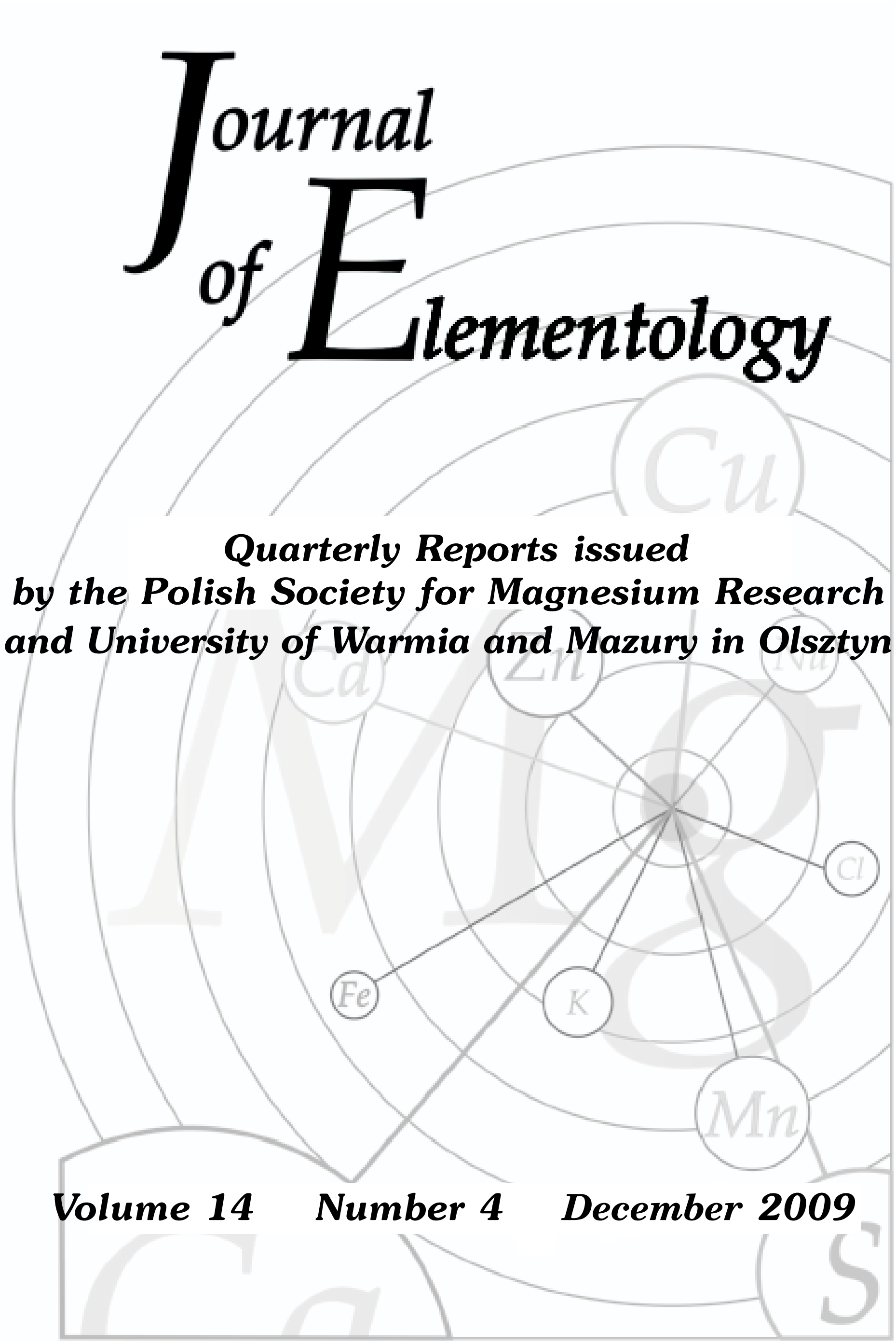

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THE EFFECT OF VARIOUS FORMS OF SULPHUR AND NITROGEN ON CALCIUM AND MAGNESIUM CONTENT AND UPTAKE IN SPRING WHEAT (*TRITICUM AESTIVUM* L.) AND COCKSFOOT *(DACTYLIS GLOMERATA* L.)

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Abstract

The study assessed the effect of various forms of sulphur ($Na_2S_2O_3$, elemental S and Na_2SO_4) and nitrogen (UAN-30, NH_4NO_3) on calcium and magnesium content and uptake in spring wheat and cocksfoot. A two-year pot experiment was conducted on soil material of clayey silt granulometric composition. Before the experiment, the soil was characterized by slight acidity and low content of assimilable forms of phosphorus, potassium, magnesium and sulphur. The results show that the experimental factors caused noticeable variation in the content and uptake of calcium and magnesium in spring wheat and cocksfoot. Among the sulphur fertilizers, the greatest increase in calcium and magnesium content and uptake was produced by application of sodium sulphate. The increase in calcium and magnesium uptake was more marked in the case of plants fertilized with nitrogen in the form of ammonium nitrate. The effect of nitrogen fertilization on the analyzed parameters also depended on the species of plant. Wheat grown in the series with ammonium nitrate was characterized by higher Ca and Mg content and uptake than plants fertilized with nitrogen in the form of liquid UAN 30. Calcium uptake by wheat fertilized with NH_4NO_3 was on average 15% higher for grain and 9% higher for straw compared to wheat fertilized with UAN 30. As for magnesium, the increase was 24.5% and 18%, respectively. Concerning cocksfoot, fertilization with UAN 30 had a greater affect on content and uptake of the analyzed nutrients than ammonium nitrate.

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Key words: calcium content, magnesium content, uptake, form of sulphur, nitrogen fertilization, spring wheat, cocksfoot.

WPŁYW RÓŻNYCH FORM SIARKI I AZOTU NA ZAWARTOŚĆ ORAZ POBRANIE WAPNIA I MAGNEZU PRZEZ PSZENICĘ JARĄ *(TRITICUM AESTIVUM* L.*)* I KUPKÓWKĘ POSPOLITĄ (*DACTYLIS GLOMERATA* L.*)*

Abstrakt

W pracy oceniono wpływ różnych form siarki ($Na_2S_2O_3$, S el. i Na_2SO_4) i azotu (RSM-30, NH_4NO_3) na zawartość i pobranie wapnia i magnezu przez pszenicę jarą i kupkówkę pospolitą. Dwuletnie doświadczenie wazonowe przeprowadzono na materiale glebowym o składzie granulometrycznym pyłu ilastego. Gleba przed doświadczeniem charakteryzowała się lekko kwaśnym odczynem oraz niską zawartością przyswajalnych form fosforu, potasu, magnezu i siarki. Wykazano, że czynniki doświadczalne widocznie zróżnicowały zawartość i pobranie wapnia i magnezu przez pszenicę jarą i kupkówkę pospolitą. Spośród nawozów siarkowych największy wzrost zawartości i pobrania wapnia oraz magnezu przez rośliny spowodowało zastosowanie siarczanu sodu. Wzrost pobrania wapnia i magnezu był bardziej wyraźny w przypadku roślin nawożonych azotem w postaci saletry amonowej. Wpływ nawożenia azotem na analizowane parametry był także uzależniony od gatunku uprawianej rośliny. Pszenica uprawiana w serii z saletrą amonową charakteryzowała się wyższą zawartością oraz pobraniem Ca i Mg w porównaniu z wartościami uzyskanymi dla roślin nawożonych azotem w formie płynnego nawozu RSM-30. Pobranie wapnia przez pszenicę w obiektach NH_4NO_3 było średnio o 15% większe w przypadku ziarna i o 9% w przypadku słomy w porównaniu z obiektami nawożonymi RSM-30. W przypadku magnezu wzrost ten wynosił odpowiednio 24,5 i 18%. W przypadku kupkówki, nawożenie RSM-30 w większym stopniu niż saletrą amonową wpływało na zawartość i pobranie analizowanych składników przez rośliny.

Słowa kluczowe: zawartość wapnia, zawartość magnezu, pobranie, forma siarki, nawożenie azotem, pszenica jara, kupkówka pospolita.

INTRODUCTION

Calcium is an essential nutrient for the proper growth and development of plants (Adcock et al. 2001). Magnesium is a component of plant tissues serving various physiological functions. Supplying plants with appropriate amounts of these macroelements is essential for the quantity and quality of yields. The literature indicates that fertilization with sulphur affects the uptake and utilization of nutrients by plants, including calcium and magnesium (McGrath et al. 1996), while sulphur deficiency can significantly limit their utilization of other nutrients (Sepúlveda et al. 1993, Lošák et al. 2000). At the same time, excess sulphur generally has a negative effect on the chemical composition of plants and acts antagonistically to uptake of certain ions (Skwierawska et al. 2006b). Appropriate nitrogen fertilization is also necessary for proper plant production. The amount and form of fertilizer applied are important as well (Howard et al. 2002). Hence, the aim of this study was to determine the effect of various forms of sulphur and nitrogen on calcium and magnesium content and uptake in spring wheat and cocksfoot.

MATERIALS AND METHODS

The study was based on plant material obtained in a two-year strict pot experiment conducted on soil material taken from the arable layer of brown soil of clayey silt granulometric composition. The soil was characterized by slight acidity and low content of assimilable forms of phosphorus, potassium, magnesium and sulphur.

The experiment was set up in a completely randomized design. There were two variables: the form of nitrogen fertilizer and the form of sulphur. Nitrogen was applied in the form of UAN 30 (urea ammonium nitrate solution) and NH_4NO_3 (granular form), and three forms of sulphur were used – $Na_2S_2O_3$, elemental S and anhydrous Na_2SO_4. The fertilizers were applied according to the scheme in Table 1. Sulphur in the form of $Na_2S_2O_3$ and Na_2SO_4 was applied in liquid form, and elemental sulphur was added in solid form. Before weighted portions were measured out, the granules were pulverized in an agate mortar.

This paper concerns the effect of the experimental factors on calcium and magnesium content and uptake by spring wheat (*Ismena* variety) and cocksfoot (*Bepro* variety). Nitrogen was applied to plants in the amount of 0.14 $g\ N \cdot kg^{-1}$ soil, and sulphur in the amount of 0.025 $g\ S \cdot kg^{-1}$ soil. Half of the nitrogen was applied before sowing, and the remainder after the plants were thinned to an optimal number in a pot. After fully mature wheat (straw and grain) and cocksfoot were harvested, calcium and magnesium content in average samples was determined using atomic absorption spectrometry (Hitachi Z-8200). Uptake of these elements by the plants was calculated based on the content of these nutrients and the yield during the vegetative period.

RESULTS AND DISCUSSION

Calcium and magnesium content and uptake in dry mass of the test plants depended on the experimental factors applied, the species and organ of the plant, and in the case of cocksfoot, on when it was harvested (Table 1).

Calcium content in wheat grain ranged from 0.92 to 1.32 $g\ Ca \cdot kg^{-1}$. A decrease in calcium content caused by sulphur fertilization was noted

Table 1

The effect of sulphur form and nitrogen fertilization on the calcium and magnesium content in spring wheat and cocksfoot and uptake of these elements

Object	Spring wheat				Cocksfoot			
	grain		straw		first cut		second cut	
	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg
Content of calcium and magnesium (g Ca, Mg$\cdot$kg^{-1})								
RSM-30	1.21	1.02	4.32	0.81	8.51	2.31	7.12	2.29
RSM-30 + $Na_2S_2O_3$	1.10	1.21	4.80	0.81	9.23	2.32	8.53	2.25
RSM-30 + elementary S	1.10	1.04	4.71	1.03	8.94	2.01	7.90	2.20
RSM-30 + Na_2SO_4	1.23	1.42	5.04	1.02	10.23	2.35	9.71	2.31
NH_4NO_3	0.92	1.34	4.43	0.92	8.09	2.28	7.82	2.21
NH_4NO_3 + $Na_2S_2O_3$	1.12	1.42	4.59	0.92	8.53	2.40	8.05	2.35
NH_4NO_3 + elementary S	1.23	1.20	4.68	1.01	8.00	2.41	7.72	2.20
NH_4NO_3 + Na_2SO_4	1.32	1.53	5.12	1.20	9.90	2.61	9.51	2.41
Uptake of calcium and magnesium (g Ca, Mg$\cdot$pot^{-1})								
RSM-30	0.016	0.014	0.077	0.014	0.105	0.029	0.113	0.036
RSM-30 + $Na_2S_2O_3$	0.018	0.020	0.110	0.019	0.125	0.031	0.158	0.042
RSM-30 + elementary S	0.017	0.016	0.101	0.022	0.115	0.026	0.142	0.039
RSM-30 + Na_2SO_4	0.020	0.023	0.112	0.023	0.145	0.033	0.189	0.045
NH_4NO_3	0.013	0.019	0.082	0.017	0.090	0.025	0.102	0.029
NH_4NO_3 + $Na_2S_2O_3$	0.019	0.024	0.110	0.022	0.103	0.029	0.123	0.036
NH_4NO_3 + elementary S	0.021	0.020	0.109	0.024	0.092	0.028	0.115	0.033
NH_4NO_3 + Na_2SO_4	0.023	0.027	0.126	0.029	0.133	0.035	0.155	0.039

in wheat fertilized with UAN 30 + $Na_2S_2O_3$ and UAN 30 + elemental S, where grain contained 10% less of this nutrient than in objects without sulphur. In the object with UAN 30 and sulphur applied in the form of sodium sulphate, however, no clear change in calcium content was noted in wheat grain. A more marked increase, 33% on average, was observed in the calcium content of spring wheat grain in all of the plants fertilized with ammonium nitrate and sulphur. SKWIERAWSKA et al. (2006b) also noted an increase in calcium content in the grain of cereal crops after application of sulphur in the form of sulphate and elemental S compared with objects without sulphur. Calcium content in wheat straw was higher than in the grain, ranging from 4.32 to 5.12 g $Ca \cdot kg^{-1}$. An increase in Ca content in dry mass of straw was noted in all objects to which sulphur was added, averaging 10.5%, compared with plants which were not fertilized with this nutrient. Calcium content was higher in the dry mass of the first cut of cocksfoot, ranging from 8.00 to 10.23 g $Ca \cdot kg^{-1}$, while in the plants from the second cut it ranged from 7.12 to 9.71 g $Ca \cdot kg^{-1}$. A slight decrease in calcium content in this plant was only observed in the object with NH_4NO_3+ elemental S, both in the first and second cuts. In the remaining objects, calcium content in dry mass of cocksfoot increased when sulphur was added.

In plants from most of the objects to which sulphur was applied, magnesium was higher than in the objects without sulphur. As in the case of calcium, the greatest increase in magnesium content in dry mass of the test plants occurred when sulphur was applied in the form of sodium sulphate. On the other hand, a marked decrease in magnesium content was observed in grain of wheat fertilized with NH_4NO_3 + elemental S and in cocksfoot hay from the first cut in the objects with UAN 30 + elemental S. Lower magnesium content was noted in the second cut of cocksfoot fertilized with elemental S, irrespective of the form of nitrogen applied.

The effect of nitrogen fertilizer on magnesium and calcium content in the test plants did not show a clear tendency. In the case of wheat, in some of the objects application of nitrogen in the form of ammonium nitrate was associated with an increase in calcium content compared with analogous objects in the series with nitrogen applied in the form of UAN 30. However, application of UAN 30 was associated with higher calcium content in the dry mass of the plants, both in grain of wheat that was not fertilized with sulphur and in cocksfoot, compared with the objects fertilized with NH_4NO_3.

Magnesium content in the grain and straw of spring wheat in objects where the nitrogen source was ammonium nitrate was about 15-18% higher than where UAN 30 was used. The dry mass of cocksfoot from most of the objects with nitrogen in the form of NH_4NO_3 also contained more magnesium than in objects with UAN 30. CHERNEY et al. (2004) also observed that nitrogen fertilizer in the form of ammonium nitrate stimulated an increase in magnesium content in plants.

Sulphur fertilization caused a marked increase in calcium and magnesium uptake with the yield of both test plants. The most marked increase in uptake of these nutrients compared to the objects without sulphur was observed where its source was sodium sulphate. It seems likely that the presence of sulphate ions in the soil facilitated uptake of magnesium ions (BRODOWSKA, KACZOR 2005). It should be added that the increase in calcium and magnesium uptake in these objects was more marked in the series in which nitrogen was applied in the form of ammonium nitrate than in the objects fertilized with UAN 30. The results obtained are confirmed by studies by other authors (SKWIERAWSKA et al. 2006a, b), who found that fertilization with sulphur increased total magnesium and calcium uptake by plants. The increase in uptake of these nutrients by wheat and cocksfoot is partly due to the effect of sulphur on yield of crop plants (KACZOR, BRODOWSKA 2005, 2009).

The effect of nitrogen application on calcium and magnesium uptake by the test plants was varied, as in the study by KOC and SZYMCZYK (2001). Regarding wheat (grain and straw), nitrogen in the form of NH_4NO_3 stimulated greater uptake of these elements than UAN 30. Calcium uptake by wheat fertilized with NH_4NO_3 was on average 15% higher in the case of grain and 9% higher in the case of straw, compared to objects fertilized with UAN 30. Concerning magnesium, the increase was 24.5% and 18%, respectively.

The effect of nitrogen fertilization on calcium and magnesium uptake by cocksfoot was the reverse of its effect on spring wheat. The first cut of cocksfoot took up on average 18% more calcium with the yield of plants fertilized with UAN 30 compared with analogous objects fertilized with ammonium nitrate. With respect to the second cut, the difference was 21%. Magnesium uptake by cocksfoot from the series with UAN 30, harvested in the second cut, was on average 18.5% higher than in plants fertilized with ammonium nitrate. Therefore, it can be firmly concluded that in objects fertilized with nitrogen in the form of UAN 30 calcium and magnesium uptake by cocksfoot was higher than in the case of NH_4NO_3. The only exception to this rule was magnesium uptake by plants from the first cut of cocksfoot fertilized with elemental sulphur and Na_2SO_4.

CONCLUSIONS

1. Fertilization with sulphur in the form of Na_2SO_4 caused the most marked increase in calcium and magnesium content in dry mass of the test plants.

2. Ca and Mg content in dry mass of spring wheat was higher in objects with nitrogen supplied in the form of ammonium nitrate, while in the case of cocksfoot, in objects fertilized with UAN 30.

3. Application of sulphur, especially in the form of sodium sulphate, caused an increase in uptake of the analyzed elements by spring wheat (straw and grain) and cocksfoot (both cuts).

4. Ca and Mg uptake by spring wheat was higher in the series fertilized with ammonium nitrate, while uptake by cocksfoot was higher in objects in which nitrogen was supplied in the form of UAN 30.

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CHANGES OF THE MINERAL PROFILE OF SERUM OF GOATS IN VARIOUS PHYSIOLOGICAL STATES

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Abstract

The aim of this work was to obtain comparative evaluation of the content of calcium (both the total and ionic forms), magnesium and phosphorus in the blood serum of goats during three physiological states characterized by much instability of the mineral balance.

The study involved 15 goats, divided into 3 groups in different physiological states (breeding season, pregnancy, lactation period). The study showed that the mean content of the ionic form of calcium (*A,D* – 1.210; *B,E* – 1.135; *C,F* – 1.115) and total calcium (*A,D* –1.640; *B,E* – 2.075; *C,F* – 2.045) in all the groups was within the range reference concentrations. It can be thought that the low content of calcium was caused by its deficiency in fodder and unstable hormonal balance (pregnancy and lactation period).

The reason why the mean content of calcium did not reach the reference level for this species was a high content of P (*A,D* – 1.650; *B,E* – 2.040; *C,F* – 2.125) and Mg (*A,D* – 0.970; *B,E* – 1.415; *C,F* – 0.990) in blood serum.

Key words: goats, breeding season, pregnancy, lactation, macroelements.

ZMIANY PROFILU MINERALNEGO SUROWICY KÓZ W RÓŻNYCH STANACH FIZJOLOGICZNYCH

Abstrakt

Celem doświadczenia było porównanie stężeń wapnia (całkowitego i zjonizowanego), magnezu i fosforu nieorganicznego w surowicy kóz w trzech okresach aktywności fizjologicznej, tj. w czasie dużej chwiejności gospodarki mineralnej ustroju.

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Badanie przeprowadzono na 15 kozach rasy saaneńskiej, podzielonych na 3 grupy, będących w różnych okresach fizjologicznych (stanówka, wysoka ciąża, laktacja).

Wykazano, że średnie wartości jonów wapnia (*A,D* – 1,210; *B,E* – 1,135; *C,F* – 1,115) oraz wapnia całkowitego (*A,D* – 1,640; *B,E* – 2,075; *C,F* – 2,045), w surowicy wszystkich badanych grup kóz, znajdowały się poniżej norm referencyjnych. Wytłumaczeniem niskich poziomów wapnia może być jego nieodpowiednia podaż w pożywieniu, w okresie ciąży i laktacji, kiedy następuje rozchwianie gospodarki hormonalnej, i tym samym nie ma możliwości odpowiedniej regulacji zawartości wapnia w surowicy.

Przyczyną obniżenia ilości Ca nawet poniżej norm fizjologicznych może być także stosunkowo wysoka zawartość P (*A,D* – 1,650; *B,E* – 2,040; *C,F* – 2,125) i Mg (*A,D* – 0,970; *B,E* – 1,415; *C,F* – 0,990) w surowicy. Potwierdzeniem tego okazały się wyniki otrzymane w doświadczeniu.

Słowa kluczowe: kozy, stanówka, ciąża, laktacja, makroelementy.

INTRODUCTION

The largest instability of the organism's mineral balance is observed during the perinatal period. This period is also characterized by metabolic and hormonal disorders. Mineral disorders, usually short-lasting, are a natural phenomenon during the delivery and developing lactation. They usually disappear a few days after the kidding without any influence on the animal's health and fertility. If, however, they are compounded by deficiency of minerals in fodder or by lowered absorption, complications in the course of impregnation and impaired reproductive abilities may appear as well as various complications after the delivery (Kruczyńska, Mocek 1997).

The level of daily mineral component requirements of animals, in this case goats, is important. The following factors play an important role as well: the animal's age, sex, physiological state or the type of breeding. Domesticated goats, kids or dairy goats have different requirements (Kruczyńska, Mocek 1997).

Being ruminants, goats eat fodder containing very diversified levels of dry matter and organic matter. The content of calcium, magnesium and phosphorus in fodder used for goat feeding is usually sufficient. Goats with high milk yield, during lactation as well as kids have to be given mineral mixtures (Kruczyńska, Mocek 1997).

One of the macroelements described in this paper is calcium, which is an element necessary for the proper growth and development. Goats' daily calcium requirement equals 11-17 g. Natural sources of calcium for every organism (both human and animal) are milk and milk products, nuts, sesame seeds, yeast and some types of cereal (Wierzbicka 1996).

The organism's phosphorus requirement is strictly connected with its calcium demand. The optimal Ca to P ratio in a diet should be 1 mmol Ca to 1 mmol P. The indispensable amount of phosphorus for ruminants is 0.3-0.4% in the dry matter of a fodder ration. The concentration of both P and Ca is strictly connected with the quality and value of the fodder since the content of these elements in plants decreases as their vegetation progresses (KRUCZYŃSKA, MOCEK 1992). Among natural sources of phosphorus which ruminants find in food are cereal grains (WIERZBICKA 1996).

Like calcium and phosphorus, magnesium is a component of bones (WIERZBICKA 1996). Simple nitro-compounds and potassium limit the absorption of magnesium (MADEJ et al. 1994), hence it is necessary to pay attention to the potassium-magnesium-calcium ratio in a dose. The absorption of magnesium from fodder is low, i.e. 25-30%. It is believed that the calcium-magnesium ratio should be 04:01. The determination of magnesium requirement standards depends mainly on the content of this bio-element and other elements (especially K and Ca) in fodder as well as on the animal's species, breed, age and physiological stadium (GABRYSZUK 1988).

This paper aims at the analysis of selected mineral components (total and ionized calcium, magnesium and inorganic phosphorus) of goats' blood serum depending on the physiological state of animals.

MATERIALS AND METHODS

The research comprised 15 Saanen goats. The animals came from a private farm in Świerznica near Rąbin. The research was carried out in winter and spring (December 2002 – April 2003). All the animals were clinically healthy, maintained under identical zoohygienic conditions and fed with fodder rations according to the requirements of goat feeding (oats – 0.7 kg/a goat/daily, hay – at will, 20% high-protein concentrate for goats – 0.21 kg/a goat).

The goats were divided into two age groups depending on their year of birth. Three physiological states were distinguished in every group. Animals from every age group went through consecutive physiological states, during which their blood was taken for testing and elements were marked (letters *A* to *F*).

1. The goats born in 1999 (4 goats):
   - in breeding season (marked with letter *A*),
   - in advanced pregnancy (marked with letter *B*),
   - in lactation period (marked with letter *C*).
2. The goats born in 2000 (11 goats):
   - in breeding season (marked with letter *D*),
   - in advanced pregnancy (marked with letter *E*),
   - in lactation period (marked with letter *F*).

The test material was serum obtained after centrifugation of whole blood taken each time at 9.00 a.m. from the outer jugular vein.

The following biochemical determinations were carried out in the centrifuged blood of every tested animal:

1) the colorimetric analysis, without deproteinization, was used for marking total calcium. Methylene blue was the applied indicator;
2) an electrolyte analyser AVL 9180 was used for marking ionized calcium;
3) the colorimetric analysis, without deproteinization, was used for marking magnesium, with the application of an EGTA calmagite;
4) inorganic phosphorus was also marked by means of the colorimetric analysis without deproteinization. The determination method is based on formation of a phosphomolybdenum complex in the presence of a reductant (iron sulphate). All the results were submitted to statistical calculations with the application of Statistica 6.0 software.

RESULTS AND DISCUSSION

In the analysis of ionized calcium concentration in the blood serum, no significant differences were found in comparable test periods (cf. Table 1, Figure 1). The observed values differed from those accepted to be physiological standards. The level of total calcium in the goats' serum was much higher (Table 1, Figure 2).

Table 1

Ionized calcium concentration, total calcium concentration, magnesium concentration and inorganic phosphorus concentration in the blood serum

Group	Ionized calcium (mmol dm^{-3})			Total calcium (mmol dm^{-3})			Total magnesium (mmol dm^{-3})			Inorganic phosphorus (mmol dm^{-3})		
	A and *D*	*B* and *E*	*C* and *F*	*A* and *D*	*B* and *E*	*C* and *F*	*A* and *D*	*B* and *E*	*C* and *F*	*A* and *D*	*B* and *E*	*C* and *F*
N	15	15	15	15	15	15	15	15	15	15	15	15
X	1.210	1.135	1.115	1.640	2.075	2.045	0.970	1.415	0.990	1.650	2.040	2.125
SD	0.500	0.061	0.320	0.683	0.160	0.297	0.191	0.321	0.439	0.438	0.441	0.332
Maximum	1.290	1.200	1.210	2.446	2.336	2.521	1.310	1.892	1.134	2.267	2.722	2.563
Minimum	1.145	1.045	1.055	0.706	1.891	1.184	0.717	1.020	0.762	1.215	1.428	1.549

N – number of subjects
X – arithmetic mean
SD – standard deviation
A and *D* – goats in breeding season
B and *E* – goats in advanced pregnancy
C and *F* – goats in lactation period

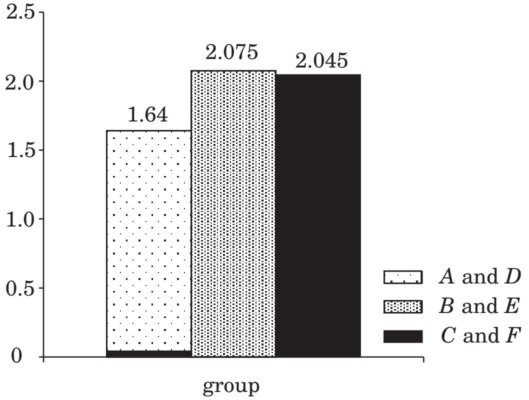

Fig. 1. The average values of ionized calcium concentration (mmol dm^{-3}) in goats' blood serum

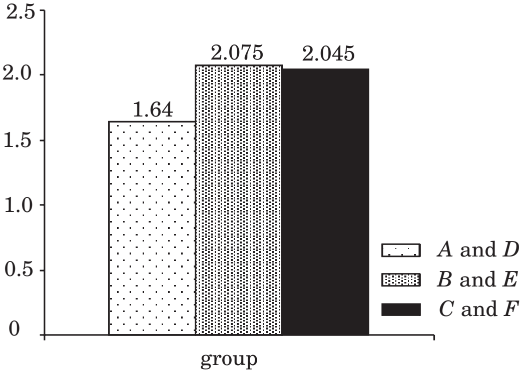

Fig. 2. The average values of total calcium concentration (mmol dm^{-3}) in goats' blood serum

The low value of calcium concentration in the tested goats' blood serum can be explained by an inadequate supply of this element in fodder given to the pregnant goats, as pregnant and breastfeeding goats usually require more mineral components (KLATA et al. 2000). How much calcium ruminants require depends largely on their physiological state, but also on the animals' productivity, and the supply of calcium is optimum when its content in dry matter of a ration equals 0.4-0.8%. High calcium supply and a broad Ca : P ratio is especially unfavourable during advanced pregnancy, just like calcium deficiency is unfavourable at the beginning of pregnancy (KRUCZYŃSKA, MOCEK 1992). The supplementation of easily assimilable calcium compounds considerably improves the calcium balance in the postnatal period. The final positive ratio is influenced by a chloride ion, which lowers the pH of the gastric contents, thus having a stimulating effect on calcium absorption.

During the three physiological periods, the content of another tested element, magnesium, also changed. During the first period, the average level of this element for *A* and *D* was 0.97 mmol dm^{-3}. During pregnancy, there was a rapid increase of magnesium concentration – *B* and *E*: 1.415 mmol dm^{-3}. This was the largest increase in the content of this macroelement. After the kidding, at the beginning of lactation, magnesium concentration was similar in blood samples and the results were much lower for *C* and F: 0.99 mmol dm^{-3} (Table 1, Figure 3). However, the results were within the standards (Winnicka 2002).

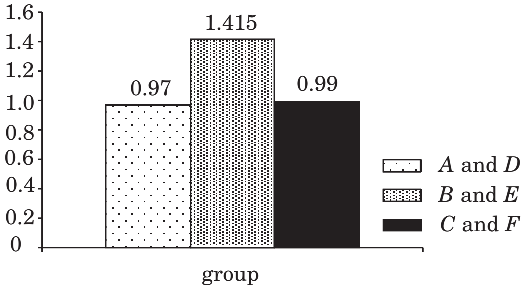

Fig. 3. The average values of magnesium concentration (mmol dm^{-3}) in goats' blood serum

The reason why magnesium level in the blood serum fell may have been the insufficient content of this element in grazing fodder characterized by a low content of dry matter. Lowered magnesium absorption, low assimilation of the macroelement from the skeleton and finally high milk yield are also important (Gabryszuk 1988).

Inorganic phosphorus concentration showed slight differences (Table 1, Figure 4). Among the goats in their breeding season, it equalled: A and *D* – 1.65 mmol dm^{-3}, which was rather low. Among all the tested goats, an increase in the inorganic phosphorus content during pregnancy was observed:

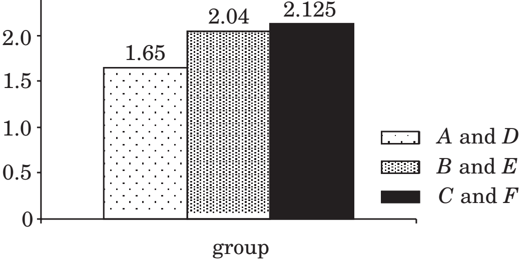

Fig. 4. The average values of inorganic phosphorus concentration (mmol dm^{-3}) in goats' blood serum

B and *F* – 2.04 mmol dm^{-3}. In the lactation period, the values were as follows: *C* and *F* – 2.125 mmol dm^{-3}. Disorders in the relations between calcium and inorganic phosphorus may be the result of worse quality fodder or wrong composition of the feeding dose. Simultaneously, in literature on ruminants, the deficiency of both elements occurring at the same time has rarely been reported, and an increase in the inorganic phosphorus concentration in fodder is usually accompanied by a decrease in calcium absorption (BRZEZIŃSKA et al. 1999).

Young animals as well as pregnant and breastfeeding females are especially sensitive to deficiency of mineral components. Milk yielding animals lose considerable amounts of mineral compounds, which have to be supplemented together with fodder (SABA et al. 2000).

Apart from protein and energy, mineral components play a very important role in the animals' growth, efficiency and physiological functions. The physiological activities are a sufficient reason for a considerable instability of the organism's mineral balance (KRUCZYŃSKA, MOCEK 1997).

CONCLUSIONS

1. In all the tested groups, the level of total and ionized calcium did not exceed the lowest reference value limit. The values of the other bio-element, magnesium, were in the lower normal range in all the tested groups. All the results concerning inorganic phosphorus in the blood serum were in the lower normal range.

2. On the basis of the research and reference data, a conclusion can be drawn that a simultaneous deficiency in calcium and inorganic phosphorus rarely occurs among ruminants, and increased inorganic phosphorus in fodder is usually accompanied by depressed calcium absorption and a considerable decrease of calcium in blood serum. This may result from using worse quality fodder or wrong composition of a feeding ration.

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EFFECT OF FERTILIZATION WITH Fe CHELATES ON THE STATE OF IRON NUTRITION OF GREENHOUSE TOMATO

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Abstract

A greenhouse experiment aimed at investigating the effect of four chelates, differing in percentage of Fe content and the kind of Fe bonding ligand: Fe 8 Forte (EDTA+ +HEEDTA), Fe 9 Premium (DTPA), Fe 13 Top (EDTA) and Librel Fe DP7 (DTPA), on the state of iron nutrition of Merkury F_1 cultivar greenhouse tomato grown traditionally in peat substrate. The second factor was iron content in the growing medium, which was established to reach the following levels: 50, 75 and 100 mg $Fe \cdot dm^{-3}$, while in the control object Fe values ranged 17.9 $Fe \cdot dm^{-3}$ (after peat liming). The experiment was established in a two-factorial design with three replications including four plants cultivated on one plot. The iron content was assayed in plant index parts according to the ASA method. On the basis of the results, significant differences were found in the state of greenhouse tomato nutrition under the influence of the examined iron chelates. The highest content of iron in tomato leaves was determined when chelate Fe 9 Premium (DTPA) was used, which points to the fact that it was the best source of Fe. The lowest iron level was recorded after the application of Fe 13 Top (EDTA). The highest mean Fe content for the years and dates of analyses appeared in leaves of plants cultivated in the growing medium containing 75 mg $Fe \cdot dm^{-3}$. In June, after the plants began to yield, there was a considerable decrease in the Fe content in plant index parts in comparison to the stage of fruit maturation and the end of yielding. The study did not demonstrate any symptoms of phytotoxicity or visible disorders regarding tomato growth and development due to the examined Fe chelates introduced in the doses of 32.1, 57.1 and 82.1 mg $Fe \cdot dm^{-3}$ to the substrate, whose initial Fe concentration after peat liming was on average 17.9 mg $Fe \cdot dm^{-3}$.

Key words: greenhouse tomato, fertilization, chelates, index parts, iron uptake.

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WPŁYW NAWOŻENIA CHELATOWMI FORMAMI Fe NA STAN ODŻYWIENIA POMIDORA SZKLARNIOWEGO ŻELAZEM

Abstrakt

W doświadczeniu szklarniowym badano wpływ czterech chelatów, różniących się procentową zawartością żelaza oraz rodzajem ligandu, jakim skompleksowano ten składnik: Fe 8 Forte (EDTA+HEEDTA), Fe 9 Premium (DTPA), Fe 13 Top (EDTA) i Librel Fe DP7 (DTPA), na stan odżywienia żelazem pomidora szklarniowego odmiany Merkury F_1 uprawianego metodą tradycyjną w substracie torfowym. Drugim czynnikiem badawczym była zróżnicowana zawartość żelaza w podłożu, którą doprowadzono do wartości: 50, 75 i 100 mg $Fe \cdot dm^{-3}$. Doświadczenie założono w układzie dwuczynnikowym, w trzech powtórzeniach. Na jednym poletku uprawiano 4 rośliny. W częściach wskaźnikowych oznaczano całkowitą zawartość żelaza metodą ASA. Stwierdzono istotne różnice w stanie odżywienia pomidora szklarniowego pod wpływem badanych chelatów żelazowych. Najwyższą zawartość żelaza w liściach pomidora odnotowano, gdy źródłem Fe był chelat Fe 9 Premium (DTPA), a najniższą po zastosowaniu Fe 13 Top (EDTA). Najwyższą średnią zawartość żelaza w liściach uprawianych roślin obliczoną dla lat i terminów analiz stwierdzono, gdy zasobność wynosiła 75 mg $Fe \cdot dm^{-3}$. W czerwcu, po rozpoczęciu plonowania roślin, następował znaczny spadek zawartości żelaza w częściach wskaźnikowych pomidora w porównaniu z pozostałmi terminami analiz. W badaniach nie stwierdzono żadnych objawów fitoksyczności, a także widocznych zaburzeń we wzroście i rozwoju pomidora pod wpływem badanych chelatów żelazowych stosowanych w dawkach 32,1, 57,1 i 82,1 mg $Fe \cdot dm^{-3}$ substratu, którego wyjściowa zasobność po odkwaszeniu torfu wynosiła średnio 17,9 mg $Fe \cdot dm^{-3}$.

Słowa kluczowe: pomidor szklarniowy, nawożenie, chelaty, części wskaźnikowe, pobieranie żelaza.

INTRODUCTION

Microelements, especially iron, play an important role in tomato nutrition. According to CHOHURA et al. (2006), the recommended Fe content in greenhouse tomato leaves should be over 60.0 mg $Fe \cdot kg^{-1}$ of dry matter.

This microelement significantly affects the quantity and quality of tomato yield, especially in greenhouses cultivation with a limited volume of the growing medium. A characteristic feature of Fe ions is their ease of transition into the forms hardly available to plants due to chemical sorption. Iron cations Fe^{+2} under aerobic conditions easily change their valence to Fe^{+3}, which makes them less available to plants (GUERINOT, YI 1994).

The problem of providing appropriate Fe nutrition of tomatoes is quite common, although organic growing media, especially those prepared from peat, contain high amounts of humus compounds, which act as natural chelators for cations. Among the causes of limited availability and Fe uptake by plants are excessively high pH, excessive contents of phosphates and carbonates in the growing medium and its excessively high moisture (TIFFIN et al. 1960).

Application of chelate forms featuring good water solubility and low value of dissociation constant (Komosa et al. 2005) is of a basic way of preventing as well as to reducing retrogradation of Fe cations in a growing medium. Following such treatment, Fe cations are gradually released to the soil solution and they can be taken up by plants in the form of complexes. According to Stuart et al. (1991), chelate Fe fertilizers most often occur as the ligands EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid) or HEEDTA (hydroxyl-2-ethylenediaminetriacetic acid). Persistance of ions and their availability to plants depend on the properties of a chelate compound which complexes Fe cations (Hoffmann, Górecki 2000).

The purpose of this investigation was to assess the effect of chelates Fe 9 Premium, Fe 8 Forte, Fe 13 Top, Librel Fe DP7 on the state of Fe nutrition of Merkury F_1 cultivar greenhouse tomato grown on peat substrate with the traditional method.

MATERIAL AND METHODS

Growing experiments were conducted in a heated greenhouse in 2006-2007. Transplants of Merkury F_1 cultivar greenhouse tomato were planted on benches into peat substrate, with 50 dm^3 of substrate per plant and 3 plants per 1 m^2. The cultivation started in the 2nd decade of April and finished in the 3rd decade of July. Plants were trained for one stem and five trusses. Peat substrate limed with chalk to pH 5.50, provided by Hartman company, was used as a growing medium. In 2006, the available Fe content after peat liming was reduced from 26.2 to 20.2 $Fe \cdot dm^{-3}$, while in 2007, it fell from 50.2 to 15.4 mg $Fe \cdot dm^{-3}$. Before planting tomatoes, the Fe content in the growing medium was standardized to the values recommended for greenhouse tomatoes by KomosA (2005): N – 220, P – 180, K – 350, Ca – 2000, Mg – 200, Mn – 20, Zn – 20, Cu – 5.0, B – 1.5, Mo – 1.5 $mg \cdot dm^{-3}$. In the 2nd decade of July, the plants were additionally fertilized with 5 g N and 10 g K per 1 m^2 of the growing medium

The experiment was established in a two-factorial design including three replications, with four plants per plot. The first factor were chelate fertilizers differing in percentage of Fe content and the kind of ligand they were complexed with, namely: Fe 8 Forte (EDTA+HEEDTA), Fe 9 Premium (DTPA), Fe 13 Top (EDTA) and Librel Fe DP7 (DTPA). The second factor was the Fe content in the growing media, which was established as 50, 75 and 100 mg $Fe \cdot dm^{-3}$. The control treatment involved the growing medium featuring native Fe content.

Fully developed leaves were used as index parts of tomatoes. The samples were collected three times in the course of plant growing period, i.e. in May – before the onset of fruit maturation, in June – at the beginning of yielding, and in July – during full yielding. Plant material, previously dried and ground, was subjected to wet mineralization in a mixture of acids HNO_3:$HClO_4$ 3:1 (v/v). Chemical analyses comprised assays of total Fe content in leaves according to the ASA method. The results were subjected statistical elaboration using analysis and the least significant differences calculated at $p = 0.05$.

RESULTS AND DISCUSSION

Mean values of the results obtained during the entire two-year-investigation, shown in Table 1, proved that the kind of Fe chelate used, as well as its dose *did* significantly differentiate the iron content in index parts of Merkury F_1 cultivar greenhouse tomato. Regardless of the term of analyses, it was possible to state that tomatoes showed of a proper state of nutrition, and the iron content was higher than its minimum value recommended by Chohura and Komosa (2003), equal 60.0 mg Fe kg^{-1} d.m. In another experiment conducted on rockwool as a growing medium, the same authors recorded the iron content in tomato index parts ranging 55-220 mg Fe kg^{-1} d.m. In our own examinations, the mean Fe content in tomato index parts was higher, reaching from 132.1 to 355.8 mg Fe kg^{-1} d.m.

In May, before fruit maturation, the average iron content in leaves of tomato fertilized with Librel Fe DP7 and Fe 9 Premium did not show any significant differences and was considerably higher than the content recorded for the other chelates as well as the control. It was also found that the application of gradually increasing Fe doses contributed to a significant increase in the level of this microelement in tomato leaves as compared to the control. In June, when tomato plants began to yield, the results were quite different. All the means of Fe content determined after the application of particular fertilizers differed significantly and were statistically higher compared to the control. The lowest iron content was recorded in the leaves of plants fertilized with Librel Fe DP7 (156.3 mg $Fe \cdot kg^{-1}$ d.m.), while the highest one – after application of Fe 9 Premium (187.0 mg $Fe \cdot kg^{-1}$ d.m).

On the last term of analyses, in July, similarly to the results of June, all means for the examined fertilizers were significantly different. The highest Fe content (304.3 mg $Fe \cdot kg^{-1}$ d.m.) was assayed in the leaves of plants fertilized with Librel Fe DP7 chelate and the lowest Fe value was obtained for Fe 13 Top (261.6 mg $Fe \cdot kg^{-1}$ d.m.).

The state of plant nutrition was also significantly dependent on the iron concentration in the growing medium. The highest Fe mean content in tomato leaves in June and July was recorded in the plants cultivated at a concentration of 75 mg $Fe \cdot dm^{-3}$ in peat substrate, while in May – at 100 mg $Fe \cdot dm^{-3}$.

Table 1

Iron content in the index part of greenhouse tomato in relation to the kind of chelates and Fe concentration in peat substrate (mean for 2006-2007, mg Fe$\cdot$kg^{-1} d.m.)

Fe fertilizer	Fe concentration in peat substrate (mg Fe$\cdot$dm^{-3})			
	50	75	100	mean
	May			
Fe 13 Top (EDTA)	193.8	283.1	272.5	249.8
Fe 8 Forte (EDTA+HEEDTA)	267.9	238.5	252.7	253.0
Librel Fe DP7 (DTPA)	267.5	279.1	320.9	289.1
Fe 9 Premium (DTPA)	317.4	276.5	269.7	287.9
Mean	261.6	269.3	278.9	
Control				191.9
LSD$_{p=0.05}$ for: fertilizer 3.7 dose 3.2 interaction 9.1				
	June			mean
Fe 13 Top (EDTA)	193.6	192.1	161.0	182.2
Fe 8 Forte (EDTA+HEEDTA)	181.7	195.4	153.8	176.9
Librel Fe DP7 (DTPA)	145.5	181.3	142.1	156.3
Fe 9 Premium (DTPA)	193.4	193.5	174.2	187.0
Mean	178.5	190.5	157.8	
Control				132.1
LSD$_{p=0.05}$ for: fertilizer 3.3 dose 2.8 interaction 8.2				
	July			mean
Fe 13 Top (EDTA)	159.2	333.7	292.1	261.6
Fe 8 Forte (EDTA+HEEDTA)	327.6	342.8	203.0	291.1
Librel Fe DP7 (DTPA)	203.9	355.8	353.4	304.3
Fe 9 Premium (DTPA)	269.3	331.2	253.1	284.5
Mean	240.0	340.9	275.4	
Control				262.5
LSD$_{p=0.05}$ for: fertilizer 4.1 dose 3.6 interaction 10.1				

In the latter term, an important role was also played by the interaction between the kind of fertilizers and their doses. The most satisfactory Fe nutritional state was recorded for Fe 8 Forte and Fe 9 Premium at the Fe concentration equal 50 mg in the growing medium, while in the case of Librel Fe DP7 it was 100 mg Fe·dm^{-3}. The lowest mean content of total iron in tomato index parts in May and June was determined for the control treatment, and in July, when the plants were grown in the medium of initial Fe concentration at the level of 50 mg Fe·dm^{-3}.

In June, on the second term of analyses, a considerable decrease in the mean content of total iron in tomato leaves was observed. This phenomenon could have been caused by the increased plant demand for that component at the beginning of yielding. A similar reaction was reported by Kowalczyk et al. (2008) regarding tomato cultivation on rockwool, as well as Komosa et al. (2005).

The results of this study indicate that the highest mean iron content, regardless of the term of analyses, occurred in the leaves of plants fertilized with Fe 9 Premium chelate (253.1 mg Fe·kg^{-1} d.m.). Similar results (249.9 mg Fe·kg^{-1} d.m.) were obtained for Librel Fe DP7 (Figure 1). The worst state of Fe nutrition was observed after application of Fe 13 Top, which could have resulted from the pH of the growing medium (5.50 at the beginning of cultivation). In the course of tomato production, owing to plant watering with tap water, the reaction of the growing medium gradually increased and when the experiment was terminated, it ranged between 6.50--6.80. According to Komosa et al. (2005) EDTA protects iron cation against retrogradation up to pH 6.20 while DTPA acts up to 9.00. Therefore, the cause of poorer nutrition of plants fertilized with Fe 13 Top could be a result

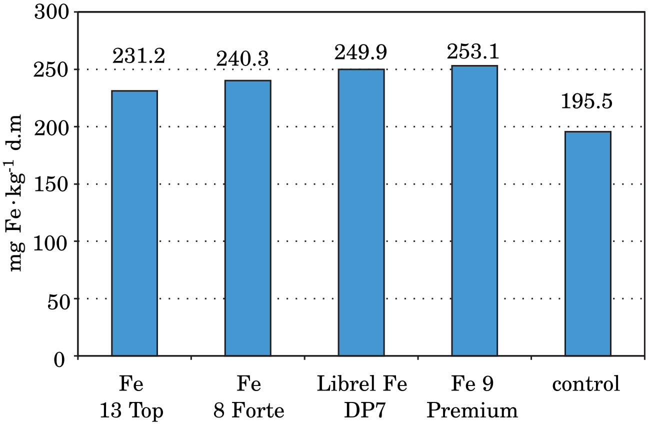

Fig. 1. Effect of the type of iron chelate on Fe content in index part of greenhouse tomato (mean for 2006-2007, mg Fe·kg^{-1} d.m.)

of partial iron retrogradation. In the case of Fe 9 Premium and Librel Fe DP7 fertilizers bound by DTPA, the state of plant nutrition was better and similar for both fertilizers.

Other authors, who examined chelates supplied to rockwool medium (Chohura et al. 2006), proved that the highest mean iron content in index parts was found in plants whose iron source was Librel Fe DP7 (135.2 mg $Fe \cdot kg^{-1}$ d.m.), while after application of Top 12 the analogous content was 123.1 mg $Fe \cdot kg^{-1}$ d.m.

Taking into account the average data for the whole growing period, Fe fertilization of greenhouse tomato up to the level of 50 $Fe \cdot dm^{-3}$ of peat contributed to the improvement of plant nutritional state in relation to the control treatment, not fertilized with iron, containing on average 17.9 mg $Fe \cdot dm^{-3}$. The increase in Fe concentration to 75 $Fe \cdot dm^{-3}$ resulted in the best state of plant nutrition while the content of 100 $Fe \cdot dm^{-3}$ caused some reduction in Fe uptake by tomato plants (Figure 2). That could have been due to the fact that some legands, especially EDTA, can produce disadvantageous effects (Lopez et al. 2007). In our own investigation, there were no symptoms of phytotoxicity or any visible disturbances in the growth and development of greenhouse tomato, despite the fact that relatively high doses of chelate fertilizers had been applied.

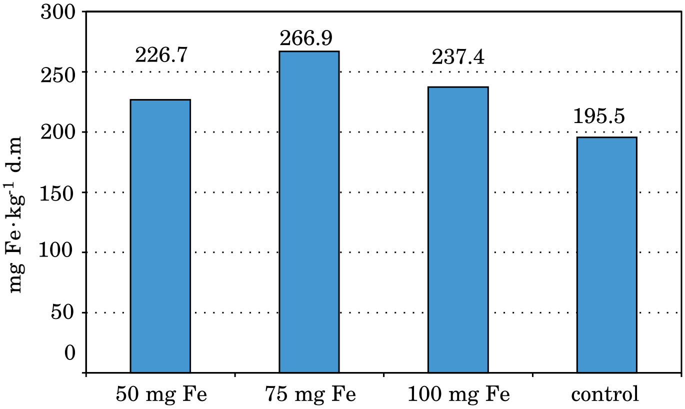

Fig. 2. Effect of iron concentration in peat substrate on Fe content in index part of greenhouse tomato (mean for 2006-2007, mg $Fe \cdot kg^{-1}$ d.m.)

CONCLUSIONS

1. The highest content of iron in tomato leaves was determined when chelate Fe 9 Premium (DTPA) was used, which points to the fact that it was the best source of Fe for this plant species.

2. The highest mean Fe content for all the terms of analyses appeared in the leaves of plants cultivated with 75 mg Fe·dm^{-3} in the growing medium. Further increase in the Fe content up to 100 mg Fe·dm^{-3} resulted in a decrease in the iron content in plant index parts.

3. In June, after the beginning of yielding, a considerable decrease in the Fe content in plant index parts occurred in comparison to the period before fruit maturation as well as the end of yielding.

4. There were no symptoms of phytotoxicity or visible disorders regarding tomato growth and development caused the examined Fe chelates supplied in the doses of 32.1, 571 and 82.1 mg Fe·dm^{-3} of the substrate whose initial Fe concentration after peat liming was on average 17.9 mg Fe·dm^{-3}.

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YIELD OF COCKSFOOT (*DACTYLIS GLOMERATA* L.) AND ITS NITROGEN AND SULPHUR CONTENT AFTER FERTILIZATION WITH VARIOUS FORMS OF THESE NUTRIENTS

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Abstract

This study has analyzed the effect of fertilization with various forms of nitrogen and sulphur on cocksfoot yield and on the content of these nutrients in the plant. The study was based on a strict experiment conducted on soil material from the arable layer of brown soil of clayey silt granulometric composition. The soil used in the experiment was characterized by slight acidity and low content of assimilable forms of phosphorus, potassium, magnesium and sulphur. The results indicate that the experimental factors caused significant variation in cocksfoot yield. Significant variations in yield also occurred as a result of the interaction between these factors. The highest yields were obtained where nitrogen was applied in the liquid form (UAN-30) and sulphur was applied in the form of Na_2SO_4. Significant increases in yield after application of elemental sulphur were not observed until the second cut was harvested, which clearly indicates that this is a slow-acting fertilizer. Fertilization with various forms of nitrogen and sulphur also caused marked variation in total S content, total N content and N-NO_3 in the plants. Total sulphur content – depending on the experimental object and on the time of harvest – ranged from 1.37 to 3.15 g $S \cdot kg^{-1}$, while total nitrogen content ranged from 29.06 to 38.72 g $N \cdot kg^{-1}$. The data obtained indicate that sulphur content in plants that were not fertilized with this nutrient was much lower than is considered optimal for grasses. This explains the effect of sulphur on yield observed in the experiment. Fertilization with sulphur also had a beneficial effect on nitrogen metabolism, manifested as a more than twofold decrease in nitrate nitrogen in the plants fertilized with sulphur.

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Key words: form of sulphur, nitrogen fertilization, sulphur content, nitrogen content, cocksfoot.

PLONOWANIE ORAZ ZAWARTOŚĆ AZOTU I SIARKI W KUPKÓWCE POSPOLITEJ (*DACTYLIS GLOMERATA* L.) NAWOŻONEJ RÓŻNYMI FORMAMI TYCH SKŁADNIKÓW

Abstrakt

W pracy przeanalizowano wpływ nawożenia kupkówki pospolitej różnymi formami azotu i siarki na plonowanie i zawartość tych składników w roślinie. Badania oparto na ścisłym doświadczeniu założonym na materiale glebowym pobranym z warstwy ornej gleby brunatnej o składzie granulometrycznym utworu pyłowego ilastego. Gleba użyta w doświadczeniu charakteryzowała się lekko kwaśnym odczynem oraz niską zawartością przyswajalnych form fosforu, potasu, magnezu i siarki. Wykazano, że czynniki doświadczalne istotnie zróżnicowały plony kupkówki pospolitej. Istotne zróżnicowanie plonów roślin wystąpiło również w efekcie interakcyjnego działania tych czynników. Największe plony roślin uzyskano w serii, w której zastosowano azot w formie płynnej (RSM-30) i siarkę w formie Na_2SO_4. Istotne zwyżki plonów rośliny testowej po zastosowaniu siarki elementarnej odnotowano dopiero przy zbiorze II pokosu, co wyraźnie wskazuje, że jest to nawóz wolno działający. Nawożenie różnymi formami azotu i siarki wpłynęło również widocznie na zróżnicowanie zawartości $S_{og.}$, $N_{og.}$ i N-NO_3 w roślinach. Zawartość siarki ogółem – w zależności od obiektu doświadczalnego i terminu zbioru – wynosiła od 1,37 do 3,15 g $S \cdot kg^{-1}$, a azotu od 29,06 do 38,72 g $N \cdot kg^{-1}$. Stwierdzono, że zawartość siarki w roślinach nie nawożonych tym składnikiem była wyraźnie niższa od wartości przyjętych za optymalne dla traw. Wyjaśnia to plonotwórcze działanie siarki w przeprowadzonym eksperymencie. Nawożenie siarką wywarło również korzystny wpływ na metabolizm azotu. Przejawił się on ponad dwukrotnym obniżeniem zawartości azotu azotanowego w roślinach nawożonych siarką.

Słowa kluczowe: forma siarki, nawożenie azotem, zawartość siarki, zawartość azotu, kupkówka pospolita.

INTRODUCTION

In recent years, there has been a deficiency of sulphur for plants in most countries of the world (KACZOR, KOZŁOWSKA 2000, SCHERER 2001). Alongside plants with high sulphur requirements, grains and grasses belonging to species with lower requirements also show increased yields in response to fertilization with sulphur (MCGRATH et al. 1996, SCHERER 2001).

The effectiveness of fertilizing crops with sulphur depends to a great extent on their nitrogen supply. It is so because proper proportions of nitrogen and sulphur determine metabolism of these nutrients and thus the quality of the yield (MESSICK, FAN 1999, KACZOR, BRODOWSKA 2005).

The aim of this study was to analyze the effect of fertilization with various forms of sulphur and nitrogen on yield and on the content of these nutrients in cocksfoot.

MATERIALS AND METHODS

The study was based on results obtained in a strict pot experiment with a completely randomized design conducted on soil material taken from the arable layer of brown soil of clayey silt granulometric composition. Before the experiment, the soil was characterized by slight acidity and low content of assimilable forms phosphorus, potassium, magnesium and sulphur. The experiment had two variables: the form of nitrogen fertilization and the form of sulphur fertilization. Two nitrogen fertilizers were used – UAN 30 (urea ammonium nitrate solution) and NH_4NO_3 (in granular form), and three forms of sulphur – $Na_2S_2O_3$, elemental S and Na_2SO_4. Both test plants were fertilized with sulphur in the amount of 0.025 g $S \cdot kg^{-1}$ soil and nitrogen in the amount of 0.14 g $N \cdot kg^{-1}$ soil according to the scheme presented in Tables 1 and 2. Sulphur in the form of $Na_2S_2O_3$ and Na_2SO_4 was applied in the liquid form, and elemental sulphur in the solid form. Before weighted portions were measured out, the granules were pulverized in an agate mortar.

Table 1

The effect of form of sulphur and nitrogen fertilization on yielding of cocksfoot (g d.m.$\cdot$pot^{-1})

Object	First cut	Second cut
RSM-30	12.35	15.82
RSM-30 + $Na_2S_2O_3$	13.50	18.50
RSM-30 + elemental S	12.83	17.92
RSM-30 + Na_2SO_4	14.20	19.49
NH_4NO_3	11.16	13.05
NH_4NO_3 + $Na_2S_2O_3$	12.11	15.24
NH_4NO_3 + elemental S	11.54	14.91
NH_4NO_3 + Na_2SO_4	13.46	16.28
LSD(p=0.01) form of sulphur (S)	1.38	1.46
Nitrogen fertilizer (N)	0.86	0.91
S × N form of sulphur x nitrogen fertilizer	1.95	2.06

In the first year of the experiment, the test plant was Ismena variety of spring wheat, and in the second year it was Bepro variety of cocksfoot, harvested twice during the vegetation period. The wheat was harvested at the full maturation stage and cocksfoot at the beginning of the heading stage. This paper comprises an analysis of the effect of the experimental factors on yield and on the total content of nitrogen, sulphur and nitrates in dry mass of cocksfoot. After cocksfoot was harvested, total nitrogen content

Table 2

The effect of form sulphur and nitrogen fertilization on the content of sulphur (g S·kg^{-1}) and nitrogen (g N·kg^{-1}) in cocksfoot

Object	Total S		Total N		$N-NO_3$ (mg N·kg^{-1})	
	first cut	second cut	first cut	second cut	first cut	second cut
RSM-30	1.95	1.42	30.51	34.25	3246.1	3051.4
RSM-30 + $Na_2S_2O_3$	3.12	2.54	33.22	38.42	926.3	1050.1
RSM-30 + elemental S	2.35	2.65	31.50	36.95	1428.0	1000.2
RSM-30 + Na_2SO_4	3.15	2.70	34.03	38.00	1051.3	911.0
NH_4NO_3	2.06	1.37	29.06	32.60	3851.4	3102.5
NH_4NO_3 + $Na_2S_2O_3$	2.85	2.35	32.51	38.72	925.3	1021.1
NH_4NO_3 + elemental S	2.23	2.32	31.06	36.94	1725.4	1312.0
NH_4NO_3 + Na_2SO_4	2.80	2.42	33.21	37.92	1235.1	1301.1

in average samples was determined by Kiejdahl method and total sulphur content was determined using Butters and Chenery's nephelometric method (1959). Nitrate nitrogen was determined colorimetrically using sodium salicylate (ŁOGINOW, WITASZEK 1964).

RESULTS AND DISCUSSION

The yields of the first cut of cocksfoot ranged from 11.16 to 14.20 g dry mass·pot^{-1}, depending on the experimental object, and the yields of the second cut ranged from 13.05 to 18.50 g dry mass·pot^{-1} (Table 1). The form of sulphur and of nitrogen fertilization caused significant variation in the yields of both cuts. The interaction between the factors was also found to be significant. In general, it can be concluded that higher yields of cocksfoot were obtained in the series where liquid UAN 30 was applied. This held for both analyzed cuts and all the forms of sulphur used in the experiment. With respect to spring wheat, ammonium nitrate in the solid form was found to be a more beneficial source of nitrogen (KACZOR, BRODOWSKA 2005).

Cocksfoot showed increased yield in response to sulphur fertilization. The most beneficial source of this element in both series was found to be sodium sulphate. Where elemental sulphur was used, significant increases in yield did not occur until the second cut. The results clearly demonstrate that sulphur applied in this form is a slow-acting fertilizer (ZHAO et al. 1996). They also indicate that even plants with low sulphur requirements, including meadow grasses (SCHERER 2001), respond positively to fertilization with this nutrient.

Total sulphur content in the cocksfoot from the first cut ranged from 1.95 to 3.15 g S·kg^{-1}, and in the plants from the second cut from 1.37 to 2.70 g S·kg^{-1} (Table 2). A study by Rychlicka (1989) demonstrated that the optimal sulphur content in grasses is from 2.0 to 4.0 g S·kg^{-1} dry mass, while less than 1.0 g S·kg^{-1} dry mass indicates a marked deficiency of this nutrient. The data in Table 2 indicate that cocksfoot which was not fertilized with sulphur, especially when harvested in the second cut, was characterized by deficiency of this element. This explains the increase in yield after application of sulphur fertilizers.

Total nitrogen content in the plants ranged from 29.06 to 38.72 g N·kg^{-1} depending on the object and the time of harvest (Table 2). The values were at the level most often observed in meadow grasses (Wiśniowska-Kielian, Lipiński 2007). The experimental factors, particularly sulphur fertilization, caused marked differences in nitrate content in the plants (Table 2). The highest content of this form of nitrogen was found in cocksfoot that was not fertilized with sulphur, where the nitrate content ranged from 3051.4 to 3851.4 mg N·kg^{-1}, while in the series fertilized with sulphur it ranged from 911.0 to 1725.4 mg N·kg^{-1}. These values confirm that fertilizing plants with sulphur has a beneficial effect on nitrogen metabolism (Messick, Fan 1999), which was manifested in this study as lower nitrate content in cocksfoot. It should be added that the nitrate content in dry mass of cocksfoot in all of the experimental objects was within the range of values considered low and optimal with respect to evaluation of grassland swards for use as fodder (Wiśniowska-Kielian, Lipiński 2007).

CONCLUSIONS

1. The highest yields of cocksfoot were obtained in the series fertilized with nitrogen in the form of UAN 30 and sulphur in the form of sodium sulphate.

2. A significant increase in cocksfoot yield as a result of elemental sulphur application was not observed until the second cut.

3. Fertilization of cocksfoot with sulphur increased the content of this nutrient in the plants to a level considered optimal.

4. Fertilization with sulphur had a beneficial effect on nitrogen metabolism in the plants, causing a more than twofold decrease in nitrate content in cocksfoot.

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PROFILE DIFFERENTIATION OF LEAD AND CHROMIUM FRACTIONS FOUND IN SOILS LOCALIZED ON A MORAINE SLOPE

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Abstract

In order to evaluate a potential threat to soil environment by heavy metals, it is important to separate and determine their fractions by means of sequential extraction.

The research aimed at evaluating the total content of lead and chromium as well as their fractions in soils localized on a moraine slope in the Siedlce Heights (transects A and B). Sequential fractionation of these elements was carried out according to Zeien and Brümmer's method. Chemical analyses revealed varied contents of seven lead and chromium fractions in the soils. The largest amounts of both heavy metals were mostly recorded in the residual fraction (F7), and those of lead also in the organic fraction (F4). The least lead was found in the exchangeable fraction (F2) (it was not detected in easily soluble fraction F1), while the least chromium appeared in the easily soluble (F1) and organic fractions (F4). Statistical processing revealed that the examined lead and chromium fractions generally depended on separated fractions, total contents of these metals, and some properties of analyzed soils.

Key words: sequential extraction, Zeien and Brümmer's method, fractions, lead, chromium, moraine slope.

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PROFILOWE ZRÓŻNICOWANIE ZAWARTOŚCI FRAKCJI OŁOWIU I CHROMU W GLEBACH POŁOŻONYCH NA STOKU MORENOWYM

Abstrakt

Dla oceny potencjalnego zagrożenia środowiska glebowego przez metale ciężkie istotne jest wydzielenie i ilościowe zbadanie ich frakcji na drodze ekstrakcji sekwencyjnej.

Celem pracy było zbadanie ogólnej zawartości ołowiu i chromu oraz ich frakcji w glebach położonych na stoku morenowym Wysoczyzny Siedleckiej (transekt A i B). Frakcjonowanie sekwencyjne tych pierwiastków przeprowadzono według metody Zeiena i Brümmera. Wykazano zróżnicowaną zawartość wydzielonych siedmiu frakcji ołowiu i chromu w badanych glebach. Najwięcej obydwu metali stwierdzono (w przeważającej większości) we frakcji rezydualnej F7, a najwięcej ołowiu we frakcji organicznej (F4). Najmniej ołowiu stwierdzono we frakcji wymiennej F2 (we frakcji łatwo rozpuszczalnej F1 nie został on wykryty), a najmniej chromu we frakcji łatwo rozpuszczalnej (F1) oraz organicznej (F4). Obliczenia statystyczne wykazały, że badane frakcje ołowiu i chromu były przeważnie istotnie zależne od wydzielonych frakcji, ogólnej zawartości tych metali oraz niektórych właściwości analizowanych gleb.

Słowa kluczowe: ekstrakcja sekwencyjna, metoda Zeiena i Brümmera, frakcje, ołów i chrom, stok morenowy.

INTRODUCTION

Behaviour of heavy metals towards in soil environment depends on their properties and chemical form (fraction) as well as on the physical and chemical features of the soil. Methods of sequential chemical extraction of heavy metals consist in the extraction of given element forms (fractions) bound to particular soil components by subsequent treatments of soil samples with different extraction solvents. Such methods allow for determining the percentage of a particular fraction of a given element in its total amount in soil, hence making possible to complete evaluation of its availability and potential toxicity to biotic elements in a trophic chain (KABATA-PENDIAS, 1998). The behavior of heavy metals in soil is predominantly determined by loamy minerals, organic matter content and acidity.

The research aimed at determining the total content of lead and chromium as well as separating fractions of these metals by means of sequential extraction according to Zeien and Brümmer's method in genetic horizons of soils localized on an eroded moraine slope.

MATERIAL AND METHODS

The soil study was carried out on a slope of a hilly terminal moraine (western exposure) formed during the Middle Polish glaciation (the Warta River Stadial) in the Siedlce Heights, in Middle-Polish Lowlands. Six outcrops were made in two transects (at about 700 m distance): transect A – one at the top (podzolized lessive soil – I) and two on the slope (Calcaric Cambisol – II and deluvial humus soil – III); transect B – at the top (regulated soil – IV), on the slope (Haplic Luvisol – V) and at the bottom (deluvial soil – VI). The soil material was collected from particular genetic horizons and subjected to determinations of the percentage of loam fraction Ø < 0.002 mm – areometric method (according to PN-R-04033); pH – potentiometry; soil sorption capacity (CEC) – calculated on the basis of hydrolytic acidity (H_h) and sum of exchangeable basic cations (S) determined by means of Kappen's method (except samples with pH > 7.5); organic carbon content (C_{org}) – oxidation-titrimetric method (Kalembasa, Kalembasa 1992); total contents of Pb and Cr – ICP-EAS (Optima 3200 RL device, Perkin Elmer) after combustion at 450°C and extraction with 20% HCl. Lead and chromium fractions were separated by means of Zeien and Brümmer's method (Table 1), which makes it possible to separate metals into seven fractions different with respect to their activity in soil environment. The analysis was performed in three replications. The reference materials (WEPAL Soil Reference Material RTH 912 – Swiss Less Soil, Perkin Elmer) and internal stand-

Table 1

Sequential extraction of heavy metals with Zeien and Brümmer's method

Fraction	Name	Extraction reagent	Extraction time (h)	pH
F1	easily soluble	1 mol $NH_4NO_3 \cdot dm^{-3}$	24	natural
F2	exchangeable	1 mol $CH_3COONH_4 \cdot dm^{-3}$	24	6.00
F3	bound to MnO_x	1 mol $NH_2OH \cdot HCl \cdot dm^{-3}$ +1 mol $CH_3COONH_4 \cdot dm^{-3}$	0.5	6.00
F4	F_{org}bound to organic matter	0.025 mol $C_{10}H_{22}N_4O_8 \cdot dm^{-3}$	1.5	4.60
F5	bound to amorphous FeO_x	0.2 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$ + 0.2 mol $H_2C_2O_4 \cdot dm^{-3}$	4	3.25
F6	bound to crystalline FeO_x	0.2 ml $(NH_4)_2C_2O_4 \cdot dm^{-3}$ + 0.2 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.1 mol $C_6H_8O_6 \cdot dm^{-3}$	0.5	3.25
F7	F_{resid} residual	calculation as difference between total content of nickel and sum of the above determined fractions	-	-

proportion soil / solution 1 g : 10 cm^3

ards were used to check the accuracy of determinations. The detection limit (the lowest concentration possible to detect applying a given method at particular probability) for lead is 0.001-0.01 mg·dm^{-3} and for chromium – 0.0001-0.001 mg·dm^{-3} .

In order to find dependencies between total content of chromium and lead, their fractions and selected soil properties (fraction Ø < 0.002 mm, C_{org}, CEC, pH_{KCl}), values of Pearson's correlation coefficient were calculated. Significant values ($p = 0.05$) were marked with an asterisk (*) in the tables.

RESULTS AND DISCUSSION

Selected physical and physicochemical properties of the soils on the examined terminal moraine slope are presented in Table 2.

The total content of lead (0.13-9.33 mg·kg^{-1}) and chromium (1.21--19.90 mg·kg^{-1}) in the soils varied between and within the profiles, reaching (in mg·kg^{-1}) 0.13-8.22 Pb and 1.21-16.81 Cr in transect A; 2.50-9.33 Pb and 2.40-19.90 Cr in transect B. In the surface humus horizons, the concentra-

Table 2

Selected properties of investigated soils*

Horizon	Depth (cm)	% fraction of diameter in mm Ø< 0.002	pH_{KCl}	CEC	Org. C
				mmol(+)·kg^{-1}	g·kg^{-1}
Transect A					
I. Albic luvisol (flat)					
A	0-25	9	4.05	45.71	6.30
Eet,fe	25-40	8	4.46	28.20	1.50
Bt,fe	40-60	7	4.80	85.00	0.70
Bt	60-90	9	7.73	-	0.50
C	90-120	0	8.87	-	0.3
II. Dystric Cambisol (slope)					
A	0-24	4	3.63	66.21	7.30
ABbr(fe)	24-37	5	3.77	56.43	2.60
Bbr1	37-47	24	4.04	123	1.80
Bbr2	47-75	21	4.57	132	1.00
Bbr3	75-100	21	4.95	122	0.94
Bbr4	100-140	10	7.49	-	0.83

cont. Table 2

III. Mollic Fluvisol (slope)					
IA1	0-15	2	6.68	127	17.71
IA2	15-35	2	6.61	126	6.70
IA3	35-46	6	6.42	124	8.10
IIA	46-68	12	6.36	213	9.90
AC	68-78	10	6.25	167	3.90
IC	78-100	1	6.26	128	1.60
IICG	100-125	15	6.32	137	1.10
Transect B					
IV. Anthropic Regosol (flat)					
Aan	0-25	5	4.26	54.70	7.73
AanA	25-50	6	4.60	48.71	2.78
Ees	50-80	4	4.18	37.51	0.78
Bhfe	80-110	8	4.20	66.22	0.77
C	110-150	17	3.87	104	0.96
V. Haplic Luvisol (slope)					
A	0-25	8	3.47	72.40	6.95
Eet	25-50	6	3.95	33.70	0.66
EB	50-80	8	4.38	146	1.21
Bt	80-120	16	3.95	96.91	0.71
C1	120-150	1	4.96	29.00	0.29
C2	150-180	3	5.12	33.92	0.14
VI. Haplic Phaeozem (foot-slope)					
A1	0-40	6	3.47	119	10.40
A2	40-64	10	3.95	135	8.49
AC	64-74	8	4.38	75	1.05
CG	74-90	6	3.95	77	0.74

*information source: KALEMBASA, MAJCHROWSKA-SAFARYAN (2007)

tion ranged (in mg·kg^{-1}) within 5.60-8.22 of lead and 4.29 -8.67 of chromium in transect A; 4.95-7.46 Pb and 5.82-7.39 Cr in transect B (Tables 3, 4). These levels of the heavy metals did not exceed permissible levels for arable lands (*Decree*.....2002) and were within the range of natural quantities according to IUNG (KABATA-PENDIAS et al. 1995). The total Pb content in lessive soils (profiles I and V), and Calcaric Cambisol (profile II) was the highest in the humus horizons and enrichment horizon B, which mainly result-

Table 3

The total content of lead and percentage contribution of lead fractions in soils in transects A and B

Horizon	Depth (cm)	Fraction							Total content
		F1	F2	F3	F4	F5	F6	F7	
		% total content							$mg \cdot kg^{-1}$
1	2	3	4	5	6	7	8	9	10
Transect A									
I. Albic luvisol (flat)									
A	0-25	n.d	6.68	13.70	40.91	11.60	6.00	20.90	5.60
Eet,fe	25-40	n.d	8.13	18.41	27.50	10.61	15.50	19.91	1.93
Bt,fe	40-60	n.d	8.48	14.42	19.31	16.60	13.12	28.10	4.62
Bt	60-90	n.d	2.91	24.90	41.00	n.d	12.60	18.32	4.77
C	90-120	n.d	n.d	25.00	20.00	n.d	19.01	35.91	1.00
Mean		n.d	5.24	19.28	35.71	7.76	13.25	24.63	3.78
II. Dystric Cambisol (slope)									
A	0-24	n.d	8.21	8.40	34.71	11.80	2.86	34.01	6.46
ABbr(fe)	24-37	n.d	1.20	14.41	26.50	7.83	14.50	38.50	5.20
Bbr1	37-47	n.d	n.d	9.30	25.51	10.52	8.60	46.52	6.93
Bbr2	47-75	n.d	1.78	13.10	25.53	12.31	8.98	38.31	7.11
Bbr3	75-100	n.d	4.40	14.62	34.00	8.25	12.80	25.82	7.11
Bbr4	100-140	n.d	n.d	21.70	32.21	3.13	6.65	36.33	6.00
Mean		n.d	2.59	13.59	29.74	8.97	9.07	36.61	6.47
III. Mollic Fluvisol (slope)									
IA1	0-15	n.d	4.51	7.62	56.01	14.60	4.67	12.50	8.22
IA2	15-35	n.d	6.36	4.92	52.62	19.61	4.75	12.63	7.26
IA3	35-46	n.d	5.95	3.65	39.70	17.32	8.16	25.30	6.70
IIA	46-68	n.d	n.d	n.d	28.92	14.70	7.35	48.92	7.51

cont. Table 3

1	2	3	4	5	6	7	8	9	10
AC	68-78	n.d	4.42	3.88	25.80	12.33	5.44	48.21	6.31
IC	78-100	n.d	n.d	8.72	36.30	8.93	11.01	35.00	5.24
IICG	100-125	n.d	n.w	15.30	43.42	15.40	7.60	17.70	0.13
Mean		n.d	3.03	6.30	40.40	14.70	7.00	28.60	5.91
Transect B									
IV. Anthropic Regosol (flat)									
Aan	0-25	n.d	n.d	15.61	38.51	14.50	10.31	20.91	6.78
AanA	25-50	n.d	16.70	13.80	22.82	13.30	12.40	21.01	4.44
Ees	50-80	n.d	6.44	13.52	25.80	4.60	9.60	40.02	2.50
Bhfe	80-110	n.d	13.51	7.97	18.83	6.04	19.12	34.60	5.18
C	110-150	n.d	4.00	10.00	18.51	6.48	20.01	45.90	6.67
Mean		n.d	8.12	12.18	24.89	9.18	14.31	31.59	5.11
V. Haplic Luvisol (slope)									
A	0-25	n.d	n.d	16.70	34.50	12.41	22.41	14.01	4.95
Eet	25-50	n.d	n.d	18.00	22.42	8.35	12.61	38.60	3.57
EB	50-80	n.d	n.d	6.44	26.00	12.42	14.00	41.00	9.33
Bt	80-120	n.d	5.30	12.62	14.81	19.60	13.51	34.13	6.30
C1	120-150	n.d	6.70	9.54	30.61	n.d	7.60	46.30	2.84
C2	150-180	n.d	11.20	22.51	37.20	n.d	2.07	26.80	2.70
Mean		n.d	3.86	14.30	27.59	8.80	12.03	33.50	4.94
VI. Haplic Phaeozem (foot-slope)									
A1	0-40	n.d	9.37	10.80	40.70	13.51	11.81	13.40	7.46
A2	40-64	n.d	8.00	14.00	30.21	10.52	16.83	20.52	5.42
AC	64-74	n.d	12.80	12.12	25.41	4.75	6.02	38.91	3.90
CG	74-90	n.d	17.01	8.36	20.50	12.60	11.01	30.50	4.64
mean		n.d	11.00	11.32	29.01	10.35	11.42	25.83	5.35

n.d – not detected

Table 4

The total content of chromium and percentage contribution fractions of this metal in the investigated soils in transect A and B

Horizon	Depth (cm)	Fraction							Total content
		F1	F2	F3	F4	F5	F6	F7	
		% total content							$mg \cdot kg^{-1}$
1	2	3	4	5	6	7	8	9	10
Transect A									
I. Albic luvisol (flat)									
A	0-25	4.96	4.54	28.50	3.40	18.80	20.91	18.90	4.29
Eet,fe	25-40	4.60	7.79	29.11	2.05	12.21	19.81	24.40	4.53
Bt,fe	40-60	2.25	13.90	15.21	2.03	9.72	12.63	45.72	9.21
Bt	60-90	2.68	14.81	13.80	2.10	6.39	16.10	44.11	9.34
C	90-120	1.27	10.90	14.00	2.10	17.00	17.90	30.90	1.21
Mean		3.15	10.38	20.12	2.34	12.80	17.47	32.82	5.72
II. Dystric Cambisol (slope)									
A	0-24	4.84	21.40	22.12	9.95	14.42	14.50	13.71	5.96
ABbr(fe)	24-37	4.43	20.92	17.71	4.09	10.70	19.20	22.80	7.34
Bbr1	37-47	1.98	10.60	9.98	1.82	7.93	12.71	54.90	13.70
Bbr2	47-75	1.92	9.56	9.67	2.45	9.52	13.13	53.50	14.91
Bbr3	75-100	1.47	9.77	9.32	2.25	7.11	18.80	56.32	15.70
Bbr4	100-140	1.93	11.60	8.54	1.09	8.08	12.41	56.33	14.82
Mean		2.70	14.00	12.91	3.61	9.62	15.13	42.90	12.08
III. Mollic Fluvisol (slope)									
IA1	0-15	2.83	16.31	14.80	4.64	9.76	20.61	35.80	8.67
IA2	15-35	3.07	14.92	14.01	3.96	7.69	20.71	35.71	8.65
IA3	35-46	3.01	14.60	12.91	4.60	11.40	19.13	34.30	9.57
IIA	46-68	1.51	9.24	9.18	1.82	11.30	10.70	56.31	15.90
AC	68-78	1.40	9.68	7.60	1.78	7.91	10.70	60.82	16.81

cont. Table 4

1	2	3	4	5	6	7	8	9	10
IC	78-100	1.70	9.75	9.40	1.55	6.62	13.41	57.61	13.90
IICG	100-125	1.92	9.53	9.95	1.82	6.02	11.50	59.30	14.50
Mean		2.20	12.01	11.12	2.88	8.67	15.25	48.55	12.57
Transect B									
IV. Anthropic Regosol (flat)									
Aan	0-25	3.88	21.20	20.31	5.62	13.50	20.40	14.73	5.82
AanA	25-50	3.89	22.31	21.01	4.28	11.01	18.30	19.01	6.21
Ees	50-80	7.60	13.12	10.10	4.93	13.03	22.91	28.30	2.80
Bhfe	80-110	2.90	16.00	13.32	3.30	8.21	13.70	42.60	9.55
C	110-150	1.50	10.20	8.54	2.23	4.20	12.51	60.81	15.00
Mean		3.95	16.56	14.66	4.07	9.98	17.56	33.12	7.87
V. Haplic Luvisol (slope)									
A	0-25	4.23	21.21	19.63	5.05	13.50	16.60	19.71	6.26
Eet	25-50	4.98	20.72	20.80	6.70	8.45	22.40	16.00	5.18
EB	50-80	1.13	7.35	7.79	1.16	6.05	8.64	67.80	19.90
Bt	80-120	1.53	11.80	10.90	0.76	9.04	11.21	54.71	14.41
C1	120-150	4.87	14.00	10.91	2.33	13.30	17.70	36.90	2.40
C2	150-180	6.50	11.51	9.70	2.71	14.11	12.73	42.80	3.00
Mean		3.87	14.43	13.29	3.95	10.71	14.90	39.65	8.52
VI. Haplic Phaeozem (foot-slope)									
A1	0-40	3.30	20.60	17.90	4.47	12.01	14.21	27.41	7.39
A2	40-64	3.13	18.22	16.81	3.58	8.75	15.80	33.70	8.11
AC	64-74	3.32	20.40	20.40	6.49	7.77	19.60	22.03	6.68
CG	74-90	2.99	16.81	14.03	1.50	11.10	17.72	35.70	8.85
Mean		3.18	19.00	17.29	4.01	9.90	16.83	29.70	7.76

ed from the soil-forming processes (lessivage and chemical erosion) shaping these soils. In deluvial soils (profiles III and IV), more Pb was associated with the humus horizons containing more organic matter. The total Cr concentration was associated with the loam fraction and organic matter in the analyzed soil horizons. More chromium was recorded in the soil horizons of transect A (10.50 $mg \cdot kg^{-1}$) than of transect B (8.10 $mg \cdot kg^{-1}$, on average), while the highest content of chromium appeared in deluvial humus soil (profile III – 12.57 $mg \cdot kg^{-1}$) and Calcaric Cambisol (profile II – 12.07 $mg \cdot kg^{-1}$) on the moraine slope, and the lowest amounts were in lessive podzolized soil (profile I – 5.72 $mg \cdot kg^{-1}$) on the hill top.

The spetiation analysis of lead in the soils on the moraine slope, performed by Zeien and Brümmer's method, indicates that the metal was bound to different parts of the soil's solid phase (forms, fractions) – Table 3. The highest lead content was found in forms bound to organic matter (F4): 29.74--40.39% of the total content in soils of transect A, mostly in deluvial humus soil, and 24.89-29.01% in soils of transect B, mainly in deluvial soil, and post-extraction residuals (F7) (residual forms indicating lead in primary and secondary silicates and aluminosilicates) in transect A: 24.63-36.61%, most in Calcaric Cambisol, and in transect B 25.83-33.50%, most in Haplic Luvisol. Lead dominated in the humus soil horizons of both transects (34.50--56.01%), which is consistent with its bio-geochemistry, and in some enrichment horizons B (namely of podzolized lessive soil and Calcaric Cambisol in transect A), which may indicate some dislocation despite the fact that this metal is considered to be less mobile in soil environment, and in mother rock C (deluvial humus soil and Haplic Luvisol), which in turn can imply the lithogenic origin of lead in these soils (KABATA-PENDIAS 1998). Similar or identical amounts of lead were found (in transects) in forms associated with manganese oxides susceptible to oxidation (F3) (6.30-19.28% in transect A and 11.32-14.30% in transect B, but most in the deepest soil horizons), and with crystalline iron oxides (F6) (7.00-13.25% in transect A and 11.41-14.30% in transect B), whose content within the profiles was more differentiated. Similar quantities of Pb (7.76-14.70%) were recorded in bonds with amorphous iron oxides (F5), the compounds that were not detected in lower horizons of lessive soils (profiles I and V), whereas within the profiles lead content was not univocally differentiated. No lead was found in easily soluble forms (F1), while its share in exchangeable forms (F2) ranged from 2.59 to 11.00% of the total content; it was detected in some horizons, indicating its reduced susceptibility to mobilization from the soil's solid phase to a solution. KARCZEWSKA (2002) also claims that lead in mineral soils is present most often in the residual fraction as well as bound to organic matter; its lowest percentage (namely in soils with natural lead content) is made up by the most mobile fractions (easily soluble and exchangeable).

The sequential extraction analysis according to Zeien and Brümmer's method revealed that chromium in the examined soils was present in more varied bindings than lead (Table 4). Particular soil horizons differed in the chromium fraction distribution. As bio-available fractions (F1 and F2), Cr content was much higher than lead, which may indicate better mobility of chromium than lead: higher in soils of transect B than A. Considerably less Cr was recorded in easily soluble fraction F1 (2.20-3.95% of the total content, on average for profiles) than in exchangeable fraction F2 (10.38--19.00%). Chromium dominated in residual forms (29.70-48.55%): more mainly

Table 5

Correlation coefficients between fractions of lead and chromium $(\mathrm{mg \cdot kg^{-1}})$ and some properties of investigated soils

Parametr	Element	Fraction						
		F1	F2	F3	F4	F5	F6	F7
Transect A								
Total content	Pb	-	0.33	0.33	0.83*	0.78*	0.61*	0.63*
	Cr	0.44	0.78*	0.61*	0.24	0.81*	0.88*	0.98*
Org. C	Pb	-	0.44	-0.27	-0.76*	0.70*	-0.05	0.09
	Cr	0.13	0.09	0.13	0.53	0.21	-0.02	-0.21
$\mathrm{pH_{KCl}}$	Pb	-	- 0.21	- 0.14	0.03	- 0.21	- 0.11	- 0.31
	Cr	- 0.44	- 0.01	- 0.44	- 0.28	- 0.18	- 0.03	0.12
CEC	Pb	-	-	- 0.49*	0.30	0.66*	0.24	0.48*
	Cr	0.27	0.48*	0.48*	0.51*	0.70*	0.59*	0.60*
$\varnothing<0.002^{a}$	Pb	-	- 0.17	- 0.12	0.44	0.47*	0.23	0.48*
	Cr	0.46*	0.70*	0.47*	0.38	0.74*	0.79*	0.72*
Transect B								
Total content	Pb	-	- 0.10	0.55*	0.75*	0.85*	0.80*	0.64*
	Cr	0.26	0.69*	0.71*	0.05	0.76*	0.86*	0.96*
Org. C	Pb	-	- 0.07	0.70*	0.81*	0.55*	0.29	- 0.37
	Cr	0.32	0.32	0.31	0.41	0.22	-	- 0.24
$\mathrm{pH_{KCl}}$	Pb	-	0.48	- 0.23	0.27	- 0.06	- 0.45	- 0.34
	Cr	- 0.26	- 0.17	- 0.19	- 0.12	- 0.17	- 0.31	- 0.26
CEC	Pb	-	- 0.07	0.34	0.65*	0.76*	0.72*	0.46
	Cr	0.33	0.70*	0.71*	0.21	0.67*	0.68*	0.70*
$\varnothing<0.02^{a}$	Pb	-	0.20	0.43	0.59*	0.60*	0.33	0.06
	Cr	0.48	0.54*	0.56*	0.25	0.49*	0.43	0.11

[a] percentage fraction of clay
* significant $p = 0.05$

in the horizons with its higher total content. Czekała (1997) reported that stable chromium bindings in the residual fraction of mineral soils made up 56-86%.

The percentage of chromium in the fractions bound to manganese oxides and hydroxides (F3), amorphous (F5) and crystalline (F6) iron oxides and hydroxides varied between within the analyzed profiles. Higher Cr amounts were found in the form occluded on crystalline iron oxides (14.90--17.56%, on average for profiles) than on amorphous ones (8.67-12.80%). Between 8.54 – 29.11% of chromium was bound to manganese oxides: more in soils of transect A than B; more in surface and sub-surface soil layers and most (13.80-29.11%) in podzolized lessive soil on the top of the slope (profile I). Little chromium was found in forms bound to organic matter (F4), and its quantity ranged at the level of easily soluble fraction (F1). Chromium content in fraction F4 was 2.34-4.07% (mean for profiles); most in anthropogenically regulated soil (profile IV) and deluvial soil (profile VI); most in surface and sub-surface layers. According to Czekała (1997), chromium share in organic fractions in humus horizons of mineral soils was 12.70% of its total amount. Kalembasa et al. (2008) found the following Cr contents in surface soil horizons localized along the ring road around Siedlce: in the fractions separated by means of Zeien and Brümmer's method (percentage of the total content): F1 3.78-6.42; F2 5.43-8.99; F3 1.98-2.75; F4 7.47-15.50; F5 31.00-40.50; F6 6.91-7.66; F7 29.20-32.50.

Significant correlations were recorded between separated Pb and Cr fractions and their total content, sorption capacity CEC (mainly chromium), organic carbon content (mainly lead), as well as loamy fraction ($\varnothing$ < 0.002 mm) in the studied soils of transects A and B (Table 5). The strongest correlations were observed between lead and chromium in bindings with amorphous iron oxides F5, in stable bindings of residual fraction F7 (transect A) and in the fraction bound to manganese oxides F3 (transect B) versus selected properties of the soils. Kalembasa et al. (2008), when examining the heavy metals fractions along the ring road around Siedlce, achieved similar values of Pearson's correlation coefficients for the analyzed metals.

CONCLUSIONS

1. Total content of lead and chromium in soils on a moraine slope did not exceed concentrations permissible by the Decree of the Ministry for Environment, and ranged within natural levels according to IUNG. These metals were slightly higher in soils of transect A than B.

2. Sequential fractionation of lead and chromium made by Zeien and Brümmer's method revealed their varied concentrations in separated fractions in particular horizons of the soils. The highest levels of the heavy

metals were predominantly recorded in the residual fraction (F7), while lead was also high in the organic fraction (F4). No lead was detected in bioavailable fraction F1, and its very small quantities were detected in fraction F2; both fractions contained much more chromium. More chromium than lead was recorded in the fraction bound to manganese oxides (F3) as well as amorphous (F5) and crystalline iron oxides and hydroxides (F6). The levels of Pb and Cr were not unambiguously differentiated in the fractions of typologically distinct soils of both transects.

3. Percentages of the heavy metals in separated fractions to their total content for soils in transects A and B can be ordered in the following sequences:

transect A Pb: F4> F7> F3> F5> F6> F2> F1 (not detected);
Cr: F7> F6> F3> F2> F5> F4> F1;
transect B Pb: F7> F4> F3> F6> F5> F2> F1 (not detected);
Cr: F7> F2> F6> F3> F5> F4> F1.

4. Statistical processing revealed significant differences between lead and chromium in the separated fractions and, in general, their fractions, total content, organic matter content and loam fraction < 0.002 mm versus CEC of analyzed soils.

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THE YIELD AND CONTENT OF TRACE ELEMENTS IN BIOMASS OF *MISCANTHUS SACCHARIFLORUS* (MAXIM.) HACK. AND IN SOIL IN THE THIRD YEAR OF A POT EXPERIMENT

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Abstract

In the third year of a pot experiment (in a greenhouse), the carryover influence of fertilization with fresh sewage sludge and, for comparison, mineral fertilization on the content and uptake of Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti by the biomass of *Miscanthus sacchariflorus* grass. The yield of silver-grass biomass was evaluated on the basis of two harvests (June and December). Trace elements in the tested grass as well as in the soil (after harvest) were determined by means of the ICP-AES technique after sample combustion in a muffle furnace. Significant influence of sewage sludge fertilization on yield of silver-grass biomass was found. Grass harvested in autumn contained higher contents of some analyzed trace elements (Fe, Mn, Sr, Ba, and Ti) than that harvested in summer. The uptake of trace elements uptake by the silver-grass biomass was higher from the objects fertilized with sewage sludge than the ones receiving mineral fertilization. After three years of cultivation, the soil contained more Fe, Mn, Ba, Sr, Ti, B, and Li as compared to the content before the experiment.

Key words: *Miscanthus sacchariflorus*, biomass, fertilization, sewage sludge, trace elements.

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PLON I ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W BIOMASIE TRAWY *MISCANTHUS SACCHARIFLORUS* (MAXIM.) HACK ORAZ W GLEBIE, W TRZECIM ROKU DOŚWIADCZENIA WAZONOWEGO

Abstrakt

W trzecim roku doświadczenia wazonowego (w warunkach szklarni) badano wpływ następczego nawożenia świeżym osadem ściekowym oraz – dla porównania – nawożenia mineralnego na zawartość i pobranie Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li i Ti przez biomasę trawy *Miscanthus sacchariflorus.* Plon biomasy określono na podstawie dwóch zbiorów miskanta (w czerwcu i grudniu). Pierwiastki śladowe w testowanej trawie oraz glebie (po zbiorze) oznaczono metodą ICP-AES, po mineralizacji próbek na sucho, w piecu muflowym. Stwierdzono istotny wpływ nawożenia osadem ściekowym na plonowanie biomasy miskanta cukrowego.

W trawie zebranej jesienią stwierdzono większą zawartość niektórych analizowanych pierwiastków (Fe, Mn, Sr, Ba i Ti) niż w trawie zebranej latem. Pobranie pierwiastków śladowych z plonem biomasy miskanta było większe z obiektów nawożonych osadem ściekowym niż z obiektu nawożonego nawozami mineralnymi. Po trzech latach uprawy stwierdzono w glebie większą zawartość Fe, Mn, Ba, Sr, Ti, B i Li, w porównaniu z zawartością przed założeniem eksperymentu.

Słowa kluczowe: *Miscanthus sacchariflorus*, biomasa, nawożenie, osad ściekowy, pierwiastki śladowe.

INTRODUCTION

Introduction of new, energy plants into cultivation is stimulated by progressing depletion of sustainable resources of fossil fuels in Poland and worldwide (EL BASSAM 1995). Among energy crops, grasses of *Miscanthus* genus are the most important ones (KOCHANOWSKA, GAMRAT 2007). Silver-grass (*Miscanthus sacchariflorus*) deserves special attention owing to its due modest soil requirements, possibility to grow it on soil amended with sewage sludge, tolerance to water deficit and growth under unfavorable habitat conditions, e.g. mine waste dumps or along roads and highways (MAJTKOWSKI, MAJTKOWSKA 1998, 2000, MALINOWSKA et al. 2006, KOCHANOWSKA, GAMRAT 2007, KALEMBASA, MALINOWSKA 2007a).

The research aimed at determining the biomass yield and total content of trace elements (Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti) in silver-grass (*Miscanthus sacchariflorus (Maxim.) Hack*) fertilized with three rates of fresh sewage sludge and mineral fertilizer (NPK) in the third years of a pot experiment.

MATERIAL AND METHODS

In spring 2005, a pot experiment was established in a greenhouse according to a completely randomized design with three replications. Pots of 20 l capacity each were filled with soil of heavy loamy sand granulometric composition (according to PTG), which was characterized by following properties: pH_{KCl} = 6.60, organic carbon content 30.5 $g \cdot kg^{-1}$, total content of some trace elements ($mg \cdot kg^{-1}$ soil): Fe – 5187; Mn – 145.8; Mo – 0.049; B – 0.673; Ba – 82.18; Sr – 29.06; As – 0.625; Sn – 0.663; Li – 1.70; Ti – 49.42. The content of organic carbon was determined by the oxidation-titrimetric method; total amounts of trace elements were analyzed applying the ICP-AES technique after soil sample combustion in a muffle furnace at 450°C. The influence of organic (fresh sewage sludge) and mineral fertilization on total content of trace elements in biomass of silver-grass (*Miscanthus sacchariflorus*) harvested on two dates (June and December 2007) in the third year of cultivation was studied.

The following objects were set up:

- control (with no fertilization);
- mineral NPK fertilization applied once before rhizomes set (mineral N was used as urea, whereas the N amount was calculated according to a dose of 20% fresh weight of sewage sludge in reference to the soil weight);
- 10% fresh weight of sewage sludge in relation to the soil weight, which corresponded to 20 g N pot^{-1};
- 20% fresh weight of sewage sludge in relation to the soil weight, i.e. 4 kg of fresh weight per pot, which corresponded to 40 g N pot^{-1};
- 30% fresh weight of sewage sludge in relation to the soil weight, i.e. 6 kg of fresh weight per pot, which corresponded to 60 g N pot^{-1}.

Fresh sewage sludge was used once (before sowing sliver-grass) by mixing it with soil in pots. Phosphorus (triple superphosphate) and potassium fertilizers (potassium sulfate) were applied to all objects, but maintaining the N:P:K ratio at 1:0.8:1.2.

The plant material samples were combusted at 450°C in a muffle furnace for 15 hours. Then, 10 ml diluted HCl (1:1) was added to the crucibles and the content was evaporated to decompose carbonates and to separate the silicates. After adding another 5 ml 10% HCl, the content was passed through hard filter paper into a measuring flask (100 cm^3 capacity) and the volume was adjusted with distilled water. The solutions thus obtained were subjected to determinations of total content of Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti by the ICP-AES technique using an emission spectrophotometer combined with inductively-coupled plasma. After silver-grass harvest, soil samples were collected from particular fertilization objects and levels of the above trace elements were determined applying the ICP-AES technique.

Based on the harvested biomass yield and the content of trace elements, their uptake by silver-grass was calculated.

The results were statistically processed, and the differences between mean values for harvest dates, fertilization objects and their interactions were verified by means of variance analysis (FR Analvar 4.1 software). Significance of differences ($NIR_{0.05}$) was assessed using Tukey's test.

RESULTS AND DISCUSSION

In the third year of growing *Miscanthus sacchariflorus*, the biomass yield harvested in June (266.9 g $\cdot$ pot^{-1}) was twice as high as in December (132.0 g$\cdot$ $\cdot$pot^{-1}; Table 1), which resembled the results from the second year (Kalembasa, Malinowska 2007b). Significant differences in the silver-grass biomass yields were found in the third year after fresh sewage sludge application.

Total amounts of the examined trace elements in silver-grass biomass varied and depended on the harvest date and fertilization rate (Table 1).

Statistical analysis revealed significant influence of the harvest date on total content of most of the studied trace elements (except molybdenum and arsenic) in silver-grass biomass. About twice as much Fe, Mn, and Sr, as well as more Ba and Ti were found in the autumn (December) than in the summer harvest. In the second year of silver-grass cultivation, Kalembasa, Malinowska (2007b) also recorded higher levels of heavy metals in the biomass harvested in autumn as compared to summer. Bio-accumulation of Mn, Mo, and Sr apparently increased on both dates due to fresh sewage sludge fertilization, while for the other elements such dependence was not observed. Much more lithium was determined in the silver-grass biomass grown on not-fertilized and mineral-fertilized soil than in that harvested from the soil amended with sewage sludge. The content of an element in a soil environment does not always condition its uptake by a plant (Grzywnowicz, Strutyński 1999). Sewage sludge fertilization under *Miscanthus sacchariflorus* (even at the highest applied rate – 30%) did not cause excessive accumulation of the tested trace elements, which may have been complexed with organic matter, being therefore converted into forms that are unavailable for plants.

A much higher uptake of the analyzed elements (Table 2) was recorded in biomass of silver-grass growing on soil fertilized with sewage sludge, which was associated with the size of yields achieved from those objects. The largest amounts of the trace elements were assimilated by yield of grass fertilized with 30% and 20% FW sewage sludge rates; more with the summer than with the autumn harvest (except Fe and Mn). Krzywy et al. (2004) reported that uptake of microelements by *Miscanthus giganteus* straw increased along with the increasing rates of sewage sludge applied.

Table 1

The content of trace elements (mg kg^{-1}) in the biomass *Miscanthus sacchariflorus* harvested in the third year of cultivation in a pot experiment

Fertilization	The yield (g pot^{-1})	Fe	Mn	Mo	B	Ba	Sr	As	Sn	Li	Ti
Summer harvest (I)											
Control object	113.3	81.9	16.6	0.41	5.70	3.57	11.3	3.09	2.02	39.9	1.09
NPK	140.0	76.9	15.2	0.43	2.40	3.13	13.6	2.95	2.77	67.6	1.19
10%	333.3	67.0	21.3	0.52	4.66	3.28	11.1	2.65	1.52	11.6	0.59
20%	373.3	92.2	36.1	1.28	6.38	3.76	16.8	2.58	2.67	14.5	1.06
30%	375.0	88.3	35.2	0.95	4.21	4.09	14.1	2.19	2.32	9.76	1.37
Mean	266.9	81.3	24.9	0.72	4.67	3.57	13.4	2.69	2.26	28.7	1.06
Autumn harvest (II)											
Conntrol object	53.3	159.2	22.8	0.59	0.80	4.86	23.0	2.51	0.21	10.3	0.97
NPK	60.0	229.0	19.2	0.44	0.98	4.90	17.3	1.77	0.22	13.1	2.47
10%	140.0	257.0	65.5	0.82	1.12	4.59	30.4	2.81	0.26	4.05	1.67
20%	206.7	153.6	69.2	0.82	1.39	5.29	23.8	2.86	0.24	3.99	1.69
30%	200.0	170.6	67.6	0.88	1.41	5.51	26.9	2.72	0.29	4.25	2.05
Mean	132.0	193.9	48.9	0.71	1.14	5.03	24.3	2.53	0.25	7.14	1.77
NIR$_{0.05}$:											
A (terms of harvest)	68.0	10.4	1.84	n.i.	0.49	0.39	1.01	n.s.	0.10	4.60	0.22
B(fertilization)	154.3	23.5	4.17	0.38	1.12	n.s.	2.30	n.s.	0.23	10.4	0.50
A/B interaction	152.1	23.2	4.11	0.37	1.11	n.s.	2.26	n.s.	0.23	10.3	0.49
B/A interaction	218.2	33.3	5.89	0.54	1.59	n.s.	3.25	n.s.	0.33	14.8	0.71

n.s. – non-significant
10% of waste activated sludge
20% of waste activated sludge
30% of waste activated sludge

The chemical analysis of the soil collected after three years of silvergrass cultivation (Table 3) revealed increase in the content of Fe, Mn, Ba, Sr, and Ti and a slight increase in the level of B and Li caused by the applied fertilization, as compared to the amounts before the experiment.

Table 2

Uptake of other elements (mg pot^{-1}) by yield of *Miscanthus sacchariflorus* in the third year of cultivation in a pot experiment

Fertilization	Fe	Mn	Mo	B	Ba	Sr	As	Sn	Li	Ti
Summer harvest (I)										
Control object	9.28	1.88	0.05	0.65	0.40	1.28	0.35	0.23	4.52	0.12
NPK	10.76	2.13	0.06	0.34	0.44	1.90	0.41	0.39	9.46	0.17
10% of waste activated sludge	22.33	7.09	0.17	1.55	1.09	3.69	0.88	0.51	3.88	0.20
20% of waste activated sludge	34.42	13.48	0.48	2.38	1.40	6.28	0.96	0.99	5.42	0.40
30% of waste activated sludge	33.10	13.19	0.36	1.58	1.53	5.27	0.82	0.87	3.66	0.51
Mean (I)	21.95	7.55	0.22	1.30	0.97	3.68	0.69	0.60	5.39	0.28
Autumn harvest (II)										
Control object	8.44	1.21	0.03	0.04	0.26	1.23	0.13	0.01	0.55	0.52
NPK	13.74	1.15	0.03	0.06	0.29	1.04	0.11	0.01	0.79	0.15
10% of waste activated sludge	35.98	9.18	0.12	0.16	0.64	4.25	0.39	0.04	0.57	0.23
20% of waste activated sludge	31.75	14.31	0.17	0.29	1.09	4.92	0.59	0.05	0.83	0.35
30% of waste activated sludge	34.12	13.52	0.18	0.28	1.10	5.37	0.54	0.06	0.85	0.41
Mean (II)	24.81	7.87	0.10	0.17	0.68	3.36	0.35	0.03	0.72	0.24
Mean (I+II)	23.38	7.71	0.16	0.73	0.83	3.52	0.52	0.32	3.05	0.26

Table 3

The content of trace elements (mg kg^{-1}) in soil after the harvest of *Miscanthus sacchariflorus*, in the third year of cultivation in a pot experiment

Fertilization	Fe	Mn	Mo	B	Ba	Sr	As	Sn	Li	Ti
Control object	3867	111.4	0.06	0.67	44.25	18.99	0.19	0.46	1.13	28.89
NPK	3077	86.2	0.12	0.58	37.68	18.98	0.66	0.35	1.25	33.63
10% of waste activated sludge	4220	123.9	0.11	0.79	41.51	19.95	0.85	0.96	1.41	30.37
20% of waste activated sludge	4323	105.7	0.12	0.63	44.12	19.17	0.93	1.11	1.45	32.02
30% of waste activated sludge	4341	112.5	0.03	0.63	41.13	19.52	1.49	0.72	1.50	30.98
Mean	3966	107.9	0.09	0.66	41.74	19.32	0.82	0.72	1.35	31.18

CONCLUSIONS

1. Significantly higher biomass yields of silver-grass cultivated on sewage sludge fertilized soil were recorded in the third year of a pot experiment.

2. Fertilization with sewage sludge enhanced the accumulation of Mn, Mo, and Sr, while mineral fertilization raised the concentration of Li in silver-grass biomass, as compared to the control object.

3. Much higher content of some examined trace elements (Fe, Mn, Sr, Ba, and Ti) was found in the test plant biomass harvested in late autumn than in summer.

4. The uptake trace elements by the biomass yields of silver-grass was higher in the objects fertilized with sewage sludge at the highest (30%) and medium rates (20%) than by plants harvested from the control and mineral–fertilized objects.

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A CARRYOVER EFFECT OF THE CHELATING AGENTS EDTA AND EDDS APPLIED TO SOILS ON THE UPTAKE OF COPPER AND IRON BY MAIZE IN THE SECOND YEAR OF A POT EXPERIMENT

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Abstract

A pot experiment was established in 2006 to examine whether induced phytoextraction can remove copper from soils polluted with emissions from copper smelters. Two soils tested in the experiment were sand and loam in texture, and contained 620 and 510 $mg \cdot kg^{-1}$ Cu, respectively. Maize was used as a testing plant. Two chelating agents: EDTA and biodagradable EDDS were introduced into the soils at the rates of 0.2; 0.5 and 1.0 $mmol \cdot kg^{-1}$ to intensify the process of Cu phytoextraction. The results that have been already published indicated that application of both chelators caused increase in Cu uptake by plants in 2006, although the concentrations of Cu in biomass were far below those required for effective phytoextraction. Additionally, both chelators caused intensive leaching of metals from soils. This paper focuses on the carryover effects observed in the subsequent year, 2007, certainly caused by the application of chelators. EDTA, particularly when applied at the highest rate, caused considerable deterioration of plant growth, reduction of plant yields and increased uptake of Cu by plants grown in both soils. The plants showed unquestionable effects of copper phytotoxicity. In the plots where EDDS was applied, a small decrease in yield was observed in the case of plants grown on sandy soil, whereas in plants grown on loamy soil a significant increase in plant yields and decrease in Cu concentrations in shoot biomass occurred compared with the control plots. Cu and Fe concentrations in plant shoots were positively correlated with each other, and the plants with the highest concentrations of Cu also contained the highest concentrations of Fe. Application of the chelating agents, particularly EDTA, in 2006 caused a long-lasting increase of Cu and Fe solubility

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in soil, and plant uptake of those elements in 2007 correlated positively with soil concentrations of soluble metal forms, extracted with 1 mol·dm^{-3} NH_4NO_3 and 0.01 mol·dm^{-3} $CaCl_2$.

Key words: soil, phytoextraction, complexing, chelator, EDTA, EDDS, copper, iron.

NASTĘPCZY WPŁYW SUBSTANCJI CHELATUJĄCYCH EDTA I EDDS NA POBRANIE MIEDZI I ŻELAZA PRZEZ KUKURYDZĘ W DRUGIM ROKU DOŚWIADCZENIA WAZONOWEGO

Abstrakt

W doświadczeniu wazonowym założonym w 2006 r., z zastosowaniem metody indukowanej fitoekstrakcji do usuwania Cu z gleb zanieczyszczonych emisjami hut miedzi, testowano 2 gleby: piaszczystą i gliniastą, zawierające odpowiednio 620 i 510 mg·kg^{-1} miedzi. Rośliną testową była kukurydza. W celu zintensyfikowania fitoekstrakcji w 2006 r. wprowadzono do gleby 3 różne dawki (0,2; 0,5 i 1,0 mmol·kg^{-1}) substancji kompleksujących: EDTA i łatwo biodegradowalnego EDDS. Opublikowane już wyniki wskazują, że w 2006 r. oba chelatory spowodowały wzrost pobrania Cu przez kukurydzę, jednak zawartość Cu w biomasie była daleko niższa od wymaganej dla skutecznej fitoekstrakcji. Dodatkowo oba odczynniki spowodowały intensywne wymywanie metali z gleb. W niniejszej pracy przedstawiono następcze efekty zastosowania substancji chelatujących do gleb w kolejnym roku doświadczenia, 2007. Zastosowane środki wpłynęły na plonowanie kukurydzy w roku następnym. EDTA, szczególnie w najwyższej dawce, spowodował na obu glebach pogorszenie wzrostu roślin i zmniejszenie plonu, wzrost koncentracji Cu w biomasie oraz silne objawy toksyczności Cu u kukurydzy. W wariantach z EDDS na glebie piaszczystej stwierdzono nieznaczne obniżenie wielkości plonu kukurydzy, a na glebie pyłowo-gliniastej – wzrost plonu roślin i zmniejszenie koncentracji Cu w częściach nadziemnych w porównaniu z wariantami kontrolnymi. Stężenia Cu i Fe w biomasie wykazywały wzajemną dodatnią korelację, a rośliny w wariantach o najwyższej koncentracji Cu zawierały też najwyższe stężenia Fe w biomasie. Zastosowane w 2006 r. chelatory, szczególnie EDTA, spowodowały długotrwały wzrost rozpuszczalności Cu i Fe w glebie. Pobranie obu pierwiastków z gleby przez rośliny w 2007 r. było dodatnio skorelowane z zawartością w glebie łatwo rozpuszczalnych form tych pierwiastków, ekstrahowanych roztworami 1 mol·dm^{-3} NH_4NO_3 i 0,01 mol·dm^{-3} $CaCl_2$.

Słowa kluczowe: gleba, fitoekstrakcja, kompleksowanie, chelatory, EDTA, EDDS, miedź, żelazo.

INTRODUCTION

Although soils polluted with heavy metals occur in Poland only on a local scale, effective and environmental-friendly soil cleaning methods are needed to enable removal of excessive amounts of pollutants from soils. Phytoextraction is considered as a potential method ofr decontamination of heavy metal-polluted soils. In particular, induced hyperaccumulation, in which chelating agents are used to mobilize metals from soil solid phase, has attracted scientists' attention in recent decades. First papers in which the results of induced phytoextraction were presented opened promising prospects for future use of this method (Blaylock 2000, Schmidt 2003). They were, however, followed by many others stressing drawbacks of the method rather than its advantages (Romkens et al. 2002, Ewangelou et al. 2007). Despite this, experiments on induced phytoextraction continue with various chelating agents different in their biodegradability and applied in different rates (Kos, Lestan 2003, Meers et al. 2005, Nascimento da et al. 2006).

The results presented in this paper refer to a pot experiment conducted in 2006-2007, in which EDTA and easily biodegradable EDDS were used for induced phytoextraction of copper from soils polluted with emissions from copper smelters. The effects of Cu removal from soils by plant uptake, which enables us to assess the phytoextraction efficiency in 2006, have already been published (Karczewska et al. 2008), and this paper focuses on carryover effects caused by chelate application in the first year,on plant growth, biomass yield and Cu and other elements uptake by maize in the following year. The plants grown in 2007 showed typical symptoms of Cu toxicity, which can be interpreted as physiological results of Fe deficiency (Kabata-Pendias 2001). Therefore, particular attention is given to Cu and Fe uptake by maize.

MATERIAL AND METHODS

Soil material used in the experiment was collected from the surface layer of soils in the vicinity of copper smelters in Legnica (soil L) and Głogów (soil G). Both soils contained enhanced concentrations of heavy metals, in particular copper. The texture of soil L corresponded to sandy loam and the soil contained 510 mg·kg^{-1} Cu whereas soil G, with the texture of loamy sand, contained 510 mg·kg^{-1} Cu. Basic properties of both soils are presented in Table 1. Maize (*Zea mays* L., var. Blaskj) was used in 2006 as the experimental plant. At the stage of plant pre-maturity, two chelates: EDTA and

Table 1

The properties of soils used in the experiment

Soil	Texture*	Percentage of grains with diameter		C org %	pH	CEC cmol(+)·kg^{-1}	Cu total concentration mg·kg^{-1}
		<0.02 mm	<0.002 mm				
G	loamy sand	15	2	0.73	6.7	6.2	510
L	sandy loam	26	6	0.95	6.6	7.8	620

*Soil textural groups and their symbols – acc. to Polish Society of Soil Sciences (2008)

EDDS were spread over the soil surface at the rates of 0.2, 0.5 and 1.0 mmol·kg^{-1}. The numbers: 1, 2 and 3 stand for those rates in the descriptions of experimental plots (Table 2, Figures 1-3). The experiment was continued with two different watering regimes, simulating „normal" weather with occasional rain (N) and „wet" with repeated heavy rainfalls (W). The design of the experiment is presented in Table 2. Under the wet regime, soil was leached with distilled water 6 times, i.e. 2, 5, 14. 28, 50, and 100 days after chelate application, while under the normal regime – 4 times: after 14, 28, 50, and 100 days. The volume of leaching water ranged from 100 to 750 cm^3 per pot, and was adjusted to obtain 200 cm^3 of leachates under the normal regime and 500 cm^3 under the wet regime. The volume of water applied depended on the maize growth and properties of the root system. Seven days after the chelate application, aerial parts of the plants were harvested. Thereafter, as well as after all the leaching treatments, the soils' moisture was kept to enable chelate biodegradation. On the basis of metal concentrations in the leachates and their volumes, the amounts of leached metals were estimated. The estimation showed that considerable amounts of Cu, up to 5 percent of total Cu, were leached from soils, and

Table 2

Design of experiment – soil from Głogów (G). For the soil from Legnica, the same design was used, with letter L instead of G in all descriptions and symbols

Experimental plot	Chelating agent	Chelator rate	Watering regime
G/0/0/N	---	0	N - normal
G/0/0/W			W - wet
G/EDTA/1/N	EDTA	1 – low (0.2 mmol·kg^{-1})	N - normal
G/EDTA/1/W			W - wet
G/EDTA/2/N		2 – medium (0.5 mmol·kg^{-1})	N - normal
G/EDTA/2/W			W - wet
G/EDTA/3/N		3 – high (1.0 mmol·kg^{-1})	N - normal
G/EDTA/3/W			W - wet
G/EDDS/1/N	EDDS	1 – low (0.2 mmol·kg^{-1})	N - normal
G/EDDS/1W			W - wet
G/EDDS/2/N		2 – medium (0.5 mmol·kg^{-1})	N - normal
G/EDDS/2/W			W - wet
G/EDDS/3/N		3 – high (1.0 mmol·kg^{-1})	N - normal
G/EDDS/3/W			W - wet

Fig. 1. Growth of maize in the year 2007: a – general view of the experiment, b – soil G, the plots with the maximum rate of EDTA and EDDS applied in 2006 (pot 67: G/EDTA/3/N, pot 71: G/EDTA/3/W, pot 91: G/EDDS/3/N, pot 95: G/EDDS/3/W), c – soil L, the plots with the maximum rate of EDTA and EDDS applied in 2006 – the pots 167, 171, 191 i 195 analogous to those with soil G: L/EDTA/3/N, L/EDTA/3/W, L/EDDS/3/N, L/EDDS/3/W

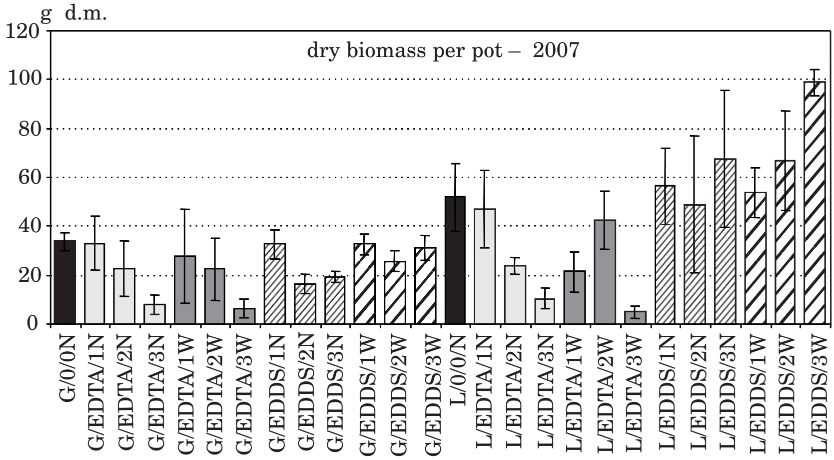

Fig. 2. Dry biomass of maize harvested in 2007 in various experimental plots, g d.m. per pot

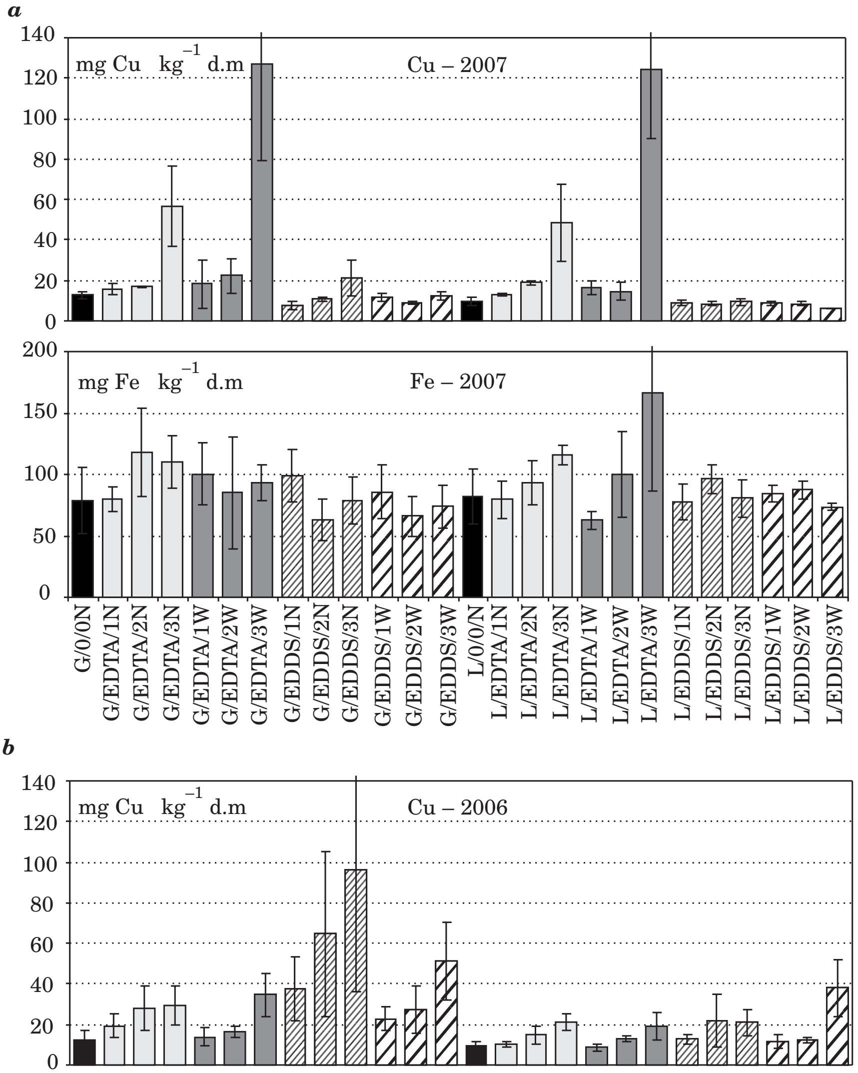

Fig. 3. Cu and Fe concentrations in dry biomass of maize: *a* – in 2007, *b* – compared with Cu in maize in 2006 (based on KARCZEWSKA et al. 2008)

the result depended on the kind and rate of a chelating agent. The highest amounts of Cu were leached from the pots with EDDS applied at the highest rates. A more detailed description of the results obtained in 2006 was presented by KARCZEWSKA et al. (2008). Figure 2b shows the mean concentrations of copper in maize biomass in 2006.

In the following year, maize was used again as an experimental plant. Before sowing, soil samples were collected and analyzed for available nutrients. Additionally, necessary fertilization with macro- and micronutrients was applied. Furthermore, easily soluble forms of Cu and Fe were analyzed in soils by extraction with 1 mol·dm^{-3} NH_4NO_3, 0.01 mol·dm^{-3} $CaCl_2$ and water (Karczewska 2002). During plant vegetation, soil moisture was maintained in the range of 60-90% of field capacity. When the plants reached the stage of maturity, their aerial parts were cut, weighed, dried and analyzed for Cu and Fe concentrations. Additionally, maize roots were collected, washed thoroughly with distilled water, dried, weighted and analyzed for Cu and Fe. The plant material was dry ashed at the temperature 450°C, and then dissolved in nitric acid (Ostrowska et al. 1991). Cu and Fe were determined in solutions by flame AAS. The results obtained for soils amended with the chelating agents were compared with control plots without chelate addition. Correlation coefficients were determined between Cu and Fe concentrations in plant material and in soil extracts.

RESULTS AND DISCUSSION

Plant growth differed considerably among experimental plots, as it is show in the photo (Figure 1) and confirmed by the data on plant biomass (Figure 2). Plant growth on soil G was much poorer than that on soil L, and related yields of biomass differed significantly. Mean biomass of maize grown in 2007 in control plots, without chelate additions, was 33.7 g d.m. per pot in the case of soil G (G/0/0/N) and 51.8 g d.m. in the case of soil L (L/0/0/N). Application of EDTA in 2006 resulted in a considerable, statistically significant reduction of plant yield in 2007, particularly in the plots with the highest EDTA rate (Figures 2 and 3). The plants in those plots indicated very strong signs of Cu toxicity, with typical symptoms such as interveinal foliar chlorosis, necrotic leaf tips and margins, leaf wilting from edges towards central part of the leaf, as well as changes in the root system (Reichmann 2002). In those pots where EDDS as a biodegradable chelator (Kos, Lestan 2003, Meers et al. 2005) was applied in 2006, different effects were observed on maize grown on soils G and L. In the plots with soil G, plant growth and biomass yield were slightly reduced in comparison with control plots, whereas in the plots with soil L, the growth of maize was affected positively, which means that maize yield increased significantly and Cu concentrations in leaves decreased when compared with control plots (Figures 2 and 3). This effect was particularly distinct in the plots with the wet watering regime (W) applied in 2006. At this stage of research, it is difficult to say what mechanism was responsible for such dependence on soil watering. Presumably, the most soluble Cu forms were intensively leached, which was followed by biodegradation of a chelating agent, which therefore did not cause any further Cu mobilization from soil. The ranges of soluble Cu and Fe in soils, determined before maize was sown, at the beginning of season 2007, as well as at the end of the season, after plant harvest, are shown in Table 3. The amounts of Cu extracted from soils with 1mol·dm^{-3} NH_4NO_3 were higher than those extracted with 0.01 mol·dm^{-3} $CaCl_2$, although the relationships between the plots were similar. The highest concentrations of soluble Cu were found in soils treated with high rates of EDTA, whereas in the plots with EDDS, the concentrations of soluble Cu were lower even then those in control plots (Table 3). Similarly, the highest concentrations of soluble Fe were found in 2007 in soils amended with EDTA. Comparison of soluble Cu in soils before the season 2007 and after plant harvesting indicates that Cu extractable with 0.01 mol·dm^{-3} $CaCl_2$ decreased significantly in both soils, by 40 percent on average, whereas in the case of Cu extractable with 1 mol·dm^{-3} NH_4NO_3, a similar decrease was confirmed only in soil L. There were no significant differences between the amounts of soluble Fe extractable from soils before and after plant cultivation.

Table 3

Soluble forms of Cu and Fe, extracted from soils with 1 mol·dm^{-3} NH_4NO_3 and 0.01 mol·dm^{-3} $CaCl_2$, mg·kg^{-1}

Plots	Value	Soil G				Soil L			
		Cu		Fe		Cu		Fe	
		the forms extracted with:							
		NH_4NO_3	$CaCl_2$	NH_4NO_3	$CaCl_2$	NH_4NO_3	$CaCl_2$	NH_4NO_3	$CaCl_2$
Before the season 2007									
Control		36.5	2.4	0.3	0.7	16.5	2.2	0.3	0.7
EDTA	min.	20.9	3.7	1.0	0.2	12.7	5.0	0.3	0.5
	max.	35.6	12.9	2.0	0.8	36.4	21.2	3.1	1.9
EDDS	min.	20.7	2.7	0.3	0.3	12.4	2.1	0.3	0.5
	max.	24.2	4.8	1.6	0.4	15.7	5.2	1.3	0.6
After maize harvesting in 2007									
Control		20.7	1.8	0.1	0.3	16.5	1.5	0.2	0.0
EDTA	min.	17.6	2.4	0.0	0.0	11.6	3.1	0.0	0.0
	max.	24.4	8.5	0.1	2.4	17.7	10.8	0.0	1.0
EDDS	min.	17.7	2.0	0.0	0.0	9.8	1.4	0.0	0.0
	max.	26.2	2.2	0.0	0.5	10.9	2.5	0.0	1.4

Copper concentrations in dry biomass of aerial parts of maize were significantly negatively correlated with plant yields (Table 4). The highest Cu concentrations, above 120 mg·kg^{-1} d.m., were found in the plants with the poorest growth and the strongest symptoms of Cu toxicity, i.e. in the plots with the highest EDTA rate and the wet watering regime: G/EDTA/3/W and L/EDTA/3/W, as it is shown in the diagram (Figure 3).

Table 4

Correlation coefficients between Cu and Fe concentrations in dry biomass, the biomass of maize shoots, and concentrations of soluble forms of metals in soils

Parameter		Metal concentrations in plant shoots ($mg \cdot kg^{-1}$ d.m.)	
		Cu	Fe
Plant yield (fresh biomass), g per pot		-0.680**	-0.450*
Plant yield (dry biomass), g d.m. per pot		-0.564**	-0.380
Cu in maize roots, $mg \cdot kg^{-1}$ d.m.		0.044	*x*
Cu in maize shoots, $mg \cdot kg^{-1}$ d.m.		*x*	-0.143
Fe in maize shoots, $mg \cdot kg^{-1}$ d.m.		0.640**	*x*
Soluble forms of elements (Cu or Fe) as determined in extraction with:	1 $mol \cdot dm^{-3}$ NH_4NO_3	0.697**	0.684**
	0.01 $mol \cdot dm^{-3}$ $CaCl_2$	0.715**	0.674**
	water	0.666**	-0.268

Correlations significant at: * p = 0.05; ** p = 0.01

Neither the analysis of Fe concentrations in the aerial parts of maize, nor the relationships between Cu and Fe concentrations in biomass confirmed any reduced uptake of Fe from soils by those plants that took up very high amounts of Cu. Under the conditions of the experiment, Cu and Fe concentrations in dry biomass of maize were positively correlated ($r = 0.640$, $p = 0.01$) – Table 4. Such relationship does not necessarily mean that there is no antagonistic effects of Cu on Fe activity at the level of cell physiology. The results of the experiment proved, however, that Fe concentrations in plant biomass increased together with increasing concentrations of Cu.

It was also proven that the concentrations of Cu and Fe in the aerial parts of maize were positively correlated with the concentrations of soluble forms of those elements present in soils, extractable with both 1 $mol \cdot dm^{-3}$ NH_4NO_3 and 0.01 $mol \cdot dm^{-3}$ $CaCl_2$, which was confirmed by high correlation coefficients ($r > 0.67$, $p = 0.01$), as indicated in Table 4. On the contrary, the concentrations of Cu and Fe in maize roots did not depend on any variable of the experiment (soil, rate of chelating agent or watering regime). Copper and iron concentrations in the aerial parts of maize did not correlate with concentrations of those elements in plant roots, either (Table 4).

CONCLUSIONS

1. EDTA applied to support copper phytoextraction from polluted soil caused long-lasting carryover effects such as raised copper phytotoxicity and its increased leachability in the subsequent year. Similar effects were not observed after application of easily biodegradable EDDS, therefore further research on induced phytoextraction of Cu from polluted soils should be carried out with biodegradable chelators.

2. Under the conditions of chelate-induced Cu phytoextraction, Cu and Fe solubility in soils increased, and plant uptake of those elements correlated well with soil concentrations of their easily soluble forms.

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EFFECT OF ADDITION OF HERBS ON BODY WEIGHT AND ASSESSMENT OF PHYSICAL AND CHEMICAL ALTERATIONS IN THE TIBIA BONES OF BROILER CHICKENS

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Abstract

Bones, even after their growth has been completed, react to both external and internal factors which include feeding. The process of bone mineralization, including limb bones, is a very important index of the effectiveness and quality of feeding procedures, aswell as a measure of the organism's health status. Antibiotics, which used to be very popular growth stimulators in feeding, have recently been replaced with natural feed additives, namely herbs. Although the usefulness of herbs has been known for a long time, little information has been found so far concerning their use in animal feeding and effect on the physical parameters and the chemical composition of the bones chickens.

The aim of the present work was to determine a potential influence of herbs added to chickens' diets on the body weight, chosen physical parameters of tibia bones: their weight, length and the content of the basic mineral components of the bone.

The experiment was conducted on 210 broiler chickens of the Ross 308 line, divided into seven feeding groups: the control group (I – a mixture containing an antibiotic) and six experimental ones (II – hops, III – lime, IV – lemon balm, V – pansy, VI – peppermint, VII – nettle). In the bone samples, their weight, length, and the chemical composition of ash: Ca, Mg and P were determined.

The results obtained in the present study reveal that an addition of nettle or lemon balm to the mixtures led to an increase in the body weight of broiler chickens. An addition of hops (II) to the mixtures led to a decrease in the length of the bones. An addition of lemon balm, pansy, peppermint or nettle to the mixtures had a negative effect on the level of Mg in the bones.

Key words: broiler chicken, herb, tibia bones, physical and chemical parameters.

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WPŁYW DODATKU ZIÓŁ DO PASZY NA MASĘ CIAŁA ORAZ CECHY FIZYCZNE I CHEMICZNE KOŚCI PISZCZELOWYCH KURCZĄT BROJLERÓW

Abstrakt

Kości, nawet po zakończeniu swego wzrostu, reagują na czynniki wewnętrzne i zewnętrzne, do których należy również żywienie. Proces mineralizacji tkanki kostnej, w tym kości kończyn, jest bardzo ważnym wskaźnikiem efektywności i jakości stosowanego żywienia, ale również i miernikiem stanu zdrowotnego organizmu. Antybiotyki, do niedawna popularne w żywieniu stymulatory wzrostu, zaczęto zastępować naturalnymi dodatkami paszowymi, np. ziołami. Mimo że przydatność ziół jest znana od dawna, to w żywieniu zwierząt, jak dotąd, nie ma jednoznacznych informacji na temat ich wpływu na organizm kurcząt oraz parametry fizyczne i skład chemiczny kości.

Celem pracy było określenie potencjalnego wpływu dodatku ziół do mieszanek paszowych na masę ciała, wybrane parametry fizyczne kości piszczelowych: masę i długość oraz zawartość podstawowych mineralnych składników kośćca.

Doświadczenie przeprowadzono na 210 kurczętach brojlerach Ross 308, podzielonych na 7 grup: kontrolną (I – antybiotyk) i 6 doświadczalnych (II – chmiel, III – lipa, IV – melisa, V – bratek, VI – mięta, VII – pokrzywa). Określono masę powietrznie suchą kości piszczelowych, długość całkowitą, a po mineralizacji – zawartość podstawowych składników mineralnych: Ca, Mg i P.

Stwierdzono, że wprowadzenie do mieszanek pokrzywy i melisy istotnie zwiększyło masę ciała kurcząt, a dodatek chmielu spowodował skrócenie kości. Zastosowanie dodatku melisy, bratka, mięty i pokrzywy wpłynęło na zmniejszenie koncentracji Mg w kościach.

Słowa kluczowe: kurczęta brojlery, zioła, kości piszczelowe, parametry fizyczne i chemiczne.

INTRODUCTION

The chemical composition of each organism is relatively fixed and determined by its genotype. Maintaining the composition on a fixed level, due to homeostasis, is essential for all tissues, including bones. Bones, even after their growth has been completed, react to both external and internal factors, which include feeding. With respect to the practice of poultry feeding, the process of bone mineralization, including limb bones, is a very important index of the effectiveness and quality of feeding procedures, as well as a measure of the organism's health status (FERRETTI et al. 1993, ŚLIWA and RADZKI 1995, KWIECIEŃ 1997, 1999, RATH et al. 2000, CRESPO et al. 2000, JANOCHA et al. 2004, KWIECIEŃ 2005).

Chickens are characterized by a fast growth rate. The mixtures used in nutrition of chickens are expected to have a high concentration of protein, energy, vitamins and minerals supplemented with stimulators (ZIMNOCH et al. 2000).

The conditions of broiler breeding and management, as well as genetic selection aimed at reaching a high body weight at the quickest rate possible, have resulted in higher requirements regarding mechanical bone resistance in chickens. The burden put on the bones, resulting from a high body weight conditioned mainly by the muscles of breasts and limbs, the imbalance between these parts of the body and an excessive ratio between the muscle weight and bone weight lead to structural deformities and distortions of the skeleton, which in most cases affect the limbs (CRESPO et al. 1999).

Recently, antibiotics which used to be very popular growth stimulators in feeding (FRITZ et al. 1993, GUO et al. 2003, DEMIR et al. 2005), have been replaced with natural feed additives, namely herbs (CRAIG 1999, KALOREY et al. 2005). This was caused by the concerns regarding an unwanted influence of antibiotics on man as a consumer, as well as on the environment (DONOGHUE 2003).

Herbs possess healing properties and they reinforce the immune system. They influence physiological processes and contribute some nutritive value. Consequently, they can affect directly or indirectly the production results (CRAIG 1999, NAGESWARA et al. 1999, HOTA et al. 2000, CROSS et al. 2004, GUO et al. 2004, MITSCH et al. 2004). Although the usefulness of herbs has been known for a long time, little information has been found so far concerning animal feeding and the remains of certain substances in the tissues, their influence on the organism or the animal products obtained. The knowledge concerning the influence of herbs on the physical parameters and the chemical composition of the bones is also scarce (KWIECIEŃ, WINIARSKA-MIECZAN 2007), which makes it impossible to verify most of the authors' own studies and induces their continuation.

The aim of the present work was to determine a potential influence of herbs added to chickens' diets on the body weight and chosen physical parameters of tibia bones: their weight, length and the content of the basic mineral components of the bone: Ca, P and Mg.

MATERIAL AND METHODS

The experiment was conducted on 210 broiler chickens of the Ross 308 line, reared in boxes under standard environmental conditions until they were 42 days old. One-day-old chickens were randomly divided into 7 groups: a control group (I) and six experimental groups (II, III, IV, V, VI and VII). Each group consisted of 30 birds in three replications.

From raising day 1 to day 10, the birds were administered a starter mixture (S), from day 11 to day 35 – a grower mixture (G) and from day 36 to day 42 – a finisher mixture (F). The control mixtures contained: maize, soybean meal, dried grass silage, soybean oil and antibiotic (Flavomycin). Composition and nutritive value of the control and experimental mixtures are presented in Table 1. In the experimental mixtures, dried grass silage was replaced by 2% addition of dried herbs: hops (*Humulus lupulus* L.), lime

Table 1

Composition (%) and nutritive value of the mixtures

Item	S		G / F	
	groups			
	I*	II-VII	I*	II-VII
Maize	55.15	55.5	57.78	57.78
Soybean meal 46%	33.0	33.0	30.0	30.0
Yeast	2.0	2.0	2.0	2.0
Dried grass silage meal	2.0	-	2.0	-
Herbal meal	-	2	-	2
Soya oil	3.0	3.0	4.0	4.0
Dicalcium phosphate	1.5	1.5	1.2	1.2
Limestone	1.5	1.5	1.5	1.5
NaCl	0.5	0.5	0.35	0.35
DL-methionine	0.15	0.15	0.15	0.15
L-lysine	0.2	0.2	0.02	0.02
Vitamin-mineral premix [a]	1.0	1.0	1.0	1.0
Total	100	100	100	100
1 kg feed mixtures contains:				
ME (MJ)	12.74	12.73	13.03	13.03
Crude protein (g)	214.1	214.1	194.2	194.2
Crude fibre (g)	34.3	34.3	33.3	33.3
Ca (g)	10.18	10.18	9.47	9.47
P total (g)	6.97	6.97	6.29	6.29
Mg (g)	1.94	1.94	1.72	1.72
Lysine (g)	12.12	12.12	9.98	9.98
Met + Cys (g)	7.77	7.77	7.71	7.71

I – control group; II-VII – experimental groups; S – starter mixture; G/F – grower/finisher mixture group

[a] Composition of premix starter/kg: vit. A 1360000 IU, vit. D_3 325000 IU, vit. E 4000 mg, vit. K3 250 mg, vit. B_1 200 mg, vit. B_2 600 mg, vit. B_6 300 mg, vit. B_{12} 2000 µg, biotin 15 mg, folic acid 125 mg, nicotinic acid 3500 mg, D-calcium panthotenate 1200 mg, choline chloride 60000 mg, Mn 9000 mg, Cu 2000 mg, Zn 10000 mg, Fe 9000 mg, J 100 mg, Se 25 mg, Co 70000 µg; Composition of premix grower/finisher/kg: vit. A 1200000 IU, vit. D_3 300000 IU, vit. E 3000 mg, vit. K3 200 mg, vit B_1 150 mg, vit. B_2 500 mg, vit. B_6 250 mg, vit. B_{12} 1500 µg, biotin 10 mg, folic acid 100 mg, nicotinic acid 2500 mg, D-calcium panthotenate 1000 mg, choline chloride 60000 mg, Mn 9000 mg, Cu 2000 mg, Zn 10000 mg, Fe 9000 mg, J 100 mg, Se 25 mg, Co 70000 µg

*antibiotic Flavomycin (0.1%)

(*Tilia cordata* L.), lemon balm (*Melissa officinalis* L.), pansy (*Viola tricolor* L.), peppermint (*Mentha piperita* L.) or nettle (*Urtica dioica* L.). Since the beginning of broiler raising, the birds were fed in accordance with the methodical system presented in Table 2.

Table 2

Design of the experiment

Group	Trestment
I (control)	antibiotic and dried grass silage – 2%
II	hops *(Humulus lupulus* L.) – 2%
III	lime (*Tilia cordata* L.) – 2%
IV	lemon balm (*Melissa officinalis* L.) – 2%
V	pansy (*Viola tricolor* L.) – 2%
VI	peppermint (*Mentha piperita* L.) – 2%
VII	nettle (*Urtica dioica* L.) – 2%

The mixtures were delivered in the form of a mass of pelets; only the nestlings were administered crumbles. Feed and water were provided *ad libitum.*

After weighing chickens on day 42, 8 birds (4 cockerels and 4 hens) from each group, about the average weight, were sacrificed and subjected to dissection. During the dissection analysis, their tibia bones were taken for preparations according to the Polish method described by ZIOŁECKI and DORUCHOWSKI (1989). The weight, length and percentage share of the bone in the total body weight were assessed.

After the incineration process at the temperature of 650°C, crude ash and basic mineral components: Ca, Mg and P were determined. Crude ash was determined by the AOAC method (1999). The spectrophotometric atomic absorption (SAA) method was used to assess the content of Ca and Mg, while the amount of P was determined with the colorimetric method on a Helios Delta apparatus.

The results were subject to a statistical analysis, using Statistica Version 5, with ANOVA single-factor variance test, adopting 0.01 as significance level (StatSoft Inc 1995). Significance of differences between means was determined by Tukey's test.

RESULTS AND DISCUSSION

The addition of herbs to the mixtures led to a significant differentiation and an increase in the body weight of broiler chickens in the experimental groups, in comparison with the body weight of the control group birds (Table 3). A different opinion is presented by KRAWCZYK et al. (2000) and

Table 3

Body weight and physical parameters of broiler chickens tibia bones

Sex	Groups						
	I	II	III	IV	V	VI	VII
Body weight (g)							
♂	2108.5±11.24	2228.5±10.11	2249.5±17.44	2365±6.94	2287.75±17.41	2297.5±9.44	2434.5±8.18
♀	2105.5±7.94	2224.75±11.70	2244.0±9,47	2370.5±10.12	2289.75±12.08	2296.2±19.61	2453.7±12.12
$\overline{x}$	2107.0^{A}	2226.6^{A}	2246.7^{A}	2367.7^{B}	2288.7^{AB}	2296.9^{AB}	2444.1^{B}
Bone weight (g)							
♂	12.96±1.45	13.77a±1.90	12.74±1.52	16.24a±1.87	14.88±2.16	17.23a±1.98	16.95a±2.02
♀	14.90±1.38	10.62b±1.65	10.21±1.23	12.08b±1.25	12.53±1.45	12.84b±2.01	13.91b±1.56
$\overline{x}$	13.93^{AB}	12.19^{B}	11.47^{B}	14.16^{AB}	13.71^{AB}	15.04^{A}	15.43^{A}
Bone lenght (mm)							
♂	103.25a±12.67	81.12±14.56	98.12±15.67	103.25a±14.32	100.75±15.08	108.6a±14.52	106.5±13.65
♀	97.00b±10.87	81.40±13.58	92.25±14.26	95.25b±13.67	99.62±14.89	100.5b±13.87	103.2±12.79
$\overline{x}$	100.12^{A}	81.26^{B}	95.19^{A}	99.25^{A}	100.19^{A}	104.6^{A}	104.9^{A}
Percentage of bone in the body weight (%)							
♂	0.62±0.03	0.65a±0.02	0.59a±0.06	0.75a±0.01	0.68±0.05	0.78a±0.06	0.76±0.04
♀	0.71±0.01	0.50b±0.04	0.47b±0.03	0.56b±0.03	0.57±0.03	0.58b±0.01	0.63±0.02
$\overline{x}$	0.66	0.57	0.53	0.65	0.62	0.68	0.69

a, b – significant differences between males and females ($P \leq 0.01$)
A, B – significant differences between groups ($P \leq 0.01$)
Groups I – VII see Table 2

by Botsoglou et al. (2002; 2004), who obtained results suggesting a negative effect of herbs on the final body weight of broiler chickens.

The weight of the chickens' tibia bones was dependent on the sex of the birds, and thus, indirectly, on their bones weight, and it was statistically higher in cockerels than in hens in the groups receiving an addition of hops (II), lemon balm (IV), peppermint (VI) and nettle (VII).

An addition of hops (II) to the mixtures led to a decrease in the length of the bones in comparison with the control group. It was also noted that the bones of the cockerels were longer than the bones of the hens, and statistically significant differences regarding the length of the bones were observed between the roosters and hens administered an addition of antibiotic (I), lemon balm (IV) and peppermint (VI).

The results of the study concerning the weight and length of tibia bones coincide with the data quoted by Kwiecień and Winiarska-Mieczan (2007), who examined the femur as a representative bone in reference to the research concerning the skeletal system. The values of the physical parameters of the tibia bone examined in the authors' own studies are similar to the results observed by Pisarski and Kwiecień (2003) and Kwiecień (2003), yet the agents affecting the physical parameters of the bones were slightly different.

Introducing herbs into feeds for poultry did not lead to a differentiation in the percentage share of the bone in the total body weight. However, statistically significant differences were observed between the cockerels and hens receiving a supplement of hops (II), lime (III), lemon balm (IV) and peppermint (VI).

All physical parameters of the bones considered in the experiment were substantially higher in roosters than in hens, which, as suggested by Blenau (1993), Śliwa and Radzki (1995), Seeman (1999) and Rath et al. (1999), results from the systemic distinctness determined by sex and growth hormones.

The results of the studies performed by Szeremeta et al. (2005) also indicate the influence of age and sex on bone parameters. The researchers found longer and heavier bones of larger diameter in male individuals. The results obtained in the authors' own studies suggest a positive effect of nettle on physical parameters of tibia bones in broiler chickens. A similar opinion is expressed in the studies by Kwiecień and Winiarska-Mieczan (2007).

One of the most serious problems in broiler raising is bone resistance, especially the resistance of the legs, which can be weakened by an inadequate composition of the feed mixture and may adversely influence the effectiveness of the production (Crespo et al. 1999).

The herbs were not a factor that would significantly modify the content of calcium and phosphorus in the chickens' tibia bones (Table 4). The level of magnesium in the bones of the birds in the control group and the chickens administered mixtures with an addition of hops and lime was statistically significantly higher than its content in the bones of the chickens fed

Table 4

Mineral composition of broiler chickens' tibia bones

Sex	Groups						
	I	II	III	IV	V	VI	VII
Crude ash (%)							
♂	48.2±4.01	46.9±1.94	46.0b±2.01	47.1±1.20	47.2±3.55	46.9±2.49	47.0±1.20
♀	46.7±3.11	47.2±1.58	49.8a±2.30	47.6±0.95	47.1±0.60	47.5±1.51	47.1±1.09
$\overline{x}$	47.5	47.1	47.9	47.4	47.1	47.2	47.1
P ($mg \cdot kg^{-1}$)							
♂	178.2±13.50	171.8±14.67	168.7b±13.90	176.8±8.90	179.2±9.00	167.1b±12.95	180.3±9.01
♀	193.8±14.70	182.6±15.02	206.3a±12.80	179.5±9.03	178.7±9.15	182.1a±11.01	178.7±8.12
$\overline{x}$	186.0	177.2	187.5	178.1	179.0	174.6	179.5
Ca ($mg \cdot kg^{-1}$)							
♂	292.7a±21.90	286.6±17.50	280.3±13.50	284.6±15.90	282.6±21.10	281.5±21.10	280.3±13.50
♀	261.9b±20.10	278.1±16.90	281.4±12.98	286.1±12.01	282.1±20.80	282.9±20.90	283.2±11.50
$\overline{x}$	277.3	282.4	280.9	285.4	282.3	282.2	281.8
Mg ($mg \cdot kg^{-1}$)							
♂	8.4±0.61	8.3±0.69	8.3a±0.65	7.3±0.59	7.3±0.45	7.2±0.48	7.1±0.49
♀	8.3±0.31	8.1±0.28	7.8b±0.19	7.1±0.12	7.0±0.11	7.1±0.14	7.0±0.30
$\overline{x}$	8.3^{A}	8.2^{A}	8.1^{A}	7.2^{B}	7.2^{B}	7.2^{B}	7.1^{B}

a, b – significant differences between males and females ($P \leq 0.01$)
A, B – significant differences between groups ($P \leq 0.01$)
Groups I – VII see Table 2

mixtures with a supplement of lemon balm, pansy, peppermint or nettle. Moreover, it was shown that the bones of the cockerels receiving a supplement of lime in the feed had a significantly higher level of magnesium than the bones of the hens.

The study has shown that the herbs added to the experimental mixtures had a positive effect on both the physical properties examined and the chemical composition of the tibia bones in broiler chickens, which is noteworthy regarding not only production results but also the welfare of the birds (PISARSKI, KWIECIEŃ 2003). It can be observed that none of the herbs we tested had an unambiguous effect on the examined parameters of the bone, whereas in the study performed by KWIECIEŃ and WINIARSKA-MIECZAN (2007) nettle had the strongest influence on the majority of the properties of chickens' femoral bones.

CONCLUSIONS

The results obtained in the present study reveal that an addition of nettle or lemon balm to the mixtures led to an increase in the body weight of broiler chickens. An addition of hops (II) to the mixtures led to an decrease in the length of the bones. An addition of lemon balm, pansy, peppermint or nettle to the mixtures indicated a negative effect on the level of Mg in the bones.

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MINERAL CONTENT OF MELON FRUIT (*CUCUMIS MELO* L.)

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Abstract

Melons are highly demanding, thermophilous plants, which is why they are unpopular among fruit growers. Melon cultivation requires special treatment methods for the improvement of microclimatic conditions. Seven Polish melon cultivars are presently grown on the domestic market. They are well adapted to the local climate. The growth rate, vigor, fruit shape, fruit size, rind color and flesh thickness of those cultivars vary. The objective of this study was to determine the mineral content of edible parts of four field-grown melon cultivars in the Warmia region (NE Poland). This study discusses the mineral content of melon fruit subject to the investigated cultivar and cultivation method. In Poland, melon production is difficult and unreliable. The main problem is the selection of an appropriate cultivar and cultivation method. The analyzed material consisted of four Polish melon cultivars: Malaga F_1, Melba, Oliwin, Seledyn F_1, grown in a field experiment without protective cover, under polyethylene (PE) sheet cover, under non-woven polypropylene (PP) cover, with soil mulching, as well as with soil mulching under PE sheet cover or non-woven PP cover. The highest concentrations of total N, K, Ca and Cu were determined in melon fruit of cv. Oliwin. Significant variations in total nitrogen and phosphorus levels in the edible parts of melon plants were noted subject to the applied cultivation method. *Cucumis melo* L. grown in the control treatment without protective cover was marked by significantly higher levels of total nitrogen and phosphorus in the fruit, compared with fruit grown with the use of other cultivation methods. The results of this study indicate that the fruit of melon plants cv. Seledyn grown in mulched soil under non-woven PP cover was characterized by the most favorable Ca:Mg and Ca:P ratios in comparison with fruit from the remaining treatments.

Key words: melon, cultivars, cultivation methods, chemical composition.

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ZAWARTOŚĆ SKŁADNIKÓW MINERALNYCH W OWOCACH MELONA (*CUCUMIS MELO* L.)

Abstrakt

Melon jest rośliną mało rozpowszechnioną w uprawie. Należy do grupy warzyw ciepłolubnym o dużych wymaganiach środowiskowych, z tego względu w jego produkcji niezbędne są zabiegi poprawiające warunki mikroklimatyczne. Obecnie w uprawie znajduje się siedem odmian polskiej hodowli, dobrze przystosowanych do uprawy w naszych warunkach klimatycznych. Odmiany te charakteryzują się zróżnicowaną siłą wzrostu, kształtem owoców, ich wielkością, zabarwieniem skórki oraz warstwą miąższu. Celem badań była ocena zawartości składników mineralnych w częściach jadalnych czterech odmian melona uprawianego w warunkach polowych Warmii, w zależności od badanej odmiany oraz metody uprawy. Uprawa melona w Polsce jest trudna i zawodna. Problem stanowi dobór odpowiedniej odmiany oraz metody jej uprawy. Do badań wytypowano cztery polskie odmiany melona: Malaga F_1, Melba, Oliwin, Seledyn F_1, uprawianego w polu bez osłon, z zastosowaniem osłaniania roślin folią PE, włókniną PP, mulczowania gleby oraz jednoczesnego mulczowania gleby i osłaniania roślin folią PE lub włókniną PP. Spośród analizowanych odmian istotnie największą zasobnością w N-ogółem, K oraz Ca i Cu charakteryzowały się owoce odmiany Oliwin. Zastosowane w uprawie melona metody uprawy spowodowały istotne zróżnicowane zawartości azotu ogółem i fosforu w jego częściach jadalnych. Uprawa *Cucumis melo* L. w obiekcie kontrolnym (bez zastosowania osłon) spowodowała istotne zwiększenie zawartości azotu ogółem i fosforu w porównaniu z innymi analizowanymi metodami uprawy. Analizując stosunki Ca:Mg i Ca:P stwierdzono, że uprawiane na glebie mulczowanej i osłanianej włókniną PP owoce odmiany Seledyn charakteryzowały się korzystną proporcją Ca:Mg oraz Ca:P w odniesieniu do pozostałych obiektów uprawy.

Słowa kluczowe: melon, odmiany, metody uprawy, skład chemiczny.

INTRODUCTION

Melon fruit enjoys widespread popularity among consumers owing to its taste and high nutritional value. However, melons are highly demanding, thermophilous plants, which makes them relatively unpopular among fruit growers. Melon cultivation requires special treatment methods for the improvement of microclimatic conditions. A number of research studies investigating melon production technologies in various regions of Poland have been initiated to investigate the effect of perforated PE sheet cover, nonwoven PP cover and soil mulching with organic and mineral material on the melon growing process. The applied cultivation measures inhibit weed infestation and improve the microclimatic environment around plants (Łotocka, Gajc 1987, Grudzień 1992, Libik, Siwek 1994, Siwek 1996, Grudzień 1998, Grudzień 2000).

Seven Polish melon cultivars are presently grown on the domestic market. They are well adapted to the local climate. The growth rate, vigor, fruit shape, fruit size, rind color and flesh thickness of those cultivars vary (*List of vegetable cultivars entered into the Polish national register* 2008).

The objective of this study was to determine the mineral content of the edible parts of four field-grown melon cultivars in the Warmia region (NE Poland).

MATERIALS AND METHODS

A two-factorial field experiment was carried out in a split-plot design, in three replications, during the years 2004-2007, at the Experimental Station of the University of Warmia and Mazury in Olsztyn. The first experimental factor were four melon cultivars: Malaga F_1, Melba, Oliwin and Seledyn F_1. The second factor were the following cultivation methods:

- melon plants grown in the control treatment;
- melon plants grown under perforated polyethylene (PE) sheet cover, 100 openings per m^2;
- melon plants grown under non-woven polypropylene (PP) cover, 17 $g \cdot m^{-2}$;
- plants grown in soil mulched with black PE sheet;
- melon plants grown in soil mulched with black PE sheet, under perforated PE sheet cover, 100 openings per m^2;
- melon plants grown in soil mulched with black PE sheet, under non-woven PP cover, 17 $g \cdot m^{-2}$.

A pot experiment was conducted in a heated greenhouse in line with generally observed standards for melon cultivation. Melon seeds were sown on 4 May, two seeds per pot filled with peat with the following chemical composition: $N\text{-}NO_3$ – 100, P – 80, K – 215, Ca – 1240, Mg – 121 $mg \cdot dm^{-3}$, pH of H_2O – 5.9 and salt concentration of 1.5 $g \cdot dm^{-3}$.

Field treatments were set up on brown soil of quality class IVb, good rye complex, developed from loamy sand on loam with pH of 6.7 and humus content of 2.8%. The chemical composition of soil was analyzed prior to the planting out of seedlings and the following results were obtained: $N\text{-}NO_3$ – 38, P – 127, K – 90, Ca – 1840, Mg – 194 ($mg \cdot dm^{-3}$). Mineral deficiencies were supplemented in accordance with standard requirements for melon plants. Soil was mulched with black PE sheet. Hardened seedlings were planted out in soil treatments on 2 June. The spacing between rows was 1.0 m, and plant spacing in a row was 80 cm.

Directly after planting out in soil treatments, seedlings were covered with perforated PE sheet, thickness of 0.02-0.05 mm, 100 openings per m^2. The other type of applied cover was Pegas-Agro 17 white non-woven PP fabric with surface density of 17 $g \cdot m^{-2}$. Both types of cover were spread directly on the plants and maintained for the first two weeks after planting.

The required cultivation measures were carried out over the growing period. The chemical protection regime was consistent with the Plant Protection Program (2004-2007). Melon fruit was harvested on ripening. Fifteen fruits were sampled from the marketable yield of each treatment for determination of the mineral content of edible melon parts. The harvested fruit was comminuted, dried to constant mass at 65°C, and ground in an electric mill. The prepared material was forwarded to the Chemical and Agricultural Station in Olsztyn, where it was mineralized and analyzed to determine the content of the following macronutrients and micronutrients: nitrogen (total) by potentiometry, phosphorus – by the vanadium-molybdate method, potassium – by flame photometry, magnesium – by atomic absorption spectrometry (AAS), calcium – by flame photometry, copper and iron – by AAS. The study was carried out under Accreditation Certificate no. AB 277 issued by the Polish Center for Accreditation.

The results were validated statistically by analysis of variance. The significance of differences between means was evaluated by constructing Tukey's confidence intervals at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Melon fruit is enjoying growing popularity among consumers owing to its taste as well as high nutritional value. Melon imports are low due to high cost and the fruit's short shelf-life (Grudzień 2000). In Poland, melon production is difficult and unreliable. The main problem is the selection of an appropriate cultivar and cultivation method.

The flesh of ripe melons has a high content of organic and mineral nutrients, which varies subject to cultivar and cultivation method (Ouzounidou et al. 2006). The results of the study carried out in 2004-2007 show that the levels of the investigated macronutrients (Table 1) were significantly affected by the cultivar, the applied cultivation method and the interactions between these experimental factors.

Nitrogen is one of the most important elements in human diet. The highest levels of this macronutrient were found in melon fruit of cv. Oliwin at 1.49 $g \cdot kg^{-1}$ d.m., while the lowest N concentrations were determined in Malaga F_1 at 1.11 $g \cdot kg^{-1}$ d.m. The applied cultivation method also affected total N concentrations in edible parts of melon plants. A significant increase in total nitrogen content was noted in the control treatment. Nitrogen levels in the fruit of melon plants grown in soil mulched with black PE sheet and under non-woven PP cover were low. Nitrogen concentrations in edible parts of melon plants were also significantly affected by the interactions between the above experimental factors. The highest quantities of total nitrogen were accumulated by melon fruit of cv. Oliwin covered with PE sheet. The growing of melon plants of cv. Melba in mulched soil under non-woven PP cover produced the opposite effect and lowered total N concentrations in the fruit by 1.3 $g \cdot kg^{-1}$ d.m.

Table 1

Total N, P, K, Mg and Ca concentrations in melon fruit (mean values for 2004-2007)

Cultivar	Cultivation method	Nutrient ($g \cdot kg^{-1}$ d.m.)				
		N	P	K	Mg	Ca
Malaga F_1	control – no cover	1.42	0.50	4.22	0.23	0.39
	PE sheet	1.09	0.37	4.10	0.20	0.34
	non-woven PP cover	0.98	0.47	4.28	0.21	0.39
	mulch	0.98	0.39	4.18	0.22	0.34
	mulch + PE sheet	1.33	0.39	5.21	0.26	0.31
	mulch + non-woven PP cover	0.86	0.36	4.28	0.25	0.38
	mean values	1.11	0.41	4.38	0.23	0.36
Melba	control – no cover	1.51	0.44	4.00	0.25	0.33
	PE sheet	1.09	0.35	4.28	0.31	0.46
	non-woven PP cover	1.24	0.49	4.85	0.30	0.60
	mulch	1.62	0.67	5.41	0.31	0.92
	mulch + PE sheet	1.04	0.39	3.88	0.22	0.37
	mulch + non-woven PP cover	0.65	0.41	3.47	0.24	0.47
	mean values	1.19	0.53	4.32	0.22	0.53
Oliwin	control – no cover	1.71	0.67	5.41	0.26	0.65
	PE sheet	1.95	0.47	5.34	0.31	0.73
	non-woven PP cover	1.83	0.58	5.21	0.31	0.54
	mulch	1.30	0.35	4.32	0.24	0.55
	mulch + PE sheet	0.83	0.28	3.34	0.23	0.51
	mulch + non-woven PP cover	1.33	0.47	4.42	0.23	0.38
	mean values	1.49	0.47	4.67	0.26	0.56
Seledyn F_1	control – no cover	1.62	0.49	4.05	0.22	0.44
	PE sheet	1.39	0.47	5.18	0.28	0.51
	non-woven PP cover	1.21	0.46	3.83	0.22	0.29
	mulch	0.89	0.50	3.52	0.15	0.37
	mulch + PE sheet	1.18	0.43	4.03	0.24	0.57
	mulch + non-woven PP cover	1.04	0.35	3.32	0.22	0.66
	mean values	1.41	0.45	4.02	0.22	0.47
Mean values	control – no cover	1.56	0.53	4.42	0.24	0.43
	PE sheet	1.38	0.41	4.73	0.28	0.51
	non-woven PP cover	1.31	0.50	4.54	0.26	0.46
	mulch	1.20	0.48	4.36	0.23	0.55
	mulch + PE sheet	1.01	0.38	4.74	0.24	0.44
	mulch + non-woven PP cover	0.98	0.39	3.87	0.24	0.47
LSD $_{\alpha=0.05}$						
cultivar (a)		0.21	n.s.	0.53	n.s.	0.10
cultivation method (b)		0.23	0.08	n.s.	n.s.	n.s.
interaction (axb)		0.18	0.12	0.96	n.s.	0.12

A well-balanced diet requires optimal phosphorus levels. According to Kunachowicz et al. (2006), melon fruit contains 0.29-0.35 g·kg^{-1} d.m. of phosphorus, subject to its dry matter content. Edible parts of the analyzed plants contained from 0.35 to 0.67 g·kg^{-1} d.m. of this nutrient. Cultivar had no statistically significant effect on phosphorus levels. Phosphorus concentrations were significantly affected by the cultivation method and by the interaction between the cultivation method and cultivar. The highest P levels were determined in edible parts of control group melons at 0.53 g·kg^{-1} d.m., while the lowest phosphorus concentrations were found in treatments with mulched soil and non-woven PP cover. Optimal phosphorus content results were noted in fruit of Oliwin plants grown in the control treatment. The highest drop in phosphorus levels in the fruit was reported when melon plants of cv. Oliwin were grown in mulched soil and covered with PE sheet.

Potassium is yet another macronutrient which is very important for the healthy function of the human body. Potassium levels in melon fruit range from 5.41 to 3.32 g·kg^{-1} d.m. The highest concentrations of this macronutrient were found in melon fruit of cv. Oliwin from the control treatment as well as in fruit of Melba plants grown in mulched soil.

Statistical analysis revealed that the investigated factors had no significant effect on magnesium levels in edible parts of melon plants. Magnesium concentrations were similar in the fruit of all analyzed cultivars, within the range of 0.15-0.31 g·kg^{-1} d.m.

Calcium is an essential mineral which builds and maintains healthy bones. On average, the analyzed melon fruit contained from 0.92 to 0.31 g·kg^{-1} d.m. of this nutrient. The highest calcium levels were determined in edible parts of cv. Oliwin plants, while the lowest calcium concentrations were noted in fruit of Malaga F_1 plants.

Iron was another element investigated in this study. Fe levels in edible parts of melon plants differed significantly (Figures 1, 2, 3) in the range from 46 to 360 mg·kg^{-1} d.m. The highest accumulation of iron was found

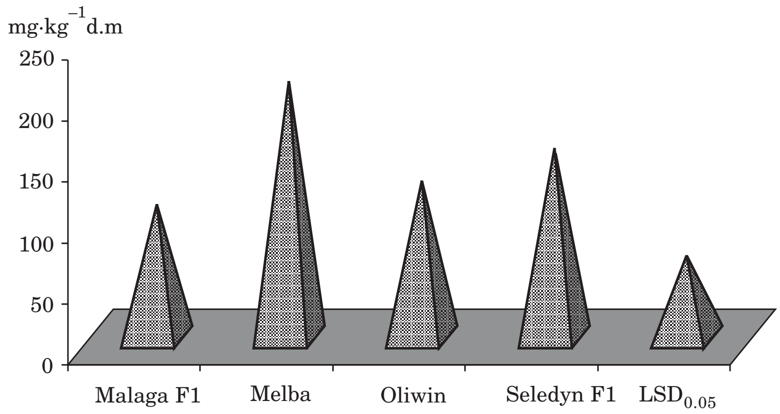

Fig. 1. The effect of cultivar on the iron content of melon fruit (mean values for 2004-2007)

in fruit of Melba plants covered with PE sheet, while a significant decrease in Fe levels was noted in fruit of melon plants grown in mulched soil under non-woven PP cover.

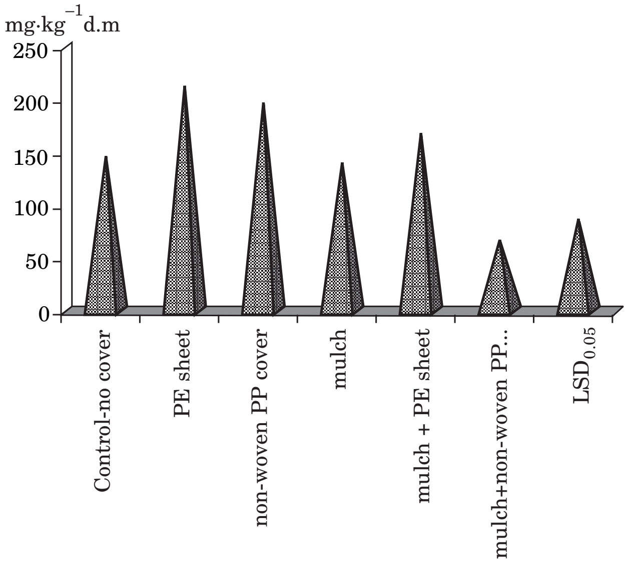

Fig. 2. The effect of cultivation method on the iron content of melon fruit (mean values for 2004-2007)

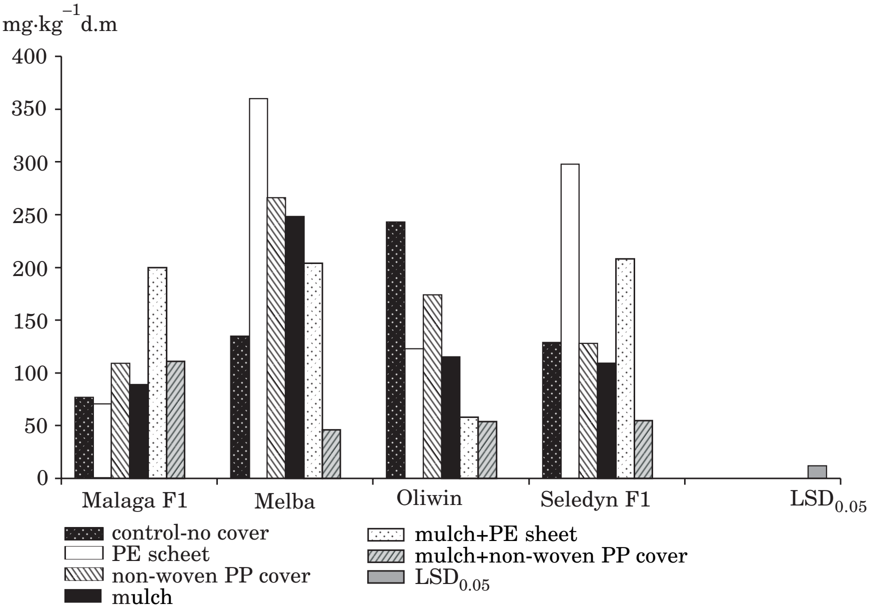

Fig. 3. The effect of interactions between the experimental factors on the iron content of melon fruit (mean values for 2004-2007)

The edible parts of melon plants were also analyzed to determine copper levels. Copper concentrations were significantly affected by the cultivar and its interactions with the cultivation method (Figures 4, 5). The highest levels of Cu were accumulated by fruit of Oliwin plants grown in mulched soil.

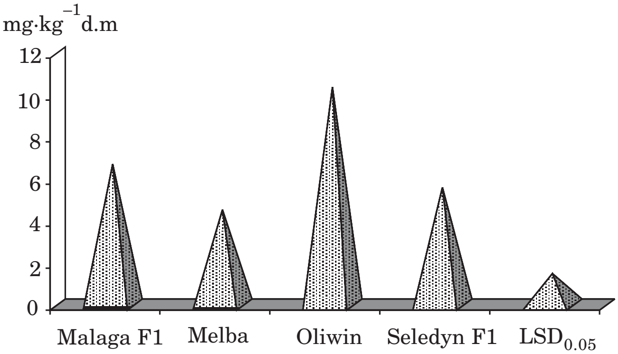

Fig. 4. The effect of cultivar on the copper content of melon fruit (mean values for 2004-2007)

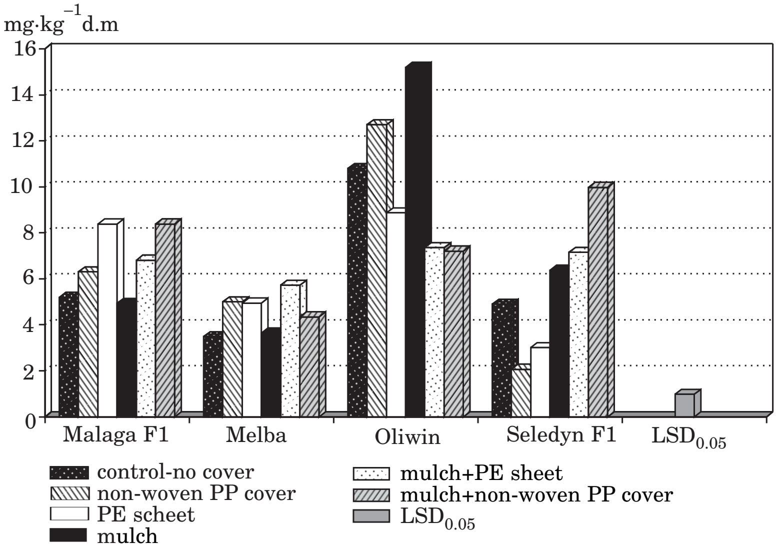

Fig. 5. The effect of interactions between the experimental factors on the copper content of melon fruit

According to Kotowska and Wybieralski (1999), the quality of plant edible parts is determined by their macronutrient and micronutrient content as well as by nutrient ratios, in particular K to Mg, Ca to Mg and K:(Mg+Ca). In the present study, nutrient ratios varied subject to the investigated cultivar and the applied cultivation method (Table 2).

Table 2

Ca:Mg, Ca:P, K:Mg and K:(Mg+Ca) ratios in melon fruit (mean values for 2004-2007)

Cultivar	Cultivation method	Ca:Mg	Ca:P	K:Mg	K:(Ca+Mg)
Malaga F_1	control – no cover	1.87	0.79	21.17	7.12
	PE sheet	2.06	0.92	20.61	7.31
	non-woven PP cover	2.69	1.12	24.42	6.47
	mulch	1.55	0.91	19.02	7.47
	mulch + PE sheet	1.20	0.80	20.05	9.16
	mulch + non-woven PP cover	1.72	1.23	17.14	6.34
	mean values	1.85	0.96	20.40	7.31
Melba	control – no cover	1.32	0.94	15.80	6.82
	PE sheet	1.60	0.94	14.87	5.61
	non-woven PP cover	2.08	0.91	17.52	5.58
	mulch	2.96	1.37	17.47	4.42
	mulch + PE sheet	1.69	0.95	17.72	6.58
	mulch + non-woven PP cover	2.37	1.15	16.76	4.89
	mean values	2.01	1.04	16.69	5.65
Oliwin	control – no cover	2.79	0.98	23.21	5.60
	PE sheet	2.36	1.55	17.27	5.14
	non-woven PP cover	1.74	0.93	16.81	6.13
	mulch	2.29	1.58	18.00	5.48
	mulch + PE sheet	2.24	1.83	14.65	4.51
	mulch + non-woven PP cover	1.65	0.81	19.24	7.27
	mean values	2.18	1.28	18.20	5.75
Seledyn F_1	control – no cover	2.03	0.90	18.69	6.14
	PE sheet	1.86	1.09	19.59	6.79
	non-woven PP cover	1.38	0.63	17.06	7.28
	mulch	2.48	0.81	23.51	6.78
	mulch + PE sheet	2.38	1.94	16.81	4.98
	mulch + non-woven PP cover	3.12	1.94	16.23	3.87
	mean values	2.21	1.22	18.65	5.97
Mean values	control – no cover	2.00	0.90	19.72	6.52
	PE sheet	1.97	1.13	18.09	6.21
	non-woven PP cover	1.97	0.90	18.95	6.37
	mulch	2.32	1.17	19.50	6.04
	mulch + PE sheet	1.88	1.38	17.31	6.31
	mulch + non-woven PP cover	2.21	1.28	17.35	5.59
LSD $_{\alpha=0.05}$					
cultivar (a)		ns	ns	ns	0.93
cultivation method (b)		ns	ns	ns	ns
interaction (axb)		0.95	0.43	ns	1.91

As demonstrated by Radkowski et al. (2005), Majkowska-Gadomska (2006), Majkowska-Gadomska and Wierzbicka (2008), the optimal Ca:Mg ratio should approximate 3, and the Ca:P ratio should be within the 1.2 – 2.2 range. A higher ratio is indicative of magnesium or phosphorus deficiency. The analyzed melon fruit was marked by a low calcium to magnesium and calcium to phosphorus ratios. The only exception was fruit of Seledyn F_1 plants grown in mulched soil under non-woven PP cover, where a satisfactory Ca:Mg ratio was noted. Ca:P ratios are a very important consideration in children's nutrition. The optimal Ca:P ratio of 1.94 was observed in fruit of Seledyn F_1 plants grown in mulched soil under PE sheet or non-woven PP cover.

All the analyzed cultivars showed a wider potassium to magnesium ratio and a wider potassium to total magnesium and calcium ions ratio. According to Radkowski et al. (2005), the optimal ratios are K:Mg – 6:1 and K:(Mg+Ca) – 1.6-2.2. The variations in the K:Mg ratio in melon fruit were not statistically validated, but a tendency to an increased K:Mg ratio was noted in Malaga F_1 fruit. The potassium to total magnesium and calcium ions ratio was significantly affected by the cultivar and its interaction with the cultivation method. The widest K:(Mg+Ca) ratio was determined in fruit of Malaga F_1 plants grown in mulched soil under PE sheet cover.

CONCLUSIONS

1. The highest total N, K, Ca and Cu concentrations were determined in melon fruit of cv. Oliwin.

2. *Cucumis melo* L. grown in the control treatment without protective cover was marked by significantly higher levels of total nitrogen and phosphorus in the fruit, compared with fruit grown with the use of other cultivation methods.

3. The fruit of melon plants cv. Seledyn F_1 grown in mulched soil under non-woven PP cover showed the optimal Ca:Mg and Ca:P ratios, in comparison with fruit from the remaining treatments.

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CONCETRATION OF COPPER, ZINC, LEAD AND CADMIUM IN PLANTS CULTIVATED IN THE SURROUNDINGS OF ŻELAZNY MOST COPPER ORE TAILINGS IMPOUNDMENT

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Abstract

Regular monitoring of soil and plants in the surroundings of Żelazny Most tailings impoundment has been held since 1996. The results presented in this paper refer to potatoes and grains of cereals such as wheat, barley, triticale and oats, which are the most popular crops planted in that area in 2004-2006. The average content of heavy metals in 2006 in cereals and potatoes was approximately: Cu – 3.7 and 1.3 mg kg^{-1} of fresh mass; Zn – 20.6 and 3.5 mg kg^{-1}; Pb – 0.14 and 0.04 mg kg^{-1}; Cd – 0.055 and 0.011 mg kg^{-1}, respectively. All those concentrations are well below threshold limit values accepted in Poland. No significant differences in Cu, Pb and Cd concentrations between the tested cereals were found. Zinc concentration in wheat and oat was significantly lower than in barley and triticale. The copper ore tailings impoundment in Żelazny Most, although very large, at present has no negative impact on the quality of crops and species of cereals and pasture plants cropped in its surroundings.

Key words: tailings impoundment, trace elements, cereals, potato.

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ZAWARTOŚĆ MIEDZI, CYNKU, OŁOWIU I KADMU W ROŚLINACH UPRAWNYCH W REJONIE SKŁADOWISKA ODPADÓW PO FLOTACJI RUD MIEDZI ŻELAZNY MOST

Abstrakt

W celu oceny ryzyka związanego z uprawą roślin konsumpcyjnych i paszowych na terenach znajdujących się pod wpływem składowiska odpadów po flotacji rud miedzi Żelazny Most, od 1996 r. prowadzony jest regularny monitoring jakości gleb i roślin uprawnych. W pracy przedstawiono zawartości Cu, Zn, Pb i Cd w ziarnie zbóż (pszenicy ozimej, jęczmienia ozimego, pszenżyta i owsa) i w bulwach ziemniaka, w latach 2004-2006. Stwierdzono następujące średnie zawartości metali (odpowiednio w ziarnie zbóż i w bulwach): Cu – 3,7 i 1,3 mg$\cdot$kg^{-1} św. m., Zn – 20,6 i 3,5 mg$\cdot$kg^{-1} św. m., Pb – 0,14 i 0,04 mg$\cdot$kg^{-1} św. m. oraz Cd – 0,055 i 0,011 mg$\cdot$kg^{-1} św. m. Nie stwierdzono istotnych różnic w zawartości Cu, Pb i Cd w ziarnie różnych gatunków zbóż. Zawartość Zn była istotnie niższa w pszenicy i owsie w porównaniu z pszenżytem i jęczmieniem. Nie stwierdzono przekroczenia dopuszczalnych zawartości pierwiastków śladowych, co świadczy o dużej skuteczności działań ograniczających negatywny wpływ składowiska na środowisko otaczających obszarów i warunki produkcji rolniczej.

Słowa kluczowe: pierwiastki śladowe, składowisko odpadów poflotacyjnych, zboża, ziemniak.

INTRODUCTION

Location of the copper industry in the Legnica – Głogów region decided about the economic structure and directions of regional development. Unfortunately, very intensive expansion of copper mining and smelting industry caused many adverse changes in natural environment (Dobrzański, Byrdziak 1995). Conditions of agricultural and forest production deteriorated as a result of air, soil and groundwater pollution (Czaban et al. 2007). Important sources of dust bearing heavy metals are impoundments containing tailings from copper ore enrichment. Fine-grained material can be blown away by wind from dry surfaces of an elevated impoundment, and transported to close surroundings as well as over very far distances. Such dust, having specific chemical composition, influences soils and plants in different ways, leading to disturbances in the life functions of soil microorganisms and cultivated plants.

Trace elements play a significant role in many metabolic processes in plant organisms, but at excessive concentrations, particularly in soluble forms and easily available to plants, can cause phytotoxic symptoms. Plant response to high contamination of soil and air with heavy metals is extremely variable and depends on many environmental factors (Kabata-Pendias, Pendias 1999, Turner 1994). Soluble and colloidal forms of heavy metals suspended in a soil solution are the most important for plant uptake, and the most important factors influencing their availability are their total concentration and soil reaction (Karczewska 2002).

Regular monitoring of soil and plant quality in the surroundings of the largest tailings impoundment located near Rudna, called Żelazny Most, has been held since 1996 with an aim of evaluating its impact on the environment and people's health (ANGEŁOW et al. 2000, KABAŁA et al. 2008, MEDYŃSKA et al. 2007). The purpose of the present study has been to asses the quality of potatoes and grain of various cereals cropped in an immediate vicinity of tailings pond, on the basis of the concentration of copper, zinc, lead, and cadmium analyzed in the years 2004-2006.

MATERIAL AND METHODS

The tailings impoundment called Żelazny Most is located in the agricultural area of three communities: Rudna, Polkowice and Grębocice in the Lower Silesia region, southwestern Poland. Soils in the surroundings of the impoundment are in general sandy in texture (prevailing sands and loamy sands), with a low or moderate content of organic matter, and nearly neutral soil reaction (ANGEŁOW et al. 2000). In 2004-2007, grain and tuber samples were taken in the phase of consumption ripeness from fields of the villages called Rudna (east of the impoundment) and Tarnówek (west of the impoundment). The quantity of samples of particular plants depended on the actual crop rotation and differed from year to year (Table 1). Four typical species of cereals (wheat, oat, barley, and triticale) and potatoes were chosen for the assessment. In accord with the reference methods, cereal grain was dried at 20°C to *ca* 12% water content, and fresh (not dried) potato tubers were washed and peeled. Additionally, dry mass of samples was determined, after weight stabilization at 105°C.

Plant samples were ignited at 450°C and ash was dissolved with concentrated nitric acid. Concentration of copper and zinc in final extracts was measured with the FAAS technique, and concentration of lead and cadmium with the GF-AAS techniques. Accuracy of the measurements was controlled by inclusion of reference plant materials (NIST-RM 8412, IAEA-V-10) with a certified content of the analyzed trace elements.

The environmental risk caused by cadmium and lead to plants was assessed according to European Commission Regulation no 1881/2006 of 19th December 2006, which sets maximum levels of certain contaminants in foodstuff (Polish transcription in Dz.U. UE L364/5). Officially allowed threshold limit values (TLV) of lead and cadmium in potatoes are 0.10 $mg \cdot kg^{-1}$ of fresh mass. In cereals TLV of Pb is 0.20 $mg \cdot kg^{-1}$ and TLV of Cd is 0.10 $mg \cdot kg^{-1}$ (except wheat, where it is 0.20 $mg \cdot kg^{-1}$). Copper and zinc concentration in foodstuff is presently not regulated by the European Community. However, for an assessment of potential contamination with these elements, unofficial limit values established by the State Institute of Plant Cultivation,

Table 1

Range and mean concentrations of trace elements (mg·kg^{-1} of f.m.) in crops as compared to TLV (threshold limit value)

Crops	Crop part	Year 2004				Year 2005				Year 2006			
		Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
Wheat	grain	2.8-3.3* 3.0**	10.8-14.0 12.8	0.15-0.19 0.17	0.03-0.04 0.03	2.2-4.0 3.4	13.8-25.1 19.4	0.15-0.19 0.17	0.05-0.08 0.06	3.3-6.2 4.1	17.0-23.0 18.5	0.14-0.19 0.16	0.05-0.08 0.06
TLV		20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.20$^{b)}$	20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.20$^{b)}$	20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.20$^{b)}$
Triticale	grain	2.6-3.9 3.1	15.6-26.2 19.5	0.08-0.17 0.14	0.02-0.2 0.07	2.7-4.0 3.4	18.9-20.1 19.5	0.15-0.17 0.16	0.05-0.08 0.06	3.2-5.3 3.9	16.5-37.2 25.6	0.12-0.18 0.15	0.05-0.07 0.06
Barley	grain	2.6-4.9 3.4	6.4-24.6 19.4	0.14-0.34 0.19	0.02-0.04 0.03	3.0-4.3 3.6	19.2-31.0 25.1	0.12-0.14 0.13	0.05-0.06 0.055	2.9-5.8 3.9	15.1-27.0 21.5	0.11-0.14 0.12	0.04-0.06 0.06
Oats	grain	-	-	-	-	-	-	-	-	2.5-3.5 3.0	8.7-21.3 16.8	0.11-0.16 0.14	0.05-0.08 0.06
TLV		20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.10$^{b)}$	20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.10$^{b)}$	20$^{a)}$	50$^{a)}$	0.20$^{b)}$	0.10$^{b)}$
Potato	tuber	0.6-1.1 0.8	2.3-3.1 2.8	0.06-0.09 0.07	0.038-0.-04 0.039	0.4-1.6 1.1	1.3-4.2 3.0	0.01-0.09 0.05	0.006-0.-02 0.013	1.1-1.7 1.3	2.8-4.4 3.5	0.014-0.084 0.04	0.007-0.018 0.011
TLV		10$^{a)}$	20$^{a)}$	0.10$^{b)}$	0.10$^{b)}$	10$^{a)}$	20$^{a)}$	0.10$^{b)}$	0.10$^{b)}$	10$^{a)}$	20$^{a)}$	0.10$^{b)}$	0.10$^{b)}$

Explanation:
*range of concentration
**arithmetic mean
$^{a)}$ TLV of Institute of Soil Science and Plant Cultivation, Puławy, Poland
$^{b)}$ TLV according to Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs

Fertilization and Soil Sciences (Puławy, Poland) were taken. The limit values of zinc in potatoes were approximated at the level of 20 $mg \cdot kg^{-1}$ of fresh mass and 50 $mg \cdot kg^{-1}$ in cereals, and the limit values of copper were 10 and 20 $mg \cdot kg^{-1}$ of fresh mass, respectively

RESULTS AND DISCUSSION

The average levels of trace metals in 2006 in the analyzed cereals and potatoes were approximated at the level of: Cu – respectively – 3.7 and 1.3 $mg \cdot kg^{-1}$ of fresh mass; Zn – 20.6 and 3.5 $mg \cdot kg^{-1}$; Pb – 0.14 and 0.04 $mg \cdot kg^{-1}$; Cd – 0.055 and 0.011 $mg \cdot kg^{-1}$. Significant differences in concentrations of trace elements in cereals and potatoes depend mainly on the dry mass content, but could be also associated with plant species and variations, phase of plant growth, concentration of trace element in soil and the local climate (Bednarek et al. 2008, Gembarzewski 2000, Kabata-Pendias, Pendias 1999, Strączyński, Strączyńska 2007). No statistically significant differences in copper, lead and cadmium concentrations between the tested cereals were found. In 2004 higher concentrations of Cu and Pb were determined in barley than in wheat grain, contrary to 2006, when wheat grain contained more Cu and Pb than barley. It seems that the crucial factor is the location of particular crops in the consecutive years. However, no significant relation between the distance to the impoundment and concentration of Cu and Pb in plants or in soils was found. Among the determined trace metals, only zinc concentration in wheat grain was significantly lower in all the years (in a range from 12.8 to 19.4 $mg \cdot kg^{-1}$) than in barley and triticale grain (range: 19.4-25.6 $mg \cdot kg^{-1}$). Oat grain, which was analyzed only in 2006, contained less zinc than all the other cereals – on average 16.8 $mg \cdot kg^{-1}$. Zinc concentration in plant material, similarly to Cu and Pb, is not statistically related to the distance to the impoundment or to the metal concentration in soils.

Although the copper level in soils in the immediate surroundings of the impoundment is elevated (Angełow et al. 2000, Kabała et al. 2008), concentrations of this metal in crops cultivated in this area did not diverge from mean values presented by Gembarzewski (2000). However, the Cu content in cereals from the nearest vicinity of the impoundment is at least 20% higher than Cu concentrations in crops cultivated on poor, sandy soils prevailing in the nearby counties. The copper level in potato tubers (in consecutive years from 0.8 to 1.3 $mg \cdot kg^{-1}$ of fresh mass) was higher then average values presented by Kabata-Pendias and Pendias (1999) – 0.7 $mg \cdot kg^{-1}$ of fresh mass, but similar to those determined in southeastern Poland, where Mikos-Bielak et al. (1996) reported 0.6-1.3 $mg \cdot kg^{-1}$ of fresh mass.

Although zinc concentrations in soils in the surroundings of the impoundment were no higher than in other areas (Angełow et al. 2000), the content of this metal in the examined cereals, like that of Cu, was *ca* 15-20% higher than the average reported from this region (KUCHARZEWSKI et al. 2002). The determined Zn concentrations did not diverge from average Polish and European values presented by KABATA-PENDIAS and PENDIAS (1999) and are significantly lower than those presented by WŁAŚNIEWSKI (2002) from the Rzeszów region. Zinc amounts in potato tubers (in a range from 2.8 to 3.5 $mg \cdot kg^{-1}$ of fresh mass) were similar to those determined in two regions of southeastern Poland (BEDNAREK et al. 2006, MIKOS-BIELAK et al. 1996), and lower than the average in the Lower Silesia region (KUCHARZEWSKI et al. 2002).

Lead concentration in soils surrounding Żelazny Most impoundment is relatively low, despite rather high pH values and organic matter content (ANGEŁOW et al. 2000), which may explain low concentrations of the element in cereal grain (0.08-0.34 $mg \cdot kg^{-1}$ of fresh mass). These amounts of Pb are much lower than found in cereals cultivated on contaminated soils near a copper smelter (BOJARSKA, BZOWSKI 1998, STRĄCZYŃSKI, STRĄCZYŃSKA 2007) and significantly lower than the average content in cereals reported from this part of the Lower Silesia region. Lead concentrations in the analyzed potato tubers (0.01-0.09 $mg \cdot kg^{-1}$ of fresh mass) were similarly lower than the mean 0.41 $mg \cdot kg^{-1}$, measured in potatoes cultivated on polluted areas of the Lower Silesia region (STRĄCZYŃSKI, STRĄCZYŃSKA 2007) but somewhat higher than in the Lublin region of southeastern Poland (BEDNAREK et al. 2006).

Concentration of cadmium in the analyzed cereal grain was in the range from 0.02 to 0.20 $mg \cdot kg^{-1}$ (average 0.055 $mg \cdot kg^{-1}$). These values, after recalculation per dry mass, are similar to those presented by KABATA-PENDIAS and PENDIAS (1999) from the entire area of Poland, and by BEDNAREK et al. (2008) from the Lublin region, but significantly lower than reported from the Rzeszów region (WŁAŚNIEWSKI 2000). Similarly, the contamination of potato tubers with cadmium was very low, with the metal contents in the range from <0.01 to 0.04 $mg \cdot kg^{-1}$ of fresh mass, which was close to results presented by KUCHARZEWSKI et al. (2002) and WŁAŚNIEWSKI (2000).

Copper concentrations in the examined cereal grain and potato tubers did not exceed approximately 20% and 13% (respectively) of the appropriate threshold limit values (TLV), and zinc concentrations – 51% and 18% of TLV according to KABATA-PENDIAS et al. (1989). Moreover, cadmium concentrations did not exceed approximately 70% and 39% (respectively), and lead concentrations – 85% and 70% of TLV set in Commission Regulation (EC) no 1881/ /2006. Trace metal concentrations in all the tested plant samples were lower than threshold limit values. It means that there are no restrictions for consumption or pasture use of cereals and potatoes planted in the surrounding of tailings impoundment Żelazny Most.

Several technologies of waste stabilization on drying surfaces had been tested during the nearly 25 years of exploitation of the impoundment to avoid dusting. The presently used technology of tailings stabilization with asphalt emulsion reduces dust emission by 95% as compared to the emission reported in the initial phase of the impoundment exploitation (DOBRZAŃSKI, BYRDZIAK 1995). Also the regular soil quality monitoring in the vicinity of the impoundment confirms decreasing emission of metal-bearing dust (KABAŁA et al. 2008, MEDYŃSKA et al. 2007). The results of our investigation on quality of crops confirm good efficiency of all the actions undertaken in order to reduce the negative impact of the copper ore tailings impoundment on the environment and conditions of agricultural production.

CONCLUSIONS

1. Copper, zinc, lead, and cadmium concentrations in all the tested samples of cereal grain and potato tubers cropped in the surroundings of tailings Żelazny Most impoundment were similar to concentrations reported from other regions of Poland and did not exceed the threshold limit values for edible plants.

2. No significant differences in copper, lead, and cadmium concentrations in grain were found among the four tested cereal species. Zinc concentration in wheat and oat grain was significantly lower than in triticale and barley grain.

3. No significant statistical relation was found between trace metal concentrations in cereal grain or potato tubers and metal contamination in soils or the distance to the tailings impoundment.

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EFFECT OF NITROGEN AND POTASSIUM FERTILISATION ON THE CONTENT OF IONS IN THE SOIL SOLUTION

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Abstract

The aim of the present research was to evaluate whether or not, and to what extent, exclusive mineral fertilisation affects the content of water-soluble ions determining the soil salinity. The soil was sampled from the arable layer of a multi-year field experiment carried out in 1974-2007. The research involved differentiated nitrogen fertilisation (factor I, *n*=3) and potassium fertilisation (factor II, *n*=4). The content of water-soluble ions was defined in water extract, in the soil to water ratio of 1:5; cations K^+, Na^+, Ca^{2+} were determined with the method of emission spectrometry and Mg^{2+} – with atomic absorption. Anions were analysed with the argentometric (Cl^-) and nephelometric (SO_4^{2-}) methods. In addition, electrolytic conductivity (R) was tested with the conductometric method, based on which the salt concentration in the solution (C) and the ionic strength (I) were calculated. The present results were statistically verified. The prolonged application of intensive nitrogen and potassium fertilisation (32 years) significantly differentiated the content of cations: K^+, Na^+, Ca^{2+} and Mg^{2+} as well as anions: Cl^- and SO_4^{2-} in soil solution. The contents of K^+, Na^+, Ca^{2+}, Mg^{2+} in the soil solutions differed and fell within the range of (mean value) 0.136-0.507 (0.281) K^+, 0.398-0.555 (0.472) Na^+, 1-2.192 (1.350) Ca^{2+} and 0.211- 0.365 (0.272) Mg^{2+} $mmol(+)\cdot kg^{-1}$. The highest nitrogen dose significantly limited the concentration of SO_4^{2-} in the soil solution, while the different doses of potassium did not result in such significant changes in the concentration of the above ions. The content of chlorine ions in the soil solution did not depend significantly on differentiated nitrogen and potassium fertilisation. No effect of the long-term mineral fertilisation on soil salinity was noted.

Key words: fertilisation, ions, salt indicator.

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WPŁYW NAWOŻENIA AZOTEM I POTASEM NA ZAWARTOŚĆ JONÓW W ROZTWORZE GLEBOWYM

Abstrakt

Celem badań była ocena, czy i na ile wyłączne nawożenie mineralne wpływa na zawartość wodnorozpuszczalnych jonów decydujących o zasoleniu gleby. Próbki gleby pobrano z warstwy ornej wieloletniego doświadczenia polowego, które prowadzono w latach 1974-2007. W badaniach stosowano zróżnicowane nawożenie azotem (I czynnik, *n*=3) i potasem (II czynnik, *n*=4). Zawartość wodnorozpuszczalnych jonów oznaczono w wyciągu wodnym, stosunek gleby do wody jak 1:5; kationy K^+, Na^+, Ca^{2+} metodą spektometrii emisyjnej, a Mg^{2+} metodą absorpcji atomowej, aniony – metodą argentometryczną (Cl^-) oraz nefelometryczną (SO_4^{2-}). Oznaczono także przewodnictwo elektrolityczne (R) metodą konduktometryczną, na podstawie którego obliczono stężenie soli w roztworze (C) i moc jonową (I) Wyniki badań opracowano statystycznie. Wieloletnie (32 lata) stosowanie intensywnego nawożenia azotem i potasem istotnie różnicowało zawartości kationów: K^+, Na^+, Ca^{2+} i Mg^{2+} oraz anionów: Cl^- i SO_4^{2-} w roztworze glebowym. Zawartość K^+, Na^+, Ca^{2+}, Mg^{2+} w roztworze glebowym wynosiła odpowiednio: 0,136-0,507 średnio (0,281), 0,398-0,555 średnio (0,472), 1-2,192 średnio (1,350), 0,211-0,365 średnio (0,272) $mmol(+)\cdot kg^{-1}$. Największe dawki azotu istotnie ograniczały koncentrację SO_4^{2-} w roztworze glebowym, natomiast zróżnicowane dawki potasu nie miały tak znaczącego wpływu. Zawartość jonów chlorowych w roztworze glebowym nie zależała istotnie od różnicowanego nawożenia azotem i potasem. Nie stwierdzono wpływu długoletniego nawożenia mineralnego na zasolenie gleby.

Słowa kluczowe: nawożenie, jony, zasolenie.

INTRODUCTION

Soil is a live formation, which shows a specific state of equilibrium between biotic and abiotic processes which determine its fertility. The concentration of respective components in the soil solution varies in time and is conditioned by many factors, both natural and anthropogenic, including brine solutions and industrial wastewater, salts applied for clearing roads from snow and mineral fertilisers (MURAWSKA 2005, KASZUBKIEWICZ et al. 2003). These factors can determine soil fertility and quality. They can also condition soil salinity, which manifests chemical degradation of environment (CAMPEBELL et al. 1989, ŁABĘTOWICZ 1995). Soil salinity in seaside soils and soils in the close vicinity of brine has been researched thoroughly (KUCHARSKI 1995, PRACZ 2005). Nonetheless, there is little evidence pertaining to long-term effect of mineral fertilisers, except for natural fertilisation and liming, on the content of cations and anions in soil, which determine its salinity (CAMPEBELL et al. 1989, ŁABĘTOWICZ, RUTKOWSKA 2001, RUTKOWSKA et al. 2009). With that in mind, the present research has been performed to find out whether or not, and if so, to what extent, long-term nitrogen and potassium fertilisation affects the content of water-soluble ions determining the soil salinity.

MATERIAL AND METHODS

The research material consisted of soil sampled from the arable layer of long-term field experiment carried out in 1974-2007. Differentiated nitrogen (factor I, n=3) and potassium (factor II, n=4) fertilisation was applied (Table 1). Detailed experimental data are provided are reported by MURAWSKA (2005).

Table 1

The application of mineral fertilisers

Fertilisation level (mean/year in kg·ha^{-1})						
N			K			
N_1	N_2	N_3	K_0	K_1	K_2	K_3
80	160	250	0	50	106	155

The following determinations were made on the soil samples: content of water-soluble ions in water extract, at the soil-to-water ratio of 1:5; cations K^+, Na^+, Ca^{2+} using emission spectrometry and Mg^{2+} with atomic absorption and anions applying the argentometric (Cl^-) and nephelometric (SO_4) methods. Additionally, electroconductivity (R) with the conductometric method was determined, based on which the salt concentration in the solution (C) and ionic power (I) were calculated from the formulas: $C=640 \cdot R$ (mg·dm^{-3}) and $I=0.013 \cdot R$ (mol·dm^{-3}). The results were statistically verified with analysis of variance according to the model compliant with the experimental design, using Tukey's test to evaluate the significance of differences.

RESULTS AND DISCUSSION

The soil phase is highly sensitive to changes in the chemical composition is the soil solution. These changes are a resultant of numerous factors, including fertilisation (ŁABĘTOWICZ, RUTKOWSKA 2001, MURAWSKA 2005). Excessively intensive mineral fertilisation increases the content of salts easily soluble in soils. Under Polish climatic conditions, fertiliser salts dissolved by precipitation waters penetrate deep into soil due to the process of migration and increase the degree of mineralization of soil- and groundwater. The present results suggest that the examined nitrogen fertilisation regime significantly determined the content of water-soluble forms of magnesium and sodium, while potassium fertilisation affected the content of potassium, magnesium and calcium (Table 2). They also depended significantly on the interaction of the factors researched. The content of K^+, Na^+, Ca^{2+}, Mg^{2+} in the

Table 2

Content of water-soluble ions in the soil samples (mmol (+)·kg^{-1})

Potassium					
Fertilisation level	K_0	K_1	K_2	K_3	Mean
N_1	0.136	0.207	0.225	0.507	0.269
N_2	0.179	0.324	0.282	0.340	0.256
N_3	0.202	0.212	0.369	0.486	0.317
Mean	0.172	0.214	0.292	0.444	0.281
LSD for I – ns, II – 0.052, IIxI – 0.090, IxII – 0.089					
Magnesium					
N_1	0.255	0.323	0.241	0.225	0.261
N_2	0.324	0.211	0.218	0.255	0.252
N_3	0.300	0.233	0.216	0.365	0.303
Mean	0.293	0.256	0.259	0.281	0.272
LSD for I – 0.034, II – 0.039, IIxI 0.067, IxII– 0.062					
Calcium					
N_1	2.192	1.275	1.000	1.017	1.371
N_2	1.542	1.050	1.033	1.173	1.200
N_3	1.400	1.617	1.500	1.400	1.479
Mean	1.711	1.314	1.178	1.197	1.350
LSD for I – n.s., II – 0.409, IIxI 0.708, IxII – 0.665					
Sodium					
N_1	0.441	0.455	0.398	0.477	0.443
N_2	0.505	0.497	0.405	0.501	0.477
N_3	0.467	0.437	0.555	0.528	0496
Mean	0.471	0.462	0.453	0.520	0.472
LSD for I – 0.048, II – n.s., IIxI – 0.109, IxII – 0.097					

soil solution varied and fell within the range of (the mean): 0.136-0.507 (0.281) K^+, 0.398-0.555 (0.472) Na^+, 1-2.192 (1.350) Ca^{2+} and 0.211-0.365 (0.272) Mg^{2+} mmol(+)·kg^{-1}.

The content of sulphate ions (VI) in the soil solution was evidently higher than that of cations and the concentration of chlorine ions fell within the concentration range of K^+, Mg^{2+} and Na^+ (Table 3). The highest nitrogen dose significantly limited the concentration of SO_4^{2-} in the soil solution, while the potassium doses did not result in such significant changes in the concentration of the above ions. The interaction of nitrogen and potassium

Table 3

Content of anions in the soil samples (mmol (+)·kg^{-1})

Sulphate (VI)					
Fertilisation level	K_0	K_1	K_2	K_3	mean
N_1	11.60	14.00	13.69	13.90	12.78
N_2	12.56	12.06	16.12	13.86	13.11
N_3	15.87	9.91	8.31	11.58	10.97
Mean	13.34	11.98	12.69	13.11	12.29
LSD for I – 2.13. II – n.s. IIxI – 4.72. IxII – 4.27					
Chlorides					
Fertilisation level	K_0	K_1	K_2	K_3	mean
N_1	0.31	0.31	0.27	0.27	0.29
N_2	0.43	0.35	0.39	0.41	0.40
N_3	0.46	0.40	0.50	0.46	0.46
Mean	0.40	0.35	0.39	0.38	0.38
LSD for I – 0.05. II – n.s. IIxI – n.s. IxII – n.s.					

fertilisation significantly differentiated the content of sulphates in the soil solution. This effect was particularly strong when the highest nitrogen dose was applied (N_3). The highest amount of sulphate (VI) was found in the soil without potassium fertilisation, which – irrespective of its rate – significantly limited their concentration. This effect could have been due to a competitive effect of chlorine ions entering soil with potassium fertilisers as well as an increased uptake of sulphates by plants well supplied with nitrogen.

The content of chlorine ions in the soil solution ranged from 0.27 to 0.50 mmol(-)·kg^{-1} (on average 0.38 mmol(-)·kg^{-1}) and it did not depend significantly on differentiated nitrogen and potassium fertilisation (Table 3).

The percentage share of the analysed cations in the pool increased in the following order: $Mg^{2+}<K^{+}<Na^{+}<Ca^{2+}$ (Figure 1*a*). Of the determined anions, sulphates (VI) made up as much as 97% (Figure 1*b*).

The measure of soil salinity is based on the electroconductivity of water-soil extracts, which in the analysed samples was on average 53.3 µS·cm^{-1} (Table 4). It was much lower than the threshold value assumed for saline soils, which is 4 mS·cm^{-1} (Pracz 2001, Hulisz 2007, Corwim, Lesch, 2005). That parameter can be applied to evaluate other indicators of soil salinity, for example salt concentration in the extract or the ionic power (Table 4), which likewise remained at a very low level in the present research.

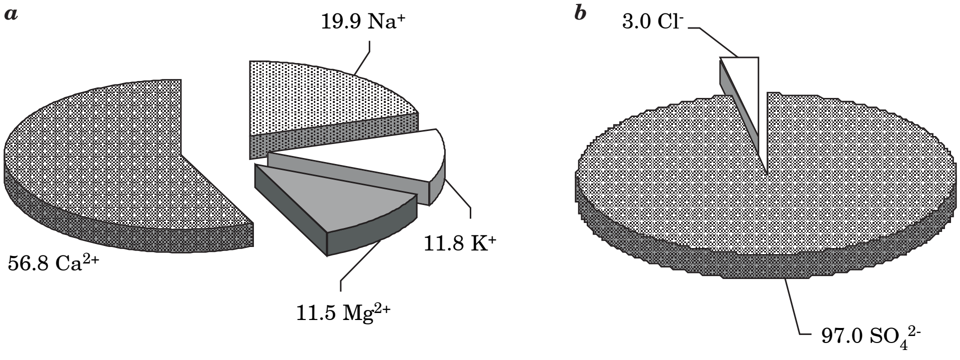

Fig. 1. Percentage share of the cations (*a*) and anions (*b*)

Table 4

Salt indicator

Parameter		Range	Mean	Median
Electroconductivity	$\mu S \cdot cm^{-1}$	35.2 - 85.90	53.30	49.21
Salt concentration	$mg \cdot dm^{-3}$	20 694 - 55 003	34 136	31 495
Ionic power	$M \cdot dm^{-3}$	0.420 - 1.117	0.693	0.640

CONCLUSIONS

The present results were statistically verified. The prolonged application of intensive nitrogen and potassium fertilisation (32 years) significantly differentiated the content of cations K^+, Na^+, Ca^{2+}, Mg^{2+} and anions Cl^-, SO_4^{2-}, although it did not lead to soil salination. It can therefore be stated that salination of the analyse soils was not directly caused by the long-term fertilisation, which under the climatic conditions prevailing in Poland can only increase the degree of mineralization of soil- and groundwater.

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THE CONTENT OF SELENIUM IN SOME SPECIES OF MEADOW PLANTS*

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Abstract

The aim of the investigation carried out in 2006-2007 was to assess differences between 5 grass species and 5 species of plants belonging to meadow herbs in their ability to accumulate selenium. According to the results, among the grass species, the samples of *Arrhenatherum elatuis* L. had the highest average Se content (46 μg $Se \cdot kg^{-1}$ d.m.), and the lowest average Se amount was found in *Holcus lanatus* L. (24 μg $Se \cdot kg^{-1}$ d.m.). The content of Se in meadow weeds (70 μg $Se \cdot kg^{-1}$ d.m.) was approximately twice as high as in grasses (32 μg $Se \cdot kg^{-1}$ dm.). Among this group of plants, the highest Se accumulation occurred in *Equisetum arvense* L. (103 μg $Se \cdot kg^{-1}$ dm.) and the lowest – in *Taraxacum officinale* (59 μg $Se \cdot kg^{-1}$ dm.). Both in grasses and in meadow weeds, the Se content significantly depended on the amount of this element in soils. In the following species: *Dactylis glomerata* L., *Arrhenatherum elatius* L., *Poa pratensis* L. and *Taraxacum officinale*, the amount of accumulated Se was also conditioned by the soil's abundance in organic and total C.

Key words: Se, soils, grasses, herbs.

ZAWARTOŚĆ SELENU W NIEKTÓRYCH GATUNKACH ROŚLIN ŁĄKOWYCH

Abstrakt

Celem badań prowadzonych w latach 2006-2007 było określenie zróżnicowania w zdolności nagromadzania selenu przez 5 gatunków traw oraz 5 gatunków roślin zaliczanych do ziół łąkowych. Wykazano, że wśród analizowanych gatunków traw najwięcej selenu zawierały próby *Arrhenatherum elatuis* L. (46 μg $Se \cdot kg^{-1}$ sm.), a najmniej *Holcus lanatus* L. (24 μg $Se \cdot kg^{-1}$ sm.), średnio dla badanych gatunków roślin.

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Zawartość Se w chwastach łąkowych (70 µg Se·kg^{-1} sm.) była ok. 2-krotnie większa niż określona dla traw (32 µg Se·kg^{-1} sm.). W tej grupie roślin największą kumulację Se wykazywał *Equisetum arvense* L. (103 µg Se·kg^{-1} sm.), najmniejszą *Taraxacum officinale* (59 µg Se·kg^{-1} sm.). Zarówno w trawach, jak i chwastach zawartość selenu była istotnie zależna od ilości tego pierwiastka w glebach. Dla gatunków: *Dactylis glomerata* L., *Arrhenatherum elatius* L., *Poa pratensis* L. oraz *Taraxacum officinale* o ilości nagromadzonego Se decydowała również zasobność gleb w C-org. i S-og.

Słowa kluczowe: Se, gleby, trawy, zioła.

INTRODUCTION

With their rich botanical composition, meadows are of special importance among permanent grasslands. The chemical composition of green forage or hay harvested from natural meadows is superior to that of simplified, more uniform meadows with high contribution of grasses. Likewise, their botanical composition and suitability for animal nutrition are better. The fact that animals receive much meadow forage, especially in spring and sumer, raises an important question of its quality.

Selenium is one of the chemical elements which are essential for good growth and development of animals. When fodders, especially those used in cattle and sheep rearing, are deficient in, selenium, animals may suffer from inferior fertility, higher incidence of miscarriages or dietary muscular dystrophy, commonly known as the white muscles disease (DĘBSKI 1992, ZABŁOCKI 1991).

The content of selenium in meadow sward is conditioned by a number of physical and chemical properties of soils, including their Se richness (ZABŁOCKI 1991, MIKKELSEN 1989, LASER 2004, WHITE et al. 2004), as well as the composition of plant species which grow on a given soil (WHITE et al. 2004, HUANG and WU 1991). GUPTA and MACLEOD (1994) as well as WHITE et al. (2004) report that differences in Se accumulated by plants become more distinct on soils rich in this element, yet they remain hardly noticeable on Se poor soils. LASER (2004) stated that even when growing on soils deficient in selenium deficit, herbs and leguminous plants featured higher content of this element than grasses.

Based on extensive research in this field, WHITE et al. (2004) classified plants regarding their ability of Se accumulation. These authors made a list of plants growing on grassland, arranging them from according to the Se content, from the lowest to the highest one: *Lolium multiflorum, Dactylis glomerata, Lolium perenne, Trifolium pratense, Phleum pratense, Rununculus repens, Holcus lanatus, Vicia villosa, Taraxacum officinale, Trifolium repens.* HUANG and WU (1991) found that deeply rooted plants contain more selenium than those possessing a shallow root system. JOHNSON (2005) has empirically demonstrated that plant species characterized by a high demand for sulfur also contain higher quantities of selenium.

The aim of this work has been to assess selenium content in soils and in selected grass species collected from 97 meadows situated in the region of Wrocław.

MATERIAL AND METHODS

The assessment of the differences between meadow plant species with respect to their ability of selenium uptake was done based on determination of Se in 10 species of meadow plants collected during the first cut from 97 meadows in the vicinity of Wrocław. Our investigation involved 5 grass species: orchard grass (*Dactylis glomerata* L.), tall cat grass (*Arrhenatherum elatius* L.), meadow bluegrass (*Poa pratensis* L.) and meadow foxtail (*Alopecurus pratensis* L.), meadow soft grass (*Holcus lanatus* L.) as well as 5 plant species of meadow herbs: common dandelion (*Taraxacum officinale*), common milfoil (*Achillea millefolium* L.), field horsetail (*Equisetum arvense* L.), ribwort plantain (*Plantago lanceolata*), and common dock (*Rumex acetosa* L.). The species selected for the examination did not occur on all grassland areas, therefore the analyzed samples were of different sample sizes. Grasses and herbs were collected from the whole area of grassland and an average sample was formed from 15-20 initial samples. Soil samples were collected from two depths: 0-5 cm and 5-20 cm, and from the same sites the plant material originated from. Soil samples underwent determination of basic physicochemical properties: granulometric composition – according to Bouyoucos-Casagrande's aerometric method, modified by Prószyński, organic C content by Tiurin's method, soil sorption capacity (T) by Kappen's method, pH in mol $KCl \cdot dm^{-3}$ using the potentiometric method, the content of total sulfur by Butters and Chenry's method. Selenium content was assayed using the AAS method combined with hydride generation in a Spectra 220 FS Varian device with a VGA-76 attachment: in soils after sample mineralization according to Beach's method (1992) and in plant material – with the method described in the Annex to the Ordinance of the Minister for Agriculture and Development of Rural Areas dated 23 January 2003 (Journal of Laws No 66).

RESULTS AND DISCUSSION

The soils subjected to the examination were characterized by considerably varied properties (Table 1). Analysis of their granulometric composition showed that 41 samples featured sand granulation, 33% was represented by loamy soils and 25% belonged to silty soils. Nearly half of the meadows was situated on very light soils (27%) or light soils (21%) of strong acid or acid

Table 1

Some properties of soils

Layer	0-5 cm				5-20 cm			
Properties	min	max	mean	*V* %	min	max	mean	*V* %
Fraction <0.02 mm					3.1	50	22	60
pH_{KCl}	3.7	7.3		18	3.8	7.5		18
Organic C, $g \cdot kg^{-1}$	7.8	72.7	24.8	43	7.4	68.0	21.2	60
Total S, $mg \cdot kg^{-1}$	88	1189	392	58	26	1260	343	67

V – coefficient of variation

reaction. Medium – heavy soils provided for 28% of the whole scope of samples. The remaining samples belonged to heavy soils. The content of organic C in the analyzed samples (Table 1) did not differ from the one determined by Kucharzewski et al. (2004) regarding meadow soils in 16 districts of Lower Silesia.

Natural content of selenium in soils ranges from 0, to 2 $mg \cdot kg^{-1}$ (Borowska, Koper 2007). According to Piotrowska (1984), its value for Polish soils reaches 40 up to 640 µg $Se \cdot kg^{-1}$ dm. Having more organic matter, meadow soils contain higher quantities of Se than arable soils (Hartfield, Bahners 1988, Trafikowska, Kuczyńska 2000). An average content of selenium assayed in the examined soil samples (Table 1) was similar to that reported by Piotrowska (1984), i.e. 277 µg $Se \cdot kg^{-1}$ dm., comparable to the mean value for soils in whole Poland. The latter value was nearly twice as high as the data reported by Zabłocki (1991), who analyzed meadow soils in the former Province of Szczecin, but half the average value determined by Trafikowska and Kuczyńska (2000) for meadow soils in the vicinity of Bydgoszcz.

When analyzing selenium content in the soil samples collected from meadows with particular plant species (Table 2), it is worth noticing that lower Se content was detected at the sites where meadow soft grass was growing, in the 0-5 cm layer, as well as in both soil levels overgrown with common dock. Except for meadow foxtail, meadow soft grass and ribwort plantain, the soil collected from the 0-5 cm level showed higher Se content than deeper layers of soil.

The content of Se in 5 grass species ranged from 7 to 199 µg $Se \cdot kg^{-1}$ dm. The average value calculated for this group of plants (32 µg $Se \cdot kg^{-1}$ dm.) did not differ from the value reported by Laser (2004). Among the 295 grass samples subjected to analysis, 33% featured Se content lower than 20 µg $Se \cdot kg^{-1}$ dm, while only 15% contained more than 50 µg $Se \cdot kg^{-1}$ dm. The highest contribution of samples featuring a very low Se content (< 20 µg

Table 2

Se content in soils under the examined plant species (µg Se·kg^{-1} dm.)

Species Layer	*Dactylis glomerata*	*Poa pratensis* L.	*Arrhenatherum elatius* L.	*Alopecurus pratensis* L.	*Holcus lanatus* L.
Grasses					
0-5 cm	290 42-851	294 70-851	284 42-851	279 80-851	265 72-708
V %	58	60	58	57	59
5-20 cm	265 43-923	272 43-923	266 43-923	308 92-923	274 93-582
V %	61	64	61	62	50
Herbs					
Species Layer	*Taraxacum officinale*	*Achillea millefolium* L.	*Plantago lanceolata*	*Equisetum arvense* L.	*Rumex acetosa* L.
0-5 cm	278 42-851	284 42-851	277 83-851	317 70-851	236 70-624
V %	57	54	56	61	52
5-20 cm	253 43-908	266 43-908	273 102-908	294 73-908	217 73-477
V %	57	62	58	64	45

V – coefficient of variation

Se·kg^{-1} dm) was detected among meadow soft grass (43%) and orchard grass (41%), and the lowest one was detected in meadow foxtail (22%). Comparing the mean values calculated for the examined grass species (Table 3), it is possible to state that the highest amount of selenium was detected in samples of tall cat grass, while the lowest value characterized meadow soft grass. In the latter species, the low Se content could have resulted from the Se content in the soil being lower than that determined for the remaining soil samples collected from underneath the other grasses, in the 0-5 cm soil layer. According to the data reported by WHITE et al. (2000), meadow soft grass is a species accumulating in its tissues higher quantities of selenium than orchard grass or meadow bluegrass. The influence of the low Se content in soils on the amount of this element in this species samples can be confirmed by the average Se content in the meadow sward from which meadow soft grass was isolated being lower than Se values determined for the remaining grass species.

Considerably more selenium than in meadow grasses was found in meadow herbs (Table 3). Similar correlations were reported by HARFIELD and BAHNERS (1988), HUANG and WU (1991), OPITZ von BOBERFELD (2002) and LASER (2004). The content of selenium in this plant group showed high diversity and

Table 3

Se content in examined grass species and in meadow sward they were collected (μg Se·kg^{-1} dm.)

Species	*Dactylis glomerata*	*Poa pratensis* L.	*Arrhenatherum elatius* L.	*Alopecurus pratensis* L.	*Holcus lanatus* L.
Number of samples	73	62	68	55	37
Mean	31	28	46	29	24
Range	7-118	7-66	9-199	7-63	8-105
V	70	56	88	49	77
Mean for grasses 32 μg Se·kg^{-1} dm., *V*=85					
Meadow sward					
Mean	41	42	40	40	35
Range	15-130	15-130	17-130	17-102	15-130
V	56	56	56	57	68
Species	*Taraxacum officinale*	*Achillea millefolium* L.	*Plantago lanceolata*	*Equisetum arvense* L.	*Rumex acetosa* L.
Number of samples	52	57	36	26	31
Mean	59	70	63	103	68
Range	15-220	16-765	15-178	16-650	16-216
V	67	137	62	131	74
Mean for herbs 70 μg Se·kg^{-1} dm., *V*=113					
Meadow sward					
Arythmetic mean	40	40	37	44	36
Range	15-130	17-130	18-102	19-130	15-130
V	55	53	47	49	74

V – coefficient of variation

ranged from 15 to 765 μg Se·kg^{-1} dm, with the variation coefficient ranging from 62 (*Plantago lanceolata*) to 137 (*Achillea milefolium* L). The calculated arithmetic mean of Se content in aerial parts of soft plants for 202 samples of this plant group equaled 70 μg Se·kg^{-1} dm. When comparing the selenium content in the five analyzed herb species, it is possible to conclue that the highest ability to accumulate this microelement was demonstrated for field horsetail (*Equisetum arvense* L). Markedly lower quantities of selenium were absorbed by common milfoil, common dock and common plantain, while the lowest accumulation rates belonged to common dandelion. However, even these species of meadow herbs accumulated twice as much selenium as grasses.

The statistical analysis proved that both selenium content in both grasses and meadow herbs was significantly dependent on the amount of this element in the both analyzed soil layers (Table 4). In the case of such species as *Dactylis glomerata, Poa pratensis* L., *Arrhenatherum elatuis* L., and *Taraxacum officinale,* the amount of accumulated Se was also affected by organic C as well as total sulfur. These properties, however, did not considerably effect the Se accumulation by *Holcus lanatus* L., *Achillea milefolium* L., oraz *Equisetum arvense* L.

Table 4

Simple correlation coefficients between Se content in plants and some properties of soils

Properties	Layer cm	Se content in plants				
		grasses				
		Dactylis glomerata	*Poa pratensis*	*Arrhenatherum elatius*	*Alopecurus pratensis*	*Holcus lanatus*
Organic C	0-5	0.63	0.43	0.46	0.31	n.s.
	5-20	0.49	0.40	0.42	0.32	n.s.
Total S	0-5	0.49	0.38	0.34	0.34	n.s.
	5-20	0.54	0.44	0.36	0.35	n.s.
Total Se	0-5	0.73	0.79	0.54	0.40	0.64
	5-20	0.67	0.71	0.53	0.37	0.45
Herbs						
		Taraxacum officinale	*Achillea millefolium*	*Plantago lanceolata*	*Equisetum arvense*	*Rumex acetosa*
Organic C	0-5	0.43	0.32	n.s.	n.s.	0.37
	5-20	0.36	n.s.	n.s.	n.s.	0.40
Total S	0-5	0.31	n.s.	0.36	n.s.	n.s.
	5-20	0.32	n.s.	0.29	n.s.	n.s.
Total Se	0-5	0.82	0.57	0.39	0.42	0.86
	5-20	0.76	0.45	0.41	0.36	0.78

significant at $p<0.05$
n.s. – not significant

CONCLUSIONS

1. The herbs subjected to examination contained significantly more selenium than grasses.

2. The examined meadow plant species showed different abilities to accumulate Se.

3. With respect to grasses, markedly more Se was determined in tall cat grass (*Arrhenatherum elatuis* L.), while field horsetail (*Equisetum arvense* L.) contained a significantly higher amount of Se than the meadow herbs.

4. Accumulation of selenium by the analyzed meadow plants was considerably dependent on the amount of this microelement in both soil layers subjected to examination.

5. The effect of organic C and total S content in plants was conditioned by properties of particular plant species.

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CONTENT OF SELENIUM IN ARABLE SOILS NEAR WROCLAW*

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Abstract

The material for this study consisted of 60 soil samples collected from the arable layer of cultivated fields located in the vicinity of Wrocław. The samples varied in their properties and reflected a whole range of soil types to be found in the region of Lower Silesia. The examinations proved that selenium content in arable soils near Wroclaw ranged from 81 to 449 $\mu g \cdot kg^{-1}$ and the average value of Se content in these soils was 202 $\mu g \cdot kg^{-1}$.

The lowest Se content appeared in sandy soils (174 $\mu g \cdot kg^{-1}$), while the highest value was found in loamy soils. The mean value of Se content calculated for this group of soils was 228 $\mu g \cdot kg^{-1}$. Selenium content in soils varied to a high degree (V=42%). The value lower than 100 $\mu g \cdot kg^{-1}$, assumed as a critical one for the quality of plant yield, was recorded for 4 samples, while in 33 soil samples the Se content fell in the range of 101--200 $\mu g \cdot kg^{-1}$ and in 14 samples it ranged from 201 to 300 $\mu g \cdot kg^{-1}$. Only 9 soils out of these subjected to investigation characterized selenium value higher than 300 $\mu g \cdot kg^{-1}$, i.e. the value regarded as medium soil fertility. Se content in soils was highly correlated with their content of silt and clay, as well as colloidal parts and also with the amount of C and total content of such chemical elements as P, S, Fe, Cu, Zn and Ni.

Key words: Se, soil properties.

ZAWARTOŚĆ SELENU W GLEBACH GRUNTÓW ORNYCH OKOLIC WROCŁAWIA

Abstrakt

Materiał do badań stanowiło 60 prób glebowych pobranych z warstwy ornej pól uprawnych położonych w okolicach Wrocławia. Ich właściwości były w znacznym stopniu zróżni-

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cowane i odzwierciedlały przekrój gleb występujących na terenie województwa dolnośląskiego. Wykazano, że zawartość selenu w glebach gruntów ornych okolic Wrocławia wahała się od 81 do 494 μg·kg^{-1}, wartość uśredniona wyniosła 202 μg·kg^{-1}.

Najniższą zawartość Se stwierdzono w glebach piaszczystych (174 μg·kg^{-1}), a najwyższą w glebach gliniastych. Określona dla tej grupy średnia zawartość Se kształtowała się na poziomie 228 μg·kg^{-1}. Zawartość selenu w glebach była w znacznym stopniu zróżnicowana (V=42%). Wartość niższą niż 100 μg·kg^{-1} – uznawaną za krytyczną dla jakości zbieranych plonów roślin – stwierdzono w 4 próbkach, a w 33 glebach zawartość Se mieściła się w przedziale 101-200 μg·kg^{-1}, natomiast w 14 od 201 do 300 μg·kg^{-1}. Spośród badanych gleb jedynie w 9 zawartość ta była większa niż 300 μg·kg^{-1} – wartość uznawana jako średnia zasobność. Zawartość selenu w glebach była wysoko istotnie skorelowaną z zawartością zarówno części spławianych, jak i koloidalnych, a także z ilością węgla oraz całkowitą zawartością P, S, Fe, Cu, Zn i Ni.

Słowa kluczowe: Se, właściwości gleb.

INTRODUCTION

Naturally occurring Se content in soils is conditioned by the origin and mineral composition of the mother rock, intensity of Se loss due to erosion and volatilization resulting from methylation (PIOTROWSKA 1984, BUTTERMAN, BROWN 2004, LASER 2004). The content of Se in soils worldwide ranges average 0.33 mg·kg^{-1}, yet it can vary between trace amounts to 230 mg·kg^{-1} (BUTTERMAN, BROWN 2004).

The soils of Poland generally feature low content of this microelement. According to PIOTROWSKA (1984), Se value equals 277 μg·kg^{-1}, while BOŻEK (1997) estimates Se content as 320 μg·kg^{-1}. BOROWSKA et al. (2007) reported that for mineral soils in the region of Pomerania and Kujawy, the Se content did not exceed 35-332 μg·kg^{-1}, with the mean content being 138 μg·kg^{-1}. The soils of arable lands in the vicinity of Bydgoszcz, examined by TRAFIKOWSKA and KUCZYŃSKA (2000), contained on average 56 μg·kg^{-1}. An equally low Se content (123 μg·kg^{-1}) for the soils of the western Pomerania was recorded by ZABŁOCKI (1991). The soils of Lower Silesia, examined by BOŻEK (1997), contained on average 240 μg·kg^{-1}.

The aim of his investigation was to determine selenium content in cultivated mineral soils in the region of Wrocław, as well as to assess the effect of some properties of these soils on the content of this microelement.

MATERIAL AND METHODS

Samples of soil from sixty cultivated fields were collected from the arable layer (0-20 cm). The sample collection was planned and performed so that soils could be considerably diversified and reflect a whole range of soil types typical for the region of Lower Silesia. Soil samples were subjected to the following determinations: granulometric composition according to the aerometric method by Bouyoucosa-Casagrande, modified by Prószyński, soil reaction in mol $KCl \cdot dm^{-3}$ with the potentiometric method, hydrolytic acidity with Kappena's method, organic C with Tiurin's method, the content of total sulfur with Butters and Chenry's method, total content of phosphorus as well as the content of Mn, Fe, Cu, Zn and Ni after mineralization of the samples with aqua regia. The Se content was assayed according to the AAS method combined with hydrides generation using a Spectr AA FS Varian device with a VGA-76 attachment, previously preparing soil samples according to the method by Beach (1992). All assays were done in three replications and the tables contain their mean values.

RESULTS AND DISCUSSION

Analysis of the granulometric composition proved that 27 of the examined soils characterized sand graining (Tables 1 and 2). The highest contribution in that group belonged to: slightly loamy (18%) and light loamy sand (12%). In the group of medium – heavy soils the highest percentage contribution featured light\loam (32%). The content of silt and clay ranged from

Table 1

Some properties of the examined soils

Soil properties	Arithmetic mean	SD	Range	*V* %
Fraction < 0.02 mm	21	10.8	5-46	50
Fraction < 0.002 mm	6.8	3.5	1-21	52
pH $mol_{KCl} \cdot dm^{-3}$	5.9	0.7	4.0-7.0	11
Hh $cmol(+) \cdot kg^{-1}$	18.1	9.9	4.4-42.0	54
Total content, $g \cdot kg^{-1}$				
Organic C	12.6	6.1	4.6-32.3	48
P	0.78	0.19	0.45-1.27	24
S	0.21	0.08	0.07-0.49	40
Total content, $mg \cdot kg^{-1}$				
Mn	303	155	62-763	51
Fe	6542	3726	1987-18168	57
Cu	11.0	8.6	3.5-37.7	78
Zn	44.7	25.6	18-128	57
Ni	8.7	5.3	2.2-24.9	61

SD – standard deviation; *V* – coefficient of variation; Hh – hydrolytic acidity

Table 2

Selenium content as dependent on soil family and soil textural group (µg·kg^{-1})

Soil textural group					
Soils	sandy		loamy		silts
Subgroup	ls, wls *n*=12	lls, sls *n*=13	ll *n*=19	lsl *n*=9	cs *n*=4
Mean Range	156 85-238	197 144-336	206 94-392	268 81-494	200 168-228
V, %	28	36	42	45	
Mean Range for group	174 85-338		228 81-494		200

V – coefficient of variation; *n* – no of samples; ls – loose sand; wls – weak loamy sand; lls – light loamy sand; sls – strong loamy sand; ll – light loam; lsl – light silt loam; cs – clay silt

Table 3

Selenium content in soils depending on granulometric composition (µg·kg^{-1}) soils

Content	*n*	Arithmetic mean	SD	Range	*V* %
Fraction <0.02 mm					
< 10	14	152	44	85-238	28
11-20	13	197	75	93-336	38
21-35	28	226	100	81-449	44
>35	5	215	45	168-278	21
Fraction <0.002 mm					
<5	23	172	68	85-338	39
5.1-10	28	212	81	81-392	38
10.1-15.0	5	298	126	154-491	42
>15.1	1	278			

SD – standard deviation; *V* – coefficient of variation; *n* – no of samples

5 to 46% (Tables 1 and 3). The highest contribution constituted medium – heavy soils (47%) and, subsequently, very light (23%) and light soils (22%). Heavy soils made up just 8% of the total soil samples, i.e. they were the least numerous.

The reaction of soil samples was highly diversified as it was found within the range of pH_{KCl} from 4.0 to 7.0 (Table 1). Most soils were slightly acid (48%). Acidic reaction was assayed in 25% of soils. A similar percentage of soils was neutral in reaction, while only one soil sample was classified as a very acid one.

Organic C content, as well as the total content of phosphorus and sulfur in the examined soils are specified in Table 1 and the number of samples in each class can be found in Tables 4 and 5.

Table 4

Content of selenium in soils depending on organic C content (µg·kg^{-1} soil)

Content organic C (g·kg^{-1})	< 11.0 *n*=33	11.1-20.0 *n*=22	> 20.1 *n*=5
Arithmetic mean	158	229	365
SD	53	68	80
Range	93-267	144-364	292-494
V, %	34	30	22

SD – standard deviation; *V* – coefficient of variation; *n* – no of samples

Table 5

Selenium content in soils as dependent on total content of *P* and S (mg·kg^{-1} soil)

Element	*P* (mg·kg^{-1})				S (mg·kg^{-1})	
Content	<500 *n*=2	501-750 *n*=27	750-1000 *n*=22	>1000 *n*=9	low *n*=26	medium *n*=34
Mean	89	184	225	220	169	221
SD		65	99	87	66	89
Range		81-307	120-491	122-364	85-307	93-491
V, %		35	44	39	116	40

SD – standard deviation; *V* – coefficient of variation; *n* – no of samples

The total content of microelements was highly varied (Table 1). The calculated values of variation coefficients ranged from 51% (Mn) to 78% (Cu). The majority of the sixty examined soils were characterized by a natural content of Mn, Fe, Cu, Zn and Ni. Considering the boundary values assumed by KABATA-PENDIAS et al. (1993), elevated values of zinc content were found only in 6 light and 4 medium-heavy soils.

Our examinations proved that the Se content in arable soils in the region of Wroclaw ranged from 81 to 449 µg·kg^{-1} and the mean value equaled 202 µg·kg^{-1}. Therefore, these values are lower than the mean values for the soils of Poland estimated by PIOTROWSKA (1984) and BOŻEK (1997).

The content of selenium in soils varied to a high degree (*V*=42%). In 4 samples it was lower than 100 µg·kg^{-1}, i.e. the value assumed as critical for the quality of plant yield (GUPTA and GUPTA 2002). In 33 soils, Se content did not exceed 101-200 µg·kg^{-1} and in 14 (23%) it reached 201 to 300 µg·kg^{-1}. By comparing these results obtained with the figures cited by ZABŁOCKI (1991) who, after Welles, claimed that Se content lower than 300 µg·kg^{-1} was regarded as Se deficit, it can be concluded that 85% of 60 examined soil samples were characterized by low Se content, while the remaining sampled contained moderate amounts of selenium.

Among the most often implied factors which condition the total Se content in soils there is soil granulometric composition. PIOTROWSKA (1984), ZABŁOCKI (1991) and BOROWSKA (1996) report that selenium content decreases as amounts of silt and clay decrease. This relationship has been confirmed by the present study.

By analyzing selenium content in soils classified to particular granulometric groups and subgroups (Table 2), it is possible to state that the lowest Se content was found in sandy soils (174 μg·kg^{-1}). Both the range of values and calculated mean values did not differ from those reported by PIOTROWSKA (1984) for soils of this group. Among sandy soils, a markedly higher Se value appeared in light loamy sand and heavy loamy sand. The table does not contain any values regarding slightly loamy sand (123 μg·kg^{-1}) and medium-heavy loam (278 μg·kg^{-1}), since these subgroups were represented only by 2 and 1 soil, respectively. Loamy soils proved to be much richer in selenium than sandy soils. Se content determined for the former group was on average 228 μg·kg^{-1}, being lower than the value reported by PIOTROWSKA (1984), who reported that the average Se content in light loamy soils was 280 μg·kg^{-1}, and for medium-heavy loam – 360 μg·kg^{-1}. Also YLÄRANTA (1983) recorded higher average Se content (290 μg·kg^{-1}) for loamy soils than that determined for the same group of soils collected in the region of Wroclaw.

According to the data reported by YLÄRANTA (1983), PIOTROWSKA (1984), ZABŁOCKI (1991) and BOROWSKA (1996), selenium content in soils *did* significantly increase as the amount of silt and clay parts they contained increased up to 35% (Table 3). Slightly lower content of this microelement was determined for heavy soils than for medium–heavy soils, which may have been due to the small number of soils (n=5) in this agronomical category. Se content in soils also increased as the amount of colloidal parts in soils increased (Tables 3 and 6). This correlation found its statistical proof. Similar relations were obtained by YLÄRANTA (1983), ZABŁOCKI (1991) and BOROWSKA (1996).

Another factor which significantly affects Se content in soils is their abundance in organic matter, although scientific reports discussing this correlation are not univocal. YLÄRANTA (1983), ZABŁOCKI (1991), BOROWSKA (1996), as well as BOROWSKA et al. (2007) proved positively significant correlation between Se content and the quantity of organic matter. In contrast, PIOTROWSKA (1984) and LASER (2004) did not find evidence supporting such correlation. Our examination proved that selenium content in soils was highly correlated with their content of organic carbon (Tables 4 and 6).

In the literature pertaining to the influence of soils properties on Se amount, there is scarce information about correlation between phosphorus and selenium. According to the results of our investigation, the increase in the total content of phosphorus in soils immediately induced an increase in the content of selenium (Table 5).

Selenium is a chemical element featuring strong geochemical relation with sulphur. In sulphur deposits of volcanic origin, as well as in sulphite minerals, Se is an accompanying component. Soils rich in humus are most often characterized by increased content of both sulfur and selenium (Butterman, Brown 2004, Laser 2004). Our examinations confirmed this correlation. Soils moderately abundant in total sulphur contained by about 24% more selenium than soils featuring low S content (Table 5). Statistical analysis proved that this was a significant correlation (Table 6).

Table 6

Correlation between selected soil properties (x) and selenium content in soils (Y), n=60

Soil properties	Content in soil Y, ($\mu g \cdot kg^{-1}$)	
	Se	
(x)	regression formula	(r)
Fraction <0.02 mm (%)	$Y= 2.32x+151.7$	0.30
Fraction <0.002 mm(%)	$Y=11.8x+121.8$	0.49
pH mol KCl$\cdot$dm^{-3}	$Y=31.6x+11.8$	n.s.
Hh (cmol(+)$\cdot$kg^{-1})	$Y=0.91x-217.9$	n.s.
Organic C (g$\cdot$kg^{-1} gleby);	$Y=10.5x+69.3$	0.75
P (g$\cdot$kg^{-1})	$Y=0.13x+96.3$	0.30
S (g$\cdot$kg^{-1})	$Y=628.1x+68.1$	0.62
Mn (mg$\cdot$kg^{-1})	$Y=0.071x+179.8$	n.s.
Fe (mg$\cdot$kg^{-1})	$Y=0.0126x+119.3$	0.55
Cu (mg$\cdot$kg^{-1})	$Y=5.91x+136.4$	0.59
Zn (mg$\cdot$kg^{-1})	$Y=1.61x+129.6$	0.48
Ni (mg$\cdot$kg^{-1})	$Y=9.07x+122.9$	0.56

r – correlation coefficient; significant ($p<0.05$); n.s. – not significant;
Hh – hydrolytic acidity

Selenium content in soils was positively significantly correlated with the total content of Fe, Cu, Zn and Ni. However, no such correlation with the Mn content in soils was found (Table 6).

According to the results obtained by Piotrowska (1984) and Bahnersa (1987), no significant effect of pH and hydrolytic acidity on selenium content in soils was recorded. Contrasting results were reported by Borowska et al. (2007).

CONCLUSIONS

1. The total content of selenium in arable soils in the region of Wrocław ranged from 81 to 494 μg·kg^{-1}, with the average Se content being 202 μg·kg^{-1}. Most of the examined soils (85%) were low in this element.

2. Loamy soils, in contrast to sandy soil, proved to be very rich in selenium.

3. Selenium content in soils depended on their granulometric composition as well as on the amount of organic C. There were also significant correlations between the total Se content and the total content of P, S, Fe, Cu, Zn and Ni.

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THE EFFECT OF VARIABLE MINERAL FERTILIZATION ON YIELD AND GRAIN MINERAL COMPOSITION OF COVERED AND NAKED OAT CULTIVARS

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Abstract

Among the cereals grown in Poland, oat grain contains the highest amount of ash, composed of macro- and microelements. It has been suggested that applying increased levels of mineral fertilization, to newer cultivars of oat could have an impact on their grain yield and mineral composition.

A two-factorial (2x2) field experiment was conducted for three years (1999-2001) in the south of Poland. The experiment involved two cultivars of oat, i.e. the covered cultivar Dukat and the naked cultivar Akt, and two fertilization levels, i.e. low (30 kg N, 30 kg P_2O_5 and 45 kg K_2O ha^{-1}) and high (60 kg N, 60 kg P_2O_5 and 90 K_2O ha^{-1}). There was no significant difference in grain yield between the studied cultivars. On the other hand, the high NPK level increased the content of Mg and Fe in the grain of Akt. At the same time, there were no significant differences in the grain content of Cu, Fe, Mn and Zn between Dukat and Akt. Overall, the high level of mineral fertilizing decreased the grain content of microelements as a result of dilution effect.

The content of Cu and Zn in oat grain was suitable for human consumption according to the IUNG-PIB standards. Generally, it was shown that cv. Akt was richer in mineral elements, especially in P, K, Ca, Mg, Fe and Zn, than cv. Dukat.

Key words: oats, fertilizing, yield, chemical composition.

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WPŁYW ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO NA PLON ORAZ SKŁAD MINERALNY ZIARNA OWSA OPLEWIONEGO I NAGOZIARNISTEGO

Abstrakt

Ziarno owsa oraz produkty jego przerobu zawierają stosunkowo dużo popiołu, w tym makro- i mikroskładników. W porównaniu z czterema innymi zbożami uprawianymi w Polsce, owies zawiera znacznie więcej składników mineralnych, dlatego też istnieje konieczność badań wpływu czynników agrotechnicznych na skład chemiczny ziarna owsa. W Polsce południowej, w latach 1999-2001, przeprowadzono dwuczynnikowe doświadczenie polowe celem określenia wpływu zróżnicowanego nawożenia mineralnego na plon oraz zawartość makro- i mikroelementów w ziarnie dwóch form owsa siewnego. Pierwszym czynnikiem badawczym były odmiany: oplewiona Dukat i nagoziarnista Akt, a drugim – zróżnicowane nawożenie mineralne, poziom pierwszy: 30 kg N, 30 kg P_2O_5 i 45 kg $K_2O \cdot ha^{-1}$, poziom drugi: 60 kg N, 60 kg P_2O_5 oraz 90 $K_2O \cdot ha^{-1}$. Badane odmiany nie różniły się istotnie plonami ziarna. Wyższy poziom nawożenia NPK wpływał na wzrost zawartości Mg i Fe w ziarnie odmiany nieoplewionej Akt. Nie stwierdzono istotnego zróżnicowania zawartości Cu, Fe Mn i Zn między oplewioną odmianą Dukat a nagoziarnistą odmianą Akt. Poziom nawożenia mineralnego wpływał na obniżenie zawartości mikroelementów, co było związane z efektem „rozcieńczenia”. Zawartość Cu i Zn w ziarnie owsa według wytycznych IUNG-PIB i Rozporządzenia MZ spełniała kryteria przydatności konsumpcyjnej. Z badań wynika, że nagoziarnisty owies był zasobniejszy w składniki mineralne, zwłaszcza w P, K, Ca, Mg, Fe, Zn, w porównaniu z formą oplewioną Dukat.

Słowa kluczowe: owies, nawożenie, plon, skład chemiczny.

INTRODUCTION

Among the major cereal crops, oat grain is characterized by particularly valuable chemical composition. Both nutrients and non-nutrients present in oat grain determine its considerable value for human and animal nutrition (PETERSON 2001, BARTNIKOWSKA 2003, GAMBUŚ et al. 2003, CUDDEFORD 1995). Until relatively recently, oat grain has been used almost exclusively for oatmeal manufacturing, whereas nowadays it is also raw material sought for health-related foods, medicines and highly valued cosmetics (PETERSON 2004, GAMBUŚ et al. 2003). In animal nutrition, oat grain is a traditional horse feed. More recently, it has also been used for feeding pigs, poultry, ruminants and husky dogs used for sledding (KEMPE et al. 2004). The nutrient content of oat grain, both covered and naked cultivars, has been described in detail in numerous papers (GĄSIOROWSKI 1995, PISULEWSKA et al. 1998), whereas relatively few research projects have focused on its concentrations of macro- and microelements.

The purpose of this study has been to assess the yield and mineral composition of covered (Dukat) and naked (Akt) cultivars of oat as affected by variable mineral fertilization.

MATERIAL AND METHODS

A two-factorial experiment was conducted using a split-splot design on soil of IIIb quality class in Nawojowa situated in Kotlina Sądecka, at an altitude of 345-360 m AMSL, in the Kamienica River catchment. The experiment was conducted over a 3-year period (1999-2001). Oat was sown as a pure culture at the rate of 500 grains/m^2. In all the years spring barley was the forecrop. Oat crop was harvested from 12 m^2 plots. The first experimental factor was the type of oat cultivar (Dukat vs. Akt), while the second one was differentiated NPK fertilization: I level: 30 kg N, 30 kg P_2O_5 and 45 kg $K_2O \cdot ha^{-1}$ vs II level: 60 kg N, 60 kg P_2O_5 and 90 $kg \cdot ha^{-1}$. The soil abundance in P, K and Mg (mg/100 g) in the consecutive years of the experiment (1999, 2000 and 2001) was as follows: 30, 37, 15; 18, 28, 12; and 7, 15 and 12. The cultivation of plots was the same for all experimental treatments (PISULEWSKA et al. 2004).

The analysis of oat grain, after combustion in a muffle furnace at 450°C for 12 hours, involved determination of Mg, Ca, P, K, Na, Cu, Fe, Mn and Zn by the ICP-AES method on a sequential JY-238 Ultrace spectrometer. The data (grain yield and mineral composition of grain) were subjected to analysis of variance using the STAT (Skierniewice) statistical programme. The significance of differences between treatment means was assessed at the level of *P*=0.95. The weather conditions in the consecutive years of the experiment are presented in Figures 1 and 2.

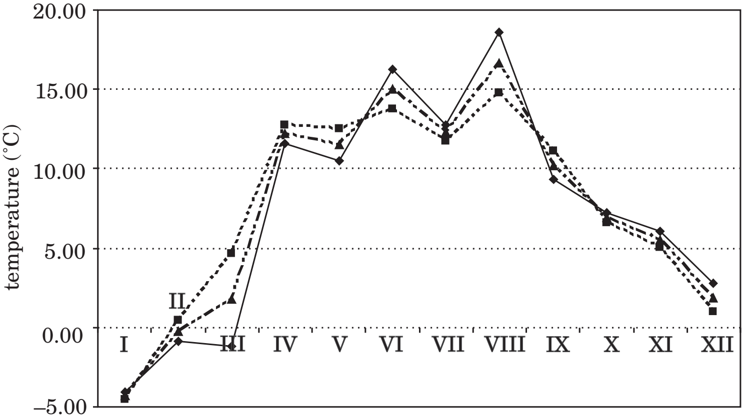

Fig. 1. Month's mean temperature during the years 1999–2001

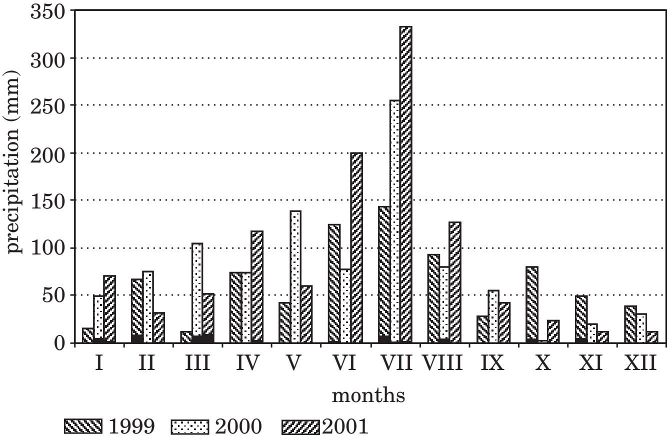

Fig. 2. Month's mean rainfall during the years 1999–2001

RESULTS AND DISCUSSION

The two different levels of mineral fertilization, tested in the field experiments, did not have any significant influence on the grain yields of the oat cultivars (Table 1). On the other hand, the weather conditions in the individual years of the experiment (Figures 1 and 2) modified the effects of the applied NPK doses. The covered cultivar Dukat gave the highest grain yields in the year with the highest rainfall and the highest mean air temperatures in July and August in 2001, whereas the naked cultivar Akt produced the highest yields in the season with the lowest rainfall in 1999. Dukat gave 27% higher yields compared with Akt. However, none of the analyzed experimental factors, nor the weather conditions in the individual vegetation seasons had any significant influence on yielding of the compared oat cultivars (Table 1). The grain yields obtained in these studies are typical for the region in which the field experiments were conducted, as has been confirmed by the literature data (Pisulewska et al. 2000).

The mineral content of cereal grain depends on many factors, of which the most important are the mineral composition of soil, applied fertilization level and the course of weather conditions during the vegetation season. In addition, the species, forms and cultivars of cereals are important (Gembarzewski 2000, Klima, Pisulewska 2000, Wróbel et al. 2003).

In the present experiment, the content of macro- and microelements in the analyzed oat cultivars was mostly affected by the course of weather conditions during the consecutive vegetation seasons. The weather conditions notably affected the mineral uptake by oat plants. In 2000, oat grain

Table 1

Effects of the level of NPK fertilization and vegetation season on the yield of studied cultivars of oat (t ha^{-1})

Years	Cultivars				Means for years	$LSD_{\alpha=0.05}$ for years
	Dukat		Akt			
	levels of fertilization					
	I	II	I	II		
	grain yield					
1999	4.06	3.25	3.08	3.13	3.38	n.s.
2000	2.93	3.13	2.48	2.99	2.88	
2001	3.90	4.39	2.00	2.03	3.08	
Means for cultivars	3.61		2.62			
$LSD_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I – 3.07		II – 3.15			
$LSD_{\alpha=0.05}$ for fertilizations	n.s.					

n.s. – not significant

had higher K content compared with the years 1999 and 2001 (Table 2). The content of P was characteristic for this species in all the years of the experiment, whereas K content in the years 1999 and 2001 was lower than stated by literature data (Gąsiorowski 1995). Low content of Na and high content of Cu and Fe in the analyzed grain was within the range stated for this species in the literature (Gąsiorowski 1995). The final year of the field experiments (2001) with very high rainfall and the highest mean air temperatures led to increased uptake of Ca, Mg and Na (Table 3) as well as Cu, Fe, Mn and Zn (Table 4). The experiment showed higher concentrations of K, Ca, Mg, Fe and Zn in the grain of the naked cultivar Akt. However, the differences between the compared cultivars were insignificant.

Oat grain and products of its processing have a relatively high mineral content, including macro- and microelements. In comparison with four other cereals cultivated in Poland, the naked cultivar Akt contains much more minerals (Petkov et al. 1999). The content of P, K, Ma and Ca in the tested oat kernels was on a similar level as in the kernels obtained in traditional and zero tillage systems (Korzeniowska, Stanisławska-Glubiak 2006). The present experiments demonstrated that naked oat was more abundant in mineral components, particularly P, K, Ca, Mg, Fe and Zn in comparison with the covered cultivar Ducat.

The higher level of NPK fertilization resulted in a slight but statistically significant increase in Mg (Table 3) and Fe (Table 4) content in the naked Akt cultivar. It seems that the naked form, developing kernels with much higher TGW (diminished by a seedling weight), has a higher relative share

Table 2

Effects of the level of N fertilization and vegetation season on the content of P and K in the grain of covered and naked cultivars of oat (g kg^{-1})

Years	Cultivars				Means for years	LSD$_{\alpha=0.05}$ for years
	Dukat		Akt			
	levels of fertilization					
	I	II	I	II		
	P					
1999	3.00	3.00	4.10	4.30	3.60	n.s.
2000	2.80	3.10	3.70	4.00	3.40	
2001	3.30	3.20	4.40	4.10	3.80	
Means for cultivars	3.00		4.10			
LSD$_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I – 3.50		II – 3.60			
LSD$_{\alpha=0.05}$ for fertilization	n.s.					
	K					
1999	2.40	2.50	2.80	2.80	2.60	0.13
2000	4.10	4.10	4.10	4.10	4.10	
2001	2.60	2.50	2.70	2.80	2.60	
Means for cultivars	3.00		3.20			
LSD$_{\alpha=0.05}$ for culti	n.s.					
Means for felrilizations	I – 3.10		II – 3.10			
LSD$_{\alpha=0.05}$ for fertilizations	n.s.					

n.s. – not significant

of minerals compared with the covered cultivar. The content of Cu and Zn in oat grain met the nutritional criteria suggested by IUNG-PIB (Kabata-Pendias et al. 1993) because it did not exceed respectively 20 and 50 mg·kg^{-1} d.m. Moreover, zinc concentration in the analyzed oat grain did not exceed the concentration limits recommended in cereal products for consumption (*Regulation of the ministry of health* 2000). On the other hand, considering needs of breeding animal, zinc content in oat kernels was insufficient because the requirements of most animal groups are on the level between 40 to 100 mg·kg^{-1} d.m. (*Nutrient reguirenents...* 2000).

The mean microelement content in the tested 474 grain samples was as follows: Mn – 66; Cu – 4.49; Zn – 1.2; Fe – 76.3 mg·kg^{-1} d.m. (Kamińska et al. 1976). The authors' own investigations showed low concentrations of Mn and Zn and higher content of Cu. The concentrations of Fe were on a similar level. Relatively low Mn content assessed in the tested oat kernels was

Table 3

Effects of N fertilization level and vegetation season on the content of Ca, Mg and Na in the grain of covered and naked cultivars of oat (g kg^{-1})

Years	Cultivars				Means for years	$LSD_{\alpha=0.05}$ for years
	Dukat		Akt			
	levels of fertilization					
	I	II	I	II		
	Ca					
1999	0.67	0.67	0.71	0.73	0.69	0.04
2000	0.68	0.68	0.72	0.73	0.70	
2001	0.76	0.75	0.74	0.71	0.74	
Means for cultivars	0.70		0.72			
$LSD_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –0.70		II – 0.71			
$LSD_{\alpha=0.05}$ for fertilizations	n.s.					
Mg						
1999	0.80	0.90	0.95	1.00	0.91	0.03
2000	0.59	0.59	0.69	0.66	0.63	
2001	0.90	0.90	1.00	0.95	0.93	
Means for cultivars	0.78		0.87			
$LSD_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –0.82		II – 0.83			
$LSD_{\alpha=0.05}$ for fertilizations	0.004					
Na						
1999	0.16	0.23	0.17	0.23	0.20	0.05
2000	0.25	0.28	0.25	0.25	0.26	
2001	0.29	0.27	0.30	0.26	0.28	
Means for cultivars	0.25		0.24			
$LSD_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I – 0.24		II – 0.25			
$LSD_{\alpha=0.05}$ for fertilizations	n.s.					

n.s. – not significant

Table 4

Effects of N fertilization level and vegetation season on the content of Cu, Fe, Mn and Zn in the grain of covered and naked cultivars of oat (g kg^{-1})

Years	Cultivars				Means for years	LSD$_{\alpha=0.05}$ for years
	Dukat		Akt			
	levels of fertilization					
	I	II	I	II		
	Cu					
1999	6.7	6.7	7.1	7.3	6.9	0.17
2000	5.0	4.3	4.1	3.7	4.2	
2001	7.6	7.5	7.4	7.1	7.4	
Means for cultivars	6.3		6.1			
LSD$_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –6.3		II – 6.1			
LSD$_{\alpha=0.05}$ for fertilizations	n.s.					
	Fe					
1999	80.0	90.0	95.0	100	91.0	0.35
2000	59.0	59.0	69.0	66.0	63.0	
2001	90.0	90.0	100	95.0	93.0	
Means for cultiva	78.0		87.0			
LSD$_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –82.0		II – 83.0			
LSD$_{\alpha=0.05}$ for fertilizations	0.04					
	Mn					
1999	16.0	23.0	17.0	23.0	20.0	0.05
2000	25.0	30.0	25.0	25.0	26.0	
2001	29.0	27.0	30.0	26.0	28.0	
Means for cultivars	0.25		0.24			
LSD$_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –25.0		II – 24.0			
LSD$_{\alpha=0.05}$ for fertilizations	n.s.					
	Zn					
1999	22.5	30.0	31.7	29.2	28.3	0.38
2000	37.8	35.7	36.1	32.3	35.4	
2001	32.2	38.0	39.1	41.7	37.7	
Means for cultivars	32.7		35.0			
LSD$_{\alpha=0.05}$ for cultivars	n.s.					
Means for felrilizations	I –33.2		II – 34.5			
LSD$_{\alpha=0.05}$ for fertilizations	n.s.					

n.s. – not significant

confirmed by the research conducted by Gembarzewski (2000). Also the study conducted by Błaziak (2007) demonstrated high Fe concentrations in oat grain, but slightly lower content of Mn. Oat has considerable requirements for Mn and a low demand for Zn, but is moderately demanding for Fe (Kaczor, Kozłowska 2000). Despite such requirements for microelements, the content of the analyzed elements in oat grain was arranged in the following order: Fe > Zn > Mn > Cu, which has been confirmed by other authors (Gąsiorowski 1995, Wróbel, Obojski 1998).

CONCLUSIONS

1. The two oat cultivars, Dukat and Akt, responded differently to the course of weather conditions during the analyzed vegetation seasons. The covered cultivar Dukat gave the highest yields in the year with the greatest rainfall, i.e. 2001, while the naked cultivar Akt gave the highest yields in the season with the lowest rainfall, i.e. 1999.
2. The course of weather conditions, different in the consecutive years of the experiment and particularly the season with very high rainfall, increased the content of macro- and microelements in oat grain.
3. The higher NPK fertilization level resulted in a slight increase in Mg and Fe content in the naked cultivar Akt. Naked oat was more abundant in minerals, especially in P, K, Ca, Mg, Fe and Zn, compared with the covered cultivar Dukat.

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EFFECT OF FERTILIZATION ON CONTENT AND UPTAKE OF CHLORINE BY OILSEED RAPE UNDER POT EXPERIMENT CONDITIONS

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Abstract

At present, chlorine counts as one of the elements which are essential for growth and development of plants because it plays an important role in main physiological processes as well as in plant protection against diseases. In Poland, the problem of chlorine shortage does not appear, therefore there are no studies on its present concentration and accumulation in field crops. However, the content of chlorine in plants and their tolerance to its excess in soil are varied. Under conditions of its high availability in the environment, its excessive accumulation is possible because chlorine is easily taken up from soil and directly from air. The aim of this study has been to find out the concentration and accumulation of chlorine in winter oilseed rape organs in dependence on N and Cl supply from the flowering up to the full maturity phase. The experiment was conducted in a greenhouse of IUNG-PIB, in Mitscherlich pots, where winter oilseed rape was cultivated. The first experimental factor was nitrogen fertilization (1.4 and 2.8 g pot^{-1}) and the second was chlorine application (0, 0.47, 0.97 and 1.42 g pot^{-1}). Chlorine concentration in plants was dependent on N dose, which caused its decrease, and on Cl dose, which resulted in its increase. The most abundant in chlorine were leaves while flowers and developing siliques contained the least of this element. Chlorine accumulated mainly in rape leaves. The accumulation of chlorine in oilseed rape increased under higher plant supply in N and Cl. The experimental plants showed a moderate supply in Cl, except the object fertilized with the highest dose of chlorine.

Key words: nitrogen, chlorine doses, yielding, dynamic of chlorine uptake.

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WPŁYW NAWOŻENIA NA ZAWARTOŚĆ I POBIERANIE CHLORU PRZEZ RZEPAK OZIMY W WARUNKACH DOŚWIADCZENIA WAZONOWEGO

Abstrakt

Obecnie chlor zaliczony jest do grupy składników pokarmowych niezbędnych do wzrostu i rozwoju roślin, ponieważ odgrywa ważną rolę w głównych procesach fizjologicznych w roślinach oraz w ich ochronie przed chorobami. W Polsce nie występuje problem niedoboru tego składnika, w związku z czym nie są prowadzone badania nad jego aktualną zawartością i akumulacją w roślinach uprawy polowej. Jednakże zawartość chloru w roślinach, a także ich tolerancja na jego nadmiar w glebie jest zróżnicowana. W warunkach dużej dostępności w środowisku może dojść do jego nadmiernej akumulacji, ponieważ chlor jest łatwo pobierany przez rośliny z gleby i bezpośrednio z powietrza. Celem badań było poznanie zawartości i akumulacji chloru w organach rzepaku ozimego, w zależności od zaopatrzenia w N i Cl, w czasie od kwitnienia do dojrzałości pełnej roślin. Doświadczenie prowadzono w hali wegetacyjnej IUNG-PIB, w wazonach Mitscherlicha, w których uprawiano rzepak ozimy. Pierwszym czynnikiem doświadczenia było nawożenie azotem (1,4 i 2,8 g wazon^{-1}), a drugim – stosowanie chloru (0, 0.47, 0.97 i 1.42 g Cl wazon^{-1}). Zawartość chloru w roślinach rzepaku zależała przede wszystkim od dawki N, która wpływała na jej obniżenie, i dawki Cl, która wpływała na wzrost koncentracji tego składnika. Najbardziej zasobne w chlor były blaszki liściowe, a najmniej – kwiaty i rozwijające się łuszczyny. Głównym miejscem gromadzenia chloru były liście. Akumulacja chloru w rzepaku wzrastała w warunkach większego zaopatrzenia roślin w azot i chlor. Rośliny doświadczalne wykazywały średnie zaopatrzenie w chlor z wyjątkiem obiektu nawożonego najwyższą dawką chloru.

Słowa kluczowe: azot, dawki chloru, plonowanie, dynamika pobierania Cl.

INTRODUCTION

Although information relating to chlorine appeared as early as the mid-19th century (Totingham 1919 – after Fixen 1993), this element was not taken into consideration in plant cultivation until the 1970s, when it was demonstrated that it could play an important role in plant production and this finding stimulated further studies on Cl^- effect on the growth and development of some crops (Johnson et al. 1957, Fixen 1993). Nowadays, chlorine as a microelement is considered as one of the 16 nutrients essential for plant growth. The main physiological role of chlorine is its participation in photosynthesis, activation of some enzymes, management of water status in the plant and plant protection against diseases (Fixen 1993). Under the conditions present in Poland, chlorine deficit in plants practically does not occur, which is why it is not taken into consideration during preparation of field crops fertilization plans. In Polish literature, there are only few reports related to chlorine concentration in field crops. However, chlorine is the aim of studies as a fertilizer component in cultivation of some vegetables (Nurzyński 1974, Uziak et al. 1982, Kowalczyk et al. 2008) or fodder plants (Michałek 1992). Is it also examined as a biomass element of energy plants (Borkowska, Lipiński 2007).

The aim of this study has been to find out the concentration and accumulation values of chlorine in oilseed rape organs in dependence on plants' supply with N and Cl.

MATERIAL AND METHODS

The experiment was conducted in a greenhouse, in Mitscherlich pots filled with 6.5 kg of soil. Winter oilseed rape var. Liropa was grown, with 5 plants per pot. The first experimental factor was nitrogen dose: 1.4 and 2.8 g N per pot and the second factor was chlorine application (g per pot): 0.47, 0.97 and 1.44, which were compared to an object without chlorine supply (control). Phosphorus, potassium, magnesium and some microelements were applied in the same doses to all the pots, and plants were watered with distilled water. Plants were harvested during the following developmental stages assigned according to BBCH scale: T1 – 61 (flowering), T2 – 71 (beginning of seed development), T3 – 81 (beginning of seed maturity) and T4 – 89 (full maturity). Chlorine concentration was analyzed using an X-Unique II device produced by Philips. Three pots from each fertilizer object were harvested on each term of harvest. The data presented in this paper are mean values for objects and years of the study. The results were statistically calculated with using of Statgraphics Plus 5.1 program.

RESULTS AND DISCUSSION

It is known nowadays that chlorine occurs in plants as free anions or loosely bound with places of exchange and is presents in more than 130 organic compounds (Engvild 1986). Chlorine concentration in cv. Liropa oilseed rape was dependent on nitrogen and chlorine doses, plant organs and, to a smaller degree, developmental phases of plants (Table 1). These observations are in accord with the research completed by Bar-Tsur and Rudich (1987) and Fixen (1993). The richest in Cl were leaves, and the poorest – flowers and developing siliques. The Cl content in stems and leaves was in the middle position. According to Kowalczyk et al. (2008) and Van Steveninck et al. (1988), concentration of chlorine in leaves reflects its availability in soil or nutrient solution. Chlorine content in leaves is closely connected with its concentration in chloroplasts because when chlorine deficiency occurs in nutrient solution, its concentration in chloroplasts decreases. High concentration of chlorine in leaves reflects its important role in photosynthesis and can have a close relationship with plants' resistance against diseases (Fixen 1993), analogously to sulphur (Podleśna et al. 2005). Accord-

Table 1

Concentration and uptake of chlorine in dependence of fertilization and developmental stage of oilseed rape

Factor	Chlorine concentration (g·kg^{-1})					Chlorine uptake (g pot^{-1})					
	leaves	stems	flowers/ /siliques*	seeds	roots	leaves	stems	flowers/ /siliques*	seeds	roots	total
Nitrogen fertilization											
N dose (g pot^{-1})											
1.4	11.2a	3.5b	0.9a	2.6a	2.8b	0.21a	0.01a	0.02a	0.07a	0.03b	0.34a
2.8	10.3a	2.3a	0.9a	3.2b	1.6a	0.25b	0.01a	0.05b	0.14b	0.02a	0.47b
Plant harvests:											
T1	9.4a	2.7a	0.4a	0.0a	2.7b	0.23a	0.10a	0.01a	0.00a	0.04d	0.38a
T2	11.1b	2.5a	0.5a	0.0a	1.7a	0.24a	0.14b	0.03b	0.00a	0.02a	0.43b
T3	11.4b	2.8a	1.2b	0.0a	1.8a	0.24a	0.13b	0.05c	0.00a	0.02a	0.44b
T4	11.2b	3.6b	1.4b	2.9b	2.7b	0.21a	0.16c	0.05c	0.10b	0.03c	0.55c
Chlorine fertilization											
Cl dose (g pot^{-1})											
0	0.5a	0.3a	0.4a	2.7a	0.4a	0.01a	0.01a	0.01a	0.09a	0.01a	0.13a
0.47	7.9b	2.0b	0.4a	2.8a	1.0b	0.17b	0.09b	0.02a	0.10a	0.01a	0.39b
0.95	13.7c	3.5c	1.2b	3.2a	3.1c	0.31c	0.17c	0.05b	0.12b	0.04b	0.69c
1.42	21.1d	6.9d	1.4b	3.2a	3.9d	0.44d	0.26d	0.07b	0.12b	0.05b	0.94d
Plant harvests:											
T1	9.4a	2.8a	0.6a	0.0a	2.5b	0.24a	0.05a	0.01a	0.00a	0.04c	0.34a
T2	11.2b	2.5a	0.5a	0.0a	1.3a	0.24a	0.14b	0.02a	0.00a	0.02a	0.42b
T3	11.4b	3.8b	0.6a	0.0a	1.8a	0.24a	0.13b	0.05b	0.00a	0.02a	0.44b
T4	11.2b	3.7b	1.7b	3.0b	2.8b	0.22a	0.16b	0.06b	0.11b	0.03b	0.58c

*T1 – flowers, T2 and T3 – siliques with seeds, T4 – siliques without seeds ing to Xu et al. (2000), flowers have less Cl than the other organs. Besides, these authors stated that fruits and seeds, which are predominantly fed by phloem, are characterized by low concentration of Cl ions. The chlorine concentration determined in seeds remained on a level of an average concentration found in stems and was not dependent on this nutrient's dose while wheat straw contained more chlorine than grain. Higher nitrogen fertilization increased chlorine concentration in seeds but decreased it in leaves, stems and roots, which can be explained by dilution effect in the enlarged mass of plants (the data are not presented). Chlorine concentration in oilseed rape increased under conditions of its greater availability, like in spring wheat (Fixen 1993) and cotton (Bar-Tsur, Rudich 1987), which results from the ease at which chlorine ions are taken up by plants and from efficient translocation of chlorine over short and long distances in plants (Marschner 1995). As oilseed rape plants matured, an increase of Cl concentration in some organs was observed, which can be explained by its passive uptake by roots and high mobility (Marschner 1995). However, Schumacher (1988 – after Fixen 1993) found that its content in spring wheat had an increasing tendency 1-2 weeks before heading and then decreased. According to Uziak et al. (1982), chlorine concentration in plants is an important indicator of their supply in this element with respect to their sensitivity to Cl. These authors observed a close relationship between retarded growth as well as inferior yielding and high chlorine concentration in bean plants. According to Johnson et al. (1957), concentration about 0.007-0.01% Cl indicates shortage of this element, while White and Broadley (2001) recognize that deficit symptoms are observed when Cl concentration in tissues is lower than 0.1-5.7 $mg \cdot g^{-1}$ dry mass. Toxicity occurs if chlorine content ranges between 4-7 $mg \cdot g^{-1}$ dry mass in chlorine sensitive plants and 15-50 $mg \cdot g^{-1}$ dry mass in Cl tolerant species. Based on these values and assuming that rape is not sensitive to Cl, it is possible to state that the experimental plants showed a moderate supply in Cl with the exception of oilseed rape, which received the highest dose of chlorine. Arnold (1955 – after Nurzyński 1974) maintains that the degree of plants' sensitivity to chlorine ions is not motivated because for chlorine there is no upper or lower limit of tolerance. However, its excess causes harm due to high salt concentration in general or to the shortage of other nutrients.

The higher dose of nitrogen applied in the experiment caused an increase of chlorine accumulation, mostly in leaves and seeds of oilseed rape (Table 1), an effect that was also found in sugar beet (Morangan 1987). Furthermore, it was observed that the total uptake of this element increased together with a Cl dose and progressing growing season. This was the consequence of elevated chlorine accumulation in leaves and stems. The smallest amounts of Cl were found in flowers, which is in agreement with the observations of White and Broadley (2001).

CONCLUSIONS

1. The biggest concentration and accumulation of chlorine was found in leaves and the smallest - in flowers and young siliques.

2. Higher doses of N and Cl applied in the experiment had varied effects on chlorine concentration in oilseed rape organs: chlorine caused an increase in its concentration in plants while nitrogen had a depressing effect.

3. The highest dose of chlorine caused excessive Cl concentration in oilseed rape plants, in contrast to its lower doses, which positively influenced the mineral composition of plants.

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EFFECT OF LONG-TERM DIFFERENTIATED FERTILIZATION WITH FARMYARD MANURE AND MINERAL FERTILIZERS ON THE CONTENT OF AVAILABLE FORMS OF P, K AND Mg IN SOIL

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Abstract

The investigations were carried out in 20022005, on proper grey-brown podsoilic soil originating from light loam (class IIIa in the soil valuation system, very good rye complex), on the basis of a two-factor experiment established in 1986 according to the random block design with four replications. The arable horizon of the soil, before the experiment, was characterized by slightly acidic reaction ($pH_{1\ mol\ KCl\ dm^{-3}}$ was 6.2) and the concentrations of available nutrients were as follows: 100.0 mg K, 53.2 mg Mg and 41.3 mg P kg^{-1} of soil. Soil samples for chemical tests were collected from the arable layer after harvesting crops grown in a rotation: sugar beet, spring barley, maize and spring wheat. The content of available forms of phosphorus and potassium were determined by Egner-Riehm method (DL), and that of manganese using Schachtschabel's method. The purpose of the study has been to determine the influence of mineral fertilization with or without FYM on the content of available macronutrients in soil. The statistical analysis of the results have shown a significant influence of manure on the level of available P, K and Mg in the tested soil. When both FYM and mineral fertilizers were introduced to soil, its abundance in available magnesium was 2.6-fold higher than after mineral fertilization alone had been applied. FYM raised nearly 3-fold the content of available forms of potassium in soil compared to the content found when only mineral fertilization was used.

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Key words: available nutrients (P, K, Mg), multi-year experiment, farmyard manure, mineral fertilization.

ODDZIAŁYWANIE WIELOLETNIEGO ZRÓŻNICOWANEGO NAWOŻENIA OBORNIKIEM I NAWOZAMI MINERALNYMI NA ZAWARTOŚĆ PRZYSWAJALNYCH FORM P, K I Mg W GLEBIE

Abstrakt

W latach 2002-2005 prowadzono badania na glebie płowej typowej wytworzonej z gliny lekkiej (klasa bonitacyjna IIIa, kompleks żytni bardzo dobry) oparte na dwuczynnikowym doświadczeniu, założonym w 1986 r. metodą losowanych bloków w czterech powtórzeniach. Warstwa orna gleby przed rozpoczęciem badań charakteryzowała się odczynem lekko kwaśnym ($pH_{1\ mol\ KCl\cdot dm^{-3}}$ wynosiło 6,2), a zawartość przyswajalnych składników pokarmowych kształtowała się na poziomie: 100,0 mg K; 53,2 mg Mg i 41,3 mg $P\cdot kg^{-1}$ gleby. Próbki gleby do analiz chemicznych pobierano z warstwy ornej po zbiorze roślin uprawianych w zmianowaniu: burak cukrowy, jęczmień jary, kukurydza, pszenica jara. Zawartość przyswajalnych form fosforu i potasu oznaczono metodą Egnera-Riehma (DL), a magnezu metodą Schachtschabela. Celem badań było określenie wpływu nawożenia mineralnego stosowanego z obornikiem lub bez obornika na zawartość przyswajalnych makroelementów w glebie. Analiza statystyczna wyników wykazała istotny wpływ obornika na zawartość przyswajanych form P, K i Mg w badanej glebie. Po zastosowaniu łącznie obornika i nawozów mineralnych stwierdzono średnio 2,4 razy więcej magnezu przyswajalnego oraz 2,6 razy więcej fosforu przyswajalnego w glebie w porównaniu z zawartością określoną po zastosowaniu nawożenia mineralnego. Nawożenie obornikiem spowodowało ponad 3-krotny wzrost zawartości przyswajalnych form potasu w glebie w porównaniu z zawartością określoną po nawożeniu mineralnym.

Słowa kluczowe: składniki przyswajalne (P, K, Mg), doświadczenie wieloletnie, obornik, nawożenie mineralne.

INTRODUCTION

The content of available nutrients (P, K and Mg) depends on the type of soil and its reaction, production intensity, rotation system, climatic conditions, organic and mineral fertilization, etc. Availability of nutrients increases under good mineral and natural fertilization (Barczak et al. 1999, Mercik et al. 2000, Sienkiewicz et al. 2004). Frequent and intensive application of natural or mineral fertilizers alone may contribute to acidification of soil, causing, for example, retardation of phosphorus and reduced availability of calcium and magnesium to plants (Łabętowicz et al. 1999, Mercik et al. 2000, Richter et al. 2000). Another undesirable effect of unbalanced natural and mineral fertilization is the transfer of biogenic substances to waters (Spychaj-Fabisiak et al. 1999, Koc et al. 2008, Skwierawski et al. 2008). Having applied full and balanced natural and mineral fertilization, one can notice an increase in the amounts of available nutrients, most probably caused by a higher capacity of the sorptive complex and improved buffer properties of soil (Sienkiewicz 2003).

The objective of this study has been to follow the effect of mineral fertilization applied with or without farmyard manure on the content of available forms of potassium, phosphorus and magnesium in soil.

MATERIAL AND METHODS

The study was conducted in 2002-2005, on proper grey-brown podsolic soil originating from light loam (class IIIa in the soil valuation system, very good rye complex), based on a two-factor experiment established in 1986 according to the random block method with four replications. The first-order factor consisted of natural fertilization (with or without FYM), while the second-order factor comprised differentiated mineral fertilization: treatments: $N_0P_0K_0$, $N_1P_1K_1$, $N_2P_1K_1$, $N_3P_1K_1$, $N_2P_1K_2$, $N_2P_1K_3$, $N_2P_1K_2$Mg, $N_2P_1K_2$MgCa. The design of the experiment as well as the rates of fertilizers can be found in Table 1. In each year, the same crop was tested on both fields (with or without FYM). Soil samples for chemical analyses were collected from the arable horizon after harvesting the crops grown in a rotation system: sugar beet, spring barley, maize and spring wheat. The content of available forms of phosphorus and potassium were determined by Egnar-Riehm method (DL), whereas that of magnesium according to Schachtschabel.

Table 1

Fertilization of crops (kg·ha^{-1})

Element	Sugar beet	Spring barley	Maize	Spring wheat
N_1	60	30	60	40
N_2	120	60	120	80
N_3	180	90	180	120
P_1 (P/P_2O_5)	34.9/80	34.9/80	26.2/60	34.9/80
K_1 (K/K_2O)	66.4/80	33.2/40	49.8/60	24.9/30
K_2 (K/K_2O)	132.8/160	66.4/80	99.7/120	49.8/60
K_3 (K/K_2O)	199.3/240	99.7/120	149.5/180	74.7/90
Mg (Mg/MgO)	48.2/80	18.1/30	24.1/40	18.1/30
Ca (Ca/CaO)	1787/2500			
FYM (t·ha^{-1})	40		40	

RESULTS AND DISCUSSION

Joint application of FYM and mineral fertilization or mineral fertilization alone over many years has largely modified the abundance of soil in the basic macronutrients (P, K and Mg). The content of available forms of phosphorus in soil fluctuated from 36.1 to 182.5 mg kg^{-1} (Table 2). FYM introduced to soil every two years improved the resources of available phospho-

Table 2

Content of available forms of phosphorus in soil (mg kg^{-1})

Factor I	Factor II								Mean
	$N_0P_0K_0$	$N_1P_1K_1$	$N_2P_1K_1$	$N_3P_1K_1$	$N_2P_1K_2$	$N_2P_1K_3$	$N_2P_1K_2$Mg	$N_2P_1K_2$MgCa	
FYM	124.7	150.0	149.8	142.1	142.0	149.9	145.5	182.5	148.3
Without FYM	36.1	57.4	51.7	47.3	51.3	53.5	61.8	87.2	55.8
Mean	80.4	103.7	100.8	94.7	96.7	101.7	103.6	134.9	

$LSD_{0.05}$ for the factor I – 6.79
$LSD_{0.05}$ for the factor II – 7.73
$LSD_{0.05}$ for interaction I×II – n.s.

rus in soil by an average of over 165%. Such beneficial influence of FYM was most evident in the soil which did not receive mineral fertilization, but was the weakest under balanced mineral fertilization including calcium and magnesium. The content of available P was less positively affected by mineral fertilization. A clear tendency appeared towards depressing the content of this nutrient in soil as the rates of nitrogen increased. This effect was most clearly seen in the soil amended only with mineral fertilizers, which was due to the action of nitrogen, whose acidifying influence was more profound in soil deprived of supply of organic substance since 1986. Liming produced a very beneficial effect on the amounts of phosphorus easily available to plants. Positive impact of FYM on abundance of soil in available P was also verified with the help of regression and correlation computation (Figure 1). Based on the analysis of the simple regression course, one can notice that regular fertilization with manure conducted for many years increased the content of available P by 90 mg kg^{-1} of soil. Should we assume that the abundance of soil in this nutrient declined to nearly zero as a result of mineral fertilization wasteful exploitation of farmland continued for then, under the very same conditions, the soil fertilized with manure should retain about 90 mg P kg^{-1} of soil.

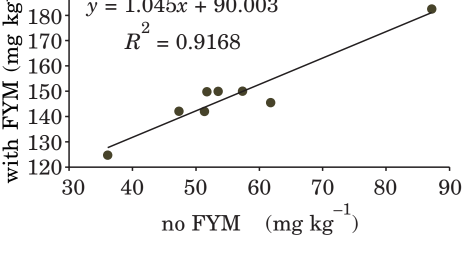

Fig. 1. Dependence between content of available P (mg kg^{-1}) in soil fertilized and not fertilized with FYM

The content of available forms of potassium in soil rose to even a higher degree than that of phosphorus owing to the long-term application of FYM (Table 3). Similarly to phosphorus, the concentration of K was most highly increased in soil fertilized with FYM alone. Increasing doses of nitrogen led to a steady decline in the abundance of soil in plant available forms of potassium. It can be assumed that the increasing acidification of soil caused by mineral nitrogen stimulated the leaching of potassium. In turn, increasing rates of potassium raised the amounts of available forms of K in soil, with the effect being evidently greater under exclusive mineral fertilization. Worth noticing is the fact that liming combined with moderate rates of N, P, K and Mg produced superior effects to the same rates of NPK.

Table 3

Content of available forms of potassium in soil (mg kg^{-1})

Factor I	Factor II								Mean
	$N_0P_0K_0$	$N_1P_1K_1$	$N_2P_1K_1$	$N_3P_1K_1$	$N_2P_1K_2$	$N_2P_1K_3$	$N_2P_1K_2$Mg	$N_2P_1K_2$MgCa	
FYM	265.8	311.5	299.2	267.4	315.8	371.3	334.3	337.6	312.9
Without FYM	64.1	86.5	77.6	66.3	107.3	161.2	109.7	129.4	100.2
Mean	165.0	199.0	188.4	166.8	211.5	266.2	222.0	233.5	

$LSD_{0.05}$ for the factor I – 14.45
$LSD_{0.05}$ for the factor II – 51.21
$LSD_{0.05}$ for interaction I×II – n.s.

Farmyard manure has been found to produce a beneficial effect on the content of available potassium (Figure 2). The availability of potassium rose on average by about 210 mg kg^{-1} following FYM fertilization. This effect is worth emphasizing because, even if the leaching of potassium was elevated or the soil was submitted to rabunkowa gospodarka, it would allow for maintaining resources of available K in soil for a longer period of time on a level that would guarantee proper functions of soil as the environment in which crops grow.

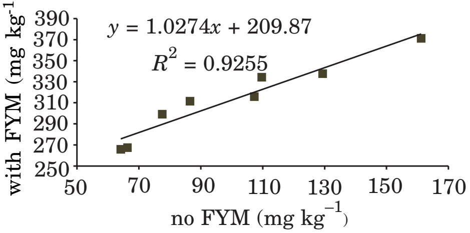

Fig. 2. Dependence between content of available K (mg kg^{-1}) in soil fertilized and not fertilized with FYM

In soil fertilized with FYM and mineral fertilizers, the content of available Mg fluctuated from 67.0 to 90.8 mg kg^{-1}, and in soil receiving only mineral fertilization it ranged from 23.3 to 45.3 mg kg^{-1} of soil (Table 4). Without any doubt, these results point to the beneficial effect produced by manure on the abundance of soil in plant available forms of magnesium. Based on the analysis of correlation and linear regression, it was determined that manure increased the content of available Mg by 46.198 mg kg^{-1} (Figure 3). Manure not only contains magnesium but it also acts as a humus creating substance. It is a known fact that manure improves the soil complex sorptive capacity, which retains cations by physicochemical sorption, thus preventing the leaching of elements, for example magnesium. Therefore, soil regularly fertilized with manure will be able to sustain soil degrading processes for a longer time and will allow for a more efficient storage of elevated amounts of available nutrients.

Table 4

Content of available forms of magnesium in soil (mg kg^{-1})

Factor I	Factor II								Mean
	$N_0P_0K_0$	$N_1P_1K_1$	$N_2P_1K_1$	$N_3P_1K_1$	$N_2P_1K_2$	$N_2P_1K_3$	$N_2P_1K_2$Mg	$N_2P_1K_2$MgCa	
FYM	78.3	71.3	75.5	67.0	67.8	71.0	90.8	83.3	75.6
Without FYM	33.0	27.3	27.3	23.3	26.8	24.3	45.3	42.0	31.1
Mean	55.6	49.3	51.4	45.1	47.3	47.6	68.0	62.6	

$LSD_{0.05}$ for the factor I – 3.09
$LSD_{0.05}$ for the factor II – 9.16
$LSD_{0.05}$ for interaction I×II – n.s.

Mineral fertilizers have also significantly affected the concentration of available magnesium in soil (Table 4). However, their effect, except compounds of magnesium or liming, was not as beneficial as that generated by manure. The highest rate of nitrogen depressed significantly the content of this element compared to its quantity observed in soil lacking mineral

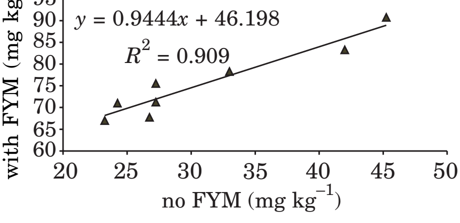

Fig. 3. Dependence between content of available Mg (mg kg^{-1}) in soil fertilized and not fertilized with FYM

fertilization. On the other hand, magnesium fertilization significantly increased the availability of Mg to plants. Liming led to a non-significant decline in the resources of Mg in soil. This could have been caused by the competition between Mg^{2+} and Ca^{2+} ions. Analogously, K^+ ions, being antagonistic to Mg^{2+} ions, considerably depressed accumulation of available magnesium in soil. The competition between potassium and magnesium was the strongest in soil which received only mineral fertilizers. Analogously to available K, nitrogen probably accelerated the leaching of magnesium.

In the present study, the effect of FYM and mineral fertilizers on the content of basic nutrients in soil (P, K and Mg) has proven to be extremely favourable. JASKULSKA and JASKULSKI (2003), who discussed both Polish and foreign research in this field, have concluded that the most rational fertilization regime, considering the soil fertility and yielding, is a combined application of organic and mineral fertilizers. The authors also emphasize the role of mineral fertilizers in balancing nutrients. They empirically demonstrated that the content of available forms of P increased in soil following FYM fertilization. The relevant literature contains papers suggesting that soil can be depleted in phosphorus after a long period of being treated with FYM alone (BARCZAK et al. 1999). In turn, ZIMNY and KUC (2005) found out that organic fertilization, and most profoundly FYM, increases the concentration of available forms of P and K in soil. There are also reports suggesting lack of response or sometimes even reduced availability of Mg in soil after it had been fertilized with magnesium (KANIUCZAK 1999). In our experiment, both manure and magnesium in mineral fertilizers considerably increased resources of available magnesium in soil. This finding is supported by PIECHOTA et al. (2000). Several researchers (ŁABĘTOWICZ et al. 1999, MURAWSKA et al. 2001, JAKULSKA and JASKULSKI 2003, SIENKIEWICZ 2003) dealing with chemical properties of soil claim that liming can perfectly well regulate the availability of P, K and Mg in soil. Our own research demonstrated a similar tendency.

CONCLUSIONS

1. When applied regularly, FYM considerably increases the content of available forms of phosphorus, potassium and magnesium in soil.

2. Nitrogen introduced to soil together with mineral fertilizers reduces the availability of phosphorus, potassium and magnesium. Fertilization with calcium and potassium significantly depresses only the availability of magnesium.

3. Exclusive mineral fertilization results in a bigger increase in the availability of nutrients used in mineral fertilizers (P, K and Mg) than mineral fertilization in combination with manure.

4. With regular application of FYM, it is possible to reduce mineral fertilization and, at the same time, maintain higher abundance of soil in basic plant nutrients.

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CONTENT OF AVAILABLE FORMS OF SOME MICRONUTRIENTS IN SOIL AFTER LONG-TERM DIFFERENTIATED FERTILIZATION

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Abstract

The objective of this study has been to follow modifications in the content of Cu, Zn and Mn in the topmost layer of soil which had been fertilized for many years with farmyard manure and mineral fertilizers or with mineral fertilizers alone. Soil samples were collected in 2002-2005 from a trial established in 1986 on proper brown podsolic soil, according to the random block design with four replication. The first factor consisted of organic fertilization (manure applied every two years or without manure). The second factor involved different rates of mineral fertilization. Rates of nutrients in the mineral fertilizers were identical in both experimental series – with or without manure. In each year, the same crop was grown on both fields, in a crop rotation system: sugar beet (2002), spring barley (2003), maize (2004) and spring wheat (2005). Plant available forms of nutrients were extracted from soil in 1 mol HCl dm^{-3} solution. After extraction, the content of metals was determined by atomic absorption spectrophotometry. The results underwent statistical processing using analysis of variance for a two-factor experiment.

The content of available forms of copper, zinc and manganese in soil regularly amended with manure was evidently higher than analogous concentrations determined in soil receiving only mineral fertilization since 1986. Manure most strongly improved the concentration of Cu (nearly 1.7-fold), while producing the weakest influence on manganese (over 1.3-fold more). In absolute values, however, the increase in availability of manganese was the highest, reaching on average 52 mg kg^{-1} of soil. Differentiated mineral fertilization with nitrogen or potassium as well as manganese and liming to a lesser extent than manure modified the availability of Cu, Zn and Mn in soil. Among these nutrients, nitrogen most often increased the content of plant assimilable forms of metals in soil, which may have been caused by its acidifying influence.

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Key words: manure, mineral fertilizers, available forms of Cu, Zn and Mn in soil.

ZAWARTOŚĆ PRZYSWAJALNYCH FORM WYBRANYCH MIKROELEMENTÓW W GLEBIE PO WIELOLETNIM ZRÓŻNICOWANYM NAWOŻENIU

Abstrakt

Celem badań było prześledzenie zmian zawartości Cu, Zn i Mn w wierzchniej warstwie gleby po wieloletnim nawożeniu obornikiem i nawozami mineralnymi lub wyłącznie nawozami mineralnymi. Próbki gleby pobierano w latach 2002-2005 z doświadczenia założonego w 1986 r. metodą losowanych bloków, w czterech powtórzeniach, na glebie płowej typowej. Pierwszym czynnikiem było nawożenie organiczne (obornik stosowany, co dwa lata lub bez tego nawozu), drugim – zróżnicowane nawożenie mineralne. Dawki składników pokarmowych w nawozach mineralnych były takie same w obydwu seriach doświadczenia – z obornikiem i bez tego nawozu. W każdym roku uprawiano tę samą roślinę na obydwu polach w zmianowaniu: burak cukrowy (2002 r.), jęczmień jary (2003 r.), kukurydza (2004 r.) i pszenica jara (2005 r.). Przyswajalne dla roślin formy metali ekstrahowano z gleby roztworem 1 mol $HCl \cdot dm^{-3}$. Po ekstrakcji zawartość metali oznaczono metodą absorpcyjnej spektrometrii atomowej. Otrzymane wyniki opracowano statystycznie metodą analizy wariancji dla doświadczenia dwuczynnikowego.

Zawartość przyswajalnych form miedzi, cynku i manganu w glebie nawożonej regularnie obornikiem zdecydowanie przewyższała ich ilość w glebie nawożonej wyłącznie mineralnie od 1986 r. Obornik najsilniej zwiększył koncentrację Cu (prawie 1,7-krtonie), a w mniejszym stopniu manganu (ponad 1,3-krotnie). W wartościach bezwzględnych jednak wzrost dostępności manganu był największy i wynosił średnio ponad 52 $mg \cdot kg^{-1}$ gleby. Różnicowane nawożenie mineralne azotem, potasem oraz magnez i wapnowanie w mniejszym zakresie niż obornik zmieniały dostępność Cu, Zn i Mn w glebie. Spośród wymienionych wyżej składników pokarmowych azot najczęściej zwiększał zawartość przyswajalnych form metali w glebie, co mogło być spowodowane jego zakwaszającym działaniem.

Słowa kluczowe: obornik, nawozy mineralne, przyswajane formy Cu, Zn i Mn w glebie.

INTRODUCTION

Micronutrients play highly important biochemical roles in plant organisms, therefore it is essential to consider them when planning fertilization (Spiak 2000). Many authors claim that good supply of plants with trace elements can only occur when fertilization is managed properly (Mazur, Mazur 2004, Rutkowska et al. 2009). On the other hand, excessive amounts of trace elements in soil can lead to their excessive uptake by plants (McBride et al. 2004, Rattan et al. 2005, Diatta 2008). In view of the above considerations, it seems recommendable that trace metals in soils should be monitored because of the consequences of excess metals for agriculture (quality and quantity of yields) and environment.

The purpose of this study has been to follow the effect of mineral fertilizers and manure on the content of plant available forms of Cu, Zn and Mn in soil.

MATERIAL AND METHODS

A two-factor experiment was set up in 1986 according to the random block design with four replications on proper brown podsolic soil originating from light loam (this paper contains the results obtained from 2002 to 2005). The first-order factor included manure fertilization and the second-order factor comprised differentiated mineral fertilization (Table 1). In each year, the same crop was tested on both fields (with and without manure) in the following rotation: sugar beet, spring barley, maize, spring wheat. Manure (40 t ha^{-1}) was used under sugar beet and maize, while liming was applied under sugar beet.

Table 1

Design of mineral fertilization

No.	Treatment	Sugar beet (maize)				Spring barley (spring wheat)			
		N	P	K	Mg	N	P	K	Mg
		dose, kg ha^{-1}							
1	$N_0P_0K_0$	0	0 (0)	0 (0)	0	0 (0)	0	0	0
2	$N_1P_1K_1$	60	34.9 (26.2)	66.4 (49.8)	0	30 (40)	34.9	33.2 (24.9)	0
3	$N_2P_1K_1$	120	34.9 (26.2)	66.4 (49.8)	0	60 (80)	34.9	33.2 (24.9)	0
4	$N_3P_1K_1$	180	34.9 (26.2)	66.4 (49.8)	0	90 (120)	34.9	33.2 (24.9)	0
5	$N_2P_1K_2$	120	34.9 (26.2)	132.8 (99.7)	0	60 (80)	34.9	66.4 (49.8)	0
6	$N_2P_1K_3$	120	34.9 (26.2)	199.3 (149.7)	0	60 (80)	34.9	99.7 (74.7)	0
7	$N_2P_1K_2Mg$	120	34.9 (26.2)	132.8 (99.7)	48.2 (24.1)	60 (80)	34.9	66.4 (49.8)	18.1
8	N_2P1K_2MCa	120	34.9 (26.2)	132.8 (99.7)	48.2 (24.1)	60 (80)	34.9	66.4 (49.8)	18.1

Soil samples for chemical analyses were collected from the arable horizon (0-25 cm) after harvest. Extraction of available forms of Cu, Zn and Mn was conducted using 1 mol HCl dm^{-3}. Afterwards, the ASA method was applied for determinations of the metals. The results were processed statistically (Statistica software).

RESULTS AND DISCUSSION

In the rotation system with manure, the content of Cu in soil ranged from 1.932 to 2.299 mg kg^{-1}, and in the system with mineral fertilization alone it varied from 1.151 to 1.437 mg kg^{-1} (Table 2). These data prove univocally that manure has a considerable effect on the content of available copper in soil.

MAZUR and MAZUR (2004) as well as RUTKOWSKA et al. (2009) demonstrated empirically that copper availability improved significantly after manure was

Table 2

Content of available cupper in soil (mg·kg^{-1})

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	2.191	1.195	1.693
$N_1P_1K_1$	2.028	1.234	1.631
$N_2P_1K_1$	2.230	1.289	1.759
$N_3P_1K_1$	2.299	1.178	1.738
$N_2P_1K_2$	2.014	1.187	1.600
$N_2P_1K_3$	1.932	1.151	1.541
$N_2P_1K_2Mg$	2.037	1.289	1.663
$N_2P_1K_2MgCa$	2.127	1.437	1.782
Mean	2.107	1.245	

$LSD_{0.05}$ for the factor I – 0.059
$LSD_{0.05}$ for the factor II – 0.088
$LSD_{0.05}$ for interaction I×II – n.s.

added to soil. Differentiated mineral fertilization did not have such a strong effect as manure on modifications in the content of plant available copper in soil. The most severe reduction in Cu availability appeared when the highest dose of potassium has been introduced to soil. Nitrogen in the treatment with manure raised the abundance of available copper in soil. In turn, when mineral fertilization was not supplemented with manure, the highest N dose reduced the availability of Cu in soil. This may have been caused by its increased uptake by crops. It is also worth noticing that liming did not limit the availability of Cu. What is more, when mineral fertilization was applied exclusively, this treatment led to a significant increase in the abundance of plant available copper in soil. Such varied influence of liming has also been reported by GONDEK (1999), SZULC et al. (2007) or RUTKOWSKA et al. (2009).

The content of available zinc in soil was evidently higher than that of copper (Table 3). By analogy to Cu, the abundance of available Zn rose significantly following long-term manure fertilization.

The lowest concentration of available Zn appeared in limed soil, which was certainly caused by the increased soil reaction. Similar results can be found in other reports (FILIPEK-MAZUR, GONDEK 1999, RUTKOWSKA et al. 2009). Nitrogen improved mobility of zinc by acidifying soil. This tendency appeared most clearly in soil amended with manure. In soil receiving only mineral fertilization, the highest rate of nitrogen limited the abundance of soil in available zinc.

Table 3

Content of available zinc in soil (mg·kg^{-1})

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	10.54	6.63	8.59
$N_1P_1K_1$	10.75	7.63	9.19
$N_2P_1K_1$	11.38	8.24	9.81
$N_3P_1K_1$	12.12	7.81	9.97
$N_2P_1K_2$	10.81	7.44	9.12
$N_2P_1K_3$	10.77	7.49	9.13
$N_2P_1K_2Mg$	10.36	6.76	8.56
$N_2P_1K_2MgCa$	9.70	5.88	7.79
Mean	10.80	7.24	

$LSD_{0.05}$ for the factor I – 0.47
$LSD_{0.05}$ for the factor II – 0.49
$LSD_{0.05}$ for interaction I×II – n.s.

Manure applied every two years considerably increased the content of available magnesium in soil, on average to over 52 mg kg^{-1}, i.e. by over 33% (Table 4). The content of Mn increased as the rate of nitrogen in the treatments with manure rose. This relationship was somewhat different in the rotation system including manure. There, the lowest four-year nitro-

Table 4

Content of available manganese in soil (mg·kg^{-1})

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	200.56	159.63	180.09
$N_1P_1K_1$	213.34	157.51	185.43
$N_2P_1K_1$	219.83	162.51	191.17
$N_3P_1K_1$	220.23	160.67	190.45
$N_2P_1K_2$	209.38	153.16	181.27
$N_2P_1K_3$	210.68	156.92	183.80
$N_2P_1K_2Mg$	200.79	150.10	175.44
$N_2P_1K_2MgCa$	193.34	148.99	171.17
Mean	208.52	156.19	

$LSD_{0.05}$ for the factor I – 6.28
$LSD_{0.05}$ for the factor II – 7.01
$LSD_{0.05}$ for interaction I×II – n.s.

gen dose (190 kg N ha^{-1}) only slightly decreased the content of Mn, but when the average dose was applied (380 kg N ha^{-1}), the content of Mn increased. Further increase in the amount of N in mineral fertilizers (from 570 kg N ha^{-1} over four years) resulted in depressed availability of magnesium, down to the level comparable to the one in the control soil. On the one hand, nitrogen may have made the soil more acidic, thus increasing the amount of manganese which was reduced to Mn^{2+}. On the other hand, however, increased solubility of manganese could have improved its uptake by plants and, possibly, raised the loss of this element caused by leaching, which could explain the relationships found in samples of soil receiving only mineral fertilization. Potassium only very slightly modified the content of Mn in soil. In turn, magnesium and calcium depressed the accumulation of available forms of manganese in soil. Both Mg and Ca are alkaline cations, which act contrary to nitrogen. Moreover, there may have been ionic antagonisms between Mg^{2+} and Ca^{2+} versus Mn^{2+}.

The elements discussed in this paper are usually present in soil in small amounts, and are available to plants as bivalent cations, which is the form that plants can assimilate. Thus, it might be expected that they will be antagonistic to one another. However, no such dependenced were verified by our results (Figures 1,2,3). The computations (regression and correlation calculations) have shown that an increase in the content of one of the metals in soil did not depress the amounts of the available forms of another metal. On the contrary, it is highly probable that changes in amounts of Cu, Zn and Mn followed the same direction.

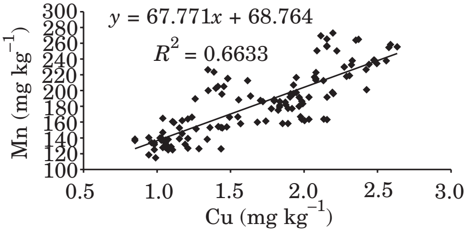

Fig. 1. Dependence between content of available forms of Cu and Mn in soil

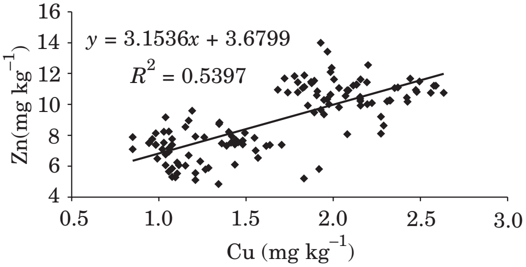

Fig. 2. Dependence between content of available forms of Cu and Zn in soil

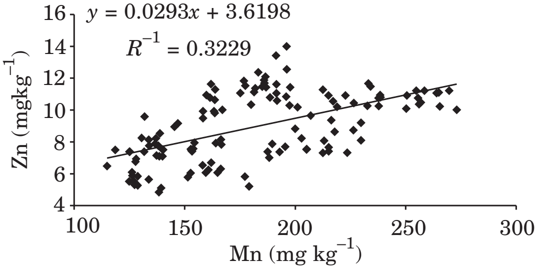

Fig. 3. Dependence between content of available forms of Mn and Zn in soil

The monitoring of the concentrations of available forms of Cu, Zn and Mn in soil is very important for two reasons. Firstly, these metals are essential for life of all living organisms, and plants must be sufficiently supplied (SPIAK 2000). Secondly, their excessive levels in soil poses a threat that plants and animals could be intoxicated (MCBRIDE et al. 2004, RATTAN et al. 2005, DIATTA 2008). The amounts of copper, zinc and manganese in soil determined in this study do not pose an ecological threat, as they range from low (Cu) to moderate (Zn and Mn) abundance. It can be hypothesised that under long-term mineral fertilization, plant may experience deficits of available copper and even regular application of FYM does not guarantee moderate abundance of soil in this element. BOWSZYS et al (2007), who investigated composted municipal waste used for fertilization, concluded that in the second year of the application of such fertilizers, zinc and magnesium in soil fell down significantly. It is worth noticing that metal elements, even when excessively accumulated in soil, do not necessarily cause their excessive accumulation in plants as organic matter strongly inhibits their uptake by plants (SAHA et al. 1999), and farmyard manure is as example of organic substance. According to GONDEK (2003), the highest differences in the content of soluble forms of trace metals are found immediately after fertilization treatments, but fertilization does not evoke their excessive mobilization. In turn, SZULC et al. (2007) found out that the concentration of available forms of Cu, Zn and Mn in soil rose under the influence of exclusive mineral fertilization, whereas manure contributed to a decrease in their soil content. In the present experiment, manure produced a stronger influence on increasing abundance of soil in Cu, Zn and Mn than mineral fertilizers, the finding that is supported by the report of MAZUR and MAZUR (2004). Nitrogen, which encourages soil acidification, can cause increased solubility of metals and their translocation to plants (DE HANN 1981). This study has demonstrated a slightly elevated content of available forms of Cu, Zn and Mn in soil under the influence of fertilization with higher nitrogen rates. However, this increase was not significant and did not create a risk of excessive uptake of the metals by plants.

CONCLUSIONS

1. Long-term fertilization with farmyard manure and mineral fertilizers or with mineral fertilizers alone does not create a risk of excessive solubility and plant availability of Cu, Zn and Mn.

2. Manure differentiated the content of available Cu, Zn and Mn in soil more strongly than mineral fertilizers.

3. Long-term mineral fertilization, which introduced to soil only macroelements can lead to soil depletion in available forms of microelements, particularly copper.

4. Manure, when was introduced to soil every other year in a long-term rotation system, it did not guarantee moderate abundance of soil in available copper.

5. Increase in the content of available forms of one of the metals (Cu, Zn or Mn) did not limit the availability of any of the other micronutrients.

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EFFECT OF DIFFERENT RATES AND FORMS OF SULPHUR ON CONTENT OF AVAILABLE PHOSPHORUS IN SOIL

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Abstract

A three-year field experiment was conducted in Byszwałd near Lubawa in 2000-2002. The aim of this study has been to determine the influence of increasing rates of sulphur on the dynamics of available phosphorus in soil at two horizons: 0-40 and 40-80 cm. The trial was set up on acid brown soil of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulphur 4.10, available phosphorus 34.5 and potassium 110.0 mg kg^{-1} of soil.

Three levels of sulphur fertilization were applied: 40, 80 and 120 kg·ha^{-1} in the sulphate form ($S\text{-}SO_4$) and as elementary sulphur ($S\text{-}S^0$). During the whole duration of the field trials, the results demonstrating the effect of fertilization with different forms and rates of sulphur on the content and transfer of available phosphorus in soil were inconsistent. Only the dose of 120 kg·ha^{-1} $S\text{-}SO_4$ caused a significant increase in the concentration of available sulphur in soil in the 0-40 and 40-80 cm layers. All the rates of elementary sulphur as well as 40 and 80 kg·ha^{-1} sulphate sulphur caused little less but an increasing tendency in the content of phosphorus in soil. The effect of elementary sulphur became apparent as late as the third year of the trials. The effect of the doses of 40 and 80 kg·ha^{-1} of sulphur on properties of soil depended on the form of sulphur, duration of the experiment.

Key words: fertilization, sulphate sulphur, elementary sulphur, available phosphorus, soil.

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WPŁYW RÓŻNYCH DAWEK I FORM SIARKI NA ZAWARTOŚĆ PRZYSWAJALNEGO FOSFORU W GLEBIE

Abstrakt

W latach 2000-2002, w Byszwałdzie, w pobliżu Lubawy, przeprowadzono 3-letnie doświadczenie polowe. W doświadczeniu badano wpływ nawożenia siarką na dynamikę przyswajalnego fosforu w glebie w dwóch poziomach: 0-40 cm i 40-80 cm. Eksperyment założono na glebie brunatnej, kwaśnej o składzie granulometrycznym piasku gliniastego mocnego. Gleba wyjściowa miała nstępujące właściwości: $pH_{(KCl)}$=5,30, azot mineralny 24,0, siarka siarczanowa 4,10, przyswajalny fosfor 34,5, potas 110,0 mg·kg^{-1} gleby. Zastosowano 3 poziomy nawożenia siarką: 40, 80 i 120 kg·ha^{-1} w formie siarczanowej (S-SO_4) i elementarnej (S-S^0). W ciągu całego okresu badań otrzymano niejednoznaczne wyniki dotyczące wpływu nawożenia różnymi formami i dawkami siarki na zawartość i przemieszczanie się przyswajalnego fosforu w glebie. Jedynie dawka 120 kg·ha^{-1} S-SO_4 przez cały okres badań wpływała na uruchamianie i migrację fosforu glebie oraz spowodowała istotne zwiększenie zawartości przyswajalnego fosforu w glebie w warstwie 0-40 cm i 40-80 cm. Wszystkie dawki siarki elementarnej oraz 40 i 80 kg siarki siarczanowej powodowały jedynie tendencję zwyżkową. Wpływ siarki elementarnej uwidocznił się dopiero w trzecim roku doświadczenia. Działanie dawek 40 i 80 kg·ha^{-1} siarki na właściwości gleby zależało od formy siarki oraz czasu trwania doświadczenia.

Słowa kluczowe: nawożenie, siarka siarczanowa, siarka elementarna, przyswajalny fosfor, gleba.

INTRODUCTION

Sulphur deficit in Europe becomes evident not only in high sulphur demanding crops but has already become a problem for farmers growing cereals (SCHUNG et al. 1993, ZHAO et al 1996, SCHERER 2001). At present, there is a growing interest in sulphur as a component of fertilisers, especially in non-industrialised areas situated far from large cities, where deficient quantities of sulphur in plants are detected (KACZOR and BRODOWSKA 2002). Phosphorus metabolism in soil is important for both agriculture and environment as different forms and levels of phosphorus play a decisive role in plant production and eutrophication of water bodies (SHARPLEY 1995). The results of studies on the effect of sulphur on fluctuations in concentrations of available sulphur in soil are inconsistent. MOTOWICKA-TERELAK and TERELAK (1998) demonstrated that sulphur, by binding aluminium sulphate, reduced phosphorus fixation in soil, while excessive amounts of sulphates may result in incomplete utilization of phosphorus supplied with fertilizers, as they inhibit the growth of crops. In contrast, LINDEMANN et al. (1991) did not determine such a relationship. In soils fertilized with elementary sulphur, access of plants to available sulphur is improved (JAGGI et al. 2005).

The purpose of the present study has been to determine the effect of fertilization with increasing rates of sulphur applied in the form of sulphates and as elementary sulphur on the content of available phosphorus forms in soil the 0-40 and 40-80 cm layers.

MATERIAL AND METHODS

A three-year field experiment was conducted from 2000 to 2002, in Byszwałd near Lubawa. The village is distant from larger industrial plants which emit sulphur compounds and lies far from any big cities. As a result, any changes in the concentration of sulphur in the soil were not caused by human pressure.

The trial was set up on acid brown soil of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulphur 4.10, available phosphorus 34.5 and potassium 110.0 mg kg^{-1} of soil. The annual rates of sulphate sulphur ($S\text{-}SO_4$) and elementary sulphur ($S\text{-}S^0$) were: S_1 – 40, S_2 – 80 and S_3 – 120 kg ha^{-1}.

The permanent experiment was established in a random block design and consisted of eight fertilisation objects with four replications: 1) 0, 2) NPK, 3) NPK + $S_1\text{-}SO_4$, 4) NPK + $S_2\text{-}SO_4$, 5) NPK +$S_3\text{-}SO_4$, 6) NPK +$S_1\text{-}S^0$, 7) NPK +$S_2\text{-}S^0$, 8) NPK +$S_3\text{-}S^0$. The NPK rates depended on the crop species and soil fertility (Table 1). The design of the experiment is presented in Tables 2-4. The following fertilisers were applied: nitrogen – ammonium nitrate or ammonium sulphate, phosphorus – triple superphosphate, potassium – potassium chloride 60% or potassium sulphate, sulphur – potassium sulphate and, as a supplement, ammonium sulphate; in addition, elementary sulphur was applied on the objects where this form of sulphur was tested.

Table 1

NPK rates applied in the trials

Crops	Year	($kg \cdot ha^{-1}$)		
		N	P	K
Head cabbage	2000	200.0	52.5	180.0
Common onion	2001	160.0	60.0	183.0
Spring barley	2002	90.0	80.0	111.0

Soil samples were collected from each plot, at 0-40 and 40-80 cm depths, prior to the establishment of the trials, after each harvest and before sowing the consecutive crop. There was one exception to the routine – in spring 2001, due to prolonged rains, soil samples were taken only from the 0-40 cm horizon. Available phosphorus was determined with Enger Riehm's method (DL) (the ratio between soil and extraction 1:50).

The concentrations of available phosphorus in soil were processed statistically using analysis of variance for two-factor experiments in a random-block design, assuming the form of sulphur as factor a and rate of sulphur

Table 2

Effect of different rates and forms of sulphur on the content of available phosphorus in soil at 0-40 cm depth (mg·kg^{-1} soil)

Treatments	2000 autumn	2001 spring	2001 autumn	2002 spring	2002 autumn
	soil at 0-40 cm depth				
0	34.8	34.1	57.0	44.1	27.4
NPK	41.0	31.6	53.1	41.0	37.5
NPK+ S_1-SO_4	50.1	38.6	91.3	43.8	47.7
NPK+ S_2-SO_4	45.2	32.1	68.0	38.5	40.3
NPK+ S_3-SO_4	35.6	33.5	91.3	43.4	49.2
NPK+S_1-S^0	39.7	33.5	55.3	35.1	38.0
NPK+S_2-S^0	48.6	33.2	56.0	35.4	39.3
NPK+S_3-S^0	45.1	33.6	66.4	42.4	44.7
NIR-*p*-0.05					
a	n.s.*	n.s.	n.s.	2.25	1.64
b	2.44	n.s.	1.68	3.19	2.32
a x *b*	n.s.	n.s.	2.38	4.51	3.29

SO_4 – sulphate sulphur; S^0 – elementary sulphur; S_1 – 40 kg·ha^{-1}, S_2 – 80 kg·ha^{-1}, S_3 – 120 kg·ha^{-1}

a – form of sulphur; *b* – dose of sulphur; *a* x *b* – interaction

* n.s. – non-significant difference

as factor b. Additional statistical analyses were performed with the software package Statistica 6.0 PL, to carry out analysis of regression with Duncan's tests in order to determine statistical differences between sets of data.

DISCUSSION OF THE RESULTS

In 2000, the amount of available phosphorus in the 0-40 cm soil layer was varied, ranging between 34.8 and 50.1 mg P·kg^{-1} of soil (Table 2). NPK as well as NPK+S fertilization caused significant increase in the concentration of available phosphorus versus the control and initial soil. When a single rate of sulphate sulphur was applied, the concentration of available phosphorus in soil increased versus the NPK fertilized object. The application of 120 kg·ha^{-1} S-SO_4 caused a significant decline in the amount of available phosphorus in soil relative all the remaining fertilization objects. This decrease could have been due to several factors, for example transfer of phosphorus to the deeper soil layer 40-80 cm (Table 3). In the 40-80 cm soil horizon, the other sulphur rates had little effect on the dynamics of available phosphorus. As the rates of sulphate sulphur applied as a fertilizer rose,

Table 3

Effect of different rates and forms of sulphur on the content of available phosphorus in soil at 40-80 cm depth (mg kg^{-1} soil)

Treatments	2000 autumn	2001 spring	2001 autumn	2002 spring	2002 autumn
	soil at 40-80 cm depth				
0	36.2	-	36.2	36.2	36.7
NPK	33.0	-	33.0	33.0	32.4
NPK+ S_1-SO_4	34.3	-	34.3	34.3	28.3
NPK+ S_2-SO_4	29.0	-	29.0	29.0	22.0
NPK+ S_3-SO_4	37.6	-	37.6	37.6	49.9
NPK+S_1-S^0	33.5	-	33.5	33.5	32.2
NPK+S_2-S^0	35.7	-	35.7	35.7	35.1
NPK+S_3-S^0	33.8	-	33.8	33.8	41.3
NIR-*p*-0.05 a *b* *a* x *b*	 1.48 2.09 * n.s.	-	 1.48 2.09 n.s.	 1.48 2.09 n.s.	 2.25 3.18 4.50

SO_4 – sulphate sulphur; S^0 – elementary sulphur; S_1 – 40 kg·ha^{-1}, S_2 – 80 kg·ha^{-1}, S_3 – 120 kg·ha^{-1}
a – form of sulphur; *b* – dose of sulphur; *a* x *b* – interaction
* n.s. – non-significant difference

a tendency towards decreasing concentration of available phosphorus in soil appeared. However, the application of elementary sulphur resulted in less regular changes.

In the second year of the experiment (2001), the concentration of available phosphorus in the 0-40 cm soil layer was uniform and independent of the sulphur fertilization (Table 2).

In autumn (2001), the level of phosphorus in soil was evidently higher in all the objects fertilized with sulphur than in the NPK fertilized object, especially after all the increasing rates of sulphate sulphur as well as a triple dose of elementary sulphur had been applied. It is most likely that the process of elementary sulphur oxidation was initiated or else increasing rates of S-SO_4 were observed to be followed by a decreasing uptake of phosphorus by onion plants Skwierawska et al (2008). In the 40-80 cm soil layer, sulphur fertilization had an ambiguous influence on the amount of available phosphorus. This form of phosphorus occurred in increased quantities in the objects which had received 120 kg·ha^{-1} S-SO_4 and 80 kg·ha^{-1} S-S^0 (Table 3). Other authors, e.g. Król et al. (1986), Motowicka-Terelak (1989), Jaggi et al. (2005) have also noticed that the content of available phosphorus in soil under the influence of sulphur tends to increase. The sulphur fertilization applied in the second year of the experiment increased the amounts of avail-

Table 4

Significance of differences in the content of available phosphorus in soil between particular objects according to Duncan's test.
Differences statistically significant at ($p \leq 0.05$)

Object	0	NPK	I-S-SO_4	II-S-SO_4	III-S-SO_4	I-S-S^0	II-S-S^0	III-S-S^0
0								
NPK	0.400789							
S_1-SO_4	0.002371	0.025297						
S_2-SO_4	0.938754	0.411004	0.002652					
S_3-SO_4	0.000667	0.010226	0.697388	0.000779				
S_1-S^0	0.772696	0.285048	0.000969	0.733427	0.000241			
S_2-S^0	0.192724	0.588087	0.075883	0.200051	0.036888	0.125709		
S_3- S^0	0.071181	0.293166	0.195560	0.075410	0.112098	0.041239	0.561581	
$\overline{x}$*	3.578	3.798	4.392	3.597	4.487	3.507	3.931	4.074

*$\overline{x}$ – average content of available phosphorus in soil in particular objects for the years 2000-2003 (mg·kg^{-1} soil); SO_4 – sulphate sulphur, S^0 – elementary sulphur, S_1 – 40 kg ha^{-1}, S_2 – 80 kg ha^{-1}, S_3 – 120 kg·ha^{-1}

able phosphorus in soil at the depths of 0-40 cm and 40-80 cm compared to the results obtained during the first year of the trials.

In the spring of 2002, the content of available phosphorus in soil sampled at 0-40 cm and 40-80 cm depth was smaller than in autumn 2001 (Tables 2,3), and ranged 29.0 and 44.1 mg P·kg^{-1} of soil.

In the autumn of 2002, all the fertilization rates of sulphate sulphur and elementary sulphur caused an increase in the amount of available phosphorus in soil sampled at 0-40 cm depth, which was particularly high after the triple sulphate sulphur dose. The increase was observed versus the control objects (Table 2). The fertilization with sulphate and elementary sulphur increased the concentration of available phosphorus in the 0-40 cm soil layer compared to the soil tested in spring, whereas the objects fertilized without sulphur became less abundant in phosphorus. At the soil depth of 40-80 cm, the concentration of available phosphorus decreased following the application of 40 and 80 kg·ha^{-1} of either sulphur form. It was only when 120 kg·ha^{-1} of S-SO_4 or S-S^0 was used that the soil was enriched with available phosphorus, which was also demonstrated in the earlier years of the trials.

During the whole duration of the field trials, the results demonstrating the effect of fertilization with different forms and rates of sulphur on the content and transfer of available phosphorus in soil were inconsistent. Only one rate of phosphorus, 120 kg·ha^{-1} S-SO$_4$ initiated mobilization and migration of phosphorus in soil throughout the whole period of the field trails.

The effect produced by elementary sulphur depended on the rate of its oxygenation in soil and its dose, which finds confirmation in studies reported by GERMID and JANZEN (1993) as well as WATKINSON and LEE (1994) and ZHOU (2002). This is proven by that fact that the concentration of available phosphorus in soil increased as late as the third year of our experiment and only in the object fertilized with 120 kg·ha^{-1} S-S^0. LINDEMANN et al. (1991) did not find any increase in available phosphorus in soil following fertilization treatments with elementary sulphur, even though the soil pH was lowered and the amount of the sulphate form in soil increased. According to JAGII et al. (2005), addition of elementary sulphur improves the availability of phosphorus in cultivated soils, irrespective of the soil initial pH.

The available references contain diverse interpretation of the influence of sulphur on the dynamics of available phosphorus in soil. The differences stem from changes in soil pH, competition among sulphate ions, mineralization of phosphorus organic forms (JAGGI et al. 1999, 2005) as well as liberation of aluminium and iron ions, which by reacting with sulphates bind fewer phosphate ions. Besides, the presence of free sulphur acid in sulphur-rich soils creates favourable conditions for the release of phosphorus from compounds which are hardly soluble (GĄDOR, MOTOWICKA-TERELAK 1986b). According to KACZOR (1996), application sulphur acid during three years cause decreasing concentration of available phosphorus in soil.

The computation of the level of significance of the differences performed with Duncan's test (Table 4) showed statistically significant differences between particular objects during the three years of the experiment. The object fertilized with the triple dose of sulphate sulphur was the most distinct one as the average content of available phosphorus determined in its soil was the highest and significantly different from the values established in the other fertilization objects.

CONCLUSIONS

1. The application of 120 kg·ha^{-1} of S-SO$_4$ caused significant increase in the content of available phosphorus in soil in the layers at 0-40 and 40--80 cm depth. All rates of elementary sulphur as well as those of 40 and 80 kg·ha^{-1} of sulphate sulphur produced only an increasing tendency in the soil concentration of phosphorus.

2. The effect of elementary sulphur on mobilization of phosphorus in soil revealed itself as late as the third year of the experiment.

3. The effect of the doses of 40 and 80 kg·ha^{-1} of sulphur on properties of soil depended on the form of sulphur, duration of the experiment.

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TRACE ELEMENTS IN SOILS OF UPPER ZONE OF SPRUCE FOREST ON SZRENICA MOUNT AND THE KOWARSKI GRZBIET RANGE IN THE KARKONOSZE MOUNTAINS

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Abstract

New regular examination of soil contamination with trace elements (Pb, Zn, Cu) in the upper zone of spruce forest in the western (Mount Szrenica) and eastern (Kowarski Grzbiet range) Karkonosze Mountains was carried out as part of the monitoring network of forest ecosystems in the Karkonosze Mountains National Park. Soil samples were taken at the following three depths: forest litter (the whole layer), 0-10 cm and 10-20 cm. Clearly raised concentrations of lead were found, particularly in forest litter (mean 83.2 $mg \cdot kg^{-1}$) and in horizons 0-10 cm (mean 73.3 $mg \cdot kg^{-1}$). Copper and zinc occurred in smaller amounts, in the ectohumus layer 47.5 mg $Zn \cdot kg^{-1}$ and 23.8 mg $Cu \cdot kg^{-1}$ (mean concentrations), and in the layer 0-10 cm – 33.7 mg $Zn \cdot kg^{-1}$ and 19.9 mg $Cu \cdot kg^{-1}$. Zinc and copper concentrations in soils of the upper spruce forest zone did not increase with altitude above mean sea level, and were slightly higher in the eastern part of Karkonosze Mts. (the Kowarski Grzbiet). Concentrations of lead were apparently higher in the western part of the Karkosze Mts. and increased with altitude AMSL.

Key words: soils, trace elements, upper spruce-zone, the Karkonosze Mountains.

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ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBACH REGLA GÓRNEGO SZRENICY I KOWARSKIEGO GRZBIETU W KARKONOSZACH

Abstrakt

W strefie regla górnego Karkonoszy zachodnich (Szrenica) i wschodnich (Kowarski Grzbiet) przeprowadzono analizę zanieczyszczenia gleb pierwiastkami śladowymi (Pb, Zn, Cu) opartą na monitoringu ekosystemów leśnych Karkonoskiego Parku Narodowego. W tym celu pobrano próbki z trzech głębokości: próchnicę nadkładową (w całej miąższości), 0-10 cm i 10-20 cm. Stwierdzono wyraźnie podwyższoną zawartość ołowiu, szczególnie w próchnicach nadkładowych (średnio 83,2 mg$\cdot$kg^{-1}) i warstwie 0-10 cm (średnio 73,3 mg$\cdot$kg^{-1}). Miedź i cynk występują w mniejszych ilościach, w ektohumusie średnio 47,5 mg Zn$\cdot$kg^{-1} i 23,8 mg Cu$\cdot$kg^{-1}, a w warstwie 0-10 cm średnio 33,7 mg Zn$\cdot$kg^{-1} i 19,9 mg Cu$\cdot$kg^{-1}. Zawartość cynku i miedzi w glebach regla górnego nie zwiększa się z wysokością n.p.m. i jest nieco wyższa we wschodniej części Karkonoszy (Kowarski Grzbiet) niż w zachodniej (Szrenica). Zawartość ołowiu jest wyraźnie wyższa w zachodniej części Karkonoszy i zwiększa się z wysokością n.p.m.

Słowa kluczowe: gleby, pierwiastki śladowe, regiel górny, Karkonosze.

INTRODUCTION

Concentration of trace elements in soils is often used as a universal indicator of degree of anthropogenic transformations in ecosystems. The ecological disaster that struck the entire Sudety Mountains in the1980s became an important impulse for undertaking extensive research on causes of that catastrophy and its effect on the soil environment (Dobrowolska 1995, Drozd et al. 1998a,b, Kabała 1995, 1998). The rapid decay of dense spruce forests caused transformation of natural habitats and the expansion of grasses, which influenced the circulation of trace elements in transformed ecosystems (Drozd et al. 1998a).

One of the consequences of a large-scale decay of forests in the Karkonosze Mountains was an implementation of permanent monitoring of forest ecosystems. The main task of the monitoring system is (i) establishing the present state of mountain ecosystems and (ii) observation of the ongoing changes resulting from anthropogenic and natural influences (Mol et al. 1998,Van Duijvenbooden 1998).

The aim of this work was to determine the gradients of spatial variability in concentrations of selected trace elements (Pb, Zn and Cu) in surface horizons of soils and forest litter in the upper zone of spruce forests in the Polish part of the Karkonosze Mountains. The analysis is based on data from the monitoring system of forest ecosystems collected in years 2006--2007. For comparison, two peripheral areas were selected: the Kowarski Grzbiet Range in the eastern periphery of the Karkonosze Mountains and Mount Szrenica in the western part of the Karkonosze Mountains (Figure 1).

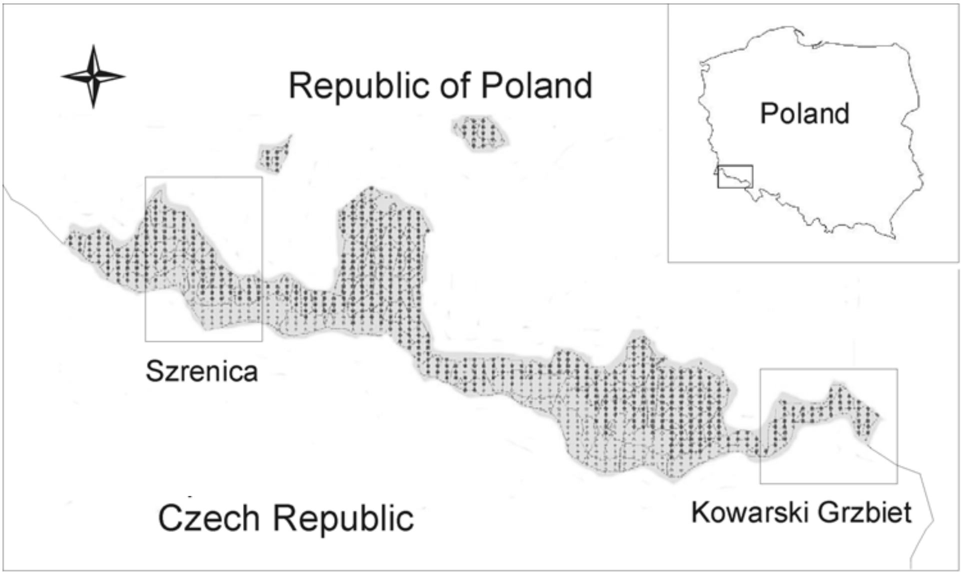

Fig. 1. Location of the investigated objects in Karkonosze Mountain National Park

METHODS

The system of forest environment monitoring in the Karkonosze Mountain National Park consists of 630 spherical areas located in forest zone and 230 areas in subalpine zone, arranged in a regular grid 200×300 m. Pedological field research was conducted in September 2006 on the Kowarski Grzbiet Range and in August 2007 on Mount Szrenica. The choice of these two mountain ranges situated on the eastern and western edges of the Karkonosze Mountains is supposed to enable the comparison of soil degradation degree as a function of the distance to the sources of atmospheric pollution, located mainly along the Czech – German – Polish border, west of the Karkonosze Mountains. Polluted air masses are moving to the Karkonosze area mainly with westerly and south-westerly winds.

Samples for analysis were generally taken in the upper zone of spruce forest in 40 monitoring areas located on the Kowarski Grzbiet Range, at the altitude of 1000-1270 m above mean sea level, and in 41 monitoring areas located on Szrenica Mount, at the altitude of 1000-1240 m AMSL. Predominating soils in these areas are Podzols, mostly with redoximorphic features (*stagnic*) and peat accumulation, locally extremely gravelly or stony (*hyperskeletic*). Podzols occurs in a mosaic with Histic Gleysols and Fibric Histosols, where the thickness of organic layer is up to 60 cm. All areas under investigation are covered with spruce mountain forests, degraded to some extent. The density of tree canopy runs up to 60-80% in the lower part of the upper zone of spruce forests, while above the altitude of 1000 m AMSL it is reduced to 40-50%. Above 1100 m AMSL, in the zone of a very strong decline of spruce stands, the density of tree canopy is generally less than 20%. Lower density of tree crowns enables the expansion of grasses and perennial plants, therefore as the altitude rises, the percentage of the surface covered with dense mossy and grassy undergrowth also increases. The entire area under investigation has very diversified microrelief resulting from numerous fallen trees with excavated roots, which strongly influences the spatial variability of the surface layers of soils and surface accumulation of organic matter.

The average field sample for analyses was prepared by mixing at least four primary soil samples taken with a pedological sampler in places randomly arranged over the monitored surface. Samples of forest litter and samples of soil taken at depths 0-10 cm and 10-20 cm were stored and analyzed separately (KARCZEWSKA et al. 2006). The ectohumus layer (forest litter) was not sampled in areas covered with grass communities, where spruce stands were extremely degraded and thinned out.

Soil and litter samples were prepared for analyses by drying, grinding and sieving through a 2 m mesh sieve. The following analyses were made on all samples: soil texture (in mineral samples taken at the depth 10-20 cm), pH in 1 $mol \cdot dm^3$ KCl – potentiometrically, organic carbon (in mineral and organic-mineral samples) – by Tiurin method, loss on ignition (in organic samples), as well as total content of trace elements (Pb, Cu and Zn) – with atomic absorption spectrometry after wet mineralization of soil samples in a mixture of nitric and hydrochloric acids in a ratio of 3:1. Mineralization was made in a microwave stove, in closed, high-pressure Teflon vessels.

Results of analyses were analyzed statistically with using Statistica 8 package (StatSoft Inc., Tulsa, USA). Statistical significance of differences between mean concentrations of trace elements was assessed using Duncan's test of multiple comparisons (at $p<0.05$) with an appointment of homogeneous groups of means.

RESULTS AND DISCUSSION

Soils on the analyzed monitoring surfaces have a texture of loamy sand and sandy loam and acid or strongly acid reaction (Table 1). Values of pH apparently increase with depth into the soil profile: the lowest pH is in the ectohumus layer (average pH_{KCl}=2.92), in the layer 0-10 cm it averages pH_{KCl}=3.16, and in the layer 10-20 cm it achieves pH_{KCl}=3.40. No statistically significant differences were found between the reaction of analogous

Table 1

Soil reaction, content of organic matter and total concentrations of trace elements in soils of the Kowarski Grzbiet and the Mount Szrenica

Localization	Kowarski Grzbiet range			Mount Szrenica		
Soil layer	ectohumus	0-10 cm	0-20 cm	ectohumus	0-10 cm	0-20 cm
pH_{KCl}	2.92^{*a} 2.6-3.4**	3.17^{a} 2.7-3.7	3.40^{a} 2.9-4.1	2.92^{a} 2.5-3.3	3.15^{a} 2.7-3.9	3.39^{a} 2.9-4.9
Organic carbon, %	-	15.3a 7.4-55.2	8.0^{a} 2.45-49.2	-	18.6^{a} 3.9-49.2	10.8^{a} 1.9-44.6
Loss on ignition, %	83.2^{a} 62.3-96.4	-	-	81.8^{a} 64.6-95.4	-	-
Zn, $mg \cdot kg^{-1}$	47.5^{a} 34.5-61.0	33.7^{a} 10.4-94.3	30.6^{a} 5.8-97.2	35.4^{b} 29.0-42.0	34.2^{a} 13.0-90.0	24.9^{a} 7.5-66.7
Cu, $mg \cdot kg^{-1}$	23.8^{a} 12.5-31.7	19.9^{a} 4.8-40.3	15.0^{a} 1.9-38.4	16.9^{b} 11.3-24.0	14.6^{a} 3.7-29.8	8.8^{b} 2.0-23.0
Pb, $mg \cdot kg^{-1}$	83.2^{a} 62.3-96.4	73.3^{a} 18.5-137.6	36.7^{a} 3.8-88.2	110.7^{b} 69.0-180.0	97.4^{b} 39.2-225.5	46.2^{b} 3.8-150.5

Explanation: *arithmetic mean, **range (minimum – maximum), $^{a,\ b}$ – homogeneous groups of Duncan's multiple range test (compared mean values of particular properties in the same soil layer on the Kowarski Grzbiet range and the Mount Szrenica)

soil horizons on the Kowarski Grzbiet Range and on Mount Szrenica (Table 1). However, slightly higher pH of litter and surface layers of soils was noticed in the zone of the expansion of grass vegetation (above 1100 m AMSL) as compared to the zone of dense spruce forests (<1100 m AMSL). Even though these differences are not statistically significant, they confirm earlier reports indicating lower pH of soils under existing spruce stands than of analogous soils existing under strongly degraded forests (Drozd et al. 1998a, Kabała 1998).

Soils under investigation have in general a high content of organic matter in surface layers, averaging from 15.3 to 18.6% in 0-10 cm layers, and from 8.0 to 10.8% in 10-20 cm layers (Table 2). Such a high content of organic carbon in surface layers, above 12%, may qualify them as belonging to organic materials. The presented mean values may, however, be somewhat inflated as a result of including peat soils (Histosols) into calculation. Accumulation of organic matter in the layers 0-10 cm of soils under degraded forests can be also remnants of forest litter covered with dense grass vegetation. Somewhat higher accumulation of organic matter in ectohumus layers of soils was identified on the Kowarski Grzbiet, whereas soils of Mount Szrenica contained more organic matter in layers 0-10 and 10-20 cm (Table 1). However, these differences are not statistically significant at $p<0.05$. Moreover, no essential and statistically significant differences in organic matter accumulation were found between altitude zones. The content of organic

Table 2

Soil reaction, content of organic matter and trace elements in soils of the Kowarski Grzbiet and Mount Szrenica in altitude zones ≤1100 and >1000 m AMSL

Localization	Kowarski Grzbiet range						Mount Szrenica					
Soil layer	ectohumus		0-10 cm		0-20 cm		ectohumus		0-10 cm		0-20 cm	
Altitude zone, m a.s.l.	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100
pH_{KCl}	2.85^a	2.91^a	3.16^a	3.20^v	3.46^a	3.38^a	2.93^a	3.00^a	3.16^a	3.13^a	3.38^a	3.40^a
Organic carbon, %	-	-	21.6^a	19.8^a	9.9^a	6.9^a	-	-	14.3^b	24.3^c	7.2^a	12.6^b
Loss on ignition, %	80.2^a	89.1^a	-	-	-	-	81.0^a	79.8^a	-	-	-	-
Zn, $mg \cdot kg^{-1}$	48.6^a	46.6^a	33.8^a	33.7^a	32.7^a	29.5^a	35.8^b	34.4^b	33.5^a	34.7^a	26.8^a	23.1^a
Cu, $mg \cdot kg^{-1}$	21.5^a	24.5^a	19.6^a	20.0^a	16.9^a	14.1^a	16.6^b	15.7^b	13.5^b	15.7^b	8.2^b	9.4^b
Pb, $mg \cdot kg^{-1}$	71.6^a	83.4^a	73.3^a	73.4^a	45.4^a	32.5^b	117.3^b	109.0^b	83.2^b	109.8c	42.4^a	49.7^a

Explanation: $^{a, b, c}$ – homogeneous groups of Duncan's multiple range test (compared mean values of particular properties
in the same soil layer
on the Kowarski Grzbiet range and Mount Szrenica in altitude zones ≤1100 i >1000 m AMSL)

matter in the ectohumus layer increases with altitude on the Kowarski Grzbiet Range but decreases on Mount Szrenica (Table 2). And inversely, in the layers 0-10 and 10-20 cm of soils on Mount Szrenica the accumulation of organic matter was apparently larger in the altitude zone >1100 m AMSL than in the zone <1100 m AMSL (Table 2). These differences may not be a consequence of the stronger decline of tree stands in the zone > 1100 m AMSL, but of greater frequency of peat soils in soil cover at this high altitude zone.

In all the analyzed soils layers, lead was found to be exceeding the content of zinc, which is the first symptom of soil pollution and imbalance of natural proportions between trace elements. Anthropogenic accumulation of lead in the soil environment is confirmed by wide differences between the minimum and the average content (almost ten-fold in the layers 0-10 cm), as well as between the content in deeper mineral layers (10-20 cm) and in forest litter. The lead content was the highest in ectohumus layers (mean value 83.2 $mg \cdot kg^{-1}$ of dry mass on the Kowarski Grzbiet Range, and 110.7 $mg \cdot kg^{-1}$ d.m. on Mount Szrenica), and decreased with depth into the soil profile to the level of 36.7 $mg \cdot kg^{-1}$ (the Kowarski Grzbiet) and 46.2 $mg \cdot kg^{-1}$ (Mount Szrenica) in the layer 10-20 cm (Table 1). In all the tested soil horizons, the concentration of lead was apparently larger on Mount Szrenica (differences between mean values are statistically significant), which agrees with some earlier reports documenting stronger pollution of soils in the western part of the Karkonosze Mountains (Drozd et al. 1998a) and confirms the permanence of soil contamination with heavy metals. Stability of lead content in soil environment rich in organic matter is related to high affinity of lead to humic substances. Correlation of total lead content and organic carbon was confirmed by good statistical significance of coefficients (Table 3). Concentration of lead in the zone >1100 m AMSL was elevated in some soil layers as compared to the zone <1100 m AMSL. It was, however, simultaneously related to differences in the content of organic matter in the compared layers (Table 2). A new, important observation was made in the zone >1100 m AMSL on Mount Szrenica, where the Pb content in ectohumus and the layers 0-10 cm was levelling, which con-

Table 3

Coefficients of correlation between organic matter and concentration of trace elements in soils of the Kowarski Grzbiet and Mount Szrenica

Localization	Kowarski Grzbiet range	Mount Szrenica
Zn	0.34**	0.12
Cu	0.26*	0.36**
Pb	0.55**	0.48**

Explanation: * significant at $p<0.05$, **significant at $p<0.01$

tradicts the regularities described earlier by DROZD et al. in. (1998a), and confirms reduced immission of lead to the mountain environments during the last decade (KARCZEWSKA et al. 2006).

In contrast to lead, concentrations of zinc and copper did not vary so significantly, both among soil layers and in spatial arrangement. Even though zinc and copper theoretically have weak affinity to humic substances and did not correlate with organic matter (Table 3), their highest concentrations were found in the ectohumus layer: average zinc contents were, respectively, 47.5 and 35.4 mg kg^{-1}, and average copper contents – 23.8 and 16.9 mg kg^{-1}, respectively on the Kowarski Grzbiet and on Mount Szrenica. The lowest concentrations, as compared among analyzed soil layers, were found in the layer 10-20 cm, where mean zinc contents were 30.6 and 24.9 mg kg^{-1}, and copper contents – 15.0 and 8.8 mg kg^{-1}, respectively. Concentrations of zinc were somewhat higher in soils of the Kowarski Grzbiet than on Mount Szrenica, but statistically significant difference was calculated only in the case of ectohumus layers (Table 1). Copper concentrations were both apparently and statistically higher on the Kowarski Grzbiet, particularly in ectohumus and in the layer 10-20 cm (Table 1). It is probably related to the kind of parent material rather than to the pollution. The Kowarski Grzbiet consists of metamorphic schists, often enriched with trace elements, while Mount Szrenica is build of granite, weathering into regoliths poor in trace metals. Some differences were found between zinc and copper concentrations in compared analogous soil levels in two altitude zones (above and below 1100 m AMSL), but in all cases the differences are statistically insignificant (Table 2). It means that there is no relation between the altitude or the degree of forest decline and the contents of Zn and Cu in soils of the upper zone of spruce forests of the Karkonosze Mountains. We found as well that differences between maximal and minimal concentrations, or minimal and average contents were not so large as in the case of lead (Table 1). The concentrations of Zn and Cu in the layers 10-20 cm, particularly in soils containing small amounts of organic matter, were similar to the so-called geochemical background established for soils derived from “acid” igneous and metamorphic rocks (KABATA-PENDIAS, PENDIAS 1992). It was concluded that the content and distribution of zinc and copper in soils of the upper zone of spruce forest in the Karkonosze Mountains are not suffering from contamination with these elements.

CONCLUSIONS

1. Elevated contents of lead in forest litters (ectohumus) and surface layers of soils in the upper zone of spruce forest in the Karkonosze Mountains indicate contamination with lead, whereas contents of zinc and copper are recognised as close to the geochemical background.

2. Significantly higher concentrations of lead in soils of Mount Szrenica (as compared to the Kowarski Grzbiet) indicate stronger anthropogenic influence on the ecosystems in the western part of the Karkonosze Mountains. Somewhat higher concentrations of zinc and copper in soils of the Kowarski Grzbiet are probably related to a geochemical abundance of metamorphic gneisses and schists building of the eastern Karkonosze Mountains.

3. Comparison of the currently measured concentrations of lead and those reported in 1990s indicate a similar level of soil contamination with this metal and lack of any improvement in the quality of soil environment during this period.

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COPPER SPECIATION IN DIFFERENT-TYPE SOIL PROFILES

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Abstract

Determination of the total content of metals in soils does not give enough information about their mobility and potential uptake by plants. The influence of heavy metals on plants depends on the type and form of a metal as well as properties of soil.

The aim of the research was to evaluate the influence of soil type (Rendzic Leptosols, Haplic Luvisols, Haplic Arenosols) on the content and speciation of copper in soil profiles.

The research was carried out in two physiographical regions: Lublin Upland and Sandomierska Valley. Samples were collected once from individual genetics horizons, in total from 30 typological differentiated soil profiles, made from chalk marl, loess and sands.

Speciation analysis of copper was carried out with the use of a three-stage sequential method of fractionation, which can isolate four fractions with BCR: fraction I – forms soluble in water, exchangeable and bounded with calcium carbonate, extractable with CH_3COOH; fraction II – forms bound with free Fe and Mn oxides, extractable with NH_2OHHCl; fraction III – forms complexed with organic matter, hot extractable with 30% H_2O_2 and next the mineralization products reextractable with CH_3COONH_4; fraction IV – residual forms (residue), i.e. the difference between the total content and the sum of three fractions I – III.

The speciation analysis indicated that in all the examined soil types, the residual form showed the largest share of copper in its total content, followed by forms bounded with organic matter and, containing the smallest proportion of copper, the soluble, exchangeable and bound with calcium carbonate forms. In rendzinas and lessive soils, the content of fraction IV in the humus horizons was significantly higher than in the parent rock, whereas in Haplic Arenosols the host rock was richer in this copper form than the humus horizons.

Key words: rendzina, Haplic Arenosols, lessive soil, forms of copper.

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SPECJACJA MIEDZI W PROFILACH GLEB ZRÓŻNICOWANYCH TYPOLOGICZNIE

Abstrakt

Określenie całkowitej zawartości metali w glebie nie daje wystarczających informacji o ich ruchliwości i możliwości pobierania przez rośliny. Oddziaływanie metali ciężkich na rośliny zależy od rodzaju metalu, formy, w jakiej występuje, a także od właściwości gleby.

Celem pracy była ocena wpływu typu gleb (rędziny, płowe, rdzawe) na zawartość i specjację miedzi w ich profilach.

Badania prowadzono na obszarze obejmującym 2 regiony fizjograficzne: Wyżynę Lubelską i Kotlinę Sandomierską. Próbki pobrano jednorazowo z poszczególnych poziomów genetycznych, w sumie z 30 profili glebowych zróżnicowanych typologicznie, wytworzonych z margli kredowych, lessów i piasków.

Analizę specjacyjną miedzi przeprowadzono z wykorzystaniem trzystopniowej metody sekwencyjnego frakcjonowania umożliwiającej wyodrębnienie 4 frakcji metodą BCR: frakcja I – formy rozpuszczalne w wodzie, wymienne i związane z węglanami, ekstrahowane CH_3COOH; frakcja II – formy zasocjowane z wolnymi tlenkami Fe i Mn ekstrahowane NH_2OHHCl; frakcja III – formy związane z materią organiczną ekstrahowane 30% H_2O_2 na gorąco i następnie reekstrahowane produkty mineralizacji CH_3COONH_4; frakcja IV – formy rezydualne (pozostałość), różnica między całkowitą zawartością a sumą trzech frakcji.

Analiza specjacyjna wykazała, że we wszystkich typach badanych gleb, forma rezydualna miedzi stanowiła największy udział w jej całkowitej zawartości, następnie formy związane z materią organiczną, a najmniejszy formy rozpuszczalne, wymienne i związane z węglanami. W rędzinach i glebach płowych poziomy próchniczne zawierały istotnie więcej IV frakcji niż skały macierzyste, natomiast w glebach rdzawych skała macierzysta zwierała więcej tej formy miedzi niż poziomy próchniczne.

Słowa kluczowe: rędziny, gleby płowe, gleby rdzawe, formy miedzi.

INTRODUCTION

The average copper content in Polish soils is 6.6 $mg \cdot kg^{-1}$ (Terelak et al. 1997). According to Terelak et al. (1997), 96.5% of arable lands area in Poland shows natural copper concentrations, while 3.1% has elevated copper levels. Soils slightly, moderately and strongly contaminated with copper make up only 0.2% of the total area. While studying the soil abundance in microelements, Czuba (1995) reported that the largest percentage of Polish soils showed boron and copper deficiencies.

Determination of the total content of metals in soil does not provide sufficient information on their mobility and potential uptake by plants. Interactions of heavy metals with plants depend on the type and form of a metal as well as soil properties (Kucharzewski et al. 2004). Methods for determinations of various metals in soil include sequential procedures, in which a variety of single agents are used for extraction. These methods are used for determining soil fractions and their sequence (Kabata-Pendias, Sadurski 2003, Karczewska 2002). Methods of sequential extraction have some advatnages and disadvantages. Different chemicals are used to determine particular metal fractions, and their selection should depend on examined soils properties, including the level of heavy metal contamination.

The aim of the present study has been to evaluate the influence of soil types (Rendzic Leptosols, Haplic Arenosols, and Haplic Leptosols) on copper content and speciation in soil profiles.

MATERIAL AND METHODS

The study was carried out in two physiographic regions: Lubelska Upland and Sandomierska Valley. Samples were collected once from particular horizons, from different types of soil profiles developed from marls, sands, and loess. Ten profiles from every soil type (5 from forest and 5 from cultivated fields) were collected (Figure1).

Fig. 1. Location of the investigated area

Soils developed from marls were classified to proper rendzic soils, and according to WRB classification – to *Rendzic Leptosols,* while those developed from sands – to *Haplic Arenosols*, and developed from loess – to *Haplic Luvisols.*

Collected soil samples were subjected to determinations of granulometric composition by means of Bouyoucos's method with modifications by Casagrande and Prószyński (OSTROWSKA et al. 1991); pH in 1 mol KCl$\cdot$dm^{-3} maintaining soil to water ratio for 1:2.5; organic carbon content applying Tiurin's method with modifications by Simakov (OSTROWSKA et al. 1991); as well as the total copper content – after digestion of soil samples in a HNO_3 and $HClO_4$ mixture (1:1) (OSTROWSKA et al. 1991) by means of the F-AAS technique.

The speciation analysis of copper was performed using the three-stage method of sequential fractionation, which makes it possible to separate 4 fractions by means of the BCR technique (URE et al. 1993, THOMAS et al. 1994): fraction I – water-soluble forms, exchangeable and bonded to carbonates, extractable with CH_3COOH at 0.11 mol$\cdot$dm^{-3} concentration and pH=2; fraction II – forms associated with free Fe and Mn oxides, extractable with NH_2OHHCl at 0.1 mol$\cdot$dm^{-3} concentration and pH=2; fraction III – forms bonded to organic matter, extractable with hot 30% H_2O_2 and then the mineralization products re-extracted with CH_3COONH_4 at 1 mol$\cdot$dm^{-3} concentration and pH=2; fraction IV – residual forms (remains), the difference between the total copper content and sum of the above three fractions. All the four fractions were determined by means of the atomic absorption spectrometry technique using a Varian Spectra-250 Plus system.

The results of these determinations were presented as arithmetic mean values, and in order to evaluate the variability of the tested characteristics, the minimum, maximum and standard deviation values were calculated. Statistical processing was made using Statistica 6.0 (StatSoft) software.

RESULTS AND DISCUSSION

Rendzic soils were characterized by the granulometric composition of heavy loams: 4-32% (mean 15%) of fraction 1-0.1 mm; 12-31% (mean 19%) of fraction 0.1-0.02 mm; 52-85% (mean 66%) of fraction <0.02 mm; haplic arenosols were loose sands containing: 83-96% (mean 91%) of fraction 1-0.1 mm, 1-13% (mean 6%) of fraction 0.1-0.02 mm; 0-7% (mean 3%) of fraction <0.02 mm; haplic luvisols were characterized as dust and contained: 0-20% (mean 3%) of fraction 1-0.1 mm; 40-65% (mean 55%) of fraction 0.1-0.02 mm; 22-60% (mean 39%) of fraction <0.02 mm.

Humus and transitional horizons of the examined rendzic soils had neutral acidity (pH 6.0-7.1), while the mother rock developed from marls was basic (pH 7.2-7.7). Haplic arenosols were strongly acidic and acidic with pH from 3.6 to 5.6. The pH value of haplic luvisols varied from strongly acidic to basic. In humus horizons, pH value was within the range of 3.8-6.7, in elution horizons (Eet) 4.0-5.0, in enrichment horizons (Bt) 4.0-7.1, and in mother rock 6.9-7.6.

The organic carbon content in humus horizons of rendzic soils ranged from 12.6 to 45.2 $g \cdot kg^{-1}$, haplic arenosols 4.2-20.4 $g \cdot kg^{-1}$, and in haplic luvisols 8.4-25.3 $g \cdot kg^{-1}$.

Total average copper content in humus horizons of rendzic soils amounted to 10.73 $mg \cdot kg^{-1}$, in transitional horizons 8.74 $mg \cdot kg^{-1}$, and in mother rock 6.44 $mg \cdot kg^{-1}$ (Table 1). In haplic arenosols, mean copper concentration did not exceed 3 $mg \cdot kg^{-1}$, while in haplic luvisols, mean copper content in humus horizons was 6.49 $mg \cdot kg^{-1}$. These were values corresponding to natural not contaminated levels (KABATA-PENDIAS et al. 1993). Low copper concentrations in haplic arenosols might be associated not only with the mother rock (KABATA-PENDIAS, PENDIAS 1999) that is typically deficient in the metal, but also a strong acidity of that soil type. Under such conditions, copper compounds are easily soluble and may migrate along with soil solution inside the soil profile; they are also faster taken by plants (GANCARCZYK-GOLA, PALOWSKI 2005).

In the analyzed soil types, copper distribution varied in particular horizons. In rendzic soils, the copper content decreased with the profile depth, whereas in haplic arenosols, particular horizons were characterized by simi-

Table 1

Total content of copper in examined soil profiles ($mg \cdot kg^{-1}$)

Genetic horizon	Minimum	Maximum	Mean
Rendzinas			
Aca	8.25	13.20	10.73
ACca	5.25	13.35	8.74
Cca	3.75	9.90	6.44
Arenosols			
A	2.00	4.25	2.96
Bv	1.25	4.25	2.35
C	0.90	3.90	2.03
Lessive soils			
A	4.45	8.00	6.49
Eet	3.40	8.00	5.98
Bt	6.10	14.75	9.31
Cca	6.50	11.60	8.03

lar copper levels. Uziak et al. (2001) reported similar dependencies in different types of soils developed from sands in eastern part of Poland. Szymańska (1996), who studied podzolic soils, found the largest copper accumulation in surface layers, revealing a decreasing tendency with the soil depth. In haplic luvisols, the elution levels (Eet) were the most deficient in copper, while enrichment levels (Bt) were characterized by its accumulation. Mean copper content in the mother rock of haplic luvisols was higher than in humus horizons. Uziak et al. (2001) recorded similar distribution of total copper contents in profiles of soils developed from dusts. Also Jaworska (1996), in studies upon haplic luvisols developed from dusts and loams in Ziemia Dobrzyńska, found two centers of copper accumulation in profiles: humus and illuvial horizons.

Copper fraction I (water-soluble, exchangeable and bonded to carbonates forms) in humus horizons of rendzic soils was within the range from 0.09 to 0.32 mg·kg^{-1} – 0.19 mg·kg^{-1}, on average (Table 2). Transitional horizon and mother rock contained higher amounts of that fraction as compared to humus horizon. In haplic arenosols, the fraction in all horizons was at similar trace levels – 0.09 mg·kg^{-1}, on average (Table 3). In haplic luvisols, the mean content of fraction I in particular horizons varied from 0.07 to 0.17 mg·kg^{-1}, and the mother rock contained the largest quantities of that

Table 2

Content of copper fractions in rendzina profiles (mg·kg^{-1})

Genetic horizon	Fraction	Minimum	Maximum	Mean	Standard deviation
A	I	0.09	0.32	0.19	0.07
	II	0.004	0.36	0.22	0.11
	III	0.26	3.01	1.54	0.86
	IV	4.80	12.81	8.78	2.64
ACca	I	0.14	0.42	0.31	0.09
	II	0.07	0.39	0.30	0.10
	III	0.46	2.79	1.56	0.66
	IV	2.85	12.68	6.58	3.02
Cca	I	0.08	0.43	0.33	0.12
	II	0.04	0.49	0.30	0.14
	III	0.35	2.08	1.61	0.54
	IV	1.03	9.03	4.20	2.71

Explanations: I – forms soluble in water, exchangable and bound to calcium carbonate; II – forms associated with free Fe and Mn oxides; III – forms bound to organic matter; IV – residual forms

Table 3

Content of copper fraction in Haplic Arenosol profiles (mg·kg^{-1})

Genetic horizon	Fraction	Minimum	Maximum	Mean	Standard deviation
A	I	0.01	0.13	0.09	0.04
	II	0.02	0.16	0.08	0.05
	III	0.28	0.89	0.52	0.19
	IV	1.35	3.57	2.27	0.84
Bv	I	0.06	0.16	0.10	0.03
	II	0.01	0.20	0.08	0.06
	III	0.18	0.34	0.26	0.06
	IV	0.66	3.81	1.91	1.03
C	I	0.03	0.18	0.09	0.05
	II	0.03	0.15	0.06	0.04
	III	0.04	0.44	0.24	0.12
	IV	0.13	3.46	1.64	1.13

Explanations as in Table 2

fraction (Table 4). For all the studied soil types, this fraction – the most available one for plants – was a small percentage of the total copper content (in humus horizons of the soils: haplic luvisols 1.26%, haplic arenosols 2.97%, rendzic soils 1.79%). Taking into account all the horizons, mother rocks of all the studied soils were characterized by the highest content of this copper fraction.

Copper fraction II (associated with iron and manganese oxides), like fraction I, was less than 3% of the total copper quantity in all the studied soil types. McLaren, Crawford (1973) reported that free manganese oxides play a very important role in binding copper in soil. This finding was not confirmed in the soil types we assayed, analogously to chernozems analyzed by Dąbkowska-Naskręt, Kędzia (1996).

The content of copper fraction III (bonded to humus) in rendzic soils and Haplic Luvisols was much higher than in Haplic Arenosols. In Haplic Arenosols and Luvisols, humus horizons were more abundant in this copper form as compared to the other horizons. Copper fraction III made up from 17.6% to 21.8% of the total metal content. The results confirmed strong copper affinity to form complexes with functional groups of humic and fulvic acids, which affects the mobility, thus availability of the element in the soil (McLaren, Crawford 1973, Kabata-Pendias, Pendias 1999). In rendzic soils, the content of copper bonded to humus was similar in all horizons and amounted to 14.3% of the total copper quantity. It may have resulted from imperfections of the method for extraction of the organic fraction from soils at high

Table 4

Content of copper fraction in lessive soil profiles (mg·kg^{-1})

Genetic horizon	Fraction	Minimum	Maximum	Mean	Standard deviation
A	I	0.02	0.17	0.08	0.05
	II	0.08	0.19	0.14	0.04
	III	0.51	2.14	1.42	0.60
	IV	3.23	6.69	4.85	1.26
Eet	I	0.01	0.10	0.07	0.04
	II	0.11	0.17	0.14	0.03
	III	0.49	2.36	1.25	0.73
	IV	2.30	7.26	4.52	1.79
Bt	I	0.05	0.20	0.11	0.05
	II	0.10	0.22	0.17	0.04
	III	0.33	2.50	1.01	0.57
	IV	4.52	13.92	8.02	2.46
Cca	I	0.09	0.33	0.17	0.07
	II	0.01	0.30	0.16	0.07
	III	0.35	1.45	0.79	0.31
	IV	4.75	10.81	6.90	2.12

Explanations as in Table 2

pH because under such conditions strong oxidizers make additional metal precipitation from other fractions (KARCZEWSKA 2002).

Fraction IV (residual) of copper made up the largest percentage in its total content in all the studied soil types. Aslo GONDEK and FILIPEK-MAZUR (2005), when determining the copper concentrations in soil by means of Zeinen and Brümmer's sequential extraction, recorded the highest levels of copper in a fraction bonded to organic matter and the residual one. Studies performed by DĄBKOWSKA-NASKRĘT, KĘDZIA (1996) on chernozems also revealed the highest amounts of the form bonded to organic matter and the residual fraction. Similar results were achieved by CHAO et al. (2007) for cultivated soils in China. Such fraction distribution in profiles depended on a soil type. In Haplic Arenosols, the content of the fraction was the highest in humus horizons and gradually decreased with the depth, falling two-fold in the mother rock. Also in Haplic Arenosols, the content of the residual fraction decreased along with the depth, but not to the same extent in rendzic soils. That fraction was most accumulated in enrichment horizons (Bt) of haplic luvisols (Table 4). In particular horizons, the residual fraction contents could be lined up in a following sequence: Bt>Cca>A>Eet.

CONCLUSIONS

1. Humus horizons of studied soils were characterized by varied natural copper contents. Rendzic soils were the most abundant in copper, haplic luvisols contained less copper, while haplic arenosols the least.

2. The speciation analysis revealed that for all soil types, the residual form of copper made up the largest percentage in its total content, then forms bonded to organic matter, and soluble, exchangeable, and bonded to carbonates.

3. The low contents of mobile copper forms indicated its poor migration and bio-availability.

4. Speciation analysis revealed a significant role of humus in binding potentially mobile copper fractions in studied soil types.

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