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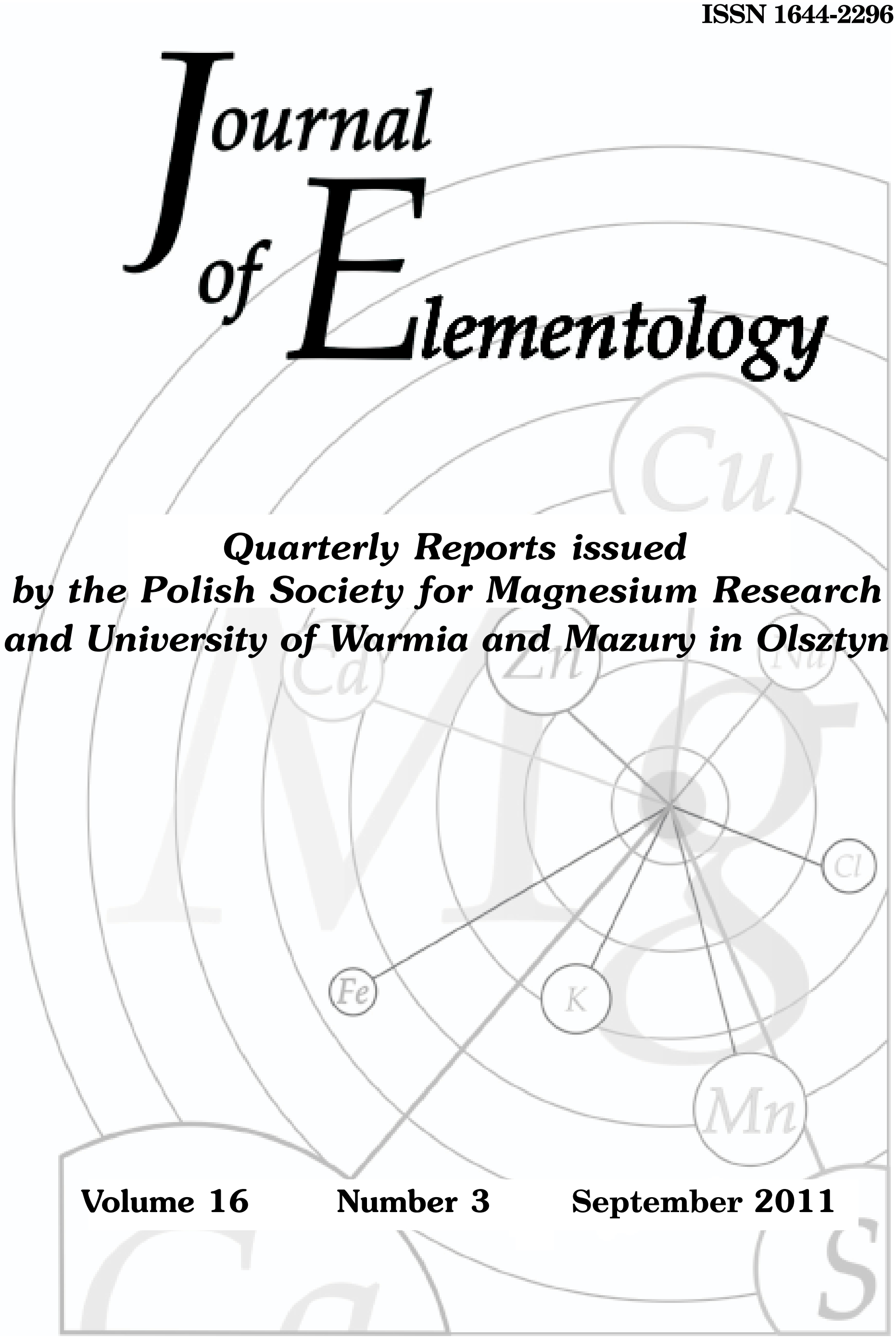

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ORIGINAL PAPERS

PHYSIOLOGICAL RESPONSE OF PLANTS AND CADMIUM ACCUMULATION IN HEADS OF TWO CULTIVARS OF WHITE CABBAGE*

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Abstract

Plants of the *Brassicaceae* family are considered useful for phytoremediation owing to their tolerance to high concentrations of heavy metals, which may be hyperaccumulated in the tissues. Cabbage seems to be a useful phytoextractor because of the high biomass concentrated in the head and cabbage cultivation technologies which ensure high yield. In a pot experiment, the response of plantlets of two cabbage cultivars: Ditmarska Najwcześniejsza (DN) and Kamienna Głowa (KG) to 10 and 40 mg Cd kg^{-1} DM of soil (Cd10 and Cd40, respectively) was studied. In addition, the content of Cd in the heads after the growing season was assayed. It was established that the Cd-induced stress was temporary and did not prevent head formation by cabbage plants. Higher leaf membrane leakiness and lower chlorophyll content, which were noticed during the 3rd week of vegetation, disappeared by the 8th week. Cd stimulated production of glucosinolates by plants. The

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higher dose of cadmium (40 mg Cd kg^{-1} DW of soil) diminished the fresh weight of heads of DN by ca 33%, and KG by 15%. However, the Cd accumulation recalculated to dry weight was high, and increased with the Cd dose. DN heads harvested from Cd40 contained up to 260-fold more Cd than control heads; for KG heads, the Cd content was over 560-fold higher. Hence, white cabbage can be used for phytoextraction of cadmium polluted soil. Higher resistance of KG than DN cultivar to stress caused by heavy metals may be attributable to a more efficient biosynthesis of organic sulphur compounds in the former cultivar, as reflected by the GLS content in both control and Cd-exposed KG specimens.

Key words: cadmium, chlorophyll, cell membrane, cabbage, phytoextraction.

REAKCJA FIZJOLOGICZNA ROŚLIN I AKUMULACJA KADMU W GŁÓWKACH DWÓCH ODMIAN KAPUSTY BIAŁEJ

Abstrakt

Rośliny z rodziny *Brassicaceae* są uważane za przydatne do celów fitoremediacyjnych w związku z tolerancją wysokich stężeń metali ciężkich, które mogą ulec hiperakumulacji w tkankach. Kapusta wydaje się rośliną, która może być wykorzystana jako fitoekstraktor w związku z dużą biomasą skoncentrowaną w główce i techniką uprawy tego warzywa umożliwiającą uzyskanie wysokiej wydajności. W doświadczeniu wazonowym badano reakcję sadzonek dwóch odmian kapusty białej głowiastej: Ditmarska Najwcześniejsza (DN) i Kamienna Głowa (KG) na kadm zastosowany w ilości 10 i 40 mg Cd kg^{-1} s.m. gleby (Cd10 i Cd40) oraz zawartość Cd w główkach po zakończeniu okresu wegetacji. Stwierdzono, że stres wywołany Cd był przejściowy, co umożliwiło roślinom wytworzenie główek. Zwiększenie przepuszczalności błon komórkowych liści oraz zmniejszenie w nich zawartości chlorofilu stwierdzone w 3. tygodniu wegetacji nie pojawiło się już w 8. tygodniu. Cd stymulował w roślinach produkcję glukozynolanów (GLS). Większa z zastosowanych dawek kadmu (40 mg Cd kg^{-1} s.m. gleby) wpłynęła na zmniejszenie świeżej masy główek DN o ok. 33%, a KG o 15%. Akumulacja Cd w jednostce suchej masy główek była jednak bardzo wysoka i wzrastała wraz ze wzrostem dawki. Główki DN pochodzące z uprawy z zastosowaniem Cd40 zawierały do 260 razy więcej Cd niż główki pochodzące z kontroli, analogiczne główki KG zakumulowały nawet ponad 560 razy więcej Cd w stosunku do kontroli. Zatem kapustę głowiastą białą można wykorzystać do fitoremediacji gleby zanieczyszczonej kadmem. Większa odporność odmiany KG niż DN na stres wywołany metalami ciężkimi może wynikać z bardziej wydajnej biosyntezy związków siarkoorganicznych, co znalazło odbicie w zawartości GLS, wyższej zarówno u roślin kontrolnych, jak i eksponowanej na Cd odmiany KG.

Słowa kluczowe: kadm, chlorofil, błony komórkowe, kapusta, fitoekstrakcja.

INTRODUCTION

Phytoextraction is a phytoremediation technique which employs metal-accumulating plants, able to translocate chemical elements from the soil and accumulate them in harvestable parts. The species belonging to the botanical family *Brassicaceae* are often considered as usable for phytoextraction of heavy metal contaminated soils. So far, Indian mustard *Brassica juncea* (L.) Czern., *Cardaminopsis halleri* Hayek and *Thlaspi caerulescens* J.

Presl & C. Presl have been taken into consideration (Kumar et al. 1995, Cunningham, Ow 1996). Here, we are discussing a possible use of white cabbage for the soil cleanup of cadmium by phytoextraction. White cabbage has already been studied in this context, but the analyzed plants were harvested from fields with a relatively low Cd content (Ciura et al. 2005, Sękara et al. 2005). The advantages of using cabbage are as follows: high biomass concentrated in a relatively small volume of the head, the plant structure which prevents big loss of plant parts, and well-known methods of cabbage cultivation.

In the present study, relatively high doses of Cd were introduced to soil (according to Antonkiewicz et al. 2006). These doses exceeded the permissible levels set by the Ordinance of the Minister for the Environment of 9.09.2002 on quality standards of soils and ground (Journal of Law, 2002, no. 165, item 1359.) The study evaluated the degree of stress to young plants transplanted to the contaminated soil and, should they survive under such chemical exposure, their ability to accumulate Cd in the heads. Analyses of the cell membrane status, chlorophyll content and F_v/F_m parameter of chlorophyll *a*, which were carried out, are often used in environmental studies performed on plants subjected to heavy metals, where they serve as a measure of the physiological stress (Chaoui et al. 1997, Jasiewicz et al. 1997, 2004, Sikora et al. 2009). Another interesting goal of this research has been to elucidate the effect of Cd on the biosynthesis of glucosinolates (GLS). GLS are secondary metabolites specific to the *Brassicaceae* family, and their synthesis is often stimulated by environmental stress (chemical or biological one) (Jensen et al. 1996, Kusznierewicz et al. 2008). As the cabbage species embraces numerous cultivars growing in different seasons, two have been selected for this experiment: Ditmarska Najwcześniejsza (DN; early), and Kamienna Głowa (KG; late). These cultivars are popular in Poland because they enable farmers to produce high yield and are resistant to changeable weather conditions.

MATERIAL AND METHODS

The experiment was performed in 2009-2010. Cabbage plants were grown in a phytotron at the University of Agriculture in Krakow, in 10 dm^3 pots filled with local soil (clay silt, 35% silt and clay, pH 7.0) containing 0.38 mg Cd dm^{-3} DM of soil. Two cabbage (*Brassica oleracea subsp. capitata f. alba*) cultivars Ditmarska Najwcześniejsza (DN; early, vegetation period 65-75 days), and Kamienna Głowa (KG; late, 150-160 days), were used. Plantlets were produced from seeds and transplanted into soil at the stage of 6-8 leaves.

The soil and the plants were fertilized according to the agricultural standards, but at the minimal level ensuring proper growth and development of the plants: N (NO_3-N + NH_4-N) – 105 (early cultivar) and 120 mg dm^{-3} DM of soil (late cultivar), P ($Ca(HPO_4)_2$ –50 and 60 mg dm^{-3}, K (KCl, 60% potassium salt) – 160 and 180 mg dm^{-3}, respectively. Cadmium was added to the soil 10 days before the planting, as $CdSO_4 \cdot 8H_2O$, in the amount of 10 and 40 mg Cd kg^{-1} DM of soil (according to ANTONKIEWICZ et al. 2006). Control pots contained the same soil but without added Cd. The level of the stress to plants was estimated during the 3rd and 8th week of plantlets growing in the pots. The cell membrane disturbance was assayed conductometrically and expressed as the ion leakage index (MARKOWSKI, SKRUDLIK 1995, BĄCZEK-KWINTA, KOŚCIELNIAK 2009). The chlorophyll content was measured photometrically with a SPAD chlorophyllometer (Konica Minolta, Japan). Additionally, in the 8th week, the photosynthetic apparatus was assayed by analyzing the parameters of chlorophyll *a* fluorescence (FMS-2, Hansatech, UK). Moreover, the maximal photochemical efficiency of photosystem II (PSII), F_v/F_m, was taken into consideration. The measurements and analyses were conducted on non-senescent, fully developed leaves (3rd to 5th, counting from the developing head).

The plants were grown in pots for 113 days (DN) and 134 (KG). After harvesting, the heads were dried and mineralized at 450°C. The content of Cd in plants was assayed by inductively coupled plasma atomic emission spectroscopy ICP-AES JY-238 Ultrace. The content of glucosinolates (GLS) in plants was determined according to the EU official method (ISO 9167-1). From freeze-dried plant material, GLS were extracted with boiling MeOH. The extract was purified on anion-exchange resin with concomitant enzymatic hydrolysis of sulfate. Desulfo-GLS were analyzed using an Agilent Model 1100 HPLC system on a Lichrosphere RP-18e column. The separation was performed by linear gradient elution (A – H_2O, B – 20% acetonitrile; 0-25 min 0-100% B). The identification and quantification of desulfo-GLS relied on glucotropaeolin used as an internal standard and reference material (BCR-367 R, rapeseed). The detailed protocol of GLS determination has been described elsewhere (KUSZNIEREWICZ et al. 2008).

Statistical analysis was carried out by one-way Anova and Duncan test on the data for each cultivar.

RESULTS AND DISCUSSION

In the 3rd week of cultivation, the plantlets were stressed by Cd presence in the soil. Leaf cell membranes were injured, as the index of ion leakage was generally higher in the case of Cd-treated plants than in the control ones. However, DN plants were more severely affected by Cd than those of KG, because their ion leakage was raised by just as little as 10 mg Cd kg^{-1} DM of soil. There was no such increase in KG plantlets. Additionally, the higher dose of Cd (40 mg Cd kg^{-1} DM of soil) resulted in higher electrolyte leakage values in DN that in KG compared to the control plants (Figure 1). Degradation of the cell membrane due to lipid peroxidation is a typical effect produced by heavy metals on plants (Ouriti et al. 1997). The reason is the overproduction of reactive oxygen species, which cause membrane lipid peroxidation, leading to increased membrane leakiness to ions (Chaoui et al. 1997). Interestingly, in the 8th week, plants exhibited no symptoms of membrane injury. All the values determined were similar for each treatment and the cultivar (Figure 1). This suggests immobilization of the metal in vacuoles and cell walls, mainly in the older parts of the plant, or in the stem, so that younger parts revealed no injury symptoms.

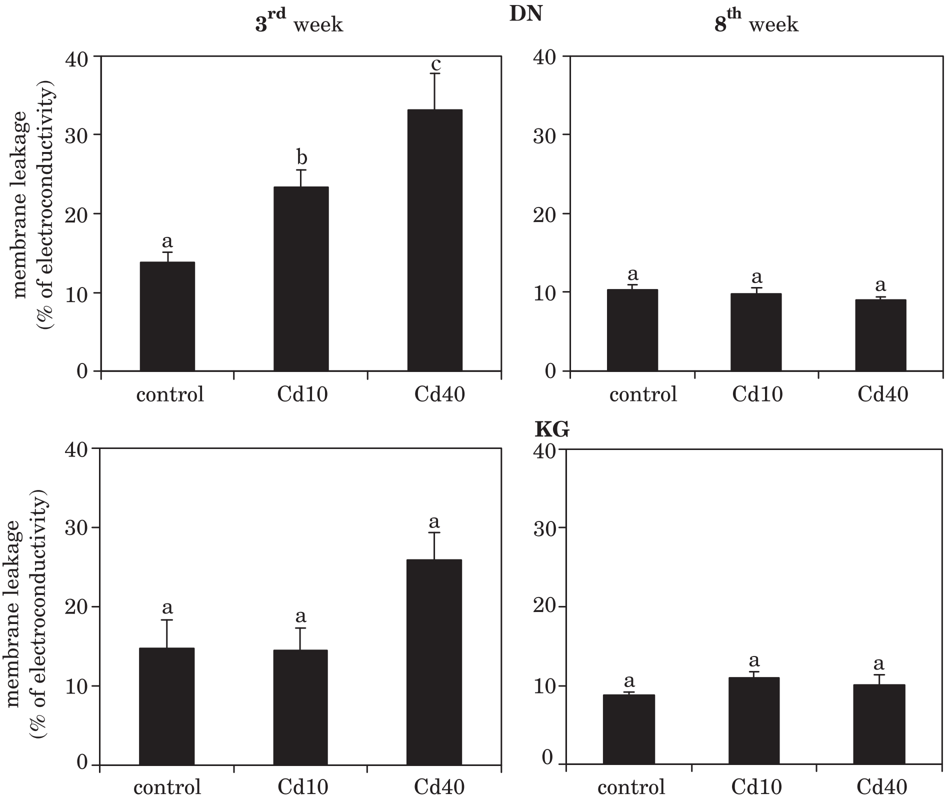

Fig. 1. The influence of Cd on the leaf cell membrane status, assayed conductometrically as ion leakage. Mean ± SE was given (n=5). Means denoted with the same letters do not differ significantly among the cultivar and the stage (Duncan's multiple range test; p=0.05)

In the 3rd week, the chlorophyll content was depressed in leaves, but the response of plants of both cultivars was not identical (Figure 2). In leaves of DN, even the smaller dose of cadmium (Cd10) depressed the SPAD values, which was similar to the effect produced by Cd40. In KG plants, the decline was caused only by Cd40, and it was smaller versus the control than that established for DN. The chlorophyll content as well as the chlorophyll *a* fluorescence parameter F_v/F_m are important markers providing information on the photosynthetic ability of plants grown on media containing a heavy metal (Jasiewicz et al. 2004, Ebbs, Uchil 2008). Chlorophyll may be destroyed by the substitution of Mg in its central part with Cd (Küpper et al. 1998) or else the synthesis of the pigment may be disturbed at the level of its precursor, i.e. aminolevulinic acid (Ala, Stobart et al. 1985, Nikolić et al. 2008).

In DN plants, the inhibitory effect of Cd40 on SPAD persisted until the 8th week (Figure 2). However, at this stage, the difference in the chlorophyll content between the control and Cd40 plants was smaller than ob-

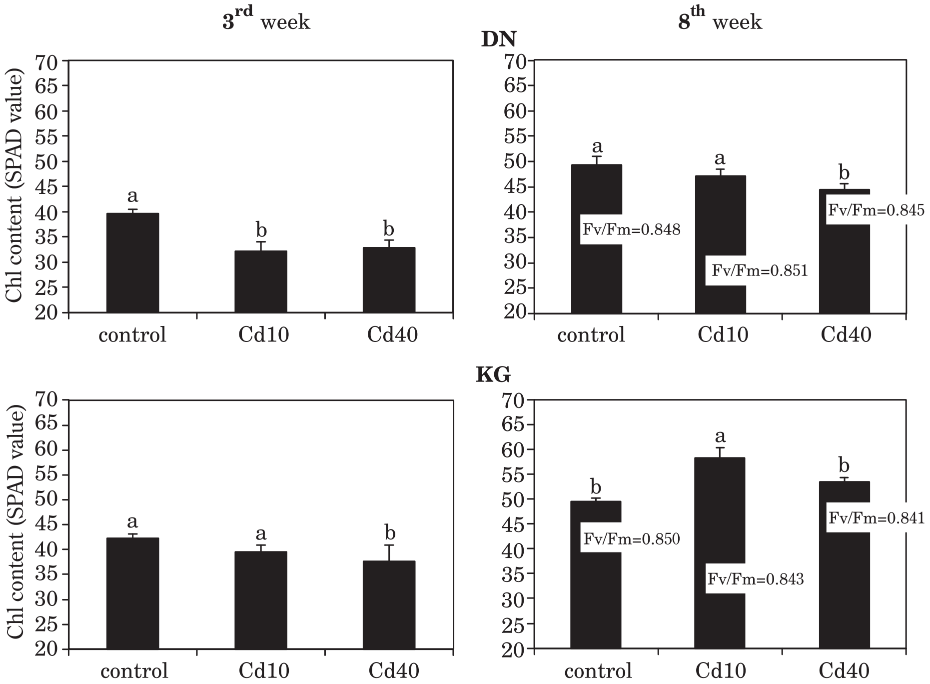

Fig. 2. The influence of Cd on the leaf chlorophyll content, assayed photometrically as the SPAD index. Data in frames: values of the fluorescence parameter F_v/F_m, measured parallel on the same leaves. Mean ± SE was given (n=5). Means denoted with the same letters do not differ significantly among the cultivar and the stage (Duncan's multiple range test; p=0.05)

served before (in the 3rd week). In KG plants, no such decline was observable in the 8th week (Figure 2), and in Cd10 plants an increase in chlorophyll was even noticed. The analysis of the chlorophyll *a* fluorescence parameter F_v/F_m revealed that in the 8th week the photochemical efficiency of photosystem II of all plants grown on Cd-contaminated soil was at the control level. Additionally, all SPAD values were higher in the 8th than in the 3rd week (Figure 2). Such an effect was also observed by SCHEPERS et al. (1992) or COSTA et al. (2003). This may suggest that Cd was incorporated into older leaves and the stem of contaminated plants, thus not affecting chlorophyll synthesis in younger plant parts. Thereby, plants were able to maintain an adequate level of photosynthesis, the source of biomass production.

However, the initial chemical stress to which the plants grown on Cd40 contaminated substrate were subjected, had a residual effect on the yield of heads. Cd40 diminished the fresh mass of DN by *ca* 30%, and that of KG by 15% in relation to the respective controls (Table 1).

Table 1

The influence of Cd on the yield and Cd content of heads of two cabbage cultivars. Mean ± SE was given (n=5). Means denoted with the same letters do not differ significantly (Duncan's multiple range test; p=0.05)

Treatment	DN		KG	
	yield of the head FW (% of ontrol)	Cd content in the head (mg kg^{-1} DW)	yield of the head FW (% of ontrol)	Cd content in the head (mg kg^{-1} DW)
Control	100 +/- 6.66 *a*	0.35 +/- 0.04 *a*	100 +/- 6.49 *a*	0.38 +/- 0.09 *a*
Cd10	95.7 +/- 17.5 *a*	5.01 +/- 0.25 *b*	99 +/- 21.9 *a*	4.62 +/- 0.53 *b*
Cd40	66.3 +/- 12.1 *b*	8.45 +/- 0.61 *c*	84 +/- 14.9 *b*	18.84 +/- 2.27 *c*

The accumulation of Cd in the dry mass of heads was high, as could have been anticipated, and tended to rise with the increasing Cd content in the soil. The highest Cd concentration was noticed in KG plants treated with Cd40. Their heads accumulated *ca* 19 mg kg^{-1} DM of biomass, which was about 560-fold more than accumulated in the control plants.

The post-harvest content of glucosinolates (GLS) is presented in Table 2. As can be seen, plants of the cultivar KG are characterized by more efficient biosynthesis (over 30%, in untreated and Cd exposed KG cabbage) of GLS when compared to DN plants. In both cultivars, the exposure to Cd stimulated GLS production. Importantly, the GLS synthesis capacity was parallel to the plants' resistance to Cd, which was tolerated better by KG plants. In sum, the data presented in Table 2 suggest that the synthesis of these secondary metabolites may help to select the most appropriate cultivar for phytoremediation.

Table 2

The influence of Cd on the glucosinalate (GLS) content in two cabbage cultivars. Mean ± SE was given (n=5). Means denoted with the same letters do not differ significantly (Duncan's multiple range test; p=0.05)

Treatment	DN	KG
	GLS content (nmoles kg^{-1} DW)	GLS content (nmoles kg^{-1} DW)
Control	3.60 +/- 0.239 *a*	6.17 +/- 0.038 *a*
Cd10	4.12 +/- 0.058 *a*	8.56 +/- 0.807 *b*
Cd40	8.10 +/- 0.071 *b*	12.0 +/- 0.595 *c*

All these results suggest that cabbage has a potential to be exploited for ion phytoextraction of Cd-polluted soil. *Thlaspi caerulescens*, well-known as a Cd hyperaccumulator tested in field trials, may accumulate up to 3,600 mg kg^{-1} DW (ROBINSON et al. 1998). However, the shoot biomass of *Thlaspi* is up to 3.89 t ha^{-1} (YANAI et al. 2006), whereas cabbage biomass is 60--90 t ha^{-1} (JABŁOŃSKA-CEGLAREK, ROSA 2002). Therefore, the capacity of cabbage to remove cadmium from soil is 8–fold lower than that of *Thlaspi caerulescens*. However, technologies for cultivation and harvesting cabbage have been well designed and tested, in contrast to *Thlaspi*. Additionally, mineral fertilization of the soil and the plants, which was implemented to optimize vegetation, might have restrained the phytoextractive potential of cabbage (GORLACH, GAMBUŚ 1991). The use of synthetic chelators, e.g. EDDS ((S,S-ethylenediaminedisuccinic acid), increases Cd accumulation in plants used for phytoextracion (LUO et al. 2002), so it would be worthwhile elucidating the benefits of EDDS addition in further experiments.

CONCLUSIONS

1. Cabbage plants are able to survive cadmium stress (40 mg Cd kg^{-1} DM of soil) and form the heads, which accumulate Cd.

2. The late cultivar Kamienna Głowa accumulates more Cd and reveals less severe phytotoxic symptoms than cv. Ditmarska Najwcześniejsza, thereby it has a better potential for phytoextraction.

3. The higher resistance to chemical stress, observed for the plants of cv. Kamienna Głowa, may result from their more efficient biosynthesis of organic sulphur compounds, as reflected by the GLS content, which both in untreated and Cd-exposed KG cabbage is about 30% higher than in the cultivar Ditmarska Najwcześniejsza.

REFERENCES

ANTONKIEWICZ J., JASIEWICZ CZ., LOŠAK T. 2006. *Wykorzystanie ślazowca pensylwańskiego do ekstrakcji metali ciężkich z gleby [Using Virginia fanpetals for extraction of heavy metals from soil].* Acta Sci. Pol., Formatio Circumiectus, 5 (1): 63–73. (in Polish)

BĄCZEK-KWINTA R., KOŚCIELNIAK J. 2009. *The mitigating role of environmental factors in seedling injury and chill-dependent depression of catalase activity in maize leaves.* Biol. Plant., 53: 278-284.

CHAOUI A., MAZHOUDI S., GHORBAL M.H., FERJANI E. 1997. *Cadmium and zinc induction of lipid peroxidation and effects on antioxidant enzyme activities in bean (Phaseolus vulgaris L.).* Plant Sci., 127: 139-147.

CIURA J., PONIEDZIAŁEK M., SĘKARA A., JĘDRSZCZYK E. 2005. *The possibility of using crops as metal phytoremediants.* Pol. J. Environ. Stud., 14: 17-22.

COSTA C., FRIGON D., DUTILLEUL P., DWYER L.M., PILLAR V.D., STEWART D.W., SMITH D.L. 2003. *Sample size determination for chlorophyll meter reading on maize hybrids with a broad range of canopy type.* J. Plant Nutr., 26: 1117-1130.

CUNNINGHAM S.D., OW D. 1996. *Promises and prospects of phytoremediation.* Plant Physiol., 110: 715-719.

EBBS S., UCHIL S. 2008. *Cadmium and zinc induced chlorosis in Indian mustard (Brassica juncea (L.) Czern) involves preferential loss of chlorophyll b.* Photosynthetica, 46: 49-55.

GORLACH E., GAMBUŚ F. 1991. *The effect of liming, adding peat, and phosphorus fertilization on the uptake of heavy metals by plants.* Pol. J. Soil Sci., 24(2): 199-204.

JABŁOŃSKA-CEGLAREK R., ROSA R. 2002. *Wpływ różnych form nawożenia organicznego na plonowanie i skład chemiczny kapusty głowiastej białej [Effect of different forms of organic fertilization on yields and chemical composition of white head cabbage].* Acta Sci. Pol., 1(2): 25-32. (in Polish)

JASIEWICZ CZ., ZEMANEK M., ANTONKIEWICZ J. 2004. *Influence of cadmium on photosynthetic pigment in maize.* Chem. Inż. Ekol., 11(7): 587-593.

JASIEWICZ CZ., ZEMANEK M., BĄCZEK-KWINTA R. 1999. *Wpływ kadmu na fluorescencję chlorofilu i aktywność dysmutazy ponadtlenkowej w liściach kukurydzy [Influence of cadmium on chlorophyll fluorescence and activity of superoxide dismutase in maize leaves].* Zesz. Probl. Post. Nauk Rol., 411-416. (in Polish)

JENSEN C.R., MOGENSEN V.O., MORTENSEN G., FIELDSEND J.K., MILFORD G. F.J., ANDERSON M.N. 1996. *Seed glucosinolate, oil, protein content of field grown rape (Brassica L.) affected by soil drying and evaporative demand.* Field Crops Res., 47: 93-105.

KUMAR N.P.B.A., DUSHENKOV V., MOTTO H., RASKIN I. 1995. *Phytoextraction. The use of plants to remove heavy metals from soils.* Environ. Sci. Technol., 29: 1232-1238.

KUSZNIEREWICZ B., BARTOSZEK A., WOLSKA L., DRZEWIECKI J., GORINSTEIN S., NAMIEŚNIK J. 2008. *Partial characterization of white cabbages (Brassica oleracea var. capitata f. alba) from different regions by glucosinolates, bioactive compounds, total antioxidant activities and proteins.* LWT- Food Sci. Technol., 41: 1–9.

KÜPPER H., KÜPPER F., SPILLER M. 1998. In situ detection of heavy metal substituted chlorophylls in water plants. Phytosynthesis Res., 58: 123-133.

LUO CH., SHEN Z., LI X. 2002. *Enhanced phytoextraction of Cu, Pb, Zn and Cd with EDTA and EDDS.* Chemosphere, 59 (2005): 1–11.

MARKOWSKI, A., SKRUDLIK G. 1995. *Electrolyte leakage, ATP content in leaves and intensity of net photosynthesis in maize seedlings at permanent or different daily exposure to low temperature.* J. Agron. Crop Sci., 175: 109-117.

Nikolić N., Kojić D., Pilipović A., Pajević S., Krstić B., Borišev M., Orlović S. 2008. *Responses of hybrid poplar to cadmium stress: photosynthetic characteristics, cadmium and proline accumulation, and antioxidant enzyme activity.* Acta Biol. Cracov. Ser. Bot., 50(2): 95-103.

Ouriti O., Boussama N., Zarrouk M., Cherif A., Mohamed H.G. 1997. *Cadmium- and copper-induced changes in tomato membrane lipids.* Phytochemistry, 7: 1343–1350.

Robinson B.H., Leblanc M., Petit D., Brooks R.R., Kirkman J.H., Gregg P.E.H. 1998. *The potential of Thlaspi caerulescens for phytoremediation of contaminated soils.* Plant Soil, 203: 47-56.

Schepers J.S., Francis D.D., Vigil M., Blow F.E. 1992. *Comparison of maize leaf nitrogen concentration and chlorophyll meter readings.* Soil Sci. Plant Anal., 23: 2173-2187.

Sękara A., Poniedziałek M., Ciura J., Jędrszczyk E. 2005. *Cadmium and lead accumulation and distribution in the organs of nine crops: implications for phytoremediation.* Pol. J. Environ. Stud., 14: 509-516.

Sikora J., Żurawski J., Rutkowska J., Poniedziałek B., Wiktorowicz K., Dudkowiak A. 2009. *Wpływ metali ciężkich na fluorescencję chlorofilu Synechocystis aquatilis [Effect of heavy metals on the fluorescence of chlorophyll in Synechocystis aquatilis].* Ochr. Środ. Zas. Nat., 41: 293-301. (in Polish)

Stobart A.K., Griffiths W.T., Ameen-Bukhari I., Sherwood R.P. 1985. *The effect of* Cd^{2+} *on the biosynthesis of chlorophyll in leaves of barley.* Physiol. Plant., 63: 293-298.

Yanai Y., Zhao F.-J., McGrath S.P, Kosaki T. 2006. *Effect of soil characteristics on Cd uptake by the hyperaccumulator Thlaspi caerulescens.* Environ. Poll., 139: 67-175.

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SOIL FUNGAL COMMUNITIES SHAPED UNDER THE INFLUENCE OF ORGANIC FERTILIZATION

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Abstract

The results presented in this paper have been obtained during a three-year experiment (from the second cycle of four-year trials set up in 2004) established in Bałcyny. The following crops were grown in succession: potato, fodder barley, winter oilseed rape and winter wheat. The fertilization treatments included: mineral NPK, FYM and organic fertilization with composted and dried sewage sludge and composted municipal waste. Treatments without soil enrichment or with mineral NPK fertilization were taken for comparison. Farmyard manure and organic fertilizers were applied in two different ways: as a single dose of 10 t ha^{-1} before planting the potato or in two doses, each 5 t d.m. ha^{-1}, before planting the potato and before sowing the oilseed rape. The effect of the applied fertilizers on assemblages of soil fungi was tested. The fungi were cultured on Martin medium.

The fertilizers were determined to have affected the populations of soil fungi. Yeast-like fungi prevailed among the isolated colonies (60-85% of the total isolates). The richest fungal community was obtained from the soil amended with dried and pelleted sewage sludge or municipal green waste compost. However, suppressed growth of pathogenic fungi represented by the species *Aureobasidium pullulans, Botrytis cinerea*, of the genus *Fusarium* and *Sclerotinia sclerotiorum* was observed in the soil amended with natural fertilizers and composts. The growth of pathogens was most strongly inhibited in the soil enriched with a double dose of FYM, composted urban green waste or with dried and pelleted sewage sludge in either of the two application variants. The pathogen-antagonistic fungi, represented by three species of *Gliocladium* and four species of the genera *Paecilomyces* and *Trichoderma*, were more often isolated from the soil fertilized with FYM or organic fertilizers than the unfertilized or NPK-nourished soil. The soil enriched with Dano compost applied in a single rate of 10 t d.m. ha^{-1} was most abundantly populated by these fungi. Among the remaining saprotrophs, fungi of the genus *Penicillium* and the orders *Mucorales* and *Sporotrichum olivaceum* were isolated.

Key words: organic fertility, NPK fertility, soil pathogens, antagonists.

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ZBIOROWISKO GRZYBÓW GLEBOWYCH UKSZTAŁTOWANE POD WPŁYWEM NAWOŻENIA ORGANICZNEGO

Abstrakt

Pezentowane w pracy wyniki pochodzą z 3-letniego doświadczenia (z 2. cyklu 4-letnich doświadczeń założonych w 2004 r.) założonego w Bałcynach. Uprawiano po sobie następujące gatunki roślin: ziemniak, jęczmień paszowy, rzepak ozimy i pszenicę ozimą. Zastosowano nawożenie mineralne NPK, naturalne obornikiem i organiczne: kompostowanymi i suszonymi osadami ściekowymi oraz kompostowanymi odpadami komunalnymi. Kombinacje bez nawożenia i z nawożeniem mineralnym NPK uwzględniono jako porównawcze. Obornik i nawozy organiczne aplikowano w dwojaki sposób: jednorazowo w dawce 10 t ha^{-1} przed sadzeniem ziemniaka lub dwukrotnie w dawce po 5 t s.m. ha^{-1} przed sadzeniem ziemniaka i przed siewem rzepaku. W badaniach określono wpływ aplikowanych nawozów na skład zbiorowiska grzybów glebowych. Hodowlę grzybów prowadzono na podłożu Martina.

Stwierdzono wpływ zastosowanych nawozów na populację grzybów glebowych. Najczęściej izolowano z gleby grzyby drożdżopodobne (60-85% ogółu izolatów). Najbogatsze zbiorowisko grzybów otrzymano z gleby użyźnionej osadem suszonym i granulowanym oraz kompostem z odpadów zieleni miejskiej. Jednak w glebie z zastosowanym nawożeniem naturalnym i kompostami stwierdzono ograniczenie liczebności grzybów patogenicznych reprezentowanych przez gatunki: *Aureobasidium pullulans, Botrytis cinerea*, rodzaju *Fusarium*, *Sclerotinia sclerotiorum*. Najbardziej zahamowany rozwój patogenów zanotowano w glebie z wniesionym dwukrotnie obornikiem, kompostem z odpadów zieleni miejskiej oraz osadem suszonym i granulowanym zastosowanymi w obydwu wariantach. Grzyby antagonistyczne względem patogenów, reprezentowane przez 3 gatunki *Gliocladium*, 4 gatunki rodzaju *Paecilomyces* i *Trichoderma*, częściej niż z gleby bez nawożenia i z nawożeniem NPK izolowano z gleby nawożonej obornikiem i organicznie, z najliczniej zasiedloną glebą użyźnioną Dano w dawce 10 t s.m. ha^{-1}. Wśród pozostałych saprotrofów wyodrębniono grzyby rodzaju *Penicillium*, rzędu *Mucorales* i *Sporotrichum olivaceum*.

Słowa kluczowe: nawożenie organiczne, nawożenie NPK, patogeny glebowe, antagoniści.

INTRODUCTION

Organic substances are added to soil in order to improve its quality by changing the physical (aggregation of soil particles) and microbiological properties (increased biomass content, microbial diversity and enzymatic activity) (DISSANAYAKE, HOY 1999, PUGET et al. 2000, CESPEDES LEON et al. 2006). Soil improvement is achieved, *inter alies*, by adding more carbon to soil (SIKORA, STOTT 1996, van BRUGGEN, SEMENOV 2000). In a study reported by KUNDU and NANDI (1985), a broader C:N ratio stimulated the development of bacteria while inhibiting that of fungi. This effect depended on the concentration of chemical and biological components in organic matter. Natural fertilizers applied in adequate doses, apart from large amounts of organic matter, enrich soil with some macro- and micronutrients. Certain characteristic microbial communities develop in soil under the influence of these fertilizers. For the phytosanitary safety, the share of fungi demonstrating antibiotic and parasitic activity is important. The fungi whose presence in soil is particularly desirable are the ones with enzymatic properties belonging to the genera *Gliocldium* and *Trichoderma*, which can inhibit the development of pathogens (not only the soil ones) by activating the following mechanisms: antibiosis, competition and hyperparasitism (CHERNIN, CHET 2002). Organic fertilizers (SARAIVA et al. 2004), composted plant waste (MAZZOLA, MULLINIX 2005), municipal waste and sewage sludge (LEWIS et al. 1992, TRANKNER 1992) as well as paper-mill residue (COOPERBAND 2001, STONE et al. 2003) provide effective plant protection against such pathogens as *Botrytis cinerea, Pythium* spp., *Phytophthora* spp., *Rhizoctonia solani, Sclerotinia sclerotiorum.*

This paper contains an analysis of the structure of soil fungal assemblages shaped under the influence of mineral, FYM or organic fertilization.

MATERIAL AND METHODS

The experiment was carried out in 2008-2010 (the second cycle of a four-year experiment started in 2004) on experimental plots in Bałcyny, on grey-brown podzolic soil originating from light silty loam, complex 4 class III (the Polish Norms, BN-78/9180-11). Prior to the experiment, the concentration of P (38.2 mg kg $^{-1}$), K (105.8 mg kg $^{-1}$) and Mg (48.3 mg kg $^{-1}$) in the soil as well as the soil pH = 5.04 were determined. The following crops were grown in succession: potato, fodder barley, winter oilseed rape and winter wheat. The applied fertilization consisted of natural fertilizer: mixed farmyard manure or organic fertilizers: sewage sludge composted with straw (municipal sewage sludge from the WTP in Działdowo, mixed with cereal straw in a 1 : 0.5 ratio and composted in heaps), dried and pelleted sludge (sludge from the WTP in Iława), sludge composted with no added substances (sludge from the WTP in Ostróda), municipal waste compost (Dano compost from unsorted municipal waste in Suwałki), and urban green waste compost from Suwałki. The chemical composition of the organic fertilizers is presented in Table 1. The treatments without fertilization or with the NPK mineral fertilization were taken for comparison. The farmyard manure and organic fertilizers were applied in two ways: in a single dose of 10 t d.m. ha^{-1} before planting the potato or as two doses, each of 5 t d.m. ha^{-1} before planting the potato and before sowing the oilseed rape. For the treatments with the organic fertilizers, depending on their N-total content, nitrogen was balanced to 150 kg ha^{-1} (under potato) and to 120 kg ha^{-1} (under oilseed rape). Spring barley and winter wheat received only mineral fertilization.

For determination of the quantitative and qualitative composition of soil fungal assemblages, in the early August each year, soil samples were collected from the depth of 10 cm from all the plots (at three sites) which made up a given experimental treatment. In the laboratory, the soil samples were shaken and portions of 10 g each were weighed out to place in 250 ml flasks, in which they were shaken for 20 minutes in 90 ml of sterile water, thus obtaining 10^{-1} dilution. The suspension was further diluted (from 10^{-2} to 10^{-4}). Fungi were cultured on Martin medium at 22-23°C. Fungal colonies grown after 5-day incubation were re-calculated per 1 gram of dry matter of soil (Dhingra, Sinclair 1995). Next, the fungi were inoculated onto agar slabs for further species identification. The results of the *in vitro* tests, carried out in a completely randomized design, were processed statistically using analysis of variance (Statistica® 9.0 2010). The means were compared with Duncan's test at the significance level of 0.01.

Table 1

Chemical composition of organic fert

Fertilizer	C org.	N	P	K	Mg	C : N
	($g\ kg^{-1}$ d. m.)					
FYM	364.00	20.00	3.72	20.80	4.80	18.2
Sludge composted with straw	276.00	20.56	23.15	9.81	6.11	13.4
Dried and pelleted sludge	386.00	35.15	24.48	3.56	5.65	11.0
Sludge composted with no added substances	410.00	50.45	31.82	3.18	7.27	8.1
Municipal waste compost (Dano)	151.00	12.57	6.92	7.83	5.46	12.0
Urban green waste compost	59.40	5.00	1.88	3.25	4.25	11.9

RESULTS AND DISCUSSION

The applied natural and organic fertilization differentiated counts of the soil fungal populations; in total, 6,192 colonies of fungi were obtained, in which yeast-like fungi made up 76.3%. Filamentous fungi were represented by 50 species. The phytopathological tests have demonstrated that most of the colony-forming units were obtained from the soil amended with urban waste compost and dried and pelleted sludge (Figure 1). The literature contains contradictory reports on the influence of soil organic amendments on assemblages of soil fungi. Górska and Stępień (2007) as well as Pratt (2008) claim that organic fertilization does not differentiate the abundance of filamentous fungal populations. Awad and Fawn (2004) formulate contradictory conclusions as they suggest that increasing rates of sewage sludge stimulate the development of soil microorganisms and increase their diversity (Weyman-Kaczmarkowa et al. 2002). As researchers claim, the amount of organic carbon added to soil plays an important role; to a lesser degree, added nitrogen affects microbial communities.

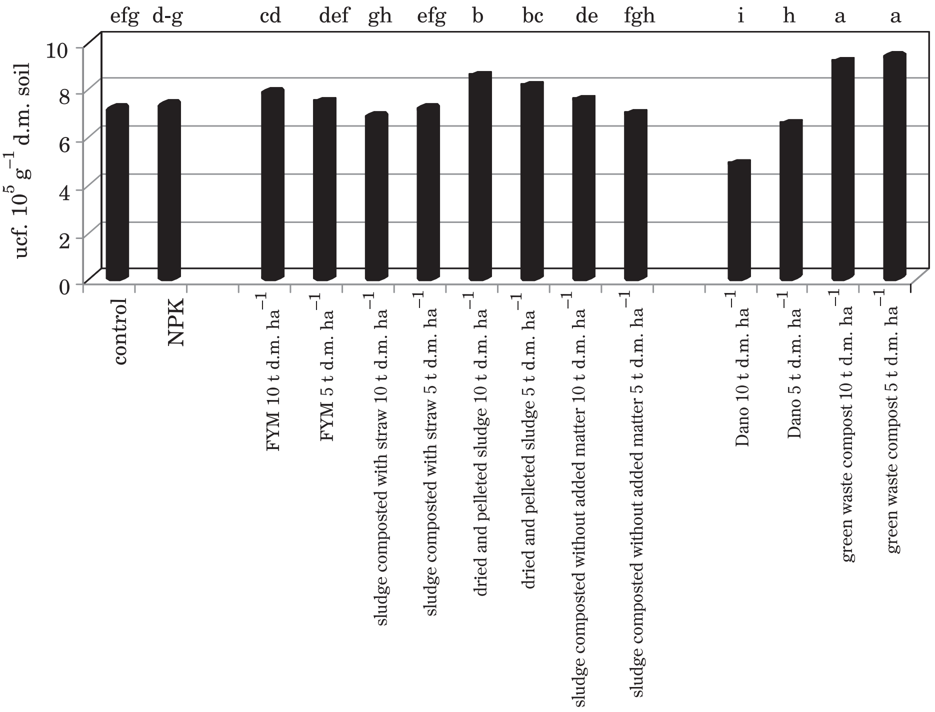


Fig. 1 Number of colony-forming units of fungi in the soil

In the present study, the dominant organisms in the fungal assemblages were yeast-like fungi, which made up from 63 to 85% of total communities (in the treatment with municipal waste compost 10 t d. m. ha^{-1} and urban waste compost in both application variants, respectively) – Figures 2a,c,d. Fifty species and non-sporulating colonies were identified among the filamentous fungi The pathogenic fungi, important for the phytosanitary soil condition, were represented by the following species: *Aureobasidium pullulans, Botrytis cinerea*, four species of the genus *Fusarium* and *Sclerotinia sclerotiorum,* most frequently colonizing the unfertilized and NPK-fertilized soil: 4.6 and 3.6%, respectively, of the total number of isolates (Figures 3a, 2b). The smallest population of the above fungi was cultured from the soil fertilized twice with FYM and urban green waste compost, under spring barley (Figures 3d, 2d). A single application of these fertilizers stimulated the development of potentially pathogenic fungi. However, this effect was accompanied by a growing number of antagonistic fungi, whose presence in soil is desirable (3 species of the genus *Gliocladium*, 5 – *Paecilomyces* and 4 – *Trichoderma*). Based on their experiments, SERRA-WITTLING et al. (1996) concluded that natural fertilizers and composts inhibited the development of *Fusarium* spp. fungi as well as those of *Pythium* and *Phytophthora*, all wide-

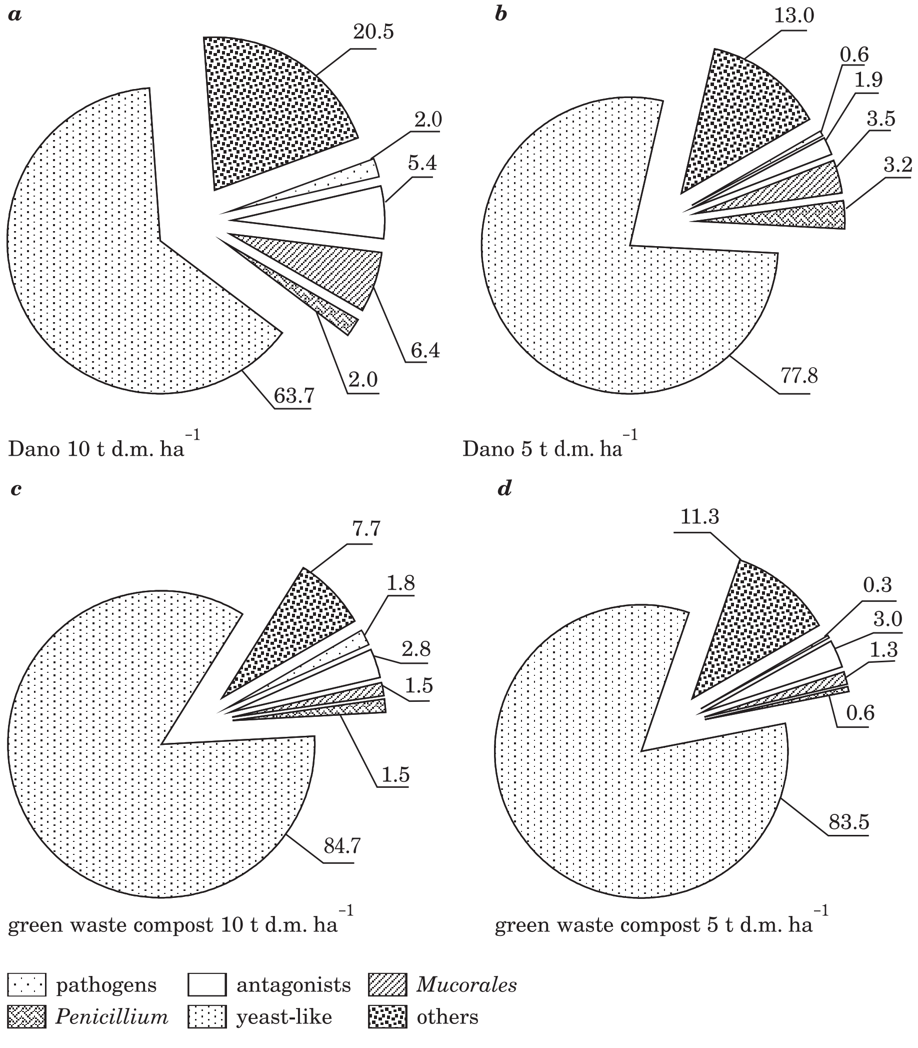


Fig. 2. Fungi isolated from soil fertilized with composted industrial waste (%)

spread in soil. Tsror Lakhim et al. (2001) as well as Lazarovitz et al. (2008) report that the infection of potato by *Rhizoctonia solani* and *Streptomyces scabies* is less severe in soil fertilized with cattle manure. Other researchers (Mills et al. 2002) point to less severe infection of solanaceous plants by *P. capsici, Alternaria solani* and *Septoria lycopersici* in soil amended with composted plant waste. Catxarrera et al. (2002) observed weaker symptoms of *Fusarium* wilt of tomato plants when the soil had been enriched with the fungus *Trichoderma asperellum* and compost. Barakat and Al.-Masri (2009) found out a similar effect for the soil enriched with *T. harzianum* and sheep manure.

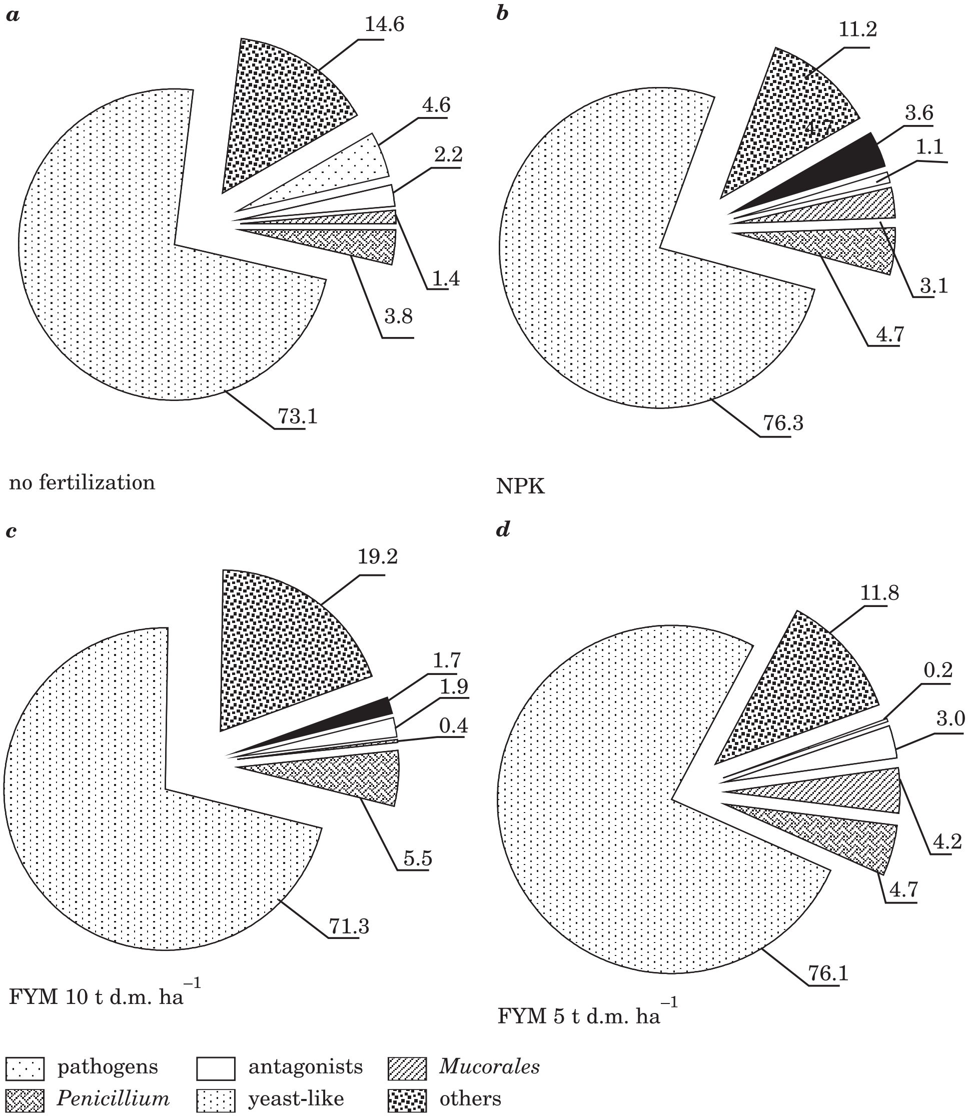
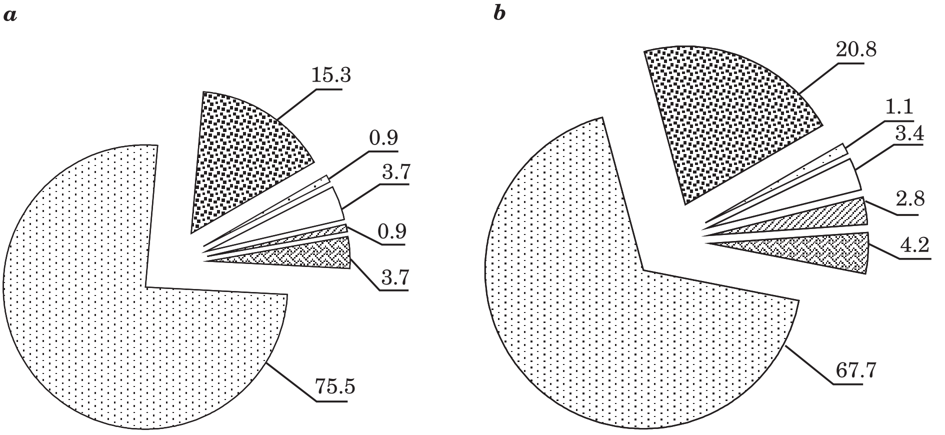
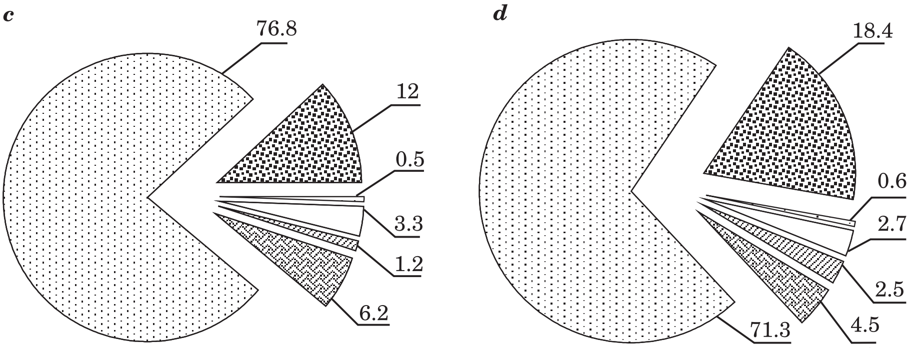


Fig. 3. Fungi isolated from unfertilized, NPK and FYM fertilized soil (%)

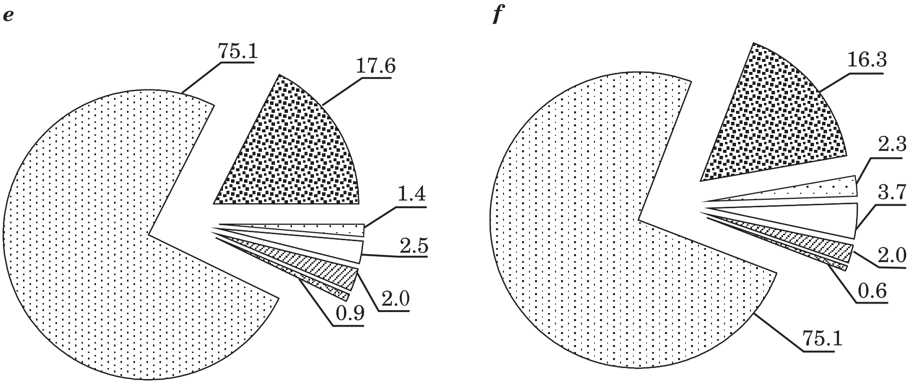
Our comparison of the analysed composted sewage sludge has demonstrated that the most favourable soil conditions, in respect of the plants' health, prevailed in the soil amended with dried and pelleted sludge, applied in either of the two systems: 0.6% of the pathogens and 3% of the antagonists (Figure 4c,d). However, the highest number of antagonists colonized the soil enriched with the compost made from unsorted municipal waste,



sludge composted with straw 10 t d.m. ha^{-1} sludge composted with straw 5 t d.m. ha^{-1}



dried and pelleted sludge 10 t d.m. ha^{-1} dried and pelleted sludge 10 t d.m. ha^{-1}



sludge composted without added matter 10 t d.m. ha^{-1} sludge composted without added matter 5 t d.m. ha^{-1}

⬚ pathogens ☐ antagonists ▨ *Mucorales*
▩ *Penicillium* ⬚ yeast-like ▦ others

Fig. 4. Fungi isolated from soil fertilized with composted sewage sludge (%)

applied in a single dose under fodder barley (Figure 2a). For the phytosanitary safety of crops, it is desirable to maintain dynamic changes of fungal populations in the soil. Organic fertilizers added to soil create favourable conditions for the development of antagonistic fungi (HOITIN, BOEHM 1999, PANDEY et al. 2006), especially the ones belonging to the genus (BULLOCK et al. 2002). Such fungi produce antibiotic and parasitic effects on pathogenic organisms, which means that they can be employed for the biological control of plant pathogens (PAPAVIZAS 1985, NELSON et al. 1983, ZAK et al. 2003). Soil cropped with *Brassicaceae* has been demonstrated to contain a growing population of the antagonists *Streptomyces* spp., which produce secondary metabolites inhibiting the development of plant pathogens, e.g. *Rhizoctonia solani* (MAZZOLA, MULLINIX 2005).

Among the saprotrophic fungi, the species of the order *Mucorales* produced the most numerous populations in the soil amended with the municipal waste compost added in a dose of 10 t d.m. ha^{-1} (6.4%, Figure 2a). In the treatments fertilized with composted sewage sludge and FYM (Figures 3c,d, 4a-f), the highest counts of saprotrophs were isolated from the soil amended with a double application of the fertilizers, except sewage sludge composted with no added substances. Species of the genus *Penicillium* had a similar share in the total number of fungi as saptrotrophs, and their development was promoted by the soil environment amended with a single dose of FYM or dried and pelleted sludge (Figures 3c, 4c). The saprotrophs of the genus *Penicillium*, analogously to those of the genus *Aspergillus*, as well as the pathogens belonging to *Fusarium* spp. are the most common components of fungal assemblages dwelling in soil enriched with organic fertilizers (SARAIVA et al. 2004).

Recapitulating, the positive influence of farmyard manure as well as sewage sludge or composted municipal waste applied as soil amending substances on the structure of soil fungal assemblages is noteworthy. These fertilizers have reduced the development of potential plant pathogens but stimulated that of antagonistic fungi.

CONCLUSIONS

In brief, the experiment has demonstrated a suppressed growth of populations of pathogenic fungi in soil amended with farmyard manure or organic fertilizers. The highest count of fungal colonies was obtained from the soil enriched with dried and pelleted sludge. At the same time, the soil from this treatment presented the most desirable phytosanitary conditions, i.e. a small count of pathogens but a high number of antagonistic fungi.

REFERENCES

Awad N.M., Fawzy K.S.M. 2004. *Assessment of sewage sludge application on microbial diversity, soil properties, and quality of wheat plants grown in a sandy soil.* Ann. Agric. Sci., (Cairo), 49(2): 485-499.

Barakat R.M., Al.-Masri M.L. 2009. *Trichoderma harzianum in combination with sheep manure amendment enhances soil suppressiveness of Fusarium wilt of tomato.* Phytopathol. Mediterranea, 48(3): 385-395.

Bullock L.R., Barker K.R., Ristaino J.B. 2002. *Influences or organic and synthetic soil fertility amendments on nematode trophic groups and community dynamics under tomato.* Appl. Soil Ecol., 21: 233-250.

Cespedes-Leon, M.C., Stone A. G., Dick R. P. 2006. *Organic soil amendments: impacts on snap bean common root rot and soil quality.* Appl. Soil Ecol., 31:199-210.

Chernin L., Chet L. In: Burns R. G., Dick R. P. 2002. *Enzymes in the environment. Activity, ecology and applications*. Marcel Dekker Inc., New York, Basel.

Cooperband L. 2001. *Intermediate-term effects of building soil carbon on soil properties and crop production using paper-mill residues.* Proc. of the Wisconsin's Annual Potato Meeting, Madison, Wisconsin.

Cotxarrera L., Trillas-Gay M.I., Steinberg C., Alabouvette C. 2002. *Use of sewage sludge compost and Trichoderma asperellum isolates to suppress Fusarium wilt of tomato.* Soil Biol. Biochem., 34(4): 467-476.

Dhingra O. D., Sinclair J. B. 1995. *Basic plant pathology methods*, Appendix A, 345-394. Lewis Publishers. CRC Press. Boca Raton, FL, USA.

Dissanayake N., Hoy J. W. 1999. *Organic material soil amendment effects on root rot and sugarcane growth and characterization of the materials.* Plant Dis., 83: 1039-1046.

Górska E. B., Stępień W., Russel S. 2007. *Wpływ dodatku osadu ściekowego, kurzeńca i kompostu Dano na aktywność mikrobiologiczną gleby i plony buraka ćwikłowego [Effect of added sewage sludge, poultry manure and Dano compost on the soil microbial activity and edible beetroot yield].* Zesz. Probl. Post Nauk Rol., 520: 287-293. (in Polish)

Hoitink H. A. J., Boehm M. J. 1999. *Biocontrol within the context of soil microbial communities a substrate-dependent phenomenon.* Ann. Rev. Phytopathol., 37: 427-446.

Kundu P. K., Nandi B. 1985. *Control of Rhizoctonia disease of cauliflower by competitive inhibition of the pathogen using organic amendments in soil.* Plant Soil, 83: 357-362.

Lazarovitz G., Hill J., Patterson G., Conn K. L., Crump N. S. 2007. *Edaphic soil levels of mineral nutrients, pH, organic matter, and cationic exchange capacity in the geocaulosphere associated with potato common scab.* Phytopathology, 97(9): 1071-1082.

Lewis J. A., Lumsden R. D., Millner P. D., Keinath A. P. 1992. *Suppression of damping-off of peas and cotton in the field with composted sewage sludge.* Crop. Prot., 11: 260-266.

Mazzola M, Mullinix K. 2005. *Comparative field efficacy of management strategies containing Brassica napus seed meal or green manure for the control of apple replant disease.* Plant Dis., 89: 1207–1213.

Mills D. J., Hoffman C. B., Teasdale J. R. 2002. *Factors associated with foliar disease of staked fresh tomatoes grown under differing bed strategies.* Plant Dis., 86: 356-361.

Nelson E.B., Kuter G.A., Hoitink H.A.J. 1983. *Effects of fungal antagonists and compost age on suppression of rhizoctonia damping-off in container media amended with composted hardwood bark.* Phytopathology, 73: 1457-1462.

Pandey A.K., Gopinath K.A., Chattacharya P., Hooda K.S., Sushil S.N, Kundu S., Selvakumar G., Gupta H.S. 2006. *Effect of source and rate of organic manures on yield attributes. Pod yield and economics of organic garden pea (Pisum sativum subsp. hortense) in north west Himalaya.* Ind. J. Agric. Sci., 76(4): 230-234.

Papavizas G.G. 1985. *Trichoderma* and *Gliocladium. Biology, ecology and potential for biocontrol.* Ann. Rev. Phytopath., 23: 23-54.

Pratt R. G. 2008. *Fungal population levels in soils of commercial swine waste disposal sites and relationships to soil nutrient concentrations.* Appl. Soil Ecol., 38(3): 223-229.

Puget P. Chenu C., Balesdent J. 2000. *Dynamics of soil organic matter associated with particle-size fractions of water-stable aggregates.* Eur. J. Soil Sci., 51: 595-605.

Saraiva V.P., Araujo E., Araujo-Filho J.O.T., Bruno G.B., Bruno R.L.A., Coelho R.R.P. 2004. *Populations of three fungi in soils treated with different forms of cattle manure and sown with carrot.* Proc. of Interamerican Soc. Trop. Horticul., 47: 43-44.

Serra-Wittling C., Houot S., Alabouvette C. 1996. *Increased soil suppressiveness to Fusarium wilt of flax after addition of municipal solid waste compost.* Soil Biol. Biochem., 28: 1207-1214.

Sikora L. J., Stott D. E. 1996. *Soil organic carbon and nitrogen*. In: *Methods for assessing soil quality.* SSSA Special Publication 49, Madison, WI, 247-271.

Stone A. G., Vallad G. E., Cooperband L. R., Rotenberg D., Darby H. M., James R. V., Stevenson W. R., Goodman R. M. 2003. *The effect of organic amendments on soil borne and foliar diseases in field-grown snap bean and cucumber.* Plant Dis., 87: 1037-1042.

Trankner A. 1992. *Use of agricultural and municipal wastes to develop suppressiveness to plant pathogens*: 35-42. In: *Biological control of plants diseases*. Tjamos E.C., Papavizas G.C., Cook R.J.*,* eds. Plenum Press, New York.

Tsror /Lahkim/ L., Barak R., Sneh B. 2001. *Biological control of black scurf on potato under organic management.* Crop Protect., 20: 145-150.

Van Bruggen A. H. C., Semenov A. M. 2000. *In search of biological indicators for soil health and disease suppression.* Appl. Soil Ecol., 15: 13-24.

Weyman-Kaczmarkowa W., Wójcik-Wojtkowiak D., Politycka B. 2002. *Greenhouse medium enrichment with composted pig slurry; effect on the rooting of Pelargoniom peltatum Hort. Cuttings and development of rhizospere microflora*. Pol. J. Environ. Stud., 11: 67-70.

Zak R.D, Holmes W.E, White D.C, Peacock A.D, Tilman D. 2003. *Plant diversity, soil microbial communities and ecosystem function: Are there any links?* Ecology, 84: 2042-2050.

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ASSESSMENT OF THE QUALITY OF THE ENVIRONMENT IN THE VICINITY OF A PESTICIDE BURIAL SITE*

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Abstract

Biologically active substances of plant pesticides deposited on pesticide burial sites can be a source of toxic substances threatening underground and surface waters and consequently drinking water. Mercury usually makes up about 0.7% of the total waste content, copper - 4.3%, zinc – 4%, and chloroorganic compounds – 29.9%. The aim of the work was to evaluate the quality of the environment in the vicinity of a pesticide burial site in Podlasie, Poland. The study was carried out in September-November 2009. The burial site comprised three containers consisting of concrete circles insulated with roofing paper and cement. Samples for determinations were collected from the immediate surroundings of the pesticide burial site. Soil samples were also taken from three holes made to the depth of 0.2-0.4 m and situated 15 m away from the burial site depth and from two sites under the concrete well (0.5 m and 1.0 m). Moreover, water samples from two piezometers and samples of plants growing up to 30 m distance (pine needles, grasses, mushrooms, birch and alder leaves and twigs, cabbage, and maize) were collected as well. Copper, mercury and zinc were determined in samples of waters, soils and plants. The metal content in soils corresponded to the natural levels; the concentrations in plant samples indicated no accumulation and the water samples were not determined to contain elevated concentrations of the above metals. It has been proven that the concrete wells were hermetic and the environment around the pesticide burial site has not been polluted.

Key words: dump, metals, pesticide, water, soil, plant.

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OKREŚLENIE JAKOŚCI ŚRODOWISKA NATURALNEGO W POBLIŻU MOGILNIKA PESTYCYDOWEGO

Abstrakt

Biologicznie aktywne substancje pestycydów składowanych w mogilnikach mogą być źródłem substancji toksycznych migrujących do wód podziemnych, powierzchniowych, a w konsekwencji do wody pitnej. W przeciętnym mogilniku ilość rtęci wynosi 0,7% masy wszystkich odpadów, miedzi 4,3%, cynku 4%, zaś związków chloroorganicznych 29,9%. Praca przedstawia jakość środowiska otaczającego mogilnik pestycydowy na Podlasiu. Badania prowadzono w okresie wrzesień-listopad 2009 roku. Mogilnik zbudowany jest z betonowych kręgów studziennych izolowanych lepikiem. Próbki do badań pobierano w bezpośrednim sąsiedztwie mogilnika. Próbki gleby pobierano z głębokości 0,2-0,4 m w odległości do 15 m od mogilnika, próbki gleby spod studni z głębokości 0,5 oraz 1,0 m pod dnem. Próbki wody pobierano z dwóch piezometrów, zaś roślin w promieniu 30 m od mogilnika (igły sosny, trawy, grzyby, dynie, brokuły). W próbkach wody, gleby i roślin oznaczono miedź, cynk i rtęć. Gleby cechują się naturalną zawartością tych pierwiastków, stężenia metali w próbkach roślinnych można określić jako akumulację małą, a rośliny jako nie zanieczyszczone, nie zanotowano także zwiększonej ilości pierwiastków śladowych w wodach podziemnych. Może to świadczyć, że ten mogilnik jest szczelny, a środowisko wokół niego nie jest zanieczyszczone.

Słowa kluczowe: mogilnik, metale ciężkie, pestycydy, woda, gleba, rośliny

INTRODUCTION

Dumps leaking to soil and water have been one of the most difficult problems to solve for years; they make an extreme hazard for people as well as the natural environment. Pesticides past the expiry date or unused, often containing heavy metals compounds, become very dangerous waste that, when inappropriately stored, penetrate the natural environment uncontrollably, which poses a serious threat to all life forms (BAGIŃSKA at al. 2008, BIZIUK 2001, CONESA et al. 2007). The Ministry of the Natural Environment Protection estimates that the total weight of pesticide waste in Poland could be as high as 60 000 tons. Recent supervision of the technical condition of p[esticide burial sites has revealed that the situation is the worst in eastern Poland. In total, there are 10 pesticide burial sites (including 5 liquidated ones) and 13 storage sites with pesticide waste in the Province of Białystok (IGNATOWICZ 2009). Previously binding design and construction procedures did not take into account effects of long-term exploitation of pesticide burial sites. Pesticide waste stored at former state farms is the most severe threat because of the disastrous technical condition of those burial stores. Besides, many burial sites are unsealed ground dumps. They are a source of toxins and poisons emitted into the natural environment: soil, water and air. The ground- and surface water, especially underground water reservoirs near dumps, is contaminated (IGNATOWICZ 2007).

On an average dumping site, mercury makes 0.7% of total waste, copper 4.3%, zinc 4%, and chloroorganic compounds 29.9% (Biziuk 2001, Ignatowicz 2009). In the past, heavy metals were also a component of pesticides. Those compounds, as toxic ones by definition, are cancerogenic, teratogenic, embryotoxic and mutagenic. They are detected in all elements of the natural environment: atmosphere, hydrosphere, geosphere, flora, fauna, and even in human bodies. Water, soil and air near dumps are very rarely monitored, hence the present study comprised analyses of water, soil and plants samples collected near pesticide burial sites in order to find out whether pesticides past the expiry date and stored in leaky and corroded concrete containers could migrate into the environment. The paper presents results of analyses of environmental samples collected from near operating, unsealed and corroded concrete burials localized in Podlasi, performed in order to assess the risk of migration of heavy metals, which are pesticide components. It is an important issue because pesticides and some metals (Cd, Pb, Hg, Ni), as stated by the European Parliament Directive 2008/105/WE on environmental quality norms for water policies, are among priority substances. The aim of the research was to assess the quality of the environment in the vicinity of pesticide burial sites.

MATERIAL AND METHODS

The study was carried out from September to November 2009 near an operating pesticide burial site, which comprised three containers consisting of concrete circles insulated with roofing paper and cement (Figure 1). The estimated amount of stored waste (according to an inventory made in 2009 by the Regional Directorate for the Environmental Protection in Białystok) was 3.39 Mg. The burials were set on varied and medium-grain sands, which are highly permeable (the filtration coefficient $k = 10^{-7}$ ms^{-1}). Any of the stored hazardous substance can easily migrate from leaky containers along with rainfall water. The burial is built at the level of about 1.6-3.0 m, while the groundwater lies 3.0-5.0 m deep. The burial site lies close to an arable cultivated field, 20 m away from crop plantations (maize, carrot, broccoli, cabbage) and 100 m from a fruit orchard.

Samples for determinations were collected from the immediate surroundings of the pesticide burial site (Figure 2). Soil samples from the depth of 0.2-0.4 m were gathered by making three holes (S8, S9, S10) at a 15-meter distance; additionally two samples under the concrete well (0.5 m and 1.0 m) were taken (St. 3). Moreover, water samples from two piezometers (S8, S9) and samples of plants growing up to 30 m away from the burial site (pine needles, grasses, mushrooms, birch and alder leaves and twigs, cabbage, and maize) were collected.

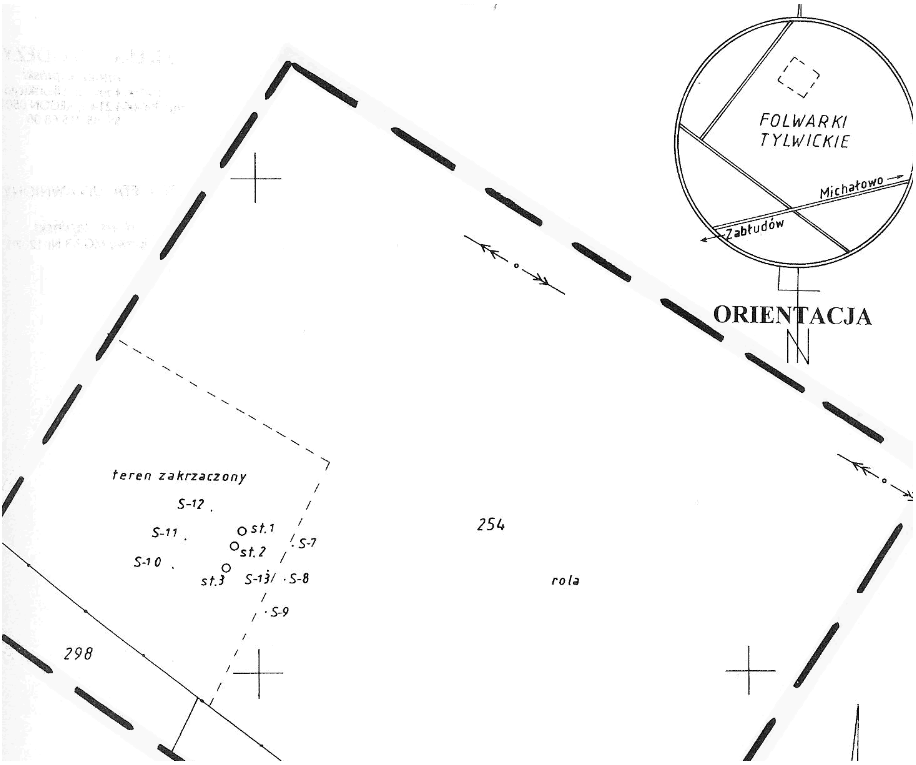

Fig. 1. Location of the pesticide burial site and the sampling points in Folwarki Tylwickie. st 1, st 2, st 3 – three containers; S-7 - S-13 – sampling point

The analyzed metals included copper, mercury and zinc. Soil was mineralized using a microwave system Mars 5 according to the EPA 3015 and EPA 3051 procedures. Determinations of copper and zinc were made with the ICP-AES technique, while mercury was analyzed with the CV-AAS technique in an AMA-254 analyzer (SIEPAK 1995, SIEPAK et al. 2008).

Fig. 2. A view of the pesticide burial site in Folwarki Tylwickie

RESULTS AND DISCUSSION

The content of the heavy metals determined in the soil samples is presented in Table 1. The values ranged from 22.76 to 41.76 mg Cu kg^{-1} (mean 31.42), 23.94 to 39.53 mg Zn kg^{-1} (mean 31.59), and less than 0.0005 to 0.025 mg Hg kg^{-1} (0.009, on average). The content of available and extractable trace elements in soils did not exceed permissible values set in the Ordinance of the Minister for the Environment of 9.09.2002, and the soils were classified as group B soils. With respect to the Ordinance of the Minister for the Agriculture and Rural Development of 21.03.2002, the analyzed soils were light ones, i.e. containing up to 20% of the finest fraction. Comparing the determined concentrations of the heavy metals with the limit values given by KABATA-PENDIAS (1999), it can be concluded that the soils near the burial site did not contain elevated levels of these contaminants. Their amounts were described as natural for group A soils with the zero contamination level. These soils can be used for agricultural production. These findings may be explained by the fact that the examined pesticide burial site lies on light sandy soil, low in sorption capacity. Ion such soils, trace elements are more easily available. However, in general, most of trace elements are eluted from such soils and penetrate to the ground- and surface water. The determined concentrations of copper were several-fold higher than the geochemical background. Therefore, copper concentrations were elevated in relation to the average levels present in soils. This was probably due to some leakage of pesticides containing copper. Copper forms hardly mobile bonds with organic matter, sulfates or carbonates in soil (Wiater, Łukowski 2010), and therefore it is accumulated in soil layers beneath the burial site, where they can be transported with groundwater. The presence of heavy metals around the pesticide burial site has been confirmed. Out of all the biosphere elements, soils are not only the main medium where many chemicals accumulate, but they also act as some kind of a protective filter for both components migrating to water and for volatile elements (Kabata-Pendias 1999, Witczak, Adamczyk 1995). Artificial fertilizers and some plant protection chemicals are an important source of trace elements in soils, especially in their topmost layers. Long-term application and storage of pesticides can lead to significant concentrations of As, Cu, Hg, and Pb in soils (Kabata-Pendias 1999, Wiater, Łukowski 2009).

It has been found that the Zn and Hg content was higher directly under the well chamber and decreased with the soil sampling depth (Table 1). This can be attributed to constant leakage of the metals from the unsealed well. Considering the fact that zinc is one of the most mobile metals, it is probably further transported in light soils alongside the groundwater runoff.

Table 1

Content of Cu, Zn ad Hg in soil

Sample	Soil around burial site			Soil under burial site		NDS for group B soil*
Depth (m)	0.2	0.3	0.4	0.5	1.0	
Cu (mg kg^{-1})	26.55	31.61	35.40	22.76	41.76	100
Zn (mg kg^{-1})	23.94	39.53	25.85	38.58	30.03	350
Hg (mg kg^{-1})	<0.005	<0.005	<0.005	0.025	<0.005	3

*The Ordinance of the Minister for the Environment of 9.09.2002 classifies the examined soil as group B soils.

The concentrations of the metals determined in the water samples are presented in Table 2. These values were below the detection limit for mercury; for copper, they reached 0.003 mg dm^{-3} for both piezometers (the geochemical background 0.001 mg dm^{-3}), while for zinc they ranged from 0.013 to 0.023 mg dm^{-3} (the geochemical background 0.001 mg dm^{-3}). The concentrations of the heavy metals in samples of underground water collected from the piezometers did not attain increased values. The content of Cu, Hg and Zn did not exceed the permissible levels for potable water as set in the Ordinance of the Minister for Health of 29.03.2007 on potable water quality (Journal of Law, 2006, no 123, item 858). The values were lower than those obtained by the author in a study on natural water contamination around a pesticide burial site (Ignatowicz 2010). However, the zinc con-

Table 2

Concentration of Cu. Zn and Hg in piezometer water

Parameters	Piezometr		NDS	
	1	2	groundwater (I class)*	drinking water**
pH	7.41	7.44	6.5-9.5	6.5-9.5
Conductivity (µS cm^{-1})	384	358	700	2500
Cu (mg dm^{-3})	0.003	0.003	0.01	2
Zn (mg dm^{-3})	0.023	0.013	0.05	-
Hg (mg dm^{-3})	<0.00005	<0.00005	0.001	0.001

* The Ordinance of the Minister for the Environment of 23.07.2008 on groundwater quality.
** The Ordinance of the Minister for Health of 29.03.2007 on drinking water quality.

centration in spring 2009 (0.12 mg dm^{-3} in a dug and 1.43 mg dm^{-3} in a drilled well) sugegsts that the analyzed water requires special protection (Zn>0.2 mg dm^{-3}) and treatment before supplied as potable water (Zn>0.8 mg dm^{-3}).

The concentrations of the metals determined in the plant samples are presented in Table 3. All the metals were detected in the collected plant samples (max Cu 0.927, Zn 2.288, Hg 0.02 mg kg^{-1}). According to the Ordinance of the Minister for Health of 27.12.2000 (Journal of Law, 2001, no 9, item 72) and the limit values given by KABATA-PENDIAS (1999), the recorded concentrations can be considered as low accumulation and the plants as not contaminated. Plants growing on metal-contaminated soils develop adaptation or protection mechanisms. On strongly polluted soils, those characteristics weaken and concentrations of metals increase proportionally to their occurrence in the subsoil (TERELAK et al. 2000). Beside the phytotoxic action, excessive amounts of trace elements can pollute the whole feeding chain. The issue requires special attention when elements hazardous to animals and people are involved. In view of the Ordinance of the Minister for Health

Table 3

Content of Cu, Zn ad Hg in plants

Metal	Max content	NDS in food	
		*	**
Cu (mg kg^{-1} d. m.)	0.927	<20.0	-
Zn (mg kg^{-1} d. m.)	2.288	<50.0	-
Hg (mg kg^{-1} d. m.)	0.02	-	0.01-0.05

* The Ordinance of the Minister for Health of 27.12.2000
** The Ordinance of the Minister for Health of 13.01.2003on maximum levels of chemical and biological contaminants allowed in food

of 13.01.2003 on the maximum levels of chemical and biological contaminants allowed in food from, the collected edible plant samples (cabbage, maize and mushrooms) contained excessive levels of mercury, whose concentration reached 0.02 mg Hg kg^{-1}, whereas the permissible value is 0.01 mg Hg kg^{-1}.

Table 4 presents the coefficients of correlation between the analyzed metals in soil and plant samples. For the soil, the strongest dependencies were determined for Hg and Cu as well as Hg and Zn. Among the plant samples Cu and Zn were most strongly correlated.

Table 4

Pearson's correlation coefficients between the metals Cu, Zn and Hg in soil and plant samples (correlation significant at $p \leq 0.05$)

Metal	Soil		Plants	
	Zn	Hg	Zn	Hg
Cu	-0.24	-0.63	0.62	-0.38
Zn		0.55		-0.25

CONCLUSIONS

The determined level of pesticide contamination has demonstrated that the concrete wells did not leak. The determined concentrations of the heavy metals in soil, water and plants proved no pollution of cooper, zinc and mercury originating from the pesticide waste. The soil was characterized by a natural content of these elements and can be used for all agricultural and horticultural crop cultivation. Particular concentrations of the metals in plant samples can be considered as low accumulation and plants were not contaminated. Likewise, the groundwater was not detected to contain higher amounts of the analyzed trace elements.

REFERENCES

Babinska I., Szarek J., Binkowski L., Skibniewska K., Wojtacka J., Markiewicz E., Felsmann M.Z., Zakrzewska M., Gesek M., Dublan K. 2008. *Grey herons (Ardea cinera L.) as a tool for monitoring the environment for metal concentrations in the vicinity of a pesticide tomb in the Ilawskie lake district.* Fres. Environ. Bull., 14(5): 357-362.

Ignatowicz K. 2007. *Evaluation of pesticide remains and heavy metals concentrations near burial grounds.* Pol. J. Environ. Stud., 16(2): 234-240.

Ignatowicz K. 2009. *Kompleksowe badania nad zastosowaniem sorpcji do ograniczenia emisji pestycydów z mogilników [Complex studies on the applicability of sorption for reduction of emission of pesticides from pesticide burial sites].* Oficyna Wydawnicza Politechniki Białostockiej, Białystok. (in Polish)

IGNATOWICZ K. 2010. *Zawartość wybranych metali w środowisku naturalnym w okolicy mogilnika [Content of some metals in the natural environment near a pesticide burial site]*. Ekol. Tech., 1(104): 54-60. (in Polish)

KABATA-PENDIAS A. 2010. *Trace elements in soils and plant.* CRC Press I Llc.

SIEPAK J., KOWALSKI A., ASTEL A., BARAŃSKI A., GWOREK B. 2008. *Mercury mobility and bioavailability in soil from contaminated area.* Environ. Geol., 55 (5): 1075-1087.

Influence of the pesticide dump on the environment. Ed. SKIBNIEWSKA K.A. 2010. Faculty of Environmental Management and Agriculture University of Warmia and Mazury in Olsztyn.

TERELAK H., MOTOWICKA-TERELAK T., STUCZYŃSKI T, PIETRUCH C. 2000. *Trace elements (Cd, Cu, Ni, Pb, Zn) in agricultural soils of Poland*. Biblioteka Monitoringu Środowiska. Warszawa.

WIATER J. ŁUKOWSKI A. 2010. *Mobility of heavy metals in agricultural soils of Podlasie region*. Fresenius Environ. Bull. 19(4): 547-552.

WIATER J. ŁUKOWSKI A. 2009. *The influence of mineral fertilization on heavy metal fraction contents in soil.* Part II. C*opper and nickel*. Pol. J. Environ. Stud., 18(4): 645-650.

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CHANGES IN THE CHEMICAL COMPOSITION OF THE RHIZOSPHERE OF TOMATO GROWN ON INERT SUBSTRATES IN A PROLONGED CYCLE

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Abstract

The aim of this study, conducted in 2005-2007, was to determine changes in the chemical composition of extracts from the rhizosphere of tomatoes and of drainage water in tomato culture set up on rockwool, perlite and expanded clay and nourished with one of the two nutrient solutions containing different concentrations of macronutrients (EC I: 2.4 mS cm^{-1} and EC II: 3.6 mS cm^{-1}). Perlite and extended clay were placed in foil sleeves, whose shape and volume corresponded to the weight of rockwool. The tomatoes were grown with a dripping fertilization system and a closed nutrient solution circulation system, without recirculation, for watering. The solution supply frequency, controlled by a soltimer, depended on the intensity of solar radiation. The concentration and proportions of macronutrients in the nutrient solutions were adjusted to the requirements of particular developmental phases of the plants, in accordance with the current recommendations. The plants were grown in a prolonged cycle for 22 clusters (from the beginning of February to mid-October). Extracts from the rhizosphere and drainage water for analyses were sampled at a set time of the day, every four weeks, since the plants were placed on the mats. The analysis of the results revealed significantly more nitrate ions, phosphorus, potassium, calcium, magnesium, sulphates and sodium in extracts from the rhizosphere and in drainage waters sampled from treatments fertilized with the concentrated solution (EC II), compared to the basic solution. In the drainage water from treatments fertilized with a solution of the basic macronutrient composition (EC I), the increase of ion concentrations appeared in the following order: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > S\text{-}SO_4 > K > N\text{-}NO_3 > Mg$, whereas in the drainage water flowing from the treatments fertilized with the solution containing 25% more macronutrients (EC II), the ion concentration range was as follows: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > N\text{-}NO_3 > S\text{-}SO_4 > K > Mg$. In the present study, the sodium content in drainage water was depressed compared to the nutrient solution dosed under plants with either of the two liquid feeds.

Key words: rockwool, perlite, extended clay, EC of nutrient solution, rhisosphere, drainage waters.

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ZMIANY SKŁADU CHEMICZNEGO ŚRODOWISKA KORZENIOWEGO POMIDORA UPRAWIANEGO W PODŁOŻACH INERTNYCH W CYKLU WYDŁUŻONYM

Abstrakt

Celem badań przeprowadzonych w latach 2005-2007 było określenie zmian składu chemicznego wyciągów ze środowiska korzeniowego oraz wód drenarskich w uprawie pomidora w wełnie mineralnej, perlicie i keramzycie z zastosowaniem dwu pożywek o zróżnicowanej koncentracji makroskładników (EC I: 2.4 mS cm^{-1} oraz EC II: 3.6 mS cm^{-1}). Perlit i keramzyt umieszczono w rękawach foliowych, formując kształt i ustalając objętość odpowiadającą macie wełny mineralnej. W uprawie wykorzystano kroplowy system nawożenia i nawadniania z zamkniętym obiegiem pożywki, bez recyrkulacji. Częstotliwość dostarczania pożywki, sterowana „soltimerem", była uzależniona od natężenia promieniowania słonecznego. Koncentracja oraz proporcje makroskładników w pożywce były różnicowane względem wymagań poszczególnych faz rozwojowych roślin zgodnie z aktualnymi zaleceniami. Rośliny uprawiano w cyklu wydłużonym na 22 grona (od początku lutego do połowy października). Wyciągi ze środowiska korzeniowego oraz wody drenarskie do analiz pobierano o ustalonej porze dnia co 4 tygodnie, począwszy od ustawienia roślin na matach. Analiza wyników wykazała istotnie więcej jonów azotanowych, fosforu, potasu, wapnia, magnezu, siarczanów i sodu w wyciągach ze środowiska korzeniowego i w wodach drenarskich pobranych z obiektów nawożonych pożywką zatężoną (EC II), w porównaniu z pożywką podstawową. W wodach drenarskich z obiektów nawożonych pożywką o podstawowym składzie makroelementów (EC I) stwierdzono wzrost zatężenia jonów w kolejności: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > S\text{-}SO_4 > K > N\text{-}NO_3 > Mg$, natomiast w wodach drenarskich wypływających z obiektów nawożonych pożywką zawierającą 25% więcej makroelementów (EC II) szereg zatężenia jonów był następujący: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > N\text{-}NO_3 > S\text{-}SO_4 > K > Mg$. W badaniach wykazano zmniejszenie zawartości sodu w wodach drenarskich w porównaniu z roztworem pokarmowym dozowanym pod rośliny z wykorzystaniem obu rodzajów pożywki.

Słowa kluczowe: wełna mineralna, perlit, keramzyt, EC pożywki, środowisko korzeniowe, wody drenarskie.

INTRODUCTION

Growing plants on inert substrates with a precise fertilization and watering system is gaining in popularity as it ensures high and good quality fruit yield (JAROSZ, DZIDA 2005, GAJC-WOLSKA et al. 2008). According to many authors (BREŚ, RUPRIK 2006, KOMOSA, KLEIBER 2007), systems allowing for recirculation of liquid solution dosed under plants are a necessity created by ecological and economical reasons. Implementation of nutrient solution recirculation, however, requires the knowledge of changes in nutrient concentrations in the plant rhizosphere and in drainage waters, compared to the solution dosed under plants (KLEIBER, KOMOSA 2008). The rhizosphere as well as in drainage water typically contain high concentrations of nutrients, a result of an increased water uptake and selective ion uptake by plants. According to DYŚKO and KOWALCZYK (2005), changes in the rhizosphere's chemical composition are also significantly affected by a developing root system and interactions between particular nutrients. Modifications in the composition of the rhizosphere and drainage water, however, depend on the substratum, crop species and even on a cultivation system.

When growing tomatoes on inert substrates, the general ion concentration (EC) in a nutrient solution is frequently elevated, which improves the taste and certain biological value parameters of fruit (Grava et al. 2001, Hao, Papadopoulos 2004). However, this solution may lead to excessive concentrations of certain ions in the rhizosphere, which disturbs the uptake and distribution of ions in plants (Grava et al. 2001).

The objective of this study has been to determine changes in the chemical composition of the rhizosphere and drainage water in a tomato cv. Cunero F_1 culture, depending on growing substrate (rockwool, perlite, extended clay) and two nutrient solutions with different concentrations of macronutrients.

MATERIAL AND METHODS

The study were conducted 2005-2007, in a greenhouse of the Department of Soil Cultivation and Fertilization of Horticultural Plants, University of Life Sciences in Lublin. Tomato plants of the cultivar Cunero F_1 were grown on rockwool (Grodan), perlite (Agroperlit) and extended clay (Optiroc-Gniew). Perlite and extended clay were placed in foil sleeves, with their shape and volume corresponding to the weight of rockwool. The tomato culture was conducted with a dripping fertilization and watering system with a closed solution circuit but no recirculation. Two types of nutrient solution were applied:

a) basic solution (I) with EC 2.4 mS cm^{-1}, containing on average (in mg dm^{-3}): N-NH_4 – 17.0; N-NO_3 – 188; P-PO_4 – 45; K – 280; Ca – 205; Mg – 75; S-SO_4 – 140; Na – 14.7; Cl – 12.3 ; Fe – 1.25; Mn – 0,55; B – 0.30 Cu – 0.05; Zn – 0,30; Mo – 0.03 and pH_{H_2O} – 5,60;

b) concentrated solution (II) by EC 3.6 mS cm^{-1} containing 25% more macronutrients, of the average composition (in mg dm^{-3}): N-NH_4 – 21.2; N-NO_3 – 235; P-PO_4 – 56.5; K – 350; Ca – 256; Mg – 94; S-SO_4 – 185; Na – 26; Cl – 18.5; Fe – 1.25; Mn – 0.55; B – 0.30; Cu – 0.05; Zn – 0.30; Mo – 0.03 and pH_{H_2O} – 5.65.

The concentration and proportions of macronutrients in the nutrient solutions were adjusted to the requirements of particular developmental phases of plants, in accordance with the current recommendations (Adamicki et al. 2005). The solutions were prepared taking the following chemical composition of water into account (in mg dm^{-3}): N-NH_4 – 0.02; N-NO_3 – 5.0; P-PO_4 – 4.0; K – 1.4; Ca – 121; Mg –13.8; S-SO_4 – 32.0; Cl – 9.5; Na – 2.7; Fe – 0.24; Mn – 0,026; Cu – 0.001; Zn – 0.038; pH_{H_2O} – 7.44, EC – 0.71 mS cm^{-1}. The daily outflow of the solution, depending on the developmental phase of plants ranged from 1.8 to 4.2 dm^3 $plant^{-1}$. The frequency of solution supply, controlled by a soltimer, depended on the intensity of solar radiation. A two-factorial experiment was established in a completely randomized design, with seven replications. Each replication was a culture slab, on which two plants grew. The plants were placed on the substrates in the first decade of February (04.02.2005; 07.02.2006; 09.02.2007). The cultivation was conducted in a prolonged cycle (22 clusters), at the plant density of 2.3 plants m^{-2}, until mid-October (20.10.2005; 17.10.2006; 12.10.2007). Plant protection and other treatments were performed in accordance with the recommendations (ADAMICKI et al. 2005).

Extracts from the rhizosphere and drainage water for analyses were sampled at a set time of the day, every four weeks, since the plants started to grow on the mats. Extracts from the cultivation mats were taken with a syringe, mid-way between the plants and from central part of the mat's height. Each time, the following determinations were completed in the collected samples: ammonium and nitrate nitrogen with Bremner's method (as modified by Starck), phosphorus by colorimetry with ammonium vanadomolybdate (Thermo, Evolution 300), potassium, calcium, magnesium and sodium with the ASA method (Perkin-Elmer, Analyst 300), sulphates by nephelometry with barium chloride, and electric conductivity (EC) by conductometry (NOWOSIELSKI 1988).

Statistical elaboration of the results was performed with the variance analysis method on mean values, applying Tukey's test for assessing differences at the significance level of α=0.05. The results are average values for all the dates of analyses from the three years of the experiment.

RESULTS AND DISCUSSION

A closed nutrient solution circuit system with recirculation saves significant amounts of water and mineral fertilizers (VAN OS 2001). It also limits the pollution of soil and groundwater with biogenic elements (KOMOSA, KLEIBER 2007). However, re-using a nutrient solution flowing out in the form of drainage water requires purification, disinfection and regulation of the concentrations of particular nutrients. Although there are many successful methods for disinfecting a nutrient solution before its reintroduction into cultivation, it is still necessary to know exactly the ranges of an increase or a decrease in the concentrations of particular elements in drainage water depending on a crop species, substrate and a cultivation technology (VAN OS 2001, KOMOSA, KLEIBER 2007, KLEIBER, KOMOSA 2008).

The statistical analysis of our results revealed significant changes in the concentrations of elements in the rhizosphere and in drainage water, compared to those in the supplied nutrient solutions, depending on both of the examined factors (Table 1). The highest increase in the ion concentrations in drainage water flowing out of the mats was reported for ammonium cati-

Table 1

Nutrient content (mg dm^{-3}) and conductivity (mS cm^{-1}) in the rhizosphere and drainage water depending on the type of substrate and concentration of macronutrients in the nutrient solution (average of all analysis from 2005-2007)

Element/ /compound	Nutrient solution	Sampling source				Mean
		rockwool	perlite	expanded clay	drainage water	
N-NH$_4$	EC I	27.78*a*	24.94*a*	38.83*a*	33.38*a*	31.24*a*
	EC II	30.89*a*	31.06*a*	36.61*a*	47.67*a*	36.55*a*
	Mean	29.33*ab*	28.00*a*	37.72*ab*	40.53*b*	
N-NO$_3$	EC I	268.6*a*	268.8*a*	250.2*a*	261.6*a*	262.3*a*
	EC II	322.1*a*	308.2*a*	305.5*a*	295.8*a*	307.9*b*
	Mean	295.4*a*	288.5*a*	277.9*a*	278.7*a*	
P-PO$_4$	EC I	79.72*a*	82.89*a*	70.94*a*	79.78*a*	78.33*a*
	EC II	96.33*a*	94.28*a*	81.83*a*	86.67*a*	89.78*b*
	Mean	88.03*b*	88.58*b*	76.39*a*	83.22*ab*	
K	EC I	381.6*a*	380.6*a*	381.7*a*	390.5*a*	383.5*a*
	EC II	477.3*a*	473.6*a*	459.0*a*	431.8*a*	460.4*b*
	Mean	429.5*a*	427.1*a*	420.2*a*	411.2*a*	
Ca	EC I	318.9*a*	316.9*a*	313.7*a*	296.2*a*	311.4*a*
	EC II	385.9*a*	379.2*a*	409.5*a*	354.8*a*	382.3*b*
	Mean	352.4*a*	348.1*a*	361.6*a*	325.5*a*	
Mg	EC I	92.41*a*	91.12*a*	91.00*a*	92.82*a*	91.84*a*
	EC II	106.1*a*	107.5*a*	116.0*a*	105.8a	108.8*b*
	Mean	99.23*a*	99.29*a*	103.5*a*	99.32*a*	
S-SO$_4$	EC I	185.9*a*	195.4*a*	191.4*a*	199.5*a*	193.1*a*
	EC II	233.2*a*	238.6*a*	230.3*a*	232.8*a*	233.7*b*
	Mean	209.6*a*	217.3*a*	210.9*a*	216.2*a*	
Na	EC I	18.67*a*	18.60*a*	17.58*a*	13.50*a*	17.10*a*
	EC II	25.33*a*	25.75*a*	20.00*a*	18.41*a*	22.37*b*
	Mean	22.00*b*	22.21*b*	18.79*ab*	15.95*a*	
Conductivity	EC I	3.179*a*	3.312*a*	3.330*a*	3.131*a*	3.239*a*
	EC II	3.713*a*	3.789*a*	3.707*a*	3.617*a*	3.706*b*
	Mean	3.446*a*	3.550*a*	3.520*a*	3.374*a*	

Values marked with the same letter are not differ significantly at α=0.05, according to Tukey's test.

ons (Table 2). This increase, compared to the nutrient solution supplied to plants, was on average + 96.41% for the basic solution (EC I) and +124.9% for the solution with an increased content of macronutrients (EC II). Contrary results were obtained by Komosa et al. (2010), who demonstrated a decrease in ammonium nitrogen from 11.7 to 26.6% in the rhizosphere of tomato grown on rockwool and fiber wood. Irrespective of the type of the applied solution, the content of N-NH_4 in drainage water (40.53 mg dm^{-3}) was significantly higher than the concentration of these ions in the rhizosphere of tomato grown on perlite (28.00 mg dm^{-3}). Many articles emphasize that the concentration of ammonium cations in tomato rhizosphere should not exceed 10% of the total amount of mineral nitrogen, as an excess of NH_4^+ may inhibit the uptake of calcium and magnesium (Ho et al.

Table 2

Percentage change (increase or decrease) in the composition of the extract from the rhizosphere and drainage water compared to a nutrient solution from a dripper (average of all analysis from 2005-2007)

Element/ /compound	Nutrient solution	Sampling source			
		rockwool	perlite	expanded clay	drainage water
N-NH_4	EC I	+63.41	+46.70	+128.4	+96.41
	EC II	+45.71	+46.51	+72.69	+124.9
N-NO_3	EC I	+42.87	+42.98	+33.08	+39.15
	EC II	+37.06	+31.15	+30.00	+25.87
P-PO_4	EC I	+77.15	+84.2	+57.64	+77.29
	EC II	+70.49	+66.87	+44.83	+53.40
K	EC I	+36.28	+35.93	+36.25	+39.46
	EC II	+36.37	+35.31	+31.14	+23.37
Ca	EC I	+55.56	+54.58	+53.02	+43.02
	EC II	+50.74	+48.12	+59.96	+38.28
Mg	EC I	+23.21	+21.49	+21.33	+23.76
	EC II	+12.87	+14.36	+23.40	+12.55
S-SO_4	EC I	+32.78	+39.57	+36.71	+42.50
	EC II	+26.05	+28.97	+24.49	+25.83
Na	EC I	+27.01	+26.53	+19.59	- 8.160
	EC II	-3.321	-1.72	-23.66	-29.69
EC	EC I	+24.50	+37.96	+38.92	+30.46
	EC II	+3.139	+5.250	+2.972	+0.472

Values marked with the same letter are not differ significantly at α=0.05, according to Tukey's test.

1999). While analyzing the composition of extracts from the rhizosphere in the examined treatments, it was noticed that proper ratios between these ammonium cations and mineral nitrogen became unbalanced when growing tomato on extended clay.

In the present experiment, no significant differences were found in the concentration of nitrate ions in the rhizosphere of tomato growing on the examined substrates and in drainage water flowing out of the mats. Irrespective of a sampling site, significantly more N-NO_3 (307.9 mg dm^{-3}) was reported in treatments fertilized with solution containing 25% more macroelements (EC II). The increased concentration of nitrates in drainage water compared to the nutrient solution dosed under plants ranged from 25.87 to 39.15% (Table 2). An event of nitrate ion concentration rise in plant rhizosphere and drainage water compared to a nutrient solution has been reported in other studies (Dyśko and Kowalczyk 2005, Komosa et al. 2009)

The analysis of extracts from the rhizosphere of tomato growing on extended clay revealed significantly less phosphorus (76.39 mg dm^{-3}) compared to the remaining substrates (Table 1). Dyśko at al. (2008) demonstrated that the content of phosphorus available to plants is closely related to the reaction of the rhizosphere. In their study, an increase in the pH in the dosed nutritional solution was followed by a higher reaction in the rhizosphere reaction, which in turn was accompanied by a significant decrease in the content of plant-available phosphorus. As it is well known, extended clay granules are characterized by high primary reaction, which causes alkalization of the rhizosphere of plants growing on this substrate in the initial weeks of cultivation. This phenomenon, also observed in the authors' own research, might have affected the results. Besides, Meinken (1997) points to possible temporary accumulation of certain nutrients, including phosphate ions, inside extended clay granules, which an considerably modify the composition of the rhizosphere.

In this experiment, significantly more phosphorus was found in extracts and drainage water from treatments fertilized with the solution containing a higher concentration of macroelements. Compared to the liquid fed through a dripper, an increase in the phosphate ion concentration in drainage water was 77.29% for the basic solution (EC I) and 53.40% for the concentrated solution (EC II). Breś and Ruprik (2006), as well as Komosa et al. (2010) reported a decrease in the phosphate content in the rhizosphere and drainage water compared to the solution dosed under plants.

In the present tests, no significant differences were found in the concentrations of potassium, calcium and magnesium in the rhizosphere and drainage water of the tomato grown on the examined substrates. Significantly more of these elements (460.4 mg K dm^{-3}, 382.3 mg Ca dm^{-3} and 108.8 mg Mg dm^{-3}) were found after the application of the concentrated solution (EC II) compared to the basic one (EC I). The analysis of the results demonstrated distinctly higher concentrations of potassium, calcium and magnesium in drainage water flowing out of the cultivation mats compared to the liquid feed dosed through a dripper. Depending on the applied solution, the increase of potassium concentration ranged from 23.37% to 39.46%, calcium 38.28%-43.02% and magnesium 12.55%-23.76%. Similar results are presented by Komosa et al. (2009). A much higher concentration of these elements was reported by Breś, Ruprik (2006). In another study completed by Komosa et al. (2010), a decrease in magnesium was reported in the rhizosphere of tomato grown on rockwool and wood fiber, compared to the solution dosed through a dripper.

Interesting results showing changes in sodium concentration in the examined treatments are noteworthy. Most of the references claim that it is a ballast element, reaching the highest concentration in drainage water, which therefore should be diluted before eing re-introduced under plants (Dyśko, Kowalczyk 2005, Komosa, Kleiber 2007, Komosa et al. 2009, 2010). In the present study, a decrease in thesodium ion content was observed (from -8.160 to -29.69%) compared to the amount of this element supplied under plants in the form of a nutrient solution.

The analysis of the results obtained from the present experiment has demonstrated differences in the composition of drainage water depending on the applied nutrient solution. In the drainage water from the treatments fertilized with the solution of basic macronutrient composition (EC I), the following ion concentration range was found: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > S\text{-}SO_4 > K > N\text{-}NO_3 > Mg$. In the drainage water flowing out of the treatments fertilized with the solution containing 25% more macronutrients (EC II), the ion concentration range was the following: $N\text{-}NH_4 > P\text{-}PO_4 > Ca > N\text{-}NO_3 > S\text{-}SO_4 > K > Mg$. The ranges of ion concentrations in drainage water produced while growing tomato on inert substrates, quoted in the literature, are different (Komosa et al. 2009, 2010). Thus, the composition of drainage water depends on the concentration of nutrients in the initial solution, as well as on the quantity of ions selectively taken up by particular cultivars. These results prove that it is necessary to monitor the chemical composition of drainage water before its reintroduction under plants through a fertigation system which allows solution recirculation.

CONCLUSIONS

1. Significantly more ions of nitrates, phosphorus, potassium, calcium, magnesium, sulphates and sodium were found in extracts from the rhizosphere and in drainage water collected from the treatments fertilized with the concentrated solution (EC II).

2. In the drainage water from the treatments fertilized with the basic solution (EC I), the increase in ion concentrations appeared in the following order: N-NH_4 > P-PO_4 > Ca > S-SO_4 > K > N-NO_3 > Mg, whereas when the concentrated solution (EC II) was applied, it turned to be: N-NH_4 > P-PO_4 > Ca > N-NO_3 > S-SO_4 > K > Mg.

3. A decrease in the sodium concentration in drainage water was demonstrated compared to the nutrient solution dosed under plants with either of the two liquid feeds.

REFERENCES

Adamicki F., Dyśko J., Nawrocka B., Ślusarski C., Wysocka-Owczarek M. 2005. *Metodyka integrowanej produkcji pomidorów pod osłonami [Methodology of integrated undercover tomato production].* PIORIN, Warszawa. (in Polish)

Breś W., Ruprik B. 2006. *Uprawa drobnoowocowych odmian pomidora szklarniowego we włóknie kokosowym przy zróżnicowanym nawożeniu azotem i potasem.* Cz. II. *Zmiany składu chemicznego pożywek zachodzące w środowisku korzeniowym [Growing greenhouse cherry tomato on coconut fibre with differentiated nitrogen and potassium fertilization.* Part II. *Changes in chemical composition of nutrient solutions in root environment.]* Acta Agroph., 7(3): 539-548. (in Polish).

Dyśko J., Kowalczyk W. 2005. *Changes of macro- and micronutrients concentration in root medium and drainage water during tomato cultivation in rockwool.* Veget. Crops Res. Bull., 62: 97-112.

Dyśko J., Kaniszewski S., Kowalczyk W. 2008. *The effect of nutrient solution pH on phosphorus availability in soilless culture of tomato.* J. Elementol., 13(2): 189-198.

Gajc-Wolska J., Bujalski D., Chrzanowska A. 2008. *Effect of a substrate on yielding and quality of greenhouse cucumber fruit.* J. Elementol., 13(2): 205-210.

Grava A., MAtan E., Yhezkel Ch., Abitan A., Samuel D. Plaut Z. 2001. *Ion uptake and distribution in tomato plants grown in sand and irrigated brackish water.* Acta Hort., 554: 121-130.

Hao X, Papadopoulos A.P. 2004. *Effect of diurnal EC variations on fruit yield and quality of greenhouse tomatoes grown in rockwool.* Acta Hort., 633: 263-269.

Ho L.C., Hand D.J., Fussel M. 1999. *Improvement of tomato fruit quality by calcium nutrition.* Acta Hort., 481: 463-468.

Jarosz Z., Dzida K. 2005. *The effect of inert substrates on yielding and fruits mineral composition of tomato grown in greenhouse.* Ann. UMSC, EEE, 15: 59-64.

Kleiber T., Komosa A. 2008. *Differentiated of microelements contents in nutrient solution and drainage water in growing of anthurium (Anthurium cultorum Birdsey) in expanded clay.* Acta Sci. Pol., Hort. Cult., 7(1): 53-62.

Komosa A., Kleiber T. 2007. *Sód i chlorki w wodach drenarskich w uprawie anturium (Anthurium cultorum Schoot) w keramzycie. [Sodium and chlorides in drainage water in growing of anthurium (Anthurium cultorum Schoot) in expanded clay.]* Rocz. AR Pozn., CCCLXXXIII, Ogrodnictwo, 41: 63-68. (in Polish)

Komosa A., Kleiber T., Piróg J. 2010. *Contents of macro- and microelements in root environment of greenhouse tomato grown in rockwool and wood fiber depending on nitrogen levels in nutrient solutions.* Acta Sci. Pol., Hort. Cult., 9(3): 59-68.

Komosa A., Piróg J., Kleiber T. 2009. *Changes of macro- and micronutrients contents in the root environment of greenhouse tomato grown in fiber wood.* Veget. Crops Res. Bull., 70: 71:80.

MEINKEN E. 1997. *Accumulation of nutrients In expanded clay used for indoor plantings.* Acta Hort., 450: 321-327.

NOWOSIELSKI O. 1988. *Opracowywanie zaleceń nawozowych w ogrodnictwie [Elaboration of the fertilization recommendations in horticulture].* PWRiL, Warszawa. (in Polish)

VAN OS E.A. 2001. *New developments in recirculation systems and disinfection methods for greenhouse crop*. Hortic. Engin., 16 (2): 2-5.

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SORPTION COMPLEX OF SELECTED SOILS OF THE DRAWSKIE LAKELAND*

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Abstract

Magnesium, calcium, potassium and sodium occur in soil in various forms but for plant nutrition their exchangeable forms are the most important. Cations bonded in soil colloids constitute a specific reservoir of nutrients.

The aim of this research was to determine sorption properties and to evaluate the distribution of exchangeable cations in the profiles of soils of the Drawskie Lakeland. Samples were taken from 6 soil profiles formed from glacial till of the Baltic glaciation in the vicinity of Złocieniec and Czaplinek. In general, the sampled soils had the grain-size composition of loams. The reaction of most soil samples was acid. Exchangeable cations were extracted with the $BaCl_2$ solution according to PN-ISO 11260. The cation exchange capacity (CEC) ranged from 52.6 to 216.6 mmol(+) kg^{-1} of soil. The soils, despite acid reaction, were sorption-saturated. Alkaline cations were dominated by calcium, whose highest share in the sorption capacity was identified in the horizons of the parent material of all the examined soils. The lowest amounts of exchangeable calcium and magnesium were found in horizons Ap and Eet. The horizons rich in clay fraction contained higher contents of Ca^{2+} and Mg^{2+}, which was confirmed by significantly positive correlation. The acid reaction did not affect significantly either the content of exchangeable cations or their distribution in the soil profiles. The highest content of K^+ in arable-humus horizons of some of the soils can be related to potassium fertilisation and the weathering of minerals containing that metal. The highest content of magnesium and calcium cations in horizons Bg and the parent material of Gleysols point to the possibility of some overlapping of the top-down gleyic process features with *lessivage* features.

Key words: Luvisols and Gleysols, glacial till, exchangeable cations.

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KOMPLEKS SORPCYJNY WYBRANYCH GLEB POJEZIERZA DRAWSKIEGO

Abstrakt

Magnez, wapń, potas i sód występują w glebie w różnych formach, z których najważniejsze w aspekcie odżywiania roślin są ich formy wymienne. Zasorbowane w koloidach glebowych kationy stanowią swoisty rezerwuar składników pokarmowych.

Celem badań było określenie właściwości sorpcyjnych oraz ocena rozmieszczenia kationów wymiennych w profilach gleb Pojezierza Drawskiego. Próbki do badań pobrano z 6 profili gleb wytworzonych z gliny zwałowej zlodowacenia bałtyckiego z okolic Złocieńca i Czaplinka. Badane gleby charakteryzowały się na ogół uziarnieniem glin. Większość próbek glebowych miała odczyn kwaśny. Kationy wymienne ekstrahowano roztworem $BaCl_2$ zgodnie z normą PN-ISO 11260. Pojemność wymienna (CEC) wynosiła od 52,6 do 216,6 mmol(+) kg^{-1} gleby. Badane gleby pomimo kwaśnego odczynu były sorpcyjnie nasycone. Wśród kationów zasadowych dominował wapń, którego najwyższy udział w pojemności sorpcyjnej stwierdzono w poziomach skały macierzystej wszystkich badanych gleb. Najmniej wymiennego wapnia i magnezu stwierdzono w poziomach Ap i Eet. Poziomy zasobne w ił koloidalny zawierały wiecej Ca^{2+} i Mg^{2+}, co potwierdziła istotnie dodatnia korelacja. Kwaśny odczyn nie wpłynął w istotny sposób na zawartość kationów wymiennych oraz ich rozmieszczenie w profilach gleb. Najwyższą zawartość K^+ w poziomach orno-próchnicznych kilku gleb można wiązać z nawożeniem potasem oraz wietrzeniem minerałów zawierających ten metal. Najwyższe zawartości kationów magnezu i wapnia w poziomach Bg oraz stropie skały macierzystej gleb opadowo-glejowych wskazują na możliwość nakładania się cech procesu odgórnego oglejenia na cechy procesu *lessivage*.

Słowa kluczowe: gleby płowe i opadowo-glejowe, glina zwałowa, kationy wymienne.

INTRODUCTION

The chemical composition of soil is mostly determined by the origin and the mineral composition of parent material, the effect of which on soil properties decreases along with its development. As a result of the effect of different soil-formation processes in genetically-homogenous parent material, soils representing different soil types can be formed (TARGULIAN, KRASILNIKOV 2005). In arable soils, the differentiation of their physicochemical properties is strengthened by agrotechnical treatments (PATERSON, RICHTER 1986). The soil sorption properties connected with the ionic exchange between the soil solution and the sorption complex determine the plant uptake of nutrients or their leaching deep into the soil profile (HARTMANN et al. 1998). In soils poor in nutrients, the highest content of nutrients available to plants is usually observed in arable-humus horizons (JOBBÁGY, JACKSON 2001). The mineral soil sorption capacity depends on the grain size composition, the type of minerals, the humus content and on the fertilisation level (ASKEGAARD et al. 2005, ERSAHIN et al. 2006). The type of the fertilisation applied considerably affects the quantitative and qualitative composition of exchangeable cations in arable soils. In many cases, high nitrogen fertilisation doses result in a decrease in the saturation of the sorption complex with cations

Ca^{+2}, Mg^{+2}, Na^{+} (Panak et al. 1996). A decisive effect on the content of cations bonded in soil colloids is also attributed to oxydo-reducing conditions of soils. The dynamics of aerobic conditions transformations to the total anaerobiosis of the soil environment depends on the amount of precipitation and the infiltration process. The intensity of that process is also affected by the grain size composition, reaction and the content of organic matter, especially visible in Gleysols, which, beside Luvisols, have been covered by the present research. In Gleysols profiles, stagnating water generally covers the eluvial horizon and illuvial horizons, determining their reducing conditions, thus changing the availability of many nutrients, and the oxygen anaerobic states can trigger permanent changes in the chemical composition of the crops (Stępniewski, Przywara 1992).

The aim of the present research was to evaluate the sorption complex of Luvisols and Gleysols formed from glacial till of the Baltic glaciation.

MATERIAL AND METHODS

The soil was sampled from 6 soil profiles formed from glacial till in the vicinity of Złocieniec and Czaplinek in the Drawskie Lakeland (Figure 1). Profiles PD1, PD2, PD5 represented Luvisols, while PD3, PD4 and PD6 were qualified as Gleysols. All the analyses were performed in air-dry samples passed through a sieve with the mesh 2.0 mm in diameter. The grain size composition was determined with the Cassagrande erometric method modified by Prószyński; the exchangeable acidity – potentiometrically in the solution of 1 M KCl; the content of organic carbon – with Tiurin method: the hydrolytic acidity with Kappen method. Exchangeable cations were extracted with barium chloride solution, (ISO 11260), and their content was determined with an atomic absorption spectrometer (Philips PU 9100X). The results were statistically verified, using Statistica 8.0 software.

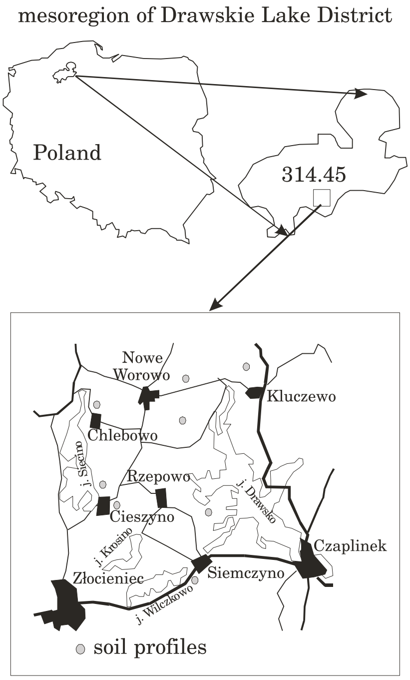

Fig. 1. A map showing the analyzed area and location of the soil profiles

RESULTS AND DISCUSSION

The Luvisols and Gleysols demonstrated the grain size composition of loams (PTG 2009), except for the parent material horizon (IIC) of soil PD5, which showed the grain-size-composition of medium sand (Table 1). A detailed analysis demonstrated very fine sandy loam and sandy loam in arable-humus horizons (Ap) as well as sandy clay loam and clay loam in the enrichment horizons. Total organic carbon (TOC) ranged from 8.2 to 11.9 g kg^{-1} in Ap horizons. As for the reaction, in most samples it was acidic. The pH values determined in 1 M KCl ranged from 3.8 to 5.3. The samples from the parent material formation of soil PD1 and the sample from horizon C of soil PD6 were neutral and alkaline in their reaction (Table 1). The alkaline reaction in those horizons was caused by the presence of calcium carbonate, whose content ranged from 7.5 to 9.5%. The hydrolytic acidity (Hh) ranged from 2.0 to 57.5 mmol(+) kg^{-1} (Table 2). The highest Hh values were observed in the arable-humus horizon, and in soil PD6 – in Bg horizon. The values of cation exchange capacity (CEC) of the soils ranged from 52.6 to 216.6 mmol(+) kg^{-1} of soil. The content of exchangeable magnesium cations ranged from 1.2 to 23.0 mmol(+) kg^{-1}. A slightly higher content of Mg^{2+} was identified in the soils formed from glacial till of the Krajeńskie Lakeland mesoregion (Kobierski, Pytlarz 2006). The parent material of those soils, however, showed a higher content of the clay fraction than the parent material of soils of the Drawskie Lakeland.

The examined soils, despite the acid reaction, must be considered as sorption-saturated ones. It was only in horizon Ap of soil PD3 that the degree of saturation of the sorption complex with alkaline cations (V) was below 50%. The highest share of alkaline cations was identified in the parent material horizons of all the soils. The base saturation was dominated by Ca^{2+}, the content of which was significantly positively correlated with the cation exchange capacity (Table 3). The highest share of calcium cations in CEC was observed in illuvial horizons and the roof of the parent material. The ratio of cations Ca^{+2}/Mg^{+2} was narrowing with the soil depth, which could have been due to its partial leaching and magnesium uptake by plants when exposed to insufficient magnesium fertilisation. In soils PD1, PD2, PD6, the arable-humus horizons were richest in exchangeable potassium, which must be related to potassium fertilisation and the process of mineral weathering. The lowest content of exchangeable potassium was found in the horizons rich in the clay fraction, which is significantly confirmed by the negative correlation between those parameters (Table 3). The amounts of potassium released to the soil solution as a result of the weathering of minerals and K^{+} desorption depend on the content of exchangeable potassium and the type of clay minerals, mostly illites (Kobierski et al. 2005). The content of exchangeable sodium varied across the soils researched and

Table 1

Selected properties and texture of the analyzed soils

Profile No	Horizon	Depth (cm)	PH KCl	TOC ($g\ kg^{-1}$)	Particle size fractions			Texture classa	
					sand	silt	clay	PTG*	USDA**
					(%)				
PD1	Ap	0-25	4.6	8.6	63	20	17	gl	SL
	Btg1	25-50	4.8	2.7	56	23	21	gpi	SCL
	Btg2	50-80	5.0	1.5	50	25	25	gpi	SCL
	Bt	80-95	5.0	0.7	57	21	22	gpi	SCL
	B/C	95-120	5.0	0.3	61	19	20	gl	SL
	Cca1	120-180	7.3	-	62	19	19	gl	SL
	Cca2	180-200	7.4	-	62	20	18	gl	SL
PD2	Ap	0-30	50	10.9	64	22	14	gl	SL
	AE	30-46	5.1	4.7	66	22	12	gp	FSL
	Eet	46-74	4.9	2.8	69	19	12	gp	FSL
	Eetg	74-125	4.5	1.3	68	21	11	gp	FSL
	Bt	125-180	4.4	0.6	32	37	31	gi	CL
	C	180-200	5.1	-	60	23	17	gl	SL
PD5	Ap	0-28	4.9	9.0	62	24	14	gl	SL
	Bt	28-72	5.1	3.4	55	24	21	gpi	SCL
	BC	72-90	5.3	1.4	70	14	16	gp	FSL
	C	90-120	4.9	0.5	57	24	19	gl	SL
	IIC	120-180	4.9	-	95	3	2	pl	S
PD3	Ap	0-25	4.0	11.9	61	23	16	gl	SL
	Gg	25-57	4.0	3.6	57	25	18	gl	SL
	Bg	57-115	4.1	1.4	55	26	19	gl	SL
	Cg	115-180	4.1	0.4	62	23	15	gl	SL
	C	190-200	4.2	-	59	23	18	gl	SL
PD4	Ap	0-28	4.4	10.1	69	23	8	gp	FSL
	Gg1	28-50	4.4	4.7	67	25	8	gp	FSL
	Gg2	50-83	4.3	1.1	65	24	11	gp	FSL
	Gg3	83-114	4.0	0.4	69	26	5	gp	FSL
	Bg	114-170	3.8	-	55	27	18	gl	SL
	C	170-200	5.2	-	58	26	16	gl	SL
PD6	Ap	0-26	4.5	8.2	70	26	4	gp	FSL
	Gg1	26-55	4.3	1.7	56	24	20	gl	SL
	Gg2	55-81	4.1	1.2	64	19	17	gl	SL
	Bg	81-120	3.7	0.5	55	23	22	gpi	SCL
	Cg	120-180	3.9	-	57	24	19	gl	SL
	C	180-200	7.0	-	61	23	16	gl	SL

TOC – total organic carbon; sand: 2.0-0.05 mm; silt: 0.05-0.002 mm; clay: <0.002 mm;
The texture classes are based on PTG 2008 and USDA classification.
*PTG: pl – sand; gp – sandy loam; gl – sandy loam; gpi – sandy clay loam; gi – clay loam
**USDA: S – sand; FSL – fine sandy loam; SL – sandy loam; SCL – sandy clay loam; CL – clay loam

Table 2

Content of exchangeable cations and sorptive capacity parameters

Profile No	Horizon	Ca^{2+}	Mg^{2+}	K^+	Na^+	Hh	S	CEC	V
		(mmol kg^{-1})							(%)
PD1	Ap	59.6	3.4	12.3	2.9	34.5	78.2	112.7	69.4
	Btg1	71.6	4.1	3.3	2.8	18.0	81.8	99.8	82.0
	Btg2	84.9	7.5	3.6	2.6	16.0	98.6	114.6	86.0
	Bt	82.4	7.2	2.5	2.0	11.5	94.1	105.6	89.1
	B/C	73.7	6.9	2.3	2.2	11.0	85.1	96.1	88.6
	Cca1	88.5	3.4	2.2	1.6	2.0	95.7	97.7	98.0
	Cca2	85.9	4.4	2.1	1.8	2.5	94.2	96.7	97.4
PD2	Ap	54.8	3.3	16.7	2.5	33.5	77.3	110.8	69.8
	AE	45.9	1.8	2.1	2.1	24.0	51.9	75.9	68.4
	Eet	44.7	1.7	3.5	2.3	26.5	52.2	78.7	66.3
	Eetg	37.1	1.7	5.5	2.2	25.5	46.5	72.0	64.6
	Bt	108.8	15.7	11.6	5.1	30.0	14.2	171.2	82.5
	C	85.5	8.6	14.1	4.3	15.0	112.5	127.5	88.2
PD5	Ap	96.2	14.2	22.8	10.4	28.0	143.6	171.6	83.7
	Bt	133.9	18.4	16.2	15.7	15.0	184.2	199.2	92.5
	BC	111.0	11.8	17.5	10.6	13.0	150.9	163.9	92.1
	C	126.3	20.7	24.7	13.0	17.0	184.7	201.7	91.6
	IIC	24.1	1.2	9.2	11.1	7.0	45.6	52.6	86.7
PD3	Ap	34.5	4.7	1.6	2.0	44.0	42.8	86.8	49.3
	Gg	40.8	7.1	2.6	5.0	38.5	55.5	94.0	59.0
	Bg	45.9	13.5	2.2	4.0	28.5	65.6	94.1	69.7
	Cg	98.0	23.0	9.5	7.7	24.5	138.2	162.7	84.9
	C	98.2	21.4	17.5	12.3	22.0	149.4	171.4	87.2
PD4	Ap	69.9	4.9	12.8	10.9	42.0	98.5	140.5	70.1
	Gg1	61.9	1.6	11.5	9.6	34.0	84.6	118.6	71.3
	Gg2	66.4	3.6	14.6	9.6	22.5	94.2	116.7	80.7
	Gg3	46.7	6.8	27.7	12.1	28.0	93.3	121.3	76.9
	Bg	12.,3	20.4	18.3	11.1	30.5	174.1	204.6	85.1
	C	148.1	14.2	26.5	15.8	12.0	204.6	216.6	94.5
PD6	Ap	80.2	2.0	29.2	13.4	40.5	124.8	165.3	75.5
	Gg1	98.3	7.9	16.5	14.3	26.5	137.0	163.5	83.8
	Gg2	93.4	10.5	12.3	14.5	33.0	130.7	163.7	79.8
	Bg	63.2	10.6	2.5	1.1	57.5	77.4	134.9	57.4
	Cg	107.5	4.7	2.1	1.4	27.5	115.7	143.2	80.8
	C	78,3	8.3	2.5	0.9	4.0	90.0	94.0	95.7

S – base saturation; CEC – cation-exchange capacity; $V=S/CEC \cdot 100$

Table 3

Correlation coefficients between the investigated parameters (n = 35)

Parameters	Mg^{2+}	Ca^{2+}	K^+	Na^+	S	CEC
Clay	0.44	0.46	-0.34			
Mg^{2+}		0.64	0.36	0.44	0.76	0.75
Ca^{2+}			0.39	0.42	0.87	0.81
K^+				0.81	0.67	0.70
Na^+					0.68	0.70

S – base sturation; CEC – cation-exchange capacity; confidence level $p<0.05$

ranged from 0.9 to 15.8 mmol(+) kg^{-1}, and the share of Na^+ in CEC ranged from 1.0 to 21.1%. The share of magnesium cations in the cation exchange capacity ranged from 1.2 to 14.9%. A similar share of Mg^{2+} in CEC (from 5.3 to 10.6%) was recorded in Luvisols and Cambisols formed from glacial till of the Inowrocławska Plain (Kobierski et al. 2005).

Analysing the exchangeable magnesium distribution in the profiles of the soils, it was found that their content varied in respective genetic horizons. The highest content of that cation was noted in the sorption complex of the horizons richest in the clay fraction. The statistical analysis of the results demonstrated a significantly positive correlation between the content of exchangeable magnesium and the content of the clay fraction (Table 3). A similar relationship was reported by Błaszczyk (1998) who found that exchangeable Mg resources in soils formed from glacial tills increased with the increasing amount of clay fraction. The lowest share of magnesium cations in CEC, whose mean content of Mg^{2+} was 1.7 mmol(+) kg^{-1}, was identified in the sorption complex of eluvial horizons (Eet) of soils PD2. Arable-humus horizons of soils demonstrated a lower variation in the content of that cation, and its average content was 5.4 mmol(+) kg^{-1}, thus being similar to the average content of Mg^{2+} in gleyic horizons (6.2 mmol(+) kg^{-1}). The highest content of exchangeable magnesium was reported in illuvial horizons of soils PD1, PD2, PD4, PD6, for which the values of the Mg^{2+} distribution index across the profiles were the highest (1.0-1.8). The values of the distribution index calculated from the ratio of the content of cations in the solum genetic horizon to its mean content in the parent material also confirm the pedogenic nature of Ca^{2+} accumulation in the profiles of Luvisols. Magnesium is very easily leached from genetic horizons within the solum. Exchangeable cations triggered as a result of chemical weathering of minerals reach the soil solution, from which they are taken up by plants, can be bonded by soil colloids or leached deep down the soil profile. In the examined Gleysols of the mesoregion, the highest content of exchangeable magnesium cations in the deepest genetic horizons of solum and the roof of the parent material was identified. A similar relationship was recorded for calcium cations. These findings can suggest some overlapping of the features of the surface gleyic process involving precipitation waters with *lessivage* features, characteristic for Luvisols. The distribution of nutrients in the soil profile depends considerably on the grain size composition and the physicochemical properties of soil, especially pH, an increase of which results in a clear increase in the content of easily-soluble magnesium (LIPIŃSKI, BEDNAREK 1998). The present results, however, did not coincide with a significant effect of the reaction on the content of exchangeable magnesium in the profiles of the investigated soils. The nature and the durability of organic-mineral bonds of the sorption complex depend on the existing acidic-alkaline equilibrium of soil. The properties determine the form of occurrence of elements and their leaching down the soil profile, which concerns mostly soils under intensive agricultural use, in which agrotechnical treatments affect the rate and the direction of changes in physicochemical properties (SKŁODOWSKI, ZARZYCKA 1995).

CONCLUSIONS

1. In the Luvisols of the Drawskie Lakeland, the lowest amount of exchangeable calcium

and magnesium was observed in arable-humus and eluvial horizons. The highest content of Ca^{2+} and Mg^{2+}, both in the profiles of Luvisols and Gleysols, was identified in the deepest genetic horizons of the solum and in the roof of the parent material, which points to the possibility of overlapping of the features of the surface gleyic process with the *lessivage* features. The exchangeable potassium and sodium distribution in the profiles of the analysed soils varied.

2. Horizons rich in the clay fraction contained a significantly higher content of Ca^{2+} and Mg^{2+} and a significantly lower content of K^+, which is confirmed by the results of the analysis of correlation.

3. The acidic reaction did not affect significantly either the content of exchangeable cations or their distribution in soil profiles.

REFERENCES

ASKEGAARD, M., HANSEN, H.C.B., SCHJOERRING, J.K. 2005. *A cation exchange resin method for measuring long-term potassium release rates from soil*. Plant Soil., 271: 63-74.

BŁASZCZYK W.H. 1998. *Ilościowe zróżnicowanie form magnezu i potasu w glebach różnie użytkowanych. [Quantitative variation of magnesium and potassium forms in differently used soils]*. Rocz. Glebozn., 49,(3/4): 85-95. (in Polish)

ERSAHIN S., GUNAL H., KUTLU T., YETGIN B., COBAN S. 2006. *Estimating specific surface area and cation exchange capacity in soils using fractal dimension of particle-size distribution*. Geoderma, 136: 588-597.

Hartmann A., Gräsle W., Horn R. 1998. *Cation exchange processes in structured soils at various hydraulic properties*. Soil Tillage Res., 47: 67-72.

Jobbágy E.G., Jackson R.B. 2001. *The distribution of soil nutrients with depth: Global patterns and the imprint of plants*. Biogeochemistry., 53: 51-77.

Kobierski M., Dąbkowska-Naskręt H., Jaworska H. 2005. *Właściwości sorpcyjne i skład kationów wymiennych intensywnie użytkowanych rolniczo gleb w regionie Równiny Inowrocławskiej [Sorption properties and cation-exchange capacity of arable soils from Inowrocław Plain region]*. Zesz. Probl. Post. Nauk Rol., 507: 285-294. (in Polish)

Kobierski M. Pytlarz K. 2006. *Potassium and magnesium in orchard and arable cambisols developed on glacial till. Macro- and trace element.* Mengen und Spurenelemente, 23: 439-444.

Lipiński W., Bednarek W. 1998. *Występowanie łatwo rozpuszczalnych form metali w glebach Lubelszczyzny w zależności od odczynu i składu granulometrycznego [Occurrence of readily soluble forms of metals in the soils of Lublin region depending on soil reaction and grain size composition]*. Zesz. Probl. Post. Nauk Rol., 456: 399-404. (in Polish)

Panak H., Wojnowska T., Sienkiewicz S. 1996. *Zmiany niektórych właściwości chemicznych i fizycznych czarnych ziem kętrzyńskich pod wpływem intensywnego nawożenia azotem [Changes in some chemical and physical properties of black earth near Kętrzyn as the influence of intensive nitrogen fertilization]*. Rocz. Glebozn., 47 (2/4): 41-46. (in Polish)

Paterson J., Richter A.C. 1986. Effect of long-term fertilizer application on exchangeable and acid-soluble potassium. Agron. J., 58: 589-595.

Polskie Towarzystwo Gleboznawcze 2009. *Klasyfikacja uziarnienia gleb i utworów mineralnych – PTG 2008*. [*Grain size composition of soils and mineral formations – PTG 2008*.] Rocz. Glebozn., 60 (2): 5-16. (in Polish)

Skłodowski P., Zarzycka H. 1995. *Wpływ rolniczego użytkowania gleb na ich niektóre właściwości chemiczne [The influence of agricultural use of soils on the selected chemical properties]*. Rocz. Glebozn., 46 (3/4): 37-44. (in Polish)

Stępniewski W., Przywara G. 1992: *The influence of soil oxygen availability on yield and nutrient uptake (N, P, K, Ca, Mg, Na) by winter rye (secale cereale*). Plant Soil, 143: 267--274.

Targulian V.O., Krasilnikov P.V. 2005. *Soil system and pedogenic processes: Self-organization, time, scales, and environmental significance*. Catena, 71: 373-381.

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CONTENT OF SOME ELEMENTS IN GRAIN OF SPRING WHEAT CV. ZEBRA DEPENDING ON SOIL TILLAGE SYSTEMS AND CATCH CROPS

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Abstract

The aim of the present study was to evaluate the effect of plough and conservation tillage treatment as well as various catch crops on the chemical composition of the grain of spring wheat grown in monoculture. The study was carried out in 2006–2008, using an experiment established in 2005. The experimental field was located on medium and heavy mixed rendzina soil. The design of a static two-factor experiment, set up using the split-plot method in four replications, included the plough tillage system (A) and two conservation tillage methods – with autumn (B) or spring (C) disking of catch crops. The other factor comprised four methods for regeneration of the spring wheat monoculture stand using the following catch crops: undersown red clover (b) and Westerwolds ryegrass (e); lacy phacelia (c) and white mustard stubble crops (d); and the control treatment without catch crops (a). The concentrations of potassium, manganese and sulphur in the spring wheat grain harvested from the ploughed plots were higher than in the conservation tillage treatment. In the plough tillage treatments, grain Mg content was higher than in the conservation tillage variant with spring disking of the catch crops. Conservation tillage had an effect on the increase in phosphorus and copper content in spring wheat grain compared to plough tillage. Zn and Fe content in the grain from the conservation tillage treatments with autumn disking of the catch crops was lower than in that from the plough and conservation tillage treatments with spring incorporation of the catch crops. Iron content in the grain obtained from the treatments with red clover and lacy phacelia was the highest. At the same time, phosphorus content in spring wheat grain was the highest in the control treatments and in the treatment with Westerwolds ryegrass and white mustard. In the plots where a lacy phacelia stubble crop had been sown, zinc and copper content in grain was determined to be the highest. In turn, the highest manganese content was found in the grain from the control treatments, whereas total sulphur content was the highest in the control plots and in the plots with the stubble crops.

Key words: conservation tillage, plough tillage, catch crops, spring wheat, chemical composition of grain.

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ZAWARTOŚĆ WYBRANYCH PIERWIASTKÓW W ZIARNIE PSZENICY JAREJ ODMIANY ZEBRA W ZALEŻNOŚCI OD SYSTEMÓW UPRAWY ROLI ORAZ MIĘDZYPLONÓW

Abstrakt

Celem badań była ocena wpływu uprawy płużnej i konserwujących sposobów uprawy roli oraz różnych międzyplonów na skład chemiczny ziarna pszenicy jarej uprawianej w monokulturze. Badania przeprowadzono w latach 2006-2008, wykorzystując doświadczenie założone w 2005 r. Pole doświadczalne było położone na średniej i ciężkiej rędzinie mieszanej. Schemat statycznego, dwuczynnikowego doświadczenia założonego metodą split-plot, w 4 powtórzeniach, uwzględniał płużny system uprawy roli (A) oraz 2 sposoby uprawy konserwującej – z jesiennym (B) lub wiosennym (C) talerzowaniem międzyplonów. Drugim czynnikiem były 4 sposoby regeneracji stanowiska w monokulturze pszenicy jarej w postaci takich międzyplonów, jak: wsiewki międzyplonowe koniczyny czerwonej (b) i życicy westerwoldzkiej (e), międzyplony ścierniskowe facelii błękitnej (c) i gorczycy białej (d) oraz obiekt kontrolny bez międzyplonów (a). Zawartość potasu, manganu i siarki w ziarnie pszenicy jarej z obiektów uprawianych płużnie była większa niż z uprawy konserwującej. W obiektach z uprawą płużną zawartość Mg w ziarnie była większa niż w wariancie uprawy konserwującej z wiosennym talerzowaniem międzyplonów. Konserwująca uprawa roli wpływała na wzrost zawartości fosforu i miedzi w ziarnie pszenicy jarej, w porównaniu z uprawą płużną. Zawartość Zn i Fe w ziarnie z uprawy konserwującej z jesiennym talerzowaniem międzyplonów była mniejsza niż z uprawy płużnej i konserwującej z wiosennym talerzowaniem międzyplonów. Zawartość żelaza w ziarnie z obiektów z koniczyną czerwoną i facelią błękitną była największa. Jednocześnie zawartość fosforu w ziarnie pszenicy jarej była największa w obiektach kontrolnych, z życicą westerwoldzką oraz z gorczycą białą. Największą zawartość cynku i miedzi w ziarnie stwierdzono w obiektach, na których wysiewano międzyplon ścierniskowy facelii błękitnej. Z kolei największą zawartość manganu stwierdzono w ziarnie z obiektów kontrolnych, natomiast siarki ogólnej z poletek kontrolnych oraz z międzyplonami ścierniskowymi.

Słowa kluczowe: uprawa konserwująca, uprawa płużna, międzyplony, pszenica jara, skład chemiczny ziarna.

INTRODUCTION

The quality of cereal grain plays an important role in obtaining high quality food product. In recent years, attempts have been made to reduce expenditure related to cereal growing technology. Conservation tillage, while reducing expenditure on soil tillage, at the same time limits water and wind erosion, stimulates biological diversity and increases the content of organic substances and macronutrients in the topsoil (ZIMNY 1999, DZIENIA et al. 2006, WEBER 2010). The growing proportion of cereals in the crop structure leads to adverse changes in the soil, the infection of plants with stem base diseases that become more severe over time, and an increased level of weed infestation. This affects grain quality and yield (WOŹNIAK, 2004). Plants sown as catch crops can largely reduce the negative effects of cereal-cropping frequency in crop rotations (ANDRZEJEWSKA 1999, KURASZKIEWICZ 2004). Catch crops influence soil properties as well as the growth and development of the main crop, ultimately affecting yield quality (Kuraszkiewicz 2004, Kwiatkowski, 2009). They can be a significant source of nutrients, including microminerals (Łoginow, 1985).

The long-term production use of crop fields may lead to the depletion of reserves of available micronutrients in the plough layer, which results in an insufficient supply of these minerals to crop plants (Wróbel 2000). The uptake of copper, manganese and zinc by the plant root system in soils with a high pH, even when the average soil availability of these elements is moderate, is inferior so that the three elements can become the mineral components reducing the yield amount and quality (Czuba 2000, Łabętowicz, Rutkowska, 2000). An adequate content of micronutrients in grain of high quality wheat is an important trait for the consumer and for the nutritive value of grain as raw product (Zięba et al. 1992, Stanisławska-Glubiak et al. 1996, Czuba 2000, Gembarzewski 2000, Kocoń 2005). Deficiency of both micro‾ and macronutrients in the plant first of all depresses its resistance to adverse environmental conditions and subsequently decreases the yield and its quality (Stanisławska-Glubiak, Korzeniowska 2007, Korzeniowska 2008). Gembarzewski (2000) emphasizes that the micronutrient content in yield is important for its nutritive and feeding value. At the same time, Ruszkowska et al. (1996) express the opinion that obtaining high yields for a number of consecutive years entails the need to control the status of micronutrient supply to plants.

The aim of the present study was to evaluate the effect of plough and conservation tillage systems as well as of various catch crops on the chemical composition of grain of spring wheat grown in monoculture on rendzina soil under the conditions prevailing in south-eastern Poland.

MATERIAL AND METHODS

The study was carried out in 2006-2008, using an experiment established in 2005 at Bezek Experimental Farm (N: 51° 19', E: 23° 25'), owned by the Lublin University of Life Sciences. The experimental field was located on medium and heavy mixed rendzina soil developed from chalk rock with the grain size distribution of medium silty loam. This soil was characterized by alkaline pH (7.35), a high content of phosphorus (117.8) and potassium (242.4) as well as a very low content of magnesium (19) (the values are expressed in mg kg^{-1} of soil), while the organic carbon content was 24.7 g kg^{-1}. The soil was classified as soil quality class IIIb and defective wheat complex.

The total rainfall from April to August in 2006 was higher than the long-term average, but it was attributable to the heavy rainfall that occurred in August. In 2008, the total rainfall during the analogous period was similar to the long-term norm, whereas in 2007 it was distinctly higher. The mean air temperatures in all those years were higher than the long-term mean (Table 1). In order to make a more complete analysis of the weather conditions, Selyaninov's hydrothermic index (K) was calculated:

$$K = \frac{p}{\Sigma t},$$

where:

P – monthly total rainfall in mm,

Σt – sum of mean daily temperatures for a given month in °C.

Table 1

Rainfall and air temperatures in April-August in 2006-2008 as compared to the long-term means (1974-2003) according to the Meteorological Station at Bezek

Years	Months					Total
	Apr	May	June	July	Aug	
	rainfall in mm					
2006	25.1	56.7	23.2	26.2	240.9	372.1
2007	12.9	93.6	87.5	130.7	79.9	404.6
2008	47.9	74.2	38.4	93.9	60.9	315.3
Means for 1974-2003	40.1	53.0	77.6	80.3	61.6	312.6
	Temperature in °C					mean
2006	8.9	13.5	16.7	21.7	18.1	15.8
2007	8.3	15.3	18.6	19.4	18.9	16.1
2008	9.1	12.7	17.4	18.3	19.3	15.4
Means for 1974-2003	7.6	13.6	16.2	17.9	17.5	14.6

The values of Selyaninov's hydrothermic index indicate that a significant water deficit occurred in June and July 2006 (Table 2).

The design of a static two-factor experiment, set up using the split-plot method in four replications, included the plough tillage system (A) and two conservation tillage methods – with autumn (B) or spring (C) disking of the catch crops. The other factor comprised four methods for regeneration of the spring wheat monoculture stand in the form of undersown crops (red clover – b; Westerwolds ryegrass – e) or stubble crops (lacy phacelia – c; white mustard – d). The plots without catch crops were the control treatment (a). The harvest plot area was 30 m^2. Winter wheat grown in this field for 3 years was the forecrop for spring wheat. In 2005, spring wheat and all the catch crops, both the intercrops and stubble crops, were sown

Table 2

Values of Selyaninov's hydrothermic index (K)

Years	Months				
	Apr	May	June	July	Aug
2006	*0.94	1.35	**0.46	**0.39	4.30
2007	*0.52	1.98	1.57	2.17	1.36
2008	1.76	1.88	*0.74	1.65	1.02
Means for 1974-2003	1.76	1.26	1.60	1.45	1.14

*$K < 1.0$ – dry spell
** $K < 0.5$ – drought

and the soil tillage was carried out in accordance with the methodological assumptions, taking this year as the preliminary one.

Plough tillage, preparing the field for spring wheat, started with skimming and harrowing after harvesting the forecrop. Ploughing was done to an average depth before the winter. In the spring, harrowing was performed and, before sowing, both cultivating and harrowing were completed. Phosphorus and potassium fertilizers were introduced during this period; the first portion of nitrogen fertilizers was also applied at the rate of 60 kg N ha^{-1} N in the form of ammonium nitrate. Phosphorus fertilizers were applied at the rate of 30.5 kg P ha^{-1} in the form of triple superphosphate, while potassium fertilizers were incorporated in the spring at 74.7 kg K ha^{-1} in the form of 60% potassium salt. The second dose of nitrogen at the rate of 40 kg ha^{-1} was introduced at the beginning of shooting (BBCH growth stages 30-33). Spring wheat cv. Zebra (technological value E – elite wheat) was sown at the rate of 5 million seeds per ha at a row spacing of 10 cm. Seeds were dressed with the seed dressing Panoctine 350 SL (350 g dm^{-3} guazatine in the form of acetate). Red clover cv. Dajana (20 kg ha^{-1}) and Westerwolds ryegrass cv. Mowester (20 kg ha^{-1}) were sown on the date of spring wheat sowing. Lacy phacelia cv. Stala (20 kg ha^{-1}) and white mustard cv. Borowska (20 kg ha^{-1}) were sown following the harvest of spring wheat and after performing post-harvest treatments.

In the conservation tillage treatments (B and C), after the forecrop was harvested in the plots without undersown red clover and Westerwolds ryegrass, grubbing to a depth of 18-20 cm and harrowing were done. Subsequently, lacy phacelia and white mustard were sown, in the same way as in the plough tillage treatment. In treatment (B) the cover crops were disked before the winter, whereas in treatment (C) they were left as mulch for the winter and disking was done in the spring. In the treatments with autumn disking of the catch crops (B), spring tillage was the same as in the plough tillage treatment. In the plots with the other conservation tillage treatment (C), the field was harrowed after disking had been done, and then harrowing was repeated before sowing spring wheat. The wheat crop protection programme included Chwastox Extra 300 SL 3.5 dm^3 ha^{-1} (300 g dm^{-3} MCPA) – (BBCH 23-29), and Alert 375 SC 1 dm^3 ha^{-1} (125 g dm^{-3} flusilazole and 250 g dm^{-3} carbendazim) – (BBCH 26-29).

The elements were determined in collective samples in three replications using the following methods: P – colorimetric method; K – flame photometry; Mg, Cu, Zn, Mn, Fe – atomic absorption spectrometry (AAS); total S – nephelometric method. The results were statistically processed using the analysis of variance. The means were compared using least significant differences (LSD) based on Tukey's test.

RESULTS

Compared to plough tillage, conservation soil tillage had a significant effect on the increase in phosphorus and copper content in spring wheat grain, whereas plough tillage promoted a significantly higher total sulphur content compared to conservation tillage (Table 3). The spring wheat grain from the conservation tillage treatment with spring disking of the catch crops had the lowest potassium content, while a significantly higher content of potassium was found in the grain obtained from the plough and conservation tillage treatments with autumn incorporation of the catch crops. The grain harvested from the ploughed plots was characterized by a significantly higher content of magnesium than that from the conservation tillage treatment in which the catch crops were left for the winter period (Table 3).

The highest zinc and iron content was found in the grain from the plots where conservation tillage with spring disking of the catch crops had been used; the zinc content was significantly lower for the plough tillage treatment, being the lowest when conservation tillage with autumn incorporation of the catch crops had been applied (Table 3). The grain harvested from the plots where conservation tillage with autumn incorporation of the catch crops had been used was characterized by the lowest content of manganese; the grain manganese content was significantly higher in the case of conservation tillage with spring incorporation of catch crop biomass, but the highest content of this mineral was determined in the grain from the plough tillage treatment (Table 3).

The phosphorus content in the spring wheat grain harvested from the plots with Westerwolds ryegrass and white mustard as well as from the control treatment was significantly higher than in the grain from the plots where red clover and lacy phacelia had been sown (Table 4). Catch cropping did not have a significant effect on potassium and magnesium content in spring wheat grain (Table 4). Sowing a lacy phacelia stubble crop increased significantly zinc and copper content in spring wheat grain compared to the other plants sown as catch crops. The grain obtained from the control treatment without catch cropping was characterized by the lowest content of the above elements (Table 4).

Table 3

Chemical composition of spring wheat grain depending on tillage systems (means for the period 2006-2008)

Specification	Tillage systems			LSD (p = 0.05)
	*A	B	C	
P content in grain (g kg^{-1} DM)	4.32	4.75	4.69	0.118
K content in grain (g kg^{-1} DM)	4.16	4.12	4.06	0.057
Mg content in grain (g kg^{-1} DM)	1.14	1.13	1.10	0.032
Zn content in grain (mg kg^{-1} DM)	26.33	26.22	26.95	0.104
Cu content in grain (mg kg^{-1} DM)	3.98	4.12	4.13	0.040
Mn content in grain (mg kg^{-1} DM)	21.18	19.97	20.86	0.137
Fe content in grain (mg kg^{-1} DM)	32.76	30.42	32.93	0.142
Total S content in grain (g kg^{-1})	1.25	1.20	1.19	0.015

*A – plough tillage
B – conservation tillage with autumn disking of catch crops
C – conservation tillage with spring disking of catch crops

Table 4

Chemical composition of spring wheat grain depending on catch crops (means for the period 2006-2008)

Specification	Catch crops					LSD (p = 0.05)
	*a	b	c	d	e	
P content in grain (g kg^{-1} DM)	4.78	4.13	4.44	4.69	4.90	0.178
K content in grain (g kg^{-1} DM)	4.12	4.09	4.09	4.13	4.14	**ns
Mg content in grain (g kg^{-1} DM)	1.12	1.13	1.11	1.13	1.14	**ns
Zn content in grain (mg kg^{-1} DM)	25.83	26.30	27.99	26.05	26.32	0.157
Cu content in grain (mg kg^{-1} DM)	3.82	4.12	4.27	4.19	3.98	0.061
Mn content in grain (mg kg^{-1} DM)	21.45	20.24	20.66	20.70	20.30	0.207
Fe content in grain (mg kg^{-1} DM)	31.59	34.44	33.01	31.23	29.90	0.214
Total S content in grain (g kg^{-1})	1.22	1.18	1.24	1.23	1.18	0.023

*a – control without catch crops
b – undersown red clover
c – lacy phacelia stubble crop
d – white mustard stubble crop
e – undersown Westerwolds ryegrass
**ns – non-significant difference

The significantly lowest content of manganese was found in the grain from the treatments with the red clover and Westerwolds ryegrass undersown crops, while this content was significantly higher in the grain from the plots with the lacy phacelia and white mustard stubble crops and the highest in the control treatment (Table 4). The highest iron content was found in the spring wheat grain in the treatment with the red clover intercrop, a significantly lower content in the grain from the plot with the lacy phacelia stubble crop, in the control plots without catch crops, and in the treatment with white mustard. Iron content in the grain from the plots where Westerwolds ryegrass had been undersown was the lowest (Table 4). The lowest grain sulphur content was obtained in the treatments with undersown red clover and Westerwolds ryegrass, while it was significantly higher in the plots with the stubble crops and in the control plots (Table 4).

Among the analyzed elements, the largest amounts of zinc, manganese and iron in spring wheat grain were found in 2008, copper in 2007, and phosphorus in the first year of the study (Table 5). Magnesium and total sulphur content in grain in 2007 and 2008 was significantly higher than in 2006, whereas potassium content was higher in 2006 and 2008 compared to 2007 (Table 5).

Table 5

Chemical composition of spring wheat grain in 2006-2008

Specification	Years			LSD (p = 0.05)
	2006	2007	2008	
P content in grain (g kg^{-1} DM)	5.88	3.69	4.19	0.118
K content in grain (g kg^{-1} DM)	4.16	4.02	4.16	0.057
Mg content in grain (g kg^{-1} DM)	1.03	1.18	1.17	0.032
Zn content in grain (mg kg^{-1} DM)	26.30	24.02	29.18	0.104
Cu content in grain (mg kg^{-1} DM)	3.06	5.68	3.48	0.040
Mn content in grain (mg kg^{-1} DM)	18.38	15.43	28.20	0.137
Fe content in grain (mg kg^{-1} DM)	23.12	30.38	42.60	0.142
Total S content in grain (g kg^{-1})	0.97	1.34	1.33	0.023

DISCUSSION

Phosphorus content in the grain of spring wheat grown using plough tillage was lower by 7.9% to 9.1% compared to both conservation tillage methods. At the same time, phosphorus content in the grain harvested from the plots where red clover had been undersown was lower by 7.0% to 15.7% compared to the other treatments. In the study of Ruszkowska et al. (1993), phosphorus content in spring wheat grain ranging 2.8-4.4 g kg^{-1} was lower than that obtained in the present study. This could have resulted from a good phosphorus supply to spring wheat grown on rendzina soil that was characterized by high phosphorus availability. At the same time, many authors indicate the accumulation of phosphorus in the topsoil under no¯tillage systems (Włodek et al. 2003, Blecharczyk et al. 2007, Weber 2010). The content of phosphorus, potassium and magnesium found in spring wheat grain was higher than obtained by Kraska (2007) in winter wheat grain for wheat crops grown on the same soil.

Conservation soil tillage with spring incorporation of the catch crops promoted higher content of zinc and iron in grain; zinc content was higher by 2.4% to 2.8%, while iron content increased by 0.5% to 8.3% compared to plough and conservation tillage with autumn disking of the catch crops. Moreover, copper content was higher by 3.5% to 3.8% in the grain obtained from both conservation tillage treatments compared to that harvested from the ploughed plots. This could have been attributable to higher availability of these elements in the soil, thereby the possibility of their uptake by wheat in the conservation tillage treatments. Zimny (1999) and Weber (2010) report that conservation tillage promotes higher availability of nutrients in the arable layer compared to plough tillage. At the same time, the introduction of catch crops as a factor mitigating the negative consequences of monoculture cropping of spring wheat increased zinc and copper content in grain compared to the control treatment without catch cropping. Many authors consider catch crops as a source of nutrients, thus increasing nutrient availability in the surface soil layer and thereby improving the level of nutrient supply to plants (Andrzejewska 1999, Zimny 1999, Małecka et al. 2004, Weber 2010). Zinc content in the grain of cv. Zebra wheat was lower than that given by Gembarzewski et al. (1995) in their study in which zinc content ranged from 31 to 38 mg kg^{-1}. Spiak and Wall (2000) found that zinc content in winter wheat grain was related to the concentration of available forms of this element in the soils. Similarly, Stanisławska-Glubiak et al. (1996) think that changes in micronutrient content in spring wheat grain is conditioned by the level of yield and the richness of the soil in available forms of micronutrients. In turn, in the study of Parylak et al. (2000) Cu, Zn and Mn content in wheat grain was not dependent on the availability of these minerals in the soil. Likewise, Nowak (2000) shows that the type of forecrop and the amount of organic biomass ploughed-in had no effect on micronutrient content in winter wheat grain. However, Parylak et al. (2000) found grain zinc concentration to have decreased by 3.8% after the application of green manure. A slightly different correlation was found in the present study. Zinc content in the grain from the catch-cropped treatments was higher by 0.9% to 8.4% compared to the control.

Gembarzewski (2000) draws attention to copper deficiency in cereal grain. A decrease of copper content in plant products in Poland is a significant threat to the health of humans and animals. Korzeniowska (2008) thinks that copper deficiency in soil can cause a reduction in grain yields by as much as 20% and a decrease in grain copper content. Gembarzewski et al. (1995) report that Polish wheats contain an average of 3.1-3.4 mg of copper per kg of grain. In our study, grain copper content was slightly larger, and in 2007 it was distinctly higher (5.68 mg kg^{-1}), but that was the season in which grain yield was the lowest. After the application of green manure, Parylak et al. (2000) recorded a slight decrease (3.7%) of copper content in wheat grain. In the present study, the introduction of catch crops increased copper content in wheat grain from 4.2% to 11.8% compared to the control without catch cropping.

The spring wheat grain from the plough tillage treatments was characterized by a higher content of manganese by 1.5% to 6.1% relative to that from the conservation tillage treatments. At the same time, the use of catch crops promoted a decrease in manganese content in grain from 3.5% to 5.6% relative to the control treatment. The application of green manure in the study of Parylak et al. (2000) also caused a decreasing tendency in the content of this nutrient in wheat grain by 16.6% compared to the results obtained in the stands fertilized with NPK alone. Stanisławska-Glubiak et al. (1996) found that manganese content in spring wheat grain was dependent on soil pH. When wheat was grown on soil with a slightly acidic pH (6.1), manganese accumulated in the grain as the level of yield increased. In soil with neutral pH (6.7), grain manganese concentration gradually decreased. The low concentration of manganese in the grain determined in the present study, compared to its content reported by Gembarzewski et al. (1995), could have arisen from the fact that the results were obtained in an experiment set up on rendzina soil with alkaline pH.

Undersowing Westerwolds ryegrass resulted in decreased grain iron content from 4.3% to 13.2% compared to the other catch-cropped treatments. In this study, iron content in spring wheat grain was lower than that given by Gembarzewski et al. (1995), which ranged from 47 to 56 mg kg^{-1} depending on wheat grain yield. Łabętowicz and Rutkowska (2000) as well as Kocoń (2005) report that the uptake of copper, iron, manganese and zinc by the plant root system in soils with a high pH, even with an average availability of these elements in the soil, is worse and they can become the mineral components that reduce yield amount and quality.

Similarly to manganese and potassium, total sulphur content in the wheat grain from the ploughed plots was higher than in that from the conservation tillage treatments. The application of stubble crops promoted higher sulphur content in grain compared to the undersown crops. Motowicka-Terelak et al. (1993) as well as Motowicka-Terelak and Terelak (2000) report that sulphur content in most plants, including crop plants, ranges from 0.5 to 15.0 g kg^{-1}. In wheat grain, this range of sulphur content is between 0.3 and 3.1 g kg^{-1}.

The content of most minerals in spring wheat grain in the last year of the study (2008) was higher than in the first year (2006). This could have resulted from the adverse weather conditions in 2006. Water deficit occurred in June and July, which could have affected the rate of nutrient uptake by the plants. Only grain copper content was the highest in the second year of the study, while for phosphorus this happened in the first year of the study; however, the potassium content was similar in all the analyzed seasons. Catch cropping, which improves chemical properties of soil and consequently the nutrient supply to plants, could have contributed to this outcome. TRZEBSKA-JESKE et al. (1976) also found that Fe, Zn, Mn and Cu content in wheat grain depended on weather conditions prevailing in the successive years of the study. MAKARSKA and MICHALAK (2003) obtained similar correlations with respect to the chemical composition of spring barley grain. Likewise, investigating the chemical composition of spring wheat grain, CHRZANOWSKA-DROŻDŻ et al. (1999) found it to be primarily dependent on weather patterns and genetic properties of cultivars, and to a lesser degree on agricultural practices.

CONCLUSIONS

1. Higher potassium, manganese and sulphur content was found in the grain of spring wheat grown using plough tillage compared to the conservation tillage treatments. Magnesium content in the grain from the ploughed plots was higher than in the conservation tillage treatments in which the catch crops had been disked in the spring.

2. Phosphorus and copper content in the grain obtained from the conservation tillage treatments was higher than in the grain from the plough tillage treatments. In turn, zinc and iron content in the grain from the conservation tillage treatments with autumn disking of the catch crops was lower than in the other tillage treatments.

3. Copper and zinc content in the grain of spring wheat grown after the catch crops was higher, while manganese content was lower, compared to the treatments without catch cropping. The highest zinc and copper content was found in the grain of wheat grown after lacy phacelia.

4. Iron content in the grain harvested from the plots with the undersown red clover and the lacy phacelia stubble crop was higher, whereas phosphorus content was lower than in the grain from the other treatments under evaluation.

5. In the grain obtained from the plots with undersown red clover and Westerwolds ryegrass, sulphur content was lower than in the grain from the plots where the stubble crops had been sown.

6. Meteorological conditions in the successive years affected the content of the analyzed elements in spring wheat grain. In the last year of the study, the content of most of these elements in the grain were higher than in the first year.

REFERENCES

ANDRZEJEWSKA J. 1999. *Intercrops in cereal crop rotations*. Post. Nauk Rol., 1: 19-31. (in Polish)

BLECHARCZYK A., MAŁECKA I., SIERPOWSKI J. 2007. *Long-term effects of tillage systems on physico-chemical soil properties*. Fragm. Agron., 1: 7-13. (in Polish)

CHRZANOWSKA-DROŻDŻ B., JASIŃSKA Z. GIL Z. 1999. *Qualitative value of spring wheat grain in pure sowing and cultivar mixtures*. Pam. Puł., 118: 67-75. (in Polish)

CZUBA R. 2000. *The micronutrients in recent fertilization systems*. Zesz. Probl. Post. Nauk Rol., 471: 161–169. (in Polish)

DZIENIA S., ZIMNY L., WEBER R. 2006. *The newest trends in soil tillage and techniques of sowing*. Fragm. Agron., 2, 227-241. (in Polish)

GEMBARZEWSKI H. 2000. *Content of microelements and tendencies of their modifications in soils and plants from arable fields in Poland*. Zesz. Probl. Post. Nauk Rol., 471: 171--179. (in Polish)

GEMBARZEWSKI H., OBOJSKI J., STRĄCZYŃSKI S., SIENKIEWICZ U. 1995. *The content of macro- and micronutrients in soils as well as in potato and winter wheat plants grown on high productivity fields*. IUNG Puławy, S(80): 1-38. (in Polish)

KOCOŃ A. 2005. *Fertilization of quality spring and winter wheat and its impact on yield and grain quality*. Pam. Puł., 139: 55-64. (in Polish)

KORZENIOWSKA J. 2008. *Importance of copper deficiency in wheat cultivation*. Post. Nauk Rol., 4-5: 15-31. (in Polish)

KRASKA P. 2007. *The influence of different doses of herbicides on yielding and macroelement content in winter wheat grain*. Biul. IHAR, 246: 23-30. (in Polish)

KURASZKIEWICZ R. 2004. *The residual effect of undersown crops on the yielding of spring barley on light soil*. Ann. UMCS, sect. E, 59 (4): 1815-1821. (in Polish)

KWIATKOWSKI C. 2009. *Studies on the yielding of naked and husked spring barley in crop rotation and monoculture*. Rozpr. Nauk. Uniw. Przyr. w Lublinie, 336: 5-117. (in Polish)

ŁABĘTOWICZ J., RUTKOWSKA B. 2000. *An attempt to include the chemical composition of soil solution into microelement fertilization diagnostics*. Zesz. Probl. Post. Nauk Rol., 471: 45-51. (in Polish)

ŁOGINOW W. 1985. *The modern basis for organic fertilization*. Post. Nauk Rol., 6: 25-37. (in Polish)

MAKARSKA E., MICHALAK M. 2003. *The effect of the system on the content and rations of nutrient elements in the grain of spring barley*. J. Elementol., 8(2): 65-74. (in Polish)

MAŁECKA I., BLECHARCZYK A., PUDEŁKO J. 2004. *Fertilizer value of catch crops in different tillage systems*. Pr. Kom. Nauk Rol. Kom. Nauk Leśn. PTPN, 97: 41-48. (in Polish)

MOTOWICKA-TERELAK T., TERELAK H. 2000. *Sulphur in soils and plants of Poland*. Fol. Univ. Agric. Stetin., 204, Agricultura, 81: 7-16. (in Polish)

MOTOWICKA-TERELAK T., TERELAK H., WITEK T. 1993. *Threshold limit values for the estimation of sulphur content in soils and plants*. [In]: *Assessment of soil and plant contamination with heavy metals and sulphur*. IUNG-Puławy, P(53): 15-20. (in Polish)

NOWAK W. 2000. *Effect of forecrops and nitrogen fertilization on the content of some microelements in winter wheat grain.* Zesz. Probl. Post. Nauk Rol., 471: 403-409. (in Polish)

PARYLAK D., WACŁAWOWICZ R., MAJCHROWSKI P. 2000. *Residual effect of organic fertilizers on microelement contents in soil and wheat.* Zesz. Probl. Post. Nauk Rol., 471: 427-432. (in Polish)

RUSZKOWSKA M., SYKUT S., KUSIO M. 1996. *Trace element supply of plants as influenced by fertilization in a long-term lysimetric experiment.* Zesz. Prob. Post. Nauk Rol., 434: 43-47. (in Polish)

RUSZKOWSKA M., RĘBOWSKA Z., SYKUT S., KUSIO M. 1993. *Nutrient balance in a lysimeter experiment (1985-1989) I. Balance of nitrogen, phosphorus and potassium.* Pam. Puł., 103: 57-77. (in Polish)

SPIAK Z., WALL Ł. 2000. *Relationship between zinc content in plants and soils under field conditions.* Zesz. Prob. Post. Nauk Rol., 471: 145-152. (in Polish)

STANISŁAWSKA-GLUBIAK E., KORZENIOWSKA J. 2007. *Principles of micronutrient fertilization of crop plants.* Studia i Rozprawy IUNG – PIB, 8: 99-110. (in Polish)

STANISŁAWSKA-GLUBIAK E., STRĄCZYŃSKI S., SIENKIEWICZ-CHOLEWA U. 1996. *Effect of yield level differentiation on micronutrient content in wheat grain.* Zesz. Probl. Post. Nauk Rol., 434: 77-81. (in Polish)

TRZEBSKA-JESKE I., RUTKOWSKA U., RUSZKOWSKI M., ZIELIŃSKA Z. 1976. *Content of certain mineral components in winter wheat in relation to mineral fertilizer application and the site of cultivation.* Rocz. PZH, 27 (4): 357-369. (in Polish)

WEBER R. 2010. *Soil properties as affected by the duration of using zero¯tillage systems.* Post. Nauk Rol., 1: 63-75. (in Polish)

WŁODEK S., HRYŃCZUK B., PABIN J., BISKUPSKI A. 2003. *The content of nutrients in the humus profile of differently cultivated soils.* Zesz. Probl. Post. Nauk. Rol., 493: 727-732. (in Polish)

WOŹNIAK A. 2004. *The yield and quality of grain of spring wheat in different crop rotations*. Zesz. Nauk. Akad. Rol. we Wrocławiu 487, Rolnictwo, 85: 219-227. (in Polish)

WRÓBEL S. 2000. *Effect of long-term arable land use on soil and spring wheat supply with microelements*. Zesz. Probl. Post. Nauk Rol., 471: 619-626. (in Polish)

ZIĘBA K., SCHLEGEL-ZAWADZKA M., HENNIG J. 1992. *Zinc, copper and manganese content in daily food rations of children.* Pol. J. Food Nutr. Sci., 42(1): 59-64.

ZIMNY L. 1999. *Conservation tillage*. Post. Nauk Rol., 5: 41-52. (in Polish)

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RESPONSE OF TWO WETLAND GRAMINOIDS TO N:K SUPPLY RATIOS IN A TWO-YEAR GROWTH EXPERIMENT

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Abstract

Changes in nutrient availability in wetlands have been observed during the recent years, mostly due to human pressure. A shift from N limitation to P or K limitation causes changes in plant species composition, nutrient use efficiency, plant growth, interspecific competition and plant species performance. Several studies have shown that stoichiometry indices such as N:P and N:K ratios in plant biomass can be a good indicator of nutrient limitation. However, the implications of an N:K ratio for wetland vegetation have hardly been investigated.

In order to estimate a critical N:K ratio that can indicate the type of nutrient limitations, a greenhouse experiment has been established. The response of two grass species: *Holcus lanatus* and *Molinia caerulea*, to the range of N and K supply was analysed for two years. The effect of six combinations of N:K supply ratios (from 0.5 to 225), combined with two levels of fertility in a factorial design, on aerial biomass production, nutrient concentrations and nutrient resorption efficiency was tested.

The aerial biomass increased with an increasing N:K supply ratio during both vegetation seasons at the low level of supply. Significant differences were observed not only between species but also between the N:K ratios during the two years. In the first year, the optimal N:K supply ratio was 4.5 for *Holcus lanatus* and 225 for *Molinia careluea* at the high fertility level. In 2010, the optimal N:K supply ratio was similar for both grasses. At the high fertility level, the shoot biomass was the highest at an N:K supply ratio of 13.5; at the low level, shoot productivity reached the peak at a 225 N:K supply ratio. Moreover, both plant species showed the same pattern of aerial biomass production to N:K supply ratios at both fertility levels, but differences in the N:K biomass ratios make it impossible to determine a critical N:K ratio. The N:K nutrient supply ratio was a better indicator of plant performance than the N:K biomass ratio of the analysed species. The tested graminoids did not show a similar response to N:K supply ratios at the high and low levels of supply, indicating that nitrogen was the most important factor limiting the plant growth during the two years, and that these plant species were less sensitive to K shortage than to N deficiency.

Key words: N:K ratio, fertilisation, growth experiment, stoichiometry indices, wetlands.

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REAKCJA DWÓCH GATUNKÓW TRAW Z SIEDLISK PODMOKŁYCH NA ZRÓŻNICOWANE DAWKI N:K W DWULETNIM DOŚWIADCZENIU KONTROLOWANYM

Abstrakt

W ostatnich latach w wyniku antropopresji na obszarach wodno-błotnych obserwuje się zmiany dostępności związków biogennych. Zmiana czynnika limitującego, w szczególności azotu, na rzecz fosforu i potasu wpływa na zmiany składu gatunkowego roślinności, efektowność poboru związków biogennych przez rośliny, wzrost roślin, konkurencję międzygatunkową oraz inne ich parametry. Badania wskazują, że wskaźniki stechiometryczne zawartości biogenów w roślinach, takie jak N:P i N:K, mogą być dobrymi indykatorami czynnika limitującego wzrost roślin na mokradłach. Jednak zastosowanie stosunku N:K w odniesieniu do roślinności mokradeł jest dotąd w niewielkim stopniu rozpoznane.

W celu wyznaczenia krytycznej wartości stosunku zawartości azotu do potasu (N:K) w biomasie roślin, wskazującego, który z biogenów jest czynnikiem limitującym wzrost roślin na obszarach podmokłych, przeprowadzono doświadczenie kontrolowane w warunkach szklarniowych. Reakcja dwóch gatunków roślin *Holcus lanatus* i *Molinia caerulea* na nawożenie zróżnicowanymi dawkami azotu i potasu była badana w okresie dwóch lat. Wpływ nawożenia N i K na produkcję nadziemnej biomasy roślin, zawartość związków biogennych oraz resorpcję biogenów badano w sześciu kombinacjach stosunku N do K (od 0.5 do 225) na dwóch poziomach nawożenia – niskim i wysokim (3 x niski). Dawki azotu przy niskim poziomie nawożenia wahały się od 9.30 mg do 146.69 mg wazon^{-1} rok^{-1}, a potasu od 18.53 do 0.65 mg wazon^{-1} rok^{-1}. Nadziemna biomasa roślin zwiększała się wraz ze wzrostem stosunku N:K w przypadku niskiego poziomu nawożenia w ciągu dwóch lat. Statystycznie istotne różnice stwierdzono nie tylko między badanymi gatunkami traw, ale także między analizowanymi latami. W pierwszym roku badań największą biomasę wytworzył *Holcus lanatus,* gdy stosunek N:K wynosił 4,5, natomiast *Molinia caerulea,* gdy stosunek N:K wynosił 225. W drugim roku wegetacji największą biomasę wytworzyły obydwa gatunki w przypadku nawożenia N:K równego 13,5, ale tylko przy wysokim poziomie nawożenia. Mimo iż reakcja badanych traw na nawożenie była analogiczna, to różnice w zawartości N i K w komórkach tych roślin uniemożliwiają wyznaczenie granicznej wartości N:K, która wskazałaby składnik limitujący wzrost roślin. Wykazano, że stosunek N:K w aplikowanych nawozach był lepszym wskaźnikiem oceny reakcji roślin na zmianę dostępności związków biogennych niż stosunek N:K wyznaczony na postawie koncentracji N i K w roślinach. Zróżnicowane reakcje badanych traw w przypadku wysokiego i niskiego poziomu nawożenia wykazały, że azot był głównym czynnikiem limitującym wzrost roślin. Analizowane trawy były mniej wrażliwe na niedobory potasu niż na niedobór azotu. Niedobór potasu był obserwowany tylko wówczas, gdy dawki nawożenia azotowego były bardzo wysokie.

Słowa kluczowe: stosunek N:K, nawożenie, eksperyment kontrolowany, wskaźniki stechiometryczne, mokradła.

INTRODUCTION

Human activities such as farming, flood control, mowing, grazing, natural environment conservation and management have impacts on natural or semi-natural vegetation. Global environmental changes, e.g. anthropogenic eutrophication, high atmospheric N deposition or acidification, have resulted in changes in nutrient availability (VITOUSEK, HOWARTH 1991, VERHOEVEN et al.

1996a,b, Bobbink et al. 1998, Rustad et al. 2001). Nutrient enrichment of an ecosystem causes changes of plant species composition, primary productivity, nutrient use efficiency, plant growth, interspecific competition and plant species performance (Verhoeven et al. 1996a,b, Güsewell et al. 2005). It is usually associated with an increase in biomass productivity and a decrease in the diversity of plant communities in all the succession stages and with shifts in the dominance of species (Olde Venterink et al. 2003, Roem, Berendse 2000, Güsewell et al. 2005).

The biomass production by wetland plants is most commonly limited by the availability of N, P and/or K. Fertilization experiments have shown that biomass production is generally limited by N in young fens, whereas old fens, which are mown and harvested for over 40 years, tend to be limited by P and/or by K (Oomes et al. 1996, Olde Venterink et al. 2003, Olde Venterink et al. 2009). It has been suggested that addition of a limiting nutrient enhances the biomass production but supplementation with a non-limiting nutrient will have little or no effect (Vitousek, Howarth 1991, Verhoeven et al. 1996b). However, simultaneous limitation by two nutrients might also occur. Besides, different species may show different responses to various nutrients, depending on their ability to take up and use a certain nutrient, their nutrient requirements or on their responsiveness to enhanced nutrient supply (Perez-Corona, Verhoeven 1999, El-Kahloun et al. 2000, Güsewell et al. 2003b).

The relative availability of N and P in soil is reflected in the concentrations of these nutrients in plant tissues (Verhoeven et al. 1996a, Güsewell, Koerselman 2002). Several fertilization studies carried out on wetlands have shown that N:P ratios in plant biomass are a good indicator of nutrient limitation (Koerselman, Meuleman 1996, Güsewell et al. 2003a). Some studies have suggested that a decreased species diversity, changes in nutrient use efficiency, plants growth, interspecific competition and plant species performance are associated with increasing N:P or N:K ratios (Verhoeven et al. 1996a, Roem, Berendse 2000, Seastedt, Vaccaro 2001) but these mechanisms are not well understood. The N:K and P:K ratios are less frequently used as indicators due to shortage of information (Hoosbeek et al. 2002, Olde Venterink et al. 2003, Lawniczak et al. 2009). Therefore, the recognition of a N:K ratio in wetland plant tissues can be a useful method for diagnosing nutrient limitation, which can be a helpful tool for wetland protection (Olde Venterink et al. 2009).

According to field studies, a critical N:K biomass ratio ranges from 1.75 to 2.1 (de Wit, 1963, Olde Venterink et al. 2003). Hoosbeek et al. (2002) suggested a critical N:K ratio of 1.2 and 1.4 for bog vegetation, indicating that either N or K can be a limiting factor. The N:K ratio < 1.2 indicated N-limitation and sites with N:K > 1.4 were characterised by K-limitation, whereas the ones with N:K between 1.2 and 1.4 were co-limited by N and K. In fertilisation experiments, limitation by K was observed only where the

N:K ratio for whole vegetation was higher than 2.1 (Olde Venterink et al. 2003). However, a study of Lawniczak et al. (2009) in a controlled experiment showed an increase in biomass production following K fertilisation at a biomass N:K ratio around 4.0. However, that experiment was conducted only for one year. As suggested by a study of Güsewell et al. (2003b), a similar response of the shoot biomass N:P ratio to N and P nutrient supply was observed after many years, as determined in field fertilisation experiments. This raised the need to study the N:K ratio over more than one vegetation season (Lawniczak et al. 2009) in order to recognise whether it can be used as an indicator of nutrient limitation in wetlands.

In order to estimate a critical N:K ratio which can indicate the type of nutrient limitations, a greenhouse experiment has been established. Another aim of the study has been to test the response of two grass species to the range of N and K supply within two years.

MATERIAL AND METHODS

The two plant species included in the experiment are common herbaceous grasses: *Holcus landaus* L. (Yorkshire-fog) and *Molinia caerulea* (L.) Moench, Meth. (Purple Moor Grass). These species occur at sites different in nutrient availability. *Holcus lanatus* prefers nutrient-rich wet meadows, in contrast to *Molinia caerulea*, which favours nutrient-poor sites with fluctuating groundwater levels (El-Kahloun et al. 2000).

The experiment was carried out in a greenhouse of the Department of Ecology and Environmental Protection, at the Poznan University of Life Sciences, from April 2009 to September 2010. In March 2009, seeds of two grasses were sown on wet substrate and germinated until a sufficient number of plants reached the height of 6 cm. Seeds were obtained from the Plant Breeding and Acclimatization Institute (IHAR) in Bydgoszcz. At the beginning of May, seedlings were transplanted to polyethylene pots of 15×15 cm width and 25 cm height. Pots were filled with pure quartz sand (source: Antoninek Glassworks, Poznań) and placed in 4 l buckets filled with deionised water. Pots were regularly shifted around the greenhouse to prevent heterogeneity in light and temperature. In winter, the plants were stored outdoors. However, all the pots were isolated to prevent nutrient and water supply. In March, the plants were moved back to the greenhouse to continue the experiment. Some specimens died during the first vegetation season or did not survive the winter. Therefore, some combinations consisted of only three replicates.

The design of the experiment was based on some previous greenhouse investigations, which focused on the effect N:K and N:P supply ratios on plant growth (Güsewell et al. 2003b, Lawniczak et al. 2009). The treatments combined six N:K supply ratios with two nutrient levels of fertility (high and low). Each combination consisted of four replicates. In total, 48 pots of *Holcus lanatus* and 48 pots of *Molinia caerulea* were analysed.

Each plant received 5 ml of KCl and NH_4NO_3 solution and 2 ml of the appropriate solution weekly during 15 weeks in 2009 (June-September) and during 16 weeks in 2010 (May-August). The first application of nutrients began three weeks after transplanting seedlings into their pots. The fertility levels were calculated using the geometric mean of the total amount of N and K supplied per plant over the entire growth period (Table 1). Additionally, an N:K ratio supply of 225 was added. The high nutrient supply level was three-fold higher than the low one (Table 1). Furthermore, all other nutrients were supplied in non-limiting amounts (10 mg P, 52 mg Ca, 16 mg Mg, 15 mg S, 5 mg Fe, 0.03 mg Cu, 0.5 mg B, 0.24 mg Mn, 0.1 mg Mo, 0.12 mg Zn per pot). Stock solutions and water were prepared every two weeks. Every week, the applied solution was adjusted to pH of approximately 7.0, using diluted HCl, and added to pots using a pipette. Every three weeks, pots were leached with deionised water to prevent toxic effect of nutrient accumulation.

Table 1

Annual amounts of N and K supplied per pot at six N : K supply ratios and two fertility levels (high supply = 3 x low supply)

N : K supply ratio	Level of supply	mg N	mg K
0.5	high	27.90	55.60
1.5	high	48.30	32.10
4.5	high	83.50	18.60
13.5	high	144.50	10.70
40.5	high	250.00	6.17
225	high	440.07	1.96
0.5	low	9.30	18.53
1.5	low	16.10	10.70
4.5	low	27.83	6.20
13.5	low	48.17	3.57
40.5	low	83.33	2.06
225	low	146.69	0.65

Every year, plants were harvested after 3-4 months of growth, i.e. on 4th September in the first year and on 5th September in the second year. Shoots were clipped 1 cm above ground. The collected material was separated into living and senescent parts. During the growing seasons, senescent leaves were collected every two weeks, dried and weighed. All harvested material was dried for 48 h to constant mass and weighed. For further nutrient analyses, four replicates per species and treatment were ground and digested with a modified Kjeldahl procedure (1 h at 200°C and 340°C in a mixture of concentrated sulphuric acid, salicylic acid, copper, and selenium) (Bremner and

Mulvaney 1982). N concentrations in the diluted digested material were determined colorimetrically on a Srecord 40, and K concentrations were assessed with flame emission spectroscopy, on a Shewood Model 425.

Statistical analysis

All statistical analyses were performed using Statistica (StatSoft, Poland) software. Shoot biomass (living parts only), senescent shoot biomass, N and K concentrations and the N:K ratio of shoots and senescent leaves were square-transformed to assess the homogeneity of variance. Four-way interactions of the effect of species, N:K supply ratios, nutrient supply levels and time on the studied variables were tested with analyses of variance (ANOVA).

RESULTS

Nutrient supply influenced significantly all variables used to describe the plant growth of the analysed species (Table 2). In general, the shoot biomass depended more strongly on the fertility levels than on N:K supply ratios, whereas the N and K concentrations, as well as N:K biomass ratios were determined by the N:K supply ratios. Four-way differences between N:K supply ratios, fertility levels, plant species and studied years were significant with respect to N:K biomass ratios and senescent biomass. However, this effect was much weaker than the main effects (Table 2).

The aerial biomass increased with an increasing N:K ratio supply during the first vegetation season (Table 2). The shoot biomass ranged from 1.15 g to over 93.23 g during the first year and from 18.68 to 314.8 g during the second year (Figure 1). In 2009, the biomass was significantly lower than in 2010, particularly at the low fertility level. *Holcus lanatus* had higher shoot biomass than *Molinia caerulea* during both years. The maximum shoot biomass differed not only between the species but also among the N:K ratios. In 2009, the optimal N:K supply ratio was 4.5 for *Holcus lanatus* at the high fertility level. At the low fertility level for both species, as well as at the high fertility level for *Molinia caerulea*, the maximum shoot biomass occurred at the 13.5 supply ratio (Figure 1). In 2010, the optimal N:K supply ratio was similar for both grasses; at the high fertility level, the shoot biomass was the highest for the N:K supply ratio of 13.5; at the low level, the shoot productivity reached the peak at the 225 N:K supply ratio.

The senescent biomass increased with increasing N:K supply ratios (Figure 2). It was significantly higher at the high fertility level and improved during the second vegetation season. *Holcus lanatus* was characterised by significantly faster senescence than *Molinia caerulea*, suggesting its higher biomass turnover.

Table 2

Results of the factorial four-way ANOVA testing of the effects of a N : K supply ratio, level of nutrient supply (low and high; high = 3 x low), time (two vegetation seasons) and plant species on aerial biomass, living shoot biomass, senescent shoot mass, nutrient concentrations (mg g^{-1}) and N : K ratios in shoot biomass. All variables were square-root transformed. Data are F-ratios and significance levels given as***.$p < 0.001$; ***.$p < 0.01$; *.$p < 0.05$; ns.$p \leq 0.05$

Effect	df	Aerial biomass		Shoot biomass		Senescent biomass		N con.		K con.		N : K	
		F	Sig	F	F	Sig.	F	F	Sig.	F	Sig.	F	Sig.
Species	1	57.41	***	54.99	***	501.20	***	0.12	ns	101.72	***	146.73	***
N : K supply ratio	5	31.90	***	31.70	***	58.26	***	489.19	***	292.05	***	420.38	***
Fertility level	1	210.96	***	210.64	***	31.92	***	298.63	***	16.44	***	73.25	***
Year	1	966.44	***	960.66	***	487.70	***	700.07	***	92.65	***	58.56	***
N : K × species	5	4.00	**	4.12	**	6.77	***	17.95	***	3.44	**	5.89	***
Species × level	1	0.09	ns	0.09	ns	1.49	ns	0.04	ns	35.99	***	1.34	ns
Species × year	1	293.31	***	294.66	***	6.34	*	163.02	***	293.16	***	135.95	***
N : K × level	5	21.71	***	21.66	***	7.77	***	100.42	***	23.24	***	35.84	***
N : K × year	5	4.22	**	4.26	**	3.49	**	3.62	**	13.36	***	21.81	***
Level × year	1	4.02	*	3.97	*	4.97	*	39.62	***	34.62	***	24.01	***
Species × N : K × level	5	10.71	***	10.73	***	9.83	***	2.97	*	7.95	***	6.06	***
Species × N : K × year	5	4.14	**	4.20	**	8.20	***	18.59	***	13.85	***	6.55	***
Species × level × year	1	0.04	ns	0.04	ns	3.84	ns	23.22	***	7.61	**	10.84	**
N : K × level × year	5	18.90	***	18.98	***	2.22	ns	21.72	***	2.97	*	7.78	***
Species × N : K × level × year	5	1.20	ns	1.21	ns	2.78	*	2.85	*	2.02	ns	6.43	***

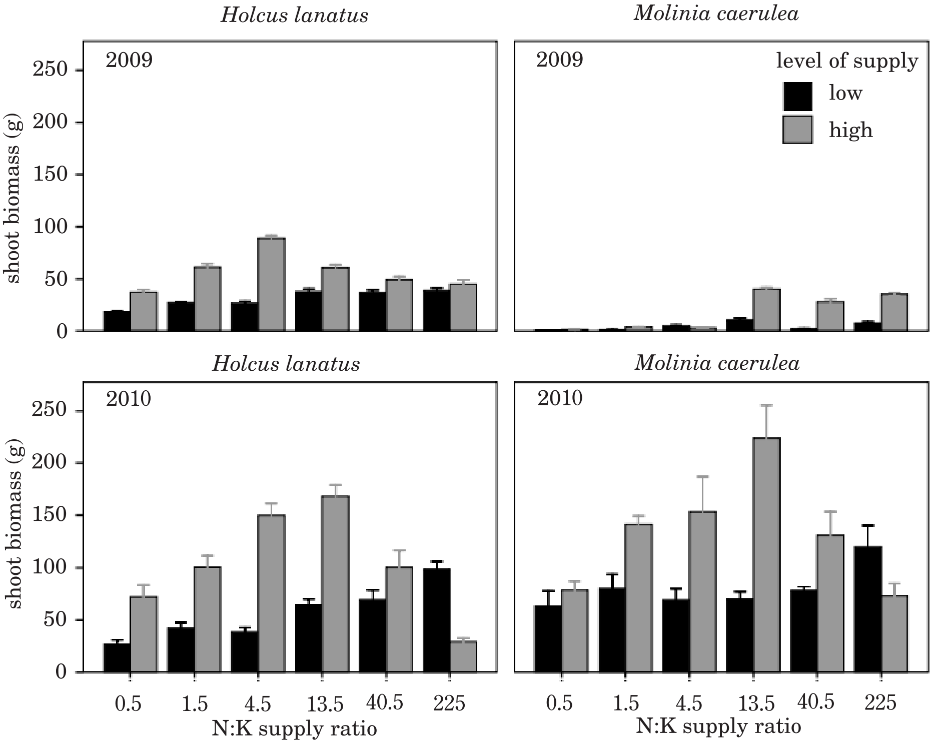

Fig. 1. Shoot biomass of two grass species grown for two years (2009 and 2010) at six N : K supply ratios and two levels of nutrient supply (low and high supply; high supply = 3 * low supply). Data are means ± se. $n = 4$

Nutrient concentrations in both species differed between the nutrient treatments (Table 2, Figs 3, 4). N concentrations generally increased with high N supply (Figure 3), whereas K concentrations increased with high K and declined with high N supply (Figure 4). In the first year, this effect was much stronger than in the second one. However, increased N concentrations were mostly observed at N:K supply ratios above 13.5 at the high fertilization level. During the second year, this effect was detected at 40.5 and 225 N:K supply ratios. At the low level, reduction of N was observed during both years, except for *Holcus lanatus*. K concentrations decreased twofold between the lowest and highest N:K supply ratios. The grasses responded quite similarly to the treatments. However, some differences between the species were observed. *Holcus lanatus* had higher K concentrations in the second year than *Molinia caerulea*.

The N:K ratio of shoot biomass increased eleven-fold across the range of N:K supply ratios (Figure 5). In the first year, the N:K ratios of *Holcus lanatus* and *Molinia caerulea* covered the same range of values in response to the N:K supply ratios. In the second year, the biggest changes were ob-

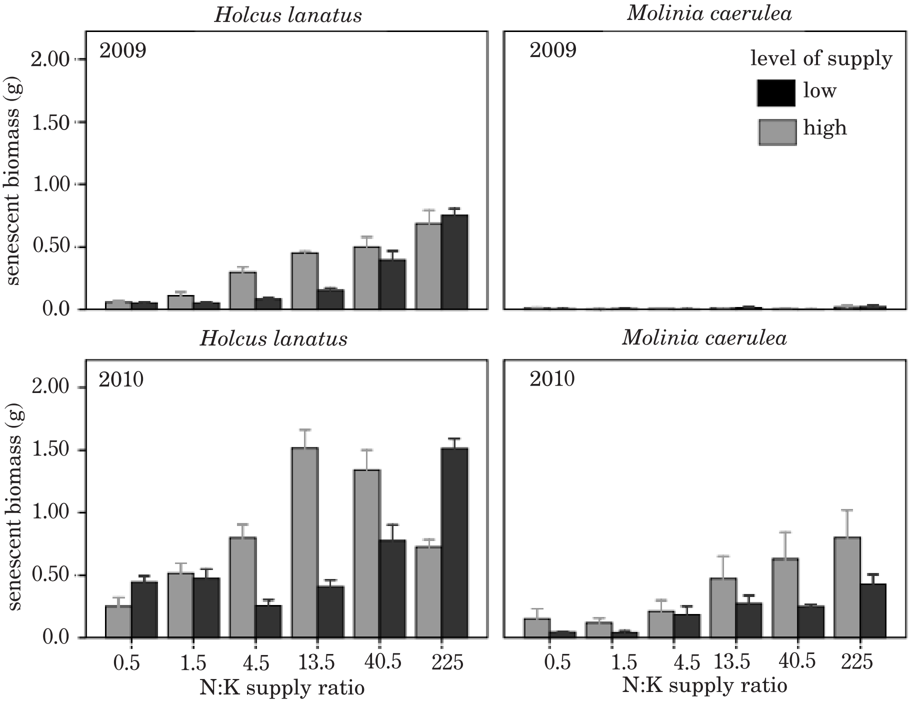

Fig. 2. Senescent biomass of two grass species grown for two years (2009 and 2010) at six N:K supply ratios and two levels of nutrient supply (low and high supply; high supply = 3 × low supply). Data are means ± se. n = 4

served in *Molinia caerulea*; its N:K biomass ratios increased twenty-fold at the high fertility level. At the N:K supply ratio of 13.5, the N:K biomass ratio was the highest and remained at that level even when N supplies increased. The N:K biomass ratios in *Holcus lanatus* increased with enhanced N:K supply ratios during both years.

Nutrient concentrations in senescent leaves, analysed only during the second year of growth, strongly depended on the nutrient treatments and varied considerably between the plant species. N concentrations during leaf senescence decreased by 5-65% (Figure 6a). The main differences appeared in *Holcus lanatus* at both fertilisation levels. K concentrations decreased by 25-98% during senescence (Figure 6b). Reduction of K was generally similar in both grass species, except *Holcus lanatus* at the 225 N:K supply ratio at the high fertility level. At the highest N:K supply ratios, K concentrations in senescent shoot parts were 77–97% lower than in living shoots. These differences were comparable to the results obtained in one-year fertilisation experiments (LAWNICZAK et al. 2009). Nutrient concentrations in senescent leaves indicate that substantial parts of K were withdrawn from leaves before senescence. This is one of the indicators of K deficiency, because leaching by rainfall or watering was excluded.

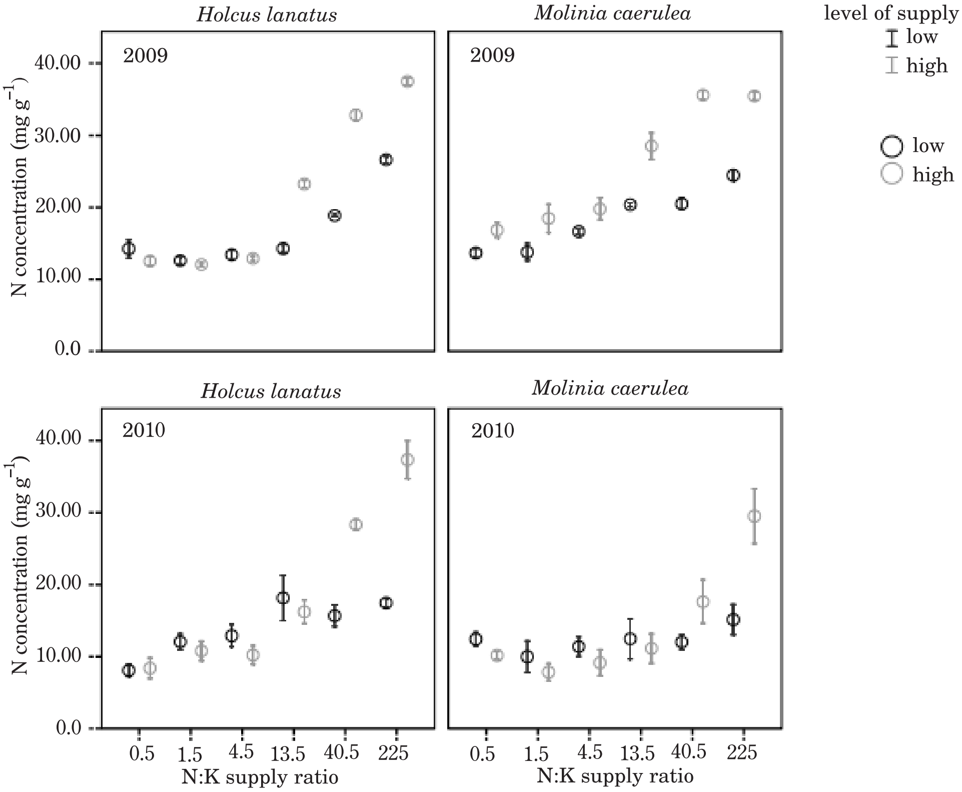

Fig. 3. Nitrogen concentrations in the living shoot parts of two grass species grown for two years at six N:K supply ratios and two levels of nutrient supply (high supply = 3 x low supply). Data are means ± se. *n* = 4

DISCUSSION

The results showed a significant effect of the N:K supply ratios on growth of the two grasses. During the first year, in both species, the biomass increased with an enhanced N:K supply ratio at the low fertility level and in *Molinia carulea* it also rose at the high fertility level, indicating that N was a limiting factor of the plant growth. At the high fertility level, *Holcus lantus* produced the highest biomass at the 4.5 N:K supply ratio, indicating the influence of K shortage on the plant growth. A shift from N-limited to K-limited growth was observed especially during the second vegetation season at the high level of nutrient supply. At the 13.5 N:K supply ratio and the high fertility level, the biomass production was the highest in both species over the entire range of N:K supply ratios. At the 40.5 and 225 N:K supply ratios, a decrease in the aerial biomass was observed, suggesting

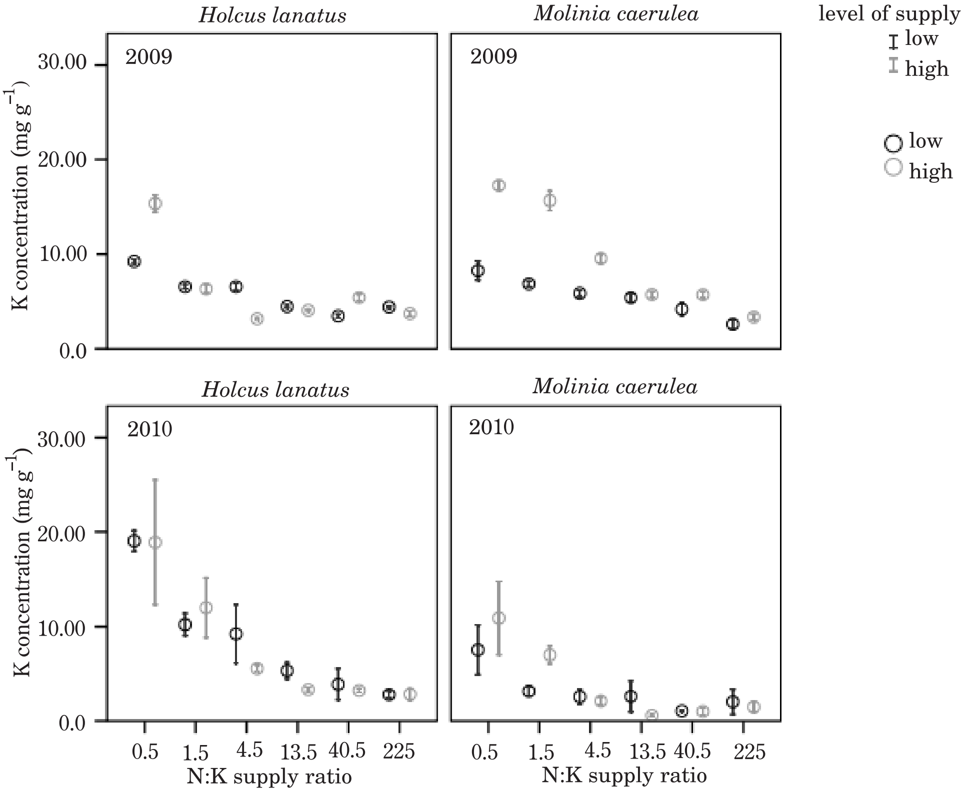

Fig. 4. Potassium concentrations in the living shoot parts of two grass species grown for two years at six N:K supply ratios and two levels of nutrient supply (high supply = 3 x low supply). Data are means ± se. *n* = 4

strong K deficiency. At the low nutrient supply level, during both years, a significant increase in biomass production between the N:K supply ratios above 13.5, 40.5 and 225 indicated that the plant growth at the 13.5 N:K supply continued to be N-limited.

However, a similar pattern of biomass production during the second year of growth occurred in both species across the range of N:K supply ratios but the N:K biomass ratios differed significantly. At the highest biomass, the N:K biomass ratio in *Holcus lanatus* was 4.5 while the N:K biomass ratio *in Molinia careulea* was very high, namely 58. These results seem to indicate that the species have different strategies of nutrient use, thus making it difficult to determine a critical N:K biomass ratio.

The shoot biomass of the tested grasses in the second year of the study was significantly higher, even at the high fertility level. This was in contrast to the N:P supply ratios, for which the biomass in the second year of experiment was higher at the low rather than high N:P supply ratios. This

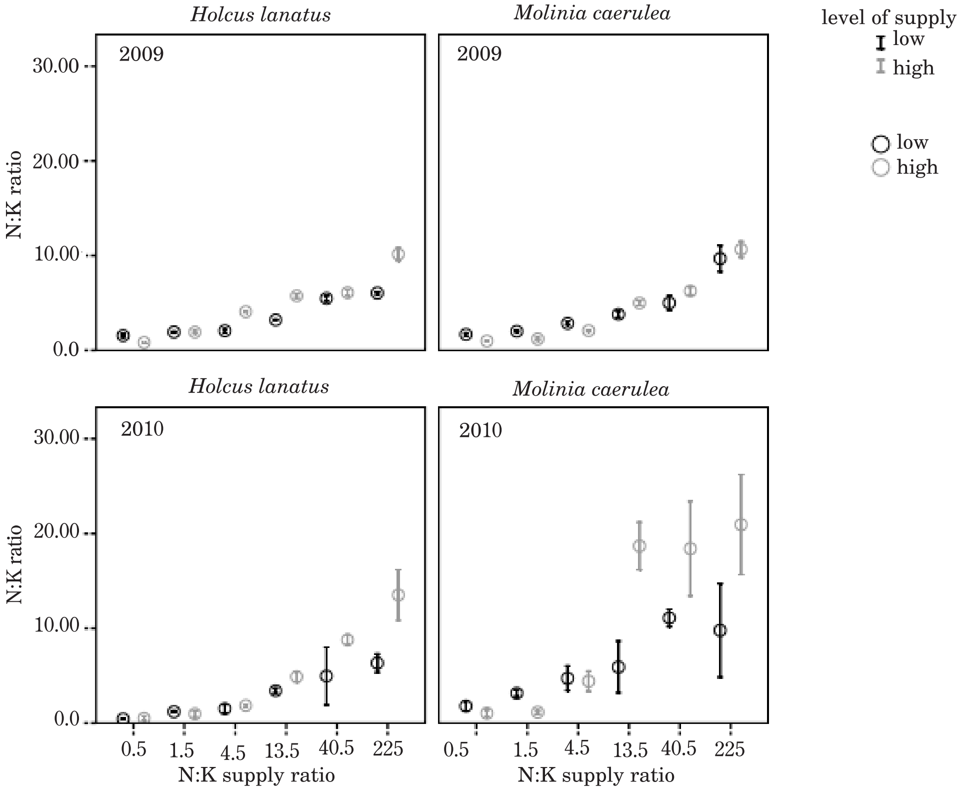

Fig. 5. The N:K biomass ratio of two grass species grown for two years at six N:K supply ratios and two levels of nutrient supply (high supply = 3 x low supply). Data are means ± se. *n* = 4

suggested that N was more important than K in limiting the plant growth between the two years.

Decreased biomass production at the 13.5 N:K supply ratio was observed in both years, indicating that strong K shortage may influence the plant growth. Lawniczak et al. (2009), in a similar type of experiment, did not observe a sharp decrease in shoot biomass between N:K supply ratios of 13.5 and 40.5, as recorded in this study. These variations may have occurred due to some specific differences between the species. On the other hand, Szczepaniak (2004) suggested that the real effect of potassium fertilization on plant yields may be expected at low available K content in soil and under water stress during the plant growth.

On the other hand, at very high N:K supply ratios, a negative effect of NH_4^+ could have occurred due to some imbalance between Mg^{+2}, Ca^{+2} and other cations (Krupa 2003). Although all pots were washed with deionised water every three weeks to prevent negative effect of NH_4^+ accumulation,

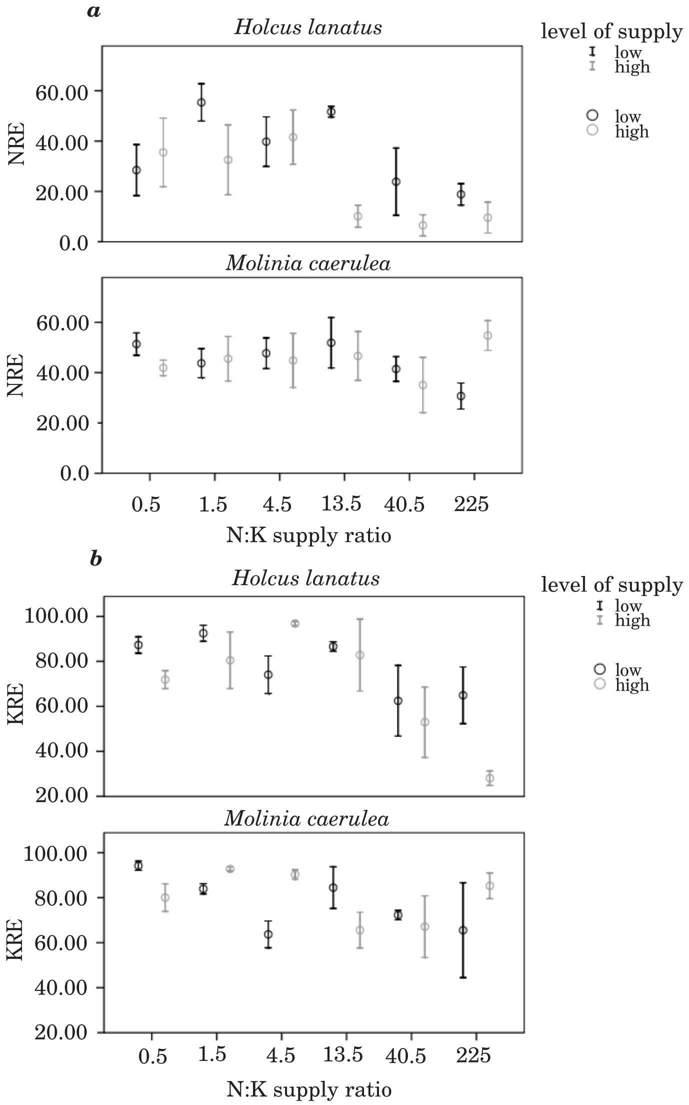

Fig. 6. Reduction in a) nitrogen and b) potassium concentrations during senescence for the two grass species in relation to the N:K supply ratios and levels of nutrient supply during the second vegetation season. Values represent the difference in nutrient concentrations between living and senesced shoot parts. as percentage of concentration in living shoot parts. Data are means ± se.

high amounts of nitrogen were added weakly. Compared to other growth experiments (Wassen et al. 1995), N concentrations of the analysed plants at the high N:K supply ratios such as 13.5 and 40.5 were generally low, with values below 20 mg g^{-1}, i.e. similar to the concentrations in the same species growing on a field (El Kahloun 2004). It was only at the high level of 225 N:K supply ratio that *Molinia caerulea* accumulated a high amount of N in plant tissues, suggesting some toxic effect of NH_4^+ accumulation. Alternatively, K concentrations were rather low, with values below 8 mg g^{-1}, which indicated strong K deficiency according to de Wit (1963) and Wassen et al. (1995). Cumulative effects of these factors could have caused decreased shoot biomass at the high level of nutrient supply.

Also, this diverse response of the studied graminoids to the N:K supply ratio may have resulted from some interspecific differences. *Holcus lanatus* is characteristic for moderately nutrient-rich sites and *Molina caerulea* grows on sites of lower fertility, particularly with strong P-limitation (El-Kahloun et al. 2000). According to Ellenberg et al. (1991), on a 1 to 9 scale, the nutrient indicator value of *H. lanatus* is 5 and that of *M. caerulea* just 1, indicating different preferences of these species to N availability in soil. In the first year of growth, these species positively correlated with Ellenberg's values; *Holcus* grew faster than *Molinia*. These results are also confirmed by the studies of Güsewell (2004) and Ryster, Lambers (1995), who observed stronger growth of species from nutrient-rich sites than from nutrient-poor ones despite low nutrient supply only in the first year of fertilisation. In the current study, this relationship disappeared in the second year only for *Molinia,* which suggested that it was less sensitive to K shortage than *Holcus*. *Molinia* was characterized by luxury consumption of the nutrient during the second year of growth. This species, at the low and high levels of nutrient supply, benefited more from available nutrients than *H. lanatus* by producing higher aerial biomass. My observations confirm the hypothesis stated by Güsewell et al. (2003b) that species from nutrient-poor sites react more readily to N supply than species from nutrient-rich sites. Also, Perez-Cordona, Verhoeven (1996) observed higher adaptation of species from poor-nutrient sites to enhanced nutrient availability.

Difficulties in estimating a critical N:K biomass ratio may have also been caused by different physiological roles of these nutrients. In an agricultural study, Marschner et al. (1996) suggested that nitrogen uptake is sufficient only at a certain amount of potassium. Gaj (2010) showed that it is important to analyse additionally Ca ions since, together with Mg and other solutes, they may partly replace K in some processes (Lindhauer et al. 1990).

Moreover, the current study did not show a similar response of the two grasses to the N:K supply ratio in the second year of growth. This response should be studied in a long-term experiment and include more species. In short-term experiments, plant species tend to produce very high biomass in a very short time (Ryster 1996, Güsewell 2004, 2005), but these differences may become smaller or disappear altogether with time (Elberse, Berendse 1993, Ryster 1996).

CONCLUSIONS

1. The response of the two grass species to the N:K supply ratios showed different patterns between the first and second years of the plant growth. During the second growing season, at the N:K supply ratio o 13.5 and the high fertility level as well as the 225 N:K supply ratio and the low fertility level, aerial biomass production was the highest in the both species.

2. The N:K biomass ratio differed between the two tested species at the maximum stand, which makes it impossible to determine a critical N:K ratio based on N and K concentrations in plant tissues.

3. The N:K nutrient supply ratio was a better indicator of plant performance than the N:K biomass ratio of the examined species.

4. The analysed graminoids did not show a similar response to N:K supply ratios at the high and low levels of supply, indicating that nitrogen was the most important factor limiting the plant growth during the two years, and that these plant species were less sensitive to K shortage than to N deficiency.

REFERNCES

BOBBINK R., HORNUNG M., ROELOFS J.G.M. 1998. *The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation a review*. J. Ecol., 86: 717-738.

DE WIT C.T., DIJKSHOORN W., NOGGLE J.G. 1963. *Ionic balance and growth of plants*. Wageningen, The Netherlands: Verslagen Van Landbouwkundige Onderzoeken, 69.15.

ELBERSE W.T., BERENDSE F. 1993. *A comparative study of the growth and morphology of eight grass species from habitats with different nutrient availabilities*. Funct. Ecol., 7: 223-229.

EL-KAHLOUN M., BOEYE D., VERHAGEN B., VAN HAESEBROECK V. 2000. *A comparison of the nutrient status of Molinia caerulea and neighbouring vegetation in a rich fen*. Belgian J. Botany, 133: 91–102.

ELLENBERG H., WEBER H.E., DÜLL R., WIRTH V., WERNER W., PAULISSEN D. 1991. *Zeigerwerte von Pflanzen in Mitteleuropa [Indicator values of plants in Central Europe]*. Scripta Geobotanica, 18: 1-248. (in German)

GAJ R. 2010. *Influence of different potassium fertilization level on nutritional status of winter wheat and on yield during critical growth stage*. J. Elementol., 15(4): 629-637.

GÜSEWELL S., KOERSELMAN W. 2002. *Variation in nitrogen and phosphorus concentrations of wetland plants.* Persp. Plant Ecol. Evol. System., 5(1): 37-61.

GÜSEWELL S, KOERSELMAN W, VERHOEVEN J.T.A. 2003a. *N:P ratios as indicators of nutrient limitation for plant populations in wetlands*. Ecol. Appl., 13: 372-384.

GÜSEWELL S., BOLLENS U., RYSER P., KLÖTZLI F. 2003b. *Contrasting effects of nitrogen, phosphorus and water regime on first- and second-year growth of 16 wetland plant species*. Funct. Ecol., 11: 754-765.

GÜSEWELL S. 2004. *Responses of wetland graminoids to the relative supply of nitrogen and phosphorus*. Plant Ecol., 176(1): 35-55.

GÜSEWELL S. 2005. *High N:P ratios reduce nutrient retention and second-year growth of wetland sedges*. New Phytologist, 165: 537–550.

GÜSEWELL S., BAILEY K. M., ROEM W. J., BEDFORD B.L. 2005. *Nutrient limitation and botanical diversity in wetlands: can fertilisation raise species richness*? OIKOS, 109: 1-71.

Hoosbeek M.R., Van Breemen N., Vasander H., Buttler A., Berendse F. 2002. *Potassium limits potential growth of bog vegetation under elevated atmospheric* CO_2 *and N deposition*. Global Change Biology, 8(11): 1130-1138.

Koerselman W., Meuleman A.F.M. 1996. *The vegetation N : P ratio: a new tool to detect the nature of nutrient limitation*. J. Appl. Ecol., 33: 1441-1450.

Krupa S.V. 2003. *Effects of atmospheric ammonia* (NH_3) *on terrestrial vegetation: a review*. Environ. Pollut., 124: 179-221.

Lawniczak A.E., Güsewell S., Verhoeven J.T.A. 2009. *Effect of N:K supply ratios on the performance of three grass species from herbaceous wetlands*. Basic Appl. Ecol., 10(8): 715-725.

Lindhauer M.G., Haeder H.E., Beringer, H. 1990. *Osmotic potentials and solute concentrations in sugar beet plants cultivated with varying potassium/sodium ratios*. Zeitschrift für Pflanzenernährung und Bodenkunde, 153: 25-32.

Marschner, H., Kirkby, E. A., Cakmak, I. 1996. *Effect of mineral nutritional status on shoot-root partitioning of photo assimilates and cycling of mineral nutrients*. J. Exp. Bot., 47: 1255-1263.

Olde Venterink H., Wassen M., Verkroost A.W.M., de Ruiter P.C. 2003. *Species richness-productivity patterns differ between N-, P-, and K-limited wetlands*. Ecology, 84: 2191-2199.

Olde Venterink H., Kardel I., Kotowski W., Peeters W., Wassen M.J. 2009. *Long-term effects of drainage and hay-removal on nutrient dynamics and limitation in the Biebrza mires, Poland*. Biogeochemistry, 93: 235–252.

Oomes M.J.M., Olff H., Altena H.J. 1996. *Effects of vegetation management and raising the water table on nutrient dynamics and vegetation change in a wet grassland*. J. Appl. Ecol., 33: 576-588.

Perez-Corona M.E., Verhoeven J.T.A. 1999. *Biomass allocation and phosphorus productivity of Carex species in relation to soil phosphorus status*. Israel J. Plant Sci., 47, 97-102.

Roem W.J., Berendse F. 2000. *Soil acidity and nutrient supply ratio as possible factors determining changes in plant species diversity in grassland and heathland communities*. Biol. Conserv., 92: 151-161.

Rustad L.E., Campbell J.L., Marion G.M., Norby R.J., Mitchell M.J., Hartley A.E., Cornelissen J.H.C., Gurevitch J., GCTE-NEWS. 2001. *A meta-analysis of the response of soil respiration, net nitrogen minerlization, and aboveground plant growth to experimental ecosystem warming*. Oecologia, 126: 543-562.

Ryster P. 1996. *The importance of tissue density for growth and life span of leaves and roots: a comparison of five ecologically contrasting grasses*. Funct. Ecol., 10: 717-723.

Ryster P., Lambers H. 1995. *Root and leaf attributes accounting for the performance of fast- and slow-growing grasses at different nutrient supply*. Plant Soil, 170: 251-265.

Seastedt T.R., Vaccaro L. 2001. *Plant species richness, productivity and nitrogen and phosphorus limitations across a snowpack gradient in alpine tundra, Colorado, USA*. Arctic, Antarctic and Alpine Res., 33: 100–106.

Szczepaniak W. 2004. *The effect of potassium fertilization on the yielding of cultivated plants*. J.Elementol., 9(4): 57-66.

Verhoeven J.T.A., Beltman B., de Caluwe H. 1996a. *Changes in plant biomass in fens in the Vechtplassen area, as related to nutrient enrichment*. Nether. J. Aquat. Ecol., 30: 227-237.

Verhoeven J.T.A., Koerselman W., Meuleman A.F.M. 1996b. *Nitrogen- or phosphorus-limited growth in herbaceous, wet vegetation: relations with atmospheric inputs and management*. Trends Ecol. Evol., 11: 494-497.

Vitousek P.M., Howarth R.W. 1991. *Nitrogen limitation on land and in the sea: how can it occur?* Biogeochemistry, 13: 87-115.

Wassen M, Olde Venterink H., de Swart E. 1995. *Nutrient concentrations in mire vegetation as a measure of nutrient limitation in mire ecosystem*. J.Veg.Sci., 6: 5-16.

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CONTENT OF BIOELEMENTS AND TOXIC METALS IN HONEY OF VARIOUS BOTANICAL ORGIN FROM LOWER SILESIA

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Abstract

Analyzing the content of bioelements and toxic metals in honeys of various botanical origin is important for the consumers' health. In addition, many authors notice that results of such analyses can help to identify the botanical and geographical origin of honey and to use the product as a bioindicator of the overall contamination of the environment.

The content of As, Cd, Pb, Zn, Cu, Mn, Ni, Mg, Fe, Cr was determined in samples of nectar honey (acacia, linden, goldenrod, multifloral, buckwheat, oilseed rape) originating from some areas in the Province of Lower Silesia unexposed to industrial and traffic emissions. In order to demonstrate differences in concentrations of the metals in particular honey samples, one-factor analysis of variance or the Kruskal-Wallis test was applied, and the correlation between levels of individual metals in the honeys was investigated. Similarities between the honeys with regard to the metal content were determined using Ward's method of cluster analysis.

Among the analyzed nectar honeys from Lower Silesia, the content of zinc was the highest in linden flower honey (13.41 mg kg^{-1}), copper and manganese – in buckwheat (1.50 mg kg^{-1} and 9.40 mg kg^{-1}, respectively), nickel – in multifloral (1.03 mg kg^{-1}) and buckwheat (1.25 mg kg^{-1}), magnesium – in goldenrod (29.6 mg kg^{-1}) and iron – in linden flower (2.11 mg kg^{-1}) and goldenrod (2.00 mg kg^{-1}) honeys. The content of arsenic, cadmium and lead did not exceed the permissible values, i.e. 0.20, 0.03 and 0.30 mg kg^{-1}. The correlation analysis performed on the concentrations of the metals in the honeys demonstrated that manganese was positively correlated with copper and nickel, while iron correlated with zinc.

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Oilseed rape and acacia, as well as multifloral and goldenrod honeys were most similar to each other in the accumulation of the metals. Using the accumulation of metals in honey as a bioindicator of environmental pollution should be verified on material originating from areas where there are differences in the content of especially dangerous metals, cadmium and lead in particular.

Key words: honey, honey variety, bioelements, metals, bioindicator.

ZAWARTOŚĆ BIOPIERWIASTKÓW I METALI TOKSYCZNYCH W MIODACH O RÓŻNYM POCHODZENIU BOTANICZNYM Z DOLNEGO ŚLĄSKA

Abstrakt

Badanie zawartości biopierwiastków i metali toksycznych w miodach o różnym pochodzeniu botanicznym ma przede wszystkim znaczenie z uwagi na zdrowie konsumentów. Wielu autorów zauważa też możliwość kategoryzacji na tej podstawie pochodzenia botanicznego i geograficznego miodu, a także stosowania tego produktu jako bioindykatora łącznego skażenia środowiska.

W próbkach miodów nektarowych: akacjowego, lipowego, nawłociowego, wielokwiatowego, gryczanego i rzepakowego pochodzących z terenów województwa dolnośląskiego w niewielkim stopniu narażonych na oddziaływanie emisji przemysłowych i komunikacyjnych określono zawartość: As, Cd, Pb, Zn, Cu, Mn, Ni, Mg, Fe, Cr. Do wykazania różnic w zawartości metali w poszczególnych odmianach miodu zastosowano test jednoczynnikowej analizy wariancji lub test Kruskala-Wallisa. Zbadano korelacje między zawartością poszczególnych metali w miodach. Do określenia podobieństwa odmian miodów pod względem gromadzenia metali zastosowano analizę skupień, używając metody Warda.

Spośród miodów nektarowych pochodzących z Dolnego Śląska najwięcej cynku zawierał miód lipowy (13,41 mg kg^{-1}), miedzi i manganu – gryczany (odpowiednio 1,50 mg kg^{-1} i 9,40 mg kg^{-1}), niklu – wielokwiatowy (1,03 mg kg^{-1}) i gryczany (1,25 mg kg^{-1}), magnezu – nawłociowy (29,6 mg kg^{-1}), a żelaza – lipowy (2,11 mg kg^{-1}) i nawłociowy (2,00 mg kg^{-1}). Zawartość arsenu, kadmu i ołowiu nie przekroczyła dopuszczalnych wartości, tj. odpowiednio 0,20, 0,03 i 0,30 mg kg^{-1}. Analiza korelacji zawartości poszczególnych metali w miodach pozwoliła stwierdzić, że zawartość manganu była dodatnio skorelowana z zawartością miedzi i niklu, a żelaza z cynkiem.

Największe podobieństwo, jeśli chodzi o kumulację metali, wykazały miody rzepakowy i akacjowy oraz wielokwiatowy i nawłociowy. Wykorzystując ten fakt do bioindykacji skażenia środowiska, należałoby zweryfikować go na materiale pochodzącym z obszarów, gdzie wystąpiłyby różnice w zawartości metali szczególnie niebezpiecznych, zwłaszcza kadmu i ołowiu.

Słowak kluczowe: miód, odmiana miodu, biopierwiastki, metale, bioindykator.

INTRODUCTION

In recent years, there has been an increasing interest in analyzing metallic elements in bee honey, reflected by a growing body of the relevant literature (POHL 2009). The research is stimulated by the importance of honey in human diet. Honey is a source of many vital elements (KOT, ZARĘBA 2008). However, when present in excessive amounts, some of these elements may become a health hazard.

The content of mineral components in honey is affected by the soil in the area where the nectar is collected and by the plant speciation. Studying the content of elements in honeys may therefore be useful for classification of honeys with respect to their geographical and botanical origin, and for verification of the information given by the producers (Bogdanov et al. 2007, Madejczyk, Baralkiewicz 2008, Pohl 2009).

The metals in honey are also of anthropogenic origin (mines, smelters, industrial and urbanized areas, transportation routes). Hence, the product may serve as a bioindicator of the overall contamination of soil, plants, water and air of the area where bees collect the nectar (Pohl 2009, Yazgan et al. 2006, Spodniewska, Romaniuk 2007). Cadmium and lead are among the most toxic elements in honey that have an anthropogenic origin (Bogdanov et al. 2007). However, these authors indicate difficulties in using honey for bioindication due to differences in its botanical origin.

In view of the above, it seemed recommendable to determine whether honeys of various botanical origin produced in Lower Silesia were safe for consumers, and to compare their content of bioelements, thus finding the varieties which accumulate metals to a similar extent.

MATERIAL AND METHODS

Tests have been performed on honeys made in 2007 at movable apiaries set in areas very slightly exposed to industrial and traffic emissions and situated in Lower Silesia. The content of arsenic, zinc, copper, manganese, nickel, magnesium, iron, chromium, cadmium and lead was determined in samples of acacia, linden, goldenrod, multifloral, buckwheat and oilseed rape honeys.

Honey samples were mineralized in concentrated nitric acid under pressure, in a CEM Mars 5 mineralizer. The content of the metals was assayed with the plasma spectrometry method (emission) ICP-AES and the results were expressed as mg kg^{-1} of dry mass.

In order to determine the differences in the content of the metals between the honey types, one-way analysis of variance (Fisher's test) was applied. The means were compared using Tukey's test. When the data did not meet the criteria of the classical variance analysis (a negative result of the variance homogeneity test), the non-parametric Kruskal-Wallis test was used (Statistica 7).

Correlation between the levels of individual metals in the honeys was investigated, i.e. correlation coefficients were found at the corresponding probability levels.

Similarities between the honey types in the accumulation of the metallic elements were determined by the cluster analysis of standardized data, using Ward's method and the Euclidean distance.

RESULTS AND DISCUSSION

None of the honey samples contained arsenic, cadmium and lead in excess of the allowable levels of contamination, i.e. 0.20, 0.03 and 0.30 mg kg^{-1}, respectively (*Regulation of the Minister for Health 2003*) – Table 1. Hence, in this respect, they can be deemed as safe for the health.

The highest mean content of zinc (13.41 mg kg^{-1}) was found in linden flower honey. The content of Zn in the other honey types ranged from 1.54 to 2.87 mg kg^{-1}. Significantly less zinc than in linden honey appeared in buckwheat and oilseed rape honeys (Table 1). Linden honey was found to contain more zinc than acacia or oilseed rape honey in a study conducted in Switzerland by BOGDANOV et al. (2007). In unpolluted areas of Romania, the zinc content was the highest in linden honey and the smallest in oilseed rape honey (BRATU, GEORGESCU 2005), analogously to our tests completed in Lower Silesia. In honey samples collected in various regions of Poland, the Zn content was the largest in oilseed rape and linden honeys (KOT, ZARĘBA 2008). The zinc content in linden, buckwheat and oilseed rape honeys collected in Pomerania was on average: 4.33, 6.66 and 4.17 mg kg^{-1}, respectively (PRZYBYŁOWSKI, WILCZYŃSKA 2001).

Significantly the highest amounts of copper (on average 1.40 mg kg^{-1}) were in buckwheat honey, compared to all the other varieties. Less copper in honeys was found by BOGDANOV et al. (2007): 0.180 mg kg^{-1} in acacia, 0.382 mg kg^{-1} in linden and 0.265 mg kg^{-1} in oilseed rape honey. The experiment conducted in Poland by KOT and ZARĘBA (2008) showed that buckwheat honey accumulated the largest amounts of copper (0.30 mg kg^{-1}), with linden, oilseed rape and acacia honeys to follow. A high content of copper in buckwheat honey may be due to buckwheat's ability to absorb from the soil some hardly available elements, including copper, which in soil occurs in its hardly mobile forms.

The highest content of manganese (9.40 mg kg^{-1}) was characteristic for buckwheat honey, being significantly lower in acacia (0.27 mg kg^{-1}) and oilseed rape honeys (0.45 mg kg^{-1}). Similarly to our experiment in the Lower Silesia, BOGDANOV et al. (2007) found a higher content of manganese in linden than in acacia and oilseed rape honeys, whereas KOT and ZARĘBA (2008) reported the highest manganese content in acacia and buckwheat honeys.

The content of nickel in multifloral (1.03 mg kg^{-1}) and buckwheat honey (1.25 mg kg^{-1}) was significantly higher than in oilseed rape honey (0.54 mg kg^{-1}). The study in Switzerland (BOGDANOV et al. 2007) showed less nickel (on average 0.152 mg kg^{-1}) in nectar honeys than in those of Lower Silesia.

Table 1

Range, mean and significant differences in the content of elements in various types of honey collected in the Province of Lower Silesia (mg kg^{-1})

Element	Type of honey						Mean	Significant statistical differences
	acacia (A)	linden (L)	golden-rod (GR)	multifloral (MF)	buckwheat (B)	rape (R)		
Cadmium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02		
Lead	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17		
Arsenic	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14		
Zinc	1.69-2.21 1.96	11.64-15.20 13.41	2.70-3.07 2.87	1.74-2.20 1.92	1.41-1.67 1.55	1.32-1.79 1.54	3.87	L → B. R*
Copper	0.31-0.56 0.44	0.37-.70 0.52	0.51-0.81 0.65	0.43-0.89 0.65	1.02-1.89 1.40	0.63-1.14 0.85	0.75	B → A. L. GR. MF. R**
Manganese	0.23-0.34 0.27	1.07-1.74 1.39	1.94-2.86 2.37	2.51-3.40 2.98	8.11-11.03 9.40	0.39-0.53 0.45	2.80	B → A. R*
Nickel	0.71-0.98 0.85	0.68-1.10 0.89	0.74-1.00 0.87	0.84-1.26 1.03	0.97-1.83 1.25	0.42-0.67 0.54	0.90	MF. B → R**
Magnesium	12.4-15.2 13.8	11.8-14.4 13.0	26.4-32.8 29.6	24.1-26.5 25.4	13.6-15.2 14.4	14.3-20.5 17.4	18.93	GR → A. L. MF. B. R; MF → A. L. B. R R → L**
Iron	0.86-1.30 1.08	1.78-2.44 2.11	1.87-2.13 2.00	0.98-1.32 1.15	0.93-1.37 1.15	1.16-1.70 1.43	1.49	L. GR → A. MF. B. R**
Chrome	0.071-0.137	<0.005	<0.005	<0.005	<0.005	<0.005		

Explanation: *Kruskal-Wallis test used, **Fisher test used
a → b – content of the element significantly higher in a than in b honey

The highest content of magnesium was characteristic for goldenrod (29.6 mg kg^{-1}), multifloral (25.4 mg kg^{-1}) and oilseed rape (17.4 mg kg^{-1}) honeys. More detailed information on the differences in the Ni content between honeys of different botanical origin can be found in Table 1. Higher magnesium content in nectar honeys (38.1 mg kg^{-1} on average) was found in the Czech Republic (LACHMAN et al. 2007).

Significantly more iron was determined in linden and goldenrod honeys (2.11 and 2.00 mg kg^{-1}, respectively) than in the other varieties. KOT and ZARĘBA (2008) found the highest Fe content in linden honey and the lowest - in acacia one. The Swiss experiment (BOGDANOV et al. 2007) demonstrated that acacia honey was the poorest in iron.

The content of chromium exceeded 0.005 mg kg^{-1} only in acacia honey. BOGDANOV et al. (2007) obtained values lower than 0.005 mg kg^{-1} for all the honey varieties they studied.

Differences in the content of metals between particular honey types from areas only slightly exposed to pollution are a result of the differentiated accumulation of metals in nectars of the respective varieties, which depends on the species-specific physiology of plants and the environmental conditions, especially the properties of the soil on which the nectar-bearing plants grow.

Our analysis of the correlations between the concentrations of the metals in the honeys demonstrated that manganese was positively correlated with the content of copper and nickel, while iron correlated with zinc (Table 2).

Table 2

Correlation between the analyzed elements

Element	Zn	Cu	Mn	Ni	Mg	Fe
Zn	x	-0.29	-0.22	-0.03	-0.33	**0.67**
Cu	x	x	**0.75**	0.21	-0.10	-0.18
Mn	x	x	x	**0.63**	-0.05	-0.23
Ni	x	x	x	x	0.03	-0.12
Mg	x	x	x	x	x	0.34
Fe	x	x	x	x	x	x

Explanation: in bold – significant at 0.05

The cluster analysis showed that oilseed rape and acacia honeys were the most similar varieties in terms of the content of the analyzed metals, followed by multifloral and goldenrod honeys. In this respect, buckwheat honey differed the most (Figure 1). This fact may be taken into account when verifying the botanical origin of honey and when using honey as an environmental bioindicator.

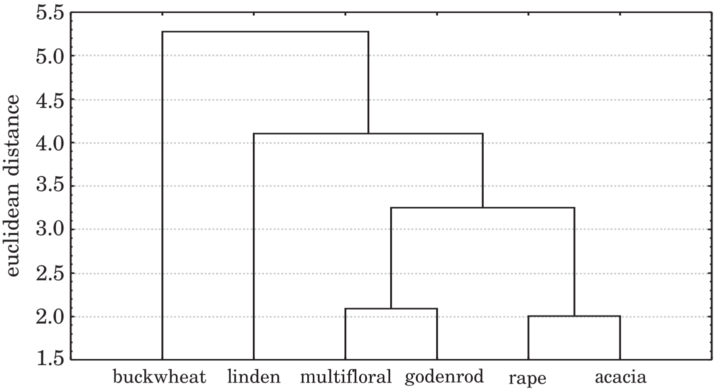

Fig. 1. Dendrogram of cluster analysis for types of honey

CONCLUSIONS

1. Among the analyzed nectar honeys made in Lower Silesia, the content of zinc was the highest in linden honey, copper and manganese – in buckwheat, nickel – in multifloral and buckwheat, magnesium – in goldenrod, and iron – in linden and goldenrod honey. The content of arsenic, cadmium and lead did not exceed the permissible values.

2. With respect to the accumulation of metals, oilseed rape and acacia honeys were most similar to each other, followed by multifloral and goldenrod honey types. Using the accumulation of metals in honey as a bioindicator of environmental pollution should be verified on material originating from areas where there are differences in the content of especially dangerous metals, cadmium and lead in particular.

REFERENCES

Bbratu I., Georgescu C. 2005. *Chemical contamination of bee honey – identifying sensor of the environment pollution.* J. Central Europ. Agric., 6 (1): 95-98.

Bogdanov S., Haldimann M., Luginbühl1 W., Gallmann P. 2007. *Minerals in honey: environmental, geographical and botanical aspects.* J. Apicultural Res. Bee World, 46(4): 269-275.

Kot A., Zaręba S. 2008. *The content of copper, zinc, iron and manganese in honey*. Ann. UMCS, Pharmacia, 21: 77-80.

Lachman J., Kolihová D., Miholová D., Košata J. ,. Titera D,. Kult K. 2007. *Analysis of minority honey components: Possible use for the evaluation of honey quality.* Food Chem., 101: 973-979.

Madejczyk M., Baralkiewicz D. 2008. *Characterization of Polish rape and honeydew honey according to their mineral contents using ICP-MS and F-AAS/AES*. Anal. Chim. Acta, 617: 11-17.

POHL P. 2009. *Determination of metal content in honey by atomic absorption and emission spectrometries*. TrAC-trend Anal. Chem., 28: 117-128.

PRZYBYŁOWSKI P., WILCZYŃSKA A. 2001. *Honey as an environmental marker*. Food Chem. 74: 289-291.

Regulation of the Minister for Health of 13th of January 2003. Journal of Law of the Poland. No 37. (*Rozporządzenie Ministra Zdrowia z dnia 13 stycznia 2003 r*. D.U. Nr 37 (in Polish).

SPODNIEWSKA A., ROMANIUK K. 2007. *Concentration of lead and cadmium in honey in randomly chosen apiaries of the Warmia and Mazury province*. Med. Wet., 63(5): 602-603). (in Polish)

YAZGAN S., HORN H., ISENGARD H.D. 2006. *Honey as a bio-indicator by screening the heavy metal content of the environment*. Deutsche Lebensmittel-Rundschau, 102(5): 192-194.

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ACCUMULATION OF POTASSIUM, MAGNESIUM, CALCIUM IN FRESH AND COLD STORED LEAVES OF LETTUCE (*LACTUCA SATIVA* L.) AFTER $CaCl_2$ FOLIAR TREATMENT BEFORE HARVEST

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Abstract

The aim of this study has been to determine the effect of foliar application of $CaCl_2$ before harvest on the accumulation of K, Mg and Ca in fresh and stored lettuce heads. The experimental material comprised cv. Omega lettuce, which was grown in a greenhouse at the Department of Cultivation and Fertilization of Horticultural Plants of the University of Life Sciences in Lublin. $CaCl_2$ solutions of the concentrations of 0.1 M and 0.2 M were sprayed over plants 20 and 10 days before harvest. After harvest, some plants were analysed immediately (fresh plants), while the remaining lettuce heads were cold-stored at 4°C for 7 and 14 days in dark polyethylene bags. The levels of dry matter, K, Mg and Ca were determined in whole leaves and leaf blades (without the midrib) of fresh and stored plants. The accumulation of dry matter, K, Mg and Ca varied depending on the leaf part, $CaCl_2$ treatment and time of storage. The Ca content was lower leaf blades than in whole leaves of fresh plants not treated with $CaCl_2$, but the K and Mg concentrations were on a similar level in both parts of leaves. The results of this study indicated that $CaCl_2$ foliar spray of plants caused higher K and Mg concentrations in whole leaves compared to the control plants (no $CaCl_2$ treatment) but decreasing Ca and K levels were observed in leaf blades without the midrib from fresh plants treated with 0.2 M $CaCl_2$. During the 14-day cold storage of lettuce, the Ca and Mg levels in decreased whole leaves but increased in leaf blades of the control plants and after the 0.2 M $CaCl_2$ treatment. Changes in the K, Mg and Ca accumulation affected the K:Mg and K:(Ca+Mg) ratios, which rose in whole leaves of stored plants compared to fresh ones.

Key words: lettuce, $CaCl_2$ treatment, potassium, magnesium, calcium, cold storage.

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AKUMULACJA POTASU, MAGNEZU I WAPNIA W ŚWIEŻYCH I PRZECHOWYWANYCH W WARUNKACH CHŁODNICZYCH LIŚCIACH SAŁATY (*LACTUCA SATIVA* L.) PO DOLISTNYM TRAKTOWANIU $CaCl_2$ PRZED ZBIOREM

Abstrakt

Celem pracy było określenie wpływu dolistnego traktowania $CaCl_2$ sałaty przed zbiorem na akumulację K, Mg i Ca w świeżych i przechowywanych główkach. Materiał badawczy stanowiła sałata odmiany Omega, uprawiana w szklarni Katedry Uprawy i Nawożenia Roślin Ogrodniczych Uniwersytetu Przyrodniczego w Lublinie. Na rośliny 20 i 10 dni przed zbiorem zastosowano roztwory $CaCl_2$ o stężeniu 0,1 M i 0,2 M. Część roślin analizowano bezpośrednio po zbiorze (rośliny świeże), natomiast pozostałe przechowywano w temp. 4°C przez 7 i 14 dni w ciemnych foliach polietylenowych. Zawartość suchej masy, K, Mg, i Ca oznaczono w całych liściach i blaszkach liściowych (bez głównego nerwu liściowego) roślin świeżych i przechowywanych. Stwierdzono, że akumulacja suchej masy, K, Mg i Ca była zróżnicowana w zależności od części liścia, stosowania $CaCl_2$ i okresu przechowywania. Zawartość Ca w blaszkach liściowych była mniejsza w świeżych roślinach nie traktowanych $CaCl_2$ niż w całych liściach, natomiast zawartość K i Mg była podobna w obu częściach liści. Wykazano, że dolistne traktowanie roślin $CaCl_2$ spowodowało zwiększenie koncentracji K i Mg w całych liściach w porównaniu z roślinami kontrolnymi (bez traktowania $CaCl_2$) natomiast w blaszkach liściowych bez głównego nerwu liściowego zaobserwowano zmniejszenie zawartości Ca i K w świeżych roślinach traktowanych $CaCl_2$ w stężeniu 0,2 M. Podczas 14 dni przechowywania sałaty w warunkach chłodniczych zawartość Ca i Mg w całych liściach zmalała, natomiast wzrosła w blaszkach liściowych roślin kontrolnych i po zastosowaniu $CaCl_2$ w stężeniu 0,2 M. Zmiany w akumulacji K, Mg i Ca miały wpływ na stosunki K:Mg i K:(Ca+Mg). Zanotowano ich zwiększenie w całych liściach roślin przechowywanych w porównaniu ze świeżymi.

Słowa kluczowe: sałata, traktowanie $CaCl_2$, potas, magnez, wapń, przechowywanie chłodnicze.

INTRODUCTION

Leaf vegetables are an important component of a balanced diet, which promotes consumption of more fruit and vegetables. Lettuce leaves, which contain vitamins C and E, carotenoids, phenolic acids with anti-free radical activity, and minerals, are an important part of the human diet. There is evidence which supports the role of mineral elements in cardiovascular diseases. Magnesium is important for the metabolic activity because it is related to many enzymes controlling the metabolism of carbohydrates, fats, proteins and electrolytes (Chakraborti et al. 2002, Haarenen 2003). Magnesium deficit and anomalies in metabolism are an important aspect when considering the aetiology of diabetes and the pathophysiology of many cardiovascular diseases in humans, such as cardiac arrhythmia, congestive heart failure, dyslipidemia, hypertension, myocardial ischaemia, atheromatosis and myocardial infraction. Its deficit gradually contracts coronary vessels, significantly blocking the flow of oxygen and nutrients to muscle fibres of the heart (Singh et al. 1997, Gazmuri et al. 2001, Chakraborti et al. 2002, Haarenen

2003). It is known that magnesium deficit distorts the balance of other important macrominerals such as calcium, potassium and sodium. This suggests some dependence between cellular ion transport mechanisms and magnesium levels (Bijvelds et al. 1997). Magnesium deficit may increase the level of intracellular Ca^{2+}, support the formation of oxygen radicals, proinflammatory factors, and induce changes in the membrane permeability and transport processes in the heart muscles (Singh et al. 1997). A high Ca:Mg ratio favours blood coagulation (Seelig 1994, Haarenen 2003).

The main macroelements, i.e. potassium, magnesium and calcium, are vital nutrients for metabolism and transport across cell membranes. They support different cellular functions, such as controlling ion charge and concentration gradients in membranes which are used in transport processes, osmosis, cytoplasmic pH regulation, stabilisation of ribosome and nucleic acid structure, activation of DNA, RNA and protein synthesis enzymes (Campo et al. 2000, Gharieb 2001).

Calcium increases the membrane permeability (Bharti et al. 1996) and may influence the growth and ageing of plants (Maksymiec, Baszyński 1998). It is one of the key initiators of signal processing in cells of higher plants, including processes such as bud formation, polar growth, control of gas exchange, light- and hormone-controlled growth and development (Bharti et al. 1996, Huber et al. 1996, Saure 1998, Ruiz et al. 1999, Burton et al. 2000).

Certain disorders in plants, for example tipburn, are related to Ca^{2+} deficiency (Saure 1998, Barta, Tibbitts 2000). It was found that calcium salts can be used for shelf stability as a firming agent in different fruit (Luna-Guzman, Barrett 2000). Lettuce is one of the vegetables whose quality is limited by a short shelf life.

The objective of this study was to determine the effect of pre-harvest foliar application of different concentrations of $CaCl_2$ on the accumulation of K^+, Mg^{2+} and Ca^{2+} in whole leaves and leaf blades (without the midrib) of fresh and cold-stored lettuce heads.

MATERIAL AND METHODS

The study involved a pot experiment conducted in a greenhouse of the Department of Cultivation and Fertilization of Horticultural Plants of the University of Life Sciences in Lublin. The experimental material comprised cultivar Omega lettuce. Two-litre pots were filled with transitional peat with the pH of 5.4 and limed to 6.4 with calcium carbonate. The peat was enriched with 4 g of superphosphate, equivalent to 0.8 g of phosphorus, per pot. The micronutrient concentrations in 2 L of the substrate were: Cu – 26.6 mg, Mn – 10.2 mg, B – 3.2 mg, Mo – 7.4 mg, Zn – 1.48 mg. The culture medium was added to the pots three times: before planting the lettuce on 17th March and twice afterwards, on 31th March and 7th April. The total content of mineral components in the medium was after planting in experiment: N – 0.7 g, K – 1.5 g and Mg – 0.45 g. The temperature in the greenhouse was maintained at 18°C at night and 23°C during the day. Two weeks after planting, the vegetables were sprayed with $CaCl_2$ solutions of two different concentrations. For this purpose, plants were divided into three groups. The first group was treated with a $CaCl_2$ solution of the concentration 0.1 M, the second one – 0.2 M, while the third group, which served as the control, was sprayed with water. The plants were sprayed twice until the first drop, 20 and 10 days before harvest. The applied $CaCl_2$ concentrations were determined during the preliminary study (Perucka et al. 2007). The experiments were carried out in a randomized block design with five replications. After harvest, some plants were analysed immediately (fresh plants), while the remaining lettuce heads were cold-stored at 4°C for 7 and 14 days in dark polyethylene bags. Five plants were sampled from each plot for chemical analysis. The plants were washed with distilled water before analysis. Leaf blades (without the midrib) and whole leaves were dissected. The prepared material was dried at room temperature, ground and mineralized in a muffle furnace at 300-500°C. The levels of K, Mg and Ca were determined in an atomic absorption spectrometer (Unicam 939/395). The content of macronutrients was determined according to the analytical curve with the method described by Perucka et al (2007). The weight ratios of Ca:Mg, K:Ca, K:Mg, K:(Ca+Mg) were also calculated.

Statistical analysis consisted of an analysis of variance (Anova), using Statgraphics v 3.1 for Windows. Tukey's test ($P<0.05$) was used to detect significant differences among the means from three replicates.

RESULTS AND DISCUSSION

The results of the study on the effect of pre-harvest $CaCl_2$ foliar application on the accumulation of potassium, magnesium, calcium and dry matter in fresh and cold-stored lettuce are presented in Tables 1 and 2. The data indicate that the dry matter ranged from 3.17% to 4.19% and depended on the concentration of $CaCl_2$ and time of storage (Table 1). Foliar $CaCl_2$ application had a statistically significant influence on modifications in the content of dry matter. It was found that more dry matter was accumulated in the whole leaves of plants treated with the $CaCl_2$ solution of the concentration of 0.2 M and in leaf blades after using the $CaCl_2$ solution of either concentration. During the storage, the level of dry matter increased in whole leaves and leaf blades compared to the control plants due to water loss.

Potassium in lettuce leaves was within the range of 43.75-63.76 g kg^{-1} of dry matter (Table 1). It generally depended on a $CaCl_2$ solution concentra-

Table 1

Concentration of dry matter and potassium in fresh and stored leaves of lettuce after foliar $CaCl_2$ treatment

Analyzed part of plant	$CaCl_2$ (M)	Dry matter (%)				K (g kg^{-1} d.m.)			
		storage time – days			$\bar{x}$	storage time – days			$\bar{x}$
		0	7	14		0	7	14	
Whole leaves	0	3.226	3.505	3.924	3.552	55.63	52.39	60.64	56.22
	0.1	3.166	3.309	3.251	3.242	63.76	55.74	63.76	61.09
	0.2	3.548	3.788	3.875	3.737	61.46	51.74	62.76	58.65
	$\bar{x}$	3.313	3.534	3.683	3.510	60.283	53.29	62.39	58.65
	$LSD_{0.05}$ for: $CaCl_2$ – I storage time – II interaction – I x II	 0.215 0.173 0.273				 3.202 4.227 5.845			
Leaf blades	0	3.265	3.737	3.428	3.477	56.91	48.32	60.49	55.24
	0.1	3.627	4.188	3.668	3.828	55.72	45.77	50.89	50.79
	0.2	3.648	3.914	3.631	3.731	43.75	54.94	60.61	53.10
	$\bar{x}$	3.513	3.946	3.576	3.379	52.127	49.677	57.33	53.04
	$LSD_{0.05}$ for: $CaCl_2$ – I storage time – II interaction – I x II	 0.144 0.175 0.257				 4.816 5.279 6.840			

tion applied during the pre-harvest foliar treatment. More potassium was noticed in the whole leaves of fresh plants after the $CaCl_2$ treatment with a solution of either 0.1 M or 0.2 M concentration; the lowest potassium content appeared in the leaf blades of plants treated with $CaCl_2$ of the concentration of 0.2 M, compared to the control. During the 14-day storage under cold conditions, the potassium level was observed to be higher in whole leaves of the control plants and after the $CaCl_2$ treatment with a solution of the higher concentration than in fresh plants.

Magnesium ranged from 3.88-6.67 g kg^{-1} of dry matter. It depended on the level of $CaCl_2$ treatment and time of storage (Table 2). In fresh plants, it increased in the whole leaves of plants after the application of $CaCl_2$ in either concentration whereas while in leaf blades it rose only when the 0.1 M solution was applied. During the 14 days of storage in cold, the magnesium concentration increased in leaf blades of the control plants and treated with the $CaCl_2$ solution of the concentration of 0.2 M, but Mg decreased in whole leaves compared to fresh plants treated with calcium chloride in the same dose.

Table 2

Concentration of magnesium and calcium in fresh and stored leaves of lettuce after foliar $CaCl_2$ treatment

Analyzed part of plant	$CaCl_2$ (M)	Mg (g kg^{-1} d.m.)				Ca (g kg^{-1} d.m.)			
		storage time – days			$\bar{x}$	storage time – days			$\bar{x}$
		0	7	14		0	7	14	
Whole leaves	0	4.074	5.285	3.929	4.429	13.42	9.321	8.190	10.31
	0.1	5.088	4.181	4.663	4.644	13.42	10.070	8.431	10.6
	0.2	5.641	4.008	4.379	4.676	12.98	10.550	9.071	10.87
	$\bar{x}$	4.934	4.491	4.324	4.583	13.27	9.982	8.564	10.60
	$LSD_{0.05}$ for: $CaCl_2$ – I storage time – II interaction – I x II	0.614 0.643 0.811				0.797 1.803 1.137			
Leaf blades	0	4.596	4.948	6.671	5.405	10.98	9.669	12.720	11.12
	0.1	5.235	3.884	4.097	4.405	11.07	9.148	9.782	10.00
	0.2	4.399	4.962	5.827	5.063	8.95	10.620	10.060	9.877
	$\bar{x}$	4.743	4.598	5.532	4.958	10.33	9.812	10.85	10.33
	$LSD_{0.05}$ for: $CaCl_2$ – I storage time – II interaction – I x II	0.527 0.643 0.888				1.497 1.467 1.951			

Calcium in cv. Omega lettuce ranged from 8.19 to 13.42 g kg^{-1} d.m. (Table 2). The accumulation of this element was distinctly affected by both $CaCl_2$ solution concentrations, part of leaves and storage time. A statistically significant higher calcium content was noted in whole leaves of fresh control plants than in leaf blades. During the 14-day storage, the calcium concentration decreased in whole leaves, in contrast to leaf blades, in which the accumulation of this element increased in the control plants and after the application of $CaCl_2$ of the concentration of 0.2 M.

These results correspond to the ones obtained by MICHAŁOJĆ and HORODKO (2006), who found that foliar treatment of sweet pepper plants with calcium ions had a weak effect on the potassium and magnesium content but the level of dry matter was higher in fruit of plants treated with Ca^{2+} ions. Foliar spray with calcium ions, both as $CaCl_2$ and $Ca(NO_3)_2$, increased the content of this ion in leaves and fruit of pepper compared to the control. Lettuce belongs to vegetables that have a low demand for nutrients but are sensitive to the ion concentration in soil, both during germination and in the vegetative period (CHIBA, SHIMIZU 2008, NURZYŃSKI at al. 2009).

The results obtained in our preliminary experiments on lettuce plants indicated that the application of $CaCl_2$ in the concentration 0.1 M decreased

Table 3

The Ca:Mg, K:Ca, K:Mg, K:(Ca+Mg) ratios in fresh and stored leaves of lettuce after $CaCl_2$ foliar treatment

Analyzed part of plant	$CaCl_2$ (M)	Ca:Mg				K:Ca				K:Mg				K:(Ca+Mg)			
		storage time – days			$\overline{x}$	storage time – days			$\overline{x}$	storage time – days			$\overline{x}$	storage time – days			$\overline{x}$
		0	7	14		0	7	14		0	7	14		0	7	14	
Whole leaves	0	3.294	1.764	2.084	2.381	4.145	5.621	7.404	5.723	13.65	9.913	15.43	12.99	3.179	3.587	5.004	3.923
	0.1	2.594	2.408	1.808	2.270	4.751	5.535	7.562	5.949	12.53	13.33	13.67	13.18	3.445	3.911	4.869	4.075
	0.2	2.303	2.633	2.071	2.336	4.735	4.904	6.919	5.519	10.89	12.91	14.33	12.71	3.298	3.553	4.666	3.839
	$\overline{x}$	2.730	2.268	1.988	2.239	4.544	5.353	7.295	5.730	12.36	12.05	14.48	12.96	3.307	3.684	4.846	3.946
Leaf blades	0	2.389	1.954	1.907	2.083	5.183	4.997	4.755	4.978	12.38	9.765	9.068	10.40	3.654	3.306	3.119	3.359
	0.1	2.115	2.355	2.388	2.286	5.033	5.003	5.202	5.079	10.64	11.78	12.42	11.61	3.417	3.512	3.667	3.532
	0.2	2.035	2.140	1.726	1.967	4.888	5.173	6.025	5.362	9.945	11.07	10.40	10.47	3.277	3.526	3.815	3.539
	$\overline{x}$	2.180	2.150	2.007	1.939	5.035	5.058	5.327	5.139	10.98	10.87	10.63	10.83	3.449	3.448	3.534	3.477

the level of Mg^{2+} and increased Ca^{2+} in fresh whole leaves (Perucka et al. 2007). The increasing soil calcium content had an effect on potassium and calcium concentrations in lettuce. Calcium increased but potassium slightly decreased in plants when calcium in soil reached the highest level (Nurzyński et al. 2009).

An increase in the calcium chloride level in soil caused a proportional rise in calcium concentrations in both roots and leaves of other plants. In tobacco plants, calcium ions were more likely to accumulate in leaves than in roots, indicating that the ion permeation system differs in roots and leaves (Ruiz et al. 1999). Identical results were obtained by other authors in experiments on *Sesamum indicum* (Bharti et al. 1996). In a study on bean plants, higher calcium levels in the substrate resulted in greater accumulation of calcium in the plant (Maksymiec, Baszyński 1998).

Bres and Weston (1992) concluded that the accumulation of calcium and magnesium in lettuce leaves was cultivar-dependent and significantly higher in cv. Summer Bibb than in cv. Buttercrunch. Lower calcium levels in cv. Buttercrunch could be responsible for a higher incidence of disease observed in this cultivar, most likely due to its increased sensitivity to adverse environmental conditions, as manifested by lower calcium concentrations in young leaves. According to a study conducted by Lazof and Bernstein (1999) into the transport of micronutrients to the youngest leaves of lettuce, it was found that the transport of calcium ions was halved in comparison with potassium ions, but no changes in the transport of magnesium ions to the youngest lettuce leaves were noted.

The results obtained in our experiments indicated that the concentrations of Mg and Ca in leaf blades were higher than in whole leaves during the 14 days storage of lettuce under cold conditions (Table 2). It may be affected by the transport of these elements from the midrib of whole leaves to leaf blades.

The ratios of mineral nutrients are an important indicator of the nutritive value of a diet. According to the present results (Table 3), the Ca:Mg ratio in whole leaves of fresh plant of cv. Omega lettuce was optimum, but the K:Mg and K:Ca ratios were twice as high as the optimum ones in a diet: less than 6.0 for K:Mg, 2.0 for K:Ca and 3.0 for Ca:Mg (Kotowska, Wybieralski 1999, Francke 2010).

It was noticed that the Ca:Mg and K:Mg ratios in the whole leaves of cv. Omega lettuce were higher than in the leaf blades, but K:(Ca+Mg) was on the same level in both parts of fresh plants (Table 3). The $CaCl_2$ treatment of lettuce before harvest caused a decrease in the Ca:Mg and K:Mg ratios compared to the control, which was a result of the increasing content of Mg in whole leaves in response to a higher $CaCl_2$ concentration. During the 14 days of storage under cold conditions, the K:Mg, K:(Ca+Mg) ratios increased in the whole leaves depending on the $CaCl_2$ doses versus the fresh plants.

CONCLUSIONS

The results show that foliar treatment of lettuce with $CaCl_2$ in rising concentration stimulated the K and Mg accumulation in whole leaves of fresh plants. No significant changes in the Ca content were observed. In leaf blades without the midrib, the application of the higher $CaCl_2$ dose caused a decline in the Ca^{2+} and K^+ concentrations in fresh plants. This depressed the Ca:Mg and K:Mg ratios. During 14-day storage of lettuce in the cold, a decrease in the Ca levels in whole leaves and an increase in leaf blades in the control plants and after the application of the $CaCl_2$ solution of the concentration of 0.2 M were observed. The same tendency was noticed for the Mg content. In general, the changes in the K levels under the same conditions were not statistically significant but the K:Mg and K:(Ca+Mg) ratios increased in whole leaves compared to fresh plants.

REFERENCES

Barta D., Tibbitts T.W. 2000**.** *Calcium localization and tipburn development in lettuce leaves during early enlargement*. J. Amer. Soc. Hort. Sci., 125(5): 294-298.

Bharti N., Singh P., Sinha S.K. 1996. *Effect of calcium chloride on heavy metal induced lateration in growth and nitrate assimilation of Sesamium indicum seedlings*. Phytochemistry, 41: 105-109.

Bijvelds M.J.C., Flik G., Bonga S.E.W. 1997. *Mineral balance in Oreochromis mossambicus: dependence on magnesium in diet and water*. Fish. Physiol. Bioch., 16: 323-331.

Bres W., Weston L.A. 1992. *Nutrient accumulation and tipburn in NFT-grown lettuce at several potassium and pH levels*. Hort Sci., 27 (7): 790-792.

Burton M.G., Lauer M.J., Mcdonald M.B. 2000. *Calcium effects on soybean seed production, elemental concentration and seed quality*. Crop. Sci., 40: 476-482.

Campo J., Maass J.M., Jaramillo V.J., Yrizar A.M. 2000. *Calcium, potassium and magnesium cycling in a Mexican tropical dry forest ecosystem*. Biogeochemistry, 49: 21-36.

Chakraborti S., Chakraborti T., Mandal M., Mandal A., DAS S., Ghosh S. 2002. *Protective role of magnesium in cardiovascular diseases: A review*. Mol. Cell. Bioch., 238: 163-179.

Chiba S., Shimizu S. 2008. *Effect of conditions at germination and nursery stages on fresh weight of plantlet and leaf weight at harvest in Lactuca sativa* L. *cv. Greenwave.* Environ. Control Biol., 46(2): 115-121.

Francke A. 2010. *The effect of potassium fertilization on the macronutrient content of pepino dulce (Solanum muricatum* Ait.*) fruit.* Acta Sci. Pol., Hort. Cult., 9(3): 51-57.

Gazmuri R.J., Hoffner E., Kalcheim J., Ho H., Patel M., Ayoub I.M., Epstein M., Kingston S., Han YE. 2001. *Myocardial protection during ventricular fibrillation by reduction of proton-driven sarcolemmal sodium influx.* J. Lab. Clin. Med., 137: 43-55.

Gharieb M.M. 2001. *Pattern of cadmium accumulation and essential cations during growth of cadmium-tolerant fungi*. BioMetals, 14: 143-151.

Haarenen S. 2003. *Does high plant feed magnesium and potassium protect healthy ruminants from atherosclerosis? A review*. Pathophysiology, 10: 1-6.

Huber S.C., Bachman M., Huber J.L. 1996. *Post-translational regulation of nitrate reductase activity: a role for Ca^{2+} and 14-3-3 proteins*. Trends Plant. Sci., 1(12): 432-438.

KOTOWSKA J., WYBIERALSKI J. 1999. *Kształtowanie się stosunków ilościowych między K, Ca i Mg w glebie i roślinach [Quantitative ratios between K, Ca and Mg in soil and plants].* Biul. Magnezol., 4(1): 104-110. (in Polish)

LAZOF D., BERNSTEIN N. 1999. *Effect of salinization on nutrient transport to lettuce leaves: consideration of leaf developmental stage*. New Phytol., 144: 85-94.

LUNA-GUMZAN I., BARRETT D.M. 2000. *Comparison of calcium chloride and calcium lactate effectiveness in maintaining shelf stability and quality of fresh-cut cantaloupes.* Postharvest Biol. Technol., 19: 61-72.

MAKSYMIEC W., BASZYŃSKI T. 1998. *The role of Ca ions in changes induced by excess* Cu^{2+} *in bean plants. Growth parameters*. Acta Physiol. Plant., 20(4): 411-417.

MICHAŁOJĆ Z., HORODKO K. 2006. *Wpływ dokarmiania pozakorzeniowego wapniem na plonowanie i skład chemiczny papryki słodkiej [Effect of extra-root lime nutrition on yield and chemical composition of sweet pepper].* Acta Agroph., 7(3): 671-679. (in Polish)

NURZYŃSKI J., DZIDA K., NOWAK L. 2009. *Plonowanie i skład chemiczny sałaty w zależności od nawożenia azotowego i wapniowego [Yield and chemical composition of lettuce depending on the nitrogen and calcium fertilization].* Acta Agroph., 14(3): 683-689. (in Polish)

PERUCKA I., NURZYŃSKI J., OLSZÓWKA K. 2007. *Wpływ* $CaCl_2$ *na zawartość składników mineralnych w liściach sałaty [Effect of* $CaCl_2$ *on the content of mineral components in lettuce leaves].* J. Elementol., 12(3): 181-190. (in Polish)

RUIZ J.M., RIVERO R.M., GARCIA P.C., BAGHOUR M., ROMERO L. 1999. *Role of* $CaCl_2$ *in nitrate assimilation in leaves and roots of tobacco plants* (*Nicotiana tabacum* L.). Plant Sci. 141: 107-115.

SAURE M.C. 1998. *Causes of the tipburn disorder in leaves of vegetables*. Sci. Hort., 76: 131-147.

SEELIG M.S. 1994. *Consequences of magnesium deficiency on the enhancement of stress reaction: preventive and therapeutic implications (a review).* J. Am. Coll. Nutr., 13: 429-446.

SINGH J., HUSTLER B.I., WARING J.J., HOWARTH F.C. 1997. *Dietary and physiological studies to investigate the relationship between calcium and magnesium signaling in the mammalian myocardium*. Mol. Cell. Biochm., 176: 127-134,.

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USING TWO METHODS FOR PLANT MATERIAL PREPARATION IN ORDER TO DETERMINE THE CONTENT OF BIOELEMENTS IN RED CABBAGE (*BRASSICA OLERACEA* L. VAR. *CAPITATA* L. F. *RUBRA*)

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Abstract

Mineral components (bioelements) are one of the five major groups of nutrients in human diet, next to proteins, lipids, carbohydrates and vitamins. The required daily amounts per capita are over 100 mg of macroelements and less than 100 mg of microelements. Every industrial processing technology applied to vegetable produce causes precipitation of bioelements and consequently undesirable losses of these components.

The purpose of this study has been to analyze the content of bioelements (Ca, Mg, Zn, and Fe) determined in homogenizates and extracts from three red cabbage cultivars (Koda, Haco POL, Kissendrup SWE). Correlation coefficients served to assess the concordance between the plant material preparation methods used for determination of bioelements. The correlation between the content of Mg versus Ca and Zn versus Fe in edible parts of cabbage (homogenizates) compared to the levels of these metals in red cabbage extracts was tested.

Two methods for the preparation of plant material for chemical analyses were used: homogenization and extraction. Citric acid solution of the concentration of 0.1 mol dm^{-3} was used for extraction. The content of bioelements was determined using atomic absorption spectrophotometry (AAS).

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The content of Ca and Zn in red cabbage depended on the method applied to the plant material preparation, i.e. homogenization or extraction. The content of Mg and Fe depended on the cabbage cultivars. Irrespective of the plant material preparation methods, the red cabbage cultivars Kissendrup SWE and Koda contained the highest average levels of Ca, Mg, Zn, and Fe, while the lowest ones were determined in cv. Haco POL. High correlation obtained for Mg enables us to convert the content of this element in homogenizates (A) into its content of extracts (B) – conversion factor A:B = 0.9. Positive and highly significant correlations were found between the content of the bioelements: Ca and Mg, Zn and Fe in cabbage homogenizates.

Key words: red cabbage, homogenizates, extracts, bioelements, atomic absorption spectrophotometry.

UŻYCIE DWÓCH METOD PRZYGOTOWANIA MATERIAŁU ROŚLINNEGO DO OKREŚLENIA ZAWARTOŚCI BIOPIERWIASTKÓW W KAPUŚCIE CZERWONEJ (*BRASSICA OLERACEA* L. VAR. *CAPITATA* L. F. *RUBRA*)

Abstrakt

Składniki mineralne (biopierwiastki) z żywieniowego punktu widzenia stanowią jedną z pięciu podstawowych grup składników odżywczych dla człowieka, oprócz białek, tłuszczów, węglowodanów i witamin. Dzienne zapotrzebowanie na składniki mineralne dla 1 osoby wynosi: makroelementy powyżej 100 mg i mikroelementy poniżej 100 mg. Każda obróbka przemysłowa produktów roślinnych powoduje wytrącenie się biopierwiastków, i w konsekwencji niepożądane straty tych składników.

Celem pracy było zbadanie zawartości biopierwiastków (Ca, Mg, Zn i Fe) oznaczonych w homogenizatach i w ekstraktach z trzech odmian kapusty czerwonej (Koda, Haco POL, Kissendrup SWE). Oceniono zgodność zastosowanych metod przygotowania materiału roślinnego do oznaczania biopierwiastków za pomocą współczynnika korelacji. Poszukiwano korelacji między zawartością Mg a Ca oraz Zn i Fe w części jadalnej kapusty czerwonej (homogenizatach) i w otrzymanych z niej ekstraktach.

Zastosowano dwie metody przygotowania materiału roślinnego do analiz chemicznych: homogenizację i ekstrakcję. Do ekstrakcji zastosowano roztwór kwasu cytrynowego o stężeniu 0.1 mol dm^{-3}. Zawartość biopierwiastków oznaczono metodą atomowej spektrometrii absorpcyjnej.

Zawartość Ca i Zn w kapuście czerwonej zależała od metody przygotowania materiału roślinnego do badań, zawartość Mg i Fe – od odmiany kapusty. Niezależnie od metody przygotowania materiału roślinnego, odmiany kapusty czerwonej Kissendrup SWE i Koda zawierały najwięcej Ca, Mg, Zn i Fe, a najmniej odmiana Haco POL. Wysoka korelacja w przypadku Mg daje możliwość przeliczenia zawartości tego pierwiastka w homogenizatach (A) na zawartość w ekstraktach (B) – przelicznik A:B = 0.9. Stwierdzono dodatnią i wysoce istotną zależność między zawartością biopierwiastków Ca i Mg, Zn i Fe w homogenizatach z kapusty.

Słowa kluczowe: kapusta czerwona, homogenizaty, ekstrakty, biopierwiastki, atomowa spektrometria absorpcyjna.

INTRODUCTION

For nutritionists, mineral components (bioelements) are one of the five major groups of nutrients for humans, next to proteins, lipids, carbohydrates and vitamins. Mineral components are divided into macroelements (e.g. Ca, Mg, P, Na) and microelements (e.g. Fe, Zn, Mn, Cu, Co). The required daily amounts per capita are over 100 mg of macroelements and less than 100 mg microelements (ZIEMLAŃSKI 2001).

Deficiency of macroelements in an organism, especially that of Ca and Mg, is a problem that appears in many human populations. Supply of essential bioelements is sometimes insufficient and tends to decline (SIKORSKI 1994, WATTS 1995). One possible measure to counteract such problems involves supplementation with mineral preparations (OŻAROWSKI 2001), which in addition to bioelements contain anthocyanins, able to form complexes with metals. Ions of metals enhance the stability of anthocyanins and protect products from decoloration (SHAKED-SACHRAY et al. 2002, SALINAS et al. 2005, SMYK et al. 2008). Such preparations are produced via technological processing of fruit (chokeberry, elderberry, cranberry) or vegetables (red cabbage). It has to be added, however, that any industrial processing of plant products leads to precipitation of elements. Extraction of mineral substances, for example while boiling or scalding vegetables, causes unwanted losses of about 30-65% K, 15-70% Mg and Cu, 20-24% Zn and many other elements (NABRZYSKI 1996). The efficiency of extraction to a large degree depends on the kind of an applied solvent (PLISZKA, HUSZCZA-CIOŁKOWSKA 2009b). The literature dealing with the content of bioelements in red cabbage most often discusses homogenizates; in contrast, few references regard the issue of bioelements in extracts (SINGH et al. 2009). The question arises whether such extracts can be considered as a natural and good source of bioelements.

The objective of this study has been to assess the content of anthocyanins and several bioelements (Ca, Mg, Fe, and Zn) determined in homogenizates and extracts from cultivars of red cabbage (Koda, Haco Pol, Kissendrup SWE). Correlation coefficients served to assess the concordance between the plant material preparation methods used for determination of bioelements. The correlation between the content of Mg versus Ca and Zn versus Fe in edible parts of cabbage (homogenizates) compared to the levels of these metals in red cabbage extracts was tested.

MATERIAL AND METHODS

Sample preparation

The material consisted of three cultivars of red cabbage (*Brassica oleracea* L., var. capitata L., f. rubra), which differed in the growing season duration: Koda (an early cultivar), Haco POL (medium early) and Kissendrup SWE (medium late). The cultivars were grown in a one-year experiment (in 2003), in a garden at the Experimental Station of the University of Warmia and Mazury in Olsztyn, Poland.

Having partly removed stalks from cabbage heads, some of the heads were shredded to size 1-5 mm fragments). The plant material was stored frozen (–18°C) until it was analyzed.

Two methods for the preparation of plant material for chemical analyses were used. Edible parts of red cabbage were homogenized in a mortar (method A). For extraction (method B), 30 g of each red cabbage sample was weighed out and macerated in 300 cm^3 of citric acid solution ($C_6H_8O_7 \cdot H_2O$) of the concentration of 0.1 mol dm^{-3}. The samples were left in the dark at 2şC for 24 h, after which they were shaken in a water bath at 37°C. The extracts were filtered through Whatman No 1 filter paper.

The samples were prepared in three replicates.

Analytical measurements

In order to determine the content of bioelements, the plant material obtained from red cabbage: homogenizates (method A) and extracts (method B), was mineralized in a Teflon® microwave digestion bomb.

For mineralization, 0.2 g of homogenizates and 2 cm^3 concentrated nitric acid (HNO_3) were used. When the extracts were mineralized, 1 cm^3 extract and 2 cm^3 concentrated HNO_3 acid were used. Once mineralized, the samples were quantitatively transferred to 25 cm^3 measuring flasks, which were filled up to full capacity with deionized water. The content of bioelements (Ca, Mg, Zn and Fe) was determined using atomic absorption spectrophotometry (AAS).

Analytical grade reagents were used for all the chemical analyses.

Statistical analysis

The results of the determinations of bioelements underwent analysis of variance. Significance of differences in the content of bioelements was tested with Student t-test at $P = 0.01$ (to demonstrate interactions), using Statistica 8.1 programme. In order to test concordance of the results obtained from the two plant preparation methods, correlation coefficients were computed for the content of each bioelement determined in homogenizates and in extracts. Regression analysis was performed on the results. In addition, correlation analysis was completed to test the content of Mg versus Ca and Zn versus Fe in homogenizates and in extracts from red cabbage.

RESULTS AND DISCUSSION

Concentrations of macroelements (Ca, Mg) and microelements (Zn, Fe) in homogenizates (method A) and extracts (method B) from red cabbage are presented in Table 1.

Calcium

High mean concentrations of Ca were determined in two red cabbage cultivars: Kissendrup SWE and Koda (20.70 and 18.76 mg 100 g^{-1}, respectively), which did not differ statistically in the content of this element. In contrast, cv. Haco POL contained significantly less calcium (15.27 mg 100 g^{-1}).

The average Ca content in red cabbage was more strongly dependent on the sample preparation method than on the cultivar of this vegetable. Likewise, the interaction between these factors was significantly high. In the homogenizates (method A), the mean Ca content was ca 5-fold higher than in extracts (method B).

In the material obtained with method A, significant differences in the content of Ca were established for all the three cultivars. The highest Ca content was found in cv. Kissendrup SWE (35.48 mg 100 g^{-1}), and the lowest one – in cv. Haco POL (25.38 mg 100 g^{-1}). According to Majkowska-Gadomska and Wierzbicka (2008), the highest Ca content in red cabbage (in dry matter) appeared in cv. Koda (0.69 g 100 g^{-1}), and the lowest one – in cv. Kissendrup SWE (0.41 g 100 g^{-1}). Other authors (Kunachowicz et al. 2003, 2005) report that red cabbage can contain 46 mg Ca 100 g^{-1} of edible parts.

In our study, the extracts (method B) of red cabbage of all the three cultivars contained similar levels of Ca (from 5.17 to 7.51 mg 100 g^{-1}). Another experiment completed by Pliszka and Huszcza-Ciołkowska (2009a) also demonstrated a low level of calcium in extracts from red cabbage (nearly six-fold less than in edible parts). Further tests are needed to clarify the reasons why Ca appears in such low amounts. Singh et al. (2009) report that the content of Ca in cabbage extracts ranged from 19.3 to 68.5 mg 100 g^{-1} fresh matter.

No significant correlation was found between the Ca content in the plant material prepared by the two methods; the correlation coefficient was low ($r = 0.350$).

Table 1

Content of bioelements in three cultivars of red cabbage depending on the method of plant material preparation (mg 100 g^{-1} of fresh matter)

Bioelements	Ca			Mg			Zn			Fe		
Method / Cultivar	A*	B**	mean	A	B	mean	A	B	mean	A	B	mean
Koda	30.00	7.51	**18.76**	14.30	12.23	**13.27**	0.39	0.31	**0.35**	0.45	0.66	**0.56**
Haco POL	25.38	5.17	**15.27**	10.81	10.66	**10.73**	0.35	0.24	**0.29**	0.28	0.10	**0.19**
Kissendrup SWE	35.48	5.92	**20.70**	16.31	14.10	**15.21**	0.63	0.17	**0.40**	0.62	0.42	**0.52**
Mean	**30.28**	**6.20**		**13.81**	**12.33**		**0.46**	**0.24**		**0.45**	**0.39**	
LSD for method	1.964			0.288			0.069			n.s.		
LSD for cultivar			2.406			0.353			0.085			0.152
LSD for method × cultivar interaction		3.403			0.499			0.120			0.214	

*Method A – homogenizates from red cabbage
**Method B – extracts from red cabbage
$LSD_{P=0.01}$; n.s. – no significant differences

Magnesium

Among all the tested factors, it was the cabbage cultivar that most strongly differentiated the content of Mg. Independently from the method applied to prepare tested samples of plant material, the mean Mg ranged between 10.73 to 15.21 mg 100 g^{-1}. All the three cultivars were significantly different in the content of this element. The highest Mg level was found in cv. Kissendrup SWE (16.31 and 14.10 mg 100 g^{-1}, method A and B respectively) and the lowest one in cv. Haco POL (10.81 and 10.66 mg 100 g^{-1}, method A and B respectively). Kunachowicz et al. (2005) report that red cabbage contains 12 mg Mg 100 g^{-1} of edible parts, which is similar to the present result (13.81 mg Mg 100 g^{-1}). Majkowska-Gadomska and Wierzbicka (2008) demonstrated that the three cultivars of red cabbage (Koda, Haco Pol, Kissendrup SWE) had identical levels of Mg (0.13 g 100 g^{-1} of dry matter).

The content of Mg in homogenizates obtained from red cabbage (method A) was significantly higher than in extracts (method B), and the values obtained in the tested samples produced with both methods were correlated ($r = 0.974$, significant at $P = 0.01$). Such high correlation suggests that it is feasible to use only one method of sample preparation for determination of Mg in red cabbage. Results obtained from tests on homogenizates can be converted into the ones produced by tests on plant extracts using the following regression equation: $y = 0.6079x + 3.9358$, where: y – content of Mg in extract; x – content of Mg in homogenizates. Both sample preparation methods proved to be comparably efficient in evaluating differences between the three red cabbage cultivars in magnesium content. The conversion factor for converting the content of Mg in homogenizates (method A) into the content of this element in extracts (method B) is A:B = 0.9.

Zinc

Like calcium, the content of Zn in red cabbage was more strongly related to the sample preparation method than to the cultivar. Analogously, the interaction between these factors was high. The highest mean Zn content was determined in cv. Kissendrup SWE (0.40 mg 100 g^{-1}) and cv. Koda (0.35 mg 100 g^{-1}), with no statistically significant differences in the level of this element between these two cultivars. In turn, statistically significant less zinc was found in cv. Haco POL (0.29 mg 100 g^{-1}).

Among the homogenizates, cv. Kissendrup SWE had the highest Zn content (0.63 mg 100 g^{-1}), while the cultivars Koda and Haco POL contained much less zinc (0.39 and 0.35 mg 100 g^{-1}, respectively). Kunachowicz et al. (2003, 2005) report that red cabbage contains 0.43 mg Zn 100 g^{-1} of edible parts.

The average Zn content in homogenizates from red cabbage was twofold higher than in extracts (0.46 mg 100 g^{-1} versus 0.24 mg 100 g^{-1}). As Singh et al. (2009) determined, the content of Zn in red cabbage extracts ranged from 211.7 to 266.7 μg 100 g^{-1} of fresh matter, thus being similar to our determinations. The relationships between the content of Zn in particular cultivars determined in the samples prepared by the two methods were different, which confirmed the significance of the cultivar´sample preparation method interaction.

No correlation was found for the content of Zn between samples prepared by the two methods. The correlation coefficient $r = -0.499$ indicated a tendency towards a negative relationship between the results obtained from homogenizates and extracts.

Iron

The content of Fe in red cabbage, like that of magnesium, was significantly differentiated by the cultivar. It did not depend on the sample preparation method (methods A and B).

High and similar mean content of Fe (0.52-0.56 mg 100 g^{-1}) in red cabbage was determined for two cultivars: Koda and Kissendrup SWE, irrespective of the sample preparation method. Less iron was detected in cv. Haco POL (0.19 mg 100 g^{-1}) (about 2.8-fold less than in the other two varieties). Majkowska-Gadomska and Wierzbicka (2008) report that the Fe content (converted into dry matter) was the highest in cv. Koda (57.50 mg kg^{-1}), and the lowest in cv. Kissendrup SWE and cv. Haco Pol (52.0 and 50.0 mg kg^{-1}, respectively). Other authors (Kunachowicz et al. 2003, 2005) demonstrated that red cabbage contained 0.5 mg Fe 100 g^{-1} of edible parts. Singh et al. (2009) in turn report that the content of Fe in red cabbage extracts varied from 327.7 to 1146.0 μg 100 g^{-1} of fresh matter. The present results of the determinations of the Fe content in the extracts are within the limits cited by Singh et al. (2009).

No correlation was found between the amounts of Fe determined in the tested material obtained by the two methods. The correlation coefficient $r = 0.559$ indicated a tendency towards a positive relationship between the results.

Correlation between the content of Ca and Mg, and between Zn and Fe

Positive and highly significant correlation was determined between the content of the following pairs of elements: Ca and Mg ($r = 0.930$; significant at $P = 0.01$) and Zn and Fe ($r = 0.860$; significant at $P = 0.01$) in homogenizates (method A) – Figure 1. Jędrzejczak et al. (1999), who determined the content of Ca and Mg in homogenized vegetables and fruit, demonstrated the presence of positive correlation between these bioelements in carrot ($r = 0.5986$) and strawberries ($r = 0.5764$).

In our study, no such correlation was found in red cabbage extracts (method B), either for Ca and Mg ($r = 0.288$), whereas for Zn and Fe, a tendency for positive correlation was observed ($r = 0.427$). There are no

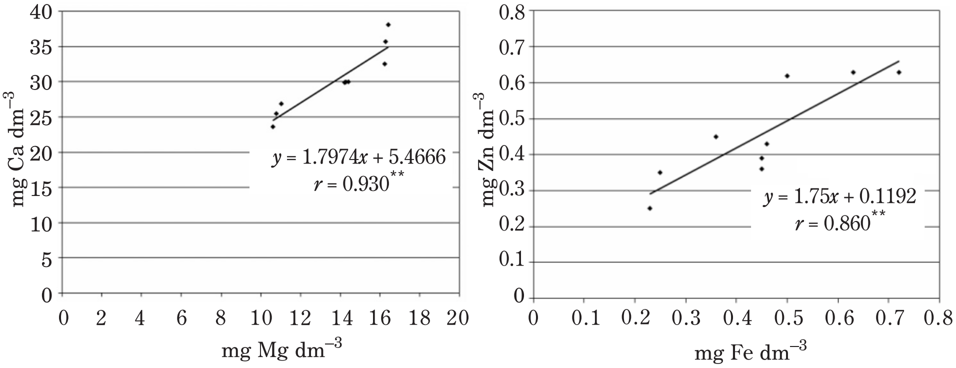

Fig. 1. Correlation between the content of Ca and Mg as well as Zn and Fe in homogenizates from red cabbage (method A)

data in the literature on mutual dependences between Ca, Mg, Zn and Fe in red cabbage extracts.

Some earlier studies on bioelements in fruit extracts revealed correlation between the content of Ca and Mg, which was independent from the extraction method (H_2O and HCl methods). However, no such correlation was proven for the content of Zn and Fe in fruit extracts obtained by the above methods (Pliszka et al. 2008).

The mean Ca content in the homogenizates of red cabbage (irrespective of the cultivar) was higher than that of Mg, unlike in the extracts, which contained more Mg and Ca. No differences were observed in the mean content of Zn and Fe in homogenizates, while in extracts the content of Fe was higher than that of Zn. Content of bioelements in fruit and vegetable extracts heavily depends on the method applied for extraction (Pliszka et al. 2008, Nascentes et al. 2009, Pliszka, Huszcza-Ciołkowska 2009b, Singh et al. 2009).

When searching for natural and good sources of bioelements (Ca, Mg, Zn and Fe) from red cabbage, one should take into consideration both cultivar-dependent traits and a method applied to plant material preparation for consumption.

CONCLUSIONS

1. The content of Ca and Zn in the three red cabbage cultivars depended on the sample preparation methods: homogenization and extraction. A very high level of Ca and Zn as well as some differences in the content of this element between the cultivars occurred in homogenizates.

2. Determination of the content of Mg and Fe was mainly dependent on the cabbage cultivar. In general, higher content of Mg and Fe was determined in the homogenizates rather than the extracts from the particular red cabbage cultivars.

3. Irrespective of the plant material preparation method, the red cabbage cultivars Kissendrup SWE and Koda were characterised by the highest mean content of bioelements, while cv. Haco POL was the lowest content of the bioelements among the tested cabbage varieties.

4. It was only for Mg that it proved possible, owing to the high correlation for Mg, to convert the amount of this element present in homogenized material (method A) into its corresponding quantity in an extract (method B). The conversion factor was A:B = 0.9.

5. Positive and highly significant correlations were found between the content of the bioelements: Ca and Mg as well as Zn and Fe in red cabbage homogenizates.

REFERENCES

Jędrzejczak R., Ręczajska W., Szteke B. 1999. *Magnez i inne makroelementy w roślinnych surowcach jadalnych [Magnesium and other macronutrients in edible plant raw materials]*. Biul. Magnezol., 4 (1): 72-76. (in Polish)

Kunachowicz H., Nadolna I., Przygoda B., Iwanow K. 2005. *Tabele składu i wartości odżywczej żywności [Tables of composition and nutritive value of food].* PZWL, Warszawa, p. 242. (in Polish)

Majkowska-Gadomska J., Wierzbicka B. 2008. *Content of basic nutrients and minerals in Heads of selected varieties of red cabbage* (*Brasicca oleracea* var. *capitata* f. *rubra*). Pol. J. Environ. Stud., 17 (2): 295-298.

Nabrzyski M. 1996. *Mineral components*. In: *The chemical and functional properties of food components*. Ed. by Z.E. Sikorski. Lancaster, Technomic, pp. 35-63.

Nascentes C.C., Korn M., Arruda M.A.Z. 2001. *A fast ultrasound-assisted extraction of Ca, Mg, Mn and Zn from vegetables*. Microchem. J., 69: 37-43.

Ożarowski A. 2001. *I znów winna dieta. [It's the diet to blame again]. Zdrowa Żywność – Zdrowy Styl Życia,* 1 (51): 9-11. (in Polish)

Pliszka B., Huszcza-Ciołkowska G. 2009a. *Effect of technological processing on the content of anthocyanins and bioelements (Ca, Mg and Zn) in plant material*. Conf. of Bioactive Plant Compounds, Structural and Applicative Aspects, September 2-4, 2009, Puławy Poland, Acta Biochim. Pol., 56, Supl. 2: 30-31.

Pliszka B., Huszcza-Ciołkowska G. 2009b. *Comparison of the content of anthocyanins and bioelements (Ca, Mg, Zn and Fe) in extracts from berry fruits depending on extraction methods.* 2nd Environmental Best Practices Conference, 14-18 September, Kraków, Poland, and Agfes Educational Workshop, p. 109.

Pliszka B., Huszcza-Ciołkowska G., Wierzbicka E. 2008. *Effects of extraction conditions on the content of anthocyanins and bioelements in berry fruit extracts*. Commun. Soil Sci. Plant Anal., 39 (5&6): 753–762.

Salinas Í., Esparza I., Gómez S., Santamaria C., Fernández J.M. 2005. *A study of heavy metal complexation in grape juice*. Electroanalysis., 17 (5-6): 469–475.

SHAKED-SACHRAY L., WEISS D., REUVENI M., NISSIM-LEVI A., OREN-SHAMIR M. 2002. *Increased anthocyanin accumulation in aster flowers at elevated temperatures due to magnesium treatment*. Physiol. Plant., 114 (4): 559–565.

SIKORSKI Z.E. 1994. *Chemiczne i funkcjonalne właściwości składników żywności [Chemical and functional proprieties of food components].* WNT, Warszawa, pp. 414-422. (in Polish)

SINGH B.K., SHARMA S.R., SINGH B. 2009. *Heterosis for mineral elements in single cross-hybrids of cabbage* (*Brassica oleracea* var. *capitata* L.). Sci. Hortic., 122: 32-36.

SMYK B., PLISZKA B., DRABENT R. 2008. *Interaction between cyanidin 3-glucoside and Cu(II) ions.* Food Chem., 107: 1616–1622.

WATTS D.L. 1995. *Trace elements and other essential nutrients*. Meltdown Intl: Dallas, Tex. 62 (2): 294-296.

ZIEMLAŃSKI Ś. 2001. *Normy żywienia człowieka. Fizjologiczne podstawy [Norms of human nourishment. Physiological grounds].* PZWL, Warszawa, pp. 314-398. (in Polish)

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Na, K, Ca AND Mg CONCENTRATIONS IN EFFLUENT WATER DRAINED FROM AGRICULTURAL CATCHMENT BASINS IN LOWER SILESIA

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Abstract

This paper contains the results of research of the content Na, K, Ca and Mg in waters drained from three agricultural river basins in Lower Silesia. The investigations covered two objects situated close to Wrocław and one in the border region between the Bolków-Wałbrzych Plateau and the Wałbrzych Mountains. The effect of the agricultural use of the land on changes in the concentrations of the analyzed macroelements in the water flowing from the river basins has been assessed. Between 58 and 91 samples of waters for chemical analyses were taken once a month.

Our analysis has shown that the concentrations of the analyzed elements were considerably different, both in the water flowing into and from the basins. The effluent water from the river basins was characterized by an elevated content of calcium and low concentrations of potassium. However, the content of magnesium was typical for the conditions in Poland.

The content of magnesium in waters drained from all the river basins was higher than in the water flowing into the basins and the correlation coefficients for the concentrations in both of these cross-sections ranged from 0.7846 to 0.8603. Likewise, for sodium, calcium and potassium, dependences were found between the concentrations of these elements above and below the analyzed objects but the correlation coefficients were lower. Distinctly lower values of the correlation coefficients were obtained for the village of Samotwór. The agricultural use of the river basin area contributed to a higher magnesium and calcium content in waters and an insignificantly raised content of sodium. These changes were accompanied by a decrease in the concentration of potassium.

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It has been found out that differences in the Na : K : Ca : Mg ratio between the seasons of the year (early spring, late summer) are connected with the dynamics of the calcium concentration. The growth in the concentration of this element caused evident differences in the Ca : Mg ratio, reaching 0.7 to 1.2. An increase in the value of the Ca : Mg ratio in late summer reduces the outflow of potassium in most cases. Agricultural practice does not show any direct influence on seasonal changes of the Ca : Mg ratio and its effect on the value of this ratio is not unambiguous.

Key words: water, river basin, sodium, potassium, calcium, magnesium.

STĘŻENIE Na, K, Ca I Mg W WODACH ODPŁYWAJĄCYCH ZE ZLEWNI UŻYTKOWANYCH ROLNICZO NA DOLNYM ŚLĄSKU

Abstrakt

W pracy przedstawiono wyniki badań zawartości: Na, K, Ca i Mg w wodach odpływających z trzech zlewni użytkowanych rolniczo na Dolnym Śląsku. Badania realizowano na dwóch obiektach położonych w pobliżu Wrocławia i jednym na pograniczu Pogórza Bolkowsko-Wałbrzyskiego i Gór Wałbrzyskich. Ocenie poddano wpływ sposobu rolniczego użytkowania gleb na zmiany stężenia analizowanych makroelementów w wodzie odpływającej ze zlewni. Próbki wody do analiz chemicznych pobierane były raz w miesiącu, ich liczba wynosiła od 58 do 91.

Analiza wykazała że stężenia tych składników, zarówno w wodzie dopływającej, jak i odpływającej z tych obiektów, istotnie się różnią. Woda odpływająca ze zlewni miała podwyższoną zawartość wapnia i niskie stężenie potasu. Natomiast zawartość magnezu była typowa dla warunków polskich.

Zawartość magnezu w wodach odpływających ze wszystkich zlewni była wyższa niż w wodzie dopływającej, współczynnik korelacji między stężeniami w obu tych przekrojach wynosił od 0,7846 do 0,8603. Dla sodu, wapnia i potasu również uzyskano istotne zależności między stężeniem powyżej i poniżej obiektu, ale współczynniki korelacji były niższe. Zdecydowanie niższe wartości współczynnika korelacji uzyskano dla Samotworu. Rolnicze użytkowanie zlewni sprzyjało zwiększeniu w wodach zawartości magnezu, wapnia i w niewielkim stopniu sodu oraz obniżeniu koncentracji potasu.

Stwierdzono, że zróżnicowanie stosunku Na : K : Ca : Mg w poszczególnych okresach (przedwiośnie, późne lato) jest związane z dynamiką stężenia wapnia. Wzrost stężenia tego pierwiastka spowodował widoczne różnice w stosunku stężeń Ca:Mg, wynoszące od 0,7 do 1,2. Wzrost wartości stosunku Ca : Mg w okresie późnego lata sprzyja w większości przypadków ograniczeniu odpływu potasu w tym okresie. Działalność rolnicza nie wykazuje bezpośredniego wpływu na sezonowe zmiany stosunku Ca : Mg, również jej oddziaływanie na wartość tego stosunku nie jest jednoznaczne.

Słowa kluczowe: woda, zlewnia, sód, potas, wapń, magnez.

INTRODUCTION

Protection of water resources is one of the major challenges for the contemporary society. Assurance of suitable quantity and quality of water determines further development of civilization on our planet. The crucial role in this process is performed by agriculture because arable lands often make up a large percentage of the area of many countries. This makes the water outflow from parts of river basins used for agriculture affect significantly the water quality in watercourses and water bodies. It is important to provide a suitable quantity of water for agriculture as the competition on behalf of other water users is growing stronger (De Fraiture, Wichelns 2010). With the food demand on the increase, the water balance can be improved by using low-grade water (De Fraiture et al. 2010), implementing economic irrigation systems (Pokladek, Nyc 2005) and changing people's eating habits. Production of vegetarian food requires just about 40% of the water used up for production of food for a diet based on beef (Renault, Wallender 2000).

Water is a very good solvent, which enables plants to obtain substances essential for their growth. Any excess of water in soil, however, causes an undesirable outflow of nutrients. The mass of nutrients removed with water depends mainly on the volume of water discharged from a given area (Pulikowski 2004). Most of this mass is composed of macronutrients and alkaline elements (Orzepowski, Pulikowski 2008). These elements are highly important for the physiology of plants and their content in water is essential when using water for the purposes connected with the supply of human population and industry.

The content of elements in water drained from river basins used agriculturally depends on the kind of soils and on the land management (Cymes, Szymczyk 2005). Irrigation and drainage also play a crucial role. Irrational use of irrigation, for example, can cause some accumulation of magnesium (Karaimov et al. 2009) whereas a depressed Ca : Mg ratio favours the release of potassium (Jalali 2008). Drainage elevates the outflow indicator and consequently depletes soil from macronutrients. Drainage systems can be used for soil desalination (Kelleners et al. 2000).

The purpose of this work has been to assess the influence of agricultural use of land on changes in concentrations of several macronutrients in water flowing from river basins situated in Lower Silesia and used agriculturally.

MATERIAL AND METHODS

This study was conducted in 1996-2008 and comprised analyses of selected elements in water sampled at three locations: Bogaczowice, Mękinia and Samowtór.

Bogaczowice is situated on the border between the Bolków-Wałbrzych Plateau and the Wałbrzych Mountains, in the region of the Central Sudetes. The research included the basin of a ditch, covering a total area of 29 hectares, within the B-II section. This ditch basin is located at an altitude of 400-500 meters above sea level, on northern and north-eastern slopes. The slopes are very steep, of the gradient from 52 to 84‰. About 50% of the area of this basin is covered by fields drained by a drainage system. In the upper part of the B-II section, an area of 6.6 hectares was distinguished and marked as the B-I section. This basin covers a cultivated field which is not drained. Between sections B-I and B-II, there is an outflow of water from a drainage system which drains 14.47 hectares of arable land. Samples of water for chemical analyses were taken from sections B-I and B-II.

In the Bogaczowice object, there are pseudo-podsolic soils of the grain size composition of medium and heavy clays with a large content of the skeleton. Soil profiles are shallow, reaching 1.2 m deep, and rest on rocky rubble. The main crops are cereals such as barley, wheat and maize.

The second object (Miękinia) is a compact, 720-hectare complex of drained cropland and forest areas situated in a small basin of a watercourse called the Zdrojek, which flows into the Jeziorka River. The Zdrojek runs through the centre of the object, along a distance of about 3 kilometres, and locally is the main water source. At the turn of 1980/90, the object was drained by regulating the main section of the watercourse, developing regular water gates on the watercourse and reconstructing an irregular network of single ditches carrying water into the Zdrojek. This pattern of ditches and water gates on the Zdrojek River, located centrally in relation to the borders of the object, ensures effective influence of the water heads. Over the recent years, there have been some changes in the use of the land within the basin of the Zdrojek River. At present, cropland makes 54% and forests cover 20%, including approx. 3%of new forests; the remaining 26% of the land is occupied by industrial or residential areas as well as some land left for future investment projects.

The soils in the object are permeable mineral (52%) and organic (48%) deposits, lying mostly on weak loamy sands and loose sands. Permanent grasslands cover mainly muck and mineral soils as well as some local low peats. Arable lands most often lie on degraded black soils and pseudo-podsolic soils of different soil classes and good hydraulic conduction.

The fall of the ground surface is mostly within 3.0-6.0‰, and locally up to15 ‰. Samples of waters for chemical analyses were taken in section M-I (above the object) and M-II (below the object).

The village of Samotwór, the third of the examined objects, is situated 20 kilometres west of the centre of Wrocław, in the lower part of the Bystrzyca River basin. This is a 100-hectare complex of arable fields, which constitutes a closed, local hydrological basin. The drainage system consists of the main ditch A with its tributary. These ditches receive waters from drainage outlets. In the lower part of the object, on the main ditch A, there is a water gate used for annual regulation of the water outflow. The fall of the ground surface is within 1-5‰, and locally 0.5-1‰. In the past, the object was used as cropland but at present above 50% of this area is wasteland. Distances between hydrometric sections on the main water flow (S-I and S-II), at which the quality of inflowing and outflowing water was assessed, are about 600 meters. This is a typical object irrigated by water from own retention and dependent on atmospheric precipitation. It is only some periodic excess of rainfall that is drained outside the system.

The soils of the object are shallow and medium deep deposits, moderately permeable and permeable, of the grain size composition of heavy loamy sand and also light sandy loam. They lie on permeable sandy or sand and gravel deposits. These are mainly brown soils, and in the valley of the Bystrzyca River, there are also fen soils, classified as good and very good rye complex as well as good rye soils.

Samples of water for chemical analyses were taken once a month. The content of magnesium and calcium was determined with the versenate method, whereas concentrations sodium and potassium were assayed using flame photometry. All the determinations were carried out at the Laboratory of Water and Sewage of the Institute of the Environmental Development and Protection of the Wrocław University of Environmental and Life Sciences. Each series consisted of 58 to 91 of samples. The evaluation of differences in the average composition of water originating from different measuring sections was performed based on a one-way analysis of variance (the F test) at the significance level equal p=0.05. The significance of the linear correlation between concentrations in inflowing and effluent water was tested at the significance level p=0.05. For statistical calculations, a Statistica software package was applied.

RESULTS AND DISCUSSION

The results of our tests deal with the objects differentiated in respect of the landscape, soils and water management. Our analysis of the Na, K, Ca and Mg concentrations showed that waters flowing to these objects differed significantly in the content of sodium, potassium, calcium and magnesium (Figure 1).

An analogous situation occurred in reference to the water flowing away from these objects (Figure 2). The average concentrations of sodium, potassium and calcium were highly varied. Magnesium was an exception in that that its average concentration was from 18.2 mg Mg dm^{-3} in Samotwór to 25.3 mg Mg dm^{-3} in Bogaczowice. These concentrations are higher than determined in agricultural river basins in north-eastern Poland (Glińska-

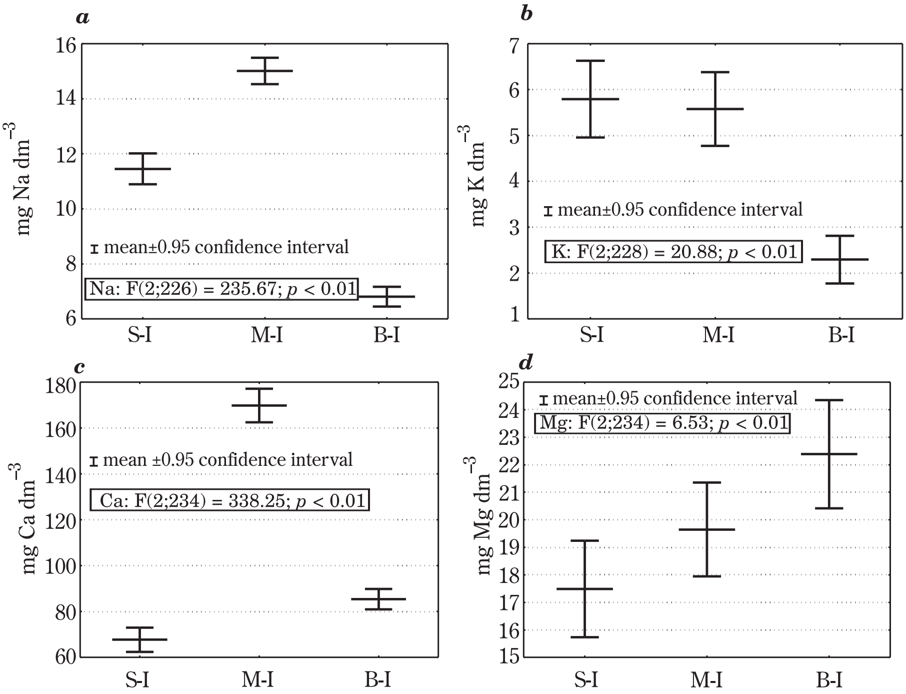

Fig. 1. Concentrations of elements in inflowing waters:
a – sodium, *b* – potassium, *c* – calcium, *d* – magnesium

-Lewczuk, Kobus 2005) but lower than reported by Terelak and Pondel (1990) for the Lubartów Plain. Notable is the high concentration of calcium in both inflow and effluent water from Miękinia – it is significantly higher than determined at the remaining objects or given in literature (Glińska-Lewczuk, Kobus 2005, Koc, Duda 2009). A very high Ca : Mg ratio, i.e. 3.6:1 in Samotwór up to 9.1:1 in Miękinia, does not favour the leaching of potassium (Jalali 2008). The determined concentrations of potassium are significantly lower than given by Durkowski, Woroniecki (2001) and Durkowski (2005).

For a number of reasons, and particularly for the physiology of plants, it is not only essential to have proper concentrations of elements but also to secure proper ratios between these elements in water available to plants. This study involved an analysis of the Na : K : Ca : Mg ratio as well as a detailed Ca : Mg ratio over a year relation and during two characteristic seasons of the year, namely early spring and late summer (Table 1).

It was demonstrated that the differentiation of the above ratios in the analyzed seasons of the year (early spring, late summer) was connected with the dynamics of the calcium concentration. Concentrations of this element were significantly higher in summer, at a smaller outflow of water from the

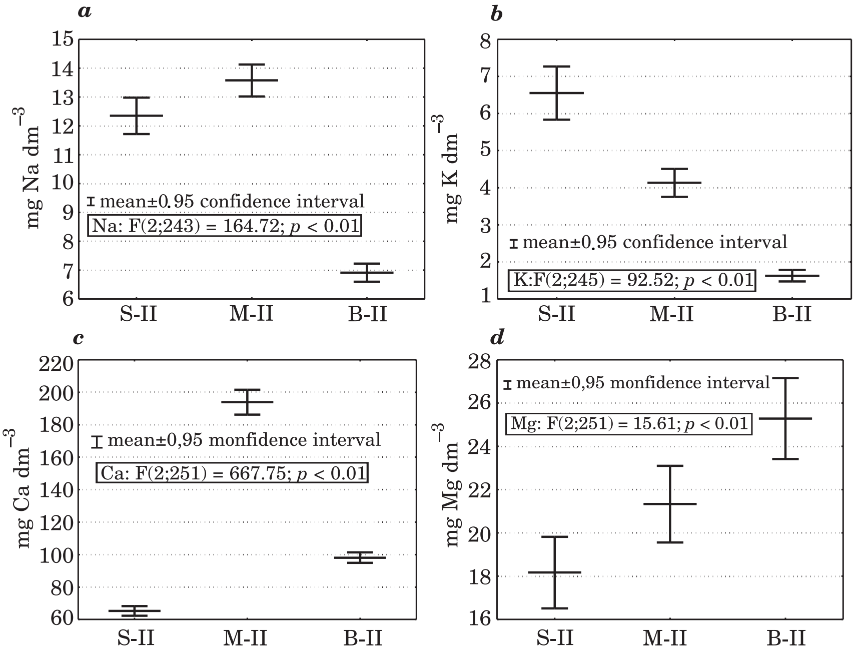

Fig. 2. Concentrations of elements in effluent waters:
a – sodium, *b* – potassium, *c* – calcium, *d* – magnesium

objects Considering the fact that this element is easily leached, one ought to suppose that the amount of leached calcium was analogous to that leached in, which obviously corresponded to higher concentrations of calcium. This caused visible differences in the Ca : Mg ratio, which ranged from 0.7 to 1.2. An increase of the value of the Ca : Mg ratio in late summer limits the outflow of potassium; concentrations of this element late summer tended to be lower. In Bogaczowice, the Ca : Mg ratios in inflow and effluent water were almost identical, although in the other two objects this ratio was variable. In Miękinia, for example, this ratio increased by about 0.4 ÷ 0.5 below the object (in this cross-section, a significant growth in the concentration of calcium in the water flowing to to the object was determined. In Samotwór, the value of this ratio below the object was lower by about 0.3÷0.4. However, seasonal changes did not show any connected with the agricultural activity because they were almost identical in sections above and below the objects.

Another analyzed dependence was the concentration of the macronutrients in effluent water versus their concentration in inflow water. The correlation coefficients for this dependence are presented in Table 2. All the correlations were significant at $p = 0.05$. For sodium, calcium and potassium, the correlation coefficients for each object were similar, with significantly smaller values obtained in Samotwór (Table 2). In all the objects, the maxi-

Table 1

Ratios of selected macroelements in early spring (Feb-April), late summer (Aug-Oct) and all year

Bogaczowice				
Season	inflow		effluent	
	Na : K : Ca : Mg	Ca : Mg	Na : K : Ca : Mg	Ca : Mg
P*	3.0:1.0:34.5:9.6	3.6	4.1:1.0:53.8:14.8	3.6
L*	2.6:1.0:34.2:8.0	4.3	4.1:1.0:65.5:15.4	4.3
Year	3.0:1.0:37.3:9.8	3.8	4.2:1.0:60.2:15.5	3.9
Miękinia				
Season	inflow		effluent	
	Na : K : Ca : Mg	Ca : Mg	Na : K : Ca : Mg	Ca : Mg
P	2.6:1.0:26.3:3.3	8.0	3.2:1.0:40.3:4.8	8.4
L	2.8:1.0:33.4:3.6	9.2	3.4:1.0:51.5:5.4	9.6
Year	2.7:1.0:30.5:3.5	8.6	3.3:1.0:48.0:5.3	9.1
Samotwór				
Season	inflow		effluent	
	Na : K : Ca : Mg	Ca : Mg	Na : K : Ca : Mg	Ca : Mg
P	2.2:1.0:12.7:3.5	3.7	1.5:1.0:8.0:2.4	3.3
L	1.9:1.0:11.2:2.5	4.5	2.0:1.0:10.5:2.6	4.1
Year	2.0:1.0:11.8:3.1	3.9	1.9:1.0:10.0:2.8	3.6

*early spring
**late summer

Table 2

Correlation coefficients between inflow and effluent water from the river basins

Element	Bogaczowice	Miękinia	Samotwór
Sodium	0.6802	0.6433	0.2332
Potassium	0.5181	0.6686	0.3601
Calcium	0.6758	0.7072	0.3136
Magnesium	0.7846	0.8064	0.8603

mum values of the correlation coefficients were calculated for magnesium, and the maximum value for this element, in contrast to the other ones, appeared (Figure 3). From the above analysis, it can be concluded that the concentration of magnesium in water flowing from a basin area used agriculturally is to a small extent relative to the type of water management.

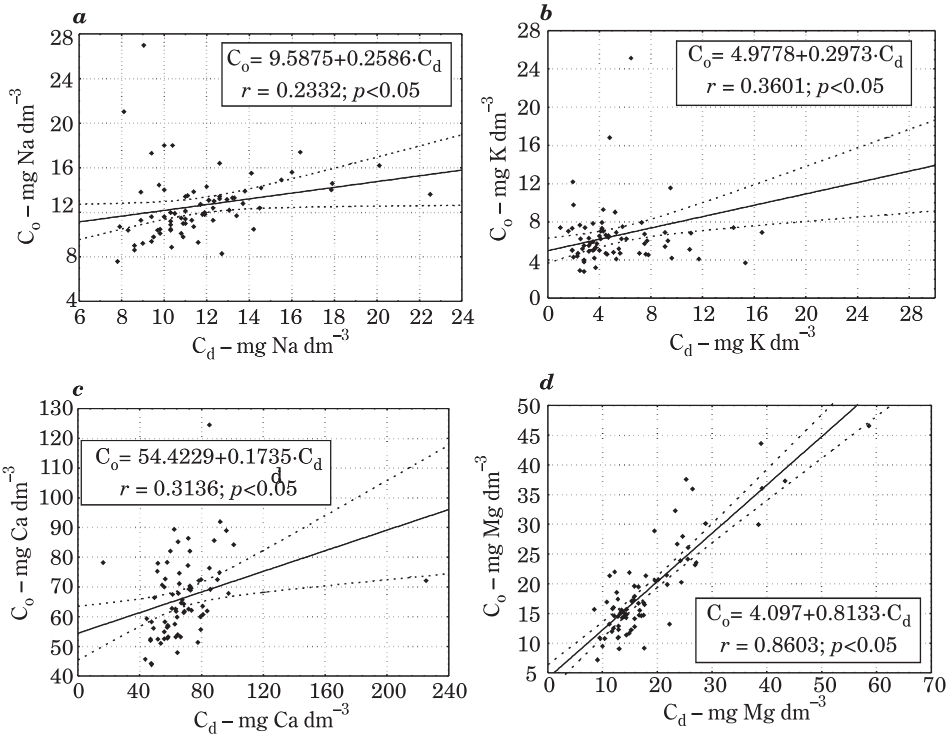

Fig. 3. Relations between concentrations of elements in inflow (Cd) and effluent (Co) water in Samotwór: *a* – sodium, *b* – potassium, *c* – calcium, *d* – magnesium

Finally, differences between concentrations of elements in inflow and effluent water from the objects were analyzed. For sodium, it was evident that drainage affects the leaching of this element as its concentration was higher in water from both drained objects, although these differences were not always significant. In the water flowing away from Mękinia, the concentration of sodium was actually smaller than its concentration above the object (Figure 4). The concentrations of potassium in the outflow water were actually smaller in Bogaczowice and Mękinia, whereas in Samotwór a somewhat higher value was determined in the water below the object, although the difference was not significant. In Bogaczowice and Mękinia, a higher concentration of calcium was found below the objects, which can suggest the leaching of this element from the river basin. Such a situation did not appear in Samotwór. Unambiguous results were obtained only for magnesium (Figure 5), whose concentration rose in the water flowing away from all the objects, but it was only in Bogaczowice that this difference was significant at the assumed level of significance of $p = 0.05$.

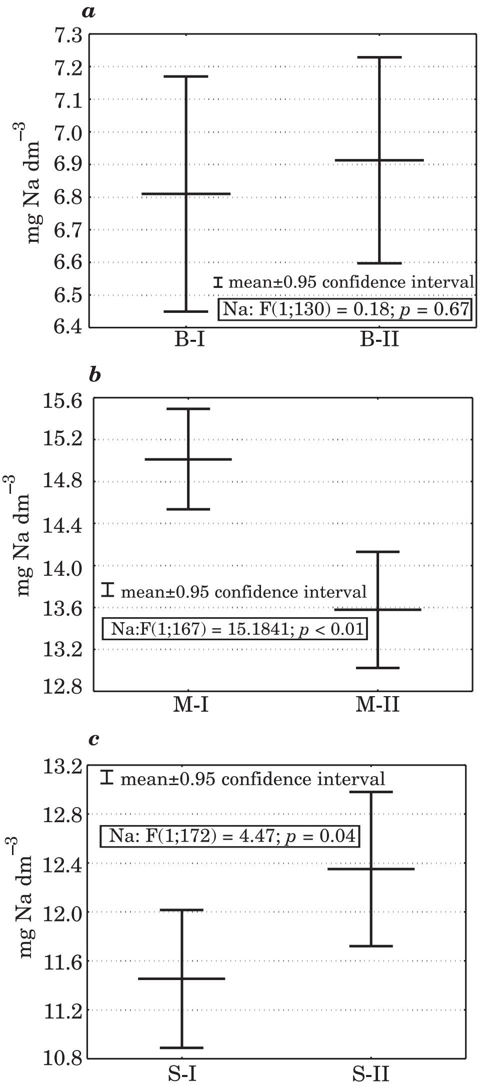

Fig. 4. Concentration of sodium in inflow and effluent waters in:
a – Bogaczowice, *b* – Miękinia, *c* – Samotwór

It can be concluded that the agricultural use of the river basins favoured an increase in the concentration of magnesium, calcium and, slightly, sodium but depressed the concentration of potassium.

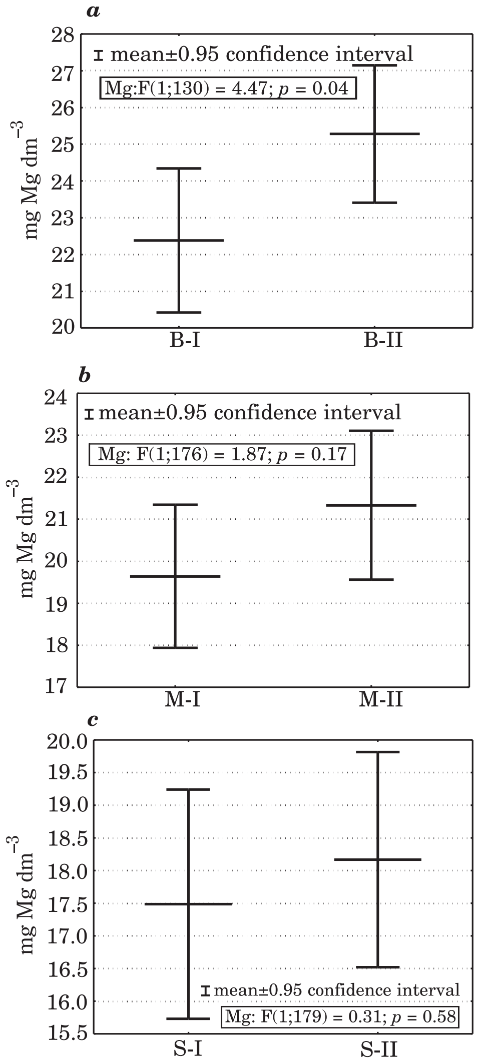

Fig. 5. Concentration of magnesium in inflow and effluent waters in: *a* – Bogaczowice, *b* – Miękinia, *c* – Samotwór – Samotwór

CONCLUSIONS

1. The magnesium content in effluent waters from all the river basins was higher than in the inflow water, with the correlation coefficients for the concentrations of the element in both sections varying from 0.7846 to 0.8603. As or the remaining elements, significant dependences were found between

their the concentrations above and below the objects, but the correlation coefficients were lower than for magnesium.

2. The differentiation of the Na : K : Ca : Mg ratio in particular seasons of the year (early spring, late summer) is connected with the dynamics of the calcium concentration. Concentrations of this element were significantly higher in summer.

3. An increase in the in value of the Ca : Mg ratio during late summer reduces the leaching of potassium; concentrations of this element tended to be lower during this season.

4. Agricultural activity does not show any direct influence on seasonal changes of the Ca : Mg ratio. Likewise, its effect on the value of this ratio is not univocal.

REFERENCES

CYMES I., SZYMCZYK S. 2005. *Wpływ użytkowania i typy gleb na zawartość sodu, wapnia i magnezu w wodzie śródpolnych małych zbiorników [Influence of land management and soil type on concentrations of sodium, calcium and magnesium in waters of small, field water bodies].* J. Elementol., 10(2): 249-257. (in Polish)

DE FRAITURE CH., MOLDEN D., WICHELNS D. 2010. *Investing in water for food, ecosystems, and livelihoods: An overview of the comprehensive assessment of water management in agriculture*. Agric. Water Manag., 97: 495-501.

DE FRAITURE CH., WICHELNS D. 2010. *Satisfying future water demands for agriculture.* Agric. Water Manag., 97: 502-511.

DURKOWSKI T. 2005. *Jakość wód gruntowych i powierzchniowych na obszarze szczególnie narażonym (zlewnia jeziora Miedwie) [Quality of ground and surface waters in a particularly exposed area (the basin of Miedwie Lake)].* Zesz. Probl. Post. Nauk Rol., 505: 107-113. (in Polish)

DURKOWSKI T., WORONIECKI T. 2001. *Jakość wód powierzchniowych obszarów wiejskich Pomorza Zachodniego [Quality of surface waters in rural areas of Western Pomerania].* Zesz. Probl. Post. Nauk Rol., 476: 365-371. (in Polish)

JALALI M. 2008. *Effect of sodium and magnesium on kinetics of potassium release in some calcareous solis of western Iran.* Geoderma, 145: 207-215.

KARAIMOV A., QADIR M., NOBLE A., VYSHPOLSKY F. ANZELM K. 2009. *Development of magnesium-dominant soils under irrigated agriculture in Southern Kazakhstan.* Pedosphere, 19(3): 331-343.

KELLENERS T.J., KAMRA S.K., JHORAR R.K. 2000. *Predication of long term drainage water salinity of pipe drains.* J. Hydrol., 234: 249-236.

GLIŃSKA-LEWCZUK K., KOBUS S. 2005. *Obieg skladników mineralnych w dolinie rzecznej na przykładzie środkowej Łyny.* Cz. II. *Wapń i magnez [Circulation of mineral components in a river valley based; a case study of the middle Lyna River].* J. Elementol., 10(3)/1: 493-501. (in Polish)

KOC J., DUDA M. 2009. *The role of storage reservoirs in reducing calcium migration from agricultural catchment.* J. Elementol., 14(3): 467-476.

ORZEPOWSKI W., PULIKOWSKI K. 2008. *Magnesium, calcium, potassium and sodium content in groundwater and surface water in arable lands in the commune of Kąty Wrocławskie* J. Elementol., 13(4): 605-614.

POKŁADEK R., NYC K. 2005. *Efekty gospodarowania wodą z zasobów retencji własnej [Effects of water management from own retention resources]*. Zesz. Probl. Post. Nauk Rol., 506: 325-333. (in Polish)

PULIKOWSKI K. 2004. *Zanieczyszczenia obszarowe w małych zlewniach rolniczych [Area pollution in small agricultural basins]*. Zesz. Nauk. AR we Wrocławiu, ser. Rozpr. CCXI, 479: 137. (in Polish)

RENAULT D., WALLENDER W.W. 2000. *Nutritional water productivity and diets*. Agric. Water Manag., 45: 275-296.

TERELAK H., Pondel H. 1990. *Wpływ nawozowej chemizacji rolnictwa na wymywanie składników mineralnych z gleb okolic Puław*. W: *Ochrona wód przed wpływem zanieczyszczeń obszarowych. [Influence of chemical fertilizers in agriculture on leaching of mineral components from soils located near Puławy. In: Protection of waters against influence of area pollutions]*. Mat. Sem. 27, Falenty, 131-141 (in Polish)

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HAIR ZINC LEVELS IN PET AND FERAL CATS *(FELIS CATUS)*

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Abstract

Zinc is an essential element for maintaining proper functions of animal bodies. It is a component of many hormones and enzymes and a participant in the metabolism of carbohydrates or the synthesis of nucleic acids and proteins. Animal tissues typically contain 10-200 mg of zinc kg^{-1}. Most of this amount (98%) can be found inside the cells. Zinc toxicity is associated mainly with the secondary copper deficit. The aim of the present investigation has been to assess zinc contamination of the environment with coats of domestic and feral cats being the indicator. Urban feral cats are synantrophic animals, living in an urbanized environment and scavenging on human food waste. Thus, they can be treated as a bioindicator of the presence of certain elements in the environment. Analyses of the zinc content in cats' hair have been performed to check whether the zinc level is connected with cats' coat colour, living conditions and gender. The coat samples were collected from the middle abdominal region. Then they were degreased and mineralized in a microwave apparatus, in concentrated nitric acid under increased pressure. The zinc content was determined by the ICP-OES method. The mean zinc content in the investigated coat samples was 238.9 mg kg^{-1}. The lowest zinc content was observed in white hair and the highest – in tortoiseshell hair. The results have confirmed that the content of zinc depends on the hair saturation with melanin. Statistical analysis has shown significant differences between the group of female cats living in the wild (268.09 mg kg^{-1}) and the group of breeding female cats (214.49 mg kg^{-1}) at p=0.05. A higher zinc content was observed in the group of older cats. The mean values did not differ from mean values of the zinc content in the coat and hair of other mammals. Considering the living conditions of the animals, the highest zinc content was noted in the group of animals living in the wild (feral ones).

Key words: zinc, hair, feral cats, domestic cats.

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ZAWARTOŚĆ CYNKU W SIERŚCI KOTÓW DOMOWYCH I WOLNO ŻYJĄCYCH *(FELIS CATUS)*

Abstrakt

Cynk jest pierwiastkiem niezbędnym do prawidłowego funkcjonowania organizmów zwierząt. Stanowi składnik wielu hormonów i enzymów, a także bierze udział w metabolizmie węglowodanów, syntezie kwasów nukleinowych oraz białek. Jego zawartość w tkankach zwierząt wynosi od 10 do 200 mg kg^{-1}, przy czym 98% znajduje się w przestrzeniach wewnątrzkomórkowych. Działanie toksyczne tego pierwiastka jest związane głównie z wtórnymi niedoborami miedzi. Celem badań było użycie sierści kota jako indykatora skażenia środowiska cynkiem z wykorzystaniem okrywy włosowej kotów domowych oraz zdziczałych kotów miejskich. Koty zdziczałe jako zwierzęta synantropijne bytujące w zurbanizowanym otoczeniu miejskim żywią się głównie odpadkami pokonsumpcyjnymi człowieka, dlatego mogą być traktowane jako bioindykator zwartości wybranych pierwiastków w środowisku. Analizy zawartości cynku przeprowadzono z uwzględnieniem wpływu czynników, takich jak: zabarwienie włosa, warunki bytowania oraz płeć zwierząt. Próby sierści pobrano z okolicy śródbrzusza. Poddano je odtłuszczaniu i mineralizacji w aparacie mikrofalowym z dodatkiem stężonego kwasu azotowego pod ciśnieniem. Zawartość cynku w badanym materiale określono metodą ICP-OES. Średnia zawartość cynku w sierści kotów była na poziomie 238.9 mg kg^{-1}. Najniższą wartość stwierdzono w sierści koloru białego, najwyższą zaś w okrywie włosowej zwierząt o umaszczeniu szylkretowym. Uzyskane wyniki potwierdziły zależność między zawartością cynku we włosie a jego wysyceniem melaniną. Odnotowano istotne statystycznie różnice p=0.05 między grupą samic wolno żyjących (268.09 mg kg^{-1}) oraz samic domowych (214.49 mg kg^{-1}). Wyższą zawartość cynku stwierdzono w sierści pozyskanej od zwierząt starszych. Średnia zawartość cynku w sierści kotów nie różniła się od wartości odnotowanych u innych gatunków ssaków. Uwzględniając warunki bytowania zwierząt, wyższe wartości zaobserwowano w grupie kotów wolno żyjących.

Słowa kluczowe: cynk, sierść, koty wolno żyjące, koty domowe.

INTRODUCTION

Zinc is an essential element for maintaining proper functions of animal bodies. It is a component of many hormones and enzymes and a participant in the metabolism of carbohydrates or the synthesis of nucleic acids and proteins. Zinc stimulates the formation and mineralization of bones. Zinc is necessary for the synthesis of collagen and activity of alkaline phosphatase (Kirsch et al. 2000, Zhang et al. 2003, Palacios 2006). On the other hand, zinc inhibits the activity of osteoclasts, which reabsorb the osseous tissue (Lai, Yamaguchi 2005). Zinc is stored in the liver, kidneys, pancreas, heart and hair. Bodies of older animals contain more zinc than those of newborns and the content of zinc in an animal's organism mainly depends on its amount in the feed (Sadurski 1984). Zinc deficiency may lead to the growth inhibition and disorders in sexual development (hypogonadism). Animals suffering from zinc shortage have decreased glucose tolerance, which causes infections, hair loss and improper growth of hair, wool or bird feathers. Zinc toxicity is associated mainly with the secondary copper deficit but zinc shows a relatively low toxicity to animals (Pasternak, Majdanik 1999).

Zinc may prevent carcinogenesis by inhibiting the formation of free radicals as a SOD (superoxide dismuthase) cofactor. However, its toxicity can result in harmful health effects (AL-EBRACHEEM et al. 2009). It has been concluded from animal studies that Zn plays an important role in the mechanism of Cd carcinogenesis. The exact mechanism by which Zn modifies this process has not been fully elucidated. It is known that Zn may participate in many stages of the carcinogenesis including the growth of cells, inactivation of reactive free radicals and the repair of DNA (BRZÓSKA, MONIUSZKO-JAKONIUK 2001).

A feline population living in towns could be divided into several categories: (a) cats living exclusively in human houses, totally depending on people's care, whose impact on the state of sanitary environment is only slight; (b) stray and feral animals living close to human houses. These animals use human food resources either indirectly (waste) or directly (intentional extra feeding); (c) domestic cats which are let out; an intermediate group between animals from groups (a) and (b) (NATOLI 1994, GUNTHER, TERKEL 2002).

The skeleton, coat and blood serum are considered to be the zinc index tissues in the organism (BODKOWSKI et al. 2006, UNKIEWICZ-WINIARCZYK et al. 2009). Hair is good material for investigating the state of supply of mineral components, especially microelements, in the organism because their content in hair is usually higher than in blood. It is also useful for determination of the status of trace elements in the organism, especially *intra vitam* (RADOMSKA et al. 1991, ANKE et al. 1994, BODKOWSKI et al. 2006). In recent years, the human hair trace element content has become a subject of toxicological, ecological, hygienic and clinical research (DIETZ et al. 2001, RASHED, SOLTAN 2005). Animal coat is a better indicator of environmental pollution than human hair because of its exposure to the soil contamination through the trophic chain (SMOLIANINOW, ASHURBEKOV 1974). Until now, hair samples from domesticated and wild species such as cattle, horse, goat, sheep, camel, European bison, moose, brown bear, wild boar, squirrel and seal have been used as a bioindicator of metal pollution (MEDVEDEV 1999, LIU 2003, IKEMOTO et al. 2004, RASHED, SOLTAN 2005, HAWKINS, RAGNARSDOTTIR 2009, SKIBNIEWSKI et al. 2010).

The aim of the present study has been to determine the zinc content in cats' coat, depending on their living conditions, gender and hair colour.

MATERIAL AND METHODS

The investigation material (n=40) comprised cats kept at home (10 females and 10 males) and living in the wild (10 females and 10 males). The free living animals were caught alive in Ursynów, an area of Warsaw, as part of the effort to limit the population of stray and feral cats. They were all typical European cats. Having been caught into special traps, the animals were subjected to surgical spaying. The group of domestic cats consisted of animals of documented origin. On the basis of clinical examination, a group of twenty males and twenty females which did not show any pathological signs was selected. The males were subjected to the procedure of orchiectomy and the females underwent ovariohysterectomy. The age of the homeless animals was determined on the basis of dentition. Coat samples, which were the indicators of zinc contamination of the organisms, were collected from the middle abdominal area. Topographically this area consisted of two regions: *regio umbilicalis* and *regio abdominis lateralis*, and the coat samples were collected from both of these regions. The samples were degreased in 70% ethanol in a Soxlete apparatus, washed in hot distilled water, rinsed in redistilled water and then transferred into Teflon containers. Next, they were mineralized in concentrated nitric acid under pressure in a microwave apparatus. The zinc content in the cats' hair was determined using the method of emission atomic spectrometry with inductively coupled plasma optical emission spectrometry (ICP-OES) in an accredited laboratory, standardizing the results with reference samples. The results were processed statistically with the programme Statistica™.

RESULTS

The results of the zinc content in the cats' coat depending on their living conditions and gender are presented in Table 1. The average zinc content in the analyzed coat samples reached 238.9 mg kg^{-1} of air dried hair. In the group of free living cats (feral ones), the mean zinc content was at the level of 250.52 mg kg^{-1} of air dried hair, and in the group of domestic (breeding) cats, it equalled 227.28 mg kg^{-1}. The statistical test showed significant differences between the group of free living female cats (268.09 mg kg^{-1}) and the group of breeding female cats (214.49 mg kg^{-1}) at p=0.05. The content of zinc in hair depending on the cats' age is presented in Table 2. Although a higher zinc content was observed in the group of older cats (242.14 mg kg^{-1}), the age of cats did not affect the hair level of zinc in a statistically significant way.

In addition, analyses of the zinc content in the cats' coat depending on the colour were performed, assuming that the colour depends on the hair saturation with melanin, thus testing whether zinc is melanin-dependent. The results are presented in Table 3. The lowest zinc content was found in white hair, higher in red and then in black hair; yet higher zinc levels were determined in the feral cats' hair, i.e. in brownish grey, and the highest – in tortoiseshell hair. The results confirmed that the content of zinc depends on the hair saturation with melanin.

Table 1

Zinc content in the cats' hair depending on gender and living conditions (mg kg^{-1} of air dried hair)

Statistical parameters	Living conditions		Females		Males		Total number of animals
	free living (feral)	domestic	free living (feral)	domestic	free living (feral)	domestic	
n	20	20	10	10	10	10	40
Arithmetic mean	250.52	227.28	268.09*	214.49*	232.95	240.07	238.90
Standard deviation	61.16	25.89	78.00	19.59	33.57	25.84	47.83
Lower quartile (25%)	216.10	208.10	228.16	203.00	214.00	231.00	209.00
Median	232.50	226.48	240.36	208.10	229.50	238.90	230.50
Upper quartile (75%)	265.00	240.74	276.00	221.96	262.40	243.60	249.41

*significant differences at $P \leq 0.05$

Table 2

Zinc content in the cats' hair depending on age (mg kg^{-1} of air dried hair)

Statistical parameters	Cats up to 2 years	Cats over 2 years
n	11	29
Arithmetic mean	230.36	242.14
Standard deviation	33.35	52.44
Lower quartile (25%)	203.00	209.00
Median	215.00	232.61
Upper quartile (75%)	257.00	248.10

Table 3

Zinc content in the cats' hair depending on the hair colour (mg kg^{-1} of air dried hair)

Statistical parameters	White	Red	Black	Brownish grey	Tortoiseshell
n	8	4	12	7	9
Arithmetic mean	219.05	233.84	235.90	245.35	257.76
Standard deviation	14.75	33.09	32.80	28.50	87.22
Lower quartile (25%)	208.10	213.40	211.00	215.00	208.98
Median	213.50	240.17	233.90	248.10	228.16
Upper quartile (75%)	231.80	254.24	252.60	262.40	250.71

DISCUSSION

The values detected in our study do not differ from the mean zinc content in the coat and hair of other mammals (ANKE et al. 1994, CZAPSKA et al. 1999, HOUSE 1999, CHYLA, ZYRNICKI 2000). SADURSKI (1984) reports that the mean zinc content in animal hair was within 40-480 mg kg^{-1}, which agrees with the values obtained in our own investigations. Our results demonstrate that free living cats have a higher zinc content in their coats, which suggests that they consumed feed with a higher content of this element. Urban feral cats are synanthropic animals, whose staple food is human food waste.

The highest zinc content was noted in the group of free living females (268.09 mg kg^{-1}). Similar results were obtained by other authors (DEEMING, WEBER 1978, CZAPSKA et al. 1999, UNKIEWICZ-WINIARCZYK et al. 2009). A higher zinc level in women's hair of was observed by DEEMING and WEBER (1978). Statistical analysis revealed a significant difference in the zinc content between women's (208 mg kg^{-1}) and men's hair (176 mg kg^{-1}). While investigating the zinc content in human hair, UNKIEWICZ-WINIARCZYK et al. (2009) also observed a generally higher content of this element in women as compared to men. In a group of women aged 20-30 years, the zinc content was at the level of 272.75 mg kg^{-1}, while in an older group, aged 50-60 years, the content of this element was lower, namely 229.6 mg kg^{-1}. Among men, the zinc level was distinctly lower in younger men (203 mg kg^{-1}) and higher in older ones (251.75 mg kg^{-1}). The results obtained in our investigation concerning the zinc content coincide with the results reported by UNKIEWICZ-WINIARCZYK et al. (2009), except the zinc content in hair obtained from young men, where a lower zinc content was observed than in our study.

A higher level of zinc in women's hair was also observed by other authors (ŁUKASIAK et al. 1998, CZAPSKA et al. 1999). A study on the zinc content in the coat of European bison (Kośla et al. 2004) showed a reverse dependence, i.e. a lower amount of this element in females (181.5 mg kg^{-1}) than in males (199.5 mg kg^{-1}).

CONCLUSIONS

The following conclusions could be drawn on the basis of the performed analyses:

1. The observed mean values of zinc in the analyzed samples of cats' hair do not differ from the zinc content in the coat or hair of other mammals.
2. Considering the living conditions of the cats, the highest zinc content was found in the group of free living animals (feral ones).

REFERENCES

Al-Ebraheem A., Farquharson M.J., Ryan E. 2009. *The evaluation of biologically important trace metals in liver, kidney and breast tissue.* Appl. Radiat. Isotop., 67: 470-474.

Anke M., Groppel B., Angelow L. 1994. *Der Einfluss des Mangan-, Zink-, Kupfer-, Jod-, und Selenmangels auf die Fortpflanzungsleistung des Wiederkäuers [The influence of manganese, zinc, copper, iodine and selenium deficiency on reproductive ability of ruminants].* Rek. J., 1: 23-28. (in German)

Bodkowski R., Patkowska-Sokoła B., Dobrzyński Z., Janczar M., Zygadlik K. 2006. *Wykorzystanie wełny owczej do oceny stopnia skażenia środowiska metalami ciężkimi [Sheep wool as an indicator of environmental pollution by heavy metals].* Rocz. Nauk. PTZ, 1: 105-111. (in Polish)

Brzóska M.M, Moniuszko-Jakoniuk J. 2001. *Interactions between cadmium and zinc in the organism.* Food Chem. Toxicol., 39: 967-980.

Chyla M.A., Zyrnicki W. 2000. *Determination of metal concentrations in animals hair by the ICP method: comparison of various washing procedures.* Biol. Trace Res., 75(1-3): 187-194.

Czapska D., Karczewski J., Ostrowska L. 1999. *Zawartość magnezu i cynku we włosach studentów Akademii Medycznej w Białymstoku [Magnesium and zinc content in the hair of students of the Białystok Medical Academy].* Biul. Magnezol., 4(2): 297-301 (in Polish)

Deeming S. B., Weber C.W. 1978. *Hair analysis of trace minerals in human subjects as influenced by age, sex and contraceptive drug.* Am. J. Clin. Nutr., 31: 1175-1180.

Dietz M. C., Ihring A., Wrazidło W., Bader M., Jansen O., Triebig G. 2001. *Results of magnetic resonance imaging in long-term manganese dioxide exposed workers.* Environ. Res., 62(2): 242-250.

Gunther I., Terkel J. 2002. *Regulation of free-roaming cat (Felis Silvestris Catus) populations: a survey of the literature and its application to Israel.* Anim. Wel., 11: 171-188.

Hawkins D.P, Ragnarsdottir K.V. 2009. *The Cu, Mn and Zn concentration of sheep wool: Influence of washing procedures, age and colour of matrix.* Sci. Total Environ., 407: 4140-4148.

House W.A. 1999. *Trace element bioavailability as exemplified by iron and zinc.* Field Crop Res., 60: 115-141.

IKEMOTO T., KUNITO T., WATANABE I., YASUNAGA G., BABA N., MIYAZAKI N., PETROV E.A., TANABE S. 2004. *Comparison of trace element accumulation in Baikal seals (Pusa sibirica), Caspian seals (Pusa caspica) and northern fur seals (Callorhinus ursinus).* Environ. Pollut., 127: 83-97.

KIRSCH T., HARRISON G., WORCH K.P., GOLUG E.E. 2000. *Regulatory roles of zinc in matrix vesiclemediated mineralization of growth plate cartilage.* J. Bone Miner. Res., 15(2): 261-270.

KOŚLA T., SKIBNIEWSKI M., SKIBNIEWSKA E.M., URBAŃSKA-SŁOMKA G. 2004. *The zinc status in free living European Bisons.* Acta Aliment. Hung., 33(3): 269-273.

LAI Y.L., YAMAGUCHI M. 2005. *Effects of copper on bone component in the femoral tissues of rats: anabolic effect of zinc in weakened by copper.* Biol. Pharm. Bull., 28(12): 2296-2301.

LIU Z.P. 2003. *Lead poisoning combined with cadmium in sheep and horses in the vicinity of non-ferrous metal smelters.* Sci. Total. Environ., 309: 117-126.

ŁUKASIAK J., CAZJER D., DABROWSKA E., FALKIEWICZ B. 1998. *Zawartość wapnia, magnezu i cynku we włosach studentów Akademii Medycznej w Gdańsku. [Analysis of calcium, magnesium, and zinc levels in hair of students of the Medical University of Gdańsk].* Żyw. Człow. Metabol., 25(1): 68-72. (in Polish)

MEDVEDEV N. 1999. *Levels of heavy metals in Karelian wildlife 1989-91' Environ.* Monitor. Assess., 56 (2): 177-193.

NATOLI E. 1994. *Urban feral cats (Felis Catus L.): perspectives for a demographic control respecting the psycho-biological welfare of the species.* Ann. Ist. Super. Sanita, 30(2): 223-227.

PALACIOS C. 20006. *The role of nutrients in bone health, from A to Z.* Crit. Rev. F. Sci. Nutr., 46(8): 621-628.

PASTERNAK K., MAJDANIK M. 1999. *Rola cynku w przyrodzie [The role of zinc in nature].* Biul. Magnezol., 4:547-553. (in Polish)

RADOMSKA K., GRACZYK A., KONARSKI J. 1991. *Analiza włosów jako metoda oceny stanu mineralnego organizmu [Hair analysis as an evaluation method of the mineral status in an organism].* Pol. Tyg. Lek., 46: 479-481. (in Polish).

RASHED M. N., SOLTAN M. E. 2005. *Animal hair as a biological indicator for heavy metal pollution in urban and rural areas.* Environ. Monitor. Asses., 110: 41-53.

SADURSKI T. 1984. *Schorzenia wywołane niedoborem cynku [Diseases caused by zinc deficiency].* Med. Wet., 8: 489-493. (in Polish)

SKIBNIEWSKI M., KOŚLA T., SKIBNIEWSKA E.M. 2010. *Manganese status in free ranging European bison from Bialowieza primeval forest.* Bull. Vet. Inst. Pulawy, 54: 429-432.

SMOLIANINOW V. M., ASHURBOKOV T.R. 1974. *Changes in the trace element composition of the hair as a tool in the expert criteria of species and sex identification (dogs, cats and swine as models).* Sud. Med. Ekspert., 17: 17-25.

ZHANG Y.H., CHENG Y.Y., HONG Y., WANG D.L., LI S.T. 2003. *Effects of zinc deficiency on bone mineralization and its mechanism in rats.* Zhonghua Yu Fang Yi Xue Za Zhi., 37(2): 121-124.

UNKIEWICZ-WINIARCZYK A., BAGNIUK A., GROMYSZ-KAŁKOWSKA K. 2009. *Calcium, magnesium, iron, zinc and copper concentration in the hair of tobacco smokers.* Biol. Trace Elem. Res., 128: 152-160.

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REVIEW PAPER

SILICON IN MEDICINE AND THERAPY

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Abstract

Trace elements are a very important factor affecting functions of living organisms. Silicon, the third most abundant trace element in the human body, is present in all healthy tissues of people. It is especially strongly associated with connective tissues, as it has been found to participate in bone development, collagen formation and mineralization of bone matrix. Silicon has also been suggested to be involved in mammalian hormonal control and to protect people from heart diseases.

An average dietary intake of silicon is about 20-30 mg/person/day, with higher intakes for men than women. Silicic acid or orthosilicic acid are the bioavailable forms of silicon, found mainly in food rich in fibre and whole grains, in vegetables, fruit and in drinking water. Various alcoholic beverages such as beer or wine also contain considerable amounts of silicon. Silicon provided with food is digested in the gastrointestinal tract to silicic acid, which is then absorbed. With blood, it is distributed into various tissues and organs, where it can exerts its action. The highest amounts of silicon are accumulated in the kidneys, liver, bone, skin, spleen, lungs, while free orthosilicic acid, not bounded to proteins, occurs in blood. The amount of silicon in tissues decreases with age. Depleted levels of silicon have also been observed in some pathological states e.g. atherosclerosis.

The aim of the paper has been to present the role of dietary silicon in living organisms. Silicon is necessary for the growth and bone calcification and as a biological cross-linking agent of connective-tissue-based membrane structures. This element is considered to have beneficial effects on several human disorders, including osteoporosis, ageing of skin, hair and nails or atherosclerosis. It has also been suggested that silicon and silicic acid may decrease the bioavailability of aluminium by blocking the uptake of the latter by the gastrointestinal tract and impeding its reabsorption in the kidneys, thus protecting an organism against the toxic (especially neurotoxic) action of aluminium. Anticancer, antiatherosclerotic and antidiabetic effects of silicon have also been suggested.

Key words: silicon, silicon metabolism, bone, connective tissue, aluminium toxicity.

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KRZEM W MEDYCYNIE I LECZNICTWIE

Abstrakt

Pierwiastki śladowe są bardzo ważnym czynnikiem warunkującym prawidłowe funkcjonowanie organizmów żywych. Krzem, trzeci pierwiastek śladowy pod względem rozpowszechnienia w organizmie człowieka, jest obecny we wszystkich zdrowych tkankach. Szczególną rolę odgrywa krzem w tworzeniu i funkcjonowaniu tkanki łącznej, ponieważ bierze on udział w rozwoju kości, tworzeniu kolagenu i mineralizacji macierzy kostnej. Krzem uczestniczy również w kontroli hormonalnej u ssaków oraz w ochronie przed chorobami serca u ludzi.

Dzienna dawka krzemu dla dorosłego człowieka powinna wynosić 20-30 mg, przy czym zapotrzebowanie na krzem jest większe u mężczyzn niż u kobiet. Przyswajalną formą krzemu jest kwas krzemowy lub kwas ortokrzemowy, którego źródłem w diecie są zboża, warzywa, owoce oraz woda pitna. Krzemiany z pożywienia są w przewodzie pokarmowym hydrolizowane do łatwo przyswajalnego kwasu ortokrzemowego, który wraz z krwią jest rozprowadzany do wszystkich tkanek i organów. Najbogatsze w krzem są nerki, wątroba, kości, skóra, śledziona oraz płuca, a we krwi krzem występuje w postaci wolnego kwasu ortokrzemowego, niezwiązanego z białkami. Wszystkie tkanki zawierają dużo krzemu, gdy są całkowicie zdrowe, natomiast jego poziom zmniejsza się w nich wraz z wiekiem człowieka i tkanki ulegają wówczas stopniowej degeneracji. Zaniżony poziom krzemu obserwuje się również w pewnych stanach chorobowych, na przykład w miażdżycy.

Celem pracy była prezentacja zależności między krzemem przyswajanym z pożywienia a wpływem, jaki wywiera on na organizmy żywe. Krzem jest niezbędny w procesie wzrostu oraz wapnienia i mineralizacji kości, jest również czynnikiem sieciującym struktury tkanki łącznej. Pierwiastek ten wywiera korzystny wpływ w pewnych schorzeniach, takich jak osteoporoza, starzenie się skóry, włosów i paznokci, miażdżyca. Krzem ma unikatowe właściwości wiązania metali ciężkich w nierozpuszczalne kompleksy, ograniczając ich szkodliwe działanie. Dodatkowo, kwas krzemowy hamuje wchłanianie glinu i jest antidotum na jego toksyczne działanie. Sugeruje się również jego działanie przeciwcukrzycowe, przeciwmiażdżycowe oraz przeciwnowotworowe.

Słowa kluczowe: krzem, metabolizm krzemu, kości, tkanka łączna, toksyczność glinu.

INTRODUCTION

Trace elements are a very important factor, affecting functions of living organisms. Although silicon is the second most abundant element in biosphere after oxygen, due to its very poor bioavailability to the human organism, its influence on metabolic processes is only fragmentarily known and poorly understood (BIRCHALL et al. 1996).

The daily recommended intake (DRI) has not been determined yet, although a suggested daily dose of silicon should reach 20-30 mg for an adult, which corresponds to 0.28-0.43 mg kg^{-1} b.w. a day for a man weighing 70 kg. Dietary sources of silicon are grains (rice, barley, oat, wheat) and grain products (breakfast cereals, bread, pasta), root vegetables (carrots, beetroot, radish, onion, potatoes), bean, corn, fruit (especially bananas) as well as dried fruit (raisins) and nuts. Silicon is highly available from drinking water and its concentration depends upon the geology of water intake surroundings because Si is derived from weathering rocks and soil minerals (JUGDAOHSINGH et al. 2002, SRIPANYAKORN et al. 2005). Beer and wine are also rich sources of dietary silicon, containing quite high amounts of orthosilicic acid, a Si bioavailable form (THIEL et al. 2004, GONZÁLEZ-MUÑOZ et al. 2008). Drinking infusions of silicon containing herbs (like Common Horsetail, Knotweed, Red Hemp-nettle, Lungwort) can supplement dietary deficits of that element as well as to alleviate symptoms of some diseases (ZIELECKA 1996).

Silicates from food are hydrolyzed into readily available orthosilicic acid in the gastrointestinal tract (BAREL et al. 2005). The exact site where silicic acid is absorbed from the gastrointestinal canal has not been established, although it has been suggested that silicon compounds from food in the presence of hydrochloric acid and other gastric acids in the stomach are broken down into orthosilicic acid, which easily diffuses through mucous membranes into the blood circulation system. In the Framingham and Framingham Offspring studies, values of an average daily silicon availability have been determined as 12.1-13.5 mg for men and 9.9-10.2 mg for women (JUGDAOHSINGH et al. 2002, JUGDAOHSINGH et al. 2004). The peak increase in the serum silicon concentration was observed 60-84 minutes after orthosilicic acid consumption (REFFITT et al. 1999) and 100-120 minutes after ingestion of a silicon-rich meal (13.15 mg) (JUGDAOHSINGH et al. 2002). Kidneys play a key role in silicon turnover. Silicon is readily filtered by the renal glomerulus because it does not form any bonds with plasma proteins (SRIPANYAKORN et al. 2005). Hence, about 70-80% of plasma silicon is eliminated by kidneys within 3-8 hours after meal ingestion (POPPLEWELL et al. 1998). Thus, urinary Si excretion is a good surrogate marker of silicon absorption (WIDNER et al. 1998, REFFITT et al. 1999). Silicon in the form of inorganic silicate occurs in large quantities in kidneys and is a constant component of urine. Silica also fulfils a role of protective colloid preventing appearance of urinary stones, although silicon excess may lead to formation of renal deposits and calculus (ZIELECKA 1996). Studies on kinetics of silicon absorption and elimination demonstrated that the organs and tissues characterized by the highest concentrations of silicon are connective tissues, bone, skin liver, heart, muscle, kidneys and lungs (POPPLEWELL et al. 1998, JUGDAOHSINGH 2007). The amount of silicon in tissues decreases with age, probably because the organ responsible for silicon absorption and turnover in an organism is the thymus, which undergoes atrophy with age.

INFLUENCE OF SILICON ON THE DEVELOPMENT AND FUNCTIONS OF A LIVING ORGANISM

For a long time, silicon has been thought to be an inactive substance, not participating in biochemical processes due to its overall unavailability to living organisms. Only recently it has been recognized as one of the most essential trace elements in human metabolism.

The highest concentrations of silicon have been found in organs consisting of connective tissues such as the aorta, trachea, bones and skin. The content of silicon in human skin is 49.5 μg g^{-1} of tissue, in hair 42.0 μg g^{-1} of tissue and in nails 26.12 μg g^{-1} of tissue. A high content of silicon in the connective tissue is attributed to its presence in protein complexes, which form the structure of the tissue as a cross-linking entity (ZIELECKA 1996). In animal studies, the aorta, trachea and tendons were found 4 or 5-fold richer in silicon than the liver, heart and muscles. In blood, silicon occurs in the form of free orthosilicic acid, not bounded with proteins, reaching a concentration from 50 to 200 μg L^{-1}, depending on its content in a diet (D'HAESE et al. 1995). The overall silicon content in a man weighing 70 kg is from 140 to 700 mg, which classifies that element as the third most abundant macroelement, after zinc and iron (SRIPANYAKORN et al. 2005). All tissues contain large amounts of silicon when they are perfectly healthy, but its amount decreases with age and then the tissues undergo gradual degradation. Depleted levels of silicon have also been observed in some pathological states like atherosclerosis or neoplastic diseases (BISSÉ et al. 2005).

In vitro studies showed that orthosilicic acid in a physiological concentration stimulates collagen synthesis and, through an increase in prolylhydroxylase activity in human osteoblasts, it stimulates their differentiation (REFFITT et al. 2003, JUGDAOHSINGH et al. 2004). Much silicon has also been found in human osteoblasts, highly metabolically active cells. In the human organism, silicon is mainly accumulated in sites of active bone growth. Numerous studies have confirmed that silicon actively participates in the process of bone calcification and accelerates the rate of bone mineralization. Silicon deficiency causes deformations or delay in bones formation as well as disorders in joint cartilage and connective tissue formation (RICO et al. 2000).

There is evidence that dietary silicon is able to lower the plasma total, VLDL and LDL cholesterol level (WACHTER et al. 1998) and to significantly inhibit the atherosclerotic process induced by a cholesterol rich diet (PELUSO, SCHNEEMAN 1994). According to some authors, silicon exerts antiatherosclerotic action mainly through increasing membrane permeability and the basal substance of arteries. Studies carried out on animals proved that silicon administered in the form of silica prevented occurrence of endoxan or streptozotocin-induced diabetes (OSCHILEWSKI et al. 1986). Antineoplastic properties of silicon, which can be associated with its influence on the connective tissue synthesis, thereby reducing progress and propagation cancer, have been reported. Synthetic silicon compounds, e.g. silitrans derivatives, applied together with cytostatics, improved manifold the effectiveness of the latter (Janczarski, Janczarski 1991). Silicon also plays a role in immune functions influencing lymphocytes proliferation (Seaborn et al. 2002).

Silicon has a unique property of binding heavy metals into insoluble complexes, thereby limiting their possible harmful effects. Additionally, silicic acid inhibits the gastrointestinal absorption of aluminium, a metal of neurodegenerative action, whose role in the pathogenesis of Alzheimer's disease is stated to be significant. Silicon is reported to be an antidote to aluminium toxicity as it reduces Al bioavailability (Bellia et al. 1996, Reffitt et al. 1999, Domingo 2006).

Silicon metabolism is connected with the turnover of numerous macro- and microelements. With calcium, silicon is involved in the processes of bone decalcification as well as calcification. Silicon is calcium-antagonist, therefore it can regulate calcium and magnesium turnover. It acts synergistically with copper, thus depressing the zinc concentration in tissues. It also antagonises harmful effects of aluminium on osteogenesis. Additionally, silicon influences the metabolism of such elements as P, Cl, Na, K, S, Mo, Co (O'Connor et al. 2008). This element is required to remove harmful and toxic heavy metals from the brain (Birchall et al. 1996, Perry, Keeling-Tucker 1998, Boguszewska et al. 2003).

Disturbances in silicon turnover have been reported in patients suffering from different skin problems or tuberculosis and in persons treated with antibiotics and chemotherapeutics for a long time (Ożarowski 1996, Calomme, Vanden Berghe 1997).

SILICON AND BONE

In the 1980s, the earliest studies on silicon biochemistry, carried out by Carlise, suggested strong connection between a proper level of dietary silicon intake and normal growth of animals (chickens and rats) (Carlisle 1980). Particularly collagenous tissues, like bones, cartilages, skin and hair were markedly abnormal in Si-deprived animals. Bone health subsequently became the main subjects for researchers studying the biological role of silicon, mainly because osteoporosis, characterized by low bone mass, is a growing health problem worldwide and leads to marked disability, increased mortality and raised health care costs (Sripanyakorn et al. 2005, Jugdaohsingh 2007).

According to recent studies, silicon is co-located with calcium in the osteoid tissue, thus some interactions between these elements were suspected to occur in processes of bone growth and mineralization (Perry, Keeling-Tucker 1998). In the earliest stage of calcification, in active calcification sites in young bones, there is a direct relationship between silicon and calcium when the calcium content of the preosseous tissue is very low. Therefore, it has been suggested that silicon is associated with calcium in the early stage of bone formation. It was demonstrated that dietary silicon increased the rate of mineralization, especially in calcium-deficient rats (Kim et al. 2009). Evidence has been obtained to indicate that when rats are fed low calcium diets, bone composition is affected by silicon deprivation: the deprivation depressed concentrations of calcium, magnesium, and phosphorus in the tibia and skull (Carlisle 1980). Additionally, silicon was found to promote the union of a bone after a fracture, in contrast to calcium, which can actually slow down the healing process or interfere with it altogether, especially when calcium levels are very high. All these facts can be interpreted as promoting bone mineralization by silicon under the conditions of a low level of calcium in a diet, but on the other hand in may also indicate interactions between calcium and silicon in the gut lumen, which can reduce the gastrointestinal absorption of silicon (Sripanyakorn et al. 2005, Jugdaohsingh 2007).

SILICON AND SKIN, HAIR AND NAILS

Many studies on silicon influence on bone and cartilage formation confirmed, that the element's primary effect is thought to be on matrix synthesis rather than mineralization (Calomme, Vanden Berghe 1997). Silicon in form of orthosilicic acid at physiological concentrations was found to stimulate collagen type 1 synthesis in human osteoblast-like cells and skin fibroblasts. Silicon treatment also enhanced osteoblastic differentiation. The suggested mechanism of orthosilicic acid is to modulate activity of prolyl hydroxylase, an enzyme involved in conversion of hydroxylate proline to hydroxyproline in the process of collagen formation, rather than alteration in collagen type 1 gene expression (Reffitt et al. 2003). Silicon was also reported to be necessary in formation of glycosaminoglycans in bone and cartilage due to its structural role in the cross-linking of glycoaminoglycans in connective tissue. As type 1 collagen and its monomer hydroxyproline are major constituents of skin, the improvement in skin parameters, like hydratation or microrelief (roughness), after silicon supplementation indicates on potential regeneration or de novo synthesis of collagen fibers. Treatment with silicon also might improve the glycosaminoglycan structure in the dermis and the keratin structure in hair and nails, what was seen through decrease in hair and nails brittleness (Barel et al. 2005).

SILICON AND ALUMINIUM TOXICITY

Despite the widespread occurrence of aluminium in the environment as well as its presence in trace amounts in almost all plants and animals, for a long time Al has been considered to be indifferent to living organisms. However, aluminium can have deleterious effects on plants, animals as well as on human beings. In the terrestrial environment, that is in plants, it is responsible for the development of a stunted and brittle root system; in animals and human it causes growth disorders and disturbed neurological functioning (Alzheimer type senile dementia, amyotrophic lateral sclerosis, a type of Parkinson's disease) (DOMINGO 2006). Aluminium is even more toxic in the aquatic environment, where it can be fatal to fish. Acute aluminium toxicity can be associated to its ability to bind to biologically important ligands, like phosphate groups in membranes, DNA and ATP. Aluminium is also able to bind to aionic sites on fish gill epithelia, stimulating excessive mucus production, which causes potentially lethal disturbances in respiration as well as ion transport (PERRY, KEELING-TUCKER 1998). The idea that silicon may be involved in a mechanism to protect against aluminium poisoning, inspired by Si-Al interactions observed in inorganic chemistry, has been checked in numerous experiments. The most recent research shows that silicic acid interacts with metal ions that are basic at physiological pH, such as aluminium. Silicon is involved in relieving Al toxicity in many different biological systems as well as in reducing aluminium bioavailability in humans by reducing its gastrointestinal absorption and enhancing its renal excretion (BIRCHALL et al. 1996, REFFITT et al. 1999). Orthosilicic acid from beer was found to increase the urinary output of aluminium, perhaps by interacting with filterable Al in renal tubules, forming hydroxyaluminosilicates and thus preventing re-absorption of aluminium (BELLIA et al. 1996). These findings may benefit transplant patients in clearing the accumulated aluminium as well as other patients, protecting them from harmful effects of aluminium excess.

The role of silicon in human biology is poorly understood, although the above findings and studies may suggest beneficial influence of silicon on the human organism in some diseases, like osteoporosis, atherosclerosis, progress of diabetes, propagation of neoplastic process as well as occurrence of heart diseases (TURNER et al. 2008). Silicon was also found to reduce negative effects of some processes as skin, hair and nails ageing (JUGDAOHSINGH et al. 2002). It is very important for regenerating tissues, activating vital processes of cells and improving the general immunity of organism. Therefore, further studies on silicon biology, biochemistry as well as silicon homeostasis and its interactions with essential mineral elements as well as with other biologically important molecules are necessary.

REFERENCES

Barel A., Calomme M., Timchenko A., De Paepe K., Demeester N., Rogiers V., Clarys P., Vanden Berghe D. 2005. *Effect of oral intake of choline-stabilized orthosilicic acid on skin, nails and hair in women with photodamaged skin*. Arch. Dermatol. Res., 297(4): 147--153.

Bellia J.P., Birchall J.D., Roberts N.B. 1996. *The role of silicic acid in the renal excretion of aluminium*. Ann. Clin. Lab. Sci., 26(3): 227-233.

Birchall J.D., Bellia J.P., Roberts N.B. 1996. *On the mechanisms underlying the essentiality of silicon – interactions with aluminium and copper*. Coord. Chem. Rev., 149: 231-240.

Bissé E., Epting T., Beil A., Lindinger G., Lang H., Wieland H. 2005. *Reference values for serum silicon in adults*. Anal. Biochem., 337(1): 130-135.

Boguszewska A., Pasternak K., Sztanke M. 2003. *Stężenie krzemu w osoczu krwi pacjentów ze świeżym zawałem mięśnia sercowego i stabilną chorobą niedokrwienną serca [Silicon concentrations in blood serum of patients soon after cardiac infarct and stable ischaemic heart disease]*. J. Elementol., 8: 4-10. (in Polish)

Calomme M.R., Vanden Berghe D.A. 1997. *Supplementation of calves with stabilized orthosilicic acid. Effect on the Si, Ca, Mg, and P concentrations in serum and the collagen concentration in skin and cartilage*. Biol. Trace Elem. Res., 56(2): 153-165.

Carlisle E.M. 1980. *Biochemical and morphological changes associated with long bone abnormalities in silicon deficiency*. J. Nutr., 110(5): 1046-1056.

D'Haese P.C., Shaheen F.A., Huraib S.O., Djukanovic L., Polenakovic M.H., Spasovski G., Shikole A., Schurgers M.L., Daneels R.F., Lamberts L.V, et al. 1995. *Increased silicon levels in dialysis patients due to high silicon content in the drinking water, inadequate water treatment procedures, and concentrate contamination: a multicentre study*. Nephrol. Dial. Transplant., 10(10): 1838-1844.

Domingo J.L. 2006. *Aluminium and other metals in Alzheimer's disease: a review of potential therapy with chelating agents*. J. Alzheimers. Dis., 10(2-3): 331-341.

González-Muńoz M.J., Peńa A., Meseguer I. 2008. *Role of beer as a possible protective factor in preventing Alzheimer's disease*. Food Chem. Toxicol., 46(1): 49-56.

Janczarski M., Janczarski D. 1991. *The role of orthosilicic acid in metabolism of living organisms*. Medycyna 2000, 9/10: 2-6. (in Polish)

Jugdaohsingh R. 2007. *Silicon and bone health.* J. Nutr. Health Aging, 11(2): 99-110.

Jugdaohsingh R., Anderson S.H., Tucker K.L., Elliott H., Kiel D.P., Thompson R.P., Powell J.J. 2002. *Dietary silicon intake and absorption*. Am. J. Clin. Nutr., 75(5): 887-893.

Jugdaohsingh R., Tucker K.L., Qiao N., Cupples L.A., Kiel D.P., Powell J.J. 2004. *Dietary silicon intake is positively associated with bone mineral density in men and premenopausal women of the Framingham Offspring cohort*. J. Bone Miner. Res., 19(2): 297-307.

Kim M.H., Bae Y.J., Choi M.K., Chung Y.S. 2009. *Silicon supplementation improves the bone mineral density of calcium-deficient ovariectomized rats by reducing bone resorption.* Biol. Trace Elem. Res., 128(3): 239-247.

O'Connor C.I., Nielsen B.D., Woodward A.D., Spooner H.S., Ventura B.A., Turner K.K. 2008. *Mineral balance in horses fed two supplemental silicon sources*. J. Anim. Physiol. Anim. Nutr., 92(2): 173-181.

Oschilewski M., Schwab E., Kiesel U., Opitz U., Stünkel K., Kolb-Bachofen V., Kolb H. 1986. *Administration of silica or monoclonal antibody to Thy-1 prevents low-dose streptozotocin-induced diabetes in mice*. Immunol. Lett., 12(5-6): 289-294.

Ożarowski A. 1996. *Common Horsetail as a medicinal herb*. Wiad. Ziel., 6: 2-4. (in Polish)

Peluso M.R., Schneeman B.O. 1994. *A food-grade silicon dioxide is hypocholesterolemic in the diet of cholesterol-fed rats.* J. Nutr., 124(6): 853-860.

PERRY C.C., KEELING-TUCKER T. 1998. *Aspects of the bioinorganic chemistry of silicon in conjunction with the biometals calcium, iron and aluminium*. J. Inorg. Biochem, 69(3): 181-191.

POPPLEWELL J.F., KING S.J., DAY J.P., ACKRILL P., FIFIELD L.K., CRESSWELL R.G., DI TADA M.L., LIU K. 1998. *Kinetics of uptake and elimination of silicic acid by a human subject: a novel application of 32Si and accelerator mass spectrometry*. J. Inorg. Biochem., 69(3): 177-180.

REFFITT D.M., JUGDAOHSINGH R., THOMPSON R.P., POWELL J.J. 1999. *Silicic acid: its gastrointestinal uptake and urinary excretion in man and effects on aluminium excretion*. J. Inorg. Biochem., 76(2): 141-147.

REFFITT D.M., OGSTON N., JUGDAOHSINGH R., CHEUNG H.F., EVANS B.A., THOMPSON R.P., POWELL J.J., HAMPSON G.N. 2003. *Orthosilicic acid stimulates collagen type 1 synthesis and osteoblastic differentiation in human osteoblast-like cells in vitro*. Bone, 32: 127-135.

RICO H., GALLEGO-LAGO J.L., HERNÁNDEZ E.R., VILLA L.F., SANCHEZ-ATRIO A., SECO C., GÉRVAS J.J. 2000. *Effect of silicon supplement on osteopenia induced by ovariectomy in rats.* Calcif. Tissue Int., 66(1): 53-55.

SEABORN C.D., BRISKE-ANDERSON M., NIELSEN F.H. 2002. *An interaction between dietary silicon and arginine affects immune function indicated by con-A-induced DNA synthesis of rat splenic T-lymphocytes.* Biol. Trace Elem. Res., 87(1-3): 133-142.

SRIPANYAKORN S., JUGDAOHSINGH R., THOMPSON R.P.H., POWELL J.J. 2005. *Dietary silicon and bone health.* Nutr. Bull., 30: 222-230.

THIEL G., GEISLER G., BLECHSCHMIDT I., DANZER K. 2004. *Determination of trace elements in wines and classification according to their provenance*. Anal. Bioanal. Chem., 378(6): 1630-1636.

TURNER K.K., NIELSEN B.D., O'CONNOR-ROBISON C.I., NIELSEN F.H., ORTH M.W. 2008. *Tissue response to a supplement high in aluminum and silicon*. Biol. Trace Elem. Res., 121(2): 134-148.

WACHTER H., LECHLEITNER M., ARTNER-DWORZAK E., HAUSEN A., JAROSCH E., WIDNER B., PATSCH J., PFEIFFER K., FUCHS D. 1998. *Diatomaceous earth lowers blood cholesterol concentrations.* Eur. J. Med. Res., 3(4): 211-215.

WIDNER B., MIRLACH A., HAUSEN A., JENEWEIN I., JENEWEIN D., DIERICH M.P., WACHTER H., FUCHS D. 1998. *Determination of silicon in urine by inductive coupled plasma-optical emission spectroscopy*. Clin. Chim. Acta., 277(1): 51-63.

ZIELECKA M. 1996. *Silicon – universal element.* Part II. Wiad. Ziel., 9: 6-7. (in Polish)

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