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COMPARISON OF QUALITATIVE TRAITS, BIOLOGICAL VALUE, CHEMICAL COMPOUNDS OF SWEET PEPPER FRUIT

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Abstract

Sweet pepper fruits have a high biological value, a rich content of minerals. At present, large-fruit cultivars, distinguishable by a thick pericarp wall, high processing efficiency, good growth on fields, under covers, dominate in sweet pepper cultivation.

The present research has been conducted to compare the qualitative traits, chemical composition of sweet pepper fruits of the Red Knight F_1 cultivar grown in a greenhouse, on open field. The evaluation of qualitative traits, biological value, chemical composition demonstrated that fruits from the greenhouse cultivation were characterized by significantly larger fruit weight, weight of edible parts as compared to those harvested from a field, although they did not differ significantly in the pericarp thickness. Fruits produced on a field had a higher ratio of the technological to total fruit weight, which proves that the cultivar is an attractive choice for field cultivation of sweet pepper, suitable for processing. Pepper fruits from a field versus the ones grown in a greenhouse contained significantly less dry matter, reducing sugars but more vitamin C. The greenhouse-grown fruits contained higher levels of nitrogen, phosphorus, potassium, calcium, magnesium than those from a field.

Key words: sweet pepper fruit, qualitative traits, biological value, chemical compounds.

PORÓWNANIE CECH JAKOŚCIOWYVCH, WARTOŚCI BIOLOGICZNEJ ORAZ SKŁADU CHEMICZNEGO OWOCÓW PAPRYKI SŁODKIEJ

Abstrakt

Owoce papryki słodkiej mają dużą wartość biologiczną i zawierają wiele składników mineralnych. Aktualnie w uprawie papryki dominują odmiany wielkoowocowe o grubej

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ściance owocni, dużej wydajności technologicznej i nadające się do uprawy zarówno w polu, jak i pod osłonami. Celem pracy było porównanie cech jakościowych oraz składu chemicznego owoców papryki słodkiej odmiany Red Knight F_1 uprawianej w szklarni oraz w otwartym polu. W badaniach dotyczących oceny cech jakościowych owoców oraz wartości biologicznej i składu chemicznego wykazano, że owoce z uprawy w szklarni odznaczały się istotnie większą masą oraz masą części jadalnej w porównaniu z zebranymi z pola, natomiast nie różniły się istotnie pod względem grubości perykarpu. W owocach stwierdzono większy udział masy technologicznej w całkowitej masie owocu z pola, co potwierdza atrakcyjność tej odmiany do uprawy w polu na potrzeby przetwórstwa. Stwierdzono też istotnie mniej suchej masy i cukrów redukujących, a więcej witaminy C w porównaniu z owocami ze szklarni. W owocach z uprawy szklarniowej wykazano większą zawartość azotu, fosforu, potasu, wapnia i magnezu niż z uprawy polowej.

Słowa kluczowe: owoce papryki słodkiej, cechy jakościowe, wartość biologiczna, skład chemiczny.

INTRODUCTION

Sweet pepper fruits are very tasty, healthy owing to their content of biologically active chemicals with antioxidant properties. The vegetable is an abundant source of vitamin C (KMIECIK, LISIEWSKA 1994, LEE, KADER 2000, BUCZKOWSKA, NAJDA 2002, GAJC-WOLSKA at el. 2005, 2007, PERUCKA, MATERSKA 2004, POKLUDA 2004, JADCZAK et al. 2010, MICHALIK 2010). Physiologically ripe fruits are abundant in carotenoid pigments (KMIECIK, LISIEWSKA 1994, PERUCKA, MATERSKA 2004, POKLUDA 2004). Sweet pepper fruits also contain phenolic compounds (PERUCKA, MATERSKA 2004). Moreover, pepper is an important source of minerals for humans (KMIECIK, LISIEWSKA 1994, BUBICZ et al. 1999, MICHALIK 2000, POKLUDA 2004, GAJC-WOLSKA et al. 2007, JADCZAK et al. 2010).

At present, commercial production of sweet pepper is dominated by heterotic, large-fruit cultivars because consumers prefer large peppers with a thick pericarp. Most of the popular cultivars are well-adapted to growing under less favorable environmental conditions, they are cultivated both in greenhouses, on fields (BUCZKOWSKA 2007, GAJC-WOLSKA et al. 2007, KORZENIEWSKA, NIEMIROWICZ-SZCZYTT 2007, JADCZAK et al. 2010).

The weight of the pericarp, i.e. the edible part of a pepper fruit, which determines the bio-technological efficiency of a given cultivar, its usefulness for industrial processing, is an important feature of sweet pepper (KMIECIK, LISIEWSKA 1994, NOWACZYK, NOWACZYK 2005, BUCZKOWSKA 2007, KORZENIEWSKA, NIEMIROWICZ-SZCZYTT 2007, JADCZAK et al. 2010).

Numerous studies on the use, biological value of sweet pepper fruits have demonstrated their dependence on many factors, mainly cultivar-specific traits (KMIECIK, LISIEWSKA 1994, GAJC-WOLSKA, SKĄPSKI 2001, BUCZKOWSKA, NAJDA 2002, POKLUDA 2004, BUCZKOWSKA 2007, KORZENIEWSKA, NIEMIROWICZ-SZCZYTT 2007, JADCZAK et al. 2010), the weather course or microclimate conditions during the growth, ripening of fruits (GAJC-WOLSKA, SKĄPSKI 2002, BUCZKOWSKA 2007, GAJ-WOLSKA et al. 2007), plant nutrition (GOLCZ 2001, GOLCZ et al. 2004a,b, PERUCKA, MATERSKA 2004, MICHAŁOJĆ, HORODKO 2006), various treatments that stimulate the yielding (GAJC-WOLSKA et al. 2007).

The present research aimed at comparing the qualitative traits, chemical composition of sweet pepper fruits of the Red Knight F_1 cultivar grown in a greenhouse, on open field.

MATERIAL, METHODS

The material comprised sweet pepper fruits of the heterotic cultivar Red Knight F_1 (Seminis Vegetable Polska S.A.). Fruits from agrotechnical experiments carried out in 2009, 2010 in an unheated greenhouse, on field were used for analytical determinations.

Pepper plants were grown in a greenhouse, in 10 dm^3 plastic cylinders, with 4 plants per m^2. They grew on horticultural peat of the initial pH equal 4.6, later limed with $CaCO_3$ to achieve pH 6.5. There were 20 plants of the cultivar Red Knight F_1, a replication consisted of a pot with a single plant (an experimental unit). Transplants were planted onto the target location at the end of April, the experiment was terminated at the beginning of October.

The following quantities of nutrients were applied during the whole growing season (in g $plant^{-1}$): N – 10 in the form of KNO_3, NH_4NO_3; P – 6.0 as $Ca(H_2PO_4)_2 \cdot H_2O$ with the content of 20.2% P; K – 15 as KNO_3, 37.3% K, 15.5% N; Mg – 7.0 in the form of $MgSO_4 \cdot H_2O$ 17.4% Mg. The microelements were used as EDTA complexes – Fe, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, H_3BO_3, $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$ at amounts as for peat subsoils. Microelements were introduced into the soil once before planting to the permanent place. Phosphorus was applied in the middle of plant setting, in the sixth vegetation week. A quarter dose of nitrogen, potassium,, magnesium was used before plant setting, while the remaining quantities were applied as post-crop in five doses every 10 days. The post-crop N, K, Mg nutrition was completed 2 weeks before the end of the experiment.

The field experiment was carried out in Zezulin (Łęczna district) on lessive soil developed from loess formations, with the organic matter content of 1.8%. The suitability of Red Knight F_1 sweet pepper fruits for food industrial processing was evaluated. The experiment was conducted in four replications, each replication consisting of 20 plants. The surface area of a replication plot was 4.8 m^2. Wheat was the forecrop for pepper in both years of the experiment. Manure at the amount of 40 t ha^{-1} was applied in autumn, while mineral nutrition was performed according to the soil analysis results. Mineral concentrations in 2009, 2010 were as follows (mg dm^{-3}): N – 60, 30; P – 160, 180; K – 320, 180; Ca – 3400, 2600; Mg – 80, 40 at pH 6.8, 6.5. Before planting the seedlings, mineral nitrogen nutrition at the level of 30 kg N ha^{-1} (2009), 50 kg N ha^{-1} (2010) in the form of nitrogen nitrate was applied. Foliar nutrition was applied as post-crop: twice with Florovit (0.5%), twice with calcium nitrate (1.0%). Transplants were prepared in pots according to the requirements for that species. They were then planted on a field at 4.2 plants m^{-2} spacing in the third decade of May. The experiment was finished at the end of September. Randomly selected, fully ripe fruits harvested at the beginning of September were chosen for analysis. In both years, the qualitative traits were determined on the basis of 20 fruits harvested from the greenhouse, from the field. The technological weight of a fruit corresponded to the weight of the pericarp weight after removing the placenta with seeds, the petiole with sepals (Kmiecik, Lisiewska 1994).

The following were determined in fresh fruits: dry matter with the dryer method, vitamin C with Tillmann's method, sugars according to Schoorl-Rogenbogen's method. Additionally, dried fruits were analyzed to determine N-total with Kjeldahl's method,, after dry combustion, P by colorimetry using ammonium vanadium molybdate, as well as K, Ca, Mg – by AAS (Perkin-Elmer). All determinations were performed in three replicates.

The results were statistically processed by means of variance analysis according to one-factor experiment in 2009, 2010. Significant differences were verified with T-Tukey multiple confidence intervals at 5% significance level.

RESULTS AND DISCUSSION

The sweet pepper cultivar Red Knight F_1 belongs to large-fruit peppers with a relatively short vegetation period. Fruits of this cultivar have distinctively high weight, a thick pericarp. For this reason, the cultivar is very popular in Poland, grown in greenhouses, foil tunnels, on open field (Gajc-Wolska et al. 2007, Korzeniewska, Niemirowicz-Szczytt 2007). Fruits harvested at the beginning of September in 2009, 2010 achieved high weight: 246 g in greenhouse, 180 g on field (Table 1). The thermal conditions during the sweet pepper vegetative growth in 2009, 2010 were suitable for thermophilic vegetables (Figure 1). The mean daily air temperature from May to September was higher than the multi-year average for the same period. High air temperatures in July, August favoured the growing, ripening of pepper fruits. Also, the moisture conditions were adequate, the water deficiency which occurred on the field in 2009 was compensated for by irrigation.

Fruits of the examined cultivar were characterized by a thick pericarp: 6.3-6.7 mm on average. No significant differences in this the trait were observed between fruits grown in the greenhouse, on the field, Korzeniewska, Niemirowicz-Szczytt (2007) reported similar results for the same cultivar concerning the mean weight of commercial fruits (176-180 g), the average thickness of the pericarp (5.8-6.0 mm).

Table 1

Qualitative traits of fruits of sweet pepper Red Knight F_1 cultivar

Place of cultivation	Fruit weight (g)			Pericarp thickness (mm)			Technological weight (g)			Share of technological weight in total weight of fruit (%)		
	2009	2010	mean	2009	2010	mean	2009	2010	mean	2009	2010	mean
Greenhouse	258	234	246	6.7	6.5	6.6	180	168	174	69.8	71.8	70.7
Field	186	174	180	6.3	6.3	6.3	158	150	154	84.9	86.2	85.5
Mean	222	204	213	6.5	6.4	6.4	169	159	164	76.1	77.9	77.0
$LSD_{\alpha=0.05}$	42.2	38.8	-	n.s.	n.s.	-	32.1	30.2	-	-	-	-

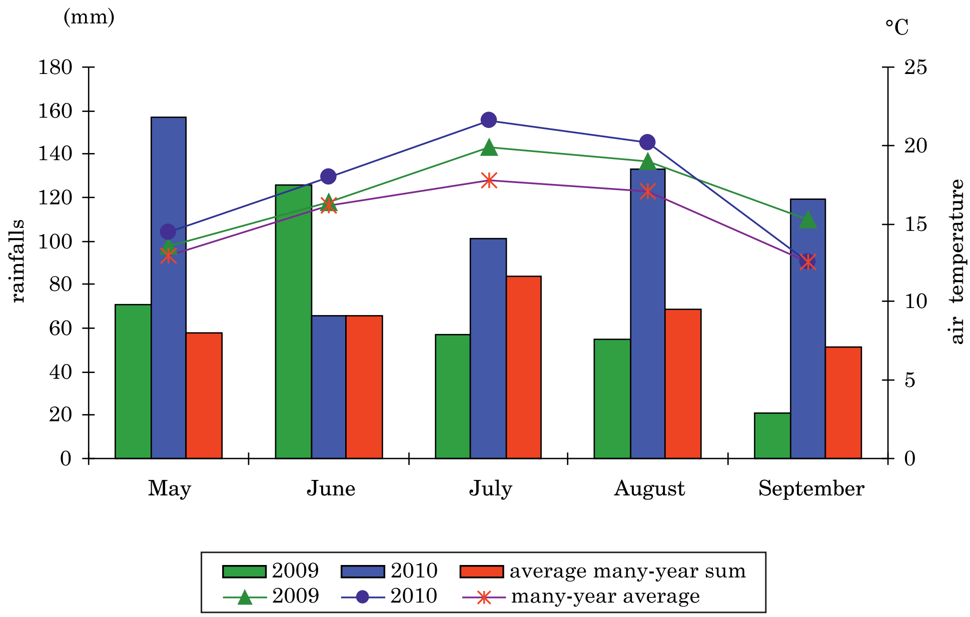

Fig. 1. Average monthly air temperature and sums of rainfalls in 2009-2010 during pepper vegetation in comparison to average multiannual values

Fruits of the examined pepper cultivar also attained a high pericarp weight. The average weight of the pericarp of fruits grown in the greenhouse was 174 g, whereas that of the fruits grown in the field 154 g. The results on the ratio of technological weight to the total weight of fruits appeared to be very interesting. For fruits harvested in the field, the percent ratio was about 85-86%, while for those from the greenhouse it was

70-72%, which was probably because fruits harvested from the field formed a lighter placenta but did not differ considerably in the pericarp thickness from the greenhouse fruits. Considering the technological value of sweet pepper cultivars, fruits whose technological weight or bio-technological efficiency is above 75% of the total fruit weight are assumed to be valuable (Kmiecik, Lisiewska 1994, Nowaczyk, Nowaczyk 2005, Jadczak et al. 2010).

The results, the literature references on qualitative traits of stable, heterotic sweet pepper cultivars demonstrate that Red Knight F_1 is very useful economically, recommendable for cultivation on fields, indoors, to be consumed fresh or processed (Kmiecik, Lisiewska 1994, Gajc-Wolska, Skąpski 2002, B uczkowska 2007, Gajc-Wolska et al. 2007, Korzeniewska, Niemirowicz-Szczytt 2007, Gajc-Wolska et al. 2007).

Fruits of Red Knight F_1 are also attractive because of their quantity, shape (Table 2). The mean shape coefficient was close to a unit (1.03-1.07), while the mean diameter, length were 8.8, 9.3 mm, respectively. Significantly larger fruits were harvested from the greenhouse.

Table 2

Biometric traits of fruits of sweet pepper Red Knight F_1 cultivar

Place of cultivation	Fruit length (cm)			Fruit diameter (cm)			Shape coefficient		
	2009	2010	mean	2009	2010	mean	2009	2010	mean
Greenhouse	9.8	9.6	9.7	9.2	9.2	9.2	1.07	1.04	1.05
Field	8.9	8.8	8.9	8.5	8.5	8.5	1.05	1.03	1.05
Mean	9.4	9.2	9.3	8.8	8.8	8.8	1.05	1.04	1.05
$LSD_{\alpha=0.05}$	0.72	0.70	-	0.58	0.61	-	-	-	-

The dry matter of the fruits was highly varied, ranging from 8.97 to 10.70% in dependence on the cultivation localization (Table 3). Less dry matter was determined in fruits harvested from the field in 2009, when the rainfall deficiency during the fruit ripening was compensated for by intensive irrigation. The results on the dry matter content in fruits from the present experiment were higher than reported by other authors for sweet pepper cultivars (5.24-10.29%) (Gajc-Wolska, Skąpski 2001, 2002, Gajc-Wolska et al. 2005, 2007, Jadczak et al. 2010), but close to the data (10.10-11.59%) recorded earlier by Buczkowska, Najda (2002) as well as Michałojć, Horodko (2006).

A higher vitamin C concentration was determined in pepper fruits from the field cultivation (200.98 mg 100 g^{-1} f.m.) as compared to the greenhouse (178.62 mg 100 g^{-1} f.m., on average). These results confirmed that insolation during fruit ripening had a positive influence on the vitamin C accumulation (Lee, Kadar, 2000). Comparable content of vitamin C in hybrid sweet pepper cultivars was reported by other authors, e.g. 168.7-202.5 mg 100 g^{-1} (Buczkowska, Najda 2002), 176.3-197.3 mg 100 g^{-1} (Gajc-Wolska, Skąpski, 2002), 150.1-242.6 mg 100 g^{-1} (Pokluda, 2004). Demonstrably more vitamin C (200.3-289.3 mg 100 g^{-1}) was determined in pepper fruits tested in 1999--2000 by Gajc-Wolska, Skąpski (2001). In contrast, less vitamin C was found in 2005-2006 by Gajc-Wolska et al. (2007; 70.39-137.46 mg 100 g^{-1}), in 2006--2008 by Michalik (2010; 110.46-148.77 mg.100 g^{-1}). These results indicate that the vitamin C concentration in sweet pepper fruits depends mainly on the cultivar-specific traits, but is also affected by weather conditions, agrotechnical treatments (Gajc-Wolska, Skąpski 2001, Gajc-Wolska et al. 2007).

Relatively high levels of total sugars (5.15%), reducing sugars (4.64%, on average) were recorded in Red Knight F_1 fruits. Slightly more sugars were determined in fruits of Red Knight F_1 in 2010. This value is comparable to that recorded in other heterotic cultivars studied by Michałojć, Horodko (2006; 5.26-6.05%), Gajc-Wolska et al. (2007; 3.80-5.26%) but lower than found by Buczkowska, Najda (2002; 3.86-4.44%). No unambiguous influence of the cultivation site on sugar accumulation was observed.

The content of total nitrogen in fruits ranged from 20.80 to 24.87 g N-tot. kg^{-1} d.m. (Table 4). Slightly higher concentrations of the element were recorded in fruits harvested from the greenhouse (24.50 g N-tot. kg^{-1} d.m.) than from the field (21.65 g N-tot. kg^{-1} d.m.). Moreover, less nitrogen was determined in fruits grown outdoors in 2010. During the fruit ripening (August-September 2010), the rainfall sum was twice as high as the multiyear average for that period (Figure 1). The nitrogen concentration in fruits of the examined cultivar is similar to that in cv. Rebeka F_1 determined by Michałojć, Horodko (2006). Jadczak et al. (2010) also confirmed a similar N-total content in fruits of several hybrid cultivars originating from Israel. Comparable quantities of N-total were also found by Golcz et al. (2004) in fruits of some hot pepper cultivars grown in an experiment on various potassium nutrition variants.

The phosphorus content in fruits harvested from the greenhouse (2.18 g P kg^{-1} d.m.) was slightly higher than that from the field (2.05 g P kg^{-1} d.m.). More phosphorus in fruits grown on field was recorded in 2009 (2.20 g P kg^{-1} d.m.) than in 2010 (1.90 g P kg^{-1} d.m.). The results on the phosphorus concentration in fruits of Red Knight F_1 obtained in the present experiment are comparable to the ones reported by Kmiecik, Lisiewska (1994), who evaluated the usefulness of stable cultivars for processing. Much more phosphorus than in sweet pepper fruits of heterotic cultivars was determined by Jadczak et al. (2010), in fruits of hot pepper cultivars in experiments performed by Golcz et al. (2004) as well as Jadczak, Grzeszczuk (2004). Gajc--Wolska et al. (2005, 2007) observed distinctly less phosphorus in fruits of heterotic cultivars, including Red Knight F_1, i.e. 0.38 g P kg^{-1} d.m.

Table 3

Content of some chemical compounds in the fruit of sweet pepper Red Knight F_1 cultivar

Place of cultivation	Dry matter (%)			Vitamin C (mg 100 g^{-1} f.m.)			Sugars (g 100^{-1} f. m.)					
							reducing			total		
	2009	2010	mean	2009	2010	mean	2009	2010	mean	2009	2010	mean
Greenhouse	10.70	10.20	10.50	176.25	180.99	178.62	5.04	4.74	4.89	5.43	4.82	5.12
Field	8.97	10.32	9.65	209.47	192.50	200.98	4.75	4.05	4.40	5.50	4.87	5.18
Mean	9.87	10.26	10.50	192.86	186.75	189.80	4.89	4.39	4.64	5.46	4.84	5.15
$LSD_{\alpha=0.05}$	0.855	n.s.	-	17.326	9.275	-	0.062	0.085	-	0.047	0.038	-

Table 4

Content of macronutrients in the fruit of sweet pepper Red Knight F_1 cultivar

Place of cultivation	Macronutrients (g kg^{-1} d.m.)														
	N-total			P			K			Ca			Mg		
	2009	2010	mean	2009	2010	mean	2009	2010	mean	2009	2010	mean	2009	2010	mean
Greenhouse	24.13	24.87	24.50	2.20	2.17	2.18	23.40	26.87	25.14	0.50	0.51	0.51	0.97	0.97	0.97
Field	22.50	20.80	21.65	2.20	1.90	2.05	20.63	20.20	20.42	0.39	0.58	0.48	0.70	0.90	0.80
Mean	23.31	22.84	23.08	2.20	2.04	2.12	22.01	23.54	22.78	0.44	0.54	0.49	0.84	0.94	0.89
$LSD_{\alpha=0.05}$	1.250	1.528	-	n.s.	0.155	-	1.562	2.375	-	0.081	0.063	-	0.187	0.057	-

The mean potassium content was 22.78 g K kg^{-1} d.m. More potassium was found in fruits from the greenhouse (mean 25.14 g K kg^{-1} d.m.), particularly in 2010 (26.87 g K kg^{-1} d.m.). The concentration of potassium in fruits harvested from the field was 20.42 g K kg^{-1} d.m., did not vary between the years of the experiment. Similar potassium levels were reported by Kmiecik, Lisiewska (1994) in sweet pepper fruits of stable cultivars,, by Gajc-Wolska et al. (2005), Golcz et al. (2004) in fruits of heterotic cultivars. Fruits of stable Czech cultivars grown on field in Moravia contained more potassium (Pokluda 2004), same as hybrid cultivars in studies on the influence of Goteo, BM 86 preparations on the yield, quality of sweet pepper fruits (Gajc-Wolska et. al. 2007). Similarly, more potassium in Delphin F_1 cultivar fruits was reported by Golcz (2001), who evaluated the effects of diverse potassium nutrition on sweet pepper yielding.

The average calcium concentration was 0.49 g Ca kg^{-1} d.m. Slightly more calcium was determined in the greenhouse fruits (0.51 g Ca kg^{-1} d.m.) than in the field ones (0.48 g Ca kg^{-1} d.m.). Much higher contents of calcium were recorded in fruits cultivated in the field in 2010 (0.58 g Ca kg^{-1} d.m.) than in 2009 (0.39 g Ca kg^{-1} d.m.). This could be the result of different moisture conditions in 2009, 2010 (Figure 1). Gajc-Wolska et al. (2007) reported comparable, while Kmiecik, Lisiewska (1994), Michalik (2000), as well as Gajc-Wolska et al. (2005) found lower calcium concentrations in sweet pepper. Much more calcium (0.90-2.62 g Ca kg^{-1} d.m.) was found in sweet pepper fruits by other authors (Bubicz et al. 1999, Golcz 2001, Golcz et al. 2004, Pokluda 2004, Jadczak et al. 2010).

The average magnesium content in fruits of the Red Knight F_1 cultivar was 0.89 g Mg kg^{-1} d.m. Significantly different concentrations of the element in fruits from the greenhouse (0.97 g Mg kg^{-1} d.m.), from the field (0.80 g Mg kg^{-1} d.m.) were recorded. The years of the experiment did not differentiate the content of magnesium in fruits grown in the greenhouse. However, fruits from the field cultivation contained more magnesium in 2010 (0.90 g Mg kg^{-1} d.m.) than in 2009 (0.70 g Mg kg^{-1} d.m.). Comparable magnesium levels in sweet pepper fruits were found by other researchers (Bubicz et al. 1999, Michałojć, Horodko 2006, Gajc-Wolska et al. 2007, Jadczak et al. 2010), whereas some reported much higher (1.90-3.18 g Mg kg^{-1} d.m.; Golcz, 2001, Golcz et al. 2004, Pokluda 2004) or much lower content (0.104 g Mg kg^{-1} d.m., Michalik 2000).

CONCLUSIONS

1. The greenhouse fruits were characterized by substantially higher fruit weight, weight of edible parts as compared to those harvested from the field, although they did not differ significantly in the pericarp thickness.

2. Fruits harvested from the field were distinguished by a higher share of the technological weight in the total weight, which makes the tested cultivar suitable for in the field for processing purposes.

3. Significantly less dry matter, reducing sugars, but more vitamin C were found in fruits from the field than from the greenhouse cultivation.

4. Higher concentrations of nitrogen, phosphorus, potassium, calcium, magnesium were determined in fruits grown in the greenhouse than in the field.

REFERENCES

BUBICZ M., PERUCKA I, MATERSKA M. 1999. *Content of bioelements of hot, sweet pepper fruit (Capsicum annuum* L.*)*. Biul. Magnezol., 4(2): 289-292. (in Polish)

BUCZKOWSKA H., NAJDA A. 2002. *A comparison of some chemical compounds in the fruit of sweet, hot pepper (Capsicum annuum* L.*).* Fol. Hort., 14(2): 59-67.

BUCZKOWSKA H. 2007. *Evaluation of yielding of Polish sweet pepper cultivars in the field cultivation in the aspect of breeding progress.* Progress in Research on Capsicum & Eggplant, K. NIEMIROWICZ-SZCZYTT (ed.) Warsaw University of Life Sciences Press, 257-265.

GAJC-WOLSKA J., SKĄPSKI H. 2001. *The evaluation of new Polish cultivars of sweet pepper in field conditions.* Fol. Hort., sup., 13(1a): 257-266. (in Polish)

GAJC-WOLSKA J., SKĄPSKI H. 2002. *Yield of field grown sweet pepper depending on cultivars, growing conditions.* Fol. Hort., 14 (1): 95-103.

GAJC-WOLSKA J., ZIELONY T., RADZANOWSKA J. 2005. *Evaluation of yield, fruit quality of new hybrids of sweet pepper (Capsicum annuum* L.*).* Zesz. Nauk. AR we Wrocławiu 515, Rolnictwo, 86: 139-147. (in Polish)

GAJC-WOLSKA J., ZIELONY T., ŁYSZKOWSKA M. 2007. *The effect of Goteo, BM86 on yield, fruit quality of sweet pepper (Capsicum annuum* L.*) in the field production.* Progress in Research on Capsicum & Eggplant. K. NIEMIROWICZ-SZCZYTT (ed.). Warsaw University of Life Sciences Press. 267-274.

GOLCZ A. 2001. *Effects of diversified pepper fertilisation with potassium*. Zesz. Nauk. ATR w Bydgoszczy, 234, Rolnictwo, 46: 53-59.

GOLCZ A., KUJAWSKI P., POTGLICKA B. 2004. *The influence of the type of fertilizer potassium on yielding hot pepper (Capsicum annuum* L.*).* Fol. Uniw. Agric. Stetin., Agriculture, 239 (95): 109-114. (in Polish)

GOLCZ A., KUJAWSKI P., ZIMOWSKA H. 2004. *Effect of potassium fertilizer type on the content of nutritive components in the leaves, fruits of hot pepper (Capsicum annuum* L.*).* Rocz. AR w Poznaniu 356, Ogrodnictwo, 37: 75-80.

JADCZAK P., GRZESZCZUK M. 2004. *Content of mineral compounds in fruit some cultivars of hot, sweet pepper (Capsicum annuum* L.*).* J. Elementol., 9(1): 15-23. (in Polish)

JADCZAK P., GRZESZCZUK M., KOSECKA D. 2010. *Quality characteristics, content of mineral components in fruit of some cultivars of sweet pepper (Capsicum annuum* L.*).* J. Elementol., 15(3): 509-515.

KMIECIK W., LISIEWSKA Z. 1994. *Evaluation of eight sweet pepper cultivars for field growing in the Kraków region from the aspect of requirements of the canning industry*. Fol. Hort., 6(2): 35-43.

KORZENIEWSKA A., NIEMIROWICZ-SZCZYTT K. 2007. *Improvement of pericarp thickness: on important goal for field-grown sweet pepper (Capsicum annuum* L.*)* in Poland. Progress in Research on Capsicum & Eggplant, K. NIEMIROWICZ-SZCZYTT (ed.). Warsaw University of Life Sciences Press, 291-296.

LEE S.K., KADER A.A. 2000. *Preharvest, postharvest factors influencing vitamin C content of horticultural crops.* Postharvest Biol. Technol., 20: 207-220.

MICHALIK Ł. 2000. *Content of some mineral constituents in sweet pepper fruits.* Ann. UMCS, Sect. EEE, 8, sup., 379-381. (in Polish)

MICHALIK Ł. 2010. *The effect of non-woven PP fabric covers on the yielding, the fruit quality of field-grown sweet peppers.* Acta Sci. Pol. Hort. Cult., 9(4): 25-32.

MICHAŁOJĆ Z.M., HORODKO K. 2006. *Effect of calcium foliar nutrition on yield, chemical composition of sweet pepper.* Acta Agroph., 7(3): 671-679. (in Polish)

NOWACZYK L., NOWACZYK P. 2005. *Usability of chosen soft-flesh hybrid forms (Capsicum frutesceus* L. *x C. annuum* L.*) for food processing*. Zesz. Nauk. AR we Wrocławiu 515, Rolnictwo, 86: 373-377. (in Polish)

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SEVERITY OF LATE BLIGHT (*PHYTOPHTHORA INFESTANS* /MONT./ DE BARY) AND EARLY BLIGHT OF POTATO (*ALTERNARIA SOLANI* SORAUER, *A. ALTERNATA* /FR./ KEISSLER) IN THREE POTATO CULTIVARS UNDER DIFFERENTIATED SOIL AND FOLIAR FERTILIZATION

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Abstract

Late blight (*Phytophthora infestans* /Mont./ de Bary) and early blight of potato (*Alternaria solani* Sorauer, *A. alternata* /Fr./ Keissler) belong to very severe potato diseases, which are able to decimate potato plantations in Poland and worldwide. In a strict plot experiment, run from 2008 to 2010, the severity of late blight (*Phytophthora infestans*) and early blight (*Alternaria* spp.) was determined, during the growing season, on three potato cultivars: medium-early cv. Adam, medium-late cv. Pasja Pomorska and late cv. Ślęza, which received NPK soil fertilization (two fertilization levels) and foliar nutrition consisting of complex fertilizers with micronutrients (Basfoliar 12-4-6, ADOB Mn, Solubor DF). The extent to which the pathogens infected potato plants was evaluated twice during each growing season, on a 9-degree scale (Pietkiewicz 1985), and the results (means from two observations) expressed as a percentage represented an infestation index. During the first two seasons, the late blight symptoms were significantly less severe on the late and medium-late rather than on the medium-early cultivar. In the last year, the cultivars Adam and Ślęza proved to be the least infected by *P. infestans*. Differences in the intensity of early blight of potato on the examined potato cultivars appeared in the third year, when cv. Adam proved to be the healthiest variety. Some non-significant differences were demon-

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strated in the severity of the diseases depending on the applied foliar fertilization and the levels of NPK fertilization.

Key words: potato, late blight, early blight, foliar fertilization.

NASILENIE ZARAZY ZIEMNIAKA (*PHYTOPHTHORA INFESTANS*) I ALTERNARIOZY (*ALTERNARIA* SPP.) NA TRZECH ODMIANACH ZIEMNIAKA PRZY ZRÓŻNICOWANYM NAWOŻENIU DOGLEBOWYM I DOLISTNYM

Abstract

Zaraza ziemniaka (*Phytophthora infestans* /Mont./ de Bary) i alternarioza (*Alternaria solani* Sorauer*, A. alternata* /Fr./ Keissler) należą do groźnych chorób ziemniaka, dewastujących uprawy tego gatunku w kraju i na świecie. W ścisłym doświadczeniu poletkowym (2008-2010) w okresie wegetacji określano nasilenie zarazy ziemniaka (*Phytophthora infestans*) i alternariozy (*Alternaria* spp.) na trzech odmianach ziemniaka: średnio wczesnej Adam, średnio późnej Pasja Pomorska i późnej Ślęza nawożonych doglebowo NPK (dwa poziomy nawożenia) i dokarmianych wieloskładnikowych nawozami dolistnymi z mikroelementami (Basfoliar 12-4-6, ADOB Mn, Solubor DF). Porażenie przez patogeny oceniano dwukrotnie w okresie wegetacji wg 9-stopniowej skali (PIETKIEWICZ 1985), a wyniki (średnie z dwóch obserwacji) podano w procentach jako indeks porażenia. Zanotowano istotnie mniejsze nasilenie zarazy na roślinach późnych odmian niż na średnio wczesnej w pierwszych dwóch analizowanych sezonach wegetacyjnych oraz mniejsze nasilenie tej choroby na roślinach średnio wczesnej i późnej odmiany niż średnio późnej w ostatnim roku badań. Zróżnicowanie w nasileniu alternariozy na badanych odmianach ziemniaka stwierdzono w ostatnim roku badań, a najzdrowsza okazała się odmiana Adam. Stwierdzono nieistotne zróżnicowanie w nasileniu chorób w zależności od stosowanego nawożenia dolistnego i poziomów nawożenia mineralnego NPK.

Słowa kluczowe: ziemniak, zaraza ziemniaka, alternarioza, nawożenie dolistne.

INTRODUCTION

The severity of late blight (*Phytophthora infestans*) and early blight (*Alternaria solani*, *A. alternata*) of potato is affected by a variety of factors, including the weather conditions, the potato cultivar (SADOWSKI 2006) or the applied plant protection chemicals (KURZAWIŃSKA, GAJDA 2004, SHAILBALA, PUNDHIR 2008). Foliar application of multi-component fertilizers is part of a modern potato cultivation technology, which gains in importance whenever organic and mineral fertilization treatments are not adequately utilized by plants. The yield-stimulating effect (including an increased percentage of large tubers) has been demonstrated to result from foliar application of N, K, P, Mg and micronutrients (BRAR, NAVDEEP-KAUR 2006) as well as the application of elemental sulphur or potassium sulphate (KLIKOCKA et al. 2005). Foliar fertilization affects the quality of tubers as well (KOZERA et al. 2006). The micronutrients such as Zn, Fe, B, Mn, Cu and Mn, found in fertilizers, shape the potato's resistance to pathogens (Haberland 2000, Mahmoud 2007, Malahouti 2008). The literature contains some reports on the limiting effect of foliar fertilization on the development of late blight (Kapsa 2002, Basu et al. 2003) and early blight of potato (Osowski 2005). However, the influence of complex foliar fertilizers on the health of potato tubers remains debatable. Boligłowa (2003) observed that infection caused by *Streptomyces scabies* was more severe under a combined fertilization treatment with Insol 7 and urea. Cooke and Little (2002) found weaker symptoms of infection caused by *P. infestans* following foliar application of phosphorus.

In the present study, the authors analyzed the severity of late and early blight on three potato cultivars grown under various systems of soil NPK mineral fertilization and foliar application of multi-component fertilizers including micronutrients.

MATERIAL AND METHODS

Our tests on the health of potatoes of three cultivars: medium-early cv. Adam, medium-late cv. Pasja Pomorska and late cv. Ślęza, were carried out in a strict plot experiment (2008-2010) set up by the staff of the Chair of Agrotechnology and Crop Production Management of the University of Warmia and Mazury in Olsztyn (with randomly chosen sub-blocks and four replications), which was located in Bałcyny, near Olsztyn (53°78'N, 20°48'E), on grey-brown podzolic soil originating from light silty clay, which belonged to complex 4 class III in the Polish soils classification system. The preceding crop consisted of cereal plants. Certified tubers were planted in rows at a 40-cm distance, with spaces between rows equal 62.5 cm. The first factor of the experiment comprised two levels of mineral fertilization: I – 80 kg N ha^{-1}, 80 kg P ha^{-1}, 120 K ha^{-1}, II – 120 kg ha^{-1} P 144 kg ha^{-1} K 156 kg ha^{-1}). The second factor included variants with foliar fertilization: A. Basfoliar 12-4-6 (8 dm^3 ha^{-1}), B. ADOB Mn (4 dm^3 ha^{-1}), C. Solubor DF (2 dm^3 ha^{-1}), D. ADOB Mn (2 dm^3 ha^{-1}) + Solubor DF (1 dm^3 ha^{-1}), E. ADOB Mn (2 dm^3 ha^{-1}) + Basfoliar 12-4-6 (4 dm^3 ha^{-1}), F. Basfoliar 12-4-6 (4 dm^3 ha^{-1}) + + Solubor DF (1 dm^3 ha^{-1}), G. Basfoliar 12-4-6 (2.7 dm^3 ha^{-1}) + ADOB Mn (1.3 dm^3 ha^{-1}) + Solubor DF (0.7 dm^3 ha^{-1}), H. control without foliar fertilization. The fertilizers were applied once, at the beginning of flowering (BBCH 61). Identical agrotechnical (as recommended by the Institute of Soil Science and Plant Cultivation – National Research Institute, Puławy) and plant protection treatments (as recommended by the Institute of Plant Protection – National Research Institute, Poznań) were performed on all the plots. The content of particular components in % weight was as follows: Basfoliar 12-4-6 (N – 12, K – 6, P – 4, Mg – 0.2, B – 0,02, Mn – 0.01, Cu – 0.01, Fe – 0.01, Zn – 0.005, Mo – 0.005), ADOB Mn (N – 6.5, Mg – 2, Mn – 10), Solubor DF (B – 17.5).

Table 1

The weather conditions (the Meteorological Station in Bałcyny)

Temperature (ºC)													
Month	2008				2009				2010				mean for 1960--1990
	monthly mean	mean for 10 days			monthly mean	mean for 10 days			monthly mean	mean for 10 days			
May	12.3	11.6	12.0	13.3	12.2	11.5	11.0	13.9	12.0	10.7	12.1	13.2	12.4
June	16.6	18.0	14.9	17.0	14.7	12.1	13.9	18.2	15.7	17.4	14.8	15.1	15.7
July	18.3	17.4	18.4	19.2	18.9	18.6	19.1	19.1	20.8	19.4	23.6	19.5	15.3
August	17.8	18.3	19.0	16.2	18.5	19.7	17.8	17.8	19.3	20.2	21.4	16.6	17.9
Mean for growing season	16.3	16.3	16.1	16.4	16.1	15.5	15.5	17.3	17.0	16.9	18.0	16.1	15.3
Rainfall (mm)													
Month	monthly sum	sum for of 10 days			monthly sum	sum or 10 days			monthly sum	sum for 10 days			sum for 1960--1990
May	48.4	41.8	2.2	4.4	89.6	11.5	1.8	76.3	105,5	19.2	38.6	47.7	56.7
June	27.8	0.0	11.2	16.6	133.1	56.7	30.4	46.0	73.7	12.0	39.8	21.9	68.3
July	47.0	10.8	23.8	12.4	82.2	60.0	10.3	11.9	87.8	16.8	21.5	49.5	81.3
August	103.1	43.0	26.0	34.1	25.7	13.4	11.2		99.3	17.4	13.8	68.1	78.1
Sum for growing season	226.3	95.6	63.2	67.5	330.6	141.6	53.7	135.3	366.3	65.4	113.7	187.2	284.4

During the plants' growth, 3 and 5 weeks after a foliar fertilization treatment carried out on 30 plants, the severity of late blight and early blight infection was assessed on a 9-degree scale (Pietkiewicz 1985), where 0 stands for no infection symptoms and 9 means the most severe infection case. The results (means from two observations) were given in percentage as an infection index Ii and then processed statistically using analysis of variance for random blocks (Statistica® 9.0 v. 2009). For comparison of the means, Duncan's test was applied at the level of significance equal 0.05.

The distribution of temperatures from May to August during the analyzed growing seasons was similar, with the average temperatures in July and August higher than the multi-year means for the same months (Table 1). In contrast, the rainfalls were varied, e.g. they were nearly 50% higher in the first than in the second and third season.

RESULTS AND DISCUSSION

The cultivars determined the intensity of late blight and early blight symptoms on potato plants in the present experiment. The resistance to potato late blight is a trait that seems to be most frequently tested in potato breeding programmes, which include new cultivars with improved resistance of leaves and tubers to late blight (Sadowski 2006). During the first two seasons, stronger symptoms of an infection by *P. infestans* appeared on potato plants belonging to cv. Adam (the infection indices from 50.5% – the variant with Solubor DF during the 2009 growing season to 68% – the combination with ADOB Mn and Solubor DF applied together, in 2008) than on the other two cultivars, at the higher and lower NPK mineral fertilization rate respectively (Table 2). When analyzing the severity of late blight on the later cultivars evaluated at the same time, the infection indices ranged from 29.1% for cv. Ślęza in the combination consisting of Basfoliar 12-4-6 in 2009 to 44.1% for cv. Pasja Pomorska in the fertilization variant with ADOB Mn in 2008 (variant II of mineral fertilization).

Basu et al. (2003) prove that foliar fertilization of potatoes with $ZnSO_4$ and $CuSO_4$ alleviated the severity of symptoms of potato late blight on leaves and tubers. Foliar application of phosphates inhibited the development of *P. infestans* on leaves (Lobato et al. 2008). Jabłoński and Bernat (2001), while concluding that the efficacy of the applied Mikrosol Zm in combination with half the recommended dose of fungicides was comparable to the whole recommended dose of the latter, perceive it as a possible way to reduce the chemical control of potato late blight. Similar results were obtained by Ann (2001): combined application of fungicides and foliar fertilizers Nutri-Phite P Foliar and Guard PK successfully limited the extent of infection caused by *P. infestans*. In his latest report, Szewczuk (2009) also implies that potato

Table 2

Symptoms of infection of potato plants by P. *infestans* during the study (% infection index), Bałcyny 2008-2010

Level of NPK	Foliar fertiliz.	2008			*x*	2009			*x*	2010			*x*
		Adam	Pasja P.*	Ślęza		Adam	Pasja P.	Ślęza		Adam	Pasja P.	Ślęza	
I**	A***	61.5^{ab}****	42.2^{c-f}	37.7^{c-g}	47.1^{a}	63.2^{a}	48.5^{cde}	35.2^{k-o}	49.0^{a}	43.7^{bc}	64.3^{a}	46.5^{bc}	51.5^{a}
	B	60.5^{ab}	39.4^{c-g}	35.5^{c-g}	45.1^{a}	59.7^{ab}	43.2^{d-j}	35.1^{k-o}	46.0^{a-e}	43.2^{bc}	62.6^{a}	48.0^{b}	51.3^{a}
	C	65.2^{ab}	40.3^{c-g}	35.5^{c-g}	47.0^{a}	62.3^{a}	43.9^{d-i}	35.2^{k-o}	47.1^{a-d}	44.3^{bc}	62.7^{a}	47.8^{b}	51.6^{a}
	D	68.0^{a}	40.6^{c-g}	35.2^{c-g}	47.9^{a}	59.9^{ab}	40.4^{f-l}	37.4^{g-n}	45.9^{a-e}	39.9^{c}	64.3^{a}	46.8^{bc}	50.3^{a}
	E	59.2^{ab}	38.7^{c-g}	36.0^{c-g}	44.6^{a}	59.8^{ab}	45.8^{def}	35.8^{j-o}	47.1^{a-d}	42.5^{bc}	63.9^{a}	46.2^{bc}	50.9^{a}
	F	63.2^{ab}	40.2^{c-g}	33.5^{efg}	45.6^{a}	60.4^{ab}	41.3^{e-l}	32.4^{mno}	44.7^{a-e}	42.1^{bc}	63.9^{a}	45.2^{bc}	50.4^{a}
	G	62.3^{ab}	39.6^{c-g}	35.2^{c-g}	45.7^{a}	59.5^{ab}	46.0^{def}	39.6^{f-m}	48.4^{ab}	44.2^{bc}	62.6^{a}	47.1^{bc}	51.3^{a}
	H	63.4^{ab}	41.1^{c-f}	34.6^{d-g}	46.4^{a}	53.2^{bc}	40.4^{f-l}	31.3^{no}	41.6^{e}	45.9^{bc}	60.8^{a}	47.2^{bc}	51.3^{a}
x		62.9^{a}	40.3^{b}	35.4^{c}	46.2^{a}	59.8^{a}	43.7^{b}	35.3^{c}	46.2^{a}	43.2^{c}	63.1^{a}	46.9^{a}	51.1*a*
II	A	59.5^{ab}	42.6^{cde}	35.6^{c-g}	45.9^{a}	61.2^{a}	40.6^{f-l}	29.1^{o}	43.6^{cde}	43.0^{bc}	61.4^{a}	45.8^{bc}	50.1^{a}
	B	58.9^{ab}	44.1^{cd}	32.0^{fg}	45.0^{a}	58.4^{ab}	38.2^{f-n}	36.3^{i-o}	44.3^{b-e}	43.0^{bc}	62.4^{a}	45.9^{bc}	50.4^{a}
	C	61.6^{ab}	41.8^{c-f}	35.2^{c-g}	46.2^{a}	50.5^{cd}	42.4^{e-k}	36.3^{i-o}	43.1^{de}	42.0^{bc}	63.3^{a}	46.3^{bc}	50.5^{a}
	D	61.1^{ab}	42.0^{c-f}	34.0^{d-g}	45.7^{a}	57.9^{ab}	39.5^{f-n}	34.3^{l-o}	43.9^{cde}	43.5^{bc}	62.7^{a}	45.6^{bc}	50.6^{a}
	E	62.2^{ab}	42.4^{c-f}	30.3^{g}	45.0^{a}	60.4^{ab}	38.4^{f-n}	33.4^{l-o}	44.1^{b-e}	42.9*bc*	60.8^{a}	46.5^{bc}	50.1^{a}
	F	57.6^{b}	40.4^{c-g}	34.8^{d-g}	44.3^{a}	60.7^{ab}	45.6^{def}	36.9^{h-n}	47.7^{abc}	42.2^{bc}	60.5^{a}	46.9^{bc}	50.0^{a}
	G	61.2^{ab}	40.3^{c-g}	33.7^{d-g}	45.0^{a}	61.0^{a}	45.2^{d-g}	37.6^{g-n}	47.9^{abc}	42.9^{bc}	64.0^{a}	45.5^{bc}	50.8^{a}
	H	65.2^{ab}	45.2^{c}	34.4^{d-g}	48.3^{a}	61.7^{a}	44.3^{d-h}	30.8^{no}	45.6^{a-e}	44.7^{bc}	61.2^{a}	47.1^{bc}	51.0^{a}
x		60.9^{a}	42.4^{b}	33.8^{c}	45.7^{a}	59.0^{a}	41.8^{b}	34.3^{c}	45.0^{a}	43.0^{c}	62.0^{a}	46.2^{a}	50.4^{a}
x for the cultivar		61.9^{a}	41.3^{b}	34.6^{c}	-	59.4^{a}	42.7^{b}	34.8^{c}	-	43.1^{c}	62.6^{a}	46.5^{b}	-

Key: *Pasja P. – Pasja Pomorska, ** I, II level of NPK (I – 80 kg N ha^{-1}, 80 kg P ha^{-1}, 120 kg K ha^{-1}, II – 120 kg N ha^{-1}, 120 kg P ha^{-1}, 180 kg ha^{-1}) ***A, B, C, D, E, F, G, H – foliar fertilization (A-Basfoliar 12-4-6, B-ADOB Mn, C-Solubor DF, D-ADOB Mn + Solubor DF, E-ADOB Mn + Basfoliar 12-4-6, F-Basfoliar 12-4-6 + Solubor DF, G-Basfoliar 12-4-6 + ADOB Mn + Solubor DF, H-control ,**** values marked with these letters do not differ significantly within the years plants can be effectively protected against this dangerous pathogen by a combined application of the foliar fertilizers Rolvit B and Plonvit and the fungicides Tattoo C 750 and Bravo 500 SC.

During the 2010 growing season, with its highest total rainfall in the summer months, more severe symptoms of late blight were observed on plants belonging to cv. Pasja Pomorska than on the other two cultivars. The infection index observed on plants of this medium-late cultivar treated with the fertilizer Basfoliar 12-4-6 and ADOB Mn + Solubor DF (in variant I of NPK fertilization) and with the three fertilizers applied conjunctively (in variant B) exceeded 64%. The infection indices assigned to potato plants of cv. Adam and Ślęza did not exceed 50%, and the differences between their values in particular fertilization treatments at both levels of mineral fertilization were non-significant.

During the whole period covered by this study, significant differences were found between the average infection indices for all the cultivars in both mineral fertilization variants. In the first two years, the medium-early cultivar Adam was the most badly infected one, but in the last year, it was the medium-late variety Pasja Pomorska that suffered the worst damage. No significant differences in the severity of infection were observed on the plots where foliar application of fertilizers was carried out and on the control plot. The mineral fertilization applied in two rates for particular macronutrients, during the three years of the experiment, did not differentiate the infection severity, although the symptoms appeared to be somewhat more severe on plants fertilized with the lower NPK dose. According to Matkowski et al. (2004), different nitrogen fertilization rates did not influence the severity of late blight of potato.

The signs of potato early blight on potato plants were weaker than those of late blight. During the first two years of the experiment, the index for infection caused by *Alternaria* spp. ranged from 18% on cv. Ślęza plants treated with the fertilizer ADOB Mn+Solubor DF (variant I of the mineral fertilization) and ADOB Mn during the first growing season (variant II of the mineral fertilization) to around 35% for cv. Adam potato plants without foliar nutrition and with the application of the fertilizer ADOB Mn+Solubor DF (variant II of the mineral fertilization), likewise in the first growing season (Table 3). The differences in the infection index values for the above cultivars grown on particular plots, at both mineral fertilization levels, were significant in 2008 and 2009, except the combination including the application of Solubor DF and the higher NPK rate (2009). In the last year of the experiment, significantly less severe infection was observed on the medium-early cultivar plants treated with foliar fertilizers, at both levels of mineral fertilization, than on plants of the medium-late and late cultivars. Osowski (2005) demonstrated the limiting effect of the fertilizer Basfoliar 12-4-6 applied in conjunction with the fungicide Antracol 70 WG and Unikat 75 WG on potato being infected by *A. alternata* during the vegetative season. Analo-

Table 3

Symptoms of infection of potato plants by *Alternaria alternata,* A. solani during the study (% infection index), Bałcyny 2008-2010

Level of NPK	Foliar fertiliz.	2008			*x*	2009			*x*	2010			*x*
		Adam	Pasja P.*	Ślęza		Adam	Pasja P.	Ślęza		Adam	Pasja P.	Ślęza	
I**	A***	30.3$^{a-h****}$	21.8*i-n*	18.5^{mn}	23.5^{a}	30.4^{a-h}	26.3^{b-m}	22.3l^{mn}	26.2^{ab}	18.2^{c}	32.2^{ab}	33.4^{ab}	27.9^{a}
	B	27.9^{a-k}	24.8^{e-n}	18.7^{mn}	23.8^{a}	29.9^{a-j}	23.0^{h-n}	18.4^{n}	23.8^{b}	19.3^{c}	32.9^{ab}	36.0^{ab}	29.4^{a}
	C	28.4^{a-j}	22.2^{i-n}	18.3^{n}	23.0^{a}	33.0^{ab}	24.5^{d-n}	22.6^{j-n}	26.7^{ab}	18.2^{c}	31.0^{ab}	34.7^{ab}	28.0^{a}
	D	32.4^{a-e}	24.7^{f-n}	18.0^{n}	25.0^{a}	33.2^{ab}	27.8*a-l*	23.3*g-n*	28.1^{a}	20.2^{c}	32.2^{ab}	36.8^{a}	29.7*a*
	E	28.6^{a-i}	25.6^{d-n}	19.3l^{mn}	24.5^{a}	32.9^{ab}	25.0^{c-n}	22.2l^{mn}	26.7^{ab}	18.2^{c}	30.2^{ab}	34.2^{ab}	27.6^{a}
	F	28.9^{a-i}	21.3^{i-n}	19.0l^{mn}	23.1^{a}	30.2^{a-i}	23.0^{h-n}	19.3^{mn}	24.2^{ab}	18.3^{c}	31.0^{ab}	33.9^{ab}	27.7^{a}
	G	30.7^{a-g}	19.6l^{mn}	20.7^{j-n}	23.7^{a}	31.5^{a-e}	21.5l^{mn}	18.9^{mn}	24.0^{ab}	19.8^{c}	31.5^{ab}	33.6^{ab}	28.3^{a}
	H	33.7^{abc}	20.4^{k-n}	18.7^{mn}	24.3^{a}	33.7^{a}	25.2^{c-m}	25.2*c-m*	28.0^{a}	19.2^{c}	31.3^{ab}	35.4^{ab}	28.6^{a}
x		30.1^{b}	22.5^{c}	18.9^{d}	23.9^{b}	31.9^{a}	24.5^{b}	21.5^{c}	26.0^{a}	18.9^{c}	31.5^{b}	34.8^{a}	28.4^{a}
II	A	31.6^{a-f}	23.2^{g-n}	20.5^{k-n}	25.1^{a}	33.0^{ab}	23.0^{h-n}	18.2^{n}	24.7^{ab}	19.9^{c}	32.5^{ab}	32.3^{ab}	28.2^{a}
	B	32.8^{a-d}	26.3^{c-m}	18.0^{n}	25.7^{a}	31.5^{a-e}	21.5l^{mn}	24.1^{f-n}	25.7^{ab}	17.2^{c}	29.2^{b}	35.6^{ab}	27.3$_{a}$
	C	34.1^{ab}	22.9^{k-n}	20.3^{k-n}	25.8^{a}	29.7^{a-k}	23.7^{f-n}	23.4^{g-n}	25.6^{ab}	18.3^{c}	33.1^{ab}	35.5^{ab}	29.0^{a}
	D	34.8^{a}	20.7^{j-n}	18.5^{mn}	24.7^{a}	31.0^{a-f}	22.3^{k-n}	22.8^{i-n}	25.4^{ab}	18.0^{c}	32.5^{ab}	34.7^{ab}	28.4^{a}
	E	32.2^{a-f}	23.1^{g-n}	18.7^{mn}	24.7^{a}	33.2^{ab}	23.2^{g-n}	25.0^{c-n}	27.1^{ab}	18.4^{c}	30.1^{ab}	34.6^{ab}	27.7^{a}
	F	32.6^{a-d}	22.1^{i-n}	18.9l^{jm}	24.5^{a}	31.9^{abc}	23.0^{h-n}	24.3^{e-n}	26.4^{ab}	19.8^{c}	31.8^{ab}	34.1^{ab}	28.6^{a}
	G	34.0^{a}	23.9^{g-n}	18.9l^{mn}	25.6^{a}	31.7^{a-d}	24.6^{c-n}	23.2^{g-n}	26.5^{ab}	19.8^{c}	30.6^{ab}	33.4^{ab}	27.9^{a}
	H	34.5^{a}	26.7^{b-l}	20.0l^{mn}	27.1^{a}	30.5^{a-g}	24.6^{c-n}	21.1l^{mn}	25.4^{ab}	19.9^{c}	33.2^{ab}	36.2^{ab}	29.8^{a}
x		33.3^{a}	23.6^{c}	19.2^{d}	25.4^{a}	31.6^{a}	23.2^{bc}	22.8^{bc}	25.9^{a}	18.9^{c}	31.6^{b}	34.6^{a}	28.4^{a}
x for the cultivar		31.8^{a}	23.1^{b}	19.1^{c}	-	31.7^{a}	23.9^{b}	22.1^{c}	-	18.9^{c}	31.6^{b}	34.7^{a}	-

Key as under Table 2

gously, in our earlier study (CWALINA-AMBROZIAK et al. 2007), less numerous isolates of *A. alternata* were obtained from aerial parts of potato plants nourished with Basfoliar 12-4-6 together with the fertilizers ADOB Mn and Solubor DF.

The statistical calculations performed on the results of our present experiment have shown that the intensity of early blight in the three examined potato cultivars was not significantly differentiated under the influence of the applied foliar fertilization in any of the analyzed growing seasons. Some non-significant differences were observed in infection indices between the two mineral fertilization levels (lower I and higher II variants), but it was only in the first growing season that more severe symptoms of early blight were found on plants receiving the higher rate of mineral fertilizers. MAC DONALD et al. (2007) claimed that high N rates reduced symptoms of late blight on potato plants. In the present study, the factor that most strongly determined the severity of symptoms of infection caused by *Alternaria* spp. was the cultivar, i.e. significant differences appeared between the mean infection indices within each examined cultivar. The most severely infected cultivar during the first two seasons was cv. Adam; cultivar Ślęza was the least infected one. In the final year of the experiment, cv. Adam proved to be the healthiest.

CONCLUSIONS

1. The cultivars determined the intensity of late blight and early blight symptoms on potato plants in the present experiment. During the first two seasons, plants of the medium-early potato cultivar Adam were the most severely infected by *P. infestans*; in the last year, they were the plants of the medium-late cultivar Pasja Pomorska. Significant differences in the intensity of early blight of potato on the examined potato cultivars appeared in the third year, when cv. Adam proved to be the healthiest variety.

2. No significant differences in the intensity of either of the diseases were found between the plots with the foliar fertilization and between the two tested NPK fertilization variants in any of the analyzed growing seasons. Only in the first year of study more severe symptoms of early blight appeared on potato plants receiving the higher rate of NPK than lower rate.

REFERENCES

ANN P. J. 2001. *Control of plant diseases with non-pesticide compound-phosphorous acid.* Plant Pathol. Bull., 10(4): 147-154.

BASU A., HOSSAIN M.M., KONAR A., CHETTRI M. 2003. *Integrated management of late blight disease of potato.* Ann. Plant Protect. Sci., 11(1): 64-66.

BOLIGŁOWA E. 2003. *Effect of foliar fertilizers on potato yield, its structure, health and storage life of tubers.* Acta Agrophys., 85: 99-106. (in Polish)

BRAR M., NAVDEEP-KAUR S. 2006. *Effect of soil and foliar applied potassium and nitrogen on yield of potato (Solanum tuberosum) in alluvial soils of Punjab, India.* Ind. J. Agricult. Sci., 76(12): 740-743.

COOKE L.R., LITTLE G. 2002. *The effect of foliar application of phosphonate formulations on the susceptibility of potato tubers to late blight.* Pest Managem. Sci., 58(1): 17-25.

CWALINA-AMBROZIAK B., CZAJKA W., BOGUCKA B., TROJAK A. 2007. *Effect of foliar fertilization of potato on a pathogenic fungal community colonizing the aerial parts of plants.* Prog. Plant Protect./Post. Ochr. Roślin, 47(2): 72-77. (in Polish)

HABERLAND R. 2000. *Do potatoes need trace element fertilizer?* Kartoffelbau, 51(6): 260-264.

JABŁOŃSKI K., BERNAT E. 2001. *The influence of Mikrosol Zm foliar fertilization on yield and quality of tubers and possible reduction of fungicide application in controlling late blight of potatoes.* Prog. Plant Protect./Post. Ochr. Roślin, 41(1): 299-305. (in Polish)

KAPSA J. 2002. *Possible reduction of fungicide rates by adding Insol 7 in the control of Phytophthora infestans (Mont.) de Bary on potato plantations.* Zesz. Nauk. AR Kraków, 387(82): 75-79. (in Polish)

KLIKOCKA H., HANEKLAUS S. BLOEM, SCHNUG E. 2005. *Influence of sulfur fertilization on infection of potato tubers with Rhizoctonia solani and Streptomyces scabies.* J. Plant Nutrit., 28(5): 819-833.

KOZERA W., NOWAK K., MAJCHERCZAK E., BARCZAK B. 2006. *Effect of foliar fertilization with microelements on the content of macroelements in potato tubers.* J. Elementol., 11(1): 29-34.

KURZAWIŃSKA H., GAJDA I. 2004. *The effectiveness of some fungicides in protection of potato against late blight.* Biul. Inst. Hod. Rośl., 233: 333-338. (in Polish)

LOBATO M.C., OLIVIERI F.P., GONZALES ALTAMIRANDA E.A.,WOLSKI E.A., DALEO G.R., CALDIZ D.O. ANDREU A.B. 2008. *Phosphite compounds reduce disease severity in potato seed tubers and foliale.* Europ. J. Plant Pathol., 122(3): 349-358.

MAC DONALD W., PETERS R.D., COFFIN R.H., LACROIX C. 2007. *Effect of strobilurin fungicides on control of early blight (Alternaria solani) and yield of potatoes grown under two N fertility regimes.* Phytoprotection, 88(1): 9-15.

MAHMOUD S.M. 2007. *Management of brown rot disease of potato.* Arab. Univ. J. Agricult. Sci., 15(2):457-463.

MALAHOUTI M.J. 2008. *The effect of micronutrients in ensuring efficient use of macronutrients*. Turkish J. Agricult. Forestry, 32(3): 215-220.

MATKOWSKI K., PROŚBA-BIAŁCZYK U., NOWAK L. 2004. *Influence of irrigation and nitrogen fertilization on the health of two potato cultivars.* Zesz. Probl. Post. Nauk Rol., 500: 351-358. (in Polish)

OSOWSKI J. 2005. *A possibility of using zinc to protect potatoes against early blight.* Biul. IHAR, 237/238: 187-193. (in Polish)

PIETKIEWICZ 1985. *Methodology of the assessment of potato haulm infection with late blight (Phytophthora infestans).* Biul. Inst. Ziemn., 32: 43-49. (in Polish)

SADOWSKI C. 2006. *Health status of the potato in Poland and threats to its production.* Zesz. Probl. Post. Nauk Rol., 511(1): 37-51. (in Polish)

SHAILBALA M., PUNDHIR V.S. 2008. *Efficacy of fungicides and bio-agents against late blight severity, infection rate and tuber field of potato.* J. Plant. Disease Sci., 3(1): 4-8.

SZEWCZUK C. 2009. *The influence of potato foliar fertilization on Phytophthora infestans infestation.* Ann. UMCS Sect. E, 64(1): 13-18. (in Polish)

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IMPACT OF NITROGEN CONCENTRATION VARIABILITY IN SUGAR BEET PLANT ORGANS THROUGHOUT THE GROWING SEASON ON DRY MATTER ACCUMULATION PATTERNS

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Abstract

Nitrogen concentration (N_c) in leaves, in each stage of sugar beet development, is the major factor stimulating the accumulation of dry matter in leaves, which in turn affects the dry matter concentration in storage roots and, consequently, determines sugar beet yields. This thesis was verified based on the data obtained from a static field experiment conducted in 2001-2003, with eight fertilizing variants: without nitrogen (absolute control, PK), without one of the main nutrients (KN, PN), with a reduced amount of phosphorus and potassium (N + 25% PK, N + 50% PK) and the recommended amount of all basic nutrients (NPK, $NP^{*}K$, P^{*} – P in the form of PAPR). Nitrogen concentrations in leaves and storage roots of sugar beet tended to decline during the growing season, but the former tendency adhered to a linear-plateau model while the latter corresponded to an exponential one. This discrepancy, revealed in the second part of the season, can be considered as an indicator of a high yield of storage roots, especially in years favorable for sugar beet vegetation. The growth analysis allowed us to determine the time and the maximum rate of canopy and storage root growth during the season. Irrespective of the fertilizing variant, both organs of sugar beet reached the maximum rate of growth from 92 to 113 day after sowing (DAS). Plants grown under conditions of ample water and nutrient supply (2001) reached a three-fold higher rate of leaf growth than in dry years (2002, 2003). The storage root showed much smaller differences in the absolute rate of growth. However, the effect of fertilizing variants was stronger, especially from 92 DAS onwards. Trends of the relative growth rate for each of the two tested plant organs were very similar. The highest growth rate for both organs occurred in early stages of sugar beet development and then progressively declined. Nevertheless, only this growth parameter responded si-

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gnificantly during the season to the variability of N_c in both sugar beet organs. The relationships showed that sugar beet plants could compensate the dry matter growth rate during early stages of sugar beet development, especially in years favorable for sugar beet growth. The impact of nitrogen concentrations in leaves on the relative storage root growth dynamics was curvilinear in 2001 but linear in the other years, i.e., the ones when droughts were frequent. At the same time, the relationship between N_c and storage root fraction was always linear. This type of a relationship clearly demonstrates the natural conservatism of the storage root to its variable nitrogen concentration during the growing season.

Key words: sugar beet, nitrogen concentration, leaves, storage root, absolute and relative rate of growth.

WPŁYW ZMIENNOŚCI KONCENTRACJI AZOTU W CZĘŚCIACH BURAKA CUKROWEGO W OKRESIE WEGETACJI NA WZORCE AKUMULACJI SUCHEJ MASY

Abstrakt

Koncentracja azotu w liściach buraka cukrowego w każdej fazie rozwoju rośliny jest głównym czynnikiem wpływającym na tempo akumulacji suchej masy liści, tym samym na koncentrację składnika w korzeniu spichrzowym, a w konsekwencji kształtującym dynamikę jego wzrostu. Tak sformułowana teza została zweryfikowana na podstawie danych uzyskanych w doświadczeniu polowym, statycznym, prowadzonym w latach 2001-2003, z ośmioma wariantami nawozowymi: bez azotu (kontrola absolutna, PK), bez jednego głównego makroskładnika (NK, NP), ze zredukowana dawką P i K (N + 25% PK; N + 50% PK) oraz z zalecaną dawką składników (NPK, NP^*K, P^* – P w nawozie fosforowym, tzw. wzbogaconym). W okresie wegetacji zawartość azotu w liściach i korzeniu spichrzowym buraka wykazywała trendy spadkowe, lecz ujawniające się odmiennie, odpowiednio jako model liniowo-plateau i potęgowy. Niezgodność ta, pojawiająca się w drugiej części sezonu, może być traktowana jako wskaźnik dużego plonu korzeni, zwłaszcza w latach optymalnych dla wegetacji buraka cukrowego. Zastosowana analiza wzrostowa pozwoliła określić termin i wartość maksymalnej szybkości wzrostu liści i korzeni w okresie wegetacji. Niezależnie od wariantu nawozowego, maksymalne wartości wzrostu obu organów wystąpiły w okresie od 92. do 113. dnia od siewu. Buraki cukrowe rosnące w warunkach optymalnego zaopatrzenia w wodę (2001) osiągnęły 3-krotnie większą szybkość wzrostu liści niż w latach z suszą (2002, 2003). W korzeniach spichrzowych wykazano znacznie mniejsze różnice wskaźnika, jakim jest absolutna szybkości wzrostu. Jednakże ujawnił się dużo większy wpływ wariantów nawozowych, zwłaszcza w drugiej części sezonu wegetacyjnego. Trendy przyrostu suchej masy, rozpatrywane oddzielnie dla obu organów buraka, były bardzo podobne. Maksymalne wartości wystąpiły w początkowym okresie wegetacji, podlegając następnie stopniowemu spadkowi. Jednakże tylko ten wskaźnik wzrostu wykazał istotny związek z koncentracją azotu w obu częściach buraka cukrowego. Zależności korelacyjne wykazały, że rośliny były w stanie kompensować szybkość wzrostu w początkowym okresie wegetacji, zwłaszcza w roku o optymalnym przebiegu pogody (2001). Wpływ koncentracji azotu w liściach na względną dynamikę wzrostu masy korzenia spichrzowego okazał się krzywoliniowy w roku 2001 i prostoliniowy w pozostałych latach (z częstymi suszami). Natomiast relacje między koncentracją azotu w korzeniu spichrzowym i jego udziałem w biomasie całkowitej buraka były zawsze liniowe. Ten model relacji podkreśla naturalny konserwatyzm korzenia spichrzowego w reakcji na zmienną koncentrację azotu w tej częsci rośliny w okresie wegetacji.

Słowa kluczowe: burak cukrowy, koncentracja azotu, liście, korzeń spichrzowy, absolutna i względna szybkość wzrostu.

INTRODUCTION

In Europe, sugar beet (*Beta vulgaris* L.) is the only crop producing sugar in amounts ensuring the feasibility of technological processing. Over a large area, from northern France to eastern Poland, potential yields of this crop determined by climatic conditions are estimated in the range of 80-85 t ha^{-1} (Supit et al. 2010). However, the harvested yields are much lower, ranging from above 70 t ha^{-1} in France to below 50 t ha^{-1} in Poland (FAOSTAT, 2011). There are two main reasons. One is the dominating weather in summer months, e.g. the impact of the continental climate (Jongman et al., 2006), experienced from the north-western to the eastern parts of the continent. Shortage of precipitation during summer months, which is responsible for frequently occurring droughts, is combined with high temperatures, significantly reducing yield of many crops, including sugar beets (Olesen et al. 2011, Supit et al. 2010).

The other significant factor shaping harvested yields of sugar beet is the fertility of soil under this crop. This term combines two soil attributes, namely the inherent soil fertility and the applied nutrient management. Sugar beet is highly sensitive to soil fertility, especially to the supply of potassium and phosphorus. The highest yields of storage roots are harvested from soils with a high potassium level. Potassium applied to currently grown crop during its critical stages of yield formation is generally considered as a factor alleviating, at least partly, the negative effects of water shortage (Cakmak, Kirkby 2008, Grzebisz et al. 2002, Milford et al. 2002).

Effects of both factors on sugar beet growth and yielding deserve much attention in regions like Central Europe, where sugar beet suffers severely from summer drought (Kenter et al. 2006). It is well recognized that under ample water supply sugar beet can fully exploit its yielding potential, provided that basic nutrients such as phosphorus and potassium do not retard the plant's growth (Freckleton et al. 1999, Hills et al. 1990, Herlichy 1992). However, the key nutrient affecting both the quantity of harvested yield of storage roots and their technological quality is nitrogen. It is well known that neither shortage nor excess of nitrogen at any stage of sugar beet growth affects negatively dry matter distribution and storage root quality (Hoffmann 2005). In Poland, sugar beet is grown on soils of different fertility, which affects the supply of nitrogen to growing plants. Therefore, nitrogen concentration in leaves, a plant organ responsible for CO_2 fixation, is considered as a factor significantly modifying the growth rate of both leaves and the storage root.

The primary objective of this study, which tested different levels of supplied nutrients such as N, P and K to sugar beet, was to determine patterns of dry matter accumulation in leaves and storage roots during a vegetative season. Another aim, in fact the key one, was to describe relationships between indices of dry matter accumulation in particular organs of sugar beet plants and nitrogen concentration in leaves and storage roots.

MATERIAL AND METHODS

A static, field experiment was carried out on a private farm in Wieszczyczyn (52°02'N17°05'E) during three consecutive growing seasons 2001, 2002, 2003. The experiment was set up on soil originating from sandy loam underlined by loam, and classified as class IVa, good rye complex according to Polish soil valuation system, and light soil in the agronomical classification. The field trials, arranged in a single-factor design with four replications, consisted of eight treatments:

1. Control (absolute control, i.e. no applied fertilizers), (Control);
2. PK (only phosphorus and potassium), (VPK, Variant PK);
3. NK (only nitrogen and potassium), (VNK);
4. NP (only nitrogen and phosphorus), (VNP);
5. NPK (basic set of nutrients, but P, K rates limited to 25% of adjusted quantity), (V25);
6. NPK (basic set of nutrients, but P, K rates limited to 50% of adjusted quantity), (V50);
7. NPK (basic set of nutrients, full rate of adjusted quantity of nutrients), (V100);
8. $NP^{*}K$ (basic set of nutrients, as in V100 variant, but P was applied as partially acidulated phosphoric rock), (V100P).

The preceding crop for sugar beet (variety *Kassandra*) was winter wheat. The main rates of phosphorus and potassium were calculated annually based on the expected yield of taproots (60 t ha^{-1}) and current soil P and K fertility for the NPK treatment. The actually applied rates of both nutrients followed the experimental design. The rate of fertilizer nitrogen was also calculated annually taking into account three parameters: (i) content of soil mineral nitrogen in the layer 0.9 m, (ii) the expected yield, and (iii) unit nitrogen accumulation of four kg N t^{-1} (taproots + respective amount of tops). All basic fertilizers and the first rate of nitrogen equal 80 kg N ha^{-1} were applied in spring before seedbed preparation. The remaining nitrogen rate was top-dressed at the stage of 3(5) leaf.

For purposes of this study, eight plants were sampled (1 m^2) on eight days of sugar beet growth after sowing (DAS): 40, 55, 77, 92, 113, 134, 155, 175. On each day, a plant sample was divided into sub-samples of leaves and a storage root, and then dried (65°C). The results were expressed on a dry matter (DM) basis. Nitrogen concentration in plant organs was determined by standard macro-Kjeldahl procedure.

The growth analysis procedure was applied to determine the Crop Growth Rate (CGR), but separately for leaves and taproots. For this study, the applied parameters are called Crop Leaves Growth Rate (CLGR) and Crop Root Growth Rate and (CRGR). The calculation was based on the formula:

$$CGR = \frac{W_2 - W_1}{T_2 - T_1}$$

Another growth parameter was the Relative Growth Rate (RGR), referred to as the Relative Growth Rate of Leaves (RGRL) and the Relative Growth Rate of Storage Roots (RGR-SR)for particular organs of sugar beet plants. It was calculated from the formula:

$$RGR = \frac{\ln W_2 - \mathrm{Ln} W_1}{T_2 - T_1}$$

where,

W_2, W_1 – yield of dry matter in two consecutive samplings (kg ha^{-1});

T_2, T_1 – two consecutive sampling dates, days after sowing (DAS)

All data were subjected to conventional analysis of variance using a computer programme package Statistica 7. Simple regression was applied to estimate the strength of relationships between some plant characteristics.

RESULTS AND DISCUSSION

General growth conditions

The experimental field was located on light but productive soil originating from post- glacial loams. Its high, natural productivity depends on the loam underlying the topsoil. During each of the growing seasons, soil content of main available nutrients such as phosphorus, potassium and magnesium (soil + applied in fertilizers) was satisfactory for harvesting good yields of storage roots. Therefore, it was assumed that on plots receiving the full recommended rate of nutrients, the weather conditions were the key factor modifying the plants' growth and final yields of beets.

The evaluation of water management by a sugar beet plantation during the growing season should take into account four components, such as i) total water demand by the sugar beet plantation, ii) annual sum of precipitation, iii) soil water reserves, iv) distribution of precipitation over the growing season, with special emphasis to summer months. The total water requirement, based on sugar beet potential evaporation, in the region where the experiment was located is calculated at the level of 740 mm. The long-term average annual precipitation (1960-2010) is significantly lower, amounting to 600 mm. During the study, it fluctuated from *ca* 400 mm in 2003 to 650 in 2001. It can therefore be concluded that even in good years, sugar beet plant growth and yielding is negatively affected by water stress. The next important parameter of field water management takes into account soil water reserves, which are related to winter precipitation. For light soil, they are assessed at 146 to 210 mm for 1 m soil layer (*Regulation*... 2002). In the analyzed period, high soil water reserves appeared in 2001 and 2002 but not in 2003. For water management by a sugar beet plantation, precipitation in July and August is important. During the study, the reported amounts were as follows 100 mm in 2001, 85 mm in 2002 and 88 in 2003. This is much below the required level (180 mm). In 2002 and especially in 2003, sugar beet plants were exposed to frequent periods of water shortages. In 2003, the first drought lasted from March to the end of June. The second one, much more severe, occurred in August and September. It can therefore be concluded that in good years, like 2001, characterized by ample water supply, the sugar beet plant growth depended on a supply of nutrients, but in other years – on supply of water. This hypothesis was fully corroborated by the experimental data.

As a result of variable growth conditions for sugar beet, the final yields of storage roots showed a distinct and year-specific response to the tested fertilizing variants (detailed data available from the authors). Based on the conducted analysis of variance, five statistically homogenous groups of fertilizing variants were distinguished:

1) 2001:
   a) reduced, comprising three treatments: absolute control, VPK, VKN, (RE), (the average yield of storage roots for this group was 69.82 t ha^{-1});
   b) limited supply of nutrients: VNP, V25, V50, (LI), (83.12 t ha^{-1});
   c) full supply of nutrients: V100, V100P (FS), (94.35 t ha^{-1}).
2) 2002 and 2003:
   a) nitrogen control (absolute control, VPK), (C-N), (42.64 t ha^{-1});
   b) fertilized with nitrogen (all other treatments), (N), (59.74 t ha^{-1}).

The detected differences between the analyzed fertilizing variants are high, clearly indicating much better growth conditions in 2001 than in the other years. In 2001, sugar beet achieved the full yielding potential, although limited by the supply of nutrients, i.e. nitrogen and phosphorus. This level of sugar beet production is possible only under ample water supply (Hills et al. 1990, Kenter et al. 2006). In the other years, yields were reduced by the limited supply of water, which minimized the importance of nutrients, except nitrogen.

Trends of nitrogen concentration in sugar beet organs

As described in the introduction, nitrogen concentration (N_c) in leaves of sugar beet is the key factor shaping the crop canopy development, which in turn is decisive for solar energy fixation (Malnou at al. 2006). Most interest in total N concentration in the storage root focuses on its technological quality (Hoffmann 2005). However, this element can be considered as a reserve used by the storage root to prolong its further growth.

The present study showed, as expected, generally different trends of nitrogen concentration in both beet organs (Table 1). The average nitrogen concentration in leaves was much higher than in storage roots, but showed less variability with respect to the years and fertilizing variants. In the case of leaves, the highest in-season variability, as indicated by the value of the determination coefficient, did not exceed 20%. The general trend, averaged over years, can be best described by the linear-plateau model. During the first part of the season, N concentration (N_c) showed a declining trend, as presented below:

$$N_c = -0.025DAS + 5.13 \text{ for } R^2 = 0.99$$

In the second part of the season, from 113 DAS, it was on a constant, stabilized level of 23 g kg^{-1} d.m.

In the storage root, the total N concentration was lower and showed slightly higher in-season variability than in leaves. The highest concentration occurred at the beginning and in the mid-season, when the lowest N_c in leaves was reported. The general trend of nitrogen concentration in storage roots, averaged over years, can be described by the exponential function, as shown below:

Table 1

Variability of nitrogen concentration in sugar beet organs during the growing season – statistical overview

Statistical parameters	Days after sowing							
	40	57	77	92	113	134	155	175
Leaves								
Average (g kg^{-1})	40.61	38.55	32.57	28.32	23.13	24.35	24.04	23.62
SD* (g kg^{-1})	6.10	4.90	3.40	5.61	2.39	4.15	3.20	2.91
CV** (%)	15.01	12.72	10.42	19.79	10.33	17.04	13.29	12.32
Min. (g kg^{-1})	27.14	27.09	25.62	20.27	17.95	16.26	18.98	18.63
Max. (g kg^{-1})	48.45	45.31	39.09	38.11	26.90	32.09	30.33	31.66
Storage root								
Average (g kg^{-1})	19.50	15.12	11.19	9.52	8.66	8.51	7.36	6.41
SD* (g kg^{-1})	4.97	1.95	1.48	1.34	1.51	1.37	0.99	1.02
CV** (%)	25.49	12.90	13.20	14.08	17.44	16.16	13.42	15.83
Min. (g kg^{-1})	11.63	9.77	7.81	7.81	6.24	6.53	5.16	4.08
Max. (g kg^{-1})	25.37	18.14	13.46	12.01	11.41	11.50	9.00	8.05

*standard deviation, **coeffcient of variation

$$N_c = 26.26DAS^{-0.72} \text{ for } R^2 = 0.98$$

The detailed analysis of the developed regression models showed that the key differences in N concentration trends occurred in the second part of the season. The constant trend as reported for leaves versus the declining one for storage roots can be considered as an improved potential of sugar beet canopy for prolonged production of assimilates (WERKER et al. 1999). These results indicate that plants demonstrating this type of N management should produce higher yields of both storage roots and sugar.

Patterns of dry matter accumulation in leaves

Dry matter yield of sugar beet plants throughout the growing season significantly depended on the fertilizing variants, whose effect was modified by the weather course in each year (Table 2). The interaction between the fertilizing variants and years was significant in three out of eight sampling dates. At harvest, however, irrespectively of the pattern of dry matter accumulation during the growing season, no significant year-to-year variability has been found.

The first estimated growth parameter describes the absolute growth rate of dry matter accumulation. In 2001, the developed curves showed almost the same shape during the course of the growing season (Figure 1). During the first period of the season, up to 92 day of vegetation (DAS), the rate

Table 2

Statistical evaluation of main factors affecting dry matter accumulation in sugar beet leaves during the growing season (Mg ha^{-1} d.m.)

Factors	Level of factor	Days after sowing, DAS							
		40	57	77	92	113	134	155	175
Experimental variants (V)	control	0.068	0.266	0.708	2.313	2.868	3.520	3.586	3.050
	PK	0.093	0.360	1.084	2.738	3.126	3.517	3.269	3.594
	KN	0.188	0.779	2.038	4.580	5.517	4.785	4.517	4.789
	PN	0.169	0.689	1.793	3.613	4.603	4.672	4.759	4.325
	W25	0.171	0.854	2.264	4.283	5.641	4.460	4.724	4.597
	W50	0.183	0.864	2.094	4.842	5.40	4.152	4.562	4.655
	W100	0.210	0.857	2.023	3.924	5.423	5.029	4.406	4.475
	W100P	0.208	0.800	2.094	4.626	4.800	4.722	4.482	4.817
$LSD_{0.05}$	0.077	0.352	0.704	1.200	1.304	2.720	1.107	0.797	Years (Y)
Years (Y)	2001	0.181	0.463	1.495	5.171	6.028	5.982	5.181	4.109
	2002	0.204	1.365	2.764	3.922	4.126	3.597	4.309	4.505
	2003	0.098	0.222	1.027	2.501	3.727	4.018	3.375	4.307
F-factor for years		***	***	***	***	***	***	***	n.s.
F-factor for years and variants		n.s.	***	*	n.s.	n.s.	n.s.	*	n.s.

*, *** – probability levels of 0.05; 0.001; n.s. – non significant

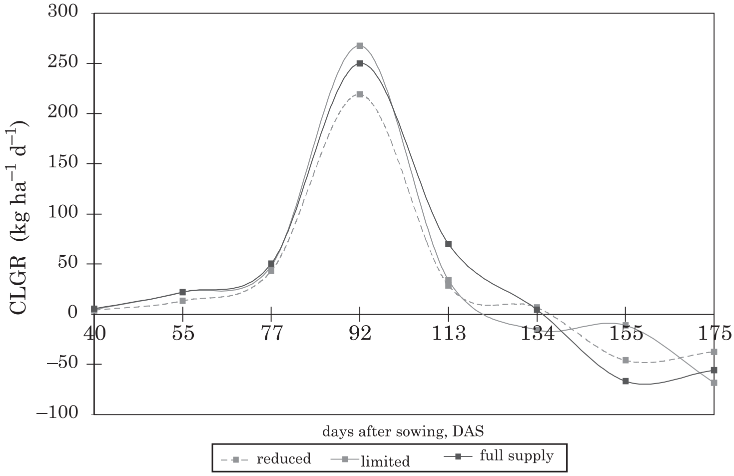

Fig. 1. Dynamics of the growth of dry matter in leaves against the background of nutrient system management, 2001 season

of the dry matter yield increase followed an exponential model, reaching the maximum. From 92 DAS on, the rate of dry matter accumulation showed a dramatic, variant-specific decline,. At this stage of the plant growth, the order of the variants was as follows:

limited > full supply > reduced.

In 2002 and 2003, patterns of dry matter accumulation by leaves were only seemingly similar to those found in 2001 (Figure 2). As in 2001, the top growth rate was reached on 92 DAS. However, on this specific day, the reported values were three-fold lower.

The second growth parameter, relative growth rate (RGR), generally confirmed the differences in dry matter accumulation in leaves. In 2001, the highest values, irrespective of the treatment, appeared at the beginning of vegetation (Figure 3). However, a secondary, but much smaller peak appeared on 92 DAS. The beginning of this secondary dry matter yield increase took place at BBCH 43 stage, when sugar beet plants reached the LAI of 3.0. This level of plant canopy is thought to fully exploit available solar radiation (MALNOU 2006). The secondary increase in sugar beet canopy can be only explained by an ample supply of soil nitrogen. At that particular period, the root system of sugar beet plants reaches the final size and enables plants to penetrate deep soil layers. In the other years, the general trend was almost identical, but the peaks were much lower, and attributed only to the Control-N treatments (Figure 4).

The main hypothesis of the study is that the N concentration in leaves determines their rate of growth. The expected relationships between N_c in

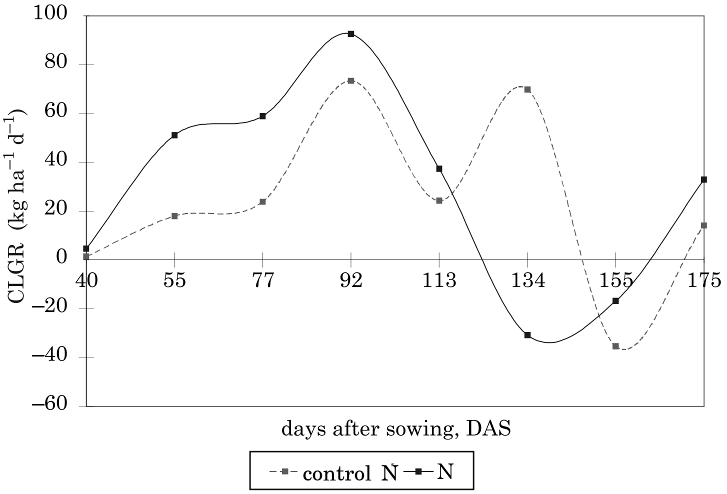

Fig. 2. Dynamics of the growth of dry matter in leaves against the background of nutrient system management, averaged over 2002 and 2003 seasons

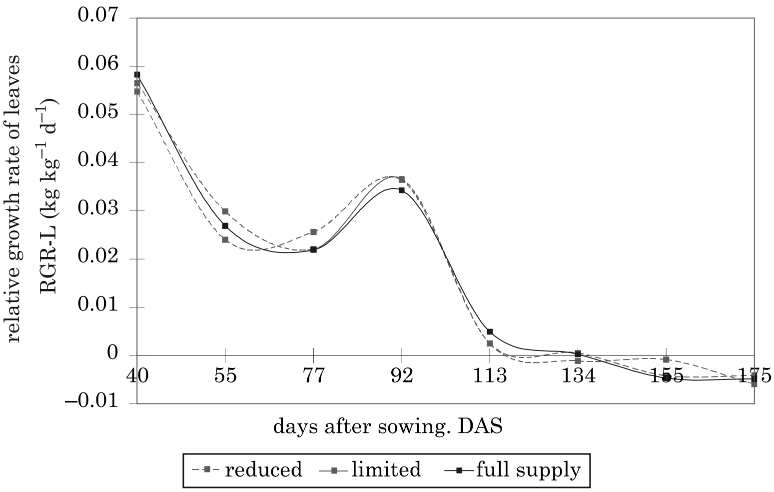

Fig. 3. The relative rate of dry matter growth in leaves against the background of nutrient system management, 2001

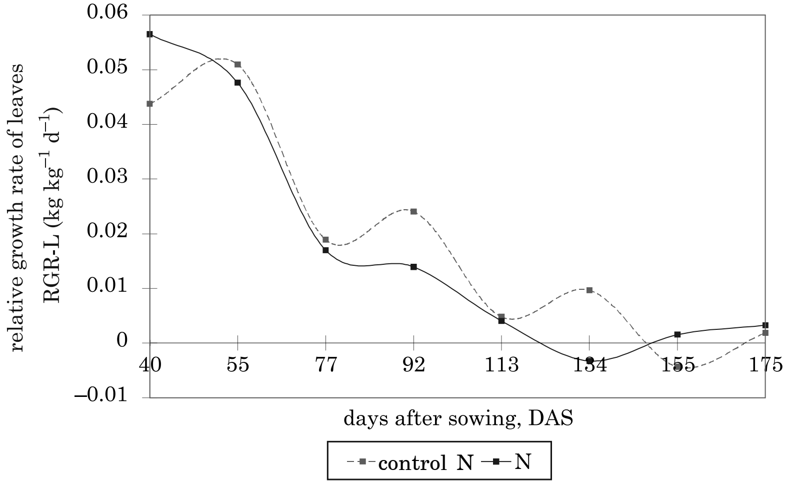

Fig. 4. The relative rate of dry matter growth in leaves against the background of nutrient system management, averaged over 2002 and 2003 seasons

leaves throughout the sugar beet growing season were revealed only for the RGR parameters. Despite the plotted trends of N concentrations during the the growing season (see Table 1), the calculated relationships were subordinated to dry matter trends:

1) 2001:
   a) reduced: $RGR = 0.018N_c - 0.032$ for $n = 8$, $R^2 = 0.70$ and $P = 0.01$;
   b) limited: $RGR = 0.020N_c - 0.041$ for $n = 8$, $R^2 = 0.73$ and $P = 0.01$;
   c) full supply: $RGR = 0.019N_c - 0.039$ for $n = 8$, $R^2 = 0.74$ and $P = 0.001$.
2) 2002+2003:
   a) control-N: $RGR = 0.041N_c - 0.088$ for $n = 8$, $R^2 = 0.88$ and $P = 0.001$;
   b) N: $RGR = 0.035N_c - 0.090$ for $n = 8$, $R^2 = 0.89$ and $P = 0.001$.

As the above equations show, in 2001 the rate of dry matter increase per unit of nitrogen was twice as low as compared in the other years. However, at harvest, dry matter yield of leaves was different only because of the N supply. Therefore, much higher dry matter yield growth per unit N concentration, as found in 2002 and 2003, can be considered as an indicator of the growth rate compensation. This does not agree with the thesis formulated by Boiffin et al. (1992), who underlined the effect of the sugar beet growth rate in the early stages of development on its capability to accumulate dry matter in subsequent stages. In the light of the present study, it can be said that sugar beet plants are able to compensate their rate of growth during the growing season.

Patterns of dry matter accumulation in storage roots

Accumulation of dry matter in storage roots during the growing season, except the earliest stages, showed significant dependence on the fertilizing treatments, i.e. groups of variants (Table 3). However, it showed high year-to-year variability, in turn modifying the effect of the tested fertilizing variants during most of the growing season. Generally, a trend of dry matter accumulation, irrespectively of the treatment, was progressive during the growing season, but year-specific. Therefore, patterns of dry matter dynamics of the storage root as described by the growth analysis were elaborated

Table 3

Statistical evaluation of main factors affecting dry matter accumulation in sugar beet storage root during the growing season (Mg ha^{-1} d.m.)

Factors	Level of factor	Days after sowing, DAS							
		40	57	77	92	113	134	155	175
Experimental variants (V)	control	0.004	0.094	0.642	2.394	5.350	7.003	8.94	14.26
	PK	0.007	0.175	1.034	2.985	5.290	8.944	11.83	15.20
	KN	0.19	0.339	1.458	4.668	7.837	9.792	13.91	14.68
	PN	0.018	0.222	1.450	3.800	7.432	9.912	13.84	13.37
	W25	0.019	0.345	1.668	4.413	8.238	9.815	14.82	17.39
	W50	0.030	0.339	1.482	4.913	8.273	10.43	14.02	18.19
	W100	0.021	0.337	1.371	4.508	9.190	11.17	14.35	17.62
	W100P	0.021	0.348	1.787	4.971	7.258	14.00	13.86	18.38
$LSD_{0.05}$	0.077	0.010	0.070	0.376	0.370	0.665	0.705	0.860	0.920
Years (Y)	2001	0.019	0.406	1.252	5.380	8.038	10.09	14.65	19.92
	2002	0.020	0.142	2.155	3.413	6.766	10.05	12.33	14.11
	2003	0.012	0.277	0.679	3.451	7.271	8.843	12.61	14.51
F-factor for years		n.s.	n.s	*	***	***	***	***	*
F-factor for years and variants		n.s.	n.s.	*	***	***	***	***	n.s.

*, *** – probability levels of 0.05; 0.001; n.s. – non significant

separately for 2001 and for the other two years. The absolute taproot growth rate of in 2001, despite some resemblances, was treatment-specific (Figure 5). Dry matter yield of taproots increased, irrespective of the fertilizing treatment, up to 92 DAS, when it peaked and then rapidly declined. At this particular stage of the beet growth, the order of fertilizing groups was as follows:

$$\text{reduced} < \text{full supply} < \text{limited.}$$

In the second part of the season, the rate of growth was highly variable, showing treatment-specific recovery. For the Reduced group, it was detectable in the first decade of September, followed by a subsequent decline.

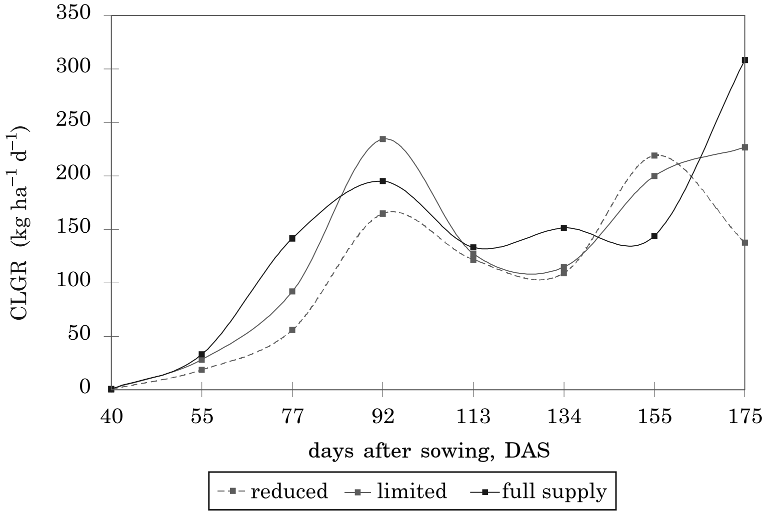

Fig. 5. Dynamics of the growth of dry matter in storage root growth against the background of nutrient system management, 2001 season

For the Limited group of variants, the secondary increase started at the same time as reported for the Reduced variants, but it progressed up to the end of vegetation. A completely different growth pattern was noted to the FS set of variants. In this case, the rate of storage dry matter yield growth was much higher during most of August than for the other treatments. The secondary growth recovery, higher than the first growth, occurred at the end of the growing season. The resulting patterns can be explained by both N the soil resource of nitrogen and its availability as guaranteed by an adequate supply of P and K. The model of the storage root growth as described for the FS group of variants, implicitly corroborate the importance of the growing season duration as the key factor responsible for attaining the sugar beet yield potential (Kenter et al. 2006).

The above hypothesis is fully confirmed by regression models developed for the other two years (Figure 6). As in 2001, the dry matter yield of taproots increased exponentially up to 92 DAS. At that particular sugar beet growth stage, the storage root reached the highest rate of absolute growth, albeit limited by the nitrogen supply. For plants fertilized with nitrogen, it was 200 kg ha^{-1} d^{-1}, whereas for the Control-N group, it reached 120 kg ha^{-1} d^{-1}. The value for the N group was at the level determined in 2001 for the Limited group of variants. In the second part of the season, its dynamics showed high variability, but went to a decline at the end. Quite a different pattern was observed for the Control-N variant, where the top rate of growth was noted on 134 DAS, preceding a decline and a subsequent increase.

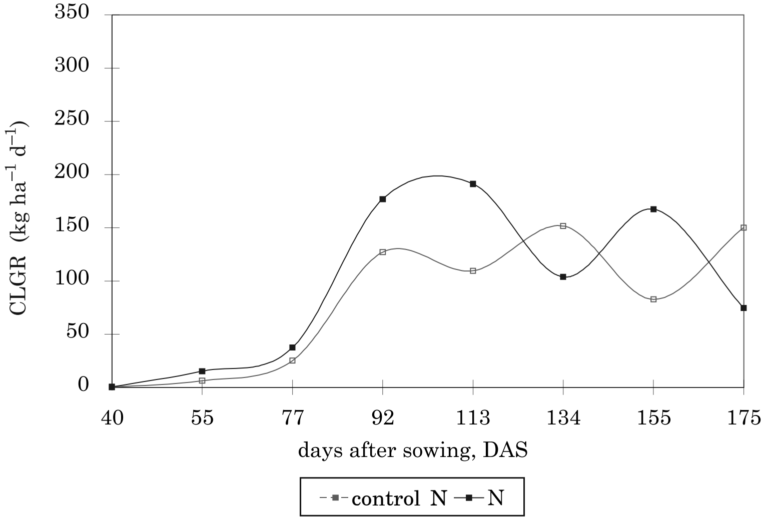

Fig. 6. Dynamics of the growth of dry matter in storage root growth against the background of nutrient system management, averaged over 2002 and 2003 seasons

The relative rate of growth, as the second indicator of the storage roots unit growth, despite significant effects of all the factors, showed strong resemblance among the treatments throughout the growing season (Figures 7 and 8). In both groups of years, two stages of growth are important. As presented by the developed models, the order of variants at the stage of

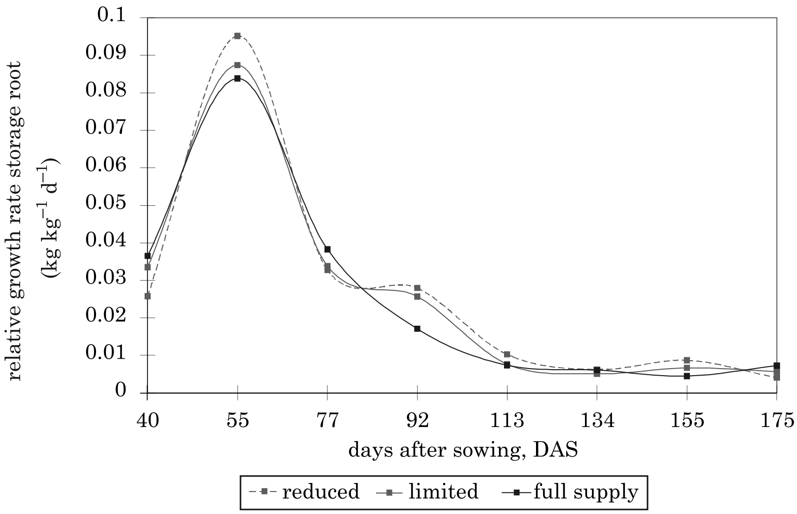

Fig. 7. The relative rate of storage roots dry matter growth against the background of nutrient system management, 2001 season

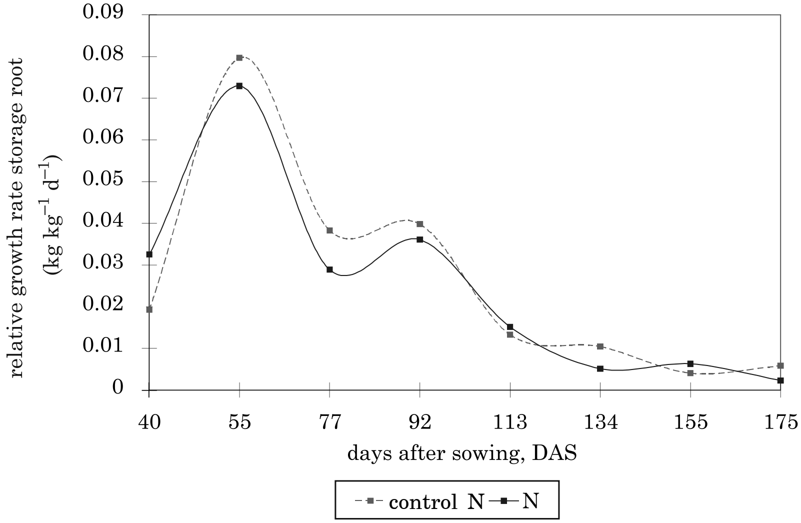

Fig. 8. The relative rate of storage roots dry matter growth against the background of nutrient system management, averaged over 2002 and 2003 seasons

7th leaf (55 DAS) is opposite to the one at the stage of 4th leaf (40 DAS). The observed compensation of the RGR of taproots was much more distinct in 2002 and 2003 than in 2001. However, the level of compensation under conditions of good water supply, i.e. in 2001, was quantitatively much higher.

The expected relationships between N concentration (N_c) in taproots throughout the sugar beet growing season were revealed only for the RGR parameter, as presented below:

1) 2001:
   a) reduced: RGR = $0.012N_c - 0.077$ for $n = 8$, $R^2 = 0.\ 89$ and $P = 0.001$;
   b) limited: RGR = $0.010N_c - 0.073$ for $n = 8$, $R^2 = 0.86$ and $P = 0.001$;
   c) full supply: RGR = $0.012N_c - 0.086$ for $n = 8$, $R^2 = 0.89$ and $P = 0.001$.

3) 2002+2003:
   a) control-N: RGR = $0.010N_c - 0.056$ for $n = 8$, $R^2 = 0.92$ and P = 0.001;
   b) N: RGR = $0.007N_c - 0.051$ for $n = 8$, $R^2 = 0.89$ and $P = 0.001$.

The developed equations clearly indicate higher productivity of a unit concentrated nitrogen in 2001 than in the other years. The mean values for the groups of variants underline the ability of sugar beet plant to compensate growth of taproots in response to the supply of nitrogen. In the other years, the unit productivity of nitrogen was much lower, in turn indicating some limitation of its supply to growing plants. It can therefore be concluded that the relative growth rate of storage roots reveals high sensitivity to the supply of nitrogen. There the thesis formulated by Boiffin et al. (1992) refers fully to this part of sugar beet crop.

Nitrogen concentration and fraction of storage root

One of the most important indices of dry matter partitioning in sugar beet crop is the storage root's fraction (SR_f). This parameter defines the dry matter fraction located in the storage root. The trends of SR_f can be described by the liner regression model (Figure 9). In 2001, its seasonal progress was highly complicated, achieving a linear trend only in the second part of the season, from 92 DAS onwards. The linear course of the trend can be considered as synchronous dry matter partitioning between leaves and the taproot. For the N group of variants, even in this period, a better fit of the real data was obtained using the quadrate model. This type of a model suggests some limitation of the taproot growth due to a prolonged leaf growth induced by the extra N supply.

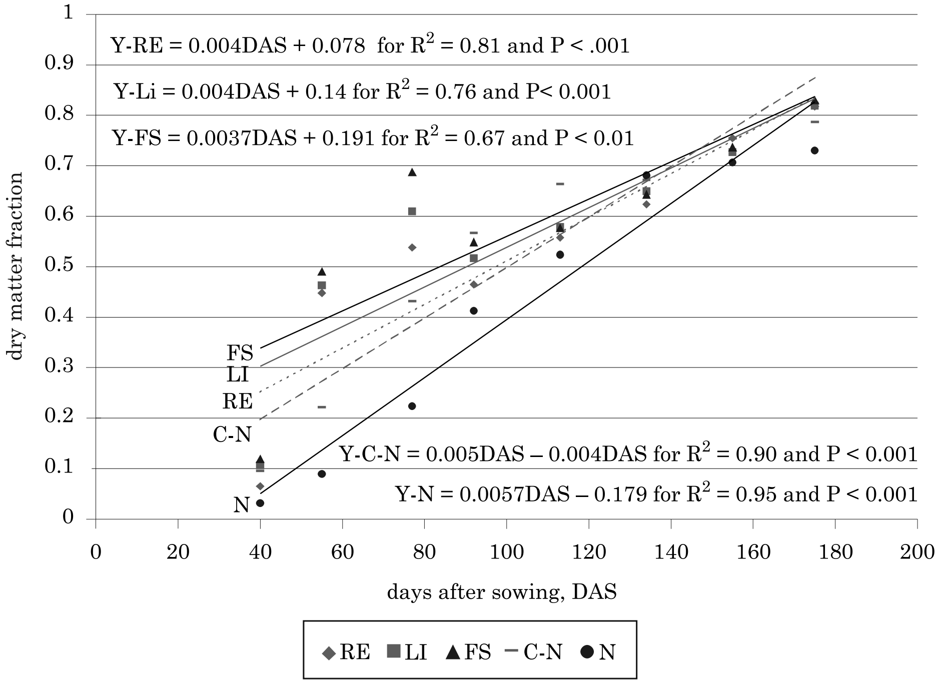

Fig. 9. Trends of storage root fraction in the course of the growing season against the background of nutrient system management

The partitioning of assimilates to leaves and the storage root is strongly influenced by the soil nitrogen dynamics (Werker et al. 1999). Hence, the storage root's fraction index depends on a nitrogen supply to sugar beet plants during the plant growth. Thus, a hypothesis was put forth, suggesting that the N concentration in both plant organs significantly affects the SR_f index. The developed equations based on the means for the distinguished groups of fertilizing variants are as follows:

1) 2001:
   a) reduced:
      i. leaves: $SR_f = -0.082N_{cL}^3 + 0.761N_{cL}^2 - 2.397N_{cL} + 3.076$ for $R^2 = 0.82$;
      ii. taproots: $SR_f = -0.349N_{cTR} + 0.908$ for $R^2 = 0.89$;
   b) limited:
      i. leaves: $SR_f = -0.256N_{cL}^3 + 2.502N_{cL}^2 - 8.029N_{cL} + 8.996$ or $R^2 = 0.94$;
      ii. taproots: $SR_f = -0.356N_{cTR} + 0.962$ for $R^2 = 0.93$;
   c) Full supply:
      i. leaves: $SR_f = -0.280N_{cL}^3 + 2.715N_{cL}^2 - 8.533N_{cL} + 9.305$ for $R^2 = 0.99$;
      ii. taproots: $SR_f = -0.366N_{cTR} + 0.989$ for $R^2 = 0.89$;
2) 2002 + 2003:
   a) control N
      i. leaves: $SR_f = -0.527N_{cL} + 1.898$ for $R^2 = 0.92$;
      ii. taproots: $SR_f = -0.699N_{cL} + 1.149$ for $R^2 = 0.97$;
   b) N
      i. leaves: $SR_f = -0.430N_{cL} + 1.741$ for $R^2 = 0.85$;
      ii. taproots: $SR_f = -0.683N_{cL} + 1.188$ for $R^2 = 0.91$.

The presented sets of equations implicitly allow us to make a simple evaluation of the weather impact during the growing season on the sugar beet growth. In 2001, characterized by an ample water supply during the critical plant growth stages, the weather effect of N concentration in leaves was highly complicated. As shown in Figure 10, this relationship shows a lag-decline phase, characterized by a decline in the of storage root fraction with respect to N concentration, termed as a transition point. The duration of

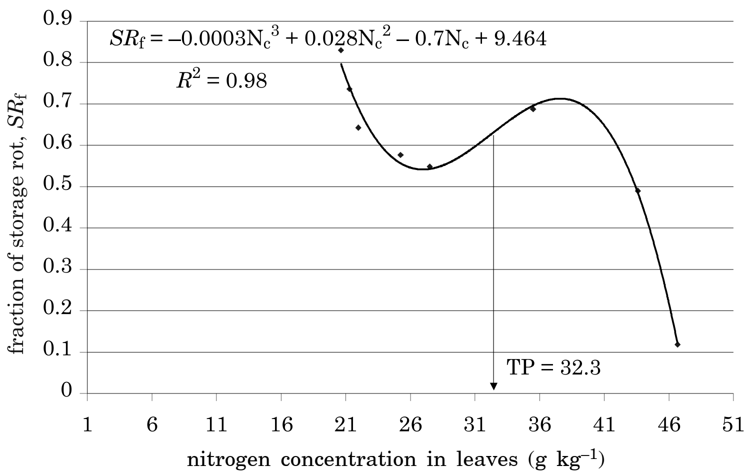

Fig. 10. Fraction of storage root as a function of nitrogen concentration in leaves, the full supply variant, 2001, TP – transition point

the phase and the position of the transition point were variant-specific, with the latter being the low for the FS (TP – 32.3 g N kg^{-1}), slightly higher for the Limited (TP – 32.6 g N kg^{-1}) and the lowest for the Reduced (TP – 30.9 g N kg^{-1}) group of fertilizing variants. Its occurrence can be explained by an extra N supply both from soil resources and the applied N fertilizers, which accelerated the rate of leaf growth. Nitrogen taken up by beet plants prolongs the period of foliage-dominated growth, but without negative impact on the storage root growth. This conclusion is supported by the linear dependence of the storage root fraction on the nitrogen concentration in this beet organ (Figure 9). This pattern of SR_f dependence on nitrogen concentration in leaves was successful, as corroborated by much higher yields of storage roots and sugar in 2001 as compared to the other years. In 2002 and 2003, the SR_f depended linearly on the N concentration in both leaves and storage roots. Therefore, the compensatory pattern of the growth sugar beet organs can be considered as a model, which ensures that sugar beet attains its full yielding potential. However, it is only possible under an ample supply of both water and nutrients. Under water shortage, sugar beet plants are not able to convert the accumulated nitrogen, as indicated by its much higher content in both leaves and storage roots, in productive biomass, observed in 2002 and 2003.

CONCLUSIONS

1. Nitrogen concentration in sugar beet organs declined during the growing season, according to a linear-plateau regression model in leaves but exponentially in storage roots.

2. The absolute rates of leaf and storage root growth peaked in the mid-season, from 92 and 113 day after sowing; the effect of the year was stronger on leaves than on roots, which responded significantly to a nutrient supply.

3. Nitrogen concentration in both organs of sugar beet significantly affected dry matter growth of leaves and the taproot.

4. Sugar beet plants can compensate their rate of growth; compensation is more efficient in years favorable to sugar beet growth.

5. Dry matter partitioning to the storage root is significantly related to nitrogen concentration in both leaves and the target plant organ; the linear dependence is typical for the storage root, underlying its internal conservatism.

6. The full realization of sugar yield production potential depends on the relationships between N concentration in leaves and the storage root; when these relationships follow a linear regression models, it is indicative of some type of limitation to the crop growth during the growing season.

REFERENCES

BOIFFIN J., DURR C., FLEURY A., MARIN-LAFLECHE A., MAILLET I. 1992. *Analysis of the* variability of sugar beet (*Beta vulgaris* L) *growth during the early stages*. I. *Influence of various conditions on crop establishment.* Agronomie, 12: 515:525.

CAKMAK I., KIRKBY E. 2008. *Role of potassium nutrition in growth and stress tolerance*. Physiol. Plant., V 133(4): 692-704.

FAOSTAT. Available online at: http://faostat.fao.org/default.aspx. (Verified 2011.12.28).

FRECKLETON R., WATKINSON A., WEEB D., THOMAS T. 1999. *Yield of sugar in relation to weather and nutrients*. Agr. Forest Meteorol., 93: 39-51.

GRZEBISZ W., MUSOLF R., BARŁOG P., POTARZYCKI J. 2002. *Potassium fertilization, water shortages during vegetation and crop yielding variability, the case of sugar beet*. Biul. IHAR, 222: 19-30.

HERLICHY M. 1992. *Effects of N, P and K on yield and quality of sugar beet*. Irish J. Agr. Food Res., 31, 35-49.

HILLS F.J., WINTER S.R., HENDERSON D.W. 1990. *Sugarbeet*. In: *Irrigation of agricultural crops*. ASA-CSSA-SSSA – Agronomy Monograph, 30: 795-810.

HOFFMANN C. 2005. *Changes in N composition of sugar beet varieties in response to increasing N supply*. J. Agron. Crop Sci., 191: 138-145.

JONGMAN R., BUNCE R., METZGER R. 2006. *Objectives and applications of a statistical environmental stratification of Europe.* Landscape Ecol., 21, 409-419.

KENTER C., HOFFMANN C., MAERLAENDER B. 2006. *Effects of weather variables on sugar beet yield development (Beta vulgaris* L.). Eur. J. Agron., 24: 62-69.

MALNOU C., JAGGARD K., SPARKES D. 2006. *A canopy approach to nitrogen fertilizer recommendation for the sugar beet.* Eur. J. Agron., 25: 254-263.

MILFORD G., ARMSTRONG M., JARVIS P., HOUGHTON B., BELLET-TRAVERS D., JONES J., LEIGH R. 2000. *Effect of potassium fertilizer on yield, quality and potassium off-take of sugar beet crops grown on soils of different potassium status*. J. Agr. Sci., Cambridge, 135: 1-10.

OLESEN J., TRNKA M., KERSEBAUM K. 2011. *Impacts and adaptation of European crop production systems to climate change.* Eur. J. Agron., 34: 96-112.

Regulation of the Minister for Environmental Protection of 23 December 2002 on criteria for determination of water bodies sensitive to nitrogen compound contamination from agricultural sources. Dz.U. Nr 241, poz. 2093. (in Polish)

SUPIT I., VAN DIEPEN C., DE WIT A. 2010. *Recent changes in the climatic yield potential of various crops in Europe*. Agr. Syst., 103: 683-694.

WERKER R., JAGGARD K., ALLISON M. 1999. *Modelling partitioning between structure and storage in sugar beet: effects of drought and soil nitrogen.* Plant Soil, 207: 97-106.

J. Elem. s. 409–419 DOI: 10.5601/jelem.2012.17.3.04

SPECIATION OF CARBON AND SELECTED METALS IN SPENT MUSHROOM SUBSTRATES

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Abstract

Increasing amounts of spent mushroom substrate in the Siedlce region and the unsolved problem of its disposal has encouraged researchers to study its properties and, subsequently, the possibility of its utilisation as fertiliser. Samples of (fresh) substrate after 6-week cultivation of the white mushroom *Agaricus bisporus* in two modern cultivation halls were used as the studied material. The determined parameters included its pH and the content of dry matter, ash, mineral nitrogen as well as total carbon and nitrogen. The main aim of the study was to determine the speciation of organic carbon and metals in spent mushroom substrates. To this end, their sequential extraction was carried out by the method described by He et al. (1995), recommended for materials with a high organic matter content. The extraction procedure yielded six operational fractions of carbon and metals and separated the humic substances into fractions of fulvic and humic acids and metals bound with them. Sequential application of extraction reagents of increasing ability to extract carbon and metal from compounds ($H_2O \rightarrow KNO_3 \rightarrow Na_4P_2O_7 \rightarrow NaOH \rightarrow HNO_3 \rightarrow$ aqua regia) allowed us to assess the potential bioavailability and resistance to biodegradation, as well as current and potential hazards to the environment (phytoavailability, mobility). It has been found that spent mushroom substrate could be recommended as fertiliser because it can enrich soils with organic matter. The largest amounts of carbon (62%) were found in the stable residual fraction, whereas the bioavailable fractions contained about 10% of carbon. Concentrations of metals (Mg, Ca, Fe, Mn, Ba, Sr, Zn, Cu, Ni, Cr, Pb) in the material were variable, but most metals were found in the fraction strongly bound with organic and mineral compounds (30.8-80.6%). Ca, Mg, Mn, Sr, Fe, and Zn were predominantly bound with mobile fulvic acids, whereas Cu, Ni, Ba, and Pb – with more stable humic acids.

Key words: spent mushroom substrate, sequential extraction, carbon fractions, metal fractions.

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SPECJACJA WĘGLA I WYBRANYCH METALI W PODŁOŻU PO UPRAWIE PIECZARKI

Abstract

Zwiększająca się ilość podłoża po uprawie pieczarek w rejonie siedleckim oraz nierozwiązany problem jego utylizacji sprowokowały do badań jego właściwości, a w perspektywie także nawozowego wykorzystania. Materiał badawczy stanowiły próbki podłoża (świeżego) po 6-tygodniowej uprawie pieczarki białej *Agaricus bisporus* z dwóch nowoczesnych hal uprawowych w regionie siedleckim. Oznaczono w nich pH, zawartość suchej masy, popiołu, azotu w formach mineralnych oraz całkowitą zawartość węgla i azotu. Celem badań było określenie specjacji węgla związków organicznych i metali w badanych podłożach popieczarkowych z zastosowaniem ich sekwencyjnej ekstrakcji, na podstawie metody HE i in. (1995) – polecanej dla materiałów o wysokiej zawartości materii organicznej. Procedura ekstrakcyjna umożliwiła wydzielenie 6 frakcji operacyjnych węgla i metali oraz rozdzielenie substancji humusowych na frakcję kwasów fulwowych i huminowych oraz metale z nimi powiązane. Sekwencyjne zastosowanie odczynników ekstrakcyjnych o zwiększających się właściwościach wydzielania węgla i metali w związkach (H_2O → KNO_3 → $Na_4P_2O_7$ → NaOH → HNO_3 → woda królewska) pozwoliło ocenić potencjalną biodostępność i odporność na biodegradację, a w przypadku metali ciężkich także aktualne i potencjalne zagrożenie dla środowiska (fitoprzyswajalność, mobilność). Stwierdzono, iż podłoże po uprawie pieczarki powinno być zalecane do nawozowego stosowania, gdyż ma znaczny potencjał wzbogacania gleb w związki organiczne. Najwięcej węgla (62%) było związane ze stabilną frakcją rezydualną, a we frakcjach biodostępnych – ok. 10%. Zawartość metali (Mg, Ca, Fe, Mn, Ba, Sr, Zn, Cu, Ni, Cr, Pb) w badanym materiale była zróżnicowana, przy czym większość z nich występowała we frakcji mocno związanej ze związkami organicznymi i mineralnymi (30,8-80,6%). Z mobilnymi kwasami fulwowymi były związane w większych ilościach Ca, Mg, Mn, Sr, Fe, i Zn, a z bardziej stabilnymi kwasami huminowymi – Cu, Ni, Ba, i Pb.

Słowa kluczowe: podłoże popieczarkowe, ekstrakcja sekwencyjna, frakcje węgla, frakcje metali.

INTRODUCTION

The cultivation of mushrooms in Poland has been developing well in the recent years and concentrated in the region near Siedlce and Łosice, where latest production technologies are implemented. With the production output of 250-300 thousand tonnes, Poland is the largest producer in Europe and the third largest one in the world. Mushroom substrate consists of mainly straw and poultry litter (frequently with added urea, gypsum, coconut fibre, highmoor peat and soybean protein). The surface cover is made of lowmoor peat with dolomite, defecation lime or meadow chalk. Modern mushroom farms cultivate mushroom mostly on phase III substrate, i.e. grown-through with mycellium outside a cultivation hall, during one of the stages of its production. Spent mushroom substrate (substrate and cover grown-through with mycelium hyphae) is obtained after 6 weeks of intensive cultivation and two or three harvests of mushrooms. The local aggregation of mushroom farming, with consequently large amounts of spent substrate, forces us to look for methods of some rational utilisation of spent substrate which would be safe to the environment. Uncontrolled dumping in the neighbourhood of large mushroom farms poses a risk that large amounts of bioelements will migrate outside prisms so that the surrounding area will become eutrophic. Rational utilisation of spent mushroom substrate and using it as fertiliser seems to be the most appropriate form of its disposal, as it will improve the balance of nutrients, especially in low-humus soils (a disadvantageous balance of organic matter). The results of scientific research have indicated that this solution is possible, especially because of relatively high concentrations of nutrients in spent substrate (Stewart et al. 1998, Zmora-Nahum et al. 2007, Jordan et al 2008, Kalembasa, Majchrowska-Safaryan 2009a,b, Medina et al. 2009, Rutkowska et al. 2009). According to the principles of modern technology, spent mushroom cultivation substrate is disinfected thermally at 70°C, which restrains infestation of agricultural ecosystems with weed seeds and pathogens when mushroom substrate is used as fertiliser. The Polish literature does not contain any thorough reports on properties of organic waste, especially on speciation of metals bound with carbon compounds. This study is an attempt at rectifying the situation, particularly because the previous studies on metal speciation have not always taken into account the main components of substrates, i.e. organic matter.

The aim of the study was to evaluate selected properties and especially to determine the speciation of organic carbon and metals in substrate after 6 weeks of cultivation of white mushrooms, with respect to its later use as fertiliser.

MATERIAL AND METHODS

Samples of spent substrate after 6 weeks of cultivation of the white mushroom *Agaricus bisporus* from two modern cultivation halls in the Siedlce region were used as the studied material. The samples (covers and substrate, together called substrate) were taken at several points (from shelves at different height), after steam disinfection and before substrate with mushrooms was removed. Each averaged sample was analysed in a laboratory in three replications. Determinations included pH (potentiometrically) and mineral nitrogen (Min-N), by the distillation method, after extraction of samples with 1 mol KCl dm^{-3}. Ash content was determined gravimetrically, following mineralisation in a muffle furnace (temp. 450°C). For other analyses, samples were dried at 40°C and ground in an agate mill (O < 0.25 mm). Total carbon (TC) and nitrogen (TN) content was determined with a Series II 2400 autoanalyser, manufactured by Perkin Elmer, with a thermal conductivity detector and acetanilide as the reference standard substance. The results were calculated with reference to absolutely dry weight of the studied material, which was determined gravimetrically after drying the substrate at 105°C.

Sequential extraction of organic carbon and metals partially bound with them was carried out by the method developed by He et al. (1995), recommended for materials with a high organic content. The extraction procedure isolates six operational fractions of carbon and metals and separates humic substances into fractions of fulvic and humic acids (Table 1). The extraction was conducted in polypropylene centrifuge flasks on a shaker-type agitator (soil sample weight-to-extraction solution ratio was 1:10) for 24 h. The solutions were clarified by centrifuging for 30 minutes (12,000 rpm) and vacuum filtering. During the stage of extraction of humic substances, potassium sul-

Table 1

Fractions of organic carbon compounds and metals isolated by the modified method developed by He et al. (1995)

Fraction	Operational fraction	Extraction reagent
F1	water-soluble	deionised water H_2O
F2	exchangeably-bound with the solid phase, mainly by electrostatic forces	potassium nitrate (V) 1 mol KNO_3 dm^{-3}
F3 $F3_{FA}$ $F3_{HA}$	metals complexed with humic substances, divided into fulvic and humic acids	tetrasodium diphosphate (V) 0.1 mol $Na_4P_2O_7$ dm^{-3}
F4 $F4_{FA}$ $F4_{HA}$	metals bound with humic substances, divided into fulvic and humic acids	sodium hydroxide 0.1 mol NaOH dm^{-3}
F5	metals strongly bound with organic and mineral solid phase	nitric (V) acid 4 mol HNO_3 dm^{-3}
F6	residual – post-extraction residue	aqua regia HCl : HNO_3, v/v =3/1

phate (VI) was added to the flocculate colloids. Some of the extract from humic substances ($Na_4P_2O_7$ and NaOH) was acidified with 3 mol H_2SO_4 dm^{-3} to precipitate the humic acid fraction (pH = 1.5); the effectiveness of separation of fulvic acids from humic acids was enhanced by centrifuging. Organic carbon content in the extracts was determined by the oxidative-titrimetric method (Kalembasa, 1991). Carbon content in the residual fraction was determined as the difference with respect to the total content of the element; carbon content as humic acids was calculated as the difference between the amount in the extract (F3 and F4) and the amount in the fulvic acid fraction. Metal content in the extracts was determined with an inductively coupled plasma atomic emission spectroscope (ICP – AES, Optima 3200 RL manufactured by Perkin Elmer), after the solutions were mineralised with nitric (V) acid and hydrogen peroxide. Metal content in the humic acid fraction was calculated in the same manner as for carbon. The total metal content was calculated by adding up the content in all fractions (F1 – F6).

The extraction procedure was modified for carbon content determination in the solutions by the oxidative-titrimetric method. According to the original guidelines, large amounts of chlorine are introduced to the extraction system (KCl solution with exchangeable fraction, HCl solution to precipitate humic acids and KCl to flocculate colloids). The content of chloride ions in a material sample elevates the results of the determination of carbon or makes it impossible to determine it due to the reduction of Cr^{6+} ions (by Cl?) in the oxidising solution (with $K_2Cr_2O_7$) during mineralization (Kalembasa 1991).

RESULTS AND DISCUSSION

The analyzed substrates were found to contain more dry matter and ash than manure; the pH was slightly acidic (Table 2). The total carbon content confirms a high potential of substrates for enriching soils with organic matter when used as fertiliser. Nitrogen content (TN) and low values of C/N ratio indicate good fertilising properties of the waste material. When added to soil, its narrow C/N ratio will positively affect mineralisation of organic matter and release of nutrients contained in substrate. Over 96% of nitrogen in the analyzed substrates was bound in organic compounds. The reduced ammonium form dominated the mineral nitrogen species (being the result of the ammonification process, which occurs during mushroom cultivation), and oxidised nitric forms were in minority. Other reports (Zmora-Nahum et al. 2007, Jordan et al. 2008, Kalembasa, Majchrowska-Safaryan 2009a, Rutkowska et al. 2009) have indicated certain differentiation of the C and N content and C/N ratio in spent mushroom substrates, depending on the method of preparation and particularly on the components used in its production.

Table 2

Some properties of analyzed spent mushroom substrates

Spent mushroom substrate	pH_{KCl}	Dry matter	Ash	TC	TN	TC/TN	Org-N	Min-N	$N-NH_4$	$N-NO_x$
		%	g kg^{-1} d.m.				% of TN		g kg^{-1} d.m.	
A	6.23	30.5	400	287	23.2	12.4	97.1	2.91	0.639	0.036
B	6.29	31.8	411	252	19.3	13.1	96.4	3.63	0.676	0.025
Mean	-	31.2	406	270	21.3	12.8	96.8	3.27	0.658	0.031

The sequential analysis resulted in the isolation (in fractions F1, F2, F3, F4, F5) of about 40% of total carbon (Table 3). The remaining part is bound in the residual fraction. Based on the average carbon content, the fractions can be arranged by increasing values: F2 < F5 < F1 ≤ F3 < F4 < F6. It is noteworthy that a large amount of carbon was extracted by water (F1). Organic carbon extracted with H_2O and KNO_3 (F1 and F2) is probably bound in soluble organic compounds. The fractions are represented mainly by simple, low-molecular organic compounds, loosely bound with mineral components of the analyzed material, potentially readily mineralized and mobile in soil, once they are introduced to soil.

Carbon isolated with solutions commonly used in extraction of humic substances – $Na_4P_2O_7$ and NaOH, (probably) represents part of the organic matter transformed in the process of humification (Tables 3, 4); in fraction F3 – humic substances, free and loosely bound as well as complexed with metals; in F4 – humic substances strongly bound with mineral components of organic material. Carbon of humic acids was found to dominate in those fractions, more markedly in fraction F4, which is indicated by the values of C_{HA}/C_{FA} ratio. Prevalence of the humic acid fraction in arable land under

Table 3

Organic carbon fractions in spent mushroom substrates

Spent mushroom substrate	Unit	Extracted organic carbon					F6 residual
		F1 H_2O	F2 KNO_3	F3 $Na_4P_2O_7$	F4 NaOH	F5 HNO_3	
A	g kg^{-1}	23.4	6.60	24.6	43.8	11.9	177
	% of TC	8.16	2.30	8.58	15.3	4.15	61.5
B	g kg^{-1}	20.9	5.25	20.2	35.1	11.0	160
	% of TC	8.28	2.08	8.02	13.9	4.37	63.3
Mean	g kg^{-1}	22.2	5.93	22.4	39.5	11.5	169
	% of TC	8.22	2.19	8.30	14.6	4.26	62.4

Table 4

Contribution of humic substances carbon (%) and ratios of humic to fulvic acids carbons

Spent mushroom substrate	Humic substances C F3 + F4	$Na_4P_2O_7$ extract F3			NaOH extract F4			C_{HA}/C_{FA} combined for humic substances
		C_{FA} (%)	C_{HA} (%)	C_{HA}/C_{FA}	C_{FA} (%)	C_{HA} (%)	C_{HA}/C_{FA}	
A	23.9	2.68	5.90	2.20	2.55	12.7	4.99	3.56
B	21.9	2.23	5.79	2.60	2.77	11.2	4.03	3.39
Mean	22.9	2.46	5.85	2.40	2.70	12.0	4.51	3.48

good soil tillage management is a desirable feature of humus, because it ensures its persistence in soil and a more beneficial effect on soil properties. Carbon contained in the residual fraction F6 in spent mushroom cultivation substrates should be regarded mainly as non-humified organic matter (rather than humus). It mostly consists of non-degradable organic waste (mainly cellulose, hemicellulose, lignin), from straw and peat used in the production of substrate and cover. These substances are highly resistant to degradation and persist the longest in soil.

The total content of the analyzed metals (Table 5) confirms that soils fertilised with spent mushroom substrate can be enriched with some nutrients essential for the proper growth and development of plants. As a result, the balance of nutrients in soil cane be improved to the benefit of a better profitability of agricultural production. Chemical analysis showed that the content of selected metals can be listed in the following sequence according to decreasing content: Ca > Mg > Fe > Mn > Zn > Sr > Ba > Cu > Pb > Cr > Ni. Compared to manure of different origin (MAĆKOWIAK, ŻEBROWSKI 2000, MAZUR, MOKRA 2009), (referred to dry weight and the element), spent mushroom substrates had a much higher content of Ca (about 30-fold more) and Mg (about 3-fold more) as well as a similar content of Fe, Mn, Zn and Cu. The heavy metal content did not exceed the permissible values for fertilisers and plant growth enhancers, which can be used as fertilisers in agriculture (*Regulation...* 2008).

Owing to the extraction procedure applied in the study, it was possible to determine the metal content in potentially bioavailable and mobile (soluble) forms, bound to a different extent with organic matter. Sequential use of extraction reagents with an increasing ability to separate carbon and metal compounds ($H_2O \rightarrow KNO_3 \rightarrow Na_4P_2O_7 \rightarrow NaOH \rightarrow HNO_3 \rightarrow$ aqua regia), allows us to list fractions of the elements according to the increasing resistance to biodegradation: F1 > F2 > F3 > F4 > F5 > F6. In heavy metals, it allows us to evaluate the current and potential hazard to the environment (phytoavailability, mobility).

Metals contained in the spent mushroom substrates have different properties and a different status in the biosphere: Mg and Ca – main bioelements; Fe, Mn, Zn, Cu, Ni – trace bioelements, essential to plants, humans and animals; Cr – a trace bioelement, essential to humans and animals; Pb – trace element with high toxicity to humans, and Sr and Ba – trace elements which have not been found to be essential to organisms.

When using spent substrate as fertiliser and for potential migration of elements and eutrophication of the environment when it is stored, the water-soluble fraction F1 (bioavailable and easily leachable), the exchangeable fraction F2 (where desorption to a solution is possible) and fraction F3 (metals in complexes with organic compounds, relatively mobile and potentially bioavailable) are of special importance (HSU, LO 2000).

Table 5

Total content and fractions of some elements in spent mushroom substrates

Element	Spent mushroom substrate	Total content (sum of fractions) (mg kg^{-1})	Content of element fractions (mg kg^{-1})					
			F1 H_2O	F2 KNO_3	F3 $Na_4P_2O_7$	F4 NaOH	F5 HNO_3	F6 residual
Mg	A	3320	619	961	431	48.0	1190	77.0
	B	2910	557	837	266	38.0	1120	91.0
Ca	A	88 100	2620	13 800	2040	948	68100	569
	B	113 000	2970	16 900	1420	936	89700	518
Fe	A	2710	9.00	11.0	442	176	1450	618
	B	2110	16.0	11.0	300	137	1240	401
Mn	A	321	6.30	10.6	45.1	8.25	245	5.52
	B	260	6.83	12.9	37.7	5.64	193	4.08
Sr	A	82.9	3.15	12.7	0.890	0.290	64.6	1.31
	B	112	3.51	15.3	0.754	0.232	90.7	1.10
Ba	A	45.1	0.499	4.31	0.716	1.03	36.3	2.24
	B	55.5	0.648	6.86	0.265	0.900	44.7	2.08
Zn	A	180	2.63	3.23	122	4.94	37.6	9.44
	B	148	2.54	2.81	94.0	5.00	34.8	8.70
Cu	A	21.6	0.845	0.902	5.03	7.18	6.57	1.11
	B	18.6	0.622	0.885	3.85	6.03	6.46	0.714
Ni	A	3.33	0.214	0.100	0.631	0.383	1.05	0.949
	B	2.88	0.155	0.125	0.539	0.244	0.865	0.950
Cr	A	4.56	0.095	0.113	n. d.	n. d.	0.743	3.61
	B	4.96	0.150	0.160	n. d.	n. d.	1.04	3.61
Pb	A	4.30	0.110	0.212	0.496	0.210	2.74	0.534
	B	5.32	0.090	0.223	0.580	0.400	3.38	0.657

n.d. – not determinated

Speciation variability between the analysed metals and similarities in the presence of metals in fractions have been found between the analyzed mushroom cultivation substrates (Tables 5, 6). A decreasing content of metals in the isolated fractions is shown in sequences for Mg: F5 > F2 > F1 > F3 > F6 > F4; Ca: F5 > F2 > F1 > F3 ≥ F4 = F6; Fe: F5 > F6 > F3 > F4 > F1 ≥ F2; Mn: F5 > F3 > F4 > F2 > F1 > F6; Zn: F3 > F5 > F6 > F4 > F2 ≥ F1; Cu: F4 ≥ F5 > F3 > F6 > F2 > F; Ni: F5 ≥ F6 > F3 > F4 > F1 >

Table 6

Contribution of separated fractions of elements (mean for spent mushroom substrates)

Element	Fractions (%)					
	F1 H_2O	F2 KNO_3	F3 $Na_4P_2O_7$	F4 NaOH	F5 HNO_3	F6 residual
Mg	18.9	28.8	11.1	1.38	37.2	2.73
Ca	2.81	15.4	1.79	0.955	78.6	0.56
Fe	0.54	0.46	15.3	6.50	56.3	20.9
Mn	2.30	4.14	14.3	2.37	75.3	1.65
Sr	3.47	14.5	0.88	0.28	79.6	1.28
Ba	1.14	11.0	1.04	1.96	80.6	4.36
Zn	1.60	1.85	65.7	3.07	22.3	5.57
Cu	3.63	4.47	22.0	32.9	32.6	4.50
Ni	5.91	3.68	18.9	9.99	30.8	30.8
Cr	2.56	2.85	n.w.	n.w.	18.6	76.0
Pb	2.13	4.56	11.2	6.21	63.6	12.4

F2; Cr: F6 > F5 > F2 ≥ F1 (w F3 and F4 not found); Pb: F5 > F6 > F3 > F4 > F2 > F1; Sr: F5 > F2 > F1 > F6 ≥ F3 ≥ F4; Ba: F5 > F2 > F6 > F4 ≥ F1 ≥ F3.

Most of the metals (Ba > Sr > Ca > Mn > Pb > Fe > Mg > Ni) were bound strongly with organic and mineral compounds of the mushroom substrates (fraction F5). The fraction dominated especially in the case of Ba, Sr and Ca, which are similar metals and co-occur in the environment. The main source of these elements in mushroom substrates are additives, usually added as carbonates, which raise the pH value at the stage of substrate and cover production. A characteristic feature of Ca, Sr, Ba and Mg was their considerably high content in the exchangeable fraction F2. A positive property of the substrates is that the heavy metals Pb and Cr dominated in stable fractions F5 and F6 and were present only in small quantities in F1 and F2 (potentially bioavailable fractions). An analogously low content of heavy metals in extracts (H_2O and $CaCl_2$ solution) from manure and composts was found by GONDEK (2007). Unlike other metals, chromium was bound in the residual fraction F6 to the greatest extent – actually, it was not found in compounds with humic substances in fractions F3 and F4. More than half of the amount of Zn and Cu was bound in those fractions (F3, F4), and Ni, Fe, Pb and Mn were present at 16.7-28.8% (Table 7), mainly in the fraction complexed with humic substances (F3) or- in the case of Cu – metals bound by humic substances (F4).

Table 7

Contribution of fractions of fulvic and humic acids bounded metals

Element	F3 $Na_4P_2O_7$		F4 NaOH	
	$F3_{FA}$	$F3_{HA}$	$F4_{FA}$	$F4_{HA}$
Mg	86.6	13.4	87.0	13.0
Ca	85.8	14.2	91.6	8.38
Fe	75.4	24.6	81.7	18.3
Sr	78.4	21.6	83.3	16.7
Ba	66.5	33.5	36.5	63.5
Mn	76.6	23.4	88.4	11.6
Zn	76.0	24.0	70.4	29.6
Cu	20.6	79.4	14.0	86.0
Ni	1.00	99.0	18.3	81.7
Pb	81.3	18.7	41.0	59.0

The majority of the metals in the humic substance fractions were found in the fulvic acid fractions ($F3_{FA}$ i $F4_{HA}$). The significance of humic acids (a more stable fraction of humic substances) was higher for speciation of Cu and Ni, and slightly weaker for Ba and Pb (in $F4_{HA}$).

CONCLUSIONS

1. Spent mushroom substrate should be used as fertiliser because of its high potential for enriching soil with organic compounds. Moreover, it contains much more Ca and Mg than manure and comparable amounts of micronutrients.

2. The highest amounts of carbon in the substrates (62%) were bound with the stable residual fraction, while 10% was present in the bioavailable fractions.

3. The content of the metals in the fractions varied, with most of them (Ba > Sr > Ca > Mn > Pb > Fe > Mn > Ni) (80.6-30.8% of the total content) being strongly bound with organic and mineral compounds (fraction F5).

4. Considerable amounts of Ca, Mg, Mn, Sr, Fe and Zn were bound with fulvic acids and Cu, Ni, Ba and Pb – with more stable humic acids. The fractions bound with humic substances (F3 and F4) were of the highest quantitative importance in speciation of zinc and copper.

5. It would be advisable to carry out further studies of speciation of metals bound with organic compounds in waste organic materials with respect to their environmental hazard and potential use as fertilisers.

REFERENCES

DZIADOWIEC H., GONET S.S. 1999. *A guidebook of methodology for research on organic matter*. Pr. Kom. Nauk. PTG, 120,Warszawa. (in Polish)

GONDEK K. 2007. *Content of carbon, nitrogen and selected heavy metals in composts.* J. Elementol., 12 (1): 13-23.

HE X.T., LOGAN T. L., TRAINA S. J. 1995. *Physical and chemical characteristics of selected U.S. municipal solid waste composts*. J. Environ. Qual., 24: 543-552.

HSU J.H., LO S.L. 2001. *Effect of composting on characterization and leaching of copper, manganesse, and zinc from swine manure*. Environ. Pollut.,114: 119-127.

JORDAN S.N., MULLEN G.J., MURPHY M.C. 2008. *Composition variability of spent mushroom compost In Ireland*. Biores. Technol., 99: 411-418.

KALEMBASA D., MAJCHROWSKA-SAFARYAN A. 2009a. *Nutrient abundance of spent mushroom substrate*. Zesz. Probl. Post. Nauk Rol., 535: 195-200. (in Polish)

KALEMBASA D., MAJCHROWSKA-SAFARYAN A. 2009b. *Fractions of heavy metals in spent mushroom substrates*. Ochr. Środ. Zas. Nat., 41: 572-577. (in Polish)

KALEMBASA S. 1991. *Quick method of determination of organic carbon in soil*. Pol. J. Soil Sci., 24(1): 17-22.

MAĆKOWIAK C. ŻEBROWSKI J. 2000. *Chemical composition of manure in Poland*. Nawozy i Nawożenie, 4(5): 119-130. (in Polish)

MAZUR Z., MOKRA O. 2009. *Concentration of macronutrients in natural fertilizers in Poland in 2003-2005*. Zesz. Probl. Post. Nauk Rol., 537: 243-247. (in Polish)

MEDINA E., PAREDES C., PEREZ-MURIA M.D., BUSTAMANTE M.A., MORAL R. 2009. *Spent mushroom substrates as component of growing media for germination and growth of horticultural plamts*. Biores. Technol., 100: 4227-4232.

Regulation of the Minister for Agriculture and Rural Development of 18 June 2008. Journal of Law 119 item 765. (in Polish)

RUTKOWSKA B., SZULC W., STĘPIEŃ W., JOBDA J. 2009. *Possible use of spent mushroom substrates in agriculture*. Zesz. Probl. Post. Nauk Rol., 535: 349-356. (in Polish)

STEWART D.P.C., CAMERON K.C., CONFORT I.S. 1998. *Effect of spent mushrum substrate on soil chemical conditions and plant growth in an intensive horticultural system: a comparison with inorganic fertiliser*. Austr. J. Soil Res., 36(2): 75-83.

ZMORA-NAHUM S., HADAR Y., CHEN Y. 2007. *Physico-chemical properties of commercial composts varying in their Skurce materials and country of origin*. Soil Biol. Biochem., 39: 1263-1276.

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EFFECT OF THE RATE OF NITROGEN AND ZINC ON THE ZINC AND COPPER ACCUMULATION IN GRAIN OF SPRING TRITICALE CULTIVAR KARGO

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Abstract

Modest stand requirements, high yielding potential and high nutritive value have made triticale an alternative crop to other cereals in Poland. The grain of that cereal is mostly used for making animal feed, although it can also be processed by the food industry. Triticale yields and the quality of grain are largely determined by agro-technical factors, including mineral fertilisation. Over the recent years, more attention has been attracted to the favourable effect of cereal fertilisation with microelements, especially more intensive nitrogen nutrition. In 2005–2007, a two-factor field experiment in a split-plot design was set up at the Agricultural Experimental Station in Minikowo, which belongs to the University of Technology and Life Sciences in Bydgoszcz. The aim of the paper was to evaluate the effect of different nitrogen rates and foliar zinc application on the content of zinc and copper in grain of cv. Kargo spring triticale. The plots, 20 m^2 each, were treated with two nitrogen fertilisation rates (factor I, n=2): 80 kg N ha^{-1} (N_{80}) and 120 kg N ha^{-1} (N_{120}) and three zinc fertilisation rates (factor II, n=3): Zn_0 (without zinc), Zn_1 (0.1 kg ha^{-1}) and Zn_2 (0.3 kg ha^{-1}) against fixed, pre-sowing phosphorus and potassium fertilisation. It was found that the rate of 120 kg N ha^{-1} resulted in a significant increase in the zinc content and a decrease in the copper concentration in grain of the cultivar Kargo spring triticale, as compared with the treatment which received 80 kg N ha^{-1}. Foliar zinc application, in all the rates applied, resulted in a significant increase in the zinc content and a decrease in the copper concentration in spring triticale grain.

Key words: spring triticale, nitrogen and zinc fertilisation, microelements.

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ODDZIAŁYWANIE DAWKI AZOTU I CYNKU NA AKUMULACJĘ CYNKU I MIEDZI W ZIARNIE PSZENŻYTA JAREGO ODMIANY KARGO

Abstrakt

Niewielkie wymagania w stosunku do stanowiska, duży potencjał plonowania i wysoka wartość pokarmowa spowodowały, że pszenżyto stanowi alternatywę dla uprawy innych zbóż w Polsce. Ziarno tego zboża wykorzystywane jest przede wszystkim na cele pastewne, ale może być również stosowane w przemyśle spożywczym. Plonowanie i jakość ziarna pszenżyta są determinowane w dużym stopniu czynnikami agrotechnicznymi, w tym nawożeniem mineralnym. W ostatnich latach coraz większą uwagę zwraca się na korzystny wpływ nawożenia zbóż mikroelementami, szczególnie w przypadku intensyfikacji nawożenia azotem. W latach 2005-2007 w Rolniczym Zakładzie Doświadczalnym Uniwersytetu Technologiczno-Przyrodniczego w Minikowie przeprowadzono dwuczynnikowe doświadczenie polowe, założone metodą losowanych podbloków. Celem pracy była ocena wpływu zróżnicowanych dawek azotu i dolistnej aplikacji cynku na zawartość cynku i miedzi w ziarnie pszenżyta jarego odmiany Kargo. Na poletkach o powierzchni 20 m^2 zastosowano dwa poziomy nawożenia azotem (I czynnik, n=2): 80 kg N ha^{-1} (N_{80}) i 120 kg N ha^{-1} (N_{120}) i trzy poziomy nawożenia cynkiem (II czynnik, n=3): Zn_0 (bez cynku), Zn_1 (0,1 kg ha^{-1}) i Zn_2 (0,3 kg ha^{-1}) na tle stałego przedsiewnego nawożenia fosforem i potasem. W wyniku badań stwierdzono, że dawka 120 kg N ha^{-1} istotnie wpłynęła na wzrost zawartości cynku oraz zmniejszenie koncentracji miedzi w ziarnie pszenżyta jarego odmiany Kargo, w porównaniu z obiektem, gdzie stosowano 80 kg N ha^{-1}. Dolistna aplikacja cynku, w całym zakresie stosowanych dawek, powodowała istotny wzrost zawartości cynku i zmniejszenie koncentracji miedzi w ziarnie pszenżyta jarego.

Słowa kluczowe: pszenżyto jare, nawożenie azotem i cynkiem, mikroelementy.

INTRODUCTION

For maintaining proper bodily functions, animals need a daily supply of basic nutrients (carbohydrates, proteins, fats) and the elements, often in trace amounts, participating in the metabolism (BORKOWSKA 2004). A crucial role in animal nutrition is played by processed cereal grains, of which triticale grain is gaining in importance. Owing to a big progress in breeding, triticale has become the fifth cereal species grown in Poland (MAĆKOWIAK 2003). Modest stand requirements, high yielding potential and high nutritive value have made it an alternative crop to other cereals in Poland. Triticale grain is used most often for animal feed, although it can also be processed by the food industry (KARCZMARCZYK et al. 2000, TOHVER et al. 2005, KNAPOWSKI et al. 2009). Triticale yielding and grain quality are largely determined by agro-technical factors, including mineral fertilisation, especially with nitrogen (PISULEWSKA et al. 1998, BORKOWSKA 2004, MUT et al. 2005, SPYCHAJ-FABISIAK et al. 2005). Over the recent years, more attention has also been paid to the effect of cereal fertilisation with microelements, especially more intensive nitrogen nutrition (CZUBA 2000, WOJTKOWIAK 2004, KNAPOWSKI et al. 2009). The need for fertilisation of cereals with microelements, including zinc, is indicated by KORZENIOWSKA (2004), who demonstrated a distinct decrease in the amount of zinc in grain. Microelements regulate enzymatic processes, participate in carbohydrate and protein transformations and improve the effect of fertilisation with macroelements, which is why they help to achieve higher yields and better biological yield value (GRZYŚ 2004, BARCZAK et al. 2006, MAJCHERCZAK et al. 2006). Fertilisation with macro- and microelements affects concentrations of minerals in grain and, consequently, contributes to the nutritive value of animal feeds given to farm animals (PISULEWSKA et al. 1998).

Zinc participates in transformations of proteins, carbohydrates and nucleic acids in human and animal bodies; it also activates enzymes essential for the immune system. Copper is indispensable for triggering the reserves of iron needed for the synthesis of haemoglobin and erythrocyte production; it is also incorporated in many tissue enzymes and participates in the metabolism. Therefore, the content of microelements in rations should meet animal requirements. Both a deficit and an excess of macro- and microelements in the grain can induce unfavourable changes in an animal's metabolism (WHITAKER et al. 1997, KOROL et al. 2006, KLEBANIUK, GRELA 2008). Thus, it is necessary to assess the impact of mineral fertilisation on the chemical composition of grain.

The aim of the present paper was to evaluate to what extent different nitrogen and zinc rates determine the accumulation of zinc and copper in grain of the spring triticale cultivar Kargo.

MATERIAL AND METHODS

The research consisted of a two-factor field experiment in a split-plot design carried out in 2005–2007 at the Agricultural Experimental Station in Minikowo (the Kujawy and Pomorze Province), which belongs to the University of Technology and Life Sciences in Bydgoszcz. The spring triticale cultivar Kargo (C1 certified material) was the tested plant. It was grown under different nitrogen fertilisation and foliar zinc application. The experiment, with three replications, was performed on proper grey soil (good wheat complex), classified as Albic Luvisols according to the international FAO-UNESCO classification (MARCINEK, KOMISAREK 2011). The soil reaction was neutral and the content of available phosphorus, potassium and magnesium was very high or high. The copper content, on the other hand, was moderate and manganese and zinc appeared in amounts below the lower threshold values. The detailed physicochemical properties of the soil are given in Table 1.

20 m^2 plots were treated with two nitrogen fertilisation rates (factor I, $n=2$): 80 kg N ha^{-1} (N_{80}) and 120 kg N ha^{-1} (N_{120}) and three zinc fertilisation rates (factor II, n=3): Zn_0 (with no zinc), Zn_1 (0.1 kg ha^{-1}) and Zn_2 (0.3 kg ha^{-1}) against fixed, pre-sowing phosphorus fertilisation at

Table 1

Physicochemical properties of soil

Parameter			Range	Mean
Total N		$g\ kg^{-1}$	0.75 - 0.89	0.82
Organic C			6.96 - 8.64	7.85
Available	P	$mg\ kg^{-1}$	69.9 - 83.8	78.3
	K		179 - 219	206
	Mg		51.7 - 94.7	76.0
	Zn		6.94 - 13.8	8.76
	Cu		5.50 - 7.10	6.40
	Mn		205 - 417	380
pH in KCl			6.3 - 7.0	6.7
Hydrolityc acidity		$mmol(+)\ kg^{-1}$	11.9 - 17.5	14.9

60 kg P_2O_5 ha^{-1} as triple superphosphate (46% P_2O_5) and potassium at 120 kg K_2O ha^{-1} as potassium salt (57% K_2O). Nitrogen fertilisation was applied in the form of urea (46% N) according to the following schedule:

– the rate of 80 kg N ha^{-1} (N_{80}) was divided into 40 kg applied pre-sowing to soil and 40 kg as foliar fertilisation (10% urea solution) at the full stem elongation stage (stage 34 on the Zadoks scale);
– the rate of 120 kg N ha^{-1} (N_{120}) was divided into 40 kg applied pre-sowing into soil, 40 kg as foliar fertilisation (10% urea solution) at the full stem elongation stage (stage 34 on the Zadoks scale) and 40 kg as a foliar fertiliser (5% urea solution) at early inflorescence emergence (stage 50-51 on the Zadoks scale).

The foliar application of zinc consisted of $ZnCl_2$ sprays applied to triticale plants at the full stem elongation phase (stage 34 on the Zadoks scale). The preceding crop was oat harvested for grain. Spring triticale cv. Kargo was sown as ORIUS 060 FS-seed-dressed grain (60 g of the active substance per 1 dm^3) at the density of 5.5 mln ha^{-1}. All the soil tillage treatments, sowing and the cereal harvest were performed compliant with the agrotechnical guidelines for this species. The content of zinc and copper in the grain was determined by atomic absorption spectroscopy (AAS), having mineralized the plant material in a mixture of chloric and nitric(V) acids. The research results were statistically verified with the analysis of variance and using Tukey's test to determine the significance of differences.

The weather conditions throughout the experiment (2005-2007) are presented according to Sielianinov's hydrothermal coefficient (Table 2). The values of this coefficient confirm the changeability of the weather conditions in the subsequent years. The highest temperature and precipitation fluctuations occurred in the 2006 growing season, which had the biggest water

Table 2

Sielianinov's coefficient values throughout the research period

Years	Months				
	Apr	May	June	July	Aug
2005	0.99	2.19	0.68	0.75	0.84
2006	2.86	1.53	0.44	0.70	2.14
2007	0.71	1.71	1.94	1.88	0.76

deficits (Sielianinov's hydrothermal coefficient reached an average value of 0.44 in June, and 0.70 in July). In the April of that year, the coefficient reached the highest mean value (K=2.86), which proved the occurrence of very moist conditions. The year 2005 was more stable in terms of temperature and precipitation than the other years. Besides, it had little rainfall from June to August.

RESULTS AND DISCUSSION

The relevant literature suggests that, among all agro-technical factors, mineral fertilisation plays a special role and significantly determines cereal yields and grain quality (NIERÓBCA 2004, MUT et al. 2005, SPYCHAJ-FABISIAK et al. 2005, BARCZAK et al. 2006, MAJCHERCZAK et al. 2006, KNAPOWSKI et al. 2009, WARECHOWSKA 2009).

The zinc requirements in most animal groups can be defined as 30 mg kg^{-1} d.m. (SMULIKOWSKA, RUTKOWSKI 2005, JAMROZ 2009). In the present experiment, the annual average content of zinc in triticale grain was 28.01 mg kg^{-1} (Table 3). A relatively low zinc content in cereal grain was also reported by KULCZYCKI and GROCHOLSKI (2004) as well as MEDYŃSKA et al. (2009): 20.8-29.0 and 19.4-25.1 mg kg^{-1}, respectively. In contrast, a content higher than reported by those authors or found in the present experiment is claimed by KARCZMARCZYK et al. (2000) – 34.50-37.80 mg kg^{-1}, JACKOWSKA and BORKOWSKA (2002) – 33.43 mg kg^{-1}, WARECHOWSKA (2009) – 28.47-31.05 mg kg^{-1} and MAKARSKA et al. (2010) – 47.5-72.3 mg kg^{-1}.

In the present experiment, analogously to the reports by DZIAMBA and JACKOWSKA (2001), JACKOWSKA and BORKOWSKA (2002) and BORKOWSKA (2004), most zinc (the mean for the whole equal 29.85 mg kg^{-1} d.m.) was reported in grain after the application of the higher nitrogen rate (Table 3). The use of 120 kg N ha^{-1} resulted in a significant increase in the zinc content (by 3.68 mg kg^{-1} d.m.), as compared with the value reported for the treatment with 80 kg N ha^{-1}. Interestingly, similar relationships were recorded for all the research years, although the increase in the concentration of that

Table 3

Content of zinc (mg kg^{-1} d.m.) in spring triticale grain

Years	N fertilisation	Zn fertilisation (kg ha^{-1})			Mean	$LSD_{p=0.05}$ for fertilisation	
		Zn_0	Zn_1	Zn_2		N	Zn
2005	80 (N_{80})	23.95	25.65	27.80	25.80	interaction IxII- n.s.	IIxI- n.s.
	120 (N_{120})	25.41	28.22	29.90	27.84		
Mean		24.68	26.94	28.85	26.82	2.03	1.01
2006	80 (N_{80})	26.99	27.85	31.51	28.78	interaction IxII- n.s.	IIxI- n.s.
	120 (N_{120})	31.95	33.72	37.90	34.52		
Mean		29.47	30.78	34.71	31.65	4.80	2.55
2007	80 (N_{80})	20.38	24.04	27.36	23.93	interaction IxII- n.s.	IIxI- n.s.
	120 (N_{120})	23.49	27.30	30.76	27.18		
Mean		21.93	25.67	29.06	25.55	0.26	2.23
2005-2007	80 (N_{80})	23.77	25.85	28.89	26.17	interaction IxII- n.s.	IIxI- n.s.
	120 (N_{120})	26.95	29.75	32.85	29.85		
Mean		25.36	27.80	30.87	28.01	1.24	0.80

microelement in cv. Kargo spring triticale grain ranged from 2.04 to 5.74 mg kg^{-1} d.m., which agrees with the results reported by WARECHOWSKA (2004) who, having applied 120 kg N ha^{-1}, noted a significant increase in the zinc content in spring triticale grain, as compared with the fertilisation treatments of 80 kg N ha^{-1}. KARCZMARCZYK et al. (2000), on the other hand, noted an increase in the Zn concentration in spring triticale grain as a result of increasing the nitrogen rate to 150 kg ha^{-1}.

Similarly, the increasing zinc fertilisation modified the content of this nutrient in grain (Table 3). The highest (mean for the three years) zinc content in spring triticale grain (30.87 mg kg^{-1} d.m.) was noted after foliar application of Zn at the rate of 0.3 kg ha^{-1}. The value was significantly higher than that of the control and than the treatment where 0.1 kg Zn ha^{-1} was applied (5.51 and 3.07 mg kg^{-1} d.m., respectively). On the other hand, WARECHOWSKA (2009) recorded a lower concentration of this nutrient in wheat grain after the foliar application of 0.2 kg Zn ha^{-1} than in the control.

The average copper content in triticale grain was 4.62 mg kg^{-1} d.m. (Table 4) and it was higher than in the grain of the cereals investigated by JACKOWSKA and BORKOWSKA (2002) – 2.05-2.58 mg kg^{-1}, KULCZYCKI and GROCHOLSKI (2004) – 2.8-3.3 mg kg^{-1}, MEDYŃSKA et al. (2009) – 3.1-3.9 mg kg^{-1} and RACHOŃ and SZUMIŁO (2009) – 2.84-3.86 mg kg^{-1}. BORKOWSKA (2004) reported a higher content of this nutrient in the grain of all the tested spring wheat cultivars (6.07-7.75 mg kg^{-1}) than in the present research.

Table 4

Content of copper (mg kg^{-1} d.m.) in spring triticale grain

Years	N fertilisation	Zn fertilisation (kg ha^{-1})			Mean	$LSD_{p=0.05}$ for fertilisation	
		Zn_0	Zn_1	Zn_2		N	Zn
2005	80 (N_{80})	4.90	4.40	4.32	4.54	interaction IxII - 0.32	IIxI - 0.15
	120 (N_{120})	4.03	4.24	4.27	4.18		
Mean		4.47	4.32	4.30	4.36	0.31	0.11
2006	80 (N_{80})	4.49	4.26	4.21	4.32	interaction IxII- n.s.	IIxI- n.s.
	120 (N_{120})	3.84	4.10	4.10	4.01		
Mean		4.16	4.18	4.15	4.17	0.10	n.i. n.s.
2007	80 (N_{80})	5.77	5.44	5.27	5.49	interaction IxII - 0.14	IIxI - 0.13
	120 (N_{120})	5.13	5.23	5.20	5.19		
Mean		5.45	5.34	5.23	5.34	0.11	0.09
2005-2007	80 (N_{80})	5.05	4.70	4.60	4.78	interaction IxII - 0.08	IIxI - 0.05
	120 (N_{120})	4.33	4.52	4.52	4.46		
Mean		4.69	4.61	4.56	4.62	0.08	0.03

The results given in Table 4 point to a relatively high variation across the years. The average copper content in the grain in 2007 was higher than in 2005 and in 2006 (22.5% and 28.1% more, respectively). Similar relationships, showing variation in the content of copper in spring wheat grain over years, were noted by Borkowska (2004). For example, an average content of this nutrient was almost 50% higher in 1998 than in 1999.

The analysis of variance, both throughout the research period and in particular years, confirmed a significant effect of the different nitrogen fertilisation rates on the copper content in spring triticale grain (Table 4). The increase in the nitrogen fertilisation level from 80 to 120 kg ha^{-1} resulted ina 6.7% decrease (an average for the three years) in the copper concentration in grain. The increase in the Cu content in spring wheat grain as a result of the increasing nitrogen fertilisation level was recorded by Dziamba and Jackowska (2001). Borkowska (2004), on the other hand, recorded a lower copper content in grain following the application of 150 kg N ha^{-1}, as compared with the fertilisation treatment which involved 50 kg N ha^{-1}.

The copper content in the grain was also determined by the increasing zinc fertilisation (Table 4). As an average for the three years, the highest Cu content in spring triticale grain (4.69 mg kg^{-1} d.m.) was reported for the treatment with no zinc fertilisation. It was significantly higher than the values recorded for the treatments treated with 0.1 kg Zn ha^{-1} and 0.3 kg Zn ha^{-1}, by 0.08 and 0.13 mg kg^{-1} d.m., respectively.

On average, a significant effect of the interaction between the nitrogen and zinc fertilisation on the copper concentration in grain was noted. The highest Cu content was found for the triticale grain harvested from the $N_{80}Zn_0$ treatments, where it equalled 5.05 mg kg^{-1} d.m. (Table 4).

CONCLUSIONS

1. The rate of 120 kg N ha^{-1} significantly increased the zinc content and decreased the copper concentration in the Kargo cultivar spring triticale grain, as compared with the treatment where 80 kg N ha^{-1} was applied.

2. The foliar zinc application resulted in a significant increase in the zinc content and a decrease in the copper concentration in spring triticale grain.

REFERENCES

Barczak B., Nowak K., Kozera W., Majcherczak E. 2006. *Effect of fertilization with microelements on the content of cations in oat grain.* J. Elementol., 11(1): 13–20. (in Polish)

Borkowska H. 2004. *The influence of nitrogen fertilization on the content of the choice of microelements in spring wheat grain.* Ann. UMCS, Sect. E, 59(2): 747-753. (in Polish)

Czuba R. 2000. *The micronutrients in recent fertilization systems.* Zesz. Probl. Post. Nauk Rol., 471: 161-170. (in Polish)

Dziamba S., Jackowska I. 2001. *Effect of some factors on chemical composition of spring wheat grain.* Biul. IHAR, 218/219: 217-222. (in Polish)

Grzyś E. 2004. *The role and importance of micronutrients in plant nutrition.* Zesz. Probl. Post. Nauk Rol., 502: 89-99. (in Polish)

Jackowska I., Borkowska H. 2002. *The influence of nitrogen fertilization on the content of trace elements in grain of some winter wheat cultivars.* Ann. UMCS, Sect. E, 57: 87-91.

Jamroz D. (ed.) 2009. *Animal nutrition and feed science.* Part 1. *Physiological and biochemical basis of animal nutrition.* Wyd. Nauk. PWN, Warszawa, 440 ss. (in Polish)

Karczmarczyk S., Koszański Z., Zbieć I., Tyrakowska-Bielec U. 2000. *Response of spring triticale to sprinkling and mineral fertilization.* Part II. Fol. Univ. Agric. Stetin., 206, Agricultura, 82: 117-124. (in Polish)

Klebaniuk R., Grela E.R. 2008. *Effectiveness of various dietary zinc and copper sources in cow nutrition*. Med. Wet., 64(10): 1252-1255. (in Polish)

Knapowski T., Ralcewicz M., Barczak B., Kozera W. 2009. *The effect of fertilization with nitrogen and zinc on the bread-making quality of spring triticale cultivated in the Noteć Valley*. Pol. J. Environ. Stud., 18(2): 227-233.

Korol W., Nieściór H., Zygmunt B., Bielecka G. 2006. *Evaluation of the content of iron, manganese, zinc and copper in compound feeds for poultry*. Rocz. Nauk. Zoot., 33(1): 95-104. (in Polish)

Korzeniowska J. 2004. *Fertilizer needs of spring wheat with zinc.* Part 1. Zesz. Probl. Post. Nauk. Rol., 502: 141-146.

Kulczycki G., Grocholski J. 2004. *The content of microelements in grain and straw of selected winter wheat cultivars*. Zesz. Probl. Post. Nauk. Rol., 502: 215-221. (in Polish)

Maćkowiak W. 2003. *Estimation of progress and strategic directions of triticale breeding in Poland*. Biul. IHAR, 230: 127-141. (in Polish)

Majcherczak E., Kozera W., Nowak K., Barczak B. 2006. *The content of macroelements and ionic ratios in spring barley grain under foliar fertilization with microelements.* J. Elementol., 11(1): 43-48. (in Polish)

Makarska E., Ciołek A., Kociuba W. 2010. *Influence of parental forms on changes in the content of mineral elements in grain of new winter triticale hybryd strains*. J. Elementol., 15(1): 131-140.

Marcinek J., Komisarek J. (ed.) 2011. *Classification of Polish soils.* Rocz. Glebozn., 62(3): 146. (in Polish)

Medyńska A., Kabała C., Chodak T., Jezierski P. 2009. *Concentration of copper, zinc, lead and cadmium in plants cultivated in the surroundings of Żelazny Most copper ore tailings impoundment.* J. Elementol., 14(4): 729-736.

Mut Z., Sezer I., Gulumser A. 2005. *Effect of different sowing rates and nitrogen levels on grain yield, yield components and some quality traits of triticale***.** Asian J. Plant Sci., 4(5): 533-539.

Nieróbca P. 2004. *The effect of nitrogen fertilization, sowing time and sowing density on yield and yield components in the spring triticale.* Biul. IHAR, 231: 231-236. (in Polish)

Pisulewska E., Zając T., Oleksy A. 1998. *Mineral composition of grain of some triticale cultivars under differentiated nitrogen fertilization.* Biul. IHAR, 205/206: 179-188. (in Polish)

Rachoń L., Szumiło G. 2009. *Comparison of chemical composition of selected winter wheat species*. J. Elementol., 14(1): 135-146.

Smulikowska S., Rutkowski A. (ed.) 2005. *Nutrition guidelines and the nutritive value of feeds. Poultry nutrition standards.* Institute of Animal Physiology and Nutrition of the Polish Academy of Sciences, 4th edition, 93-95.

Spychaj-Fabisiak E., Lozek O., Knapowski T., Ralcewicz M. 2005. *Evaluation of the effect of sowing date and nitrogen fertilization on yield and content of protein in triticale grain*. Fragm. Agron., 22(1): 550-562. (in Polish)

Tohver M., Kann A., Täht R., Mihhalevski A., Hakman J. 2005. *Quality of triticale cultivars suitable for growing and bread-making in northern conditions*. Food Chem., 89(1): 125-132.

Warechowska M. 2004. *Qualitative evaluation of spring triticale grain fertilized with different nitrogen and zinc doses.* Zesz. Probl. Post. Nauk. Rol., 502: 411-417. (in Polish)

Warechowska M. 2009. *Zinc and protein content in the spring wheat grain depending on zinc fertilization techniques.* Zesz. Probl. Post. Nauk. Rol., 541: 457-464. (in Polish)

Whitaker D.A., Eayres H.F., Aitchison K., Kelly J.M. 1997. *No effect of the dietary zinc proteinate on clinical mastitis, infection rate, recovery rate and somatic cell count in dairy cows.* Vet. J., 153: 197-204.

Wojtkowiak K. 2004. *The effect of fertilization technique on the quality and yielding of the triticale grain.* Part I. Zesz. Probl. Post. Nauk. Rol., 502: 43-50. (in Polish)

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EFFECT OF THE GWDA COMPOST AND PRP SOL FERTILISATION ON THE TOTAL CONTENT OF NICKEL, MANGANESE AND LEAD AND THEIR SOLUBLE FORMS IN SOIL

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Abstract

A field experiment was carried out at the Agricultural Experimental Station in Lipnik near Stargard Szczeciński in 2008-2009. It was set up on soil classified as soil quality class IVa and good rye complex (5). In the study, the GWDA compost produced at the Municipal Sewage Treatment Plant in Stargard Szczeciński was used. This compost was characterised by neutral reaction (pH_{H_2O} 7.15). The total content of heavy metals, which limits its possible use as fertiliser, did not exceed the standards given in the Regulation of the Minister of Agriculture and Rural Development (Official Journal of Law No. 119, item 765 of 2008). Compost doses were determined based on the total nitrogen content. It was assumed that 100 kg N ha^{-1} was added to soil with the 1st dose, 200 kg N with the 2nd dose, and 300 kg N with the 3rd dose. The experiment was carried out in two series: with and without addition of the active substance PRP SOL. In autumn 2007, respective compost doses were introduced into soil on established plots according to the experimental design. The active substance PRP SOL was applied at a 150 kg ha^{-1} dose before sowing or seeding test plants. The whole experimental area was fertilised with multicomponent fertiliser Polifoska 6 in a 200 kg ha^{-1} dose in 2008 and 2009. Due to a small content of nitrogen in Polifoska 6 (6% N), top-dressing nitrogen fertilisation was applied in the form of urea (46% N) at a 100 kg N ha^{-1} dose. The test plants were winter wheat cultivar Korweta in 2008 and spring rape cultivar Bosman in 2009.

The results indicate that the total average manganese, lead and nickel content in soil increased by 15.1%, 5.0% and 3.0%, respectively, under organic fertilisation with and without the active substance compared to the initial content. In the course of time, manganese, nickel and lead content decreased to a different extent. This resulted from these microelements being taken up by the cultivated crop or their leaching outside the rhizo-

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sphere. With respect to the soil abundance, it can be stated that it is characterised by medium abundance in manganese soluble forms.

Key words: municipal sewage sludge, compost, active substance PRP SOL, soil, nickel, manganese, lead.

WPŁYW NAWOŻENIA KOMPOSTEM GWDA I PRP SOL NA ZAWARTOŚĆ OGÓLNĄ ORAZ FORM ROZPUSZCZALNYCH NIKLU, MANGANU I OŁOWIU W GLEBIE

Abstrakt

Doświadczenie polowe przeprowadzono w Rolniczej Stacji Doświadczalnej w Lipniku k. Stargardu Szczecińskiego w latach 2008-2009, na glebie zaliczanej do klasy bonitacyjnej IV_a, kompleksu przydatności rolniczej żytniego dobrego (5). Do badań użyto kompostu GWDA wyprodukowanego w Komunalnej Oczyszczalni Ścieków w Stargardzie Szczecińskim. Kompost ten miał odczyn obojętny (pH_{H_2O} 7,15). Zawartość ogólna metali ciężkich, która limituje możliwość wykorzystania go do celów nawozowych, nie przekraczała norm podanych w Rozporządzeniu Ministra Rolnictwa i Rozwoju Wsi (Dz.U. 08.119.765). Dawki kompostu ustalono na podstawie zawartości azotu ogólnego. Przyjęto, że z I dawką wniesiono 100 kg N, z II – 200 kg N, a z III – 300 kg N ha^{-1}. Doświadczenie prowadzono w dwóch seriach: bez dodatku i z dodatkiem substancji czynnej PRP Sol. Jesienią 2007 r. zgodnie ze schematem badań na wyznaczonych poletkach wprowadzono do gleby odpowiednie dawki kompostu. Substancję czynną PRP Sol w dawce 150 kg ha^{-1} stosowano przed siewem lub sadzeniem roślin testowych.

Całą powierzchnię doświadczenia w 2008 i 2009 r. nawożono Polifoską 6 w dawce 200 kg ha^{-1}. Ze względu na niewielką zawartość azotu w Polifosce 6 (6% N), zastosowano pogłównie nawożenie tym pierwiastkiem w formie mocznika (46% N) w dawce 100 kg N ha^{-1}. Roślinami testowymi były w 2008 r. pszenica ozima odmiany Korweta, a 2009 rzepak jary odmiany Bosman.

Wykazano, że średnia zawartość form ogólnych manganu, ołowiu i niklu w glebie pod wpływem nawożenia organicznego bez dodatku i z dodatkiem substancji czynnej PRP Sol zwiększyła się odpowiednio o 15,1%, 5,0% i 3,0% w porównaniu z zawartością wyjściową. W miarę upływu czasu zawartość manganu, niklu i ołowiu zmniejszała się w różnym stopniu. Było to wynikiem pobrania tych mikroskładników przez uprawiane rośliny, a także wypłukania ich poza strefę korzeniową roślin. Oceniając zasobność analizowanej gleby można stwierdzić, że zasobność formy rozpuszczalnej manganu jest średnia.

Słowa kluczowe: komunalny osad ściekowy, kompost, substancja PRP Sol, gleba, nikiel, mangan, ołów.

INTRODUCTION

The livestock populations in Poland have been diminished drastically over the last years. Consequently, the production of natural fertilisers has declined as well. At the same time, prices of mineral fertilisers have risen very high, while prices paid for manufactured farm produce have increased only a little. This has reduced amounts of organic matter introduced to soils and the supply of nutrients for plants. New and less expensive sources of organic matter and nutrients for plants have been searched for. Different organic and mixed organic and mineral waste and substances have been tested in order to determine their effect on soil fertility indices, crop yield volume and quality as well as the environmental impact.

In the present experiment, attention has been paid to the use of compost produced from municipal sewage sludge originating from the Municipal Sewage Treatment Plant in Stargard Szczeciński. Many authors, including Bowszys et al. (2009), Jakubus (2006), Jasiewicz et al. (2007), Grzywnowicz (2007), Krzywy et al. (2007), Wieczorek and Gambuś (2006), Wołoszyk et al. (2009), suggest that composts produced with addition of sewage sludge may be a rich source of organic matter for soils and nutrients for plants. However, such composts may contain excessive concentrations of heavy metals, which have a toxic effect on plants, animals and humans. Therefore, municipal sewage sludge, prior to its introduction into soil, should contain permissible amounts of heavy metals specified in the *Regulation of the Minister of Agriculture and Rural Development* (Official Journal Of Law No 119, item 765 of 2008).

Trials conducted in France have demonstrated that PRP SOL mineral solution pellet contains 30% CaO, 8% MgO, 3.5% Na and 3-5% premixes, together with which 48 microelements are introduced into soil (e.g. manganese, lead, iron, boron and molybdenum). The content of PRP SOL components contributes to the improvement of soil physical properties, inducing the conversion of hardly assimilable forms of phosphorus, potassium and magnesium into compounds which can be available to plants; it also enhances soil enzymatic activity and enriches it with microelements necessary for the development of plants (Krzywy-gawrońska 2009).

Nickel, manganese and lead belong to chemical elements whose quantities in sewage sludge differ greatly depending on its origin (Kalembasa et al. 2008). On the other hand, large quantities of organic matter found in this waste and soil liming eliminate the toxicity of the above chemical elements after their application into soil (Bowszys et. al. 2005, Schufer, Seifert 2006). Some chemical elements, including manganese, lead and nickel, are essential in precisely determined doses for the normal growth and development of plants. Excessive quantities of these chemical elements in fertilisers and then in soil lead to their excessive uptake by plants, and decrease crop yields and yield quality.

The present study aimed at determination of the effect of fertilisation with increasing doses of organic fertiliser with and without addition of the active substance PRP SOL on the total content of nickel, manganese and lead and their forms soluble in 1 mol dm^{-3} HCl in soil during a two-year study period.

MATERIAL AND METHODS

A field experiment was set up and carried out at the Agricultural Experimental Station in Lipnik. It was established on brown, incomplete soil developed from light loamy silty sand with a medium-deep underlying layer of light loam. The soil belongs to soil quality class IVa and good rye complex. Fields of the Agricultural Experimental Station in Lipnik lie on brown, acid, complete (soil quality class V) and incomplete (soil quality classes IVa and IVb) soils. The examinations of the topmost soil (0-25 cm) show that its reaction was close to neutral (pH_{KCl} 6.65). The abundance of assimilable phosphorus forms in soil was high (78.2 mg kg^{-1}d.m.), whereas that of potassium and magnesium (113.9 and 38.6 mg kg^{-1}d.m., respectively) was medium (Table 1).

Table 1

Some iindices of soil fertility in the 0-25 cm layer of the experimental field

Total content (g kg^{-1} d.m. soil)						C_{org} (g kg^{-1})	Assimilable forms (mg kg^{-1} d.m. soil)			
N	P	K	Ca	Mg	S		P	K	Mg	$S\text{-}SO_4$
0.64	1.10	2.41	2.18	0.60	0.12	7.55	78.2	113.9	38.6	9.26

The GDWA compost from municipal sewage sludge used in our examinations was produced at the Municipal Sewage Treatment Plant in Stargard Szczeciński. This compost was characterised by neutral reaction (pH_{H_2O} 7.15) and contained more nitrogen (28.6 g kg^{-1}d.m.) and phosphorus (12.0 g kg^{-1}d.m.) when compared to potassium (6.70 g kg^{-1}d.m.). The total content of heavy metals, which restrains its use for fertilisation purposes, did not exceed standards given in the Regulation of the Minister of Agriculture and Rural Development (*Regulation*... 2008) – see Table 2.

In our field experiment, two factors were taken into account: factor A – increasing doses of compost, and factor B – increasing doses of compost + PRP SOL. The control consisted of plots without fertilisation (control I) and with addition of the active substances PRP SOL (control II). In the experi-

Table 2

Chemical composition of the GWDA compost used in the field experiment at the Agricultural Experimental Station in Lipnik

pH_{H_2O}	N	C	P	K	Mg	Ca	Hg	Mn	Ni	Pb	Cr
	content (g kg^{-1} d. m.)						content (g kg^{-1}d.m.)				
7.15	28.6	246	12.0	6.70	2.22	4.80	0.025	170	3.55	45.3	14.7

mental design, three doses of compost produced from municipal sewage sludge were applied, so as to supply 100, 200 and 300 kg N ha^{-1}. The tested plants were winter wheat cultivar Korweta in 2008 and spring rape cultivar Bosman in 2009.

In autumn 2007, respective doses of compost produced by the GWDA method were introduced into soil on established plots according to the experimental design. In March 2008 and 2009, the whole experimental area was fertilised with the complex fertiliser Polifoska 6 at a 200 kg ha^{-1} dose. Due to the low content of nitrogen in Polifoska 6 (6% N), top-dressing nitrogen fertilisation was applied in the form of urea (46% N) at a dose of 100 kg N ha^{-1}. The total dose of nitrogen under spring rape and winter wheat was divided into two equal parts, applied in two time periods (in spring – 50% of the dose before sowing spring rape and 50% before inter-row closing, while for winter wheat 50% at the beginning of the vegetative growth and 50% at the stem elongation stage). PRP SOL was introduced into soil at a 150 kg N ha^{-1} dose before sowing the test plants. In autumn 2008 and in 2009, the same measures were carried out in the field experiment.

Total manganese, nickel and lead were determined by the method of atomic absorption spectrometry using a Perkin Elmer AAS 300 spectrophotometer. Stock solution was obtained following wet mineralisation of soil material according to the Polish standards PN–ISO 11466 and PN-ISO 11047. The content of soluble manganese, nickel and lead forms was determined with the method commonly used at Chemical and Agricultural Stations. These determinations were made in 1 mol dm^{-3} HCl under a fume cupboard with the AAS method for fertilisation consulting purposes. The results were processed with the analysis of variance using a Statistica 8.0 computer software package. Tukey's test at the significance level $\alpha \leq 0.05$ was used to check significance of differences.

RESULTS AND DISCUSSION

The results obtained in this study are presented in Tables 3, 4 and 5. Mean total manganese, nickel and lead contents in soil following the application of increasing doses of compost without and with addition of active substance PRP SOL are compared in Table 3. In control objects (control I without compost and control II with PRP SOL), total manganese, nickel and lead contents in soil decreased when compared to the initial data (Table 3). This phenomenon is induced by uptake of the examined microelements by test plants during the experiment.

The total content of manganese, nickel and lead and their 1 mol dm^{-3} HCl soluble forms in soil was higher in 2008 than in 2009, which was due to partial leaching of these chemical elements deep into the soil profile and

Table 3

Effect of increasing doses of compost without and with addition of PRP SOL on total manganese, lead and nickel contents in soil; data are given (mg kg^{-1} d.m.)

Fertilisation treatments	Years	Mn	Pb	Ni
		(mg kg^{-1} d.m.)		
Initial content	2008	321	15.2	6.45
Control	2008 2009	315 310	15.4 14.9	6.55 6.50
Mean		312	15.1	6.52
Control with PRP SOL	2008 2009	322 318	15.2 15.0	6.30 6.40
Mean		320	15.1	6.35
1st dose of compost without PRP SOL	2008 2009	368 357	15.7 15.5	6.62 6.50
2nd dose of compost without PRP SOL	2008 2009	375 362	16.1 15.9	6.67 6.58
3rd dose of compost without PRP SOL	2008 2009	382 370	16.3 16.1	6.71 6.66
Mean for doses without PRP SOL		369	15.9	6.62
1st dose of compost with PRP SOL	2008 2009	376 363	15.9 15.7	6.68 6.55
2nd dose of compost with PRP SOL	2008 2009	382 368	16.3 16.1	6.72 6.62
3rd dose of compost with PRP SOL	2008 2009	394 381	16.5 16.3	6.83 6.72
Mean for doses with PRP SOL		387	16.1	6.68
$LSD_{0.05}$ A - compost doses B - PRP SOL effect AxB		6.436 3.251 ns	0.176 0.089 ns	0.102 ns ns

their uptake by the test plants as well as the reaction of the soil. During the experiment, the pH_{KCl} value increased as affected by organic fertilisation with and without PRP SOL addition. Higher soil reaction induces a decrease occurred in the total content of manganese, nickel and other heavy metals and the content of their soluble forms in 1 mol dm^{-3} HCl. Such a phenomenon occurred in the field experiment. ANDRZEJEWSKI and DERĘGOWSKA (1986) report a decrease in the content of heavy metals in soil fertilised with raw or composted sewage sludge. On the other hand, MERCIK and KUBIAK (1995) state that formation of chelate complexes with trace elements, including heavy metals, induces soil detoxication, which may decrease their availability for plants (Tables 3 and 4). The increasing doses of organic fertiliser (compost) as a rule caused an increase in the total content of cad-

Table 4

Effect of increasing doses of compost with and without addition of PRP SOL on the content of 1 mol dm^{-3} HCl-soluble manganese, lead and nickel forms in soil; data are given (mg kg^{-1} d.m.)

Fertilisation treatments	Years	Mn	Pb	Ni
		(mg kg^{-1} d.m.)		
Initial content	2008	246	9.20	3.35
Control	2008 2009	277 265	10.1 10.0	3.58 3.51
Mean		271	10.0	3.54
Control with PRP SOL	2008 2009	282 270	10.6 10.5	3.53 3.49
Mean		276	10.5	3.51
1st dose of compost without PRP SOL	2008 2009	291 280	11.2 10.9	3.72 3.65
2nd dose of compost without PRP SOL	2008 2009	302 295	11.5 11.0	3.78 3.70
3rd dose of compost without PRP SOL	2008 2009	310 320	11.7 11.1	3.84 3.75
Mean for doses without PRP SOL		299.7	11.2	3.74
1st dose of compost with PRP SOL	2008 2009	302 290	11.3 10.9	3.82 3.76
2nd dose of compost with PRP SOL	2008 2009	319 310	11.6 11.1	3.88 3.82
3rd dose of compost with PRP SOL	2008 2009	338 329	11.8 11.3	3.94 3.83
Mean for doses with PRP SOL		314.7	11.3	3.84
$LSD_{0.05}$ A - compost doses B - PRP SOL effect AxB		12.5 6.18 ns	0.316 0.160 ns	0.0385 0.018 0.050

mium, copper and zinc and their soluble forms in soil. This is related to the introduction of compost with sewage sludge – which was the main source of the analysed chemical elements – into soil. PRP SOL in the control treatment and in treatments with increasing compost doses contributed to a higher total content of manganese, nickel and lead and their soluble forms in soil.

The highest manganese, nickel and lead concentrations were characteristic of the soil fertilised with a triple dose of compost with PRP SOL addition (Table 3). The largest mean increase in the total manganese, nickel and lead content, by 24.2%, 8.60% and 3.91% respectively versus the control, during this two-year experiment (2008-2009) was found in the treatments fertilised with a triple dose of compost with PRP SOL (Table 3). On the other hand, the smallest mean increase in manganese, lead and nickel (by 16.2%, 3.31% and 0.61%, respectively) was found in the treatments fertilised with a single compost dose (Table 3).

Differences in the effect of the increasing compost doses significantly affected the accumulation of manganese, lead and nickel contents in soil. Significant differences in the manganese and lead content were found in the treatments fertilised with increasing doses of compost and PRP SOL, whereas differences in the nickel content under the same fertilisation were non-significant. The results show that fertilisation may be a source of manganese, nickel and lead in soil for cultivated plants.

The concentration of chemical elements analysed in soil was within natural content limits and considerably lower when compared to the total content of examined chemical elements given by the State Research Institute of Soil Science and Plant Cultivation (1995).

Most of the soluble manganese, lead and nickel forms was contained in the soil fertilised with a triple dose of compost with a PRP SOL addition. The biggest decrease in the manganese content between 2008 and 2009 (by 3.97%) was found in the treatment fertilised with a single dose of compost with PRP SOL; in the lead (3.54%) and nickel content (1.57%) – in the treatment fertilised with a triple dose of compost.

The biggest mean increase in the content of manganese, lead and nickel soluble forms (by 16.1%, 13.0% and 8.47%, respectively) was obtained in the treatments fertilised with increasing doses of compost with PRP SOL addition when compared to the control (Table 4).

Differences in the effect of the fertilisation variants on the content of soluble manganese, nickel and lead forms in soil were significant. Introduction of increasing doses of compost with and without addition of PRP SOL had a significant effect of the content of soluble forms of chemical elements analysed in soil. On the other hand, CZEKAŁA (2004) shows that sewage sludge or composts made from sewage sludge or composted sewage sludge applied in different doses did not significantly affect the content of soluble manganese in soil. When evaluating the abundance of the examined soil in 1 mol dm^{-3} HCl soluble forms, it can be stated that the manganese content was moderate.

The average percentage of manganese, nickel and lead forms soluble in 1 mol dm^{-3} HCl in their total content in the soil differed slightly between the fertilisation treatments (Table 5). Out of the analysed chemical elements, the highest percentage of their soluble forms in the total content was found for manganese (86.0%) in the treatment fertilised with a triple dose of compost with PRP SOL, while the lowest one was determined for nickel (56.1%) in the treatments fertilised with a single dose of compost without addition of PRP SOL. Based on the average percentage of soluble forms of these chemical elements in their total contents after two years, heavy metals can be arranged in the following decreasing value order: Mn > Pb > Ni. Similar results were obtained by IŻEWSKA et. al. (2009).

Table 5

Mean percentage of 1 mol dm^{-3} HCl-soluble forms of microelements in their total soil content after the harvest of the test plants according to applied fertilisation (%)

Fertilisation objects	Mn	Pb	Ni
1st dose of compost without PRP SOL	78.7	70.8	56.1
2nd dose of compost without PRP SOL	81.0	70.3	56.4
3rd dose of compost without PRP SOL	83.8	70.4	56.8
Mean	81.2	70.5	56.4
1st dose of compost with PRP SOL	81.1	70.2	57.3
2nd dose of compost with PRP SOL	83.8	70.1	57.7
3rd dose of compost with PRP SOL	86.0	70.4	57.3
Mean	83.6	70.2	57.4

CONCLUSIONS

1. The biggest average increase in the total manganese, lead and nickel content during this two-year study was found in the treatments fertilised with a triple dose of compost with PRP SOL when compared to the control.

2. The direct effect of increasing compost doses on the total content of manganese, lead and nickel and their 1 mol dm^{-3} HCl soluble forms in soil was higher than the residual effect of fertilisation.

3. The biggest average increase in the content of soluble manganese, lead and nickel forms was obtained in the treatments fertilised with increasing doses of compost with PRP SOL when compared to the control.

4. The applied organic fertilisation with and without addition of PRP SOL induced an increase in the total content of manganese, lead and nickel and their soluble forms in the first year of our study. Organic fertilisation did not induce excessive concentrations of the examined chemical elements, irrespective of the size of a compost dose.

5. The highest percentage of soluble forms in total content was found for manganese (86.0%) in the treatment fertilised with a triple dose of compost with PRP SOL addition, while the lowest one was observed for nickel (56.1%) in the treatment fertilised with a single dose of compost without addition of PRP SOL.

REFERENCES

Andrzejewski M., Deręgowska M. 1986. *Humus complexes with heavy metals as protection against contamination of the soil.* Rocz. Glebozn., 37 (2/3): 323-332. (in Polish).

Bowszys T., Ruszkowski K., Bobrzecka D., Wierzbowska J. 2005. *Effect of liming and multicomponent fertilizers on reaction and content of some heavy metals in soil.* J. Elementol., 10(1): 33-40.

Bowszys T., Wierzbowska J., Bowszys J. 2009. *Content and removal of Cu and Zn with harvested crops grown on soil fertilized with composted municipal sewage sludge.* J. Elementol., 14(1): 23-32.

Czekała J. 2004. *Effect of sewage sludge on selected soil chemical properties.* Zesz. Probl. Post. Nauk Rol., 499: 39-46. (in Polish)

Grzywnowicz I. 2007. *Dynamics of mineral nitrogen form content in soil after application of sewage sludge as fertilizer.* Ecol. Chem. Eng., 14(3-4): 303-308.

Iżewska A., Krzywy E., Wołoszyk C. 2009. *Evaluation of impact of fertilization with manure, municipal, sewage sludge and compost prepared from sewage sludge on content of Mn, Zn, Cu and Pb and Cd in light soil.* J. Elementol., 14(3): 457-466.

Jakubus M. 2006. *Effect of long-term application of sewage sludge on changes of chosen soil chemical properties*. Zesz. Probl. Post. Nauk. Rol., 512: 209-219. (in Polish)

Jasiewicz C., Antonkiewicz J., Mazur Z., Krajewski W. 2007. *Agrochemical properaties of soil fertilized with sewage sludge from sewage treatment plant at Olecko.* Ecol. Chem. Eng., 14(5-6): 457-463.

Kalembasa S., Symanowicz B., Wysokiński A. 2008. *Effect of composted sewage sludge with bark and sawdust, and their interaction with the NPK content of selected trace elements in soil and plant*. Zesz. Probl. Post. Nauk Rol., 526: 343-353. (in Polish)

Krzywy E., Krzywy-gawrońska E., Krzywy J., Wołoszyk C. 2007. *Impact of composts with participation of municipal sewage sludge on content of available forms of phosphorus for plants and on quantity of spring rape seed yield*. Pol. J. Chem. Technol., 9(4): 98-101.

Krzywy-gawrońska E. 2009. *The study on the influence of compost from municipal sewage sludge and active substance PRP Sol on the fertility and productivity of soil.* Wyd. ZUT w Szczecinie, ss. 96. (in Polish)

Mercik S., Kubik I. 1995. *Chelation of heavy metals by humic acids and the effect of peat to download Zn, Pb and Cd by plants*. Zesz. Probl. Post. Nauk Rol., 422: 19-30. (in Polish)

Regulation of the Minister for Agriculture and Rural Deevlopment of 18 June 2008 on execution of some regulations contained in the Act on Fertilisers and Fertilisation, Official Journal of Law No. 119, item 765 of 2008. (in Polish)

Schufer U., Seifert M. 2006. *Trace elements electrolytes.* J. Agric. Food Chem., 23(3): 150-161.

Wieczorek J., Gambuś F. 2006. *Comparison of manure and sewage sludge residual effects on yielding and chemical composition of the white mustard in a lysimenter experiment.* Zesz. Prob. Post. Nauk Rol., 512: 627-636. (in Polish)

Wołoszyk C., Iżewska A., Krzywy-gawrońska E. 2009. *Content, uptake and utilization by plants of copper, manganese and zinc from municipal sewage sludge and wheat straw*. J. Elementol., 14(3): 593-604.

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HEAVY METAL POLLUTION OF FOREST SOILS AFFECTED BY THE COPPER INDUSTRY

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Abstract

The study was carried out on forest soils in the vicinity of a copper ore tailings facility and a copper smelter in Lower Silesia, Poland. Soil and litter samples were collected in the surroundings of the tailings facility under pine stands different in age (50, 18 and 11 years old) and under poplar stands (same age as the pine stands) located at an increasing distance from the copper smelter (0.5 km, 1.5 km and 2.1 km). The purpose of the study was to describe the effect of copper mining and smelting on forest soils. The following were determined in the collected soil and litter samples: pH in distilled water electrometrically with a pH meter and total concentrations of Cu, Zn and Pb after digestion with perchloric acid (1:10) using the ICP-ES technique. Very high pH values were found in all organic horizons, which can evidence the alkalizing effect of dusts from the objects. In all the forest soils, the highest total concentrations of all the analyzed elements were found in humus layers, decreasing in deeper horizons of the soil profile. The total concentration of Cu, Pb and Zn was much higher in forest soils under poplar stands in the vicinity of the copper smelter. The concentration of all the elements decreased rapidly with the distance from the smelter. The concentration of Cu, Pb and Zn was higher than found in the vicinity of the objects on the arable soils. This can indicate a secondary rise in heavy metal concentration in the topsoil caused by the presence of a tree stand.

Key words: forest soils, litter, copper smelter, heavy metals.

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ZANIECZYSZCZENIE METALAMI CIĘŻKIMI GLEB LEŚNYCH W REJONIE ODDZIAŁYWANIA PRZEMYSŁU MIEDZIOWEGO

Abstrakt

Badania prowadzono na obszarach leśnych stanowiących dawną strefę ochronną składowiska odpadów flotacji rud miedzi oraz huty miedzi. Powierzchnie badawcze w rejonie składowiska odpadów zlokalizowano pod różnowiekowymi drzewostanami sosnowym (50, 18 i 11 lat). W rejonie huty miedzi powierzchnie zlokalizowano w funkcji odległości od źródła emisji (0,5 km, 1,5 km i 2,1 km od huty) w równowiekowych drzewostanach topolowych. Celem pracy było określenie wpływu przemysłu miedziowego na gleby leśne w rejonach objętych znacznym oddziaływaniem ww. obiektów. Na każdej powierzchni badawczej pobrano próbki gleb i ektopróchnic, w których analizowano pH w wodzie destylowanej i całkowitą zawartość Cu, Pb i Zn po mineralizacji w kwasie nadchlorowym (1:10) z użyciem metody ICP-ES. Bardzo wysokie wartości pH stwierdzone w ektopróchnicach świadczą o alkalizującym wpływie emisji pochodzących z obu obiektów. W ektopróchnicach wszystkich badanych gleb stwierdzono najwyższą całkowitą zawartość Cu, Zn i Pb, a zawartość pierwiastków malała w głąb profilu glebowego. Całkowita zawartość badanych pierwiastków była zdecydowanie wyższa w glebach w rejonie huty miedzi i wyraźnie malała wraz ze wzrostem odległości od źródła emisji. Zawartość Cu, Zn i Pb była zdecydowanie wyższa niż stwierdzona w tym rejonie zawartość pierwiastków w glebach uprawnych. Może to świadczyć o wtórnym nagromadzeniu Cu, Zn i Pb w glebach obszarów zadrzewionych.

Słowa kluczowe: gleby leśne, ściółka, huta miedzi, metale ciężkie.

INTRODUCTION

Mining and smelting can be a significant source of metal contamination of the environment due to mineral excavation, ore transportation, ore flotation, smelting and refining and disposal of tailings and wastewater around mines and smelters. Heavy metal pollution of soils in the Legnica-Głogów copper mining area has been the subject of several investigations in recent years (Andruszczak et al. 1986, Szerszeń et al. 1999, Angełow et al. 2000, Szerszeń et al. 2004, Kabała et al. 2008, Medyńska et al. 2009, Karczewska et. al. 2010). Many of these studies focused on arable soils and the effect on crop productivity. These days, most of the lands in the nearest surroundings of copper mining and smelting objects are afforested, but our knowledge on heavy metal pollution of forest soils is very modest. Forest ecosystems efficiently filter pollutant particles from the air (Ukonomaanaho et al. 2001). The presence of humus layers in forest soils has often been found to effectively retain heavy metals, particularly Pb and Cu (Bergkvist et al. 1989, Derome, Nieminen 1998). Therefore, forest ecosystems and forest soils can accumulate considerable amounts of trace elements. In this paper, we are describing the effect of copper mining and smelting on forest soils.

MATERIALS AND METHODS

The study was carried out on forest soils affected by dusts from two emission sources: a copper ore tailings facility and a copper smelter. The tailings facility (impoundment) has been exploited since 1977. Over 368 mln m^3 of tailings from copper ore flotation have been deposited over an area of 1 390 ha. Because of their physical properties and the storage technology, tailings are the most significant source of the local soil pollution. The main problem is the emission of dust from dry beaches surrounding the pond. Dust containing excessive amounts of heavy metals such as Cu, Pb, Zn, Cd, Ni and As becomes a potential source of soil and plant contamination. Since 1996, sixty-four sites (mostly arable soils) in the environs of the facility have been monitored. The results show long-term changes in the heavy metal contamination of the soils affected by the facility.

The copper smelter belongs to a mining and smelting complex founded in 1951, which currently includes 4 mines, 3 ore enrichment plants and 3 smelters. The complex produces approximately 500 000 tons of copper annually, a quarter of which is produced in the Legnica Smelter. The copper smelting plant in Legnica opened in 1953 and in the past was indicated as a source of high metal-containing dust emission, which was considerably reduced in the 1980s and 1990s in all the facilities of the complex (Monograph of KGHM 2007). However, the long-term pollution caused by the Legnica Copper Smelter has led to extensive soil contamination with many trace elements. In the early 1980s, the most severely contaminated soils within the so-called impact areas were planted with black poplar (*Populus nigra* L.) and black Italian poplar (*Populus euroamericana f. serotina* Hartig).

Soil and litter samples were collected from six forest sites. Three study sites were located in pine forests, in the surroundings of the Zelazny Most tailings facility (ZM), about the same distance from the smelter (approximately 400 m), east and north-east of the object (Figure 1). The coniferous stands were of different age: 50 (1 ZM), 18 years old (2 ZM) and 11 years old (3 ZM). Three other sites were located in the former impact area of the Legnica Copper Smelter (HML), in poplar plantings 0.5 km, 1.5 km and 2.1 km from the emitter (Figure 1). Litter samples were collected with a steel cylinder (d=23 cm), in four replicates. Soil profiles were made in May 2009 and samples were collected from each horizon for further analysis. The soil and litter samples were submitted to the following determinations: pH in distilled water electrometrically with a pH meter (CARTER, GREGORICH 2008), the total concentration of Cu, Zn and Pb after mineralization with perchloric acid (1:10) in an open column system (HOSSNER 1996) using the ICP-ES technique. All analysis were made in two replications.

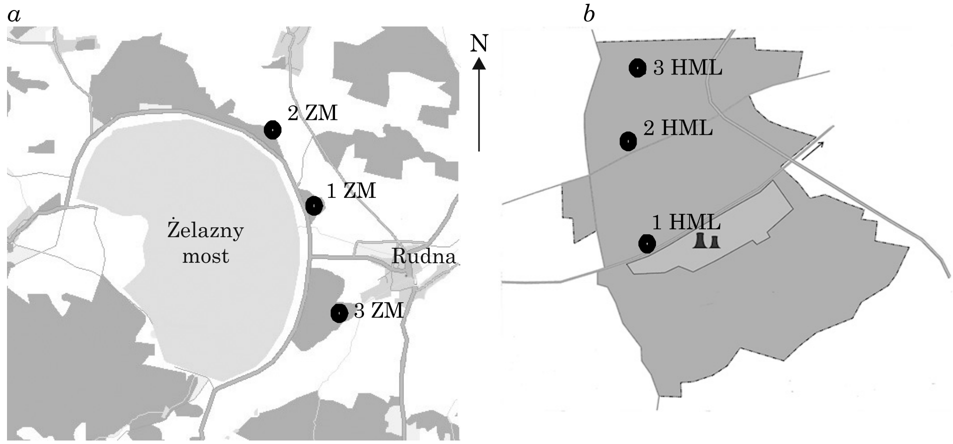

Fig. 1. Location of the study sites *a*) in the vicinity of the copper ore tailings facility in Zelazny Most, *b*) in the vicinity of the copper smelter in Legnica

RESULTS AND DISCUSSION

Forest soils in the surroundings of the copper ore tailings facility were Brunic Arenosols (Fao-Wrb 2007) developed from poor, loose sands with (proto)moder humus in different stages of development. Forest soils in the surroundings of the copper smelter were Cutanic Luvisols (FAO-WRB 2007) developed from loess-like sediments, having the texture of silt loam, mostly with mull humus. In all the forest soils, the pH values in the 0-30 cm topsoil and organic layers were higher than found in natural, unpolluted forest ecosystems (Świercz 2003, Mertens et al. 2007). Under coniferous tree stands (ZM) in the vicinity of the copper ore tailings facility, the pH reached 6.6 in O horizon (Table 1). The high soil pH was caused by two factors 1) high input of airborne calcium and magnesium from dusts from the copper tailings facility 2) high calcium content in parent rock of these soils. Previous studies demonstrated a high calcium and magnesium content in dust from the copper ore tailings facility as well as a high calcium carbonate content in C horizons. Soil under coniferous stands differed in the pH values between the sites. The pH of organic horizons increased with the age of a tree stand and was the highest under the 50-year-old tree stand ZM (Table 1). More acidic O horizons were found under the youngest tree stand, which could have been caused by the accumulation of non-decomposed organic matter, consisting mainly of fresh pine needles. Among the mineral horizons of the profiles, the highest pH – up to 7.1 – was determined under the 18-year old stand 2 ZM, and the lowest one – under the 50-year old

Table 1

Chemical properties of forest soils in the surrounding of the copper ore tailings impoundment

Profile	Horizon	Depth (cm)	pH	Total concentration of the element (mg kg^{-1}) of dried mass of soil		
				Cu	Pb	Zn
1 ZM	O	4-0	6.6	678	213	72
	Ap	0-10	5.4	16	22	26
	Bv1	10-30	4.9	9	24	35
	Bv2	30-45	4.9	9	35	26
	BvC	45-60	6.9	9	29	28
	2C	60+	7.9	5	29	16
2 ZM	O	4-0	6.5	365	119	65
	Ap1	0-10	7.0	34	33	16
	Ap2	10-20	7.1	9	30	20
	Ap3	20-30	5.0	12	27	15
	Bv1	35-45	5.4	5	18	15
	Bv2	45-60	5.3	5	19	14
	BvC	70-80	4.8	6	20	17
	C	90-100	4.9	6	20	18
3 ZM	O	5-0	6.3	115	62	50
	Ap1	0-10	6.6	35	47	17
	Ap2	10-20	6.0	25	45	15
	Ap3	28-38	5.8	17	46	14
	Bv	38-60	5.4	2	20	10
	BvCgg	60-90	5.5	2	19	8
	Cgg	90-100	6.5	1	19	4

stand 1 ZM (Table 1), which could imply stable humification processes in O horizons under the oldest pine stands (Table 1). Decomposition of organic matter from coniferous trees cause acidification of the underlying mineral horizons (Finzi et al. 1998, Berger et al. 2008).

Soils under coniferous tree stands in the surroundings of the copper ore tailings facility had lower pH than soils under poplar stands in the vicinity of the copper smelter, where the highest, sometimes even alkaline reaction in distilled water was found at site 3 HML (Table 2). The pH values of soils in the former impact zone of the copper smelter increased with the distance from the emitter, which could confirm the spatial distribution of airborne dust from the smelter. Dust speciation studies were not performed during

Table 2

Chemical properties of forest soils in the surrounding of the copper smelter

Profile	Horizon	Depth (cm)	pH	Total concentration of the element (mg kg^{-1}) of dried mass of soil		
				Cu	Pb	Zn
1 HML	O	6-0	6.7	13143	9181	3363
	Ap1	0-10	7.1	2375	681	1488
	Ap2	10-20	7.2	2875	723	327
	Ap3	20-30	7.1	1065	259	132
	EBtg1	30-50	7.1	20	37	35
	EBtg2	50-65	7.3	13	12	37
	BtgC	65-80	7.4	9	26	26
	2C1	85-95	7.4	8	25	20
	2C2	95-105	7.4	9	20	16
2 HML	O	2-0	6.8	1508	833	748
	Ap1	0-10	6.9	439	183	91
	Ap2	10-20	7.2	458	202	99
	Ap3	20-35	7.4	423	165	77
	EBt	35-55	7.4	11	16	35
	Btg	55-75	7.4	11	14	37
	BtgC	75-90	7.4	8	12	25
	2C	95-110	7.2	17	13	28
3 HML	O	2-0	6.9	855	585	718
	Ap1	0-10	6.7	200	92	55
	Ap2	10-20	7.1	207	95	61
	Ap3	20-30	7.3	208	95	63
	Eet	30-45	7.5	14	15	34
	EBt1	45-60	7.6	14	13	31
	EBt2	60-75	7.7	9	10	23
	BtC	75-95	7.7	9	10	20
	C1	95-105	7.7	8	9	17

this project but the increasing concentration of calcium and magnesium in O horizons at sites more distant from the smelter can prove these processes. Similar dependence was observed by DEROME and NIEMINEN (1998) near the Harjavalta smelter in Finland. Under the poplar standings (HML) near the copper smelter, higher pH values were found in topsoil (0-30 cm) than in organic layers. This can suggest strong decomposition processes causing acidification of the material or the acidifying effect of SO_4^- emission from the smelter on forest litter. In all the examined soil profiles in the surroundings of the copper smelter, the pH increased with the depth (Table 2), reaching the highest values in the C horizon. High pH values in deeper horizons are typical for Cutanic Luvisols, but can also be the effect of previous calcium and magnesium fertilization used while planting poplar trees.

The total concentrations of Cu, Pb and Cd varied between the sites and within the soil profiles. The total Cu, Pb and Zn concentrations were much higher in forest soils under poplar stands in the vicinity of the copper smelter than in soils impacted by the copper ore tailings facility (Tables 1, 2). This can be the evidence that the copper smelter is a bigger source of heavy metal pollution for soils than the copper ore tailings facility. The average heavy metal concentration in soils in the surroundings of the copper ore tailings facility reached 678 mg Cu kg^{-1}, 213 mg Pb kg^{-1} and 72 mg Zn kg^{-1} in O horizon and was much lower than found by Krzaklewski et al. (2004) for soils impacted by dusting from the zinc-lead ore tailings facility in southern Poland, but much higher than found in soils under natural boreal ecosystems of Poland (Gworek, Degórski 1997). No significant differences were found in the Cu and Zn concentration in the topsoil of the ZM sites. Significant differences were only found for the Pb concentration between site 3 ZM and 1 and 2 ZM.

In all the examined forest soils, the highest total concentration of all the analyzed elements was found in humus layers (Tables 1, 2). Under the coniferous forest 1 ZM, the Cu concentration was even thirty-fold higher in ectohumus than in the mineral Ap horizon. Such relations were also found for Pb and Zn at all the forest sites. There were significant differences* in heavy metal contamination in forest ectohumus horizons between the sites in the surroundings of the copper tailings facility. The highest concentrations of all the heavy metals in ectohumus were found under the oldest pine stand 1 ZM (678 mg Cu kg^{-1}, 213 mg Pb kg^{-1} and 72 mg Zn kg^{-1} in O horizon) and the lowest – under the youngest pine stand 3 ZM (115 mg Cu kg^{-1}, 62 mg Pb kg^{-1}, 50 mg Zn kg^{-1} in O horizon). Surprisingly high concentrations of Cu and Pb in O horizon under the oldest tree stand did not correspond with a higher content of the elements in the 0-30 cm mineral topsoil, what can prove that a well-developed, (proto)moder ectohumus horizon was an effective Cu and Pb filter (Table 1).

With respect to vertical concentrations of the elements downwards the soil profiles, the Cu content decreased and there was a significant difference between the 0-30 cm depth and deeper horizons. The Zn concentration also decreased with the depth into the soil profile but the differences were smaller. Changes in the Pb concentration were very irregular and there were no

*Tested with Tukey's test

significant differences between horizons. Higher Cu and Pb concentrations in the topsoil were found under younger tree stands (18 and 11 years old), which can suggest poorer retention abilities of ectohumus horizons in the early stage of development. Unlike Zn, Cu and Pb are strongly bound to organic matter and are not readily leached from the organic horizon (BERG 1986, BERGKVIST 1987). The total Zn concentration in the soil profiles under the pine stands depended more strongly on the level of contamination in ectohumus horizons than on the development stage, which can be also a proof of higher zinc leaching from O horizons. The concentrations of Cu, Pb and Cd in soils in the vicinity of copper smelter decreased rapidly with the distance from the smelter and at 2.1 km (3 HML) the concentration of Cu in O horizons was 15-fold lower than at 0.5 km from the emitter (1 HML). The differences between the sites were statistically significant*. Extremely high concentrations of heavy metals, reaching 13 143 mg Cu kg^{-1}, 9 181 mg Pb kg^{-1} and 3 363 mg Zn kg^{-1} in O horizon, were found at the site 0.5 km (1 HML) from the smelter (Table 2). The concentrations of all the analyzed heavy metals decreased rapidly with depth in the soil profile, being even 1460-fold lower in the C horizon (for Cu at site1 HML). The concentration of copper in the Ap soil horizon of at 1 HML was six-fold lower than in O horizon, which verifies the role of ectohumus horizons in heavy metal retention. The highest accumulation rate was found for Cu and Pb, whose concentrations in O horizon were six- and twelve-fold higher, respectively, than in the 0-30 cm topsoil (at site 1 HML).

At sites 2 and 3 HML, the difference was smaller (Table 2). Surprisingly, at site 1 HML zinc was mostly accumulated in O horizon, but also very high zinc amounts (only two-fold lower) were found at the 0-10 cm depth. At the depth of 10-20 cm the concentration was ten-fold lower and at 20-30 cm – it was twenty-five-fold lower (Table 2). This stratification pattern was only found for forest soil at site 1 HML, highly contaminated with Zn. At site 1 HML, the differences in the Cu and Pb content in deeper soil layers were also significant. No such regularities were found for the other sites (2 and 3 HML), where elemental concentrations decreased with the depth, but there were no significant differences between the sites. In all the forest soils under poplar stands, concentration of the elements in the mineral horizon depended more strongly on the distance from the smelter and different heavy metal content in ectohumus horizons, whereas the stage of development played a secondary role in Cu, Pb or Zn retention.

These observations indicate the importance of afforestation in the capture of pollutants but also point to significant changes in the circulation of trace elements due to introduction of trees, as well as very specific forest soils. The most characteristic element of forest soils is the occurrence of organic layer, highly capable of metal sorption, which on the one hand hin-

*Tested with Tukey's test

ders leaching of metals from the soil, but on the other hand causes major disturbances in processes of decomposition and humification of organic matter. O horizons of forest and afforested soils are often compared to a natural sink for heavy metals (Tyler 1973, Breymeyer et al. 1997, Wilcke et al. 1998, Berg 2000, Lomander, Johansson 2000). Reviews of filtration and accumulation abilities of forest soil organic horizons are usually based only on analysis of the total accumulation of metals in humus. Meanwhile, its sorption capacity depends on the type of forest humus, the dynamics of its distribution and chemical forms of elements reaching the horizon. The mechanisms of these processes and their actual impact on the cycling of elements in forest ecosystems are not yet well understood, although several important publications identified some aspects of them (Bergkvist et al. 1987, Dziadowiec 1990, Berg et al. 1991, Derome, Nieminen 1998, Andersen et al. 2004, Mertens et al. 2007). The concentration of Cu, Pb and Zn was higher than found in the vicinity of the objects on arable soils (*Bulletin...* 2009). This can be the evidence of a secondary rise in heavy metal concentration in the topsoil caused by the presence of tree stands and O horizons. Similar dependence was found by Kabała et al. (2008) in forest soils in the vicinity of a copper smelter in Głogów, SW Poland. Forest ecosystems are mainly closed systems, where all elements are cycled along internal pathways, so losses of trace elements, e.g. heavy metals, are very low. In contrast to arable land, the biomass (with a given content of metals) produced in a forest throughout a year is not removed from the ecosystem. This gradually leads toelevated concentration of heavy metals in the topsoil (Kabała et al. 2008).

CONCLUSIONS

1. Forest ectohumus horizons, its stage of development and type, play a significant role in Cu, Pb and Zn accumulation from airborne copper mining and smelting emissions.

2. In highly polluted soils with heavy metals, the total concentration of the elements in ectohumus reflects the amounts in mineral horizons.

3. The wealth of tree stands can lead to bioaccumulation of heavy metals in forest soils.

REFERENCES

Andruszczak A., Strączyński S., Czerniawska W., Radwan B. 1986. *Element content in soils and plan cultivated in the surrounding of copper smelters.* Soil Sci. Ann., 37(4): 47-66. (in Polish)

Andersen M., Raulund-Rasmussen K., Strobel B., Hansen H. 2004. *The effect of tree species and site on the solubility of Cd, Cu, Ni, Pb and Zn in soils.* Water, Air Soil Pollution, 154: 357-370. DOI:10.1023/B:WATE.0000022991.59456.01.

ANGEŁOW Z. CHODAK T., KABAŁA C., KASZUBKIEWICZ J., SZERSZEŃ L. 2000. *Impact of copper ore tailings facility in Żelazny Most on soils.* Agricultural University of Poznań Annual, 317: 327-337. (in Polish)

BERG B. 1986. *Nutrient release from litter and humus in coniferous forest soils – a mini review*. Scan. J. For. Res., 1: 359-369.

BERG B., EKBOHM G., SODERSTROM B. STAFF H. 1991. *Reduction of decomposition rates of Scots Pine needle litter due to heavy-metal pollution.* Water, Air Soil Pollution, 59: 165-177. DOI: 10.1007/BF00283179

BERG B. 2000. *Litter decomposition and organic matter turnover in Northern Forest Soils.* Forest Ecol. Managem., 133: 13-22. DOI: 10.1016/S0378-1127(99)00294-7

BERGER T., UNTERSTEINER H., SCHUME H., JOST G. 2008. *Throughfall fluxes in a secondary spruce (Picea abies), a beech (Fagus sylvatica) and a mixed spruce-beech stand.* Forest Ecol. Managem., 255: 605-618. DOI: 10.1016/j.foreco.2007.09.030

BERGKVIST B. 1987. *Soil solution chemistry and metal budgets of spruce forest ecosystems in South Sweden.* Water, Air Soil Pollution, 33: 131-154.

BERGKVIST B., FOLKESON L., BERGGREN D. 1989. *Fluxes of Cu, Zn, Pn, Cd and Ni in temperate forest ecosystems. A literature review.* Water Air Soil Pollut., 47:217-286. DOI: 10.1007/BF00279328

Bulletin of Environmental Protection KGHM 2009. Edt. by KGHM Polska Miedź S.A. (in Polish)

BREYMEYER A., DEGÓRSKI M., REED D. 1997. *Decomposition of pine-litter organic matter and chemical properties of upper soil layers: transect studies.* Environ. Pollut., 98/3: 361-367. http://dx.doi.org/10.1016/S0269-7491(97)00157-7

CARTER M., GREGORICH E. 2008. *Soil sampling and methods of analysis.* 2nd Ed. Canadian Society of Soil Science, CRC Press.

DEROME, T. NIEMINEN 1998. *Metal and macronutrient fluxes in heavy-metal polluted Scots Pine ecosystems in SW Finland.* Environ. Pollution, 103: 219-22. http://dx.doi.org/10.1016/S0269-7491(97)00157-7

DZIADOWIEC H. 1990. *Litter decomposition in forest ecosystems.* Edt. by Mikołaj Kopernik University in Toruń. (in Polish)

FINZI A., CANHAM C., VAN BREEMEN N. 1998. *Canopy-tree interactions within temperate forests: species effect on pH and cations*. Ecol. Appl., 8: 447-454. DOI 10.1890/10510761

GWOREK B., DEGÓRSKI M. 1997. *Spatial and profile distribution of iron and trace elements in soils under boreal ecosystems.* Soil Sci. Annual, 48, 1/2: 19-30. (in Polish)

HOSSNER L. 1996. *Dissolution for total analysis.* In: *Methods of soil analysis.* Part 3. *Chemical methods.* BARTELS J.M. (ed.) Soil Sci. Soc. America, Madison, Wisconsin, USA, 49-64.

KABAŁA C., CHODAK T., SZERSZEŃ L. 2008. *Influence of land use pattern on changes in copper content in soils around a copper smelter, based on a 34-year monitoring cycle.* Ţemës Űkio Mokslai, 15(3): 8-12

KARCZEWSKA A., KASZUBKIEWICZ J., JEZIERSKI P., KABAŁA C., KRÓL K. 2010. *Copper, lead and cadmium concentration in soils of Legnica smelter protective zone, in years 1982-2005.* Soil Sci. Annual, 61(1): 45-51. (in Polish)

KRZAKLEWSKI W., BARSZCZ J., MAŁEK S., KOZIOŁ K., PIETRZYKOWSKI M. 2004. *Contamination of forest soil in the vicinity of the sedimentation pond after zinc and lead ore flotation (in the region of Olkusz, southern Poland).* Water, Air Soil Pollution, 159: 151-164. DOI: 10.1023/B:WATE.0000049173.18935.71

LOMANDER A., JOHANSSON M. 2001. *Changes in concentration of Cd, Zn, Mn, Cu and Pb in spruce (Picea abies) needle litter during decomposition.* Water, Air Soil Pollution, 132: 165-184. DOI: 10.1023/A:1012035620480

MEDYŃSKA A., KABAŁA C., CHODAK T., JEZIERSKI P. 2009. *Concentration of copper, zinc, lead and cadmium in plants in the surroundings of Żelazny Most copper ore tailings impoundment.* J. Elementol., 14(4): 729-736.

MERTENS J., VAN NEVEL L., DE SCHRIJVER A., PIESSCHAERT F., OOSTERBAAN A., TACK F. M.G., VERHEYEN K. 2007. *Tree species effect on the redistribution of soil metals.* Environ. Pollut., 149: 173-181. http://dx.doi.org/10.1016/j.envpol.2007.01.002

Monograph of KGHM Polish Copper Company 2007. Ed. by KGHM Cuprum Sp.z.o.o. Research Center, Wrocław Poland. (in Polish)

SZERSZEŃ L., CHODAK T., KABAŁA C. 1999. *Monitoring studies of trace element concentration in soils impacted by copper smelters in Głogów and Legnica.* Adv. Agric. Sci. Problem Issues, 467: 405-412. (in Polish)

SZERSZEŃ L., CHODAK T., KABAŁA C. 2004. *Changes in copper, lead and zinc concentration in soils impacted by copper smelters Głogów and Legnica in years 1972-2002.* Soil Sci. Annual, 55(3): 195-205. (in Polish)

ŚWIERCZ A. 2003. *Heavy metal concentration in needles and bark of Pinus Sylvestris after decrease of alkaline emission.* Regional Monitoring of Natural Ecosystems, 4: 107-113. Ed. by Kieleckie Towarzystwo Naukowe, Kielce. (in Polish)

TYLER G. 1973. *Heavy metal pollution and decomposition of spruce needle litter*. Oikos, 24: 402-416.

UKONMAANAHO L., STARR M., MANNIO J., RUOHO-AIROLA T. 2001. *Heavy metal budgets for two headwater forested catchments in background areas of Finland.* Environ. Pollut., 114: 63-75.

WILCKE W., MOSBACH J., KOB•A J., ZECH W. 1998. *Distribution of Al and heavy metals in bulk soil and aggregates at three sites contaminated by the emissions of a central Slovak al smelter.* Water, Air, Soil Pollution, 106: 389-402. DOI: 10.1023/A:1005094624006.

World Soil Resources Reports No. 103. FAO, Rome.

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FACTORS INFLUENCING MINERAL COMPOSITION OF PLUM FRUITS

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Abstract

The study has been based on a three-factor field experiment (two rootstocks – Myrobalan and Stanley seedlings, two cultivars – Čačanska lepotica and Čačanska najbolja, three years – 2006, 2007 and 2008) set up according to the method of randomized blocks with four replications. The aim of this work was to evaluate the mineral composition of plums in Serbia. The results indicated that levels of fruit ash and minerals, except nitrogen, significantly differed between the treatments. The average content of ash in plum fruits reached 4.54%, nitrogen – 0.78%, phosphorus – 0.06%, potassium – 1.45%, calcium – 0.07%, magnesium – 0.16%, iron – 19.37 μg g^{-1}, manganese – 10.21 μg g^{-1}, copper – 3.21 μg g^{-1}, zinc – 19.29 μg g^{-1} and boron – 22.83 μg g^{-1} of dry matter. A strong rootstock/cultivar/year interaction was found for most of the minerals. Between ash and manganese or zinc, and between manganese and zinc in plums, significant correlations were observed. On the basis of the analysis of major components, we concluded that Stanley rootstock had better ability to accumulate ash and most of the minerals in fruits of both cultivars than Myrobalan rootstock.

Key words: cultivar, fruits, minerals, Myrobalan, *Prunus domestica* L., Stanley.

CZYNNIKI WPŁYWAJĄCE NA SKŁAD MINERALNY OWOCÓW ŚLIW

Abstrakt

Badania wykonano na podstawie trójczynnikowego doświadczenia polowego (dwa podkłady z sadzonek odmian Myrobalan i Stanley, dwie domiany Čačanska lepotica i Čačanska najbolja oraz trzy lata: 2006, 2007 i 2008), założonego zgodnie z metodą losowych bloków w czterech powtórzeniach. Celem pracy było ocenienie zawartości składników mineralnych w owocach śliw rosnących w Serbii. Wykazano, że zawartość popiołu oraz składników mi-

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neralnych w owocach śliw, z wyjątkiem azotu, różniła się istotnie w poszczególnych obiektach doświadczenia. Średnia zawartość popiołu w śliwkach wynosiła 4,54%, azotu – 0,78%, fosforu – 0,06%, potasu – 1,45%, wapnia – 0,07%, magnezu – 0,16%, żelaza – 19,37 µg g^{-1}, manganu – 10,21 µg g^{-1}, miedzi – 3,21 µg g^{-1}, cynku – 19,29 µg g^{-1}, boru – 22,83 µg g^{-1} suchej masy. W przypadku większości składników mineralnych stwierdzono silną interakcję między podkładem, odmianą i rokiem badań. Zauważono istotne korelacje między popiołem a manganem oraz cynkiem, a także między manganem i cynkiem w śliwkach. Na podstawie analizy głównych komponentów doświadczenia stwierdzono, iż podkład z odmiany Stanley w większym stopniu pozwalał obu odmianom akumulować popiół i większość analizowanych składników mineralnych niż podkład Myrobalan.

Słowa kluczowe: odmiana, owoce, minerały, Myrobalan, *Prunus domestica* L., Stanley.

INTRODUCTION

Prunus domestica L. is one of the most important *Prunus* species, widely grown across the world. In Serbia, this crop, known as the Domestic or European plum, is a very old, traditional fruit tree, so plums are one the most popular fruits in local diet, playing an important role in the economy and social development of the country (Milošević, Milošević 2011). Plum trees are grown throughout Serbia, except cold mountainous area. The total area of plum orchards in Serbia reached over 130,000 ha in 2010 and the production output was 426,826 tons, which makes this country the fourth largest world producer after China, Romania and USA (FAO 2012). The most important plum tree growing area is Western Serbia. Cacak, a location in this region, is the most important plum production center. Plums are eaten fresh or dried. Other main processed products made from plums include *pekmez* (special old Serbian jam without sugar), *slatko* (old Serbian specialty for guests, with added sugar), jams, compotes, mousse, pulp, candied fruit, frozen fruit, jelly products and traditional Serbian plum brandy Rakija or Šljivovica (Milošević, Milošević 2011).

Generally, plum fruits are suitable for human nutrition (Jaroszewska 2011) owing to their high energy, nutritive, dietary and health values (Walkowiak-Tomczak 2008). The high dietary value of plums results from their considerable content of organic and inorganic phytochemical constituents, such as carbohydrates (mono- and disaccharides, pectin, dietary fiber) (Stecewicz-Sapuntzakis et al. 2001), antioxidant compounds, phenolic acids, flavonoids, vitamins, proteins, fat, etc. (Auger et al. 2004). Also, plums are raw material rich in ash and minerals (Nergiz, Yýldýz 1997) such as potassium, sodium, calcium and magnesium (Bhutani, Joshi 1995, Kunachowicz et al. 2005, Çalişr et al. 2005). Additionally, plums also contain microelements, especially boron and iron (Yagmur, Taskin 2011, Jaroszewska 2011).

Many authors reported that concentrations of minerals in plums depend on the cultivar, pedo-climatic conditions, harvest date (Nergiz, Yýldýz 1997), water and fertilization regimes (Jaroszewska 2011), and especially on rootstocks. Beside its effect on the vigor of a fruit tree, a rootstock can modify fruit quality (RATO et al. 2008, DAZA et al. 2008). Myrobalan (*P. cerasifera* Ehrh.) seedlings are the most popular and traditional rootstock for European plum trees in Serbia (MILOŠEVIĆ, MILOŠEVIĆ 2011). However, this type of rootstock has some negative traits, such as inadequate compatibility with some cultivars, high vigor, only average winter-hardiness, etc. (LORETI et al. 1990). Thus, alternative rootstocks for intensively grown orchards are needed. Rootstocks of cv. Stanley seedlings have not been examined from that point of view until now. Thus, the objectives of our research were: a) to evaluate the influence of two rootstocks on the fruit quality of an individual plum cultivar with special reference to the macro- and microelements of the fruit; b) to estimate the most favorable rootstock for producing fruits from the cultivars Čačanska lepotica and Čačanska najbolja with the best mineral content.

MATERIAL AND METHODS

The present study was carried out in three successive years (2006, 2007, 2008) in a private orchard located at the village Viljusa (43°50’ N, 20°24’, 290 m above sea level) near Cacak, Western Serbia. Two cultivars (Čačanska lepotica and Čačanska najbolja) were grafted on two rootstocks (Myrobalan and Stanley seedlings). The orchard was established in 1992 at 6 m × 4 m planting distance. Trees were trained as Open vase, under non-irrigated, standard horticultural practice. A randomized complete blocks design was adopted in this trial, with five trees of each rootstock/cultivar/year combination in four replicates.

Table 1

Soil chemical properties at different soil depths

Soil pH, organic matter, and macronutrient	Units or content	Micronutrient and EC*	Content
Soil pH	4.31	Fe (mg kg^{-1})	78.0
Organic matter (%)	1.29	Mn (mg kg^{-1})	7.8
Total nitrogen (%)	0.14	Cu (mg kg^{-1})	1.6
P_2O_5 (mg kg^{-1})	34.1	Zn (mg kg^{-1})	0.52
K_2O (mg kg^{-1})	270.1	B (mg kg^{-1})	2.3
CaO (%)	0.73	Na_2O (%)	0.68
MgO (%)	2.34	EC (dS m^{-1})	0.74

*EC: Electrical conductivity

Orchard soil was Cambisol (Serbian Soil Taxonomy). The average soil chemical composition from the 0-20 cm soil depth is presented in Table 1. The data showed that the soil was highly acid, low in organic matter and in total nitrogen. The content of available P_2O_5 and K_2O was low and moderate, respectively. The content of CaO, MgO and Na_2O was low, and did not reach the standard levels for Cambisol soil of a sandy-loam texture in Serbia (Protic et al. 2003). Electrical conductivity (EC) of the soil samples was 0.74 dS m^{-1}. The soil showed broad variation in the content of available micronutrients, ranging from very high for Fe, high for Cu and B, low for Mn to very low for Zn (Ankerman, Large 1977).

The climate is maritime temperate, with moderate to strong winters and hot and semi to dry summers, characterized by the average annual temperature of 11.3°C and total annual rainfall of 690.2 mm.

Fruit samples for analysis were collected at commercial maturity, carefully rinsed with deionized water and, after recording their surface area, oven dried, weighed, ground to pass a 0.5 mm mesh and analyzed for macronutrient content according to the guidelines of the Association of Official Analytical Chemists (AOAC 1995). Nitrogen was determined by Kjeldahl analysis; phosphorus was analyzed spectrophotometrically by the phospho-vanadate colorimetric method (Hewlett Packard 8452A, Ontario, Canada); K was determined by flame photometry (Corning 405, Halstead, UK), and Ca, Mg, Fe, Mn, Cu and Zn by atomic absorption spectroscopy (Pye Unicam SP 191, Cambridge, UK); B was determined colorimetrically using quinalizarin, in a colorimeter Zeiss MK 6/6 (Carl Zeiss, Jena, Germany). The data are given as % and μg g^{-1} of dry matter for each macro- and microelement studied, respectively. The ash content was estimated after burning at 550°C and expressed as %. The values are presented as means ± standard error (SE) of triplicate analyses for each treatment per year.

A 2´2´3 factorial design was employed. The data from determinations of the minerals were analyzed by analysis of variance (ANOVA), using an MSTAT-C statistical package (Michigan State University, East Lansing, MI, USA), and mean values were grouped using an LSD test at $p \leq 0.05$ as a *post-hoc* analysis. Relationships between the minerals were evaluated by Pearson's product-moment correlation at $p \leq 0.05$. A principal component analysis (PCA) was performed to determine the relationships among rootstock/cultivar combinations and among variables using the PRINCOMP procedure of the SAS statistical package (SAS Institute Inc., North Carolina, USA).

RESULTS AND DISCUSSION

Ash and content of macroelements

Amounts of ash, P and K in plums varied significantly between the rootstocks, cultivars and years, whereas Ca and Mg significantly differed only

Table 2

Fruit ash and macroelements in Čačanska lepotica and Čačanska najbolja on different rootstocks

Parameter	Ash (%)	N (%)	P (%)	K (%)	Ca (%)	Mg (%)
Rootstock (A)						
Myrobalan	4.435±0.336^{b}	0.780±0.021^{a}	0.052±0.005^{b}	1.595±0.035^{a}	0.072±0.002^{a}	0.166±0.006^{a}
Stanley	4.640±0.261^{a}	0.790±0.010^{a}	0.066±0.004^{a}	1.375±0.005^{b}	0.076±0.005^{a}	0.150±0.028^{a}
Cultivar (B)						
Čačanska lepotica	4.838±0.291^{a}	0.798±0.031^{a}	0.054±0.007^{b}	1.505±0.133^{a}	0.078±0.005^{a}	0.169±0.015^{a}
Čačanska najbolja	4.240±0.207^{b}	0.772±0.026^{a}	0.063±0.004^{a}	1.463±0.060^{b}	0.070±0.010^{a}	0.148±0.012a
Year (C)						
2006	5.077±0.359^{a}	0.830±0.018^{a}	0.060±0.007^{b}	1.382±0.101^{c}	0.060±0.005^{b}	0.157±0.019^{b}
2007	4.347±0.134^{b}	0.710±0.011^{a}	0.064±0.008^{a}	1.588±0.105^{a}	0.068±0.009^{b}	0.155±0.021^{b}
2008	4.192±0.335^{c}	0.815±0.028^{a}	0.052±0.006^{c}	1.482±0.159^{b}	0.094±0.005^{a}	0.162±0.014^{a}
Average	4.539±1.028	0.785±0.013	0.059±0.007	1.484±0.211	0.074±0.004	0.158±0.008
ANOVA (significance)						
A × B	ns	ns	*	*	ns	ns
A × C	ns	ns	*	*	ns	ns
B × C	ns	ns	*	*	ns	ns

Different letter in columns indicate significantly different values at $p \leq 0.05$ by LSD test. The asterisk in column indicates a significant difference between means at $p \leq 0.05$ by LSD test. ns: non-significant differences.

among years (Table 2). Also, strong rootstock/cultivar/year interaction was observed for the ash, P and K content in plums. On the other hand, there were no significant differences among rootstocks, cultivars and years in the N and Mg content. The highest ash and P content were found in plums of the cultivars grafted on Stanley rootstock, whereas the K content was the highest in the cultivars grafted on Myrobalan. Fruits of Čačanska lepotica were richer in ash and K, whereas plums of Čačanska najbolja had a higher P content. Regarding the years, significantly higher ash content was determined in the first season; in the second year, the P and K content was the highest, while in the third season, the Ca and Mg content was higher. The total quantities of the macroelements accumulated in fully ripe plums followed a decreasing order: K > N > Mg > Ca > P.

Wide variations in the mineral composition of plums have been previously reported in the literature, for example Nergiz, Yýldýz (1997) claimed that the ash content was significantly affected by cultivars and geographical regions, and varied between 3.7 and 9.0 g kg^{-1}. Çalişir et al. (2005) reported that wild plum contained close to 3% ash. Our arrangement of the microelements in plums in the decreasing concentration order was in agreement with BHUTANI, JOSHI (1995), KUNACHOWICZ et al. (2005) and ÇALIŞIR et al. (2005), who all reported that K was a dominant mineral, followed by Ca and Mg. JAROSZEWSKA (2011) reported that under different water and fertilization regimes, macronutrient amounts in plums of Čacanska rana followed a decreasing order: K > N > P > Ca > Mg. Differences between the present results for some macroelements and those obtained by JAROSZEWSKA (2011) are probably due to diferent cultivars and environmental conditions. Namely, in our unpulished work, fruit of Čačanska rana had a higher water content when compared with Čačanska lepotica and Čačanska najbolja. This was connected with the solubility of minerals in water, due to which some amounts of the minerals were transferred to water (CLYDESDALE et al. 1991). On the other hand, RATO et al. (2008) reported that the content of some phytochemicals may be affected by a soil type and plum rootstock. In addition, plums of both cultivars on both rootstocks contained considerable amounts of Ca and Mg, which is in agreement with some previous studies carried out on plum (WALKOWIAK-TOMCZAK 2008, JAROSZEWSKA 2011). Finally, significant interactions between rootstocks, cultivars and years verified for some macroelements suggested that their content under the same conditions does not depend on a particular parameter alone (rootstock, cultivar or year) but on their combination, as observed previously (NERGIZ, YÝLDÝZ 1997).

Concentrations of microelements

Concentrations of microelements in two plum cultivars are shown in Table 3. Regarding rootstocks, Myrobalan induced a higher Fe concentration in plums, while plums growing from the Stanley rootstock had more B. Differences between the rootstocks in Mn, Cu and Zn concentrations were not significant. In this context, THORP et al. (2007) reported that rootstocks led to differences in the vigor of trees and had an important role in determining nutrient concentrations in fruits and leaves. According to the above authors, some rootstocks were evidently able to absorb nutrients from soil better than others, irrespective of their effect on the tree vigour. A similrar observation was previously reported by DAZA et al. (2008).

In respect of the cultivars, Čačanska lepotica had significantly higher amounts of Mn, Cu and Zn; plums of Čačanska najbolja had a higher Fe concentration, whereas no differences between the cultivars in the B content were observed. The Fe, Cu, Zn and Mn concentrations in fresh plums of *P. domestica* determined in the present study were much higher than found by YAGMUR, TASKIN (2011). L. NERGIZ, YÝLDÝZ (1997) also reported much less Fe in plums than observed in our study, whereas JAROSZEWSKA (2011) observed more Fe and less Zn in fruits of Čačanska rana than in our study. This may be due to differences in the tested cultivars. In general, our findings were similar to the data obtained by KATÝYAR et al. (1990), who reported

Table 3

Concentration of microelements in fruits of Čačanska lepotica
and Čačanska najbolja on different rootstocks

Parameter	Fe (µg g^{-1})	Mn (µg g^{-1})	Cu (µg g^{-1})	Zn (µg g^{-1})	B (µg g^{-1})
Rootstock (A)					
Myrobalan	20.50±0.832^{a}	9.800±2.638^{a}	3.300±0.431^{a}	18.92±2.091^{a}	21.56±0.567^{b}
Stanley	18.25±1.083^{b}	10.62±1.956^{a}	3.135±0.065^{a}	19.66±0.837^{a}	24.10±0.501^{a}
Cultivar (B)					
Čačanska lepotica	19.25±2.077^{a}	12.50±0.682^{a}	3.467±0.641^{a}	20.25±1.189^{a}	22.87±2.530^{a}
Čačanska najbolja	19.50±1.204^{a}	7.917±0.471^{b}	2.967±0.253^{b}	17.83±2.355^{b}	22.80±1.987^{a}
Year (C)					
2006	18.00±2.380^{b}	10.65±1.746^{a}	2.750±0.126^{c}	22.87±2.276^{a}	29.20±1.829^{a}
2007	21.62±0.746^{a}	10.30±1.692^{a}	3.125±0.382^{b}	19.00±2.406^{b}	18.20±0.804^{c}
2008	18.50±2.372^{b}	9.675±0.945^{a}	3.775±0.953^{a}	15.87±1.419^{c}	21.10±0.451^{b}
Average	19.37±1.128	10.21±0.411	3.215±0.085	19.29±0.371	22.83±1.274
ANOVA (significance)					
A × B	ns	ns	*	*	*
A × C	ns	ns	*	ns	*
B × C	*	*	*	ns	*

Different letter in columns indicate significantly different values at $p \leq 0.05$ by LSD test.
The asterisk in column indicates a significant difference between means at $p \leq 0.05$ by LSD test.
ns – non-significant differences

that plums of *P. domestica* L. contained 4-360 mg kg^{-1} Fe. The total amounts of microelements in plums followed a decreasing order: B > Fe > Zn > Mn > Cu (Table 3). These results are in good agreement with the orders reported by Stacewicz-Sapuntzakis et al. (2001) and Walkowiak-Tomczak (2008), who all emphasized that plums are an important source of B. In contrast, Çalişir et al. (2005) reported that wild plums conatined more Fe than B, and their decreasing order for five microelements was: Fe > B > Cu > Mn > Zn.

Year-by-year variations in levels of the microelements were observed; Zn and B concentrations were higher in 2006, Fe – in 2007, and Cu – in 2008. Differences between the years in Mn concentrations were not observed. Annual variations in the content of Fe, Cu, Zn and B could be due to the environmental conditions as well as the nutritional status of the plantation (Nergiz, Yýldýz 1997, Stacewicz-Sapuntzakis et al. 2001).

Finally, strong interactions between the cultivar and year with respect to Fe, and among the rootstock, cultivar and year in the case of the other microelements indicated a very complex nature of the accumulation of microelements in fruits of plum trees and the importance of a good choice of rootstocks to maximize the potential performance of a cultivar grown in an orchard for several years, both observations claimed previously by THORP et al. (2007).

Relationship among fruit minerals and principal component analysis

The data given in Table 4 showed some significant relations between the set of variables evaluated. The Mn and Zn amounts significantly correlated with the ash content. These relationships indicated that a higher ash

Table 4

Correlation matrix between the analyzed variables

Variables	Ash	N	P	K	Ca	Mg	Fe	Mn	Cu	Zn	B
Ash	1										
N	0.897	1									
P	-0.435	-0.171	1								
K	-0.133	-0.280	-0.815	1							
Ca	0.660	0.420	0.000	-0.537	1						
Mg	0.318	-0.133	-0.621	0.316	0.570	1					
Fe	-0.249	-0.117	-0.477	0.812	-0.860	-0.292	1				
Mn	0.988*	0.863	-0.565	0.022	0.580	0.366	-0.121	1			
Cu	0.714	0.718	-0.733	0.467	-0.032	0.072	0.501	0.795	1		
Zn	0.960*	0.948	-0.470	-0.015	0.428	0.121	-0.003	0.967*	0.856	1	
B	0.366	0.652	0.635	-0.843	0.322	-0.588	-0.452	0.240	0.001	0.381	1

Asterisk indicated that correlation coefficient is significant at $p \leq 0.05$.

content contained more Mn and Zn. Additionally, Zn and Mn significantly correlated with each other. Correlations between the other variables were not significant. JAROSZEWSKA (2011) noticed a strong relationship between sugars and K or Ca, which proves that the content of macro- and microelement in plums is a complex phenomenon, determined by numerous characteristics, e.g. the soil type and texture, content of soil nutrients and their ratio, amounts of rainfall, field water capacity, air temperature and horticultural practice (BERNSTEIN et al. 1956).

More than 80% of the variability obtained in this study was explained by the first two variables (Table 5). PC1 and PC2 accounted for 47.01% and 33.93% of the variability, respectively. Figure 1 represents PC1 and PC2 plotted on a two-dimensional plane. Table 6 shows correlations between the original variables and the first two principal components: PC1 represents

Table 5

Eigenvalues and proportion of total variability among rootstock/cultivar combinations as explained by the three principal components (PC)

PC	Eigenvalues	Percent of variance	Cumulative (%)
1	5.171	47.011	47.011
2	3.732	33.926	80.937
3	2.097	19.063	100.000

Table 6

Component loadings for macro- and microelements in plums for four rootstock/cultivar combinations based on three principal components

Variable	Component loadings		
	PC1, λ = 47.01	PC2, λ = 33.93	PC3, λ = 19.06
Ash (%)	0.995	-0.074	0.061
N (%)	0.908	-0.217	-0.359
P (%)	-0.485	-0.842	-0.238
K (%)	-0.061	0.998	0.020
Ca (%)	0.587	-0.515	0.625
Mg (%)	0.287	0.316	0.904
Fe (μg g^{-1})	-0.155	0.815	-0.559
Mn (μg g^{-1})	0.995	0.082	0.060
Cu (μg g^{-1})	0.777	0.522	-0.351
Zn (μg g^{-1})	0.980	0.049	-0.194
B (μg g^{-1})	0.336	-0.815	-0.472

the amounts of ash, N, Ca, Mn, Cu and Zn; PC2 represents the amounts of P, K, Mg, Fe and B. The positive PC1 values indicate that Čačanska lepotica on Stanley gives a higher amount of ash, N, Ca, Mn, Cu and Zn, as shown in Figure 1. The positive values for PC2 show that Čačanska lepotica on Myrobalan had a higher amount of K, Mg and Fe, while the negative PC2 values indicate a higher content of P and B in Čačanska najbolja on Stanley. In general, higher positive values for PC1 and PC2 indicate that Čačanska lepotica on both rootstocks had a higher content of ash, N, K, Ca, Mg, Fe, Mn, Cu and Zn, while Čačanska najbolja on Stanley rootstocks had a higher P and B content.

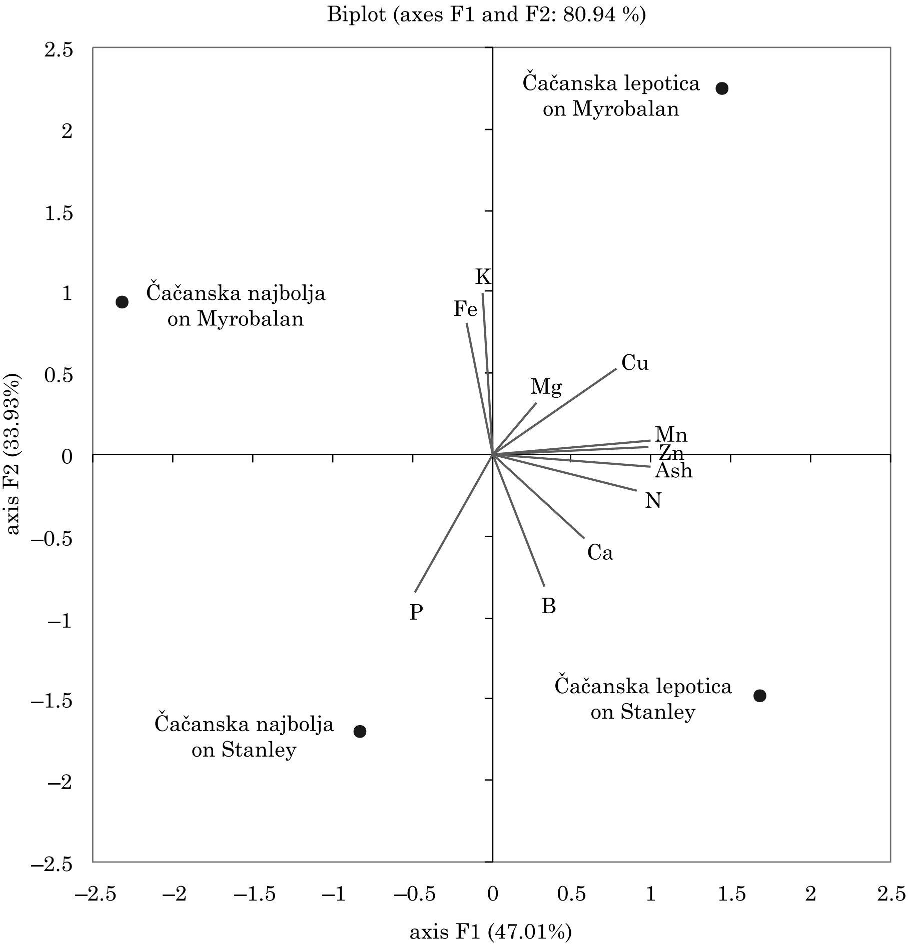

Fig. 1. Biplot based on principal component analysis (PCA) for ash, macro- (N, P, K, Ca and Mg) and microelement (Fe, Mn, Cu, Zn and B) contents in four plum cultivar/rootstock combinations

CONCLUSIONS

1. The results showed that rootstocks, cultivars, years and their mutual interaction induced a wide variation in amounts of macro- and microelements, except nitrogen, in fruit of plum trees. Stanley seedlings as a rootstock resulted in a higher content of ash, phosphorus and boron, while Myrobalan rootstock stimulated higher levels of potassium and iron in plums; fruits of Čačanska lepotica had more ash, potassium, manganese, copper

and zinc, and Čačanska najbolja fruits had more phosphorus and iron; more ash, zinc and boron was found in the 1st season; more phosphorus and potassium in the 2nd year and more calcium, magnesium and copper in the 3rd season.

2. Strong positive relationships were observed between ash and manganese or zinc, and between zinc and manganese.

3. The Principal component analysis suggested that Stanley rootstock may be better at achieving higher amounts of minerals in fruits than Mirobalan for Čačanska lepotica and Čačanska najbolja grown on Cambisol with low soil pH and deficiency of most soil nutrients.

REFERENCES

ANKERMAN D., LARGE R. 1977. *Minor elements*. In: (Ed.). *Soil and plant analysis*. Ankerman D. Soil Science Society of America, Inc., Madison, Wisconsin, USA, 34-45.

AOAC. 1995. *Official Methods of Analysis*. In: 16th Ed. Washington DC, 67-75.

AUGER C., AL-AWWADI N., BORNET A., ROUANET J.M., GASC F., CROS G., TEISSEDRE P.L. 2004. *Catechins and procyanidins in Mediterranean diets*. Food Res. Int., 37(3): 233-245.

BERNSTEIN L., BROWN J. W., HAYWARD H.E. 1956. *The influence of rootstock on growth and salt accumulation in stone-fruit trees and almonds.* Proc. Am. Soc. Hort. Sci., 68: 86-95.

BHUTANI V.P., JOSHI V.K. 1995. *Plum*. In: Salunkhe D.K. Kadam S.S. (Ed.). *Fruit science and technology, production, composition, storage and processing*. Marcel Dekker, Inc., New York, 203-241.

ÇALIŞIR S., HACÝSEFEROĐULLARÝ H., ÖZCAN M., ARSLAN D. 2005. *Some nutritional and technological properties of wild plum (Prunus spp.) fruits in Turkey*. J. Food Eng., 66(2): 233-237.

CLYDESDALE F.M., HO L.T., LEE C.Y., MONDY N.I., SHEWFWLT R.L. 1991. *The effects of postharvest treatment and chemical interactions on the bioavailibility of ascorbic acid, thiamin, vitamin A, carotenoids and minerals*. Crit. Rev. Food Sci. Nutr., 30(6): 599-638.

DAZA A., GARCIA-GALAVIS P.A., GRANDE M.J., SANTAMARIA C. 2008. *Fruit quality parameters of 'Pioneer' Japanese plums produced on eight different rootstocks*. Sci. Hort., 118(3): 206-211.

FAO Statistics Division, February 16, 2012. Available from http://faostat.fao.org.

GEORGE F.M.B. 2006. *Vitamins in foods: analysis, bioavailability and stability*. CRC Press, United States.

JAROSZEWSKA A. 2011. *Quality of fruit cherry, peach and plum cultivated under different water and fertilization regimes*. J. Elementol., 16(1): 51-58.

KATÝYAR S.K., SHARMA K., KUMAR N., BHATIA A.K. 1990. *Composition of some unconventional Himalayan wild fruits*. J. Food Sci. Technol., 27(5): 309-310.

KUNACHOWICZ H., NADOLNA I., PRZYGODA B., IWANOW K. 2005. *Food composition tables*. PZWL, Warsaw. (in Polish)

LORETI F., GUERRIERO, R., MASSAI R. 1990. *A new and promising plum rootstock selection: "Mr.S.2/5"*. Acta Hort., 283: 261-266.

MILOŠEVIĆ T., MILOŠEVIĆ N. 2011. *Growth, fruit size, yield performance and micronutrient status of plum trees (Prunus domestica* L.*)*. Plant Soil Environ., 57(12): 559-564.

NERGIZ C., YÝLDÝZ H. 1997. *Research on chemical composition of some varieties of European plums (Prunus domestica) adapted to the Aegean district of Turkey*. J. Agr. Food Chem., 45(8): 2820-2823.

PROTIC N., MARTINOVIC L., MILICIC B., STEVANOVIC D., MOJASEVIC, M. 2003. *The status of soil surveys in Serbia and Montenegro*. In: *Soil resources of Europe*. JONES R., HOUŠKOVA B., BULLOCK P., MONTANARELLA L. (Ed.). The European Soil Bureau, Luxemburg: Ispra, 297-315.

RATO E.A., AGULHEIRO C.A., BARROSO M.J., RIQUELME, F. 2008. *Soil and rootstock influence on fruit quality of plums (Prunus domestica* L.*)*. Sci. Hort., 118(3): 218-222.

STACEWICZ-SAPUNTZAKIS M., BOWEN P.E., HUSSAIN E.A., DAMAYANTI-WOOD B.I., FARNSWORTH N.R. 2001. *Chemical composition and potential health effects of prunes: a functional food?* Crit. Rev. Food Sci. Nutr., 41(4), 251-286.

THORP T.G., BOYD L.M., BARNET A.M., LOWE R.G., HOFSTEE B.J., BLATTMANN P.J., CLEARWATER M.J. 2007. *Effect of inter-specific rootstocks on inorganic nutrient concentrations and fruit quality of 'Hort16A' kiwifruit* (*Actinidia chinensis* Planch. var. *chinensis*). J. Hortic. Sci. Biotech., 82(6): 829-838.

WALKOWIAK-TOMCZAK D. 2008. *Characteristics of plums as a raw material with valuable nutritive and dietary properties – a review*. Pol. J. Food Nutr. Sci., 58(4): 401-405.

YAGMUR C., TASKIN M. 2011. *Study on changes in mineral content of plum (Prunus domestica) and strawberry (Fragaria × ananassa) during canning*. Ind. J. Agr. Sci., 81(8): 723-728.

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CHANGES IN THE CONTENT OF SOME MACRONUTRIENTS IN BASIL HERBAGE INDUCED BY DIFFERENT NITROGEN AND POTASSIUM FERTILIZATION RATES*

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Abstract

This experiment, carried out in a greenhouse from February to May in 2008-2010, was designed to determine the effect of an increased rate of nitrogen and potassium on the content of phosphorus, calcium, magnesium, chlorine and sulphur in basil herbage as well as to trace relationships between a basil cultivar and changes in the mineral composition of the herbage as influenced by the applied rates of nutrients. The mineral composition of basil herbage was determined on the basis of an analysis of the growing substrate conducted after the harvest of the experimental plants. Two Polish cultivars of basil, called Kasia and Wala, as well as a green-leaved form popular on the domestic horticultural market, were grown from seedlings in pots (4 dm^3) filled with sphagnum peat of the pH between 5.5-6.0. The following amounts of nutrients were applied, expressed in g per 1 dm^3 of the growing substrate: 0.2, 0.4, 0.6, 0.9 N in the form of ammonium nitrate; 0.4, 0.8 K in the form of potassium sulphate; 0.4 P as 20% P superphosphate; 0.3 Mg in the form of magnesium sulphate monohydrate, as well as the following micronutrients (in g per 1 dm^3 of the growing substrate): 8.0 Fe (EDTA), 5.1 Mn ($MnSO_4 \cdot H_2O$), 13.3 Cu ($CuSO_4 \cdot 5H_2O$), 0.74 Zn ($ZNSO_4 \cdot 7H_2O$), 1.6 B (H_3BO_3) and 3.7 Mo ($(NH_4)_6Mo_7)_{24} \cdot 4H_2O$).

The plants were harvested at the beginning of flowering (29 May 2008, 25 May 2009 and 27 May 2010) by cutting off the aerial part of the stem above its lignified parts. The herbage was dried at 70°C, ground and used for chemical analysis. The analysed basil herbage proved to be a good source of phosphorus, calcium, chlorine and sulphur. The increasing

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rate of nitrogen resulted in an increased concentration of the mineral nutrients determined in the basil herbage. The magnesium concentration in the basil herbage dry matter was not dependent on a cultivar and nitrogen rate, but increased under the influence of the higher amount of potassium applied. On the other hand, the raised amounts of potassium did not modify the concentrations of phosphorus and sulphur in the examined plant material.

Key words: *Ocimum basilicum* L., cultivar, nitrogen and potassium fertilization.

ZMIANY ZAWARTOŚCI NIEKTÓRYCH MAKROELEMENTÓW W ZIELU BAZYLII POD WPŁYWEM ZRÓŻNICOWANEGO ŻYWIENIA ROŚLIN AZOTEM I POTASEM

Abstrakt

Celem doświadczenia przeprowadzonego w okresie od lutego do maja 2008-2010 w szklarni było określenie wpływu zwiększonej dawki azotu oraz potasu na zawartość fosforu, wapnia, magnezu, chloru i siarki w zielu bazylii oraz prześledzenie zależności między odmianą bazylii a zmianami składu mineralnego ziela pod wpływem zastosowanych dawek składników pokarmowych. Analizę składu mineralnego ziela bazylii oparto na analizie podłoża po zbiorze roślin doświadczalnych. Bazylię dwóch polskich odmian Kasia i Wala oraz formy zielonolistnej, popularnej na krajowym rynku ogrodniczym, uprawiano z rozsady w doniczkach (4 dm^3), wypełnionych torfem sfagnowym o pH 5,5-6,0. Zastosowano następujące ilości składników pokarmowych (g dm^{-3} podłoża): 0,2; 0,4; 0,6; 0,9 N w formie saletry amonowej; 0,4; 0,8 K w postaci siarczanu potasu; 0,4 P w postaci superfosfatu 20% P; 0,3 Mg w formie jednowodnego siarczanu magnezu oraz mikroelementy (mg 1 dm^{-3} podłoża) 8,0 Fe (EDTA); 5,1 Mn ($MnSO_4 \cdot H_20$]; 13,3 Cu ($CuSO_4 \cdot 5H_2O$); 0,74 Zn ($ZNSO_4 \cdot 7H_2O$); 1,6 B (H_3BO_3) i 3,7 Mo ($(NH_4)_6Mo_7)_{24} \cdot 4H_2O$).

Zbiór roślin przeprowadzono na początku kwitnienia (29 maja 2008, 25 maja 2009 i 27 maja 2010), ścinając nadziemną część pędu powyżej jej zdrewniałych fragmentów. Ziele wysuszono w temp. 70°C, zmielono i przeznaczono do analiz chemicznych. Badane ziele bazylii okazało się dobrym źródłem fosforu, wapnia, chloru i siarki. Wzrastająca dawka azotu powodowała zwiększenie koncentracji badanych składników mineralnych w roślinie. Koncentracja magnezu w suchej masie ziela bazylii nie była uzależniona od odmiany oraz dawki azotu, natomiast zwiększała się pod wpływem wzrastającej ilości potasu. Zwiększona ilość potasu nie modyfikowała udziału fosforu i siarki w badanym materiale roślinnym.

Słowa kluczowe: *Ocimum basilicum* L., odmiana, nawożenie azotem i potasem.

INTRODUCTION

The nutritional status of plants affects yield amount and quality as well as plant resistance to stress factors. An optimal supply of macro- and micronutrients to cultivated plants, provided that light, thermal and moisture conditions are adequate, ensures high quality yield, reduces production costs and restrains the risk of environmental contamination. Herbal plants constitute valuable raw material, whose biological activity depends on the content of the major biologically active substances and accompanying macro- and micronutrients, enzymes, and vitamins. Nitrogen and potassium belong to the most important nutrients taken up by plants in the largest quantities. Nitrogen, which is called a yield-stimulating nutrient, affects both volumes of yields and the chemical composition of yield components (CHEN et al. 2004, NURZYŃSKA-WIERDAK 2006, BIESIADA, KOŁOTA 2010, BIESIADA, KUŚ 2010). The primary function of nitrogen is to participate in the formation of amino acids, which are structural elements of proteins as well as pyrimidine and purine bases, nucleotides and nucleic acids (BAHMANYAR, SOODAEE-MASHAEE 2010). As a component of these and other compounds, nitrogen participates in almost all biochemical reactions occurring in living organisms. Nitrogen uptake by plants is associated with the presence of other important mineral nutrients in the nutritional environment, including potassium. Disturbances in nitrogen metabolism, arising from potassium deficiency, manifest themselves in changes in the proportions between nitrogen fractions as well as in the accumulation of harmful amino substances in plants, such as agmatine, N-carbamoyl putrescine, putrescine or ammonium ions (NOWACKI 1980). The application of increased potassium fertilization has a clear effect on the decrease in the concentration of nitrates (HANAFY-AHMED et al. 2000, MICHAŁOJĆ 2000, NURZYŃSKA-WIERDAK 2006).

Basil responds very well to fertilization, especially organic one, and can thoroughly use up nutrients (SIFOLA, BARBIERI 2006, ZHELJAZKOV et al. 2008, SEIDLER-ŁOŻYKOWSKA et al. 2009, NURZYŃSKA-WIERDAK et al. 2011). Increased rates of nitrogen, potassium, phosphorus, sulphur and calcium modify the mineral composition of basil herbage (YAMAMOTO, TAKANO 1996, RAO et al. 2007, GEETHA et al. 2009, BIESIADA, KUŚ 2010, DZIDA 2010). Furthermore, foliar feeding stimulates the height and weight of basil plants and raises the concentration of potassium and calcium in basil herbage (NURZYŃSKA-WIERDAK, BOROWSKI 2011, NURZYŃSKA-WIERDAK et al. 2011). Calcium, phosphorus, magnesium, and sulphur, i.e. the minerals that are the major building material for bones, teeth, skin and hair, play an important physiological function in the human organism; in addition to dairy products, raw plants are a source of these mineral components (FRIEDRICH 2002). In turn, chlorine is important for the water and electrolyte management as well as for the acidic and alkaline balance. Magnesium, a poorly absorbable ion, seems to be particularly important; its deficiency raises our sensitivity to stress, which is an underlying cause of many civilization diseases (KŁOSIEWICZ-LATOSZEK 1993). The factors inhibiting magnesium bioavailability in the alimentary canal include, *inter alia*, high-protein and high-fat diet as well as foreign substances in food and addictive substances (FRIEDRICH 2002). Herbal raw materials, which are used as seasoning, therapeutic and aromatic agents, can be a valuable, although still underappreciated, source of macro- and micronutrients. The aim of the present study was to determine the effect of an increased rate of nitrogen and potassium on the content of phosphorus, calcium, magnesium, chlorine and sulphur in basil herbage as well as to trace relationships between a basil cultivar and changes in the mineral composition of the herb as influenced by the applied rates of nutrients. The mineral composition of basil herbage was determined on the basis of an analysis of the growing substrate conducted after the harvest of the experimental plants.

MATERIAL AND METHODS

The present experiment was conducted in a detached greenhouse, with the north-south orientation of the major axis. The greenhouse belonged to the Department of Vegetable Crops and Medicinal Plants, University of Life Sciences in Lublin. The experiment was conducted from February to May in 2008-2010. The temperature in the greenhouse was at 18-25°C during the day and 12-15°C at night. Two Polish cultivars of basil, Kasia and Wala (breeder and distributor: Institute of Natural Fibres and Medicinal Plants in Poznań) as well as a green-leaved form popular on the domestic horticultural market (distributor: a seed production company called PNOS Ożarów Mazowiecki), were grown from seedlings. The plants were grown in pots (4 dm^3) filled with sphagnum peat of the pH between 5.5-6.0. The experiment was conducted using a completely randomized design with 8 replicates. A single basil plant, i.e. an experimental unit, grew in each pot. Basil seeds were sown on the following dates: 28 February (2008), 12 March (2009), and 3 March (2010). Before sowing, seeds were dressed with the fungicide Dithane Neo Tec 75 WG. Emergence occurred after about 8 days. After 18-20 days from sowing, the plants were transferred into multi-cell trays filled with peat substrate. The present study was carried out under strictly controlled conditions. No presence of diseases or pests was found on the plants during the growing period, therefore no chemical protection was used. The plants were transplanted to pots about 25 days after sowing, at the 4 true-leaf stage.

The following amounts of nutrients (in g per 1 dm^3 of growing substrate) were applied in the experiment: 0.2, 0.4, 0.6, 0.9 N in the form of ammonium nitrate; 0.4, 0.8 K in the form of potassium sulphate; 0.4 P as 20% P superphosphate; 0.3 Mg in the form of magnesium sulphate monohydrate, and the following micronutrients (in g per 1 dm^3 of growing substrate): 8.0 Fe (EDTA), 5.1 Mn ($MnSO_4 \cdot H_2O$), 13.3 Cu ($CuSO_4 \cdot 5H_2O$), 0.74 Zn ($ZNSO_4 \cdot 7H_2O$), 1.6 B (H_3BO_3), and 3.7 Mo [$(NH_4)_6Mo_7)_{24} \cdot 4H_2O$]. During the experiment, the plants were watered with the same amount of water (250-300 ml) every 1-2 days. The plants were harvested at the beginning of flowering (29 May 2008, 25 May 2009, and 27 May 2010) by cutting off the aerial portion of the stem above its lignified parts. The herbage was dried at 70°C, ground and the following were determined in 2% CH_3COOH extract: chlorine (colourimetrically with $AgNO_3$) and sulphates with $BaCL_2$. After dry combustion at 550°C, phosphorus was determined colourimetrically with ammonium vanadium and molybdate, while potassium, calcium, and magnesium were determined with the atomic absorption method using a Perkin-Elmer Analyst 300 spectrometer.

Immediately after plant harvest, samples of the growing substrate were taken for chemical analysis and the following were determined in the substrate: in 0.03 M acetic acid extract, the content of phosphorus, calcium, magnesium, chlorine and sulphates using the same method as applied for the plant material, substrate's pH – potentiometrically in H_2O, and ion concentration (EC) – conductometrically. The results of chemical assays were statistically described using analysis of variance for three-way cross-classification, evaluating the significance of differences with Tukey's confidence intervals and performing LSD calculations at the level of significance α=0.05.

RESULTS AND DISCUSSION

The herbage of the basil cultivars differed significantly in the content of the macronutrients, except for magnesium (Table 1). The cultivar Kasia was characterized by the highest concentration of phosphorus and calcium, while the green-leaved form accumulated the highest amount of chlorine and sulphur. These results are in agreement with those obtained by Dzida (2010), who confirms cultivar-specific differences in this respect. The mineral composition of the investigated herbal material was generally comparable to the literature data (Khalid 2006, Rao et al. 2007, Seidler-Łożykowska et al. 2009, Biesiada, Kuś 2010, Dzida 2010). The biggest differences appeared in the proportion of phosphorus (Rao et al. 2007, Dzida 2010), calcium and magnesium (Seidler-Łożykowska et al. 2009, Dzida, 2010), and were probably induced by different amounts of mineral nutrients in the nutritional environment of the cultivated plants as well as cultivar-specific differences. The growth dynamics of basil plants, like their morphological characteristics, is highly varied (Labra et al. 2004, Nurzyńska-Wierdak 2007, Abduelrahman et al. 2009, Svecova, Neugebauerova 2010). The leaf/stem ratio (LS) and the leaf area index (LAI) in basil are significantly affected by both a nitrogen rate (LAI) and a cultivar (LS and LAI) (Sifola, Barbieri 2006), which should also be attributable to the plant's mineral balance.

The applied nitrogen rate significantly modified the concentrations of phosphorus, magnesium, chlorine and sulphur in the basil plants (Table 1). The study showed that the concentrations of the these macronutrients in the basil herbage increased with the increasing rate of nitrogen; phosphorus was an exception, since it increased only in the series from the lowest to the second highest rate of nitrogen. The level of macronutrients in the basil herbage depends on the rate of nitrogen and irrigation (Biesiada, Kuś 2010). These relationships partly arise from the yield-stimulating role of nitrogen and from the interactions between macronutrients. It should be noted here that the analysis of the growing substrate after plant harvest did not confirm the significant effect of the nitrogen rate on its chemical composition, which should be attributable to the uptake of minerals by the plants during their growth (Table 2). The concentration of phosphorus, which is always taken up by plants against its concentration gradient, was the highest in the analyzed basil herbage under the substrate rate of nitrogen, but de-

Table 1

Phosphorus, calcium, magnesium, chlorine and sulphur content in sweet basil herbage (mean for 2008-2010)

Cultivar (A)	N dose (B)	K dose (C)	P	Ca	Mg	Cl	$S\text{-}SO_4$
	(g dm^{-3})		(% d.m.)				
Kasia	0.2	0.4	0.69	1.54	0.20	0.24	0.18
		0.8	0.59	1.52	0.22	0.53	0.24
	0.4	0.4	0.71	1.64	0.22	0.62	0.22
		0.8	0.77	1.56	0.25	0.65	0.23
	0.6	0.4	0.72	1.69	0.27	0.62	0.23
		0.8	0.76	1.69	0.28	0.64	0.24
	0.9	0.4	0.63	1.95	0.30	0.86	0.23
		0.8	0.71	1.62	0.34	0.98	0.23
Mean (A)			0.69	1.65	0.26	0.64	0.22
Wala	0.2	0.4	0.59	1.33	0.16	0.79	0.24
		0.8	0.48	1.23	0.18	0.52	0.28
	0.4	0.4	0.64	1.45	0.21	0.47	0.28
		0.8	0.61	1.30	0.23	0.66	0.29
	0.6	0.4	0.58	1.55	0.24	0.47	0.32
		0.8	0.55	1.26	0.26	0.60	0.34
	0.9	0.4	0.63	1.61	0.27	1.14	0.28
		0.8	0.53	1.25	0.31	1.20	0.31
Mean (A)			0.58	1.37	0.23	0.69	0.27
Green	0.2	0.4	0.54	1.41	0.16	0.46	0.28
		0.8	0.54	1.23	0.18	0.64	0.31
	0.4	0.4	0.62	1.59	0.21	0.59	0.31
		0.8	0.59	1.47	0.23	0.73	0.32
	0.6	0.4	0.82	1.64	0.24	0.75	0.34
		0.8	0.69	1.55	0.26	0.72	0.37
	0.9	0.4	0.80	1.96	0.27	1.44	0.34
		0.8	0.72	1.41	0.31	1.64	0.40
Mean (A)			0.66	1.53	0.25	0.87	0.33
Nean (B)	0.2		0.57	1.38	0.19	0.48	0.24
	0.4		0.66	1.50	0.23	0.62	0.27
	0.6		0.68	1.56	0.26	0.63	0.29
	0.9		0.67	1.63	0.30	1.21	0.31
Mean (C)	0.4		0.66	1.61	0.23	0.68	0.27
	0.8		0.63	1.42	0.26	0.79	0.29
Mean			0.64	1.52	0.25	0.73	0.28
$LSD_{0.05}$							
A			0.10	0.23	n. s.	0.10	0.03
B			0.13	0.11	0.05	0.12	0.04
C			n. s.	0.15	n. s.	0.06	n. s.
AxB			n. s.	n. s.	n. s.	0.28	n. s.

n.s. – not significance

creased under a higher dose of nitrogen; at the same time, this mineral remained in the substrate in a larger amount. Given the fact that only some of phosphates introduced into the nutritional environment are used by plants during the same growing season, the above relationship is a logical consequence of mineral nutrition of plants. The phosphorus content determined in the basil herbage was comparable to the results reported by other authors (ÖZCAN 2004, ÖZCAN et al. 2005, 2007). The calcium content in the investigated herbage averaged 1.52% of dry weight (DW) and it was lower than in some other described basil plants (ÖZCAN 2004, SEIDLER-ŁOŻYKOWSKA et al. 2009, BIESIADA, KUŚ 2010, DZIDA 2010), which could have resulted from cultivar-specific differences and from the level of nutrients in soil, in particular under increased calcium fertilization (DZIDA 2010). The concentration of the above nutrient increased under the influence of the increasing rate of nitrogen, but the differences in the calcium content in plants fertilized with the substrate rates of nitrogen were not statistically significant. The magnesium concentration in the investigated plant material was on average 0.25% DW, being much lower than determined by ÖZCAN (2004), but was higher under the increasing rate of nitrogen. Similar relationships were shown by BIESIADA and KUŚ (2010) in the cultivation of a red-leaved form of basil. Excessively high levels of NH_4^+ and K^+ ions in the nutritional environment reduce magnesium uptake by plants. Good supply of magnesium to the analyzed basil plants can be explained by the adequate concentration of ions in the substrate and its optimal pH. The concentrations of chlorine and sulphur in the investigated basil herbage increased with the increasing rate of nitrogen (Table 1). These relationships should be attributable to the increase in the basil plant biomass under the increasing rate of nitrogen (NURZYŃSKA-WIERDAK et al. 2012) rather than to the correlation between the ions.

The mineral composition of the investigated basil herb was affected by the potassium rate, but significant differences were shown only for the concentration of calcium and chlorine (Table 1). The increased concentration of potassium in the nutritional environment of the plants caused a decrease in calcium in the basil herbage dry matter, most probably due to the antagonism between these two mineral nutrients. In turn, the chlorine concentration significantly increased under the influence of the increasing rate of potassium. Different concentrations of elements in the plant, as compared to their concentration in the nutritional environment, indicate selective, active uptake of elements, frequently against their concentration gradient in the plant. Moreover, the accumulation of macronutrients by the plant under the increased mineral fertilization occurred at different intensity in particular plant organs (ALI et al. 2003, DZIDA 2010, SHEHU et al. 2010, MARKIEWICZ et al. 2011).

The growing substrate after the harvest of the basil plants was characterized by a pH in the range of 4.50-6.10 and an ion concentration (EC) of 1.3-2.3 mS cm^{-1}, depending on the rate of nitrogen and potassium (Table 2).

Table 2

pH values and EC in substrate after sweet basil harvest (2008-2010)

Cultivar (A)	N dose (B)	K dose (C)	pH_{H_2O} (range)	EC (mS cm^{-1})
	(g dm^{-3})			
Kasia	0.2	0.4	5.5-6.1	1.1
		0.8	5.4-5.8	1.4
	0.4	0.4	5.3-5.6	1.5
		0.8	4.9-5.6	1.7
	0.6	0.4	4.9-5.6	1.7
		0.8	4.9-5.4	1.8
	0.9	0.4	4.9-5.4	2.1
		0.8	4.8-5.3	2.1
Range / Mean (A)			4.8-6.1	1.7
Wala	0.2	0.4	5.6-6.0	1.4
		0.8	5.5-5.8	1.6
	0.4	0.4	5.3-5.5	1.7
		0.8	5.0-5.5	1.9
	0.6	0.4	4.9-5.2	2.1
		0.8	4.8-5.2	2.3
	0.9	0.4	4.8-5.1	2.5
		0.8	4.7-5.0	2.6
Range / Mean (A)			4.7-6.0	2.0
Green	0.2	0.4	5.5-6.1	1.0
		0.8	5.2-6.1	1.4
	0.4	0.4	4.8-5.8	1.7
		0.8	4.7-5.7	1.8
	0.6	0.4	4.7-5.6	1.9
		0.8	4.6-5.5	2.1
	0.9	0.4	4.6-5.5	2.1
		0.8	4.5-5.4	2.4
Range / Mean (A)			4.5-6.1	1.8
Range / Mean (B)			5.2-6.1 4.7-5.8 4.6-5.6 4.5-5.5	1.3 1.7 2.0 2.3
Mean (C)			4.6-6.1 4.5-6.1	1.7 1.9
Mean			4.5-6.1	1.8
$LSD_{0.05}$ A B C				 0.2 0.3 0.1

n.s. – not significance

The substrate on which the basil cultivars were grown differed in terms of the value of both pH and EC, which could indicate different nutritional requirements of the cultivars, associated even with a different growth dynamics (NURZYŃSKA-WIERDAK et al. 2011). On the other hand, the analysis of the nutrient content in the substrate does not confirm this hypothesis (Table 3). Residues of the macronutrients in the substrate show that the basil plants took up nutrients in a similar way and that nutrient availability was adequate. It was only in the case of calcium that significantly more of this element remained in the substrate used for growing the green-leaved basil form than in the other substrates, which could suggest its more intensive uptake. These differences have also been shown for other basil cultivars (DZIDA 2010), but these relationships could have also been caused by the increased rate of calcium carbonate applied in the nutrition of plants. The increased level of nitrogen and potassium caused an increase in the value of the substrate's EC (Table 2). Similar correlations have been shown in other papers (DZIDA 2004, DZIDA, PITURA 2008, GOLCZ et al. 2008, NURZYŃSKA-WIERDAK 2006, 2009), but more importance in this respect is generally attached to nitrate ions than to potassium ions. The applied rates of nitrogen and potassium did not have a significant effect on the content of phosphorus, calcium, magnesium and chlorine in the substrate after plant harvest. However, it was shown that the quantity of sulphates in the substrate increased with the increasing rate of potassium. SO_4^{2-} ion uptake is not inhibited by nitrates, phosphates or chlorides, but only by selenate anions, hence the above relationships should not be linked to the competition between ions, in particular given that the plants receiving more potassium also accumulated more sulphur in the herbage, but this was not statistically confirmed (Table 1). Similar correlations have been shown in our earlier papers (NURZYŃSKA-WIERDAK 2006, 2009) and they should be attributable to the type of fertilizer applied, which was potassium sulphate. When comparing the mineral composition of the plants and of the substrate on which they were grown to the concentration of salts in the substrate, the present study demonstrated that the uptake and absorption of phosphorus, calcium, magnesium, chlorine and sulphur by basil plants were not reduced at the increasing value of EC. Excessive salt concentration in the substrate results in a reduction in N, P, Ca and Mg uptake and increased concentration of Na and Cl in plant tissues (ESMAILI et al. 2008). On the other hand, however, differences in nutrient uptake by plants also arise from their cultivation on different substrates. Furthermore, nitrogen fertilization increases plant tolerance to excessive salinity through an improvement in their nutritional status (ESMAILI et al. 2008). The results obtained in this study indicate that basil plants received adequate nitrogen and potassium fertilization, which enabled their proper nutrient uptake and absorption, also under the increasing concentration of salts in the growing substrate.

Table 3

Phosphorus, calcium, magnesium, chlorine and sulphur content in a substrate from sweet basil cultivation (mean for 2008-2010)

Cultivar (A)	N dose (B)	K dose (C)	P	Ca	Mg	Cl	$S-SO_4$
	($g\ dm^{-3}$)		($mg\ d.m.^{-3}$)				
Kasia	0.2	0.4	162.3	1800.0	206.3	182.5	360.7
		0.8	174.2	1765.3	174.3	160.3	405.8
	0.4	0.4	165.8	1734.3	171.0	174.2	321.2
		0.8	251.8	1496.7	176.3	187.7	412.3
	0.6	0.4	219.0	1771.7	191.7	214.2	326.0
		0.8	269.3	1783.0	147.0	194.8	358.5
	0.9	0.4	297.7	1693.2	160.0	190.5	378.8
		0.8	287.3	1847.2	171.2	207.8	406.3
Mean (A)			229.7	1736.4	174.7	188.0	371.2
Wala	0.2	0.4	223.0	1547.0	159.7	207.2	375.0
		0.8	203.7	1457.5	122.3	191.0	380.2
	0.4	0.4	182.2	1493.2	166.5	185.0	352.3
		0.8	210.2	1607.8	228.5	212.5	402.7
	0.6	0.4	218.8	1571.7	239.3	225.3	348.8
		0.8	220.8	1741.5	195.5	227.8	392.8
	0.9	0.4	211.2	2010.5	222.8	209.5	401.2
		0.8	220.0	1860.7	236.2	220.5	399.7
Mean (A)			211.2	1662.5	196.4	232.8	381.6
Green	0.2	0.4	178.0	1368.5	161.7	210.8	347.8
		0.8	206.0	1419.3	199.5	207.0	410.0
	0.4	0.4	209.5	1576.2	222.0	225.8	365.3
		0.8	224.3	1586.3	234.5	273.8	438.7
	0.6	0.4	224.8	1406.5	205.8	241.7	361.5
		0.8	193.5	1464.3	192.3	244.2	379.8
	0.9	0.4	173.0	1416.3	155.2	246.7	322.7
		0.8	187.2	1386.7	161.5	212.5	401.3
Mean (A)			199.5	1453.0	191.6	232.8	378.4
Nean (B)	0.2		192.9	1559.6	170.6	193.1	379.9
	0.4		207.3	1582.4	199.8	210.5	382.1
	0.6		224.4	1623.1	195.3	222.7	361.3
	0.9		229.4	1704.1	184.5	214.6	385.0
Mean (C)	0.4		205.4	1616.6	188.5	208.5	355.1
	0.8		221.5	1618.0	186.6	211.9	399.0
Mean			213.5	1617.3	187.5	210.2	377.1
$LSD_{0.05}$							
A			n. s.	256.5	n. s.	n. s.	n. s.
B			n. s.	n. s.	n. s.	n. s.	n. s.
C			n. s.	n. s.	n. s.	n. s.	37.9

n.s. – not significance

CONCLUSIONS

The analyzed basil herbage proved to be a good source of phosphorus, calcium, chlorine and sulphur; the content was generally significantly affected by a cultivar, nitrogen rate and potassium rate, but a greater effect should be attributed to the cultivar-specific traits seemed to have produced a stronger effect than the nitrogen rate or potassium rate. The increasing rate of nitrogen caused an increase in the concentration of the mineral nutrients in the basil herbage. The concentration of magnesium in the basil herbage dry matter was not dependent on a cultivar and nitrogen rate, but it increased under the influence of the increasing amount of potassium applied. On the other hand, the increased amounts of potassium did not modify the share of phosphorus and sulphur in the investigated plant material. Thus, by using adequate amounts of nitrogen and potassium in the nutrition of basil plants, the content of phosphorus, calcium, magnesium, chlorine and sulphur in the herbage can be effectively increased, thereby enriching the chemical composition of raw material.

REFERENCES

Abduelrahman A.H.N., Elhussein S.A., Osman N.AL., Nour A.H. 2009. *Morphological variability and chemical composition of essential oils from nineteen varieties of basil (Ocimum basilicum* L.*) growing in Sudan.* Int. J. Chem. Technol., 1(1): 1-10.

Ali MD.A., Hossain M.A., Mondal MD.F., Farooque A.M. 2003. *Effect of nitrogen and potassium on yield and quality of carrot.* Pak. J. Biol. Sci., 6(18): 1574-1577.

Bahmanyar M.A., Soodaee-Mashaee S. 2010. *Influences of nitrogen and potassium top dressing on yield and yield components as well as their accumulation in rice (Oryza sativa).* J. Biotechnol., 9(18): 2648-2653.

Biesiada A., Kołota E. 2010. *The effect of nitrogen fertilization on yielding and chemical composition of radicchio chicory for autumn-harvest cultivation.* Acta Sci. Pol. Hort. Cult., 9(4): 85-91.

Biesiada A., Kuś A. 2010. *The effect of nitrogen fertilization and irrigation on yielding and nutritional status of sweet basil (Ocimum basilicum* L.*).* Acta Sci. Pol. Hort. Cul., 9(2): 3-12.

Chen B.M., Wang Z.H., Li S.X., Wang G.X., Song H.X., Wang X.N. 2004. *Effects of nitrate supply on plant growth, nitrate accumulation, metabolic concentration and nitrate reductase activity in three leafy vegetables.* Plant Sci., 167: 635-643.

Dzida K. 2004. *The effect of N-K nutrition on the yielding of leaf beet (Beta vulgaris var. cicla) and nutrients content in growing substrate].* Rocz. AR Pozn. CCCLVI, Ogrodnictwo, 37: 55-60. (in Polish)

Dzida K. 2010. *Nutrients contents in sweet basil (Ocimum basilicum* L.*) herb depending on calcium carbonate dose and cultivar.* Acta Sci. Pol. Hort, Cult., 9(4): 143-151.

Dzida K., Pitura K. 2008. *The influence of varied nitrogen fertilization on yield and chemical composition of swiss chard (Beta vulgaris var. cicla.* Acta Sci. Pol. Hort. Cult., 7 (3): 15-24.

Esmaili E., Kapourchal S.A., Malakouti M.J., Homaee M. 2008. *Interactive effect of salinity and two nitrogen fertilizers on growth and composition of sorghum.* Plant Soil Environ., 54(12): 537-546.

FRIEDRICH M. (ed.) 2002. *Mineral nutrients in human and animal nutrition.* Wyd. AR Szczecin. (in Polish)

GEETHA A., RAO P.V., REDDY D.V. SHAIK M. 2009. *Effect of organic and inorganic fertilizers on macro and micro nutrient uptake, oil content, quality and herbage yield in sweet basil (Ocimum basilicum)*. Res. Crops, 10(3): 740-742.

GOLCZ A., KUJAWSKI P., MARKIEWICZ B. 2008. *Effect of nitrogen and potassium fertilization on the nutritional status of hot pepper (Capsicum annuum* L.*) plants and on substrate salinity*. Acta Sci. Pol., Hort. Cult., 7(1): 45-52.

HANAFY AHMED A.H., KHALIL M.K., FARRAG AMAL M. 2000. *Nitrate accumulation, growth, yield and chemical composition of rocket (Eruca vesicaria subsp. sativa) plants as affected by NPK fertilization, kinetin and salicylic acid.* ICEHM Cairo Univ., Egypt, 495-508.

KHALID KH.A. 2006. *Influence of water stress on growth, essential oil, and chemical composition of herbs (Ocimum* sp.*)*. Int. Agrophys., 20: 289-296.

KŁOSIEWICZ-LATOSZEK L. 1993. *Magnesium deficit versus cardiac diseases.* Żyw. Człow. Metab., 20(4): 374-380. (in Polish)

LABRA M., MIELE M., LEDDA B., GRASSI F., MAZZEI M., SALA F. 2004. *Morphological characterization, Essentials oil composition and DNA genotyping of Ocimum basilicum* L. *cultivars*. Plant Sci., 167: 725-731.

MARKIEWICZ B., GOLCZ A., KLEIBER T., BOSIACKI M. 2011. *Effect of nitrogen, phosphorus and potassium fertilization on the content of macroelements in fruits of aubergine (Solanum melongena* L.*) grown on organic substrates.* J. Elementol., 16(1): 69-74.

MICHAŁOJĆ Z. 2000. *Effect of nitrogen and potassium fertilization on yield and chemical composition of lettuce, radish and spinach*. Rozpr. Nauk. AR Lublin. (in Polish)

NOWACKI E. (ed.). 1980. *Nitrogen management of crops*. PWRiL, Warszawa. (in Polish)

NURZYŃSKA-WIERDAK R. 2006. *The yield and chemical components of rocket and kohlrabi leaves in dependence on nitrogen and potassium fertilization*. Rozpr. Nauk. AR Lublin. (in Polish)

NURZYŃSKA-WIERDAK R. 2007. *Evaluation of morphological and developmental variability and essential oil composition of selected basil cultivars*. Herba Pol., 53(93): 255-261.

NURZYŃSKA-WIERDAK R. 2009. *Growth and yield of garden rocket (Eruca sativa Mill.) affected by nitrogen and potassium fertilization.* Acta Sci. Pol. Hort. Cult., 8(4): 23-33.

NURZYŃSKA-WIERDAK R., BOROWSKI B., DZIDA K. 2011. *Yield and chemical composition of basil herb depending on cultivar and foliar feeding with nitrogen.* Acta Sci. Pol. Hort. Cult., 10(1): 207-219.

NURZYŃSKA-WIERDAK R., BOROWSKI B. 2011. *Dynamics of sweet basil (Ocimum basilicum* L.*) growth affected by cultivar and foliar feeding with nitrogen*. Acta Sci. Pol. Hort. Cult., 10(3): 307-317.

NURZYŃSKA-WIERDAK R., ROŻEK E., BOROWSKI B. 2011. *Response of different basil cultivars to nitrogen and potassium fertilization: total and mineral nitrogen content in herb*. Acta Sci. Pol., Hort. Cult., 10(4): 217-232.

NURZYŃSKA-WIERDAK R., ROŻEK E., BOROWSKI B., DZIDA K. 2012. *Growth response to nitrogen and potassium fertilization of sweet basil (Ocimum basilicum* L.*) plants.* Acta Sci. Pol. Hort. Cult., 11 (in press).

ÖZCAN M. 2004. *Mineral contents of some plants used as condiments in Turkey*. Food Chem., 84: 437-440.

ÖZCAN M., ARSLAN D., UNVER A. 2005. *Effect of drying methods on the mineral content of basil (Ocimum basilicum* L.*)*. J. Food Engin., 69: 375-379.

ÖZCAN M., AKBULUT M. 2007. *Estimation of minerals, nitrate and nitrite contents of medicinal and aromatic plants used as species, condiments and herbal tea*. Food Chem., 106: 852-858.

RAO E.V.P., PUTTANA K., GANESHA RAO R.S., RAMESH S. 2007. *Nitrogen and potassium nutrition of French basil (Ocimum basilicum Linn.)*. J. Spices Aromat. Plants, 16(2): 99- 105.

SEIDLER-ŁOZYKOWSKA K., MORDALSKI R., KUCHARSKI W., GOLCZ A., KOZIK E., WÓJCIK J. 2009. *Economic and qualitative value of the raw material of chosen species of medicinal plants from organic forming*. Part II. *Yield and quality of sweet basil herb (Ocimum basilicum* L.*)*. Acta Sci. Pol. Agric., 8(3): 29-35.

SHEHU H.E., KWARI J.D., SANDABE M.K. 2010. *Effects of N, P and K fertilizers on yield, content and uptake of N, P and K by sesame (Sesamus indicum)*. Int. J. Agric. Biol., 12(6), 845-850.

SIFOLA M.I., BARBIERI G. 2006. *Growth, yield and essentials oil content of three cultivars of basil grown under different levels of nitrogen in the field.* Sci. Hort., 108: 408-413.

SVECOVA E., NEUGEBAUEROVA J. 2010. *A study of 34 cultivars of basil Ocimum* L. *and their morphological, economic and biochemical characteristics, using standardized descriptors.* Acta Univ. Sapientiae Alimentaria, 3: 118-135.

ZHELJAZKOV V.D., CANTRELL CH.L., EBELHAR M.W., ROWE D.E., COKER CH. 2008. *Productivity, oil content, and oil composition of sweet basil as a function of nitrogen and sulfur fertilization.* Hort. Sci., 43 (5): 1415-1422.

YAMAMOTO A., TAKANO T. 1996. *Effects of anion variations in a nutrient solution on the basil growth, essential oil content and composition*. Sci. Rept., Fac. Agr., Meijo Univ., 32: 47-52.

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YIELD AND CHEMICAL CONTENT OF CARROT STORAGE ROOTS DEPENDING ON FOLIAR FERTILIZATION WITH MAGNESIUM AND DURATION OF STORAGE

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Abstract

Yield amount, maturity stage, morphological as well as biological properties of carrot roots are cultivar-dependent. In 2007-2009, field experiments involving foliar fertilization of carrot with magnesium sulphate (acrid salts) on yield and selected yield constituents (dry matter, monosaccharides and total sugars) of carrot storage roots were conducted. Magnesium was applied in doses of 0, 45 and 90 kg MgO ha^{-1} in the form of 3% sprays during the intensive growth of carrot. The tested carrot belonged to five cultivars: medium-late Berjo and late Flacoro, Karotan, Koral and Perfekcja, all characterized by good shelf life.

The yields of carrot storage roots depended on a cultivar and foliar fertilization with magnesium. The cultivar Flacoro gave the highest yield of 60.82 t ha^{-1} and cv. Karotan – lowest (51.40 t ha^{-1}). The application of foliar magnesium fertilization during cultivation in the doses of 45 and 90 kg MgO ha^{-1} caused a significant increase of root yield of about 4.2 and 8.7%, respectively.

The content of dry matter, reducing sugars and total sugars was determined in carrot roots immediately after harvest and after six months of storage. Regardless of the experimental factors, storage roots of cv. Karotan contained the highest amount of dry matter (138.7 g kg^{-1}), reducing sugars (25.2 g kg^{-1}) and of total sugars (76.8 g kg^{-1}) based on fresh matter. Increasing fertilization with magnesium led to a significant increase in the content of all the analyzed constituents in carrot storage roots. The most successful was the dose of 45 kg MgO ha^{-1}, which caused the highest significant increment in dry matter, reducing and total sugars.

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The six-month storage of carrot roots caused a 2.6% increase in dry matter and an 11.2% rise in total sugars, but decreased reducing sugars by 11.1% (mean results for all cultivars and fertilization variants).

Key words: carrot, cultivar, foliar fertilization with magnesium, field, chemical content, storage.

PLONOWANIE I SKŁAD CHEMICZNY KORZENI SPICHRZOWYCH MARCHWI W ZALEŻNOŚCI OD NAWOŻENIA DOLISTEGO MAGNEZEM I CZASU PRZECHOWYWANIA

Abstrakt

Wielkość plonu, termin dojrzewania, cechy morfologiczne oraz biologiczne korzeni marchwi są zróżnicowane u poszczególnych odmian. W latach 2007-2009 przeprowadzono doświadczenie polowe dotyczące wpływu dolistnego dokarmiania siarczanem magnezu (sól gorzka) na wielkość plonu i wybrane składniki (sucha masa, cukry proste i ogółem) korzeni spichrzowych marchwi. Magnez zastosowano w dawkach: 0, 45 i 90 kg MgO ha^{-1} w formie 3% oprysku, w okresie intensywnego wzrostu marchwi. Obiektem badań było 5 odmian marchwi: średnio późna Berjo oraz późne: Flacoro, Karotan, Koral i Perfekcja, o dobrej trwałości przechowalniczej.

Plon korzeni spichrzowych marchwi zależał od odmiany i nawożenia dolistnego magnezem. Największy plon korzeni dała odmiana Flacoro – 60,82 t ha^{-1}, natomiast najmniejszy Karotan – 51,40 t ha^{-1}. Stosując podczas uprawy dolistne nawożenie magnezem w ilości 45 i 90 kg MgO ha^{-1}, uzyskano istotny wzrost plonu korzeni o 4,2 i 8,7%.

Zawartość suchej masy, cukrów redukujących i cukrów ogółem oznaczono w korzeniach marchwi bezpośrednio po zbiorze i po 6 miesiącach przechowywania. Niezależnie od czynników doświadczenia, korzenie spichrzowe marchwi odmiany Karotan zawierały najwięcej suchej masy – 138,7 g kg^{-1}, cukrów redukujących – 25,2 g kg^{-1} i cukrów ogółem – 76,8 g kg^{-1} w świeżej masie. Wzrastające nawożenie magnezem wpłynęło istotnie na wzrost zawartości wszystkich badanych składników w korzeniach spichrzowych marchwi. Najkorzystniejsza okazała się dawka 45 kg MgO ha^{-1}, która spowodowała najwyższy istotny wzrost zawartości suchej masy, cukrów redukujących i ogółem.

Okres 6 miesięcy przechowywania korzeni marchwi spowodował wzrost suchej masy o 2,6%, wzrost cukrów ogółem o 11,2% i spadek cukrów redukujących o 11,1% (średnio dla odmian i nawożenia).

Słowa kluczowe: marchew, odmiany, nawożenie dolistne magnezem, plon, skład chemiczny, przechowywanie.

INTRODUCTION

Vegetables are rich in nutrients, which stimulates a continuous rise in their production. Application of more intensive mineral fertilization certainly raises yields. But fertilization also has a significant influence on the biological value of vegetables. Excessive or deficient doses of fertilizers compared to the optimum, crop-specific requirements may cause physiological disorders and adversely influence the yield quality. One of the basic vegetables produced and consumed in Poland is carrot. The impact of basic NPK fertilization on yield and chemical content of carrot roots is thoroughly investigated (Kołota, Biesiada 2000, Nawirska, Król 2004, Wierzbicka et al. 2004, Smoleń et al. 2005, Dyśko, Kaniszewski 2007, Gajewski et al. 2007, Karkleliene et al. 2008, Gajewski et al. 2009, Smoleń, Sady 2009a,b, Gajewski et al. 2010, Majkowska-Gadomska, Wierzbicka 2010). It is also a well-known fact that carrot needs soils rich in magnesium, because a yield of 100 tons of fresh matter contains 21 kg of magnesium, of which about 15 kg falls on the marketable yield of roots. However, less is known about the influence of magnesium on changes occurring in carrot roots, and investigations in this area are rare (Smoleń, Sady 2009a,b).

Magnesium participates in the metabolism of carbohydrates, activates enzymatic changes and improves the resistance of plants to diseases, hence the present experiment was undertaken to evaluate the influence of foliar magnesium fertilization applied to chosen carrot cultivars on yield of storage roots and on their content on dry matter and sugars. Because most of the carrot yield is stored over autumn and winter, another aim of this study was to determine the yield quality over a prolonged storage period.

MATERIAL AND METHODS

The material was obtained from field experiments carried out at the Experimental Station in Mochełek (2007-2009), which belongs to the Faculty of Agriculture and Biotechnology at the University of Life Sciences in Bydgoszcz (the Province of Kuyavia and Pomerania). Field experiments were performed on light, slightly acid soil, poor in available P and K forms and very low in Mg (Table 1). Data about the temperature and precipitation during the vegetation time are presented in Figure 1. The year 2007 was most suitable for carrot cultivation. Less favourable for the growth and development of carrot was 2009, with much atmospheric precipitation and relatively low air temperatures. Furthermore, the worst was 2008, with prolonged droughts from April to June.

The experiments were set up in a split-plot design with three replications.

The Experimental design comprised:

I. Date of evaluation (after harvest, after storage)
II. Cultivars (medium-late Berjo, late: Flacoro, Karotan, Koral and Perfekcja)
III. Magnesium doses (0, 45, 90 kg MgO ha^{-1}) as magnesium sulphate (16%) under identical fertilization with nitrogen (70 kg N ha^{-1}), phosphorus (80 kg P_2O_5 ha^{-1}) and potassium (100 kg K_2O ha^{-1}). Foliar fertilization with magnesium was applied twice during the intensive growth of plants (July, August) as an aqueous solution of magnesium sulphate (3%) in the amount of 300 dm^3 ha^{-1}.

Table 1

Chemical content of soil before field experiments in 2007-2009

Parametr	Unit	Year of cultivation			Reaction/ /abundance
		2007	2008	2009	
pH H_2O	-	6.6	6.5	6.7	slightly acid soil
pH KCl	-	6.0	5.9	6.1	
Organic carbon	(g kg^{-1})	7.65	7.80	7.55	-
Total nitrogen	(g kg^{-1})	0.72	0.69	0.75	-
Available forms of phosphorus	(mg kg^{-1})	24.0	23.0	25.0	low abundance
Available forms of potassium	(mg kg^{-1})	42.0	43.0	45.0	low abundance
Available forms of magnesium	(mg kg^{-1})	18.5	20.0	17.0	very low abundance

Agro-technical treatments against plant diseases and pests were performed as required for carrot, i.e. in each year, seeds were treated with the seed dressing preparation Funaben T and the herbicide Stomp 330 EC was applied at the pre-emergence stage. During the growing season, carrot fields were manually weeded. Storage roots of carrots were harvested when fully ripe (the 1st decade of October). In order to evaluate the total yield in t ha^{-1}, the mass of roots after harvest was weighed and samples of roots from each plot were taken for analytical and storage investigations. Samples were stored in a traditional earthen mound for 6 months. Chemical content of carrot was determined with the following methods:

1. Dry matter content – oven method after Pijanowski,
2. Content of monosaccharides and total sugars – after PN-90/A-75101/07.

The results of the 3-year-long experiment were statistically verified using the method of variance analysis. The significance of differences was evaluated with the Tukey's multiple confidence intervals at the significance level of α=0.05. Coefficients of linear correlation were calculated between the evaluated quality parameters of carrot yields.

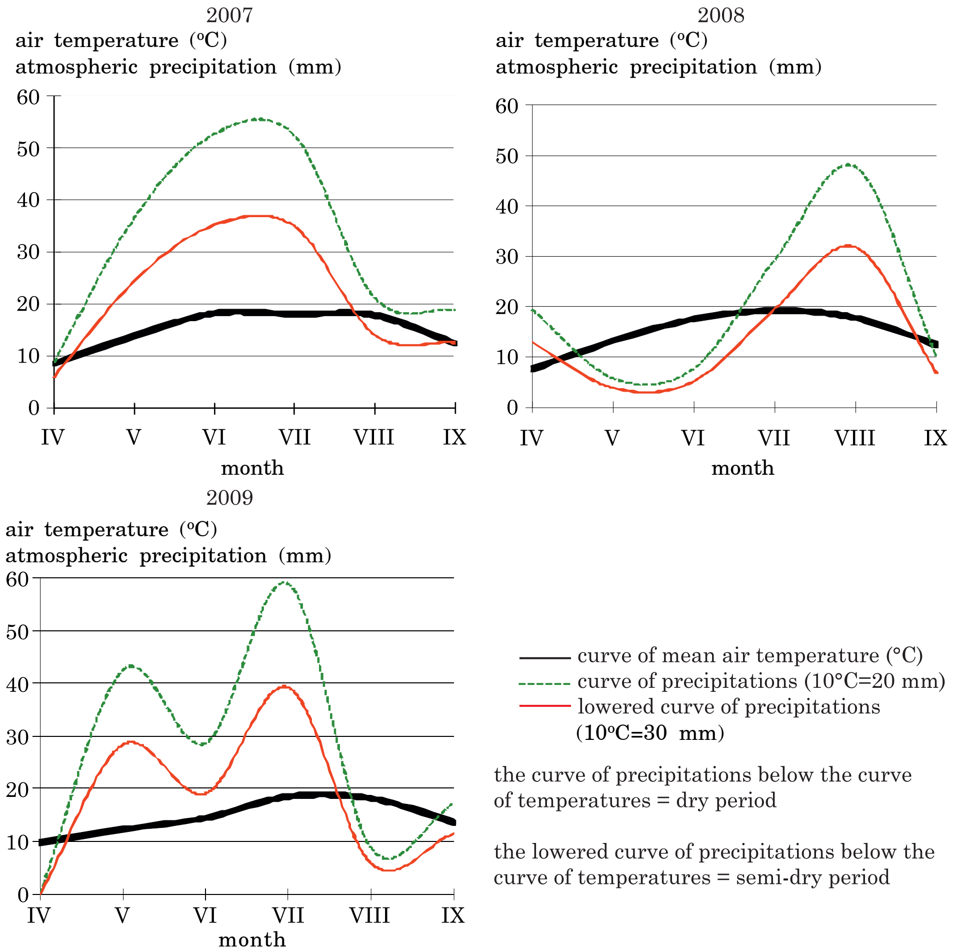

Fig. 1. Meteorological conditions according to Walter

RESULTS AND DISCUSSION

The main factors determining the yield and chemical composition of storage roots of carrot are the genotype, meteorological conditions and cultivation method (Kołota, Biesiada 2000, Alasalvar et al. 2001, Wierzbicka et al. 2004, Dyśko, Kaniszewski 2007, Majkowska-Gadomska et al. 2007, Kaniszewski, Dyśko 2008, Smoleń, Sady 2009a,b, Karkleliene et al. 2009, Majkowska-Gadomska, Wierzbicka 2010). Our results confirm the above because high significant differences were observed not only between the cultivars but also between years (Table 2). In 2007 and 2009, which were characterized by good climatic conditions for carrot cultivation (Figure 1), the yields were the highest: 67.42 and 55.36 t ha^{-1}, respectively These results confirm the findings by Dobrzański et al. (2008), who verified the influence of weather conditions on carrot yield volumes. These authors obtained the mean total carrot yield of 85.0 t ha^{-1} in 2007, favorable for carrot cultivation, and just 45.0 t ha^{-1} in less favourable 2006. Similar results were observed by Majkowska-Gadomska et al. (2007) in experiments with other cultivars in 2003-2004.

Irrespective of the year and magnesium fertilization level, out of the five cultivars, Flacoro and Berjo produced the highest yield of carrot storage roots: 60.82 t ha^{-1} and 58.22 t ha^{-1}, respectively. The lowest yield were produced by Karotan (51.40 t ha^{-1}). Majkowska-Gadomska et al. (2007), in their two-year-long experiments on yields of nine cultivars additionally fertilized with the multinutrient fertilizer Ekosol U during thegrowing season, found the highest mean yield for cv. Florida F_1 (77.2 t ha^{-1}) and the lowest one, same as in our research, for cv. Karotan (63.5 t ha^{-1}). Smoleń, Sady (2009a), who conducted an experiment in 2006-2007 on the cultivar Kazan F_1, determined the mean yield value at the level of 78.0 t ha^{-1} regardless of the applied factors. In another experiment, completed by of Majkowska-Gadomska et al. (2007), the cultivar Kazan F_1 yielded comparably high, that is 72.8 t ha^{-1}.

The applied foliar fertilization with magnesium caused a significant increase of yields of carrot storage roots from all the cultivars (Table 2). The increase was observed in each year. The highest yield was reached by the carrot cultivars Flacoro, Berjo and Perfekcja: 63.22, 60.99 and 60.95 t ha^{-1} (magnesium dose 90 kg MgO ha^{-1}), respectively. Majkowska-Gadomska, Wierzbicka (2010) observed a 6.2% increase in the total root yield and a high, 39.6% increase in the marketable yield of three carrot cultivars owing to the soil application of nutrients in the in form of the fertilizer Crop Care containing magnesium. Moreover, Smoleń et al. (2005), who used the complex fertilizer Supervit-R, also containing magnesium, demonstrated a positive influence of foliar nutrition on the total and marketable yield of carrot roots. There are also exists reports which indicate that foliar fertilization of some vegetables with multi-component fertilizers, in some combinations, decrease yields, which has been shown in the case of potato, parsley and cucumber by Jaskulski (2005).

The results of our analyses of the chemical composition of carrot roots showed some significant differences between the cultivars in the content of dry matter and total sugars (Tables 3, 4). However, no significant differences were found in the content of monosaccharides (Table 5). After Holden et al. (1999), carrot roots contain about 120.0 g kg^{-1} of dry matter and 45.0 g kg^{-1} of total sugars. In the present investigations, the highest content of dry matter and total sugars was determined in storage roots of the cultivar Karotan (137.2 and 82.0 g kg^{-1}) and the lowest one was in cv. Berjo (121.4 and 72.4 g kg^{-1}). Gajewski et al. (2007) investigated six cultivars of carrots, other than in the present experiment, but also found significant

Table 2

Yield of carrot storage roots – mean value for three years of experiment (t ha^{-1})

Cultivar (A)		Fertilization MgO kg ha^{-1} (B)			
		0	45	90	mean
Berjo	2007	68.57	69.67	73.00	70.41
	2008	44.37	48.57	50.57	47.84
	2009	53.40	56.41	59.41	56.41
	mean	55.45	58.22	60.99	58.22
Flacoro	2007	71.48	72.24	76.29	73.34
	2008	48.90	49.83	51.67	50.13
	2009	56.96	58.33	61.71	59.00
	mean	59.11	60.13	63.22	60.82
Karotan	2007	57.10	60.38	62.76	60.08
	2008	41.10	42.50	43.77	42.46
	2009	49.41	51.49	54.11	51.67
	mean	49.20	51.46	53.55	51.40
Koral	2007	57.24	64.48	64.86	62.19
	2008	47.9	51.17	52.67	50.58
	2009	51.64	56.74	57.37	55.25
	mean	52.26	57.46	58.30	56.01
Perfekcja	2007	68.43	69.52	75.33	71.09
	2008	44.83	45.33	49.57	46.58
	2009	52.43	53.04	57.94	54.47
	mean	55.23	55.96	60.95	57.38
Mean	2007	64.56	67.26	70.45	67.42
	2008	45.42	47.48	49.65	47.52
	2009	52.77	55.20	58.11	55.36
	mean	54.25	56.65	59.40	56.77
$LSD_{\alpha=0.05}$		B/A = 1.63 A/B = 8.21			

differences between the cultivars in the content of dry matter and total sugars. The mean content of dry matter and total sugars in the experiments of the aforementioned authors ranged from 95.0 g kg^{-1} to 150.0 g kg^{-1} of dry matter and from 40.0 g kg^{-1} to 70.0 g kg^{-1} of total sugars. Furthermore, the experiments showed that the cultivars containing most of dry matter were also characterized by the highest concentration of total

Table 3

Content of dry matter in carrot roots – mean of three years of experiments (g kg^{-1})

Date of investigation (A)	Cultivar (B)	Fertilization MgO kg ha^{-1} (C)			Mean
		0	45	90	
Immediate after harvest	Berjo	119.3	122.3	122.7	121.4
	Flacoro	118.2	123.1	127.7	123.0
	Karotan	131.8	137.9	141.8	137.2
	Koral	132.6	136.1	138.0	135.6
	Perfekcja	130.7	132.0	136.6	133.1
	mean	126.5	130.3	133.4	130.1
After storage	Berjo	122.3	125.1	125.9	124.4
	Flacoro	121.7	128.1	131.9	127.2
	Karotan	135.1	141.4	144.0	140.2
	Koral	134.2	141.4	142.2	139.3
	Perfekcja	133.1	136.4	138.5	136.0
	mean	129.3	134.5	136.5	133.4
Mean		127.9	132.4	134.9	131.7
$LSD_{\alpha=0.05}$		A = n.s.* B/A = n.s. A/C = n.s.	B = 7.29 A/B = n.s. C/B = n.s.	C = 1.51 C/A = n.s. B/C = n.s.	

*n.s. – not significant

sugars and this is in accordance with the results of our investigations. Similar dependencies were found by GAJEWSKI et al. (2010). PRĘDKA, GRONOWSKA-SENGER (2009), who examined carrot roots of the cultivar Nantejska grown in organic and conventional farming, found the content of dry matter 128.4 and 110.8 g kg^{-1} for raw and 121.8 and 112.3 g kg^{-1} for cooked carrot, respectively. RUTKOWSKA (2005) completed similar investigations with three cultivars Perfekcja, Koral and Regulska and obtained an average 137.2 g kg^{-1} of dry matter under organic farming and 127.8 g kg^{-1} in conventional cultivation. In her experiments, storage roots of cv. Perfekcja and Koral had less dry matter and total sugars than in our investigations, which can be the result of the positive response of carrot to foliar fertilization with magnesium, owing to the its role in the synthesis of sugars. However, DOBRZAŃSKI et al. (2008), who tested different growth stimulators on the carrot cultivar Nerac F_1, obtained an average of 123.0 g kg^{-1} of dry matter, 59.0 g kg^{-1} of total sugars and 18.2 g kg^{-1} of monosaccharides, irrespective of the experimental factors.

According to PRĘDKA, GRONOWSKA-SENGER (2009), the content of dry matter and sugars in vegetables depends not only on the cultivar, soil properties or

Table 4

Content of total sugars in fresh matter of carrot roots – mean for three yea of experiments (g kg^{-1})

Date of investigations (A)	Cultivar (B)	Fertilization MgO kg ha^{-1} (C)			Mean
		0	45	90	
Immediately after harvest	Berjo	65.8	74.2	77.3	72.4
	Flacoro	68.2	76.0	77.3	73.8
	Karotan	75.2	83.7	87.2	82.0
	Koral	75.9	79.2	84.1	79.7
	Perfekcja	71.5	73.2	75.1	73.3
	mean	71.3	77.3	80.2	76.3
After storage	Berjo	57.5	67.6	71.6	65.6
	Flacoro	61.7	68.2	69.4	66.4
	Karotan	65.9	71.2	77.5	71.5
	Koral	67.1	70.5	74.6	70.7
	Perfekcja	62.8	64.4	66.8	64.7
	mean	63.0	68.4	72.0	67.8
Mean		67.2	72.8	76.1	72.0
$LSD_{\alpha=0.05}$	A = 1.79 B/A = n.s. A/C = n.s.	B = 8.66 A/B = n.s. C/B = n.s.	C = 2.74 C/A = n.s. B/C = n.s.		

n.s. – not significant

weather conditions during the growing season, but also on the type and amount of mineral nutrition. Our own investigations confirm it, because the applied foliar fertilization caused changes in the content of the analyzed compounds. Each of the applied magnesium doses caused a significant increase in the content of dry matter and total sugars, which are its main component. Similar results were obtained in a trial by MAJKOWSKA-GADOMSKA, WIERZBICKA (2010), where carrots were soil fertilized with the multi-component fertilizer Crop Care. In the experiments of these authors, this increase was 5.4% for dry matter and 5.3% for total sugars. However, RUTKOWSKA (2005) claims that the chemical composition of vegetables is first and foremost determined genetically, and then by the method and conditions of cultivation. Although the author observed different content of dry matter and sugars in vegetables (potato, carrot) grown with different methods (organically and conventionally), the differences were not statistically proven.

Most of the carrot produced in Poland is stored before consumption, for up to 6 to 8 months, depending on a cultivar and the quality of carrot yield (GAJEWSKI et al. 2010). After KARKLELIENE et al. (2008), the lack of stable mois-

Table 5

Content of monosaccharides in fresh matter of carrot roots – mean for three years of experiments (g kg^{-1})

Date of investigations (A)	Cultivar (B)	Fertilization MgO kg ha^{-1} (C)			Mean
		0	45	90	
Immediately after harvest	Berjo	23.4	23.2	25.0	23.9
	Flacoro	23.1	24.1	25.9	24.4
	Karotan	21.6	22.5	25.0	23.0
	Koral	23.4	25.2	26.2	24.9
	Perfekcja	21.4	22.5	24.2	22.7
	mean	22.6	23.5	25.3	23.8
After storage	Berjo	23.7	24.7	26.0	24.8
	Flacoro	26.1	26.4	27.1	26.5
	Karotan	26.9	27.5	28.0	27.5
	Koral	26.2	26.6	27.3	26.7
	Perfekcja	25.1	26.9	27.2	26.4
	mean	25.6	26.4	27.1	26.4
Mean		24.1	25.0	26.2	25.1
$LSD_{\alpha=0.05}$	A = n.s. B/A = n.s. A/C = n.s.	B = n.s. A/B = n.s. C/B = n.s.	C = 0.65 C/A = n.s. B/C = n.s.		

n.s. – not significant

ture conditions during the intensive growth of carrot roots may impair the quality and resistance of these roots to decay during their storage. In turn, Suojala (2000), Seljasen et al. (2001), Gajewski et al. (2009, 2010) state that the storage conditions are among the most important factors affecting the quality of carrot roots. Zimoch-Guzowska, Flis (2006), Bombik et al. (2007), Wszelaczyńska et al. (2007), Pobereżny, Wszelaczyńska (2011) report that the scale of changes in dry matter and sugar content in vegetables depends first of all on a cultivar, fertilization during the vegetative growth, and on the duration and temperature of storage. In the present experiments, after six months of storage, the increase in the dry matter content was 2.2% for cv. Koral and Perfekcja to 3.4% for Flacoro (Figure 2). Gajewski et al. (2010), in their storage experiment on eight carrot cultivars with different coloration (white, orange and purple), after 6 months of storage, obtained similar to our results with respect to the increase in the dry matter content (an average for all the cultivars 1.5%), but the results were not statistically proven. Such a small difference is probably the result of different storage conditions, because the water transpiration rate is higher in a mound than in a con-

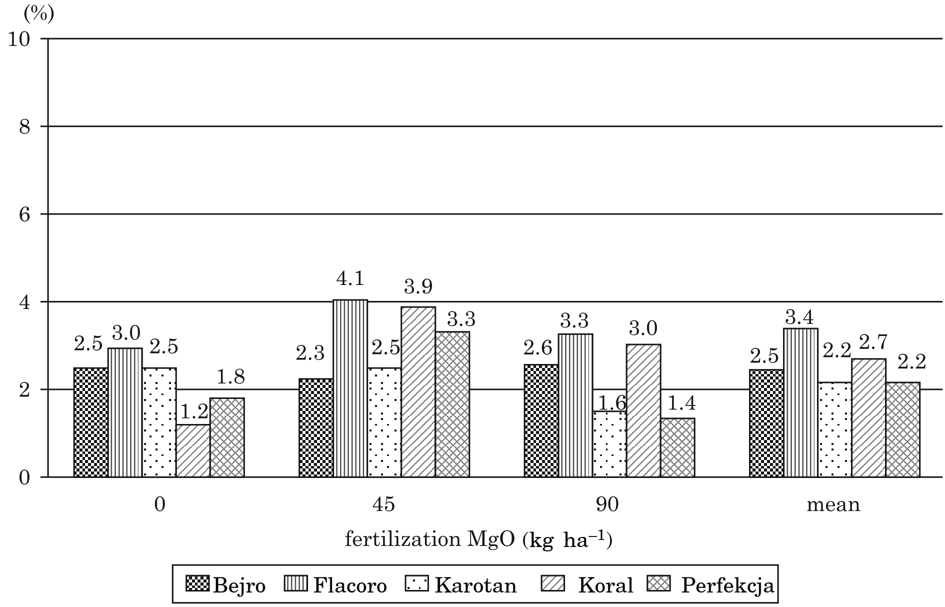

Fig. 2. Changes in percentages of dry matter content in carrot roots depending on a cultivar, fertilization and storage duration – mean value for 2007-2009

trolled environment. In the research by NAWIRSKA, KRÓL (2004), who analyzed the chemical content of roots of four carrot cultivars (Nantejska, Perfekcja, Dolanka, Flacoro) stored in a cool room for 60 days, detected a much lower mean value of the content of dry matter (21.9%) as well as the total sugars (20.7%) but a higher content of reducing sugars (8%) than in our experiment (Tables 3-5). In turn, the differences for the cultivars Perfekcja and Flacoro in dry matter and total sugars were 16.5 and 25.4 % as well as 0.6 and 34.9%, respectively. It can be presumed that such differences are caused by the cultivation method, mainly fertilization, which in our experiments was higher and more complex (additional fertilization with magnesium). It can be also concluded the above authors probably detected a lower content of dry matter and sugars in carrot roots immediately after harvest than in our research, although no such information is given in the cited articles.

The dry matter content in storage roots of the tested carrot cultivars after six-month storage in relation to the applied fertilization with magnesium was modestly different than after harvest. In this respect, 45 kg MgO ha^{-1} was most successful in raising the dry matter content after storage (Figure 2). However, it should be underlined that the presented dry matter losses are the calculated and not the real ones, which should also reflect the fresh mass losses of roots (POBEREŻNY, WSZELACZYŃSKA 2011).

The results on total sugars are contrary (Figure 3). After the long-term storage, a significant loss of total sugar was determined, which is in accordance with the results of SUOJALA (2000). In contrast, GAJEWSKI et al. (2010) obtained a significant increase in these compounds. This discrepancy could have been caused by higher temperature during the storage in a mound, which accelerates degradation of oligosaccharides

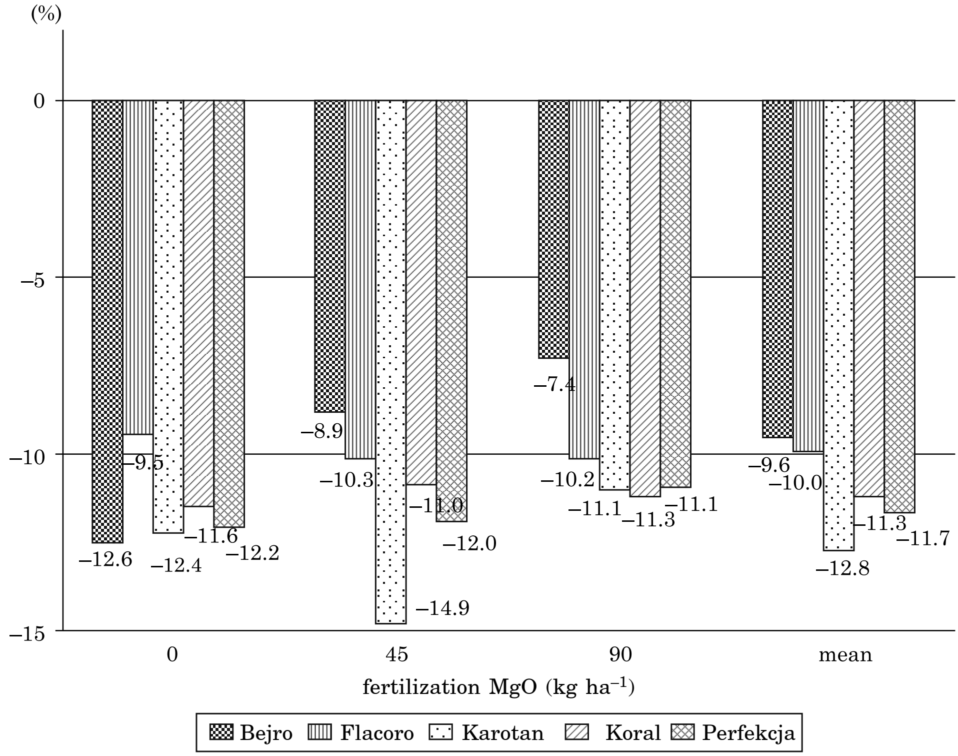

Fig. 3. Losses as percentage of total sugar content in carrot roots depending on a cultivar, fertilization and storage duration – mean value for 2007–2009

It is known that during storage decomposition exceeds synthesis. In contrast to the decrease in total sugars in all the investigated cultivars, the content of reducing sugars went up (Figure 4). This coincides with the opinion of SUOJALA (2000), who noticed that during storage the following changes in saccharides occur: there are less oligosaccharides but more monosaccharides. The increase in monosaccharides could be affected not only by a high and unstable temperature in a mound, accelerating respiration processes, but also by the intensive growth of leaves and forking at the end of storage.

The results of linear correlation are given in Tables 6 and 7. As seen in Table 6, the quantities of yield were negatively correlated with the content

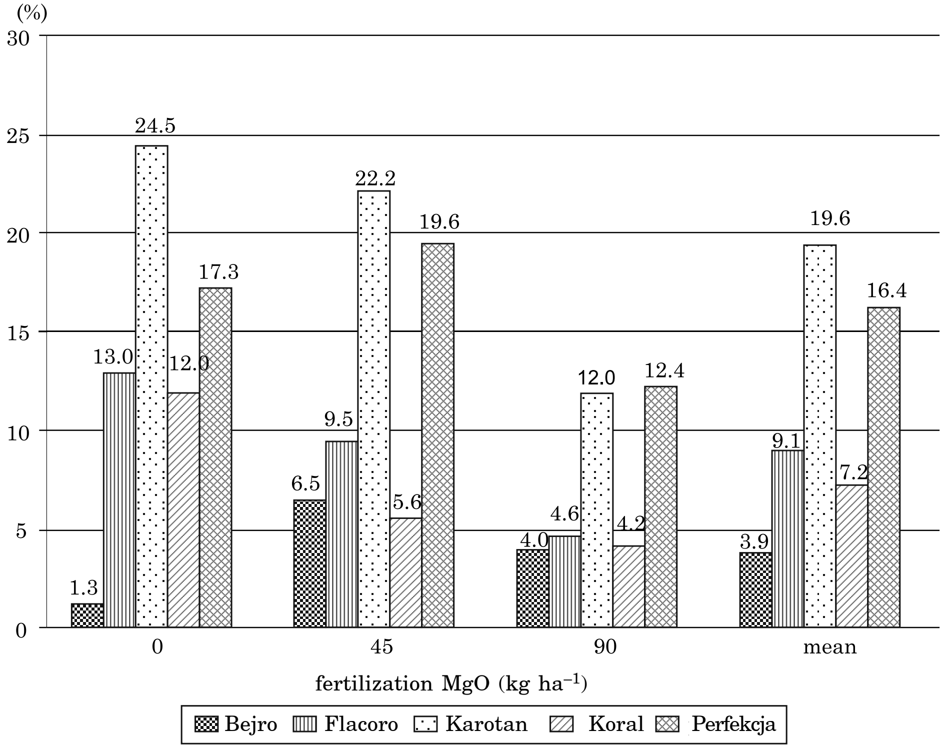

Fig. 4. Changes in percentage of monosaccharides in carrot roots depending on a cultivar, fertilization and storage duration – mean value for 2007-2009

Table 6

Significant correlation coefficients between the investigated parameters after harvest

Parameter		2.	3.	4.
1.	Field of storage roots	-0.498	0.614	
2.	Content of dry matter			0.773
3.	Content of monosaccharides			0.502
4.	Content of total sugars			

$P_{0.05}$ r = 0.497

Table 7

Significant correlation coefficients between the investigated parameters after harvest

Parameter		2.	3
1.	Content of dry matter	0.767	0.659
2.	Content of monosaccharides		
3.	Content of total sugars		

$P_{0.05}$ r = 0.497

of dry matter (r=-0.498) and positively with the content of monosaccharides (r=0.614). This means that the increase in the total yield of carrot storage roots resulted in lower dry matter but higher content of monosaccharides.

The total sugar content was positively correlated with the content of dry matter (r=0.773) and with reducing sugars (r=0.502). A similar albeit stronger dependency was also observed after storage (Table 7), i.e. r=0.767 for dry matter and r=0.659 for monosaccharides. This result is obvious because sugars are the main component of dry matter.

CONCLUSIONS

1. Irrespective of the years and magnesium fertilization level, the highest yield of storage roots of carrot was obtained from the cultivars Flacoro and Berjo; the lowest one was produced by cv. Karotan.

2. Each of the applied doses of magnesium resulted in a significant increase in the yield of carrot storage roots. The most successful was the dose of 45 kg MgO ha^{-1}, where the highest increase of yield was achieved.

3. Storage roots of carrot of cv. Karotan contained most of the dry matter and total sugars; the cultivar Berjo had the lowest content of dry matter and sugars.

4. Increasing fertilization with magnesium caused a significant increase in the dry matter content, reducing and total sugars in carrot storage roots, and the dependencies remained detectable after storage. The dose of 45 kg MgO ha^{-1} proved to be the most effective.

5. Six-month storage time caused an increase in dry matter and total sugars content and a decrease in reducing sugars in carrot roots.

REFERENCES

ALASALVAR C., GREGOR J. M., ZHANG D., QUANTICK P. C., SHAHIDI F. 2001. *Comparison of volatiles, phenolics, sugars, antioxidant vitamins, and quality of different colored carrot varieties.* J. Agric. Food Chem., 49: 1410-1416.

BOMBIK A., RYMUZA K., MARKOWSKA M., STANKIEWICZ CZ. 2007. *Variability analysis of selected quantitative characteristics in edible potato varieties.* Acta Sci. Pol., Agric., 6(3): 5-15.

DOBRZAŃSKI A., ANYSZKA Z., ELKNER K. 2008. *Response of carrots to aplication of natural extracts from seaweed (Sargassum* sp.*) – Algaminoplant and from leonardite – humiplant.* J. Res. Appl. Agric. Engin., 53(3): 53-58.

DYŚKO J., KANISZEWSKI S. 2007. *Effect of drip irrigation, N-fertigation and cultivation methods on the yield and quality of carrot.* Veg. Crops Res. Bull., 67: 25-33.

GAJEWSKI M., SZYMCZAK P., ELKNER K., DĄBROWSKA A., KRET A., DANILCENKA H. 2007. *Some aspects of nutritive and biological value of carrot cultivars with orange, yellow and purple-coloured roots.* Veg. Crops Res. Bull., 67: 149-161.

GAJEWSKI M., SZYMCZAK P., BAJER M. 2009. *The accumulation of chemical compounds in storage roots by carrots of different cultivars during vegetation period.* Acta Sci. Pol. Hort. Cult., 8(4): 69-78.

GAJEWSKI M., SZYMCZAK P., DANILCENKO H. 2010. *Changes of physical and chemical traits of roots of different carrot cultivars under cold store conditions.* Veg. Crops Res. Bull., 72: 115-127.

HOLDEN J. M., ELDRIDGE A. L., BEECHER G. R., BUZZARD M., BHAGWAT S., DAVIS C. S., DOUGLASS L. W., GEBHARDT S., HAYTOWITZ D., SCHAKEL S. 1999. *Carotenoid content of U.S. foods: an update of the base.* J. Food Comp. Anal., 12: 169-196.

JASKULSKI D. 2005. *Productivity and economic results of foliar application of Sonata fertilizers in cultivation of some field vegetables.* Fragm. Agronom., XXII, 1(85): 419-428. (in Polish)

KANISZEWSKI S., DYŚKO J. 2008. *Effect of drip irrigation and cultivation methods on the yield and quality of parsley roots.* J. Elementol., 13(2): 235–244.

KARKLELIENE R., DAMBRAUSKIENE E., RADZEVIČIUS A. 2008. *Evaluation of the morphological, physiological and biochemical parameters of edible carrot (Daucus sativus Rõhl.).* Biologija, 54(2): 101-104.

KARKLELIENE R., RADZEVIČIUS A., BOBINA Č. 2009. *Productivity and root-crop quality of Lithuanian carrot (Daucus dativus* Rőhl.*).* Breeder lines. Section, 63, 1/2, (660/661): 63-65.

KOŁOTA E., BIESIADA A. 2000. *Effect of foliar fertilization on yield and quality of carrot roots.* Rocz. AR Poznań 323, Ogrodnictwo, 31(1): 331-335. (in Polish)

MAJKOWSKA-GADOMSKA J., WIERZBICKA B., NOWAK M. 2007. *Yields of nine carrot cultivars grown for foor processing in Warmia.* Rocz. AR Poznań. ser. Ogrodn., 41: 559-563. (in Polish)

MAJKOWSKA-GADOMSKA J., WIERZBICKA B. 2010. *The yield and nutritive value of selected carrot cultivars with orange and purple- colored storage roots.* Acta Sci. Pol. Hort. Cult., 9(4): 75-84.

NAWIRSKA A., KRÓL A. 2004. *Carrot – a comparsion on selected chemical constituents of four cultivars.* Przem. Ferm., 1: 25-26. (in Polish)

POBEREŻNY J., WSZELACZYŃSKA E. 2011. *Effect of bioelements (N, K, Mg) and long-term storage of potato tubers on quantitative and qualitative losses.* Part II. *Content of dry matter and starch.* J. Elementol., 16(2): 237-246.

PRĘDKA A., GRONOWSKA-SENGER A. 2009. *Antioxidant properties of some vegetables from organic and conventional farms in oxidative stress reduction*. Żywność. Nauka. Technologia. Jakość., 4(65): 9-18. (in Polish)

RUTKOWSKA G. 2005. *Potatoes and carrot from organic and conventional farms.* Przem. Ferm. 5: 20-21. (in Polish)

SELJASEN R., BENGTSSON G., HOFTUN H., VOGT G. 2001. *Sensory and chemical changes in five varieties of carrot in response to mechanical stress and postharvest.* J. Sci. Food Agric., 81: 436-447.

SMOLEŃ S., SADY W., ROŻEK S. 2005. *Effect of differentiated nitrogen fertilization and foliar application on yield and biological quality of carrot crop.* Hortic. Veget. Grow., 24(3): 273-281.

SMOLEŃ S., SADY W. 2009a. *Effect of different nitrogen fertilization and foliar nutrition with Pentakeep V on the carrot yield volume and quality.* Zesz. Probl. Post. Nauk Rol., 539: 663-669. (in Polish)

SMOLEŃ S., SADY W. 2009b. *The effect of nitrogen fertilizer form and foliar application on the concentrations of twenty-five elements in carrot.* Fol. Hort., 21(1): 3-16.

SUOJALA T. 2000. *Variation in sugar content and composition of carrot storage roots at harvest and during storage.* Sci. Hort., 8: 1-19.

WIERZBICKA B., PIERZYNOWSKA-KORNIAK G., MAJKOWSKA-GADOMSKA J. 2004. *Yields of nine carrot cultivars for food processing grown in Warmia.* Fol. Univ. Agric. Stetin., Agric., 239(95): 415-418. (in Polish)

WSZELACZYŃSKA E, JANOWIAK J, SPYCHAJ-FABISIAK E, PIŃSKA M. 2007. *Effect of fertilization on some quality parameters of cv. Bila potato tubers.* Acta Sci. Pol. Agric., 6(4): 91-96. (in Polish)

ZIMOCH-GUZOWSKA E., FLIS B. 2006. *Geneic foundations of potato qualitative traits.* Part 1. Zesz. Probl. Post. Nauk Rol., 511: 23-36. (in Polish)

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CHANGES IN THE CONCENTRATIONS OF AVAILABLE ZINC AND COPPER IN SOIL FERTILIZED WITH SULFUR

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Abstract

The concentrations of available forms of trace elements in the soil are mostly determined by their total content and soil processes. Soil organic matter and pH are the key factors affecting the content and mobility of heavy metals in soil. According to many authors, the toxicity of heavy metals and their availability to plants increase due to soil acidification caused by sulfur deposition. The direct and residual effect of sulfur fertilization on changes in the heavy metal content of soil has to be taken into account in environmental analyses in agricultural areas, including environmental impact assessments and predictions. The objective of this study was to determine the effect of increasing doses of sulfate and elemental sulfur on changes in the concentrations of available zinc and copper in soil samples collected at a depth of 0-40 and 40-80 cm. A three-year field experiment was conducted on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. Soil samples were collected from each plot, prior to the establishment of the trials, after each harvest and before sowing the consecutive crop. The soil samples were used to determine the concentrations: Zn and Cu in soil (extractions with 1 mol HCl dm^{-3}, the ratio between soil and extraction – 1:10) was determined by the AAS method using a Schimadzu AA apparatus. The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance. The application of sulfate and elemental sulfur decreased the zinc content of 0-40 and 40-80 cm soil layers, as compared with soil sampled before the experiment. Sulfur fertilization had no effect on changes in copper concentrations in both soil horizons. The sulfur doses applied in the experiment did not affect the natural content of zinc and copper in the soil, and had no negative agricultural or environmental impacts.

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Key words: fertilizer, sulfate sulfur, elemental sulfur, available forms, zinc, copper, interaction.

ZMIANY ZAWARTOŚCI PRZYSWAJALNYCH FORM CYNKU I MIEDZI W GLEBIE NAWOŻONEJ SIARKĄ

Abstrakt

Procesy glebowe oraz ogólna zawartość metali ciężkich w glebie wpływają na zawartość ich form przyswajalnych. Materia organiczna wraz z pH gleby są najważniejszymi czynnikami kształtującymi zawartość i mobilność metali ciężkich w glebie. Nawożenie gleb siarką przez zakwaszenie może wpływać na zwiększenie toksyczności i biodostępności metali ciężkich dla roślin. Zbadanie bezpośrednich i następczych efektów nawożenia siarką na zmiany zawartości metali ciężkich w glebie ma znaczenie w ocenie skutków oraz monitorowania zmian przyrodniczych warunków na obszarach rolniczych. Celem pracy była ocena wpływu nawożenia wzrastającymi dawkami siarki siarczanowej i elementarnej na zmiany zawartości przyswajalnych form cynku i miedzi w dwóch poziomach gleby: 0-40 i 40-80 cm. Trzyletnie doświadczenie polowe założono na glebie brunatnej, kwaśnej o składzie granulometrycznym piasku gliniastego mocnego. Glebę do analiz chemicznych pobierano wiosną i jesienią. W próbkach glebowych oznaczono zawartość przyswajalnych form cynku i miedzi w wyciągu 1 mol HCl (stosunek gleby do roztworu ekstrakcyjnego wynosił 1:10) metodą absorpcyjnej spektrometrii atomowej. Wyniki analiz chemicznych gleby opracowano statystycznie metodą analizy wariancji. Po zastosowaniu siarki siarczanowej i elementarnej nastąpiło zmniejszenie zawartości Zn w glebie w poziomach 0-40 i 40-80 cm w porównaniu z glebą przed założeniem doświadczenia. Nawożenie siarką nie miało wpływu na zmiany koncentracji przyswajalnej formy miedzi w obu poziomach gleby. Wniesione dawki siarki nie zaburzyły naturalnej zawartości badanych mikroelementów w glebie w aspekcie rolniczo-przyrodniczym.

Słowa kluczowe: nawożenie, siarka siarczanowa, siarka elementarna, formy przyswajalne, cynk, miedź, interakcja.

INTRODUCTION

Concentrations of available forms of trace elements in soil are mostly determined by their total content and soil processes. Soil organic matter and pH are the key factors affecting the content and mobility of heavy metals in soil (Soliman et al. 1992, Martinez, Motto 2000, Borůvka, Drábek 2004, Šichorová et al. 2004, Terelak et al. 2001). Another important consideration is human activity, which contributes to soil contamination in some regions of Poland, thus leading to changes in the natural microelement content. As demonstrated by Żarczyński et al. (2011), also land management has a significant effect on the zinc and copper content of soil.

In the Province of Warmia and Mazury, average zinc and copper concentrations in agricultural soils are considerably lower than the average levels determined in other regions of Poland. The above soils have a natural (0°) heavy metal content (Terelak et al. 2001).

According to many authors (Nederlof, Riemsolijk 1995, Temminghoff et al. 1997, Motowicka-Terelak et al. 1998), the toxicity of heavy metals and their availability to plants increase due to soil acidification caused by sulfur deposition. However, some elements – including zinc and copper – precipitate as sulfides and sulfates, to produce forms that are relatively immobile in the soil profile (Kabata-Pendias, Pendias 1992).

The objective of this study was to determine the effect of increasing doses of sulfate and elemental sulfur on changes in the concentrations of available zinc and copper in soil samples collected at a depth of 0-40 and 40-80 cm.

MATERIAL AND METHODS

A three-year field experiment was conducted from 2000 to 2002, in a village in north-eastern Poland. The village is distant from larger industrial plants which emit sulfur compounds and lies far from any big cities. The concentration of sulfur in the soil were not caused by human activity.

The trial was set up on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulfur 4.10, available phosphorus 34.5 and potassium 110.0 mg kg^{-1} of soil. The annual rates of sulphate sulfur (SO_4^{2-}-S) and elemental sulfur (S^{-0}-S) were: S_1 – 40, S_2 – 80 and S_3 – 120 kg ha^{-1}. Air-dry soil was passed through a 1 mm mesh sieve.

The permanent experiment was established in a random block design and consisted of eight fertilization treatments with four replications: 1) unfertilized control, 2) NPK, 3) NPK + S_1-SO_4, 4) NPK + S_2-SO_4, 5) NPK +S_3-SO_4, 6) NPK +S_1-S^0, 7) NPK +S_2-S^0, 8) NPK +S_3-S^0.

Nitrogen in the form of ammonium nitrate or ammonium sulphate, phosphorus in the form of triple superphosphate, potassium in the form of potassium salt of 60% or in the form of potassium sulphate, sulfur in the form of potassium sulphate and ammonium sulphate supplementation as well as in the form of elemental sulfur. The NPK rates (Table 1) depended on the crop species and soil fertility. The experiment did not apply the soil fertilization microelements.

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. Air-dry soil was passed through a 1 mm mesh sieve. The soil samples were used to determine the concentrations: Zn and Cu in soil (extractions with 1 mol HCl dm^{-3}, the ratio between soil and extraction – 1:10) was determined by the AAS method using a Schimadzu AA apparatus.

Table 1

Applied doses of NPK in the experiment

Year	($kg\ ha^{-1}$)		
	N	P	K
2000	200.0	52.5	180.0
2001	160.0	60.0	183.0
2002	90.0	80.0	111.0

The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance for a two-factor experiment in a random block design, using the form of sulfur as factor a and rate of sulfur 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 with an aim of determining statistical differences between sets of data.

RESULTS AND DISCUSSION

A three-year field experiment was carried out to determine the effect of fertilization with sulfate or elemental sulfur at a dose of 40, 80 and 120 kg ha^{-1} on the zinc and copper content of the 0-40 cm and 40-80 cm soil horizons. Before the experiment, zinc concentrations ranged from 15.65 to 17.00 mg kg^{-1} in the 0-40 cm soil layer, and from 5.80 to 7.60 mg kg^{-1} in the 40-80 cm soil layer.

In the autumn, after cabbage harvest, considerable changes were noted in the zinc content of the 0-40 cm horizon, which reached 3.82-16.18 mg kg^{-1} (Table 2). The application of both sulfur forms led to a substantial decrease in zinc levels, compared with the NPK treatment. Sulfate and elemental sulfur applied at 80 kg contributed to a higher increase in the zinc content of soil, in comparison with other sulfur treatments. After cabbage harvest, zinc concentrations at the depth of 40-80 cm (Table 3) were significantly affected by sulfur form and dose. Increasing sulfur doses (in particular 120 kg ha^{-1} S-S^{-0}) led to an increase in the zinc content of soil.

In the spring, before sowing onion seeds, zinc concentrations in the 0-40 cm horizon (Table 2) decreased substantially, relative to the corresponding treatments before the experiment. The sulfur form had no significant influence on changes in the zinc content of soil. The sulfur doses applied in the experiment contributed to an increase in soil zinc concentrations, compared with the NPK treatment. The only exception was the treatment fertilized with 80 kg ha^{-1} S-S^0.

Table 2

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

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	17.00	7.58	6.54	4.50	8.26	2.92
NPK	16.18	16.18	4.06	7.54	6.32	2.95
NPK+ S_1-SO_4^{2-}	16.61	6.61	4.78	14.12	11.62	3.16
NPK+ S_2-SO_4^{2-}	15.65	11.65	10.46	11.28	5.36	3.44
NPK+ S_3-SO_4^{2-}	16.15	6.15	8.87	6.92	7.11	3.94
NPK+S_1-S^{-0}	15.89	5.89	9.08	4.72	6.60	3.69
NPK+S_2-S^{-0}	16.12	10.12	3.33	5.13	8.15	3.30
NPK+S_3-S^{-0}	15.82	3.82	7.25	9.17	11.81	3.99
$LSD_{-0.05}$						
a	n.s	1.4550	n.s.	1.7576	n.s.	0.2754
b	n.s.	n.s.	1.5894	2.4856	n.s.	n.s.
a x *b*	n.s.	2.9100	2.2478	3.5152	n.s.	n.s.

SO_4^{2-} – sulphate sulphur; S^0 – elementary sulphur; S_1– 40 kg h^{-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

In the autumn, after onion harvest (Table 2), the zinc content of the 0-40 soil layer was significantly affected by the sulfur form and dose. Zinc levels increased considerably in treatments fertilized with 40 and 80 kg ha^{-1} S-SO_4^{2-}. Sulfate exerted a stronger effect than elemental sulfur.

In the 40-80 cm soil layer (Table 3), zinc concentrations increased considerably compared with the initial levels and the corresponding treatments in previous years. This trend was particularly noticeable after the application of 120 kg sulfate and elemental sulfur.

In the spring, before spring barley sowing, zinc levels tended to increase in the 0-40 cm horizon (Table 2) as a result of soil fertilization with increasing elemental sulfur doses. Neither the sulfur form nor its dose had a significant effect on the zinc content of soil. A similar trend was observed in the 40-80 cm soil layer (Table 3).

At the end of the study, zinc concentrations in the 0-40 cm soil layer ranged from 2.92 to 3.99 mg kg^{-1}, irrespective of sulfur doses, and they were generally considerably lower than in the corresponding treatments in the first and second year of the study. This could be due to increased bioavailability of zinc. KAYSER et al. (2001) demonstrated that the application of elemental sulfur increased zinc solubility in the soil and utilization by plants. KAYA et al. (2009) found that the application of elemental sulfur and sulfur-

Table 3

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

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	6.72	5.72	-	6.00	1.30	1.94
NPK	6.51	3.51	-	6.80	1.80	2.32
NPK+ S_1-SO_4^{2-}	6.12	3.12	-	6.91	1.13	2.08
NPK+ S_2-SO_4^{2-}	5.99	5.99	-	6.00	1.30	1.75
NPK+ S_3-SO_4^{2-}	5.80	5.30	-	10.27	1.66	1.69
NPK+S_1-S^{-0}	7.50	6.77	-	7.42	1.59	1.57
NPK+S_2-S^{-0}	6.30	7.30	-	8.68	1.36	1.79
NPK+S_3-S^{-0}	7.60	9.60	-	18.54	1.70	1.65
$LSD_{-0.05}$						
a	n.s	1.046		1.640	n.s.	0.210
b	n.s.	1.479		2.319	n.s.	n.s.
a x *b*	n.s.	2.092	-	3.280	n.s.	n.s.

Explanations see Table 2

containing waste resulted in a decrease in soil pH, but it also increased the concentrations of nutrients available to plants, such as Zn, Cu and Mn. Different results were reported by MODAISHSH et al. (1989) and ABDOU et al. (2011) who did not observe an increase in zinc availability to plants as a result of elemental sulfur fertilization.

Zinc concentrations in soil samples collected at the depth of 40-80 cm were significantly affected only by a sulfur dose. Sulfate (in particular at 40 kg ha^{-1}) exerted a stronger effect than elemental sulfur on the soluble zinc content of soil. Zinc depletion was noted in comparison with soil samples collected before the experiment and after the first and second year of the study.

Before the experiment, the copper content of the 0-40 cm soil layer was similar in all treatments and tended to increase in the treatment with a single dose of elemental sulfur. In the 40-80 cm horizon, copper levels ranged from 1.00 to 1.26 mg kg^{-1}. In the autumn, after cabbage harvest, the copper content of the 0-40 cm soil layer remained at a stable level in all treatments (Table 4). Neither the sulfur form nor its dose had a significant effect on changes in copper concentrations, which tended to increase in the treatment with a single dose of elemental sulfur. The experimental factors had no significant influence on changes in copper concentrations in the 40-80 cm horizon (Table 5).

Table 4

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

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	1.80	1.63	1.82	1.72	1.62	1.71
NPK	1.90	1.65	1.59	1.44	1.61	1.62
NPK+ S_1-SO_4^{2-}	1.90	1.75	1.98	1.80	1.82	1.56
NPK+ S_2-SO_4^{2-}	1.80	1.77	1.85	1.82	1.87	1.78
NPK+ S_3-SO_4^{2-}	1.76	1.76	1.57	1.60	1.70	1.56
NPK+S_1-S^{0}	2.00	1.97	1.86	1.66	1.71	1.53
NPK+S_2-S^{0}	1.50	1.61	1.55	1.72	1.66	1.58
NPK+S_3-S^{0}	1.60	1.54	1.67	1.64	1.68	1.7
$LSD_{0.05}$						
a	n.s	n.s.	0.091	n.s.	n.s.	n.s.
b	n.s.	n.s.	n.s.	0.147	0.102	n.s.
a x *b*	0.299	0.299	0.183	0.208	0.144	n.s.

Explanations see Table 2

Table 5

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

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	1.20	1.15	-	1.07	1.12	0.76
NPK	1.00	1.00	-	0.93	1.04	1.15
NPK+ S_1-SO_4^{2-}	1.11	1.05	-	1.00	0.88	0.76
NPK+ S_2-SO_4^{2-}	1.15	1.15	-	0.86	0.96	0.71
NPK+ S_3-SO_4^{2-}	1.20	1.18	-	1.16	1.28	0.89
NPK+S_1-S^{0}	1.26	1.21	-	0.95	1.13	1.13
NPK+S_2-S^{0}	1.04	0.96	-	0.85	0.89	0.70
NPK+S_3-S^{0}	1.00	1.00	-	0.94	1.01	0.76
$LSD_{0.05}$						
a	n.s	n.s.		n.s.	n.s.	n.s.
b	n.s.	n.s.		n.s.	n.s.	n.s.
a x *b*	n.s.	n.s.	-	n.s.	n.s.	n.s.

Explanations see Table 2

In the spring, before sowing onion seeds, only the sulfur form had a significant effect on changes in the copper content of the 0-40 cm soil layer. Sulfate, compared with elemental sulfur, caused a significant increase in copper concentrations. This could have resulted from changes in soil pH. Sulfur decreases soil pH and increases the solubility, availability and mobility of heavy metals (TICHÝ et al. 1997, SEIDEL et al. 1998, KAYSER et al. 2000, CUI et al. 2004, MARTINEZ et al. 2000). The effect of soil pH on heavy metal mobility can be expressed as a solubility product – a decrease in soil pH by one unit causes a 100-fold increase in the potential solubility of heavy metals. In soils contaminated by several heavy metals, the so-called salt effect is observed – the presence of one ion enhances the activities of the remaining ions, thus increasing the bioavailability of heavy metals (MOTOWICKA-TERELAK, TERELAK 1998).

In the autumn, after onion harvest, sulfur fertilization increased the copper content of the 0-40 cm soil layer, compared with the NPK treatment. $S\text{-}SO_4^{2-}$ applied at 40 and 80 kg ha^{-1} led to an increase in copper concentrations, in comparison with the remaining sulfur doses. Sulfur form had no significant influence on copper levels. Increasing doses of sulfate and elemental sulfur had no significant effect on the copper content of soil samples collected at a depth of 40-80 cm (Table 5).

In the spring of the third year of the study, copper concentrations in the 0-40 cm horizon ranged from 1.61 to 1.87 mg kg^{-1}, regardless of sulfur forms (Table 4). The copper content of soil fertilized with 40 and 80 kg ha^{-1} $S\text{-}SO_4^{2-}$ increased, similarly as in the first year of the experiment. The application of different forms and doses of sulfur had no significant impact on copper concentrations in the 40-80 cm soil layer (Table 5), which increased slightly relative to the corresponding treatments in the fall of 2001.

At the end of the experiment, copper concentrations in the 0-40 cm soil layer were comparable, irrespective of sulfur forms and doses. A minor decrease in the copper content was noted compared with soil samples collected before the experiment. A similar trend was observed in the 40-80 cm horizon, which could have been due to the copper uptake by plants. (SKWIERAWSKA et al. 2008b). KAYA et al. (2009) reported that increased application of elemental sulfur led to a significant increase in the average copper content of plants. In our study, sulfur fertilization had no significant effect on changes in the copper content of soil at the depths of 0-40 and 40-80 cm throughout the experiment.

CONCLUSIONS

1. The application of sulfate and elemental sulfur decreased the zinc content of the 0-40 and 40-80 cm soil layers, as compared with soil sampled before the experiment.

2. Sulfur fertilization had no effect on changes in copper concentrations in both soil horizons.

3. The sulfur doses applied in the experiment did not affect the natural content of zinc and copper in the soil, and had no negative agricultural or environmental impacts.

REFERENCES

ABDOU A. SOAUD, FAREED H. AL DARWISH, MAHER E. SALEH, KHALED A. EL-TARABILY, M. SOFIAN-AZIRUN AND M. MOTIOR RAHMAN. 2011. *Effects of elemental sulfur, phosphorus, micronutrients and Paracoccus versutus on nutrient availability of calcareous soils*. Aust. J. Crop Sci., 5: 554-561.

BORŮVKA L., DRÁBEK O. 2004. *Heavy metal distribution between fractions of humic substances in heavily polluted soils.* Plant Soil Environ., 50(8): 339-345.

CUI Y., DONG Y., LI KAIFENG, WANG Q. 2004. *Effect of element al sulphur on solubility of soil heavy metals and their uptake by maize.* Environ. Int., 30: 323-328.

KABATA-PENDIAS A., PENDIAS H. 1992. *Trace elements in soils and plants.* 2nd Ed. CRC Press Inc. , Boca Raton. FLa.

KAYA M., KÜÇÜKYUMUK Z., ERDAL I. 2009. *Effects of elemental sulfur and sulfur-containing waste on nutrient concentrations and growth of bean and corn plants grown on calcareous soil.* Afr. J. Biotechnol., 8(18): 4481-4489.

KAYSER A., SCHRODER T.J., GRUNWALD A., SCHULIN R. 2001. *Solubilization and plant uptake of zinc and cadmium from soils treated with elemental sulfur.* Int. J. Phytoremediat., 3: 381-400.

KAYSER A., WENGER K., VELLER A., ATTINGER W., FELIX HR., GUPTA Sk. 2000. *Enhancement of phytoextraction of Zn, Cd and Cu from calcareous soil: the use of NTA and sulphur amendments.* Environ. Sci. Technol., 34: 1778-1783.

MARTINEZ C.E., MOTTO H.L. 2000. *Solubility of lead, zinc of copper added to mineral soils.* Environ. Pollut., 107: 153-158.

MODAIHSH A.S., AL-MUSTAFA W.A., METWALLY A.I. 1989. *Effect of elemental sulphur on chemical changes and nutrient availability in calcareous soil*s. Plant Soil, 116: 95-101.

MOTOWICKA-TERELAK T.,TERELAK H. 1998. *Sulphur in the soils of Poland. State and threats.* PIOŚ, Bibl. Monit. Środ., Warszawa, 1-106. (in Polish)

NEDERLOF M.M., VAN RIEMSDIJK W.H. 1995. *Effect of natural organic matter and pH on the bioavailability of metal ions in soils*. In: *Environmental impact of soil component interactions.* HUANG PM, et al., eds., CRC, Boca Raton, FL, USA, pp 73-84.

SEIDEL H., ONDRUSCHKA J., MORGENSTERN P., STOTTMEISTER U. 1998. *Bioleaching of heavy metals from contaminated aquatic sediments using a feasibility study.* Water Sci. Technol., 37: 387-394.

ŠICHOROVÁ K., TLUSTOŠ P., SZÁKOVÁ J., KOŘÍNEK K., BALÍK J.2004. *Horizontal and vertical variability of heavy metals in the soil of a polluted area.* Plant Soil Environ., 50(12): 523-534.

SKWIERAWSKA M., ZAWARTKA L., ZAWADZKI B. 2008. *The effect of different rates and forms of applied sulphur on nutrient composition of planted crops*. Plant Soil Environ., 54 (5): 179-189.

SOLIMAN MF., KOSTANDI SF., BEUSICHEM Van ML. 1992. *Influence of sulfur and nitrogen fertilizer on the uptake of iron, manganese and zinc by corn plants grown in calcareous soil.* Commun. Soil Sci. Plant Anal., 23:1289-1300.

TERELAK H., PIOTROWSKA M., MOTOWICKA-TERELAK T., STUCZYŃSKI T., BUDZYŃSKA K. 1995. *Content of heavy metals and sulphur in agricultural lands in Poland and soil contamination with these components.* Zesz. Probl. Post. Nauk Rol., 418: 45-60. (in Polish)

TERELAK H., TUJAKA A., MOTOWICKA-TERELAK T. 2001. *Content of trace elements and sulphur in farmland soils in the Province of Warmia and Mazury.* Zesz. Probl. Post. Nauk Rol., 476: 327-334. (in Polish)

TICHÝ R., FEITL J., KUZEL S., KOLAR L. 1997. *Use of elemental sulphur to enhance a cadmium solubilization and its vegetative removal from contaminated soil.* Nutr. Cycl. Agroecosys., 46: 249-255.

ŻARCZYŃSKI P., SIENKIEWICZ S., KRZEBIETKE S. 2011. *Effect of the way set-aside land is maintained on the content of available forms of selected micronutrients in soil.* J. Elementol., 16(4): 651–657.

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EFFECTS OF SULPHIDE OXIDATION ON SELECTED SOIL PROPERTIES*

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Abstract

This study covered soils containing sulphides (*Potential Acid Sulphate Soils - PASS*), located on Karsiborska Kępa Island (NW Poland). The aim was to analyse changes in some soil properties caused by the oxidation of sulphides to sulphates for developing a new methodology. Soil samples taken from one representative pedon were oxidized under laboratory conditions for 8 weeks (incubation method). During this period the concentration of sulphates and pH in the soil extract was measured at multi-day intervals. Soil organic horizons characterized by a relatively high content of total sulphur (> 0.75%) showed no decrease in pH below 4 due to the oxidation. The opposite was observed in the case of sandy horizons, poor in sulphur. The rate of pH decline during incubation was the highest in the initial period of oxidation, which justifies the need to perform some soil analyses in samples of fresh /wet soil within 48 hours of sampling. The results enabled us to propose a procedure for soils containing sulphides, which included both field and laboratory tests, with special care taken to preserve as much as possible the natural reducing environment.

Key words: potential acid sulphate soils, iron sulphides, oxidation, soil acidification.

WPŁYW UTLENIANIA SIARCZKÓW NA WYBRANE WŁAŚCIWOŚCI GLEB

Abstrakt

Badania dotyczyły gleb zawierających siarczki (*ang. Potential Acid Sulphate Soils - PASS*), zlokalizowanych na wyspie Karsiborska Kępa (wsteczna delta Świny). Celem badań było określenie zmian, jakie zachodzą w glebach przy przejściu od środowiska redukcyjnego do utleniającego, pod kątem opracowania propozycji nowej procedury badawczej. Prace takie w odniesieniu do PASS występujących w Polsce nie były dotychczas prowadzone.

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Zgodnie ze standardami międzynarodowymi pobrane próbki glebowe poddano 8-tygodniowej inkubacji (utlenianiu) w warunkach laboratoryjnych. W trakcie tego okresu wykonywano w kilkudniowych odstępach oznaczenia stężenia siarczanów, a także pomiar pH gleby.

Poziomy organiczne charakteryzujące się relatywnie wysoką zawartością siarki całkowitej (> 0,75) po utlenieniu nie wykazywały spadku pH poniżej 4. Odwrotny efekt obserwowano natomiast w przypadku poziomów piaszczystych ubogich w siarkę. Dynamika spadków wartości pH była największa w początkowym okresie inkubacji, co uzasadnia konieczność wykonania pewnych analiz glebowych w próbkach świeżych/wilgotnych maksymalnie w ciągu 48 h od momentu ich pobrania.

W przedstawionej propozycji metodyki badań PASS, obejmującej zarówno prace terenowe, jak i laboratoryjne, zwrócono szczególną uwagę na możliwie maksymalny stopień zachowywania naturalnie występującego środowisko redukcyjnego.

Słowa kluczowe: gleby zawierające siarczki, siarczki żelaza, utlenianie, kwasowość gleby.

INTRODUCTION

Sulphur is a very important element in soil, because its presence is required for proper physiological functioning of plants (KLIKOCKA 2005). An excess of certain sulphur forms (sulphides, sulphates) in soils alongside some other unfavorable environmental conditions may cause significant losses of agricultural areas. Therefore, sulphurization is a major global problem, which concerns mainly alluvial soils covering a total area of about 17.1 million hectares in the world (ANDRIESSE, MENSVOORT 2006). There are two types of acid sulphate soils. In anaerobic conditions, formation of reduced forms of sulphur (sulphides, mainly pyrite) occurs. Soils which will be potentially oxidized if drained are called potential acid sulphate soils (PASS). When these soils are exposed to air due to drainage or some disturbance, sulphuric acid is produced, often releasing toxic quantities of iron, aluminium and heavy metals. Such soils is defined as AASS – Actual Acid Sulphate Soils (DENT, PONS 1995).

In Poland, there are more than 20 sites with PASS and AASS. Most lie in the Polish Baltic coastal zone (PRACZ 1989, PRACZ, KWASOWSKI 2001, NIED•WIECKI et al. 2002). Several stands have also been found in central and southern Poland (CZERWINSKI 1996, HULISZ 2007). However, all previous studies mostly focused on the basic recognition of Polish PASS and AASS. A proposal for the classification of these soils was given by PRACZ (1989), but unfortunately it has not been included either in the old or the new version of the *Taxonomy of Polish Soils* (1989, 2011). Therefore, further studies aiming at more detailed knowledge of PASS and AASS properties are needed. In the future, it will also be necessary to add a description of these soils to the next version of the Taxonomy of Polish soils.

The aim of this study was to determine changes that occur in different soil samples during the transition from a reducing to an oxidizing environment, and to propose a procedure including both field and laboratory work.

MATERIAL AND METHODS

The field work was carried out in September 2010 in the western part of Karsiborska Kępa Island (NW Poland; 53º51'41″N, 14º19'8″E). The study area is subject to salinization due to backwater effects and seasonal flooding from the Baltic Sea. There are soils formed both under the influence of the Stara Świna river water and seawater (thin peat or muck layers on alluvial subsoils). According to the WRB classification (IUSS Working Group WRB 2007), they can be classified as Histic Fluvisols. It was previously stated that the sulphide oxidation which occurred in these soils could lead to strong acidification. The pH (in H_2O) values determined in oxidized soil samples can be lower than 3.5 (NIEDŹWIECKI et al. 2000, 2002).

In this study, the standard methods for indirect determination of sulphides in soils were used. Thus, it was possible to identify the features typical for PASS (DENT 1980). As the first criterion, which indicated the presence of strongly reducing conditions, voltage (Eh) below 30 mV was adopted (*Guidelines for Soil Description* 2006). In a field study, potential redox (Eh) was measured (potentiometric method) to obtain representative soil samples. The electrical conductivity of bulk soil (EC_a) was also determined by Time Domain Reflectrometry (TDR). The measurements were made at several points (in shallow soil pits). Afterwards, one representative pedon was selected and sampled for further analysis. The soil material (each sample about 500 g), taken from five different horizons, was put in plastic bags to avoid changes in the oxidation-reduction conditions. After the removal of air, the plastic bags are tightly closed. The samples were immediately refrigerated. The first measurements in fresh/wet samples referred to the actual field conditions. Soil extracts were prepared by using ultrapure water saturated with N_2. The following properties were determined: reaction (pH_a in H_2O) by the potentiometric method, SO_4^{2-} ion concentration by the turbidimetric method (the precipitation of sulphates from acidified solution with $BaCl_2$ and photometric measurement of the turbidity of the samples). Moreover, the actual soil moisture was determined by oven drying method. It was necessary to express ion concentrations in relation to absolutely dry soil.

According to the commonly used procedure (DENT 1980, IUSS Working Group WRB 2007, SULLIVAN et al. 2009), soil samples were placed on plastic trays, creating a layer of about 1 cm thickness, and then incubated at room temperature for a period of 8 weeks (56 days). During this period, the material was sampled in triplicate from each of the horizons for the laboratory analysis (pH in H_2O, SO_4^{2-} concentration and actual moisture). All these analyses were performed on 3, 6, 10, 14, 21, 28 and 56 day of the incubation.

Next, the following properties were determined in air-dry samples (after incubation):

- soil reaction (pH_{pox}) after oxidation with 30% H_2O_2 by the potentiometric method,
- organic carbon (C_{org}), total nitrogen (N_{tot}) and total sulphur (S_{tot}) content using a CNS Variomax analyser.

Based on the results obtained during incubation, the ratio of the concentration of sulphate ions on the different days of analysis (SO_{4x}^{2-}) to their concentration in the soil sample before incubation (SO_{4a}^{2-}) was calculated according to the formula:

$$\frac{SO_{4x}^{2-}}{SO_{4a}^{2-}}$$, where x – the day of analysis.

For interpretation of oxidation-reduction conditions in the soil, the results were transformed to rH values using the formula (IUSS Working Group WRB 2007):

$$rH = 2pH + 2Eh/59$$

The rH values over 35 indicate strongly aerated environment, between 13 and 19 – formation of Fe^{2+}/Fe^{3+} oxides and below 13 – sulphide formation.

The description of the soil horizons was made according to the WRB (*Guidelines for Soil Description* 2006).

RESULTS AND DISCUSSION

Basic soil properties

Potential acid sulphate soils are formed when seawater or sulphate-rich water mixes with waterlogged land sediments containing iron oxides and organic matter in the absence of oxygen (PRACZ 1989, FITZPATRICK et al. 1998). In freshwater environments, soil material oxidation does not usually result in soil acidification because the content of sulphates is too low (LEONARD et al. 1993).

The results of the basic soil analysis are presented in Table 1. The soil was characterized by distinct stratification. Its morphology and properties were formed by both the peat-forming and alluvial processes. The impact of the seawater intrusion was evident. The salinity of the bulk soil (EC_a) ranged from 1.43 to 2.08 dS m^{-1}.

The organic carbon content in the profile (Corg 0.33-34.5%) was related to the presence of mineral (sandy) and organic (mucky, peaty and muddy) horizons. The C:N ratio from 14 to 16 indicated progressive mineralization of organic matter and silting.

The total sulphur content in organic horizons (Ha, Her and Har) varied between 0.78% and 1.93%. It was significantly higher comparing to the average values (0.05-0.67%) found in Polish mineral-organic and organic soils (MOTOWICKA-TERELAK, TERELAK 1998). However, the mineral horizons were characterized by a low S_t content, from 0.03% (Ahr) to 0.19% (Cr).

In the analysed profile, the C:S ratio decreased with depth. Lower C:S ratios in deeper soil horizons (Har – 7 and Cr – 2) suggested some accumulation of sulphides (BLOOMFIELD 1972, PRACZ 1989). This was also confirmed by the occurrence of strong reducing conditions (Eh up to -70 mV, rH 12-14). Moreover, there were no carbonates in the whole soil profile.

In the World Reference Base for Soil Resources classification (IUSS Working Group WRB 2007) *sulphide material* is distinguished, which should fulfill the following criteria: pH of 4.0 or more and 0.75 percent or more S (dry mass) and less than three times as much of calcium carbonate equivalent as S. According to these criteria, only the organic horizons characterized by neutral reaction (pH_a), lack of carbonates and rich in sulfur can be described as *sulphidic material* (Table 1). The criteria related to S_{tot} and $CaCO_3$ content are not taken into account if the material is incubated (layer 1 cm thick) under field conditions and at room temperature. Then, pH should drop by 0.5 or more units to 4.0 or less within 8 weeks.

Table 1

Selected properties of studied soil

Horizon	Depth (cm)	C_{org} (%)	N_{tot} (%)	S_{tot} (%)	C:N	C:S	pH_a	ECa (dS m^{-1})	Eh (mV)	rH	Type of material
Ha	0-22	34.5	2.559	0.78	14	44	7.0	1.77	117	18	muck
Ahr	22-36	1.35	0.092	0.03	15	54	7.6	1.43	-3	15	loose sand
Her	36-42	33.7	2.505	1.21	14	28	7.3	2.08	-70	12	low peat
Har	42-60	13.5	1.110	1.93	15	7	7.3	2.01	-50	13	mud
Cr	>60	0.33	0.021	0.19	16	2	6.9	1.48	3	14	loose sand

Abbreviations: Ha – highly decomposed organic material, Ahr – mineral horizon with accumulation of organic matter and strong reduction, Her – moderately decomposed organic material with strong reduction, Har – highly decomposed organic material with strong reduction, Cr – mineral horizon with strong reduction

Changes in selected soil properties by oxidation

Soil pH measurements were made before (pH_a, Table 1) and after sample oxidation, which was achieved by two ways. The first oxidizing agent was a 30% hydrogen peroxide solution (pH_{pox}). This method is commonly used in the WRB classification (IUSS Working Group WRB 2007) for diagnostic recognition of *sulphidic* material under the field conditions. Forced oxidation with 30% H_2O_2 should lower pH values to 2.5 or less. It should be noted that oxidation can also be influenced by the presence of organic matter or manganese compounds. Therefore, the threshold pH value is much lower than that adopted in the incubation method.

The pH_a values ranged between 6.9 to 7.6 (Figure 1). The application of H_2O_2 resulted in a significant decrease in pH values. The difference between pH_a and pH_{pox} increased with depth (from 2.5 to 6.2 pH units). In the deeper horizons, pH_a values ??below 2.5 were recorded: Her (1.1), Har (1.4) and Cr (1.6). It allowed us to identify *sulphidic* material.

The second method was the incubation of soil samples in the laboratory. During the incubation soil material is exposed to ambient conditions to simulate natural acidification behavior (SULLIVAN et al. 2009).

The pH measured on the last day of the incubation (pH_{ox}) decreased from 0.4 (Ha) to 3.1 units (Cr) compared to pH_a – Figure 1. The response to change in the soil oxidation-reduction conditions was different at individual horizons, depending on the type of material. It should be noted that in the whole profile there was no calcium carbonate, which would have buffered pH declines.

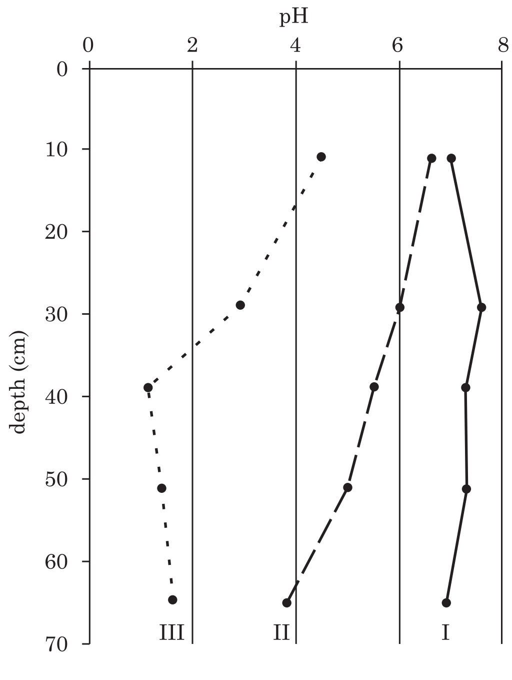

Fig. 1. Variability of soil pH in selected profile: I – before incubation (pH_a), II – after incubation (pH_{ox}), III – after oxidation by peroxide (pH_{pox})

Figure 2 presents the dynamics of soil sample oxidation. The rate of pH decline was expressed as a function of the time (ΔpH/Δt). During the incubation, certain minimum fluctuations (decrease/increase of the pH values) were noted. Namely, the variable ΔpH/Δt was greater than 0 at some points on the diagram. It can be explained by the lack of homogenization of the soil material. The fastest pH decline (already during the first three days of incubation) was recorded in sandy Cr horizon, characterized by the lowest carbon content and a relatively high content of total sulphur (C:S = 2). The value of pH_{ox} was 3.8, which allowed us to distinguish *sulphidic material*. Despite having similar texture to Cr, the oxidation test of Ahr sample gave clearly different results (pH_{ox} = 6.0). This can be linked to a higher content of Corg and lower S_{tot} (C: S = 54). In the case of organic horizons, the maximum rate of pH decline occurred after 5 days from the start of incubation. The pH_{ox} values exceeded 4.0 and thus these horizons did not fulfill the criteria for *sulphidic* material.

Finally, the biggest pH declines in the entire soil profile occurred within the first 10 days. Over the next 10 days, the fluctuations were small. However, after 20 days of analysis, relative stabilization of pH levels was recorded. Therefore, it can be concluded that almost complete oxidation of samples took place after a 4-week period of the incubation, which is shorter than recommended in the WRB classification, i.e. 8 weeks.

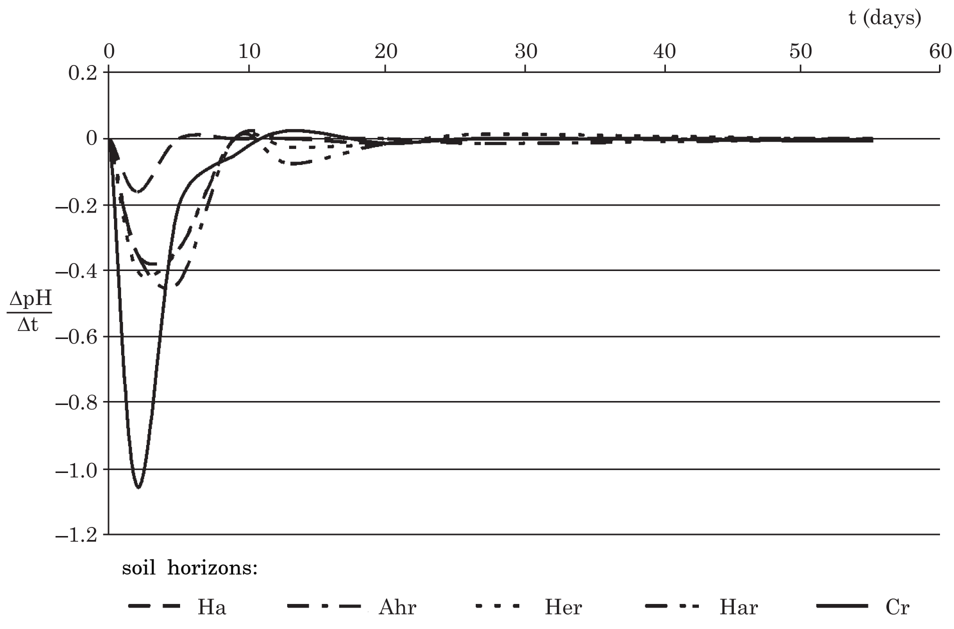

Fig. 2. Rate of pH decline caused by the soil sample incubation as a function of time

Beside the above changes in soil pH, the oxidation of sulphides causes simultaneous increase of oxidized form of sulphur, namely sulphates (VI). Comparing the results of SO_4^{2-} determinations before and after incubation, the highest increase in sulphate concentrations was observed in samples taken from organic horizons: Her (from 38.2 to 279 mg 100 g^{-1} of absolutely dry soil) and Har (from 19.7 to 131 mg 100 g^{-1} of absolutely dry soil). In Ha horizon, characterized by a relative high S_{tot} content (0.78%, Table 1), only a slight increase in SO_4^{2-} ions was noted (from 39.3 to 58.4 mg 100 g^{-1} of absolutely dry soil). The smallest changes in SO_4^{2-} concentrations appeared in mineral, poor in sulphur (S_{tot} < 0.2%) Ahr and Cr horizons (from 17.6 to 28.8 and from 10.8 do 48.3 mg 100 g^{-1} of absolutely dry soil, respectively).

Dynamics of the changes in SO_4^{2-} ion concentrations in time is shown in Figure 3. The $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio specifies how many times the content of sulphates over consecutive days of oxidation was higher than their content in the unoxidized sample. The ratio equal to 1 means that the amount of sulphates was constant during the experiment, and the soil material did not contain sulphides. The $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio for Ha and Ahr horizons ranged from 1 to about 2, while the deeper horizons (Her, Har, and Cr) were significantly richer in sulphides (4-10).

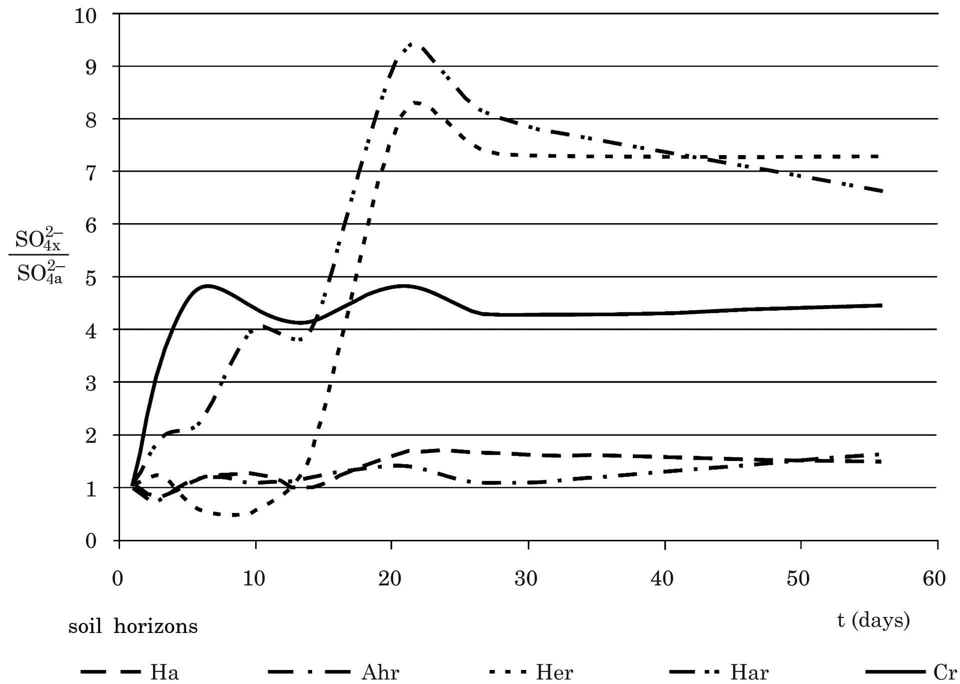

Fig. 3. Changes in the $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio as a result of sample incubation in 8 weeks

Figures 2 and 3 shows a similar dynamic changes in pH and sulphate content in the analysed soil horizons. This is understandable, given the fact that the final product of sulphide oxidation is sulphuric acid. The results suggest that the analysed soils are very sensitive to changes in redox conditions. Therefore, inadequate regulation of the groundwater level could lead to the soil degradation. This is particularly important because the studied area belongs to habitats protected under the Nature 2000 network.

However, the results of other authors indicate that soil oxidation in a laboratory gives a stronger acidification effect than oxidation caused by natural soil drainage and exposure to atmospheric oxygen (van Breemen 1973, Dent 1980, Pracz 1989). Under field conditions, the total oxidation of sulphides does not occur as quickly as in a laboratory and sulphuric acid is removed from soil by leaching (Bloomfield, Coulter 1973).

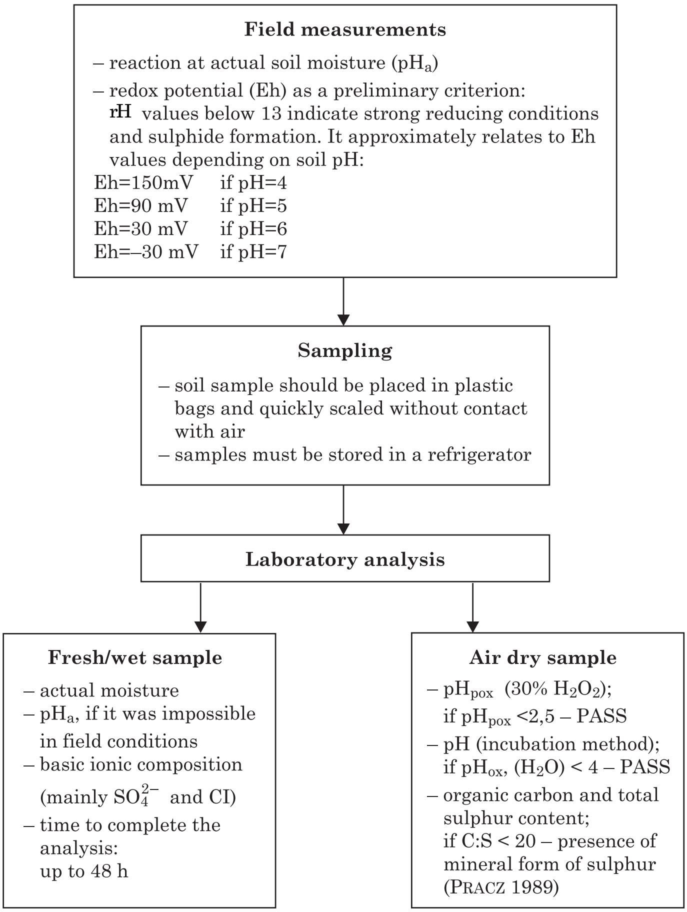

Fig. 4. Proposed methodical procedure in studies of AASS

Methodical remarks

Soils containing reduced forms of sulphur (mainly iron sulphides), due to their specific characteristics, require a special methodological approach. It should particularly take into account the unique sensitivity of these soils to changes in redox conditions (groundwater level), resulting in relatively rapid acidification.

The methodical procedure for PASS, which includes both field and laboratory work, is proposed below (Figure 4). Such a methodical approach has not yet been presented in Poland.

CONCLUSIONS

1. During the incubation of soil organic horizons, characterized by a relatively high content of total sulphur (> 0.75%), pH did not decrease below 4 as a result of oxidation. The opposite effect was observed in the case of sandy horizons, poor in sulphur.

2. The rate of pH decline and the increase in sulphate concentrations during ther incubation were the highest in the initial period of the sample oxidation, which justifies the need to perform some analysis in samples of fresh /wet within 48 hours of sampling.

3. According to the WRB classification (2007), both types of the analysed soil horizons, despite the different characteristics, fulfilled the diagnostic criteria for *sulphidic* material.

4. Soils containing reduced forms of sulphur (mainly iron sulphides), due to their specific characteristics, require a special methodical approach. A possible solutions could be the proposed procedure involving both field and laboratory work.

REFERENCES

Andriesse W., van Mensvoort M.E.F. 2006. *Acid sulfate soils: Distribution and extent*. Encyclopedia of Soil Science, 14-28. DOI: 10.1081/E-ESS-120006641

Bloomfield C. 1972. *The oxidation of iron sulphides in soils in relation to the formation of acid sulphate soils, and of ochre deposits in field drains*. J. Soil Sci., 23: 1-16.

Bloomfield C., Coulter J.K. 1973. *Genesis and management of acid sulfate soils*. Adv. Agron., 25: 265-326.

Czerwiński Z. 1996. *Salinity of waters and soils in the Cuiavian region*. Rocz. Glebozn., 47 3(4): 131-143. (in Polish)

Dent D.L. 1980. *Acid sulphate soils: morphology and prediction*. J. Soil Sci., 31: 87-99.

Dent D.L., Pons L.J. 1995. *A world perspective on acid sulphate soils*. Geoderma, 67: 263-276.

Fitzpatrick R.W., Merry R.H., Williams J., White I., Bowman G., Taylor G. 1998. *Acid sulfate soil assessment: Coastal, inland and minespoil conditions.* National Land and Water Resources Audit Methods Paper, 18 pp.

Guidelines for soil description. 2006. Food and Agriculture Organization of the United Nations Rome: 97 pp.

HULISZ P. 2007. *Proposal of the taxonomy of Polish salt-affected soils*. Rocz. Glebozn., 58(1/2): 1-10. (in Polish)

IUSS Working Group WRB. 2007. *World Reference Base for Soil Resources 2006, first update 2007*. World Soil Resources Reports No. 103. FAO, Rome, 128 pp.

KLIKOCKA H. 2005. *Sulphur status in the environment*. J. Elementol., 10(3): 625-643.

LEONARD E.N., MATTSON V.R., BENOIT D.A., HOKE R.A., ANKLEY G.T. 1993. *Seasonal variation of acid volatile sul?de concentration in sediment cores from three northeast Minnesota lakes*. Hydrobiology, 271: 87-95.

MOTOWICKA-TERELAK T., TERELAK H. 1998. *Sulphur in Polish soils – state and hazards*. Bibl. Monit. Środ., Warszawa, 106 pp. (in Polish)

NIEDŹWIECKI E., PROTASOWICKI M., WOJCIESZCZUK T., MALINOWSKI R. 2000. *Sulphur content in soils of reverse delta of Świna river on the example of organic soils in Karsiborska Kępa*. Fol. Univ. Agric. Stetin. 204, Agricultura, 81: 97-102. (in Polish)

NIEDŹWIECKI E., PROTASOWICKI M., CZYŻ H., WOJCIESZCZUK T., MALINOWSKI R.. 2002. *Chemical properties of strongly acidic soils in Karsiborska Kępa Island influenced by riverine-marine waters.* Zesz. Probl. Post. Nauk Rol., 482: 397-402. (in Polish)

PRACZ J. 1989. *Properties of soils formed under the influence of saline groundwater in the region of the Polish Baltic coast.* Rozpr. Nauk. Monogr. Wydaw. SGGW-AR, Warszawa, 92 pp. (in Polish)

PRACZ J., KWASOWSKI W. 2001. *Characteristics of the salinity of sulphide and acid sulphate soils in the area of Mrzeżyno.* Rocz. Glebozn., 52(3/4): 17-31. (in Polish)

SULLIVAN L.A., WARD N.J., BUSH R.T., BURTON E.D. 2009. *Improved identi?cation of sul?dic soil materials by a modi?ed incubation method*. Geoderma, 149: 33-38.

Taxonomy of Polish Soils. 1989. Rocz. Glebozn., 40(3/4): 150. (in Polish)

Taxonomy of Polish Soils. 2011. Rocz. Glebozn., 62(3): 194. (in Polish)

VAN BREEMEN N. 1973. *Soil forming processes in acid sulphate soils*. In: Acid sulphate soils. Dost, H. (Ed.). Int. Inst. for Land Reclamation and Improvement, Wageningen, 66-130.

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CONTENT OF MINERALS IN GRAIN OF SPRING WHEAT CV. KOKSA DEPENDING ON CULTIVATION CONDITIONS

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Abstract

A study has been undertaken to determine the effect of different cultivation conditions for spring wheat cv. Koksa on the total ash, P, K, Mg, Ca, Fe, Zn, Mn, and Cu in wheat grain. The study was conducted at Uhursk Experimental Farm (51°18'12″N, 23°36'50″E) of the University of Life Sciences in Lublin, in 2008-2010. The experimental factors were: 1) systems of soil tillage: ploughing and ploughless, 2) doses of nitrogen: 90 and 150 kg ha^{-1}, and 3) preceding crop: pea and soy. The objective was to evaluate the impact of different soil tillage systems, doses of nitrogen fertilizers and preceding crops on the content of mineral components in the grain of spring wheat cv. Koksa.

The study demonstrated that ploughless tillage increased the content of total ash, Zn and Cu, while ploughing tillage raised the content of K, Mg and Mn in the grain. A standard dose of nitrogen (90 kg ha^{-1}) facilitated the accumulation of K, Fe, Zn and Cu, whereas a higher nitrogen dose (150 kg N ha^{-1}) elevated the content of total ash and Mn in grain of spring wheat. The grain of wheat cultivated after pea was characterized by a higher content of Ca, Fe and Zn, whereas that cultivated after soy contained more total ash, K and Mn.

Key words: grain of spring wheat, mineral components, soil tillage, nitrogen dose, preceding crop.

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ZAWARTOŚĆ SKŁADNIKÓW MINERALNYCH W ZIARNIE PSZENICY JAREJ ODMIANY KOKSA W ZALEŻNOŚCI OD WARUNKÓW UPRAWY

Abstrakt

Badano wpływ zróżnicowanych warunków uprawy pszenicy jarej odmiany Koksa na zawartość w ziarnie popiołu całkowitego oraz P, K, Mg, Ca, Fe, Zn, Mn i Cu. Badania prowadzono w latach 2008-2010 w Gospodarstwie Doświadczalnym Uhrusk (51°18'12″N, 23°36'50″E) należącym do Uniwersytetu Przyrodniczego w Lublinie. Czynnikami doświadczenia były: 1) systemy uprawy roli: płużny i bezpłużny, 2) dawki azotu: 90 i 150 kg ha^{-1}, 3) przedplony: groch i soja. Celem badań była ocena wpływu zróżnicowanych systemów uprawy roli, wielkości dawek nawozów azotowych i przedplonów na zawartość składników mineralnych w ziarnie pszenicy jarej.

Wykazano, że bezpłużna uprawa roli wpłynęła na zwiększenie w ziarnie zawartości popiołu całkowitego, Zn i Cu, natomiast płużna uprawa – K, Mg i Mn. Standardowa dawka azotu (90 kg ha^{-1}) sprzyjała gromadzeniu w ziarnie K, Fe, Zn i Cu, natomiast wysoka dawka (150 kg N ha^{-1}) zwiększała udział popiołu całkowitego i Mn. W ziarnie pszenicy uprawianej po grochu stwierdzono większą zawartość Ca oraz Fe i Zn, natomiast uprawianej po soi – więcej popiołu oraz K i Mn.

Słowa kluczowe: ziarno pszenicy jarej, składniki mineralne, uprawa roli, dawka azotu, przedplon.

INTRODUCTION

Wheat is a cereal of key significance in human nutrition. Wheat flour is mainly used for bread making and pasta production. The quality of this flour is determined by the functional value of grain (raw material), which in turn is affected by the methods and conditions it is achieved with (Peltonen, Virtanen 1994, Wooding et al. 2000).

The content of mineral components in wheat grain depends on cultivar-specific characteristics as well as soil-climatic and agritechnical conditions. Among the latter, the content of ash is affected by mineral fertilization, chemical plant protection against agrophages and soil tillage system (Paris, Gavazzi 1972, Woźniak 2010). Mineral content of grain is additionally affected by the class and composition of soil as well as a cultivation site (Cubadda et al. 1969). As claimed by Morris et al. (2009), the content of ash in wheat grain is correlated more strongly with the weather course before harvest and crop localization than with the genotype. Also Budzyński et al. (2008) demonstrated stronger dependence of ash content of grain on weather conditions than on cultivar-specific traits. The mineral composition of grain is also influenced by the species and cultivar of wheat, and by the weather during grain maturation (Ranhort et al. 1995, Ruibal-Mendieta et al. 2005, Gontarz 2006). The content of ash additionally depends on cultivation conditions. Grain of wheat cultivated in a monoculture was reported to contain more minerals than wheat from crop rotation, which results from a high contribution of grain with low plumpness (WOŹNIAK 2007). For similar reasons, also ploughless soil tillage and low nitrogen fertilization are reported to increase the content of minerals in grain (WOŹNIAK 2010).

In view of the above, the objective of the study has been to evaluate the impact of different soil tillage systems, doses of nitrogen fertilizers and preceding crops on the content of mineral components in grain of spring wheat cv. Koksa.

MATERIAL AND METHODS

The experimental material was grain of spring wheat of cultivar Koksa, obtained from a field experiment conducted in 2008-2010 at the Experimental Farm in Uhrusk (51°18'12"N, 23°36'50"E) of the University of Life Sciences in Lublin. The above cultivar belongs to the class of high quality wheat (A) with good milling quality and very good flour strength as well as with high resistance to sprouting.

The experiment was conducted on limestone soil formed from light clay rich in available forms of phosphorus and potassium, of a slightly alkaline pH (pH=7.2). The experimental factors were: 1) systems of soil tillage: ploughing and ploughless, 2) doses of nitrogen: 90 and 150 kg ha^{-1}, and 3) preceding crop: pea and soy. Soil tillage in the ploughing system consisted in cultivation skimming after preceding crop harvest and deep fall ploughing. In the springtime, the soil cultivation included harrowing, pre-sowing nitrogen fertilization and ploughing pre-sowing preparation with a cultivation kit. For comparison, soil tillage in the ploughless system involved the substitution of skimming and fall ploughing by spraying Roundup 360 SL herbicide (active subtsance glifosat) in a dose of 4 dm^3 ha^{-1}, whereas cultivating measures applied in the springtime were the same as in the ploughing system. Fertilization with nitrogen was applied in two doses, i.e. 90 and 150 kg ha^{-1}, and on 4 dates. The standard dose (90 kg) was divided as follows: 1 – before sowing 40 kg ha^{-1}, 2 – propagation stage (23/24 in the BBCH scale) 20 kg ha^{-1}, 3 – shooting stage (32/33 in the BBCH scale) 20 kg ha^{-1}, 4 – ear formation stage (52/53 in the BBCH scale) 10 kg ha^{-1}. The higher dose of nitrogen (150 kg ha^{-1}) was applied at the same stages, with the broadcasting doses of 60, 40, 30 and 20 kg ha^{-1}.

Plant protection measures were identical on all plots and consisted in the eradication of fungal diseases with Alert 375 SC fungicide (flusilazole + + carbendazim) applied in a dose of 1.0 dm^3 ha^{-1} at the shooting stage (32/33 BBCH) and Tilt Plus 400 EC (propiconazol + fenpropidin) – 1.0 kg ha^{-1} at the ear formation stage (53/54 BBCH). Weed eradication in the wheat fields was performed with Aminopielik D 450 SL herbicide (2,4-D + dicamba) applied in a dose of 3.0 dm^3 ha^{-1} at the propagation stage of wheat (23/24 BBCH).

Determinations of the content of mineral components in wheat grain were conducted after dry mineralization of the samples at a temperature of 600°C. The resultant ash was dissolved in 5 mL of 6M HCl, then filled up to the volume of 50 ml with redistilled water. Measurements were carried out with Atomic Absorption Spectrometry, with excitation in acetylene-air flame in a UNICAM 939 apparatus.

The results were elaborated statistically with the analysis of variances, whereas differences were estimated with Tukey's test at a significance level of p=0.05.

RESULTS AND DISCUSSION

The content of mineral components in grain of spring wheat was found to be differentiated by the applied soil tillage systems (Table 1). The grain originating from ploughless tillage was characterized by a significantly higher content of total ash (1.85%) than that from plots cultivated in the ploughing system (1.77%). Likewise, KRASKA (2011) demonstrated a higher content of ash in wheat grain originating from fields subjected to conservation (ploughless) rather than to intensive (ploughing) tillage. It may thus be speculated that the ash content of the grain of wheat cultivated in the ploughless system is determined by a poorer development of the kernel endosperm compared to the grain from plots with the ploughing tillage. Also our previous study (WO•NIAK 2010) demonstrated that wheat grain from plots with

Table 1

Mineral content in grain of spring wheat cv. Koksa depending on the soil tillage systems (means from 2008-2010)

Specification	Soil tillage systems		Mean
	ploughing	ploughless	
Total ash (%)	1.77 *a**	1.85 *b*	1.81
P (g kg^{-1})	2.59 *a*	2.56 *a*	2.58
K (g kg^{-1})	3.36 *a*	3.29 *b*	3.32
Mg (g kg^{-1})	1.13 *a*	1.03 *b*	1.08
Ca (g kg^{-1})	0.56 *a*	0.57 *a*	0.57
Fe (mg kg^{-1})	40.42 *a*	40.16 *a*	40.29
Zn (mg kg^{-1})	34.07 *a*	35.71 *b*	34.89
Mn (mg kg^{-1})	25.76 *a*	24.18 *b*	24.97
Cu (mg kg^{-1})	6.62 *a*	7.21 *b*	6.92

* Means followed by the same letter are not significantly different at p=0.05.

ploughless tillage was characterized by lower density and poorer uniformity than grain from ploughing tillage.

The ploughless soil tillage caused a significant increase in the content of Zn and Cu in grain, as compared to the ploughing system. The reason was that the availability of microelements in well-aerated soils is lower than in less-aerated soils, hence it may be presumed that multiple aeration of ground in the ploughing system depressed the availability of Zn and Cu, unlike in the ploughless tillage. In turn, in the ploughing system the grain was characterized by higher content of K, Mg and Mn. The higher concentration of K and Mg in the grain may be explained by their higher availability to plants for they more easily migrate into deeper soil layers, especially of the intensively pulverized soil in the ploughing system. The availability of manganese (Mn) was diminished in both cases due to the alkaline pH of soil. The differentiated content of Mn in grain may be attributed to a different moisture content of soil in both tillage systems.

Furthermore, the content of mineral components in wheat grain were observed to be differentiated by nitrogen fertilization (Table 2). Grain from the plots fertilized with the higher dose of nitrogen (150 kg ha^{-1}) was characterized by a significantly higher content of ash and Mn than grain from plots fertilized with the standard nitrogen dose (90 kg ha^{-1}). Similar dependencies were observed by Jackowska and Borkowska (2002). In turn, the standard dose of nitrogen led to a significant increase in the content of K, Fe, Zn and Cu in grain compared to the higher nitrogen dose. As indicated by the literature data, low content of nitrogen in soil restricts the availability of some microelements, and thereby decreases their content in grain (Jackowska and Borkowska 2002).

Table 2

Mineral content in grain of spring wheat cv. Koksa depending on the dose of nitrogen (means from 2008-2010)

Specification	Dose of nitrogen (kg ha^{-1})		Mean
	90	150	
Total ash (%)	1.79 *a**	1.85 *b*	1.82
P (g kg^{-1})	2.62 *a*	2.57 *a*	2.59
K (g kg^{-1})	3.32 *a*	3.18 *b*	3.25
Mg (g kg^{-1})	1.11 *a*	1.07 *a*	1.09
Ca (g kg^{-1})	0.57 *a*	0.56 *a*	0.57
Fe (mg kg^{-1})	41.69 *a*	39.86 *b*	40.78
Zn (mg kg^{-1})	36.16 *a*	35.04 *b*	35.60
Mn (mg kg^{-1})	24.46 *a*	25.01 *b*	24.74
Cu (mg kg^{-1})	7.32 *a*	7.01 *b*	7.17

*Designations as in Table 1.

The content of ash as well as macro- and microelements in the grain examined was also significantly affected by the preceding crops (Table 3). On the plots with soy grown before wheat, the wheat grain was characterized by significantly higher content of total ash, K and Mn than on the plots with pea as the preceding crop. In contrast, grain of wheat cultivated after pea was characterized by considerably higher content of Ca, Fe and Zn. In a study by GONTARZ (2006), the highest content of ash was reported in grain of spring wheat harvested from a plot after 3 consecutive self-forecrops, whereas a significantly lower one – after pea followed by potato and single self-forecrop. The content of ash and minerals was also differentiated by the year of study and advanced agricultural technology. The intensive level of agricultural measures (increased fertilization with nitrogen and chemical protection against macrophages) resulted in an increased ash content of the grain, compared to the minimal level.

Table 3

Mineral content in grain of spring wheat cv. Koksa depending on the preceding crop (mean from 2008-2010)

Specification	Forecrop		Mean
	pea	soy	
Total ash (%)	1.76 *a**	1.88 *b*	1.82
P (g kg^{-1})	2.66 *a*	2.53 *a*	2.59
K (g kg^{-1})	2.89 *a*	3.62 *b*	3.25
Mg (g kg^{-1})	1.09 *a*	1.09 *a*	1.09
Ca (g kg^{-1})	0.59 *a*	0.54 *b*	0.57
Fe (mg kg^{-1})	42.43 *a*	39.11 *b*	40.77
Zn (mg kg^{-1})	37.30 *a*	33.89 *b*	35.60
Mn (mg kg^{-1})	24.35 *a*	25.15 *b*	24.75
Cu (mg kg^{-1})	7.14 *a*	7.19 *a*	7.16

*Designations as in Table 1.

CONCLUSIONS

1. The content of mineral compounds in the grain of spring wheat cv. Koksa was found to be differentiated by soil tillage systems. Ploughless tillage facilitated the accumulation of total ash, Zn and Cu, whereas ploughing tillage encouraged the accumulation of K, Mg and Mn in the grain.

2. The standard dose of nitrogen (90 kg ha^{-1}) raised the content of K, Fe, Zn and Cu in the grain of spring wheat, whereas the higher dose of nitrogen (150 kg N ha^{-1}) elevated the content of total ash and Mn.

3. The content of minerals in the grain of spring wheat significantly depended on a preceding crop. On the plot with pea grown before wheat, the wheat grain was characterized by significantly higher content of Ca, Fe and Zn, whereas on the plot with soy as a forecrop, the content of total ash, K and Mn was higher.

REFERENCES

Adamczewski K., Matysiak K. 2002. *Key to identification of plant of monocotyledons and dicotyledons on the BBCH scale*. IOR Poznań, pp.114. (in Polish)

Budzyński W., Bielski S., Borysewicz J. 2008. *Influence of nitrogen fertilization on technological quality of winter wheat grain*. Fragm. Agron., 1(97): 39-49. (in Polish)

Cubadda, R., Fabriani, G., Tranquilli, G. B. 1969. *Variability of ash content of durum wheat in relation to locality and ripening time*. Food Sci. Technol., 20: 253-63.

Gontarz D. 2006. *The yield and technological quality of wheat grains (Triticum aestivum L.) and durum wheat (Triticum durum Desf.) depending on the level of agricultural technology and forecrop*. AR Lublin, pp. 95, doctoral dissertation. (in Polish)

Jackowska I., Borkowska H. 2002. *The influence of nitrogen fertilization on the content of trace elements in grain of same winter wheat cultivars*. Ann. UMC, sect. E, 57: 87-91.

Kraska P. 2011. *Tillage systems and catch crops as factors creating physical and chemical properties of spring wheat grain cultivar Zebra*. Acta Agroph., 17(1): 117-133. (in Polish)

Morris C.F., Li Shuobi, King G.E., Engle D.A., Burns J.W., Ross A.S. 2009. *A comprehensive genotype and environment assessment of wheat grain ash content in Oregon and Washington: analysis of variation*. Cereal Chem., (86)3: 307-312.

Paris P., Gavazzi C. 1972. *The ash content of durum wheat in northern Italy*. Food Sci. Technol. Abstracts Tecnica Molitoria, 23 (22): 709-728.

Peltonen J., Virtanen A. 1994. *Effect of nitrogen fertilization on the physicochemical and functional properties of bread wheats*. Cereal Chem., 62: 427-430.

Ranhort G.S., Gerroth J.A., Glaser B.K., Lorenz K.J. 1995. *Baking and nutritional qualities of a spelt wheat sample*. Lebensm. Wiss. Technol., 28: 118-122.

Ruibal-Mendieta N.L., Delacroix D.L., Mignolet J.M.P., Marques C., Rozenberg R., Petitjean G., Habib-Jiwan J.L., Meurens M., Qeentin-Leclerco J., Delzenne N.M., Larondelle Y. 2005. *Spelt (Triticum aestivum ssp. spelta) as a source of breadmaking flours and bran naturally enriched in oleic acid and minerals but not phytic acid*. J. Agric. Food Chem., 53: 2751-2759.

Wooding A.R., Kavale S., MacRitchie F., Stoddard F.L., Wallace A. 2000. *Effects of nitrogen and sulfur fertilizer on protein composition mixing requirements, and dough strength of flour wheat cultivars*. Cereal Chem., 77(6): 798-807.

Woźniak A. 2007. *Technological parameters of winter wheat cv. Korweta in crop rotation with different wheat participation.* Acta Agroph., 10(1): 247-255. (in Polish)

Woźniak A. 2010. *Effect of chemical plant protection on grain quality of spring wheat*. Progr. Plant Protect. / Post. Ochr. Rośl., 50 (2): 1010-1013. (in Polish)

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REVEGETATION OF RECLAIMED SODA WASTE DUMPS: EFFECTS OF TOPSOIL PARAMETERS

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Abstract

The paper presents the diversity of herbaceous vegetation developing in a complex of soda waste dumps in Krakow, which were reclaimed with a topsoil over 15 years ago (1995) and left without further treatment. A total of 132 plots were selected using the systematic method to determine some physical (texture composition, depth) and chemical parameters (pH, electrolytic conductivity, content of N, C, P, K, Mg, Ca, and C:N) of the topsoil. Plant species composition in each plot was determined using the Braun-Blanquet method. In total 133 plant species, predominantly ruderal and meadow ones, were found in the soda waste dumps. The areas dominated by ruderal species were characterized by greater depth of the topsoil and abundance in nitrogen and phosphorus, which increased the average plant height and plant cover. It was concluded that the reclamation method used for the soda waste dumps gave rise to communities with the predominance of ruderal species and halted the succession at this stage. Development of vegetation into meadow communities would require the use of a topsoil of low fertility and small depth. The species composition of the seed mixture intended for sowing on the reclaimed site should be ecologically matched to local conditions. For satisfactory reclamation effects, it is necessary to define the target characteristics of a plant community when determining the method of reclamation and land management.

Key words: soda waste dumps, reclamation, topsoil, vegetation.

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ROZWÓJ ROŚLINNOŚCI NA ZREKULTYWOWANYCH OSADNIKACH POSODOWYCH: WPŁYW WŁAŚCIWOŚCI WARSTWY GLEBOWEJ

Abstrakt

W pracy przedstawiono zróżnicowanie roślinności zielnej rozwijającej się na kompleksie osadników posodowych w Krakowie zrekultywowanych przez pokrycie osadu warstwą nadkładu glebowego przed 15 laty (w 1995 r.), i pozostawionych bez dalszych zabiegów pielęgnacyjnych. W wyznaczonych metodą systematyczną 132 powierzchniach badawczych określono wybrane parametry fizyczne (skład granulometryczny, miąższość) i chemiczne (pH, przewodnictwo elektrolityczne, zawartość N, C, P, K, Mg, Ca i C:N) nadkładu glebowego. Skład gatunkowy roślinności na każdym poletku określono metodą Braun-Blanquetta. Na osadnikach stwierdzono występowanie 133 gatunków roślin, wśród których dominowały gatunki ruderalne i łąkowe. Powierzchnie z dominacją gatunków ruderalnych miały większą miąższość nadkładu glebowego i zawierały wiecej azotu i fosforu, co wpłynęło na większą średnią wysokość roślin i większe pokrycie powierzchni. Stwierdzono, że metoda rekultywacji zastosowana na osadnikach posodowych spowodowała wykształcanie się zbiorowisk roślinnych z przewagą gatunków ruderalnych i zatrzymanie się sukcesji na tym etapie. Ukierunkowanie rozwoju roślinności na zbiorowiska łąkowe wymagałoby zastosowania nadkładu glebowego o niskiej żyzności oraz niewielkiej miąższości. Skład gatunkowy mieszanki nasion przeznaczonej do wysiewu na rekultywowanym obiekcie powinien być ekologicznie dostosowany do lokalnych warunków. Aby uzyskać zadowalający efekt rekultywacji, konieczne jest określenie docelowych zbiorowisk roślinnych na etapie ustalania metody rekultywacji i zagospodarowania terenu.

Słowa kluczowe: osadniki posodowe, rekultywacja, nadkład glebowy, roślinność.

INTRODUCTION

One of the problems in many urban and industrial agglomerations is the reclamation and management of waste dumps of different origin e.g. industrial. In the past, they were located outside the city boundaries, but as the cities were growing, they were gradually incorporated into the urban structure. The soda waste dump in Krakow (Poland) occupies a large area, which is surrounded by developing housing estates. This should be preferably managed as an urban green area with recreational infrastructure, considering the shortage of such objects in the city. However, post-soda wastes represent extreme conditions for vegetation development. A very high $CaCO_3$ content and strongly alkaline reaction are not found in natural habitats. Other problems are high salinity, deficit of nitrogen and potassium as well as solidity of soda waste after sedimentation (Trzcińska-Tacik 1966, Boroń, Nagawiecka 1995, Siuta 2007). Such harsh conditions induce low floristic diversity and morfological deformations of spontaneously occurring plants (Trzcińska-Tacik 1966). Application of some reclamation measures to improve the habitat seems to be indispensable, e.g. the biological reclamation method worked out for soda waste dumps in Janików using sewage sludge (Siuta 2007).

The nature of derelict land determines the method of technical and biological reclamation, thus entailing further processes that occur in the developing ecosystem (BRADSHOW 2000). One of the reclamation procedures is to cover derelict land with a topsoil. This method enables the land to turn green rapidly by sowing conventional meadow grass seed mixtures (MARTÍNEZ-RUIZ, FERNÁNDEZ-SANTOS 2005, MARTÍNEZ-RUIZ, MARRS 2007). In such a situation, it is necessary to predetermine the target characteristics of the ecosystem and to adapt the reclamation process as well as possible cultivation measures (BLOOMFIELD et al. 1982) needed to form and maintain desired ecosystem types. Most sites can accommodate a variety of plant communities if provided sufficient topsoil (CARNELL, INSLEY 1982, BRADSHAW 1984 after ROBINSON, HANDEL 1995). However, the sites reclaimed by means of topsoil covering may create conditions that hinder the development of stable plant communities (ATHY et al. 2006). In the case of capped landfills soil degradation problems include compaction, decreased permeability, lack of organic material, diminished soil fauna, inappropriate soil texture (EWING 2002) and also shallow soil, water-logging and drought (DOBSON, MOFFAT 1993). The correlation between biomass and soil cover depth is confirmed by research conducted on different sites, e.g. a reclaimed waste dump (BOWEN et al. 2005).

After years, the reclamation of the soda waste dumps with the use of topsoil gave rise to a mosaic of vegetation patches with different species composition, plant cover and main biomass height. The technical reclamation combined with seed sowing initially produced a plant cover composed mainly of the meadow species commonly used in the reclamation of derelict land, but the abandonment of management measures caused changes in the species composition, i.e. spontaneous succession. In the case of depositional soils, it may be either primary succession, because it develops on a substratum that is not typical soil, or secondary succession, because it may contain plant propagules (REBELE 1992). That is why vegetation development on reclaimed soda waste dumps differs from succession in natural areas but also from succession taking place directly on the waste substratum, e.g. on an unreclaimed soda waste dump (ZARZYCKI, ZAJĄC 2001) or post-coal mining heaps (ROSTAŃSKI 2006).

The aim of this study was to evaluate the plant establishment pattern on soda waste dumps reclaimed by the topsoil method and to determine the effect of some physical and chemical properties of the soil cover used in the reclamation on species composition.

MATERIALS AND METHODS

The Krakow Soda Plant Solvay was in operation during 1901-1994. The basic products were raw soda, soda ash, and caustic soda, the manufacture of which generated huge amounts of waste deposited into sedimentation lagoons, called “white seas” (N 50°00´30″; E 19°56´26″). This waste consisted mainly of water, compounds of calcium, chloride and silicon dioxide (Pałka, Sanecki 1992) and was characterized by high alkalinity and salinity (Boroń et. al. 2000).

At the time of the plant’s liquidation, the area of soda waste dumps in need of reclamation totalled 84.65 ha (Małecki 1997). Reclamation work was carried out in the largest complex of soda waste dumps (17.43 ha). It involved levelling of the embankments, strengthening the scarps and covering with topsoil. Fertilizing and a grass and legume seed mixture were also applied, but no detailed information is available. The reclamation ended in 1995 and since then the soda waste dumps have been left untreated. At present, the area is overgrown with herbaceous plants and small clusters of trees. The only source of water for the vegetation is precipitation. In Krakow, the total annual precipitation usually varies between 650-700 mm. The sum of average monthly precipitation from May to September reaches 406 mm, with the maximum amount in July. The mean annual air temperature is 8.7°C. The coldest period of the year is between the second decade of January and the beginning of February, while the warmest period from the second half of July to the first decade of August. During the year, western winds prevail (about 25%), but also a very high frequency of calms (25.1%) is noted (Matuszko 2007).

The investigations were conducted in 2007-2009. A total of 132 plots, with an area of 25 m^2 each, were designated for characterizing the properties of the topsoil used for reclamation and the plant cover. The plots were laid out in a 30 by 30 m grid.

All plant species on each plot were recorded and the plant cover was estimated according to the Braun-Blanquet scale. Species were classified into meadow and ruderal ones according to Ellenberg et al. (1992). Species constancy, i.e. the percentage of plots in which a species occurred, and cover coefficient (Cc), which describes the proportion of a species in plant cover, were calculated for each species. The cover coefficient was calculated according to Braun-Blanquet (1964), where Cc = 100 Σ cover of the species in all plots divided by number of plots.

Each of the 132 designated plots was measured for depth of the topsoil and soil samples (mixed from three sub-samples) were collected for laboratory analysis and tested for:

- grain-size distribution – Bouyoucos-Casagrande method modified by Prószyński;
- pH in H_2O and KCl (soil: water ratio 1:2,5);
- electrical conductivity (EC);
- organic carbon – Tiurin method;
- total nitrogen – Kjeldahl method;
- available phosphorus and potassium – Egner-Riehm method;
- total calcium and magnesium – ICP–AES method (samples were subjected to wet mineralization, then vaporized to dryness and dissolved in acid (Zając 2009).

Diversity of species composition and the effect of topsoil parameters were analysed by multivariate analysis. Detrended Correspondence Analysis (DCA) was performed in CANOCO ver. 4.5 (ter Braak, Smilauer 2002) to order species, plots and topsoil parameters along the axis. Significance (percentage of explained variation) of each axis is expressed through eigenvalues. The gradient length, expressed in standard deviation units, is calculated by nonlinear scaling of each axis and expresses the exchange of species relative to the axis. Correlations between topsoil parameters, parameters of community structure and individual DCA axes were computed based on Pearson's correlation coefficient. For statistical analysis, the Braun-Blanquet scale was transformed into percentage scale. Square root transformation and downweighting of rare species were used. To meet the normal distribution assumption, the data were in some cases log-transformed prior to statistical analysis.

RESULTS AND DISCUSSION

The basic chemical properties of the topsoil used to reclaim the soda waste dumps (Table 1) are not significantly different from those found in natural habitats. During the reclamation process, the soda waste dumps were covered with a topsoil (average depth 0.25 m) which was composed predominantly of the clay fraction. The soil cover has a low phosphorus content. On the other hand, the content of potassium and magnesium is very high, which may be associated with the dominant soil type and the fertilization carried out as part of the reclamation operations. Noteworthy is a very high total calcium content (an average of 18 251.4 mg kg^{-1} soil), which probably results from some components of the soda waste permeating into the soil cover, also with the participation of the soil fauna (Pośpiech, Skalski 2006). This probably influences the pH, which is close to alkaline. For most samples, the C:N ratio ranges between 8:1 and 12:1, i.e. within the most common range found in the mineral soils of Poland (Lityński et al. 1976). The topsoil used in the reclamation of depositional sites is usually of low quality, often comes from deep building excavations (Robinson, Handel 1995), and sometimes contains contaminants of different origin. Also in the area of the investigated soda waste dumps, especially near the embankments, the reclamation material cover contained waste components (especially construction debris, building felt, etc.), which may influence both ecosystem development and the application of management measures (Zając 2009).

The development of vegetation in the analysed soda waste dumps showed considerable variation. Over 70% of the plots was characterized by an incomplete plant cover. The height of the main plant mass ranged from 10 cm to 130 cm. In total133 plant species were found in the investigated plots, including 47 meadow and 40 ruderal ones (Table 2). The other 46 were species of diverse habitat requirements.

Table 1

Characteristics of the topsoil

Parameter	Range	Mean value (standard deviation)	Median
Depth of topsoil (m)	0.10 - 0.68	0.25 (± 0.11)	0.22
Fraction (%):			
1.0 - 0.1 mm (sand)	13 - 68	29.70 (± 9.67)	27.00
0.1 - 0.02 mm (silt)	7 - 30	13.26 (± 3.82)	12.50
< 0.02 mm (clay)	22 - 78	57.33 (± 10.53)	59.50
pH KCl	6.75 - 7.56	7.14 (± 0.14)	7.13
pH_{H_2O}	6.75 - 7.97	7.61 (± 0.18)	7.63
EC (mS cm^{-1})	0.20 - 1.59	0.41 (± 0.20)	0.38
Organic C (g kg^{-1})	11.53 - 79.97	21.18 (± 7.64)	19.42
Total N (g kg^{-1})	1.01 - 4.82	2.14 (± 0.53)	2.06
C:N	4.68 - 27.77	9.96 (± 2.47)	9.81
P_2O_5 (mg kg^{-1} soil)	0.00 - 835.9	46.4 (± 120.9)	18.6
K_2O (mg kg^{-1} soil)	75.3 - 840.4	419.0 (± 98.2)	417.4
Ca (mg kg^{-1} soil)	3739.1 - 86332.3	18251.4 (± 11350.9)	16307.1
Mg (mg kg^{-1} soil)	1363.9 - 9539.3	4797.9 (± 1568.8)	4626.7

Although soils with a high content of clay fraction make a good insulation layer, they generally have unfavourable physical properties with poor aeration and permeability. Water-logging may occur in wet periods and excessive drying out of the topsoil in dry periods (Ewing 2002). The species composition in the dumps reflected the varying degrees of soil moisture. Some areas were colonized by species typical of dry habitats (e.g. *Campanula rapunculoides, Poa compressa, Filipendula vulgaris*) and others by species typical of wet habitats (e.g. *Lysimachia vulgaris, Phragmites australis*).

Over the past 15 years, the vegetation dominated by species that appear spontaneously has developed on the investigated area. Urban and industrial areas are often characterized by the occurrence of a relatively large number of species in a small area (Angold et al. 2006). Ruderal and meadow species predominate, but species from very diverse habitats are found. Occurrence of both ruderal and meadow species in the course of succession is typical of many areas of anthropogenic origin (Kutyna et al. 2007).

On the soda waste dumps the group of meadow species included many species of high constancy (16 species with constancy above 30%). However, their cover coefficients were low (770 at most). Ruderal species occurred with much lower constancy (10 species with constancy above 30%), but of-

Table 2

Frequency F (%) and cover coefficient (Cc) of main plant species on soda waste dumps

Ruderal species n = 40			Meadow species n = 47			Other species n = 46		
Species	F	Cc	species	F	Cc	species	F	Cc
Artemisia vulgaris L.	78	307	*Vicia cracca* L.	87	516	*Calamagrostis epigejos* (L.) ROTH	77	1911
Tanacetum vulgare L.	58	535	*Crepis biennis* L.	76	770	*Trifolium medium* L.	36	1222
Melilotus officinalis (L.) PALL.	57	302	*Potentilla anserina* L.	64	80	*Campanula rapunculoides* L.	36	236
Cirsium arvense (L.) SCOP.	53	193	*Daucus carota* L.	63	186	*Ononis arvensis* L.	33	410
Agropyron repens (L.) P.BEAUV.	52	793	*Pastinaca sativa* L. S. STR.	60	200	*Senecio jakobea* L.	24	22
Medicago sativa L.	48	720	*Lathyrus pratensis* L.	52	381	*Coronilla varia* L.	23	191
Melilotus alba MEDIK	43	217	*Taraxacum officinale* F. H. WIGG	52	135	*Euphorbia esula* L.	20	23
Medicago lupulina L.	32	41	*Trifolium pratense* L.	48	317	*Vicia sepium* L.	12	20
Erigeron annuus L. (PERS.)	33	45	*Festuca rubra* L. S. STR.	47	519	*Odontites serotina* (LAM.) RCHB. S. STR.	12	9
Solidago gigantea AITON	30	71	*Arrhenatherum elatius* (L.) P. BEAUV. EX J. PRESL & C. PRESL	45	497	*Rubus caesius* L.	8	75
Lathyrus bulbosus L.	18	145	*Dactylis glomerata* L.	45	60	*Carex acutiformis* ERH.	8	80
Symphytum officinale E.	17	22	*Lotus corniculatus* L.	45	22	*Rubus plicatus* WEIHE & NEES	7	43
Equisetum arvense L.	15	27	*Festuca pratensis* HUDS.	39	87	*Populus tremula* L.	6	21
Poa compressa L.	15	31	*Centaurea jacea* L.	39	197	*Carex spicata* HUDS.	5	3
Hypericum perforatum L.	9	8	*Poa pratensis* L. S. STR.	33	138	*Mentha arvensis* L.	5	6
Oenothera biennis L. S. STR.	9	11	*Achillea millefolium* L. S. STR.	31	47	*Robinia pseudoacacia* L.	4	5

ten dominated in individual plots. The species widely distributed and often showing a high degree of plant cover was *Calamagrostis epigejos*. Except *Trifolium medium*, the other species occurred sporadically and were characterized by a low degree of plant cover.

Similarities in species composition between individual plots were relatively small, as confirmed by the results of Detrended Correspondence Analysis (DCA) – Table 3. The gradient length of the first three axes was similar (about 3 SD). The first two axes account for 13.6% of the total variation and the first four for 22.5%.

Table 3

Summary of the DCA analysis

	Axis			
	1	2	3	4
Lengths of the gradient (standard deviation)	3.110	3.043	3.059	2.528
Cumulative percentage variance of species data	8.1	13.6	18.7	22.5

The main gradient in species composition, illustrated by the first DCA axis, is associated with an increasing depth of the topsoil, nitrogen and phosphorus content. This axis correlates positively with the proportion of the sand fraction and negatively with the proportion of clay fraction. The first axis also correlates with the proportion of the area covered by ruderal species and negatively with the area covered by meadow species. None of the analysed factors was significantly correlated with the second DCA axis. The first axis also shows a strong positive correlation with height of the main plant mass and plant cover (Table 4).

The statistical analysis showed that the proportion of the meadow and ruderal species in plant cover was related to differences in topsoil properties. The share of ruderal species increases with growing depth of topsoil and abundance of nitrogen and phosphorus (Figure 1a). According to PRACH (2003), the most important factors that influence succession towards ruderal communities are fertile substratum with high pH and location in urbanized areas, which is the case in the investigated soda waste dumps. Ruderal species (characteristic for class *Artemisietea, Agropyretea, Stellarietea*) grew more vigorously, showed higher plant cover and achieved greater biomass. Clonal species that reproduce by means of stolons, such as *Agropyron repens* and *Calamagrostis epigejos* developed particularly strongly. Especially the latter species show good tolerance to low soil depth and strong expansion on anthropogenic land (KIRNER, MACHN 2001, PRACH, PYSEK 2001).

Meadow species are relatively strongly represented in the soda waste dumps. Rather than forming typical plant communities, they occur in assemblages with ruderal and other species. The occurrence of meadow spe-

Table 4

Correlation between vegetation composition (DCA1 and DCA2 factor scores), site characteristics and vegetation characteristic. Correlation coefficient, statistically significant ($p<0.01$) are in bold

Parameter	DCA axis 1	DCA axis 2
Depth of topsoil	**0.40**	0.10
Sand	**0.29**	0.04
Silt	0.00	0.10
Clay	**-0.29**	-0.07
pH H_2O	-0.04	-0.09
pH KCl	0.05	-0.06
EC	0.06	0.01
Organic C	0.13	-0.01
Total N	**0.32**	-0.01
C:N	-0.11	-0.12
P_2O_5	**0.25**	-0.13
K_2O	0.10	-0.03
Ca	0.03	-0.01
Mg	-0.13	-0.10
Ruderal species	**0.60**	**0.39**
Meadow species	**-0.38**	0.08
Vegetation cover	**0.58**	0.06
Height of main plant mass	**0.45**	0.12

cies was associated with lower fertility and lower depth of the topsoil and higher content of clay fraction (Figure 1b). Increasing soil fertility causes high biomass production, which in turn reduces the number of species. That dependence is commonly observed in grasslands (Janssens et al. 1998, Marrs 1993). Another reason why they developed less well in the investigated dumps, if no mowing is done, is the strong competition from ruderal species. This is reflected in a lower plant cover and main biomass height on the plots dominated by meadow species. Unlike ruderal communities, meadow communities usually show greater biocenotic diversity and have better aesthetic value (Prach, Hobbs 2008), which is important in the case of sites located in urbanized areas.

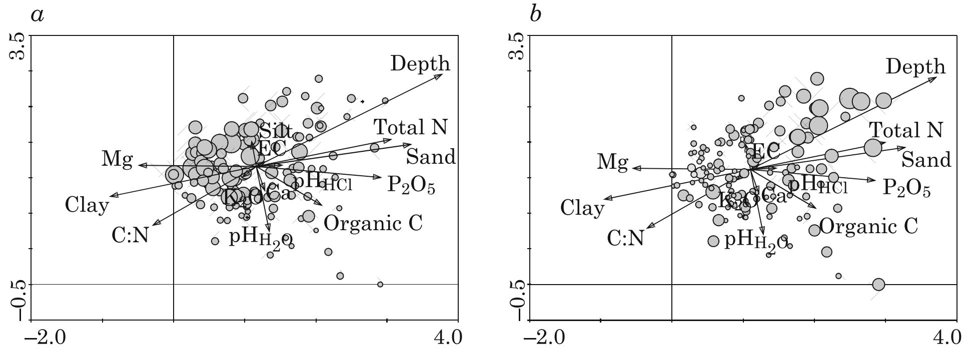

Fig. 1. DCA ordination diagram of plots displaying the major variation in species composition. The share of *a* – meadow species and *b* – ruderal species is visualised by the size of circles. The topsoil parameters were used as passive ones

CONCLUSIONS

1. The topsoil reclamation method applied in the soda waste dumps resulted in their revegetation, but due to the lack of further maintenance, communities with predominance of ruderal species have developed.

2. For satisfactory reclamation effects, it is necessary to define the target characteristics of a plant community when determining the method of reclamation and land management. This makes it possible to adapt technical reclamation procedures, topsoil conditioning, and plan possible management measures.

3. Development of vegetation into meadow communities, which are considered naturally and aesthetically more valuable, would require the use of a topsoil of low fertility and small depth. The species composition of the seed mixture intended for sowing on the reclaimed site should be ecologically matched to local conditions. Species typical of dry meadows (*Festuco-Brometea*) should be considered in the seed mixture for sites reliant on precipitation water and species typical of wet meadows (*Mollinietalia*) in constantly or periodically water-logged areas. Mowing is a necessary practice to hinder the development of highly competitive ruderal species.

REFERENCES

ANGOLD P.G., SADLER J.P., HILL M.O., PULLIN A., RUSHTON S., AUSTIN K., SMALL E., WOOD B., WADSWORTH R., SANDERSON R., THOMPSON K. 2006. *Biodiversity in urban habitat patches*. Sci. Total Environ, 360:196-204.

ATHY E.R., KEIFFER C.H., STEVENS M.H. 2006. *Effects of mulch on seedlings and soil on a closed landfill.* Restor. Ecol., 14: 233-241.

BLOOMFIELD H.E., HANDLEY J.F., BRADSHAW A.D. 1982. *Nutrient deficiencies and the aftercare of reclaimed derelict land*. J. Appl. Ecol., 19: 151-158.

BOROŃ K., ZAJĄC E., KLATKA S. 2000. *Reclamation of waste dumps of the KSP "Solvay" in Krakow*. Inż. Ekol., 1: 58-64. (in Polish)

BOROŃ K. J., NAGAWIECKA H. 1995. *The possibility of biological reclamation of soda waste reservoirs "White Seas" in Krakow, Poland*. Proc. of the Symposium Green'93., Balkema, Rotterdam, 523-526.

BOWEN C.K., SCHUMAN G.E., OLSON R.A., INGRAM L.J. 2005. *Influence of topsoil depth on plant and soil attributes of 24-year old reclaimed mined lands*. Arid Land Res. Manag., 19: 267-284.

BRADSHAW A. 2000. *The use of natural processes in reclamation - advantages and difficulties*, Landsc. Urb. Plann., 51: 89-100.

BRAUN-BLANQUET J. 1964. *Plant sociology*. 3 Aufl. Springer Verl. Wien (in German).

CARNELL R., INSELY H. 1982. *The influence of depth and type of cover material on tree establishment on a domestic refuse landfill site*. Reclam. Reveg. Res., 1: 225-230.

DOBSON M.C., MOFFAT A.J. 1993. *The potential for woodland establishment on landfill sites*. Department of the Environment HMSO, London.

ELLENBERG H., WEBER H.E., DÜLL R., WIRTH V., WERNER W., PAULIßEN D. 1992. *Indicator values of plants in Central Europe*. Scripta Geobot., 18: 1-258. (in German)

EWING K. 2002. *Mounding as a technique for restoration of Prairie on a capped landfill in the Puget Sound Lowlands*. Rest. Ecol., 10: 289-296.

JANSSENS F., PEETERS A., TALLOWIN J.R.B., BAKKER J.P., BEKKER R.M., FILLAT F., OOMES M.J.M. 1998. *Relationship between soil chemical factors and grassland diversity*. Plant Soil, 202: 69-78.

KIRMER A., MAHN E.-G. 2001. *Spontaneous and initiated succession on unvegetated slopes in the abandoned lignite-mining area of Goitsche Germany*. Appl. Veg. Sci., 4: 19-27.

KUTYNA I., NIED•WIECKI E., MALINOWSKI R. 2007. *Pioneer plant communities on newly formed sand bottom sediments within the Ostrów Grabowski dumping area in Szczecin*. Folia Universitatis Agriculturae Stetinensis Agricultura, 1 (253): 53-64 (in Polish).

LITYŃSKI T., JURKOWSKA H., GORLACH E. 1976. *Agro-chemical soil analysis. Guidelines for soil and fertilizers analysis.* PWN, Warszawa. (in Polish)

MAŁECKI Z. 1997. *Restructure-Liquidation-Management of CSE "Solvay "* [in:] Problemy Sozologiczne Aglomeracji Miejsko-Przemysłowych. Komitet Inżynierii Środowiska PAN, Kraków. (in Polish)

MATUSZKO D. (ed.). 2007. *Cracow's climate in the 20th century*. Inst. Geografii i Gospodarki Przestrzennej UJ, Kraków. (in Polish)

MARRS R.H. 1993. *Soil fertility and nature conservation in Europe: theoretical considerations and practical management solutions.* Adv. Ecol. Res., 24: 241-300.

MARTÍNEZ-RUIZ C., B. FERNÁNDEZ-SANTOS. 2005. *Natural revegetation on topsoiled mining spoils according to the exposure*. Acta Oecol., 28: 231-238.

MARTINEZ-RUIZ C., MARRS R.H. 2007. *Some factors affecting successional change on uranium mine wastes: Insights for ecological restoration*. Ecol. Eng., 30: 286-294.

PAŁKA J., SANECKI L. 1992. *The Kracow Soda Plant „Solvay" Current state report.* DDJM – Biuro Architektoniczne, Kraków. (in Polish)

POŚPIECH N., SKALSKI T. 2006. *Factors influencing earthworm communities in post-industrial areas of Krakow Soda Works*. Europ. J. Soil Biol., 42 (Suppl. 1): 278-283.

PRACH K. 2003. *Spontaneous succession in central-European man-made habitats: What information can be used in restoration practice?* Appl. Veg. Sci., 6: 125-129.

PRACH K., PYŠEK P. 2001. *Using spontaneous succession for restoration of human disturbed habitats: Experience from Central Europe*. Appl. Veg. Sci., 4: 111-114.

PRACH K., HOBBS R. J. 2008. *Spontaneous succession versus technical reclamation in the restoration of disturbed sites.* Restor. Ecol., 16: 363-366.

REBELE F. 1992. *Colonization and early succession on anthropogenic soils*. J. Veg. Sci., 3: 201-208.

ROBINSON G.R., HANDEL S.N. 1995. *Woody plant roots fail to penetrate a clay- lined landfill: Management implications.* Environ. Manage., 19 (1): 57-64.

ROSTAŃSKI A. 2006. *Spontaneous plant cover on colliery spoil heaps in Upper Silesia (Southern Poland).* Wyd. Uniw. Śląskiego, ser. Pr. Nauk. Uniw. Śląskiego, 2410. (in Polish)

SIUTA J. 2007. *System of plant cultivation and composting with the use of sewage sludge on the post-soda waste landfill at Janików.* Inż. Ekol., 19: 38-58. (in Polish)

TER BRAAK C.J.F., SMILAUER P. 2002. *CANOCO Reference manual and CanoDraw for Windows user«s guide: Software for Canonical Community Ordination (version 4.5),* Microcomputer Power (Ithaca NY USA).

TRZCIŃSKA-TACIK H. 1966. *Flora and vegetation of the spoil mounds of the Cracow Soda Factory.* Fragm. Florist. Geobot., 12(3): 342-306. (in Polish)

ZAJĄC E. 2009. *Analysis of physical and chemical properties of topsoil on reclaimed soda waste decanters of former Kracow Soda Plant Solvay.* Ochr. Środ. i Zas. Natur., 38: 388--395. (in Polish)

ZARZYCKI J., ZAJĄC E. 2001. *Vegetation development on the unreclaimed soda waste decanter of the former Krakow Soda Plant „Solvay”* Zesz. Nauk. AR w Krakowie, 390: 37-46. (in Polish)

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