	0.65 g	0.930 bcde	1480 abc
180 kg N <sub>s</sub> ha <sup>-1</sup> + PK	5.6 h	6.59 a	6.65ab	126.6 bc	0.45 def	1.038 e	1544 abc
90 kg N <sub>m</sub> ha <sup>-1</sup> + PK	5.5 fgh	7.25 ab	7.78 bc	147.6 de	0.52 efg	1.028 e	1418 a
180 kg N <sub>m</sub> ha <sup>-1</sup> + PK	5.6 gh	7.69 abc	5.78 a	134.0 cd	0.58 efg	0.990 cde	1522 abc
90 kg N <sub>s</sub> ha <sup>-1</sup>	5.1 e	10.32 fgh	8.12 c	147.2 de	0.53 efg	1.050 e	1424 ab
P	5.3 efgh	9.04 cdef	10.16 d	156.4 e	0.43 cde	1.182 f	1524abc
'0'– no fertilization	5.2 ef	9.35 def	5.33 a	151.5 de	0.42 cde	1.280 f	1390 a

\*deviation from the mean; \*\* a-h - homogeneous groups according to Fisher's test.

Iron content in soil of the +Ca series remained within the medium content class, i.e. ranged between 700 and 3800 mg kg<sup>-1</sup> soil d.m. It was found that this microelement content increased in all treatments when fertilization was applied, which suggests this element mobilization in the amounts which the meadow sward is unable to take up. Similarly in the research conducted by Woźniak [8] on acid brown soils, the content of iron extracted with hydrochloric acid was significantly bigger than the contents of the other elements.

Because of the soil reaction, the intervals of boron content classes in soil which should be considered are different. The interval considered for the assessment of this element content as medium for the series without liming ranges between 0.8 and 2.6 mg B kg<sup>-1</sup>. In the limed series, with pH between 5.15 and 5.57, the interval of boron content considered as medium was between 1 and 3.2 mg B kg<sup>-1</sup>. Boron contents in soils of both series may be considered on the border between low and medium content. This level of soil boron content, despite low meadow sward sensitivity to this element, justifies the necessity for boron fertilization.

No standard of soil abundance in cobalt has been developed. In the presented experiment cobalt content was particularly diversified by liming. In the soil of the 0Ca series the highest cobalt content was registered on the treatment receiving PK fertilization. Such notable difference in contents in comparison with the other treatments of the 0Ca series is difficult to explain. It may result from systematic application of fertilizers in which Co is bound to ballast or from specific plant composition absorbing smaller quantities of Co in comparison with plants from the other treatments.

Forms of metals extracted with 1 mole HCl dm<sup>-3</sup> are considered to be potentially available in the long period. Comparing mean contents of metals in the 3rd and in the 37th year of the experiment it was found out that these contents were smaller in the 37th year in the case of zinc by 8.5-46.6%, for manganese by 57.2-74.1% and for cobalt by 90.3-54.6%. In the case of boron its content was by 15.9% lower on some objects and on others it was higher by 39% and in the case of iron it was higher by 23-59%. The content of copper (this metal was introduced in the 27th year of the experiment) was by 10-136% higher in the 37th year than in the 3rd year of the experiment. These results indicate that metals were activated differentially and the dynamics of this process was high due to the direct and indirect influence of fertilization.

## CONCLUSIONS

1. Long-term mineral fertilization significantly diversified the content of the microelement extracted with 1 mol HCl dm<sup>-3</sup> in permanent meadow sward but the changes were multidirectional. Diversification in the contents of microelement results from unilateral phosphorus fertilization, acidifying effect of fertilizers and liming blocking microelement solubility in soil.

2. The content of the majority of microelements in mountain meadow soil fertilized by many years with mineral fertilizers ranges within the medium class of their content, except for the boron content fluctuating on the border between the medium and low class.

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#### ZMIANY ZASOBNOŚCI GLEBY W WYBRANE MIKROELEMENTY W DŁUGOTRWAŁYM DOŚWIADCZENIU NAWOZOWYM (CZARNY POTOK)

W prezentowanych badaniach określono zawartość wybranych mikroelementów w glebie oraz runi łąkowej statycznego doświadczenia w Czarnym Potoku k. Krynicy. Doświadczenie założone w 1968 na naturalnej łące górskiej, obejmuje 8 obiektów nawozowych: 1 – PK, 2 – 90 kg N<sub>s</sub>+PK, 3 – 180 kg N<sub>s</sub>+PK, 4 – 90 kg N<sub>m</sub>+PK, 5 – 180 kg N<sub>m</sub>+PK, 6 – 90 kg N<sub>s</sub>, 7 – 90 kg P, 8 – bez nawożenia (s-saletra amonowa, m – mocznik, K – 150 kg K<sub>2</sub>O, P – 90 kg P<sub>2</sub>O<sub>5</sub>). W roku 1985 przeprowadzono wapnowanie połowy każdego obiektu wprowadzając serię z wapnowaniem. W 1995 roku powtórzono zabieg wapnowania. Badania przedstawione w pracy dotyczą 36 roku trwania doświadczenia. W glebie w warstwie 0-10 cm oraz w runi łąkowej I i II pokosu oznaczono B, Mn, Zn, Fe, Cu, Mo. Ocenie poddano glebowe formy mikroelementów rozpuszczalne w 1 mol HCl · dm<sup>-3</sup> oraz wskaźniki zakwaszenia. W ocenie zawartości boru uwzględniono odczyn gleby. Zawartość boru w glebie obiektów serii bez wapnowania można zaliczyć do średniej klasy zasobności tego pierwiastka, przy czym wszystkie wartości są bliskie dolnej granicy tej klasy (0,8 mg B · kg<sup>-1</sup>). W serii wapnowanej ze względu na wyższy odczyn granica zasobności klas niskiej i średniej wynosi 1 mg B · kg<sup>-1</sup>. Przedziały ufności zawartości boru w glebie uzasadniają potrzebę nawożenia tym pierwiastkiem. Wśród pozostałych pierwiastków zawartość w glebie Zn, Cu w obu seriach oraz zawartość Mn w serii bez wapnowania mieściła się w klasie o wysokiej oraz średniej zawartości. Natomiast zawartość Fe oraz Mn w serii wapnowanej zawierała się w granicach średniej zawartości. Wieloletnie nawożenie mineralne różnicowało istotnie zawartość, ekstrahowaną 1 mol HCl · dm<sup>-3</sup>, mikroelementów w glebie łąki trwałej ale zmiany te były wielokierunkowe. Różnicowanie zawartości mikroelementów wynika z jednostronnego nawożenia fosforem, zakwaszającego wpływu nawozów oraz wapnowania blokującego rozpuszczalność mikroelementów w glebie.