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ORIGINAL PAPERS

CALCIUM AND MAGNESIUM CONTENT IN TREATED WATERS AND THEIR TOTAL HARDNESS

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Abstract

Household water is subject to special protection, as confirmed by the number of evaluated parameters, of which hardness and magnesium content deserve special attention. On the other hand, although calcium is not a limiting constituent although its concentration as well as the calcium compounds affect water hardness. Therefore, calcium is an element which is usually determined in raw water, after treatment as well as at the end-user. For hygienic reasons, particular attention is paid to magnesium concentration in water as well as quantitative relations between Mg and Ca.

The aim of the study was to determine water hardness and the content of calcium and magnesium in treated water intended for consumption by residents of the town of Leszno. The investigations were carried out in 2006-2009 on water samples derived from three water intakes and a water treatment plant. Water samples were collected in accordance with the PN-ISO 5667 standard and the aforementioned parameters were determined with the assistance of the ethylene diamine tetraacetic acid (EDTA) method (PN-ISO 6059).

Total hardness of the examined waters ranged from 192.0 to 410.0 mg $CaCO_3$ dm^{-3}, averaging 334.9±33.16 mg $CaCO_3$ dm^{-3}. The above values, despite apparently high extreme ranges with respect to mean values, were similar between the examined intakes and years, not showing any statistically significant differences.

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Calcium concentrations in the examined waters ranged from 24.7 to 152.4 mg dm^{-3}, on average 73.46±31.15 mg dm^{-3}, while those of magnesium from 1.6 to 107.1, on average 20.45±27.77 mg dm^{-3}. It is evident from the analysis of the experimental data that the overall hardness of the examined waters failed to correlate with calcium and magnesium concentrations. On the other hand, positive correlation was observed between calcium and magnesium concentrations. It was also concluded that, after treatment, household water in Leszno met the qualitative requirements of the examined parameters. The recorded mean water values showed that household waters in Leszno can be described as moderately hard of lowered magnesium concentration.

Key words: household water, hardness, calcium, magnesium.

OKREŚLENIE TWARDOŚCI OGÓLNEJ I ZAWARTOŚCI WAPNIA I MAGNEZU W WODACH UZDATNIONYCH

Abstrakt

Woda do konsumpcji podlega szczególnej ochronie, o czym świadczy liczba parametrów jej oceny. Wśród nich należy wyróżnić twardość oraz zawartość magnezu. Z kolei wapń nie jest składnikiem limitowanym, ale jego koncentracja i związki składają się na twardość wody, dlatego jest on pierwiastkiem na ogół oznaczanym zarówno w wodach surowych, po uzdatnieniu, jak i u odbiorcy. Ze względów zdrowotnych szczególną uwagę zwraca się na koncentrację magnezu w wodach oraz na relacje ilościowe między Mg i Ca.

Celem pracy było określenie twardości oraz zawartości wapnia i magnezu w wodach uzdatnionych przeznaczonych do spożycia dla mieszkańców miasta Leszna. Badania przeprowadzono w latach 2006-2009 na próbkach wód pochodzących z trzech ujęć i stacji uzdatniania wody. Próbki wód pobierano zgodnie z normą PN-ISO 5667, a powyższe parametry oznaczono metodą wersenianową (PN-ISO 6059). W okresie badań zanalizowano ogółem 270 próbek na twardość oraz po 30 próbek na zawartość wapnia i magnezu.

Twardość ogólna wód kształtowała się od 192,0 do 410,0 mg $CaCO_3$ dm^{-3}, średnio 334,9±33,16 mg $CaCO_3$ dm^{-3}. Wartości te mimo pozornie dużych zakresów skrajnych pod względem średnich są zbliżone między ujęciami i latami, co skutkowało brakiem istotnych statystycznie różnic.

Stężenie wapnia w wodach wynosiło od 24,7 do 152,4 mg dm^{-3}, średnio 73,46±31,15 mg dm^{-3} a magnezu od 1,6 do 107,1, średnio 20,45±27,77 mg dm^{-3}. Z analizy danych wynika, że twardość ogólna wód nie korelowała z koncentracją wapnia i magnezu, natomiast stwierdzono dodatnią zależność korelacyjną między koncentracją wapnia i magnezu. Stwierdzono, że po uzdatnieniu, wody do konsumpcji w Lesznie spełniały normy jakościowe badanych parametrów. Według średnich wartości, wody te zaliczono do średnio twardych o zaniżonej koncentracji magnezu.

Słowa kluczowe: woda do spożycia, twardość, wapń, magnez.

INTRODUCTION

Owing to its role in sustaining life on Earth, water is subject to special protection, necessary because of reduced water resources and growing human pressure. Changes in the chemical composition of water are among the consequences of man-made pressure (Jiang et al. 2009). Therefore, appropriate legal regulations for protection of water, nature and man are implemented in many countries. In such context, potable water gains in significance – specific bacteriological, physicochemical and sensory requirements as well as directives related to monitoring, water supply network construction etc., have been formulated in Poland (*Regulation* … 2007). Among numerous parameters of water quality assessment, magnesium content and hardness are crucial. The Polish legal acts do not contain any regulations referring to calcium limits although the element is determined during water hardness tests.

Hard water sometimes causes considerable technical and exploitation problems in public water supply mains or industrial installations, for example due to limescale formation. Magnesium present in waters mainly affects human, animal and plant health. The element can activate about 300 enzymes and takes part in many metabolic processes (Marx, Neutrta 1997). Magnesium can influence smooth muscles, thrombocytes and cardiac muscle cells (Rayssiguier Gueux 1986, Waston et al. 1986, Hattori et al. 1988, Chrysant et al. 1988). A survey conducted in many countries has indicated some dependence between magnesium concentration in drinking water and diet versus ischemic heart disease (Marx, Neutrta 1997). Thus, it is necessary to provide people with appropriate amounts of magnesium to ensure good balance of elements in our bodies (Elin 1988). Calcium present in waters should be taken into account in terms of its role in physiological processes as well as the formation of the Ca:Mg ratio (Kousa et al. 2006), which is important during metabolic magnesium transformations. Thus, presence of both elements in drinking water brings health considerations although no content limits have been set for calcium. Numerous reports also reveal dependence between hard waters and some diseases and disorders which can be associated with both magnesium and calcium concentrations. Therefore, continuous monitoring and quality assessment of treated waters that includes the three above indicators seems justifiable and reasonable.

The present study aimed at an assessment of the quality of potable water in Leszno based on three parameters: hardness, calcium content and magnesium content.

MATERIAL AND METHODS

Residents of Leszno (51°51´N and 16°34´E) are provided with drinking water at three water intake points connected to a water treatment plant, which are localized in Zaborowo, Karczma Borowa, and Strzyżewice, all within the borders of the town. Each of these intake points has its own wells 20 to 150 m^3 h^{-1} in capacity. The water intake point in Zaborowo consists of

5 drilled wells (21.2 to 28 m), which collect underground water from the Quaternary layer; the point in Karczma Borowa has 3 wells, which also exploit Quaternary waters; the water intake point in Strzyżewice has 4 wells collecting water from the Tertiary layer (down to 120 m), 4 wells (down to 30 m) from the Quaternary, and a single well (down to 60 m) from deep levels of the Quaternary layer. Fresh underground waters are characterized by elevated iron, manganese, and ammonia concentration, hence they are treated by means of open aeration in Strzyżewice (hydrosulfide presence) as well as closed aeration, filtration (rapid pressure filters), and emergency disinfection at other water intake points.

Treated water samples were collected for analyses in accordance with the norm PN-ISO 5667 (2003). Water hardness (n=270), calcium (n=30), and magnesium content (n=30) were determined according to the PN-ISO 6059 (1999) norm.

RESULTS AND DISCUSSION

In general, underground waters cannot occur in a chemically pure form because they contain dissolved gases and minerals in various concentrations and therefore they should be treated before reaching the water supply system.

Due to its unquestionable importance in man's life, water is subject to rigorous control, which the WHO's guidelines (2004) as well as latest Polish legal acts included in the Decree of the Minister for Health (2007) can prove. These acts consider the microbial, sensory, physicochemical, and radiological survey of drinking water as necessary. Besides, Appendix No 4 sets additional chemical requirements that drinking water should meet: hardness and magnesium content. Calcium has not been limited in drinking water.

Hardness is an insignificant parameter for hygienic and sanitary properties of water; however, it is important in industry and economy and that is why determination of its level is part of water quality assessment. According to the Polish Norms (*Regulation*… 2007), its permissible range is from 60 to 500 mg dm^{-3} recalculated as calcium carbonate. Treated waters in Leszno were characterized by a relatively high stability of the parameters in question over the studied period (Table 1).

For all the data (n=270), the parameter values oscillated within the range from 192 to 412 mg $CaCO_3$ dm^{-3}, with slightly higher differences between water treatment stations (SUW) than between the years: in Zaborowo 330.4 mg $CaCO_3$ dm^{-3}, in Karczma Borowa 321.5±32.89 mg $CaCO_3$ dm^{-3}, and in Strzyżewice 352.7±28.94 mg $CaCO_3$ dm^{-3}, on average. The mean water hardness value for the years and SUW's reached 334.9±33.16 mg $CaCO_3$ dm^{-3}.

Table 1

Hardness of treated water (mg $CaCO_3$ dm^{-3})

Site of water collection and processing	Years				Mean n=270	SD*
	2006	2007	2008	2009		
Zborowo	240-370	270-380	296-372	304-372	330.4±29.71	29.71
Karczma Borowa	240-390	192-370	286-382	293-412	321.5±32.89	22.89
Strzyżewice	290-410	300-410	292-394	307-380	352.7±28.94	28.94
Mean	332.0±46.39	348.4±36.83	338.0±24.75	335.9±22.84	334.9±33.16	33.16
SD	46.39	36.83	24.75	22.84	-	-

*Standard deviation

The extreme values (192 and 412 mg $CaCO_3$ dm^{-3}) occurred only once, which did not affect the total result of the parameter. The data listed in the above table classify the treated water from Leszno from 10.7°dH to 23.0°dH, with the mean level of 18.7^{0}dH. However, a problem of choosing the most appropriate hardness scale can arise, because literature contain different scales. i.e. some cite a 5-grade scale, while others rely on a 6-grade scale but in other ranges of $CaCO_3$ dm^{-3} mg content or hardness degrees (°dH). Referring the parameters of the above assessment to Biszof's norms (2010), the analyzed waters can be considered as moderately hard.

Considering water hardness, reports on less sudden deaths due to acute cardiac infarction at women from populations drinking harder waters are appearing more frequently (Rubenowitz et al. 1999). On the other hand, Miyake and Iki (2003) did not report significant dependence between hard water and mortality resulting from cardiovascular and cerebrovascular diseases. Earlier studies presented high mortality due to coronary heart disease in Australia, where large amounts of soft water are drunk, in contrast to the smallest number of deaths in western Texas, where drinking water is very hard (Sharma 2010, cit. after Ashmead 1981).

Statistical analysis of our data reveals that the hardness of treated water did not correlate with the calcium and magnesium content, which means that the former was probably determined by other substances present in water and not analyzed in the study. Instead, positive dependence between calcium and magnesium concentrations in the analyzed water samples was found (Figure 1). Interactions between both elements are common, although scientists cannot agree about an optimum ratio between these elements in waters. Conventionally, it is assumed as a 2:1 ratio (Durlach 1989), but recent studies indicate it should be modified due to higher magnesium requirements for an organism (Sharma 2010). Kiss et al. (2004) claim that the

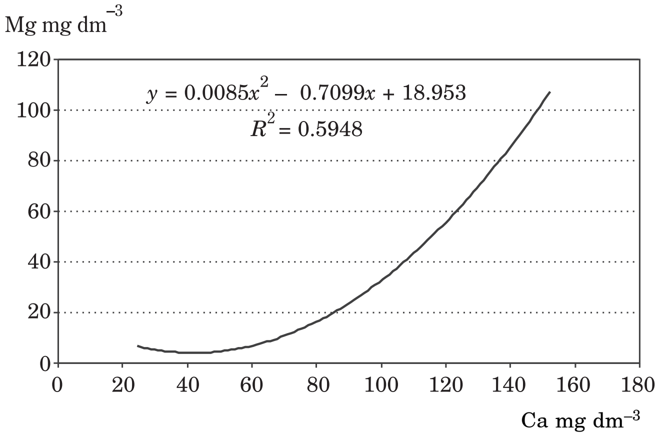

Fig. 1. Relationship between of total concentrations of calcium and of magnesium in water

ionic calcium to magnesium ratio is better for dietetic and sanitary evaluation of water than the ratio of their concentrations. It is obvious that the question of a ratio between calcium and magnesium in potable water is important because of its effect on human health.

Calcium and magnesium concentrations in the analyzed treated water samples varied, as demonstrated by their absolute content and values of standard errors (Table 2). The quantitative range for calcium oscillated around 24.7 to 152.4 mg Ca dm^{-3} (mean 73.46±31.15 mg Ca dm^{-3}) at the variability of V=42.4%. In the case of magnesium, the range was even wider: from 1.6 to 107.1 mg Mg dm^{-3}, at the average level of 20.45 mg Mg dm^{-3} and the variability coefficient V=135.8%. The quantitative variability of calcium and magnesium in waters results from numerous factors, including geological ones. It is particularly evident during the water intake and while mixing waters originating from different water-bearing layers, which usually differ in their hydrochemical properties (Buczyński, Modelska 2005). Furthermore, some authors point to the fact that the Quaternary layers can be separated from the ground level in different ways, which may increase the risk of contamination of those water layers.

Presence of many elements and substances in underground waters is a natural feature, which largely depends on the geological subsoil. Depending on the structure and elution intensity, both calcium and magnesium are transferred to waters in different amounts. However, changes in the physical and chemical composition of waters, which can occur during particular stages of its distribution, cannot be excluded (Wons 2007). It is therefore necessary to monitor water quality at each stage, not only to prevent some undesirable phenomena can arise (e.g. during industrial processes), but also to protect human health, e.g. by controlling the amounts of calcium and

Table 2

Concentrations of calcium and magnesium in water (mg dm^{-3})

Element	Site of water collection and processing			Mean n=30	SD
	Zborowo	Karczma Borowa	Strzyżewice		
Calcium (Ca)	24.7-108.1	24.9-116.8	26.4-152.4	73.46	31.15
Mean	71.61	69.89	78.88		
SD	29.43	28.81	37.14		
Magnesium (Mg)	1.6-97.4	1.6-98.3	1.6-107.1	20.45	27.77
Mean	20.32	19.09	21.94		
SD	27.67	28.12	30.41		

magnesium, which have direct impact on water hardness. For many years, medical sciences have devoted much efforts to the above issues, for example studying the correlation between hard water and various diseases, including prostate cancer (Yang et al. 2000). Besides, water quality is important in agriculture, both for animal and plant nutrition, e.g. irrigation and spraying. It is possible to hydrolyze some active substances in water in order to repress their action. On the other hand, antagonistic effects of water-soluble salts towards chemically active substances contained for example in herbicides can appear. Thus, the problem of drinking water quality gains in importance although the health aspects seem to be a priority. In such a view, the abundance and forms of magnesium in waters are doubtless one of the more important scientific issues to study in the nearest future.

CONCLUSIONS

1. The analyzed waters, after treatment, were characterized by stable hardness, regardless of the year, sample collection locality or the treatment site.

2. The treated underground waters in Leszno can be classified as moderately hard and the hardness scale did not significantly depend on the calcium and magnesium content.

3. The calcium and magnesium concentrations in the waters were characterized by high quantitative variability, first of all over time and then depending on a sampling site, indicating possible influence of geological factors on the content of both elements.

4. In most of the samples, the water contained less magnesium than recommended.

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EFFECT OF NITROGEN FERTILIZATION ON P, K, Mg, Ca AND S CONTENT IN SOIL AND EDIBLE PARTS OF WHITE CABBAGE

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Abstract

The results of three-year investigations on cv. Galaxy F_1 of cabbage grown commercially in the south Poland, an important agricultural region, are presented. In 2005-2007, a field experiment was carried out on silty clay soil containing 0.91-1.02% organic carbon and of the soil acidity pH_{H2O} 7.18-8.21.

Effects of the N form (ammonium sulfate and UAN: a solution of ammonium nitrate + urea) and the method of application (placement and broadcast techniques and complementary foliar fertilization with urea and Supervit K) on the P, K, Mg, Ca and S concentrations in edible parts of cabbage were surveyed. Nitrogen fertilizer was applied at the rate of 120 kg N ha^{-1}. In the placement treatment, fertilizer was applied on each plant while transplanting seedlings in rows 10 cm deep and spaced 10 cm from one another. Foliar nutrition with 2% urea was carried out 3 times and once 1% Supervit K was applied. The content of nutrients in cabbage leaves changed over the years. On average, the highest K and Mg content was in 2006 and the lowest P, K, Mg and Ca content appeared in 2007, with the harvest of 2005 being intermediate. The sulfur leaf content was the highest in 2007 and the lowest in 2006. The concentrations of P, K, and Mg in edible parts of cabbage were less than sufficient. The source of N affected P concentrations in cabbage leaves in 2005-2006. Slightly higher P amounts were detected in cabbage fed UAN than ammonium sulfate. None of the examined factors influenced K and Mg concentration in cabbage. In 2005-2006, slightly lower concentrations of Ca in cabbage fed UAN than ammonium sulfate were noticed. In every year, higher S concentrations in plants fed ammonium sulfate were detected. In 2005-2006, cabbage fertilized with the broadcast technique had slightly higher amount of S than the one given the placement treatment. Foliar fertilization did not affected the content of the examined nutrients in cabbage in any year of the trials.

Key words: ammonium sulphate, UAN, broadcast and placement fertilization.

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WPŁYW NAWOŻENIA AZOTEM NA ZAWARTOŚĆ P, K, Mg, Ca I S W GLEBIE I CZĘŚCIACH JADALNYCH KAPUSTY GŁOWIASTEJ BIAŁEJ

Abstrakt

Badano wpływ nawożenia azotowego siarczanem amonu i roztworem saletrzano-mocznikowym (RSM) na zawartość P, K, Mg, Ca i S w glebie i kapuście głowiastej białej. Badania z kapustą głowiastą białą odmiany Galaxy F_1 prowadzono w latach 2005-2007 w Zagorzycach k. Miechowa. Nawozy azotowe stosowano wg schematu: 1) kontrola – 100% N (120 kg ha^{-1}) rzutowo w czasie sadzenia rozsady; 2) 75% N rzutowo w czasie sadzenia rozsady + 25% N w trakcie wegetacji; 3) 75% N rzutowo w czasie sadzenia rozsady + nawożenie pozakorzeniowe; 4) 75% N w sposób zlokalizowany w czasie sadzenia rozsady, 5) 75% N w sposób zlokalizowany w czasie sadzenia rozsady + 25% N rzutowo w czasie wegetacji; 6) 75% N w sposób zlokalizowany w czasie sadzenia rozsady + nawożenie pozakorzeniowe. Dokarmianie pozakorzeniowe wykonywano 2% mocznikiem (3-krotnie) i 1% roztworem Supervitu K (1 raz).

Warunki pogodowe w kolejnych latach doświadczenia znacznie modyfikowały wpływ czynników badań na zawartość oznaczanych składników mineralnych w kapuście. Najwięcej K i Mg w roślinach oznaczono w 2006 r., najmniej P, K, Mg i Ca w 2007 r., natomiast 2005 r. był rokiem średnim, jeśli chodzi o stężenia badanych pierwiastków. Zawartość siarki w liściach kapusty była najwyższa w 2007 r., a najniższa w 2006 r. Oznaczone zawartości P, K i Mg były poniżej zakresu przyjętego za wystarczający dla części jadalnych kapusty. Rodzaj nawozu azotowego wpływał istotnie na zawartość P i Ca w roślinach. W 2005 i 2006 r. wyższe stężenia P wykazano w roślinach nawożonych RSM w porównaniu z nawożonymi siarczanem amonu. Więcej Ca oznaczano w kapuście nawożonej siarczanem amonu w porównaniu z kapustą nawożoną roztworem saletrzano-mocznikowym. Żaden z badanych czynników nie różnicował istotnie zawartości K i Mg w kapuście. W każdym roku badań rośliny nawożone siarczanem amonu zawierały więcej siarki. W 2005 i 2006 r. rzutowy sposób nawożenia siarczanem amonu wpływał istotnie na zwiększenie stężenia S w roślinach w stosunku do nawożenia zlokalizowanego. Nawożenie pozakorzeniowe nie wpływało istotnie na zawartość oznaczanych pierwiastków w roślinach.

Słowa kluczowe: siarczan amonu, RSM, nawożenie rzutowe i zlokalizowane.

INTRODUCTION

Agricultural production and productivity are directly related to nutrient availability and uptake. Relationships between the uptake of macro- and micronutrients by crops and their yield are significant (Janssen 1998, Fragaria 2009). Soils differ widely in their ability to supply the nutrients necessary to sustain plant productivity. Nutrient availability to plants is a very dynamic and complex process, consisting of the physical, chemical and biological changes that occur in the rhizosphere (Marchner 1995). Nutrients are added to soil through weathering, atmospheric deposition, fertilization, fixation and mineralization and lost or made unavailable through harvesting, leaching, biological immobilization, sorption and precipitation chemistry (Mengel et al. 2001).

Nutrient interactions in crop plants, which may be positive, negative or neutral (no interaction), are probably one of the most important factors affecting yields of annual crops. This is a very complex issue in mineral nutrition and has not been fully clarified yet (Frageria, Baligar 2005). Nutrient interactions may be a result of precipitation reactions occurring in the soil solution, which reduce availability for plant uptake, or a consequence of competition during nutrient uptake, translocation or metabolic functions in the plant. Some important nutrient interactions include ammonium-calcium and potassium-magnesium-calcium relations (Goulding 1983). Farmers often use NH_4 and K salts as fertilizer sources. Even though N-NH_4 applied as a fertilizer has a short life in agricultural soils (1-3 weeks or more depending on rates of nitrification), the K-NH_4-Ca exchange interaction controls the distribution of these cations between the exchange and solution phases during that period (Evangelou et al. 1994). Thus, the availability of K^+ and NH_4^+ in the solution phase would be affected by all ions present.

For sustainable agriculture, it is important to know how nitrogen interacts with other nutrients in order to improve efficient utilization of this element and, consequently, to enhance yields. Positive interactions between N and other nutrients have been reported by Holford et al. (1992), Zhao et al. (1997), Sady and Smoleń (2007), Smoleń and Sady (2009). Positive interactions of N with P, K, Ca and other nutrients may be associated with improved yield when N is added. Potassium application may increase plant yields although an optimal supply of N and P leads to a better response of yield to K fertilizer (Fragaria 2009).

Nitrogen also enters into positive interactions with S in crop plants It is generally considered that S availability may influence the N utilization by plants and vice versa, indicating that mineral S and N availabilities interact to affect the S and N management by plants (Zhao et al. 1997, Jackson 2000, Abdallah et al. 2010).

The main objective of the present study was to examine the influence of ammonium sulfate and UAN (solution of ammonium nitrate + urea) applied by the placement and broadcast techniques and additional foliar fertilization (urea and Supervit K) on the mineral concentration of P, K, Mg, Ca and S in cv. Galaxy F_1 white cabbage.

MATERIAL AND METHODS

In 2005-2007, a field experiment was carried out on cv. Galaxy F_1 white cabbage grown on silty clay soil containing 0.91-1.02% organic carbon and of the soil acidity pH_{H_2O} 7.18-8.21 (Table 1). The plots were located on a private farm in Zagorzyce (50°23’ and 20°04’). Farms in this area specialize in cabbage production in continuous or highly frequent cropping. In short-term

Table 1

pH values, EC (electrical conductivity) and content of macronutrients content in soil before cabbage planting in 2005-2007

Year	Soil layer (cm)	pH_{KCl}	pH_{H_2O}	EC (mS cm^{-1})	C (%)	Nutrient (mg dm^{-3} of soil)			
						P	K	Mg	Ca
2005	0-30	7.70	8.21	0.24	0.91	70.6	207	110	3218
	30-60	7.60	8.14	0.15	0.38	39.6	133	124	5159
	60-90	7.57	8.01	0.14	0.20	35.4	56.6	129	5965
2006	0-30	6.17	7.18	0.19	1.02	63.7	88.3	50.3	1572
	30-60	6.57	7.40	0.11	0.47	56.4	17.3	99.9	2826
	60-90	6.59	7.44	0.10	0.41	48.2	8.7	61.4	1462
2007	0-30	7.09	7.90	0.06	0.98	119.6	73.1	54.3	2301
	30-60	7.05	7.99	0.07	0.49	67.2	19.4	38.3	1270
	60-90	7.70	7.85	0.07	0.37	60.8	8.35	40.8	944

crop rotation systems, liming is commonly used as a control measure against club root. Calcium oxide application one month prior to planting is a practical means to control this fungal disease.

The mineral fertilization of cabbage in our experiment was designed according to the results of chemical analysis of soil samples collected in the previous autumn. The content of soil nutrients such as P, K and Mg were supplemented to the level of 50, 200 and 60 mg dm^{-3}, respectively.

Two factors were examined: the type of N fertilizer ammonium sulfate and UAN (1:1 solution of ammonium nitrate and urea), and the method of N application. The treatments were as follows:

1. Control - 100% N rate (120 kg ha^{-1}) broadcasted at planting of seedlings,
2. 75% N rate broadcasted at planting of seedlings + 25% N during plant growth,
3. 75% N rate broadcasted at planting of seedlings + foliar fertilization,
4. 75% N placement at planting of seedlings,
5. 75% N placement at planting of seedlings + 25% N during plant growth,
6. 75% N placement at planting of seedlings + foliar fertilization.

The treatments were designed in completely randomized split-plot blocks with four replications. Nitrogen fertilizer was applied at rates of 120 kg N ha^{-1} (100% N) or 75 kg N ha^{-1} (75%). With the placement method, fertilizer was applied on each plant (plant were spaced 67.5 x 67.5 cm) in rows 10 cm deep and spaced at 10 cm distance while transplanting the seedlings. Cabbage seedlings were planted in the first decade of June. Foliar sprayings started at the beginning of intensive leaf growth and continued during the growing season in two-week interval. Foliar nutrition with 2% urea was carried out 3 times and once 1% Supervit K was applied (% w/v: $N\text{-}NH_2$ – 4.4, $N\text{-}NO_3$ – 0.8, K – 3.1, Mg – 0.6, Mn – 0.05, Ti – 0.05, B – 0.03, Fe – 0.025, Mo – 0.005). The total amount of N reached 27.6 kg N ha^{-1} following the foliar urea application and 0.6 kg N ha^{-1} when Supervit was used.

Harvest took place in the last decade of October. Edible parts were analyzed after washing with distilled water and drying at 70°C for 48 h. The K, Mg and Ca content in the samples was determined by atomic absorption spectroscopy (AAS) after digestion with HNO_3 : $HClO_4$: H_2SO_4 (6 : 2 : 0.25). Phosphorus in the mineralized samples was analyzed with vanadium-molybdenum method described by Ostrowska et al. (1991) whereas S-SO_4 was assayed by Bardsley-Lancaster's method (1960).

Soils samples from three layers: 0-30 cm, 30-60 cm and 60-90 were taken in the spring before the experiment started as well as after the harvest. Organic carbon was assessed by Tiurin's method (Ostrowska et al. 1991), and the sorption complex capacity (CEC) was determined in ammonium chloride extract (Kociałkowski, Ratajczak 1984). N (N-NH_4 and N-NO_3), P, K and Mg were measured in 0.03 M CH_3COOH extract according to the universal method (Ostrowska et al. 1991). The results of determinations of the physical and chemical properties carried out in 2005-2007 are presented in Tables 1, 2 (before cabbage planting) and 3, 4 (after harvest).

The results were subjected to a two-factor analysis of variance. The means were separated by Fisher LSD test (p=0.05). Statistical calculations were performed with the Statistica 7.0 software application.

Table 2

Soil exchangeable complex characteristics in 2005-2007

Year	Soil layer (cm)	Cation (cmol kg^{-1})					CEC (cmol kg^{-1})
		Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	
2005	0-30	11.00	0.17	0.67	0.00	0.52	12.38
	30-60	12.94	0.24	0.20	0.00	0.60	13.98
	60-90	16.44	0.20	0.14	0.00	0.49	17.27
2006	0-30	6.84	0.38	0.43	0.07	0.80	8.52
	30-60	4.80	0.19	0.16	0.09	0.63	5.86
	60-90	4.87	0.20	0.15	0.08	0.56	5.86
2007	0-30	9.73	0.33	0.43	0.04	0.87	11.36
	30-60	8.77	0.25	0.19	0.04	0.84	10.09
	60-90	6.75	0.24	0.26	0.04	0.84	8.23

RESULT AND DISCUSSION

The content of nutrients in cabbage leaves changed in the years. On average, the highest K and Mg content was noted in 2006 and the lowest P, K, Mg and Ca in 2007, with the results obtained in 2005 being intermediate.

The sulfur leaf content was the highest in 2007 and the lowest in 2006. Fluctuations in the environmental factors such as the temperature and soil moisture can affect the mineral composition of leaves considerably. In our study, the rainfalls were 326 and 419 mm in 2005 and 2007, respectively (data not shown), but in 2005 they were distributed regularly. In 2007, a relatively low temperature and high rainfalls were observed in September (134 mm). The growing season of 2006 was the warmest and the driest (253 mm of rainfall). In that year, extremely dry weather appeared in July (8 mm) and October (4 mm of precipitation).

In the present experiment, the concentrations of P, K, and Mg in edible parts of cabbage were below the sufficient range of content reported for cabbage by Barker and Pilbeam (2006).

Phosphorus

Most soils readily buffer P-additions and P hardly ever appears at high levels in the soil solution. Soil concentrations of P, K, Mg and Ca are generally interpreted using the sufficiency level of available nutrients (SLAN).

Table 3

Phosphorus and potassium content (mg dm^{-3} of soil) in the 0-30 cm soil layer after cabbage harvest

Fertilizer	Method of N application		P				K			
			2005	2006	2007	mean	2005	2006	2007	mean
Mean for years			63.0	61.6	103.3		86.6	84.5	55.3	
Fertilizer	$(NH_4)_2SO_4$		61.0	65.0	108.7	78.2	103.2	76.4	49.6	76.4
	UAN		64.9	58.2	97.9	73.7	70.0	92.6	60.9	74.5
Metod of N application	broadcast	1*	60.4	59.9	104.3	74.9	66.3	31.3	43.9	47.2
		2	60.4	56.1	113.1	76.5	51.7	68.0	50.8	56.8
		3	64.4	65.2	97.6	75.7	88.6	86.3	61.7	78.9
	placement	4	66.0	61.4	95.9	74.4	133.3	106.6	47.9	95.9
		5	60.3	61.2	102.2	74.6	84.2	116.0	53.5	84.6
		6	66.3	65.8	106.8	79.6	95.6	98.5	73.8	89.3
$LSD_{0.05}$ for:	fertilizer		n.i.	6,17	n.i.		n.i.	n.i.	n.i.	
	method		n.i.	n.i.	n.i.		n.i.	n.i.	n.i.	
	fertilizer × method		n.i.	n.i.	n.i.		n.i.	n.i.	n.i.	

* 1) control – 100% N rate (120 kg ha^{-1}) broadcasted at planting of seedlings, 2) 75% N rate broadcasted at planting of seedlings + 25% N during plant growth, 3) 75% N rate broadcasted at planting of seedlings + foliar fertilization, 4) 75% N placement at seedlings planting, 5) 75% N placement at seedlings planting + 25% N during plant growth, 6) 75% N placement at seedlings planting + foliar fertilization.

Table 4

Magnesium and calcium content (mg dm^{-3} of soil) in the 0-30 cm soil layer after cabbage harvest

Fertilizer	Method of N application		Mg				Ca			
			2005	2006	2007	mean	2005	2006	2007	mean
Mean for years			54.7	54.4	69.8		1587	1361	2972	
Fertilizer	$(NH_4)_2SO_4$		56.4	52.7	73.1	60.7	1712	1405	3087	2068
	UAN		52.9	56.2	66.5	58.5	1462	1318	2856	1879
Metod of N application	broadcast	1*	50.9	51.7	73.1	58.6	1414	1350	3527	2097
		2	63.1	56.5	72.2	63.9	1569	1454	3105	2043
		3	57.3	53.3	71.6	60.7	1576	1411	2803	1930
	placement	4	55.6	58.8	73.2	62.5	2087	1320	2881	2096
		5	48.1	50.6	63.3	54.0	1310	1299	2857	1822
		6	53.1	55.6	65.7	58.1	1563	1335	2656	1851
$LSD_{0.05}$ for:	fertilizer		ns	ns	ns		233.0	ns	ns	
	method		ns	ns	ns		403.5	ns	ns	
	fertilizer × method		ns	ns	ns		570.7	ns	ns	

* see Table 3

According to the sufficiency level concept, there are definable levels of nutrient in soil below which crops will respond to added fertilizers and above which they will probably not respond (KOPITTKE, MENZIES 2007). The optimal P-concentration in soil determined by the universal method (OSTROWSKA et al. 1991) for cabbage plants is 50-70 mg P dm^{-3} of soil. In the present study, the concentrations of available phosphorus found in the soil before planting were within or above this range (Tables 1 and 3). However, the content of phosphorus in cabbage (Table 5) was low and tended to be below the sufficient range (0.38%) reported by BARKER and PILBEAM (2006). The soil test recommendation for P should be customized by a crop. However, at present, soil-test-based recommendations are generally not sufficiently sensitive to allow recommendations to accommodate the more subtle genetic variation among cultivars within crop species.

The lowest P concentrations in plants were noted in the wet year 2007 (0.25% d.m.), in comparison to 2005-2006 (0.30% d.m.). P availability is affected by soil water condition. It is generally understood that excessive water causing poor aeration would actually restrict the P uptake by crops. Usually, soil water affects soil reaction, governing the release and diffusion of P in the soil solution and ultimately the positional availability of P relative to roots (MENGEL et al. 2001). In our research, the highest yield was obtained in 2007 (88.4 t ha^{-1}) compared to 2005 r (83.8 t ha^{-1}) and 2006

Table 5

Phosphorus and potassium content (% d.m.) in cabbage after harvest in 2005-2007

Fertilizer	Method of N application		P (%)				K (%)			
			2005	2006	2007	mean	2005	2006	2007	mean
$(NH_4)_2SO_4$	broadcast	1*	0.26	0.31	0.26	0.28	2.57	2.70	2.26	2.51
		2	0.29	0.27	0.26	0.28	2.36	2.68	2.20	2.41
		3	0.26	0.26	0.27	0.26	2.26	2.81	2.38	2.48
	placement	4	0.27	0.22	0.27	0.26	2.36	2.60	2.03	2.33
		5	0.30	0.30	0.26	0.29	2.21	2.72	2.09	2.34
		6	0.29	0.31	0.26	0.29	2.34	2.76	2.10	2.40
UAN	broadcast	1	0.32	0.34	0.24	0.30	2.37	2.71	2.21	2.32
		2	0.31	0.34	0.20	0.29	2.23	2.38	2.29	2.39
		3	0.29	0.30	0.23	0.27	2.30	2.66	2.15	2.36
	placement	4	0.32	0.33	0.25	0.30	2.18	2.64	2.27	2.40
		5	0.30	0.34	0.24	0.29	1.99	2.75	2.23	2.36
		6	0.32	0.32	0.25	0.29	2.25	2.84	2.07	2.36
Mean for years			0.30	0.30	0.25		2.28	2.69	2.19	
Fertilizer	$(NH_4)_2SO_4$		0.29	0.28	0.27	0.27	2.35	2.71	2.18	2.41
	UAN		0.30	0.33	0.23	0.29	2.22	2.67	2.20	2.37
Metod of N application	broadcast	1	0.29	0.32	0.25	0.29	2.47	2.54	2.23	2.41
		2	0.30	0.31	0.23	0.28	2.29	2.67	2.25	2.40
		3	0.28	0.28	0.25	0.27	2.28	2.72	2.27	2.42
	placement	4	0.30	0.28	0.26	0.28	2.27	2.68	2.15	2.37
		5	0.30	0.32	0.25	0.29	2.1	2.78	2.16	2.35
		6	0.30	0.31	0.26	0.29	2.29	2.77	2.08	2.38
$LSD_{0.05}$ for:	fertilizer		0.017	0.041	ns		ns	ns	ns	
	method		ns	ns	ns		ns	ns	ns	
	fertilizer × method		ns	ns	ns		ns	ns	ns	

* see Table 3

(64.3 t ha^{-1}) (data not shown), which may be attributed to the effect of phosphorus ‘dilution’ in plant biomass (a decrease in its content in the dry matter). Under favorable soil moisture, the enhanced plant growth after nitrogen application caused ‘dilution’ of phosphorus without any competition occurring in its uptake.

In our investigations, the form of nitrogen fertilizers affected P concentrations in cabbage leaves in 2005-2006. Slightly higher amounts of phosphorus were detected in cabbage fed UAN than ammonium sulfate. These results are difficult to interpret conclusively. The form in which nitrogen is taken up by plants will induce the change of rhizospheric pH value. The uptake of NH_4^+ results in a decrease of the pH value. Contrary, the uptake of NO_3^- will cause an increase of the rhizospheric pH value (MARCHNER 1995). A change in the rhizospheric pH value will affect nutrient availability and thus influence the nutrient uptake and utilization by plants (TYLER and OLSSON 2001). In alkaline or neutral soils, acidification of rhizosphere by $(NH_4)_2SO_4$ should increase P-availability and amount of phosphorus taken up by plants. However, the reverse was observed.

Potassium, magnesium and calcium

The major soil cations are present partly in the structure of primary and secondary minerals, partly in an exchangeable form on cation exchange sites and partly as soluble ions in the soil solutions. Assessment of the plant-available fraction of any of three types of cations is often based on measurement of the exchangeable fraction (KOPITTKE, MENZIES 2007). Among the exchangeable cations, Ca^{2+} is usually dominant, often amounting to between 60-85% of the total in non-acid soil. In soils in humid regions, Mg normally makes up 5-30% of the total exchangeable cations and K between 2-6% (MENGEL et al. 2001). In our study, 80% (2006) to 89% (2005) of the total exchangeable cations in top soils consisted of Ca^{2+} (Table 2). Magnesium accounted for 1.4% in 2005 to 4.5% in 2006 and potassium reached from 5% in 2006 to 5.4% in 2005. According to BEAR et al. (1945), the soil cation exchange complex is satisfactory for plant growth when comprising 65% Ca, 10% Mg, 5% K and 20% H.

Each of these cations is absorbed by roots as free ions, and the relative amounts taken up are influenced by the absolute and relative concentrations of the ions in the soil solution. Potassium, magnesium and calcium appear to compete with each other in the uptake by plants (EVANGELOU et al. 1994). Nitrogen fertilizer has inconsistent effects on plant concentrations of K and Ca, but generally increases concentrations of Mg and Na (BARKER, PILBEAM 2006). When a supply of cations, especially K, is limited, any increase in the plant growth caused by N fertilizer tends to reduce their concentrations in plant tissues. However, when supplies of cations are plentiful and N is taken up mainly as nitrate, plant concentrations may increase owing to the synergistic effect between nitrate and cation uptake (WHITEHEAD 2000). In our study, N fertilizer had little or no effect on K, Ca and Mg plant concentrations (Tables 5 and 6). The tendency of ammonium N to depress plant K after the application of ammonium sulfate applied was not identified.

Table 6

Magnesium and calcium content (% d.m.) in cabbage after harvest in 2005-2007

Fertilizer	Method of N application		Mg (% d.m.)				Ca (% d.m.)			
			2005	2006	2007	mean	2005	2006	2007	mean
$(NH_4)_2SO_4$	broadcast	1*	0.13	0.14	0.11	0.13	0.60	0.67	0.50	0.59
		2	0.13	0.14	0.11	0.13	0.56	0.62	0.51	0.56
		3	0.14	0.14	0.12	0.14	0.60	0.58	0.55	0.57
	placement	4	0.13	0.15	0.12	0.13	0.61	0.61	0.54	0.59
		5	0.13	0.15	0.11	0.13	0.56	0.56	0.47	0.53
		6	0.13	0.14	0.12	0.13	0.59	0.53	0.52	0.54
UAN	broadcast	1	0.13	0.12	0.11	0.12	0.53	0.39	0.51	0.48
		2	0.13	0.14	0.11	0.13	0.51	0.48	0.51	0.50
		3	0.13	0.14	0.11	0.13	0.56	0.52	0.51	0.52
	placement	4	0.12	0.15	0.12	0.13	0.53	0.49	0.50	0.51
		5	0.12	0.15	0.11	0.13	0.52	0.51	0.44	0.49
		6	0.13	0.14	0.11	0.12	0.51	0.45	0.46	0.48
Mean for years			0.13	0.14	0.11		0.56	0.53	0.50	
Fertilizer	$(NH_4)_2SO_4$		0.13	0.14	0.11	0.13	0.59	0.59	0.51	0.56
	UAN		0.13	0.14	0.11	0.13	0.53	0.47	0.49	0.50
Metod of N application	broadcast	1	0.13	0.13	0.11	0.12	0.57	0.53	0.51	0.54
		2	0.13	0.14	0.11	0.13	0.53	0.55	0.51	0.53
		3	0.13	0.14	0.12	0.13	0.58	0.54	0.52	0.55
	placement	4	0.13	0.15	0.12	0.13	0.57	0.55	0.52	0.55
		5	0.13	0.15	0.11	0.13	0.54	0.54	0.45	0.51
		6	0.13	0.14	0.11	0.13	0.55	0.49	0.49	0.51
$LSD_{0.05}$ for:	fertilizer		ns	ns	ns		0.055	0.048	ns	
	method		ns	ns	ns		ns	ns	ns	
	fertilizer × method		ns	ns	ns		ns	ns	ns	

* see Table 3

Potassium uptake during plant growth is a dynamic process, causing K depletion in the root zone through removal of exchangeable K. Our understanding of the nature and rate of release of soil K from different pools of adsorbed and structural K is important in terms of soil fertility (Sharpley 1990).

The optimal K-concentration availability determined by the universal method for cabbage ranges between 175-225 mg K dm^{-3} of soil. In this study, the concentrations of available K in the top soil before planting were in this range only in 2005 (Table 2). In 2006-2007, the soil K content was supplemented using KCl to the level of 200 mg dm^{-3} before cabbage planting. The potassium amount determined in soil at harvest varied from 55.3 to 86.6 mg K dm^{-3} (Table 3). This indicates that both the top soils and subsoil from the cropping sites were highly K-deficient in 2006-2007 and will eventually become depleted unless K fertilizers are provided.

Water soluble K^+ depends on the clay concentration in soil and on the type of clay minerals. Some soil minerals may act as a sink for removing K from solution. When K is absorbed in the interlayer sites of illite, vermiculite and other smectit clays, the clay layers collapse and trap the K within the mineral lattice. This fixation process is relatively fast, while the release of this interlayer K is very slow (Bouabid et al. 1991, Evangelou et al. 1994, Bolan et al. 1999). Fixed K^+ is higher in high- than in low-pH soil (Goulding 1983). The most common test for plant available K is the exchangeable K^+ with ammonium acetate as an extractant. This fraction contains mainly soil solution K^+ plus potassium of the hydrated K^+ fractions and only a small part of the interlayer K. For K^+ exchange in particular, 5-10% K^+ saturation of the total exchangeable cations is most important to crops because the K^+ saturation of soil seldom exceeds 10%, even after many years of treatment with K fertilizers (Goulding 1983). In our research, the soil was characterized by about 5% K^+ saturation in the 0-30 cm topsoil layers.

The present results demonstrated that the potassium content in cabbage plants (Table 5) was below the sufficient range (3-4%) reported for *Brassica* species by Barker and Pilbeam (2006). The highest content of K in plant tissues was detected in the dry 2006, and the lowest – in the wet 2007. Monovalent cations are leached more readily than divalent ones, but when Ca^{2+} is the dominant cation in the soil, it may be leached in the highest amount (Whitehead 2000). Another possible reason, analogously to phosphorus, is the effect of K ‘dilution’ in plant biomass.

In our research, the examined factors did not influence the K concentration in cabbage. However, plants fed ammonium sulfate with the broadcast technique had a slightly higher level of potassium than fed UAN and with the placement method (Table 5). This is in contrast to the well-known phenomena of competition between NH_4^+ and K^+. Possible explanations for this is that ammonium ions have a relatively small unhydrated radius and low negative hydrogen energy, and they can displace the K^+ from interlayer clay sites (Goulding 1983). However, the chances of NH_4^+ competing with K^+ for plant uptake are more likely to occur in cool rather than warm soils because most ammonium in warmer soils is converted into nitrate by nitrification process.

Plant magnesium is most likely to be low in soils that are either sandy or acid or that have high contents of Ca or K. Calcareous or freshly limed soils often induce low plant concentrations of Mg. Calcium is strongly competitive with Mg^{2+} and the binding sites on the root plasma membrane appear to have less affinity for the highly hydrated Mg^{2+} than for Ca^{2+}

(Marchner 1995). Thus, high concentrations of substrate Ca^{2+} often result in increased leaf-Ca along with a marked reduction in leaf-Mg. It is well know that in some plants Mg^{2+} uptake is highly controlled by K^+ levels, but the reverse is not always true (Stout, Baker 1981).

The optimal Mg concentrations in *Brassica* species range between 0.17--1.08% in dry matter (Barker, Pilbeam 2006). In the present research, the amount of Mg in cabbage was low and ranged between 0.11 (2007) to 0.14 (2006) – Table 6. The highest Mg content in cabbage was determined in 2006. The soil in that year was characterized the highest Mg^{2+} saturation in total exchangeable cations (4.5% Mg) in the 0-30 cm topsoil and high saturation in the 30-90 cm subsoil layer (3.2-3.4%) (Table 2). In 2006, the soil pH values and concentration of calcium extracted by the universal method were relatively low compared to 2005-2007 (Tables 1, 4).

Nitrogen may either inhibit or promote Mg accumulation in plants, depending on the form of N. With ammonium, the Mg uptake is suppressed but with nitrate it is increased (Barker, Pilbeam 2006). In the present study, none of the examined factors influenced the Mg content in cabbage plants.

The concentration of calcium in cabbage plants tended to increase with increasing soil pH and with an increasing proportion of Ca^{2+} in the total exchangeable cations of the soil (Tables 1, 6). Soil liming generally increases plant Ca. Our research was carried out in an area specialized in cabbage production, with lime used as a control measure for club root. Every year, the amount of Ca in cabbage plants was with the sufficient range 0.1-5% d.m reported by Barker and Pilbeam (2006) for *Brassica* species. The highest concentration of Ca in cabbage was detected in 2005 (0.56%), and the lowest – in 2007 (0.50%).

Nitrogen fertilizer has an inconsistent effect on the plant Ca, partly due to the fact that some N fertilizers contain Ca and partly because of the form in which the N is taken up. Fertilizers that do not contain Ca often depress the plant Ca although, in some cases, the effect is very weak. When N fertilizer is supplied in the form of ammonium or urea, the plant Ca is lower than when N is supplied as nitrate. In this study, lower concentrations of Ca in cabbage fed UAN (solution ammonium nitrate and urea 1:1) than ammonium sulfate were noticed in 2005-2006 (Table 6). However, these differences were relatively small. K-Ca exchange behavior in soils would be influenced by addition of NH_4^+. Thus, the relative chemical potential of adsorbed monovalent cations would depend on the number and type of cations present in the soil system (Lumbanraja, Evangelou 1990).

Optimum leaf Ca/Mg ratios are considered to be approximately 2 : 1, although a Ca/Mg ratio >1 : 1 and < 5 : 1 can produce adequate growth without any expression of Mg deficiency (Barker, Pilbeam 2006). In our experiment, the Ca/Mg ratios were 4 : 1, 3.8 : 1 and 4.5 : 1 in 2005-2007 respectively.

Sulfur

Most *Brassicaceae* plants have greater S requirements than other large crop species. Sulfur availability has been decreasing in many areas of Europe during the last two decades (McGrath et al. 2002, Zhao et al. 1997).

Interactions between S and other minerals may significantly influence crop quality parameters. Sulfur and nitrogen show strong interactions in their nutritional effects on crop growth and quality (Jackson 2000). Under of S deficiency, the utilization of N will be reduced and consequently nonprotein N compounds, including NO_3^-, accumulate in the part tissue (Kopriva, Rennenberg 2004, Abdallah et al. 2010).

Our research indicated that the environmental conditions, fertilizer type, method of N application and interaction of these factors significantly affected the sulfate content in cabbage plants. The highest amount of S in the wet 2007 was noticed and the lowest one – in 2005 (Table 7). Every year, higher S concentrations in plants fed ammonium sulfate were detected. In 2005-2006, the cabbage fertilized with the broadcast technique had a slightly higher amount of S than with the placement treatment. In 2005, plants fed ammonium sulfate with the broadcast treatment had a higher S concentration than with the placement treatment. Hu et al. (2005) tested the bioavailability of water-insoluble sulfate, a sulfate-$CaCO_3$ co-precipitate labelled with ^{35}S added to calcareous soil in a pot experiment with either NH_4^+ or NO_3^- as the N source. In 29 days, wheat plants took up 10.6% and 3.0% of the ^{35}S added to the soil in the NH_4^+ and NO_3^- treatments, respectively. The results indicate that sulfate co-precipitated with $CaCO_3$ in calcareous soils may become partly available for plant uptake, depending on the rhizosphere's pH influenced by N-NH_4 treatment.

The soil sulfur cycle is driven by biological and physicochemical processes, which affect flora and fauna (McGill, Cole 1981). Seasonal variations in mineralization leaching, capillary rise and plant uptake cause temporal variations in the sulfate content in soil. Especially under humid growth conditions, plant-available soil water is the largest contributor to the S balance (Mengel et al. 2001). In the present study, high amounts of sulfates in cabbage plants in the wet 2007 were associated with a high level of nitrates (data not published). A possible explanation includes increasing microbial activity in soil in autumn. In Europe, organic matter mineralization in autumn is relatively high (Wiesler 1998). The flux of inorganic nitrogen and sulfur to soil at harvest might be regulated by the wetting up, breakdown and release of soil organic matter.

Table 7

Sulfur content (% S-SO_4 d.m.) in cabbage after harvest in 2005-2007

Fertilizer	Method of N application		S-SO_4 (% d.m.)			
			2005	2006	2007	mean
$(NH_4)_2SO_4$	broadcast	1*	0.24	0.35	0.46	0.35
		2	0.23	0.28	0.47	0.32
		3	0.23	0.30	0.45	0.33
	placement	4	0.16	0.28	0.48	0.31
		5	0.21	0.24	0.47	0.31
		6	0.25	0.24	0.41	0.30
UAN	broadcast	1	0.15	0.17	0.41	0.24
		2	0.17	0.18	0.44	0.26
		3	0.11	0.12	0.40	0.21
	placement	4	0.20	0.16	0.40	0.25
		5	0.20	0.12	0.40	0.24
		6	0.25	0.13	0.37	0.25
Mean for years			0,20	0,21	0.43	
Fertilizer	$(NH_4)_2SO_4$		0,22	0.28	0.46	0.32
	UAN		0,18	0.15	0.40	0.24
Metod of N application	broadcast	1	0.19	0.26	0.43	0.30
		2	0.20	0.23	0.46	0.29
		3	0.17	0.21	0.43	0.27
	placement	4	0.18	0.22	0.44	0.28
		5	0.20	0.18	0.43	0.27
		6	0.25	0.18	0.39	0.27
$LSD_{0.05}$ for:	fertilizer		0.022	0.026	0.033	
	method		0.038	0.045	ns	
	fertilizer × method		0.054	ns	ns	

* see Table 3

CONCLUSIONS

Efficient nutrient management is essential in modern crop production systems by providing a balance between nutrient inputs and outputs over the long term (BINDRABAN et al. 2000, BASSANINO et al. 2010). The present research has clearly showed that plant tissue tests versus specific standard concentrations that separate deficient, sufficient or toxic levels are an important diagnostic method of the plant nutrient status. Our better understanding of N interactions with other nutrients may be useful in comprehending the importance of balanced supplies of nutrients, and consequently, in obtaining improved plant growth or yields.

At present, nutrient interactions and environmental yield potential as a driving force for establishing optimal nutrient requirements are not taken advantage of in practice. Although experimental research supplies valuable information for a given site, the results can only partly be extrapolated to estimate nutrient requirements on a micro-scale in farmers' fields. It is so because of a much broader range of soil, weather, and agronomic conditions at a farm level.

The observations made in this study appear to confirm than single levels in fertilizer recommendations should be based on standard conditions that take into account the major factors governing crop response to a given nutrient. Quantitative approaches that simultaneously account for yield potential and interactions between N, P and K in estimating the crop requirement for each of the elements are likely to be more precise, particularly at high yield levels.

Sulfur availability has been decreasing in many areas of Europe. S-containing fertilizers such as ammonium sulfate or superphosphate have been replaced by fertilizers containing little or no S. Moreover, sulfur requirements of many crops, especially *Brassicaceae* plants, have increased as a result of intensive agriculture and optimization during plant breeding programmes. The present research results have demonstrated a positive effect of S applied as ammonium sulfate on the concentration of sulfur in cabbage plants.

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INLFUENCE OF INCREASING NITROGEN FERTILIZATION ON CONTENT OF MICROELEMENTS IN GRASSES CULTIVATED ON ORNAMENTAL LAWNS

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Abstract

The main aim of the study, conducted in 2007-2008, was to define the influence of nitrogen levels 0, 50, 100, 150, 200 mg N dm^{-3} applied to grass lawns on the content of metallic microelements: iron, manganese, zinc and copper and on their quantitative ratios in turf grass. The study was carried out on a 2-year-old lawn, composed of a mixture of lawn grasses species and varieties: perennial ryegrass (*Lolium perenne* L.) var. Grasslands Nui (45%), tall fescue (*Festuca arundinacea* Schreb) Finelawn (25%), red fescue (*Festuca rubra* Hack.) Olivia (10%), red fescue (*Festuca rubra* Hack.) Boreal (15%) and Kentucky bluegrass (*Poa pratensis* L.) Balin (5%). With the exception of copper, the nitrogen fertilization raised the content of iron, manganese and zinc in aerial plant parts. The application of nitrogen (as ammonium nitrate) increased the uptake of nutrients by aerial plant parts: Fe to 143.0%, Mn – 227.2%, Zn – 233.3% Cu – 180.7%, and modified the ratios between amounts of the microelements. In general, it has been demonstrated that nitrogen nutrition of plants grown on ornamental lawns, within ranges of N – 150 to N – 200, increased the ratios of Fe : Mn : Zn : Cu. The best ornamental quality of lawns was obtained where the aerial plant parts contained (in mg kg^{-1} d.m.): Fe 231.6-292.8, Mn 35.6-50.5, Zn 26.5-47.5 and Cu 16.9-17.6. These ranges could be recommended as preliminary guidelines for ornamental lawns. In practice, considering the positive and stimulating influence of nitrogen nutrition on crops, the chemical composition of plants and the uptake of microelements by a mixture of grasses on ornamental lawns, it is crucial to monitor actual fertilization by taking into account losses of nutrients. These losses are caused by intensive uptake of nutrients by the aerial plant parts and due to the leaching of nutrients from the rhizosphere. It is necessary to replenish lost elements using mineral fertilizers.

Key words: nitrogen, lawn, turf grass, microelement content, plant analysis.

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WPŁYW WZRASTAJĄCEGO NAWOŻENIA AZOTEM NA ZAWARTOŚĆ MIKROELEMENTÓW W RUNI TRAWNIKÓW DEKORACYJNYCH

Abstrakt

Celem badań w latach 2007-2008 było określenie wpływu wzrastających poziomów azotu: 0, 50, 100, 150, 200 mg N dm^{-3} na zawartość mikroelementów metalicznych żelaza, manganu, cynku i miedzi oraz stosunki ilościowe w runi trawników dekoracyjnych. Doświadczenie wegetacyjne wykonano na 2-letnim trawniku, na którym wysiano mieszankę traw o następującym składzie gatunkowym (w %): życica trwała (*Lolium perenne* L.) Grasslands Nui – 45%, kostrzewa trzcinowa (*Festuca arundinacea* Schreb.) Finelawn – 25%, kostrzewa czerwona (*Festuca rubra* Hack.) Olivia – 10%, kostrzewa czerwona (*Festuca rubra* Hack.) Boreal – 15%, wiechlina łąkowa (*Poa pratensis* L.) Balin – 5%. Z wyjątkiem miedzi, nawożenie azotem wpływało na wzrost zawartości żelaza, manganu i cynku w częściach nadziemnych traw. Nawożenie azotem (w formie saletry amonowej) zwiększało pobranie mikroelementów przez części nadziemne roślin: Fe o 143,0%, Mn – 227,2%, Zn – 233,3%, Cu – 180,7% oraz ich stosunki ilościowe. Wykazano, że wysokie nawożenie azotem trawników dekoracyjnych, od N-150 do N-200, zwiększało stosunek Fe : Mn : Zn : Cu. Najlepszymi walorami dekoracyjnymi charakteryzowała się murawa zawierająca w częściach nadziemnych (w mg kg^{-1} s.m.): Fe 231,6-292,8, Mn 35,6-50,5, Zn 26,5-47,5 i Cu 16,9-17,6. Zakresy te można zalecać jako tymczasowe zawartości wskaźnikowe dla trawników dekoracyjnych. Z praktycznego punktu widzenia, biorąc pod uwagę pozytywny i stymulujący wpływ nawożenia azotem na plonowanie, skład chemiczny roślin i pobieranie mikroelementów przez mieszankę traw na trawniku dywanowym, konieczne jest – w ich kontrolowanym nawożeniu – uwzględnienie strat wynikających z wynoszenia tych składników z gleby wraz z plonem części nadziemnych, a także ich wypłukiwania z rizosfery, i ewentualne ich uzupełnienie nawozami mineralnymi.

Słowa kluczowe: azot, trawnik, darń, zawartość mikroelementów, analiza roślin.

INTRODUCTION

Grasses, forming natural green areas, have for long been fulfilling ornamental functions. With time, grass began to be introduced to gardens, generally as lawns. Together with the development of architecture, their practical meaning gradually started to increase. In recent time, grass lawns have been treated as one of the most important components of green areas.

Despite many significant functions performed by grass plants, there are no recommended values of microelements in aerial part of grasses that would facilitate a diagnosis of the actual plant nutrient status, which is essential for controlling fertilization of ornamental lawns. The experiments conducted so far on the influence of nitrogen fertilizers have focused on the abundance of soil, harvesting of plants and values of ornamental lawns (Kleiber et al. 2009a), status of plant supply with macroelements (Kleiber et al. 2009b) and microbiological changes that occur in soil under lawns (Niewiadomska et al. 2010).

The main aim of the present study has been to determine the influence of increasing nitrogen fertilization on the content of iron, manganese, zinc and copper, their uptake by plants and quantitative ratios in aerial plant parts. Another objective has been to propse preliminary guidelines for levels of microelements in aerial parts of grass plants, which will ensure the best ornamental efects. These data are valuable in practice for controlled nitrogen fertilization of lawns.

MATERIAL AND METHODS

Vegetation experiments were carried out in 2007-2008, at the Experimental Station of the Horticulture and Landscape Architecture Department, Poznań University of Life Sciences. The increasing levels of nitrogen fertilization were tested (in mg N dm^{-3}): 0, 50, 100, 150, 200 (marked N-0 to N-200), corresponding to the doses of nitrogen such as 0, 10, 20, 30 and 40 g N m^2 (in ammonium nitrate – 35% N), on iron, manganese, zinc and copper content, their uptake and quantitative ratios in aerial plant parts. Apart from nitrogen, the other macroelements in all treatments were applied to maintain standard levels of fertilization (in mg dm^{-3}): P 100, K 200, Mg 180 (in 2007) and Mg 300 (in 2008). A detailed description of the material and methods in this experiment is given by Kleiber et al. (2009a).

The tests were carried out on 2-year-old lawn, where a mixture of lawn grasses was sown in the amount of 25 g m^{-2}, composed of perennial ryegrass (*Lolium perenne* L.) var. Grasslands Nui (45%), tall fescue (*Festuca arundinacea* Schreb) Finelawn (25%), red fescue (*Festuca rubra* Hack.) Olivia (10%), red fescue (*Festuca rubra* Hack.) Boreal (15%) and Kentucky bluegrass (*Poa pratensis* L.) Balin (5%).

During the vegetation period, samples of aerial plant parts were collected for chemical analyses. The samples were obtained after cutting the grass with of a lawn mower. The experiments were set up in four replications; each replication was a plot of 12 m^2. The samples were collected separately from each plots on the following days: 26.07 and 03.09.2007 or 18.06, 23.07 and 25.08.2008. The collected aerial plant parts were dried at the temperature of 45-50°C and ground. The plant samples were digested in a mixture of nitric and perchloric acids 3:1 (v/v). Afterwards, Fe, Mn, Zn, and Cu were determined with the AAS method (AAS3; Carl Zeiss Jena). The results of plant analyses were subjected to statistical analysis with Duncan's test (α=0.05).

RESULTS AND DISCUSSION

Nutrient status of plants

Significant influence of the application of nitrogen fertilizers on the content of iron in aerial parts of plants has been demonstrated (Table 1). The significantly highest content of this nutrient (287.5-300.5 mg Fe kg^{-1} d.m.) was found in plants that were supplied with the lower and average quantities of nitrogen (N-0 to N-100). A significant decrease in the iron content was noticed when plants were fed higher nitrogen doses (N-150 to N-200); then it ranged from 231.6 to 234.0 mg Fe kg^{-1} d.m. A higher content of iron was shown by Wiater et al. (2005), who tested a mixture of grasses nourished with sewage fertilizer; there, aerial parts of plants contained 357 to 801 mg Fe kg^{-1} d.m. In our experiment, the year of the tests modified the iron content of the plants.

Table 1

The influence of nitrogen nutrition on the content of iron, manganese, zinc and copper in aerial plant parts (mg kg^{-1} d.m.)

N level (A)	Fe			Mn			Zn			Cu		
	year											
	2007	2008	mean	2007	2008	mean	2007	2008	mean	2007	2008	mean
N-0	341.1	233.9	287.5*a*	40.8	24.9	32.9*b*	56.5	29.7	43.1*a*	18.2	18.3	18.2*a*
N-50	371.2	229.8	300.5*a*	55.7	25.2	40.4*ab*	36.3	17.5	26.9*b*	16.7	17.5	17.1*a*
N-100	368.2	217.5	292.8*a*	76.3	24.7	50.5*a*	33.2	19.8	26.5*b*	16.9	18.4	17.6*a*
N-150	307.8	160.3	234.0*b*	59.5	22.0	40.7*ab*	40.5	22.6	31.5*b*	16.6	17.5	17.0*a*
N-200	291.5	171.7	231.6*b*	48.2	23.0	35.6*b*	64.5	30.6	47.5*a*	14.5	19.3	16.9*a*
Mean	341.1*a*	233.9*b*	287.5	40.8*a*	24.9*b*	32.9	56.5*a*	29.7*b*	43.1	18.2*a*	18.3*a*	18.2

* Values designated with the same letters in columns do not significantly differ at p=0.05.

The tested nitrogen plant nutrition had a significant influence on the content of manganese in aerial plant parts. The lowest content of manganese was found under the extreme levels of nitrogen in the soil N-0 and N-200, where it reached 32.9 and 35.6 mg Mn kg^{-1} d.m., respectively. The highest content of this element (50.5 mg Mn kg^{-1} d.m.) appeared in response to N-150 fertilization. By analogy to iron, the content of manganese was significantly different between the two years of the study. Demonstrably lower content of manganese (79-119 mg Mn kg^{-1} d.m.) was determined by Wiater et al. (2005). Baryła et al. (2009) turn our attention to the important influence of grass species on nutrient accumulation. Czarnecki, Harkot (2000) express an opinion that red fescue (*Festuca rubra* Hack.) accumulates higher amounts of manganese than other grass species.

Analogously to iron and manganese, differences in the influence of nitrogen fertilizers on the content of zinc in plants were shown. The significantly highest content of this nutrient appeared in the control combination (N-0) and the treatments that had received the highest quantities of nitrogen (N-150): 43.1 and 47.5 mg Zn kg^{-1} d.m. of aerial plant parts, respectively. The content of zinc in the other treatments was as follows: from 26.5 to 31.5 mg Zn kg^{-1} d.m. The year of the experiment significantly influenced the content of zinc in aerial plant parts. Similarly to iron and manganese, in the experiment conducted earlier by WIATER et al. (2005), a higher content of zinc was discovered, ranging from 49.1 to 103.4 mg Zn kg^{-1} d.m. of aerial plant parts. In turn, BARYŁA et al. (2009), who compared the chemical composition of different grass species, demonstrated higher accumulation of zinc in aerial parts of *Phalaris arundinacea*.

Contrary to the other microelements, no significant influence of nitrogen nutrition on the content of copper in aerial parts of plants was shown. The content of copper was from 16.9 mg Cu kg^{-1} d.m. in combinations the plants fed with higher rates of nitrogen (N-200) to 18.2 mg Cu kg^{-1} d.m. in the control combination (N-0). There were no significant differences between the two years of the experiment in the content of copper in aerial parts of plants. The content of copper was higher than the data reported by WIATER et al. (2005).

Some earlier experiments, e.g. conducted by VUCKOVIC et al. (2005), did show significant influence of nitrogen fertilization levels, within ranges of 0 to 160 kg ha^{-1}, on the condition of feeding grasses with zinc and copper. The content of zinc, as shown bythe above auhtors, was higher than in our experiment, i.e. from 68 to 75 mg Zn kg^{-1} d.m. The same is true about copper, ranging from 24 to 31 mg Cu kg^{-1} d.m. It was also shown, as in our study, that the year of the experiment had some influence on the plants' nutrient status with zinc. These authors claim that an increase of nitrogen doses caused an increase of the content of copper accompanied by a decrease in the content of zinc. The content of zinc and manganese determined in our tests was higher than the results reported by COURTNEY, TIMPSON (2004), who stated that the biomass of *Lolium perenne*, in dependence on the physiochemical characteristics of the soil, contained on average from 12.1 mg to 36.3 mg Mn kg^{-1} d.m. The same authors reported that the content of zinc ranged from 15.9 mg to 33.4 mg Zn kg^{-1}. SAWICKA (1996) pointed out that higher doses of nitrogen fertilizers cause some decrease in the content of zinc and copper in plants. The influence of nitrogen nutrition on the status of plant supply with microelements and their translocation within plants has been also noticed by HU-LIN et al. (2007).

Nutrient uptake by aerial parts of plant

Some positive influence of nitrogen nutrition on the uptake of microelements by aerial parts of grass plants was noticed (Table 2). Among all treat-

Table 2

The influence of nitrogen nutrition on yield of dry matter (g m^{-2}) and uptake microelements by aerial parts of grasses (mg m^{-2}) – average from two years

Nutrient (mg m^{-2})	N level					
	N-0	N-50	N-100	N-150	N-200	mean
Dry matter	313.8*c*	452.8*b*	590.8*b*	763.8*ab*	946.6*a*	613.6
Fe	90.2*c*	136.1*b*	173.0*ab*	178.7*ab*	219.2*a*	159.4
Mn	10.3*c*	18.3*b*	29.8*a*	31.1*a*	33.7*a*	24.6
Zn	13.5*b*	12.2*b*	15.7*b*	24.1*b*	45.0*a*	22.1
Cu	5.7*c*	7.7*b*	10.4*b*	13.0*a*	16.0*a*	10.6

* Values designated with the same letters in rows do not significantly differ at p=0.05.

ments, the lowest uptake of microelements appeared in plants cultivated in the control combination. As the nutrition of plants with nitrogen rose, so did the uptake of microelements. Under the highest nitrogen nutrition (N-200), relative to the control combination (N-0), the uptake of microelements rose as follows: Fe-143.0%, Mn-227.2 %, Zn- 233.3% and Cu-180.7%. For zinc, the lowest uptake of this microelement was in the treatment fertilized with the nitrogen level N-50. The average uptake of microelements by aerial parts of plants under the tested nitrogen levels was (in mg m^{-2}): Fe 159.4, (90.2-219.2), Mn 24.6 (10.3-13.7), Zn 22.1 (12.2-45.0) and Cu 10.6 (5.7--16.0). WIATER et al. (2005) reported that the uptake of microelements, depending on the year of the experiment, was the following (in mg m^2): Fe (33.7-147.0), Mn (10.1-21.7), Zn (9.25-16.5) and Cu (0.0012-1.38).

Nutrient ratios in aerial plant parts

The influence of nitrogen nutrition on changes in ratios between microelements in aerial parts of plants grown on an ornamental lawn has been demonstrated (Table 3). Noted was also Diminishing ratios between Fe : : Mn = 1.00: 0.17 under the nitrogen levels in soil from N-100 to N-150 were also observed. When the nitrogen nutrition of plants was low (N-0 and N-50), the ratio of iron to manganese rose to Fe : Mn = 1.00: (0.11-0.13).

The ratio Fe : Zn in aerial parts of grasses also rose under the influence of the nitrogen levels from N–50 to N–150 [Fe : Zn = 1.0 : (0.09-0.13)] in comparison to the control combination N-0. The highest Fe : Zn ratio = 1.00 : 0.20 was noted in plants that had received the highest dose of nitrogen (N-200).

Together with intensive increase in plant nitrogen nutrition, the ratio between Fe : Cu kept decreasing (from 1.00 : 0.06 to 1.00 : 0.07). The average ratios between microelements (Fe : Mn : Zn : Cu) for all tested levels of nitrogen soil fertilization were 1.00 : 0.15 : 0.13 : 0.06.

Table 3

The influence of nitrogen nutrition on ratios between nutrients in aerial parts of grasses (average from the years 2007-2008)

Nutrient	N level					
	N-0	N-50	N-100	N-150	N-200	mean
Microelements						
Fe	1.00	1.00	1.00	1.00	1.00	1.00
Mn	0.11	0.13	0.17	0.17	0.15	0.15
Zn	0.15	0.09	0.09	0.13	0.20	0.13
Cu	0.06	0.06	0.06	0.07	0.07	0.06
Macroelements (KLEIBER et al. 2009b)						
N	1.00	1.00	1.00	1.00	1.00	1.00
P	0.25	0.26	0.25	0.23	0.18	0.23
K	1.26	1.32	1.28	1.20	1.06	1.22
Ca	0.39	0.48	0.52	0.35	0.23	0.39
Mg	0.21	0.24	0.23	0.20	0.16	0.21
S	0.19	0.19	0.19	0.16	0.16	0.18

In general, the results of the tests show that nitrogen nutrition of plants growing on ornamental lawns with nitrogen, within ranges of N-150 to N-200, increased the ratios of Fe : Mn : Zn : Cu. In contrast to these microelements, same as in the experiment carried out by KLEIBER et al. (2009b), high nitrogen fertilization decreased the ratio of nitrogen to the remaining macroelements in aerial plant parts.

SUMMARY

In practice, considering the positive and stimulating influence of nitrogen nutrition on crops (KLEIBER et al. 2009a), the chemical composition of plants and the uptake of microelements by a mixture of grasses on ornamental lawns, it is crucial to monitor their fertilization, taking into account losses of nutrients. These losses are caused by intensive uptake of nutrients by the aerial plant parts and due to the leaching of nutrients from the rhizosphere. It is necessary to replenish lost elements using mineral fertilizers.

CONCLUSIONS

1. The study has confirmed significant influence of nitrogen nutrition on plants growing on ornamental lawns, and in particular, on the content of iron, manganese and zinc in their aerial parts. Soil nitrogen fertilization did not have any significant influence on the content of copper.

2. Positive influence of nitrogen nutrition of grasses on the uptake of metallic microelements by aerial plant parts was shown. The lowest uptake of iron, manganese, zinc and copper was noted in grasses in the control combination (N-0). Increasing nitrogen nutrition of plants caused some increase in the uptake of these microelements.

3. Under the highest level of nitrogen fertilization (N-200), in relation to the control object (N-0), the uptake of microelements by aerial parts of plants rose as follows: Fe – 143.0%, Mn – 227.2%, Zn – 233.3% and Cu – 180.7%.

4. Increasing nitrogen nutrition of grasses modifies ratios of quantities of microelements in aerial parts of plants.

5. The lawns with the best ornamental attributes are those that are characterized with the following content of elements (in mg kg^{-1}): Fe – 231.6÷292.8, Mn – 35.6÷50.5, Zn – 26.5÷47.5 and Cu – 16.9 ÷ 17.6.

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SPATIAL VARIABILITY OF DIFFERENT MAGNESIUM FORMS IN LUVISOLS FORMED FROM GLACIAL TILL*

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Abstract

Ions occurring in the soil solution as well as exchangeable ions related to exchangeable complex are a reservoir of magnesium for plants. The content of magnesium forms important for plants can reveal a very high spatial variability of this element on a field scale. Determination of such spatial variability of elements is extremely important for the so-called precision agriculture, in which application of a fertilizer dose is by principle related to the actual deficit of elements, even in a small area.

In order to evaluate parameters connected with the spatial variability of magnesium forms, the H_2O (water) soluble (Mg-H_2O), exchangeable (Mg-E) and available magnesium (Mg-A) forms were determined. The soil samples were taken in spring 2007 from the humic Luvisols horizon under winter wheat. Fifty soil samples were taken from the sites located in a square sampling grid (10 m x 10 m). The results were evaluated with the use of classical statistical methods as well as geostatistical calculations. The raster maps illustrating the spatial variance of determined nitrogen forms were drawn on the ground of semivariograms.

The concentration of magnesium forms in the surface horizon of the soil showed significant differentiation: Mg-H_2O ranged from 0.76 to 2.89 mmol(+) kg^{-1}; Mg-E 1.69-8.06 mmol(+) kg^{-1} and Mg-A 28.50-91.40 mg kg^{-1}. The data were analyzed statistically. Coefficients of variations equaled 31.6% for Mg-H_2O; 30.5% for Mg-E and 24.9% for Mg-A. Analysis of dispersion showed the highest similarity to the mean value, reaching 1.24 mmol kg^{-1} Mg-H_2O, which was confirmed by high kurtosis (8.73). The most flattened distribution was noted for Mg-E (– 0.39 kurtosis). Geostatistical calculations demonstrated that the analyzed magnesium forms did not occur in total dispersion in the soil mass, which was confirmed by high nugget variance values equal 0.423 (mmol $kg^{-1})^2$ for Mg-E, 0.031

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(mmol kg^{-1})^2 for Mg-H_2O and 83.42 (mg kg^{-1}) for Mg-E. The highest participation of the nugget variance in sill variance (47.3%) was observed on the Mg-E semivariogram. The range of influence, defined as a maximum distance of correlations between point values, ranging 80.0-98.0 m, was higher than the real distance of soil sampling.

Key words: exchangeable magnesium, water soluble magnesium, available magnesium, spatial variability, Luvisols.

ZRÓŻNICOWANIE PRZESTRZENNE RÓŻNYCH FORM MAGNEZU W GLEBIE PŁOWEJ WYTWORZONEJ Z GLINY LODOWCOWEJ

Abstrakt

Rezerwuarem magnezu dla roślin jest gleba, głównie jony znajdujące się w roztworze wodnym, oraz jego kationy wymienne związane z kompleksem sorpcyjnym. Zawartość magnezu przyswajalnego – ważna ze względu na zabezpieczenie potrzeb pokarmowych roślin – może się charakteryzować bardzo dużym zróżnicowaniem przestrzennym w skali pola uprawnego. Określenie przestrzennego zróżnicowania tych składników jest niezmiernie istotne w rolnictwie precyzyjnym, uzależniającym dawkę nawożenia od rzeczywistego niedoboru pierwiastka, nawet na niewielkim areale pola uprawnego.

W celu oszacowania parametrów związanych z przestrzenną zmiennością form magnezu określono zawartość magnezu wodno-rozpuszczalnego (Mg-H_2O), wymiennego (Mg-W) i przyswajalnego dla roślin (Mg-P). Próbki z 50 punktów poziomu orno-próchnicznego gleby płowej pobrano wiosną 2007 r. w sieci kwadratów rozmieszczonych co 10 m. Zawartość poszczególnych form magnezu oznaczono tradycyjnymi metodami, a wyniki opracowano metodami statystycznymi i geostatystycznymi, które posłużyły do wykonania map określających ich przestrzenne zróżnicowanie.

Wykazano duże zróżnicowanie zawartości form magnezu (Mg-H_2O – 0,76-2,89 mmol(+) kg^{-1}; Mg-W – 1,69-8,06 mmol(+) kg^{-1}; Mg-P – 28,50-91,40 mg kg^{-1}) w poziomie orno-próchnicznym gleby płowej. Zróżnicowanie to potwierdzają wysokie wskaźniki zmienności, wynoszące odpowiednio: Mg-H_2O – 31,6%; Mg-W – 30,5%; Mg-P – 24,9%. Na podstawie analizy geostatystycznej wyników stwierdzono, że najbardziej skupione wokół średniej arytmetycznej, wynoszącej 1,24 mmol Mg kg^{-1}, były zawartości Mg-H_2O. Potwierdza to także obliczona dla tej formy magnezu wysoka wartość kurtozy (8,73). Najbardziej spłaszczony rozkład miały wyniki określające zawartość magnezu przyswajalnego dla roślin (kurtoza -0,39). Poszczególne formy magnezu w masie glebowej badanego pola charakteryzują się niewielkim wskaźnikiem rozproszenia, na co wskazuje wysoka wartość efektu samorodka, odpowiednio: 0,423 (mmol kg^{-1})^2 dla Mg-W; 0,031 (mmol kg^{-1})^2 dla Mg-H_2O oraz 83,42 (mg kg^{-1})^2 dla Mg-P. Największy udział efektu samorodka w wariancji progowej (47,3%) zaobserwowano na semiwariogramie określającym zawartość Mg-P. Obliczony zasięg oddziaływania, czyli korelacji między próbkami, wynosił 79,3-98,0 m i był większy niż rzeczywista odległość między poszczególnymi próbami pobranymi do badań.

Słowa kluczowe: magnez wymienny i wodno-rozpuszczalny, magnez przyswajalny dla roślin, zmienność przestrzenna, gleba płowa.

INTRODUCTION

Magnesium as a component of chlorophyll and the activator of enzymes involved in phosphorylation processes (phosphokinases, phosphotransferases) (MARSCHNER 1986, VOET, VOET 2004) participates in many important processes, which determine the quality and the quantity of crop yields. Magnesium ions occurring in the soil solution as well as exchangeable ions related to the exchangeable complex are a reservoir of magnesium for plants.

The concentration of magnesium in the soil solution depends on soil moisture, grain size distribution, organic matter content and soil microbiological activity, season of the year as well as mineral and organic fertilization (ŁABĘTOWICZ, RUTKOWSKA 2001, MARCHNER 1986). The content of magnesium forms important for plants can reveal a very high spatial variability of this element on a field scale. Determination of spatial variability of elements is extremely important for the so-called precision agriculture, in which application of a fertilizer dose as related to the actual deficit of elements, even in a small area.

The objective of this study has been to evaluate and compare the spatial variability of different magnesium forms: the H_2O (water) soluble (Mg-H_2O), exchangeable (Mg-E) and available magnesium (Mg-A) in the surface horizon of Luvisols from the Polish region called Kujawy and Pomorze.

MATERIAL AND METHODS

The area from which the soil samples were collected was localized on a 80-hectare field in the village of Orlinek near Mrocza in Kujawy and Pomorze. The area is partialy covered with typical Luvisols formed from till of the Vistulian glaciation.

Winter wheat after winter rape as the forecrop was cultivated on the selected field. The specimens were taken from the surface horizon (0-20 cm) of the soil profile at a stage of the wheat spreading (April 2007). In total, 50 soil samples were taken from points located in a square sampling grid (10 m x 10 m). Each soil sample accounted for a mean value of 10 individual samplings. The basic parameters of the investigated soils are shown in Table 1. The soil profile morphology and particle-size in respective (each) genetic horizons confirmed that the soil is Luvisols with an argic horizon, containing $CaCO_3$ in the parent material (Table 2). Soil analyses were performed on air dried and sieved (< 2 mm) soil samples according to the standard methods commonly used in soil science. Basic physicochemical parameters were determined: particle-size by Cassagrande'a method modified by Proszyński; fraction > 2 mm content by the sieving method; pH in 1 mol

Table 1

Ranges and means of basic soil physical and chemical parameters

Data	Organic carbon	Total nitrogen	pH		Fraction < 0.002 mm
	g kg^{-1}		H_2O	1M KCl	
Min – Max / Mean	5.5. – 9.0 / 7.3	0.68 – 0.99 / 0.80	4.66 –6.83 / 5.44*	4.11 – 5.77 / 4.70*	4.0 – 9.0 / 6.1

* geometric mean

Table 2

Selected properties of the Luvisols profile

Horizon	Depth	pH	$CaCO_3$	TOC	ρ_a	Particicle size (mm)		
						2-0.05	0.05-0.002	0.002
	(cm)	KCl	(%)	(g kg^{-1})	(Mg m^{-3})	(%)		
Ap	0-28	5.07	0	6.66	1.31	77	18	5
AE	28-42	4.70	0	5.24	1.55	82	14	4
Eet	42-68	5.09	0	1.05	1.59	83	13	4
EB	68-84	5.18	0	0.75	1.65	70	15	15
Bt	84-115	5.48	0	0.36	1.76	63	19	18
BC	115-135	6.32	1.81	0.22	1.78	64	20	16
C1cagg	135-150	6.92	3.18	0	1.87	69	22	9

TOC – total organic carbon; ρ_a – bulk density

KCl by the potentiometric method; organic carbon content by using a dry combustion CN analyser (Vario Max CN) and $CaCO_3$ by Scheibler procedure. The analysis of magnesium forms was completed by atomic absorption spectroscopy using the following extractants: water with 1÷5 soil: water suspension for Mg-H_2O; Schachtschabel's extractant (0.0125 mol dm^{-3} $CaCl_2 \cdot 6H_2O$) for Mg-A and $BaCl_2$ solution according to PN-ISO 13636 (2002) for Mg-E.

The results were evaluated with the use of classical statistical methods (Statistica v. 8.0 Software) by calculating arithmetic and geometric means, standard deviation, coefficients of variation as well as skewness and kurtosis. Geostatistical calculations included empirical semivariogram graphs and a theoretical mathematical model of variograms. On the basis of the models thus obtained, the following geostatistic parameters were read out: nugget, sill variance, range of influence and nugget effects ($[Co/(Co+C)] \cdot 100$ (Namysłowska-Wilczyńska 2006). On the grounds of the semivariograms, raster maps illustrating the spatial variance of the determined magnesium forms were drawn. The method of point kriging was adapted to the date estimation (DAVIS 1986) and the calculations were done using SURFER 8.0 of Golden Software.

RESULTS AND DISCUSSION

Among many forms of magnesium, the most important in agricultural practice is the available one since it is the basis for optimization of magnesium fertilizer doses. The mean value of Mg-A in the surface horizon (Ap) of the investigated Luvisols was 60.5 mg kg^{-1}, being higher than the results obtained by CZEKAŁA et al. (2001). According to our results, the investigated soil could be classified as having a high Mg-A content (IV class abundance) i.e. soil not requiring magnesium fertilization (OBOJSKI, STRACZYNSKI 1995). Such soils account for 12% of the country's area (IGRAS, LIPIŃSKI 2006) and make up from 16% (GOSEK, KOPIŃSKI 2001) to about 25% of the soils in the Province of Kujawy and Pomorze (IGRAS, LIPIŃSKI 2006). The results on the available magnesium content in the surface horizon of the examined showed, however, demonstrated significant differentiation, as indicated by the range (28.5-91.4 mg kg^{-1}), standard deviation value (15.06) and variation coefficient obtained for this form (24.9%). The negative value of kurtosis (-0.39) further confirmed the wide dispersion of Mg-A and gave evidence of a flattened distribution, whereas the skewness analysis showed right-sided asymmetry (0.245), which indicated a higher number of soil samples with values lower than the mean for the whole investigated area. Moreover, this fact was evidenced by a lower median than the mean.

Geostatistical analysis showed some spatial variability of this Mg-A form in the surface horizon in the analyzed area. This was shown by a high sill variance value equal 259.32 (mg $kg^{-1})^2$. Our semivariogram model analyses showed the appearance of nugget variance, reaching 83.42 (mg $kg^{-1})^2$ – Table 3, Figure 1), which proved that the Mg-A distribution was influenced by structural factors, resulting in a short-range variability.

The influence of the above factors was significant, as demonstrated by the nugget effect at the level 32.2%.

Hovewer, the raster map of abundance classes drawn on the basis of the semivariogram (Figure 2) did not show high Mg-A changeability because most of the investigated area (70-75%) belonged to abundance class IV (soils with high abundance). It is in agreement with the abundance classification prepared for the studied area according to the mean values.

Soil available magnesium consists of ions occuring in the soil solution (Mg-H_2O) and Mg^{2+} cations bonded to the sorption complex (Mg-E), which showed differentiation in the surface horizon of the investigated Luvisols. This fact could be evidenced by the range of aforementioned magnesium

Table 3

Basic statistical and geostatistical parameters of analyzed properties

Parameter	Magnesium		
	exchangeable	water soluble	available
	mmol(+) kg^{-1}		mg kg^{-1}
η	50	50	50
Minimum	1.90	0.77	28.5
Maximum	8.06	2.90	91.4
Arithmetical mean	4.51	1.24	60.5
Geometric mean	4.31	1.17	58.6
SD***	1.378	0.392	15.06
Median	4.24	1.16	57.9
CV (%)****	30.5	31.6	24.9
Kurtosis	0.140	8.73	-0.39
Skewness	0.585	2.61	0.245
Variance	1.90	0.15	226.67
Model	spherical	spherical	spherical
Nugget (Co)	0.423*	0.031*	83.42**
Sill (Co+C)	2.083*	0.139*	259.32**
Nugget effect (%)	20.3	22.3	32.2
Range (m)	97.3	98.0	79.9

* (mmol(+) $kg^{-1})^2$, ** (mg $kg^{-1})^2$, ***SD – standard deviation, ****CV (%) – coefficient of variation

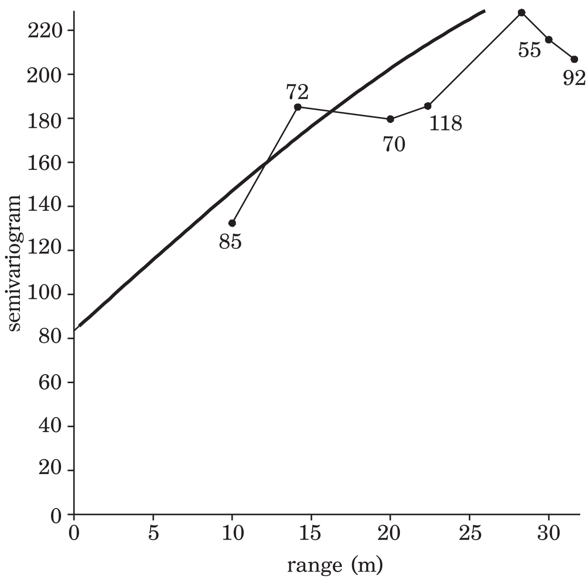

Fig. 1. Empirical semivariogram of the available magnesium content (Mg-A) obtained according to the estimated theoretical model

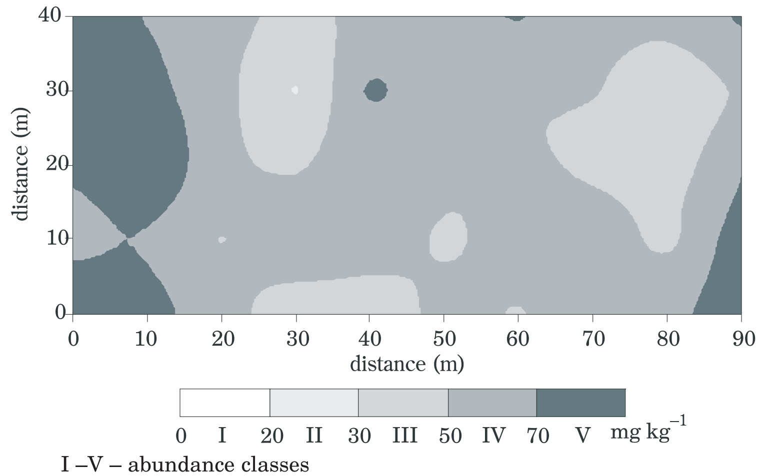

Fig. 2. Raster map of the available magnesium content (Mg-A)

forms, which varied between 1.90 and 8.06 mmol(+) kg^{-1} for Mg-E and 0.77-2.90 mmol(+) kg^{-1} for Mg-H_2O (Table 3). The differentiation was confirmed by high standard deviation values such as 1.378 mmol(+) kg^{-1} for Mg-E and 0.392 for Mg-H_2O calculated for the analyzed magnesium forms. However, the variation coefficients obtained for these Mg forms (30.5% for Mg-E and 31.6% for Mg-H_2O, respectively) pointed out that their differentiation was uniform over the investigated area. In turn, the results of dispersion analyses of Mg-H_2O were characterized by very high concentration around the mean value, which was confirmed by leptokurtic distribution (kurtosis 8.73), while the distribution of Mg-E values was similar to normal distribution (kurtosis -0.140). Although the concentration of both Mg forms displayed right-sided asymmetry, higher values were obtained for Mg-H_2O (Table 3). The right-sided Mg-H_2O distribution is further verified by the positive skewness value and lower median than mean values (Table 3).

Geostatistical analysis demonstrated spatial variability of both Mg-E and Mg-H_2O values. The distribution indicated that most of soils samples contained the Mg-H_2O concentration below the mean value. In the surface horizon of the analyzed soil, higher spatial variability was found for Mg-E than Mg-H_2O, which was indicated by the sill variance calculated for these parameters according to the experimental semivariograms and models derived from these semivariograms (Table 3, Figures 3 and 4). Additionally, they showed that the spatial variability of Mg-E and Mg-H_2O in the surface horizon of the investigated Luvisol was influenced by short-range variability, the fact that was proven by the nugget variance amounting to 0.423 $(mg\ kg^{-1})^2$ for Mg-E and 0.031 $(mg\ kg^{-1})^2$ for Mg-H_2O. The contribution of short-range variability to the total changeability of both magnesium forms (Mg-E and Mg-H_2O) was equal and reached approximately 20% (Table 3). The raster

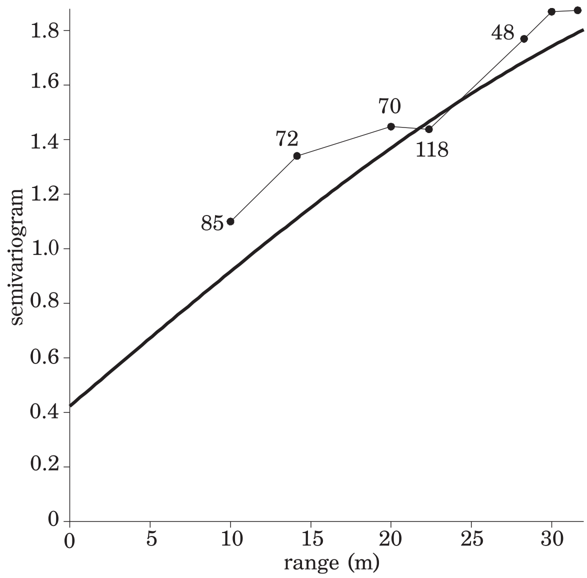

Fig. 3. Empirical semivariogram of the exchangeable magnesium content (Mg-E) obtained according to the estimated theoretical model

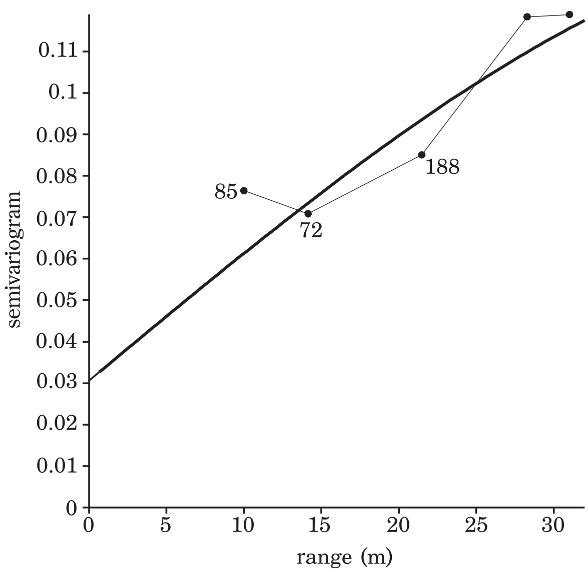

Fig. 4. Empirical semivariogram of the water-soluble magnesium content (Mg-H_2O) obtained according to the estimated theoretical model

maps displaying the spatial variability of Mg forms in the analyzed area showed higher differentiation of Mg-E than that of Mg-H_2O (Figures 5 and 6). The range of semivariograms (Table 3), showing the distance where point results could be auto-correlated, indicated that the range for each Mg forms was similar, i.e.: to 80 m for Mg-A and to 98 m for Mg-H_2O and 97.3 for Mg-E.

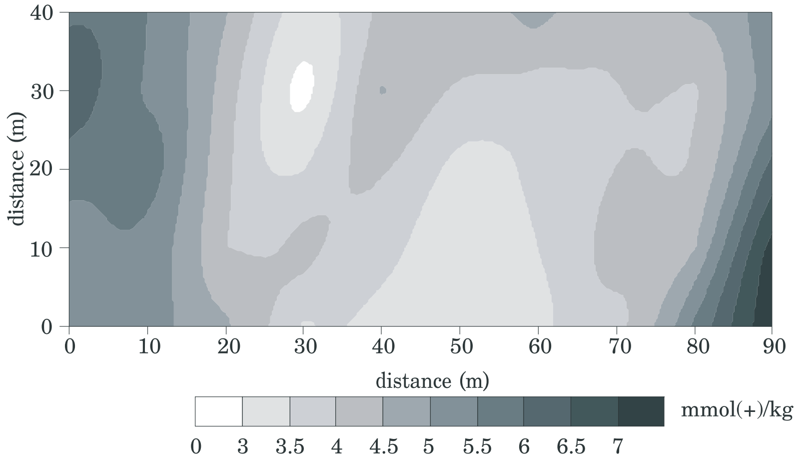

Fig. 5. Raster map of the exchangeable magnesium content (Mg-E)

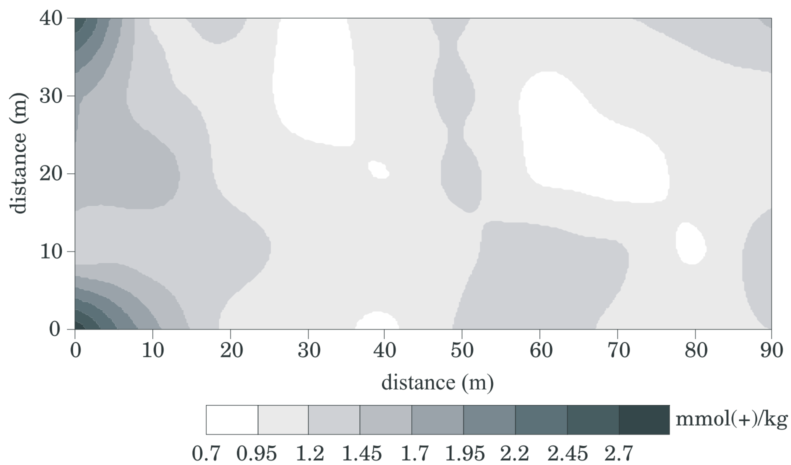

Fig. 6. Raster map of the water-soluble magnesium content (Mg-H_2O)

CONCLUSIONS

The investigation showed differentiation of the spatial variability of available magnesium as well as both water soluble and exchangeable magnesium forms in the Luvisols surface horizons on a scale of a microregion. The significant participation of short-range variability to the total changeability of all the investigated Mg forms was demonstrated and could show some irregular location Mg^{2+} cations in the soil mass, which was probably a consequence of soil heterogeneousness. The geostatistical analysis helped us to show that the maximal distance between sampling points for both Mg-H_2O and Mg-E spatial variability estimation should be about 100 m, while for the Mg-A abundance distance between estimation points should not exceed 80 m. A traditional criterion establishing abundance classes, when used for drawing maps of Mg-A variability, causes overgeneralization and homogenization of an analyzed, which could affect negatively the efficiency and accuracy of fertilization.

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EFFECT OF ASH-FLY ASH MIXTURE APPLICATION ON SOIL FERTILITY*

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Abstract

Nowadays, it is illegal to apply ashes, fly ashes and their mixtures on arable soil in Slovakia although it is allowed in many countries. The reasons why the Slovak law prohibits using these substances in agriculture are not explicitly stated but most probably it is so because of the variable and often high content of heavy metals as well as the residual radioactivity in soil treated with such mixtures. However, ashes and fly ashes are significantly different in parameters, therefore they should be classified individually. It is irrational to ignore some positive effects of ashes and fly ashes on plants if they do not pose a threat of increased input of heavy metals and residual radioactivity into soil and, subsequently, in crops. The aim of this experiment has been to find out the effect of ash-fly ash mixture (AFAM) on some soil yielding parameters and to clarify opinions on using ashes and fly ashes in agriculture.

A pot experiment was carried out in a vegetation cage located in the premises of the SAU in Nitra. Pots of the capacity of 30 kilos were filled with 24 kg of anthropogenic soil prepared by mixing two portions of Haplic Luvisol with one portion of siliceous sand. The ash-fly ash and/or NPK fertilizers were applied into the whole soil profile. The experimental design comprised 6 treatments (0, $AFAM_1$, NPK, NPK+ $AFAM_1$, NPK+ $AFAM_2$, NPK+ +$AFAM_3$), each in four replications, as follows: 1 – control treatment, 2 – AFAM in a dose of 3 t ha^{-1}, 3 – NPK mineral fertilizer, 4 – NPK mineral fertilizer + AFAM in a dose of 3 t ha^{-1}, 5 – NPK mineral fertilizer + AFAM in a dose of 30 t ha^{-1}, 6 – NPK mineral fertilizer + AFAM in a dose of 150 t ha^{-1}. The soil samples were analysed in the whole soil profile after harvest of spring barley.

The ash-fly ash mixture in the basic dose of 3 t ha^{-1} positively influenced several soil parameters. Statistically significant increase of both pH_{KCl} and pH_{H_20} as well as the con-

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tent of available calcium were noted. The total carbon content (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K also increased but not significantly. Sorption capacity (CEC)did not change. The sum of exchangeable base cations (EBC), base saturation (BS), conductivity (EC) and content of N_{in} and Mg were not significantly influenced. The AFAM with NPK combination significantly decreased the bulk density of soil (BD). Addition of AFAM to mineral NPK fertilizers at the rates of 3, 30 and 150 t ha^{-1}, respectively, influenced positively the content of C_{ox}, C_{HS}, C_{HA}, Mg and the values of CEC, EBC, BS, BD, pH_{H2O} and pH_{KCl}. This addition had a negative effect ob just two parameters: EC and content of mineral nitrogen. Application of ash-fly ash mixture alone or with NPK fertilizers improved soil parameters, which enhanced the soil productivity and its resistance against depressed fertility caused by unidirectional industrial nutrition.

Key words: ash-fly ash mixture, soil fertility, total carbon, humic acids, bulk density of soil.

WPŁYW STOSOWANIA POPIOŁÓW, POPIOŁÓW LOTNYCH I ICH MIESZANEK NA ŻYZNOŚĆ GLEBY

Abstrakt

Aplikacja popiołów, popiołów lotnych i ich mieszanek w glebach Słowacji nie jest dozwolona przez prawo, mimo że niektóre państwa pozwalają na takie wykorzystanie. Można przypuszczać, że jest to spowodowane głównie niestabilną i często wysoką zawartością metali ciężkich oraz związków promieniotwórczych w glebie. Poszczególne popioły i popioły lotne znacznie różnią się powyższymi parametrami, z tego powodu konieczna jest indywidualna ocena wykorzystania popiołów w Słowacji. Korzystnego wpływu popiołów i popiołów lotnych na rośliny nie można pominąć w przypadku surowców nie stwarzających zagrożenia związanego ze zwiększoną ilością metali ciężkich i związków radioaktywnych. Celem eksperymentu było określenie wpływu mieszanki popiołu z popiołem lotnym (AFAM) na niektóre parametry glebowe oraz sprecyzowanie poglądów na wykorzystanie popiołów i popiołów lotnych w rolnictwie.

Eksperyment przeprowadzono w wegetacyjnej klatce znajdującej się na terenie Słowackiego Uniwersytetu Rolniczego w Nitrze, w 30 kg pojemnikach z 24 kg antropogenicznej gleby, która powstała po zmieszaniu 2 części brunatno-modalnej gleby i 1 części piasku krzemionkowego. Do całego profilu glebowego powyższych pojemników aplikowano mieszankę popiołów i popiołów lotnych lub nawozów NPK w 4 powtórzeniach. Eksperyment miał 6 wariantów (0, $AFAM_1$, NPK, NPK+ $AFAM_1$, NPK+ $AFAM_2$, NPK+ $AFAM_3$): 1 – wariant kontrolny, 2 – mieszanka popiołu i popiołu lotnego w ilości 3 t ha^{-1}, 3 – nawozy sztuczne NPK, 4 – nawozy NPK + AFAM w ilości 3 t ha^{-1}, 5 – nawozy NPK + AFAM w ilości 30 t ha^{-1}, 6 – nawozy NPK + AFAM w ilości 150 t ha^{-1}.

Mieszanka popiołu i popiołu lotnego (AFAM) stosowana w ilości 3 t ha^{-1} miała pozytywny wpływ na kilka parametrów glebowych. Istotnie statystycznie zwiększyła wartość pH_{KCl}, pH_{H2O} i dostępnych zasobów Ca. W przypadku zawartości węgla całkowitego (C_{ox}), węgla substancji humusowych (C_{HS}), węgla kwasów huminowych (C_{HA}), kwasów fulvia (C_{FA}) i dostępnego K reakcja na wzrost była niejednoznaczna. Gęstość objętościowa gleby (BD) się zmniejszyła. Absorpcja (CEC) nie uległa zmianie. Statystycznie nieistotny, ale negatywny wpływ miała na ilość kationów podstawowych (EBC), stopień nasycenia kationami bazowymi (BS), przewodność (EC), zawartość N_{an} i Mg.

Dodanie AFAM do nawozów NPK w dawkach 3, 30 i 150 t ha^{-1} miało pozytywny wpływ na ilości C_{ox}, C_{HS}, C_{HA} i Mg, na wartości CEC, EBC, BS, pH_{KCl} i pH_{H_2O}, BD gleby. Negatywnie wpłynęło tylko na EC i zawartość N_{in}. Wykorzystanie mieszanki popiołu i popiołów lotnych oraz mieszanki w połączeniu z nawozami NPK poprawiło głównie te parametry gleby, które zwiększają jej wydajność, odporność na spadek plonów spowodowany jednostronnym sztucznym nawożeniem roślin.

Słowa kluczowe: mieszanka popiołów i popiołów lotnych, żyzność gleby, węgiel całkowity, kwasy huminowe, gęstość gleby.

INTRODUCTION

Thermal power stations produce approximately 500 million tons of ash and 100 million tons of fly ash annually all over the world. About 15-20% of ash and about 20-40% of fly ash are recycled (WRIGHT et al. 1998, KIKUCHI 1999). In Slovakia, however, only about 10-15% of ash and fly ash are used again and with their annual production of about 1.1-1.2 million tons it means a growing pressure for new storage space, which should be used more appropriately and ecologically. Therefore, Slovak researchers are looking for possibilities of using ashes, fly ashes and their mixtures in the building industry, mining and metallurgical industry and automobile industry (FLOREKOVÁ et al. 2001). It seems that agriculture could be another possible recipient of these substances but the Slovak law does not allow it. The negative approach to ashes, fly ashes and their mixture in Slovakia remains in contrast to the substantial international experience of using these substances in agriculture (AMRHEIN et al. 1995, LIN et al. 1998, KIKUCHI 1999, MATSI, KERAMIDAS 1999, JALA, GOYAL 2006, JEZIERSKA-TYS, FRĄC 2008, ANTONKIEWICZ 2010). The cause of negative attitudes to using ashes and fly ashes in Slovakia has never been explicitly stated but apparently it is so due to their unstable nature, frequently high content of heavy metals, high salinity and reduction of solubility of some nutrients by their high pH values as well as the residual radioactivity (AITKEN et al. 1984, KARANGELOS et al. 2004, BASU et al. 2009). It is therefore inevitable to classify specific ashes and fly ashes individually in Slovakia, on the basis of exactly defined chemical and radiological criteria (parameters) and agrochemical and environmental influence on soil and plants. It is wrong to ignore considerable qualitative differences among particular ashes and fly ashes with respect to their positive influence on crops and soil.

The aim of this experiment has been to find out the effect of AFAM (in which the content of heavy metals and also residual radioactivity were lower than the limits set by the Slovak law, KOVÁČIK, MIŠÍK 2008) on the soil yielding parameters, and to clarify opinions on using ashes and fly ashes in agriculture.

MATERIAL AND METHODS

A pot experiment was carried out in 2005 and 2006 in a vegetation cage located in the premises of the SAU in Nitra (48°18´ N, 18°05´ E). The experimental pots were filled with a mixture of 16 kg of soil (Haplic Luvisol) and 8 kg of siliceous sand; the agrochemical characteristics of the soil material are presented in Table 1. The chemical parameters of N-NH_4 were determined by Nessler's colorimetric method; N-NO_3 was assayed by the colorimetric method with phenol – 2,4 disulphonic acid and N_{in} was calculated as the sum N-NH_4 + N-NO_3. The content of available P, K, Ca and Mg was determined by Mehlich III extraction procedure (Mehlich 1984). The content of P was determined by the colorimetric method while K and Ca were measured by flame photometry; the content of Mg was assessed by atomic absorption spectrophotometry and pH_{H_20} and pH_{KCl} (in solution of 1.0 mol KCl dm^{-3}) were determined potentiometrically. The total N content (N_t) was determined according to Kjeldahl's method (Bremner 1960); total carbon content (C_{ox}) was evaluated spectrophotometrically after oxidation (Ťjurin 1966); exchangeable base cations (EBC), cation exchange capacity (CEC) and base of saturation (BS) were tested according to Kappen's method (Myślińska 1998). Soil electrical conductivity (EC) was also determined (Corwin, Lesch 2005).

The hygienic, toxicological and agrochemical parameters of the material are presented in Tables 2 and 3. The detected metal content was lower than the permitted limits for soil additives used in arable soil. The total forms of metals in the soil were determined by the means of an AAS Pye Unicam (mineralization in HF + $HClO_4$).

In the ash-fly ash mixture applied, the presence of radioactive substances was analyzed by semiconductor gamma-spectrometry using a high purity germanium detector (Canberra). The whole assembly of a detector, modular spectrometer (EG&G Ortec, Canberra) and software (GammaVision + modified modules of Nuclear Data software) passed relevant comparison tests organized by the International Atomic Energy Agency. No activity (MDA < 0.29 Bq kg^{-1}) of environmentally important man-made radionuclides (^{137}Cs, ^{134}Cs, ^{60}Co) was found in the ash-fly ash substrate. The levels of natural U and Ra in ash-fly ash mixture exceeded the levels in soil by a factor ≤ 2.0, but were more than 4.1-fold lower than the most active natural isotope ^{40}K found (382 ± 31) Bq kg^{-1}. Those levels of radioactivity are well in the range of the usual variability of natural isotopes in soils (Mazzilli et al. 2000) and therefore no build-up of radioactivity in soil and plants could be produced by introducing the ash-fly ash mixture to soil at the suggested application rate.

Into each pot, 100 spring barley grains (Express c.v.) was seeded. After germination, the seedlings was thinned to 75 plants per pot. Moisture of the soil in the pots was maintained at 60% of full water capacity by regular irrigation.

Table 1

Agrochemical characteristics of anthropogenic soil used in pot trial

Year	$N\text{-}NH_4$	$N\text{-}NO_3$	Ni_n	P	K	Ca	Mg	N_t	C_{ox} (%)	EBC	CEC	BS (%)	pH_{KCl}	EC ($mS\ cm^{-1}$)
	($mg\ kg^{-1}$)									($mmol\ kg^{-1}$)				
2005	12.48	0.24	12.72	41.3	242	1 310	250	1064	0.97	87.8	101.5	86.5	5.78	0.040
2006	9.80	2.99	12.80	18.9	182	1 643	303	1064	0.99	90.6	106.4	85.1	5.57	0.025

Table 2

The heavy metals content in ash-fly ash mixture used in the pot trial

As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
($mg\ kg^{-1}$)										
< 0.04	< 1	34.0	34.3	28	7 025	0.366	960	27	< 5	26.8
10.0*	2.0*	-	100.0*	-	-	1.0*	-	50.0*	50.0*	-

*Limited values of heavy metals for soil additives (according to Slovak Law Act No 577/2005).

Table 3

Agrochemical characteristics of ash-fly ash mixture used in the pot trial

$N\text{-}NO_3$	$N\text{-}NH_4$	N_{in}	P	K	Ca	Mg	pH_{KCl}	pH_{H_2O}	EC	$CaCO_3$	C_{ox}
($mg\ kg^{-1}$)									($mS\ cm^{-1}$)	(%)	(%)
1.1	2.6	3.7	12	109	3400	1450	12.35	12.12	0.05	1.51	4.43

The experiment consisted of 6 treatments (0, $AFAM_1$, NPK, NPK+ $AFAM_1$, NPK+ $AFAM_2$, NPK+ $AFAM_3$). Each treatment was conducted in four replications. The basic rate of ash-fly ash mixture ($AFAM_1$) was applied in treatments 2 and 4 and represented 0.1% of the total weight of soil in a pot (24 g pot^{-1}, i.e. 3 t ha^{-1}). The rate of ash-fly ash mixture applied in treatment 5 ($AFAM_2$) was 10–fold (240 g pot^{-1}, that is 30 t ha^{-1}) and in treatment 6 ($AFAM_3$) 50-fold (1200 g pot^{-1}, that is 150 t ha^{-1}) higher than the basic rate.

The rates of NPK nutrients were calculated on the basis of the content of N_{in} and available P and K in soil and the plant requirement for these nutrients to achieve planned yield. Nitrogen was applied in the form of DAM-390 fertilizer; P was added in the form of single superphosphate and potassium was introduced to soil as 60% KCl.

Spring barley was harvested at the growth stage of DC 91. After harvest, a soil sample of the whole profile from the each pot was taken and the following parameters were determined: C_{ox} – total carbon, C_{HS} – carbon of humic substances, C_{HA} – carbon of humic acids, C_{FA} – carbon of fulvic acids, soil reaction – pH_{KCl}, BD – bulk density. The parameters C_{HS}, C_{HA} and C_{FA} were detected according to the methods described by KONONOVA and BELTCHIKOVA (SHVIDENKO et al. 1997). The results were evaluated by analysis of variance, using Statgraphics, version 5 software.

RESULTS AND DISCUSSION

Application of ash-fly ash mixture (AFAM, treatment 2) at the rate of 3 t ha^{-1} positively influenced several pedological and agrochemical soil characteristics (Tables 4 and 5). The application caused statistically significant increase of both pH_{KCl} and pH_{H_2O} as well as the content of available calcium. Owing to this attribute, KOVÁČIK and SLAMKA (2008) recommend to use shes and fly ashes for adjustment of pH in acid soils. The only exception is acid ashes, which lost their alkaline elements in the process of weathering and leaching (DOSSKEY, ADRIANO 1993).

After application of AFAM, the content of total carbon (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K increased. However, this increase was not statistically significant. On the other hand, significant increase of carbon content was reported by CERVELLI et al. (1987) and SAJWAN et al. (2003).

After AFAM application, the soil bulk density (BD) decreased, which agrees with the findings of PERKINS and VANN (1997) but is in contrast to the report by CHANG et al. (1977). Sorption capacity (SC) was nearly unchanged.

The base saturation (BS), exchangeable base cations (EBC), conductivity (EC) and content of N_{in} and Mg were negatively affected, but the influence was negligible and statistically insignificant (Tables 4, 5).

Table 4

The effect of ash fly-ash mixture on some agrochemical parameters

Treatment		pH_{KCl}	pH_{H_2O}	EC	Nin	P	K	Ca	Mg
No.	designation			(mS cm^{-1})	(mg kg^{-1})				
1	0	5.63^{a}	6.80^{a}	0.06^{a}	12.55^{a}	52.5^{b}	210^{ab}	900^{a}	262^{ab}
2	$AFAM_1$	5.93^{b}	7.00^{b}	0.07^{a}	11.15^{a}	32.2^{a}	220^{b}	$1\,401^{c}$	253^{a}
3	NPK	5.60^{a}	6.71^{a}	0.14^{b}	38.83^{d}	61.5^{bc}	200^{a}	$1\,310^{c}$	241^{a}
4	NPK+$AFAM_1$	5.92^{b}	6.81^{a}	0.14^{b}	34.48^{c}	57.6^{bc}	200^{a}	$1\,173^{b}$	241^{a}
5	NPK+$AFAM_2$	6.25^{c}	7.08^{b}	0.17^{c}	27.48^{b}	65.7^{c}	218^{ab}	$1\,401^{c}$	292^{b}
6	NPK+$AFAM_3$	6.90d	7.40^{c}	0.24^{d}	25.39^{b}	91.3^{d}	255^{c}	$1\,538^{d}$	443^{c}
$LSD_{0.05}$		0.271	0.103	0.025	3.503	10.85	20.0	101.6	38.5
$LSD_{0.01}$		0.366	0.139	0.033	6.365	14.58	26.9	139.7	46.5

LSD – limit of significant difference at the level = 0.05 and = 0.01.

The degree of soil salinity and deterioration of the BS and EBC parameters were considerably lower after an application of 3 t ha^{-1} AFAM than after a standard rate of mineral NPK fertilizers. Application of NPK fertilizers (treat.3) deteriorated most of the examined pedological and agrochemical parameters (Cox, C_{HS}, C_{HA}, C_{FA}, ratio of C_{HA}:C_{FA}, CEC, EBC, BS, pH_{KCl}, pH_{H_2O}, EC) not only in comparison with the unfertilized treatment 1, but also with treatment 2 ($AFAM_1$). In contrast, addition of AFAM at the rates of 3, 30 and 150 t ha^{-1}, respectively to mineral NPK fertilizers (treatments 4, 5, 6 versus treatment 3) not only mitigated the demonstrated negative effect of NPK fertilizers on the majority of the parameters, but many affected positively (C_{ox}, C_{HS}, C_{HA}, ratio of C_{HA}:C_{HF}, CEC, EBC, BS, pH_{H_2O}, pH_{KCl}, BD). The gradually increasing rates of AFAM added to NPK fertilizers increased the values of the above parameters, except soil bulk density, which decreased with the increasing rates of AFAM, but this was considered as a positive development (Table 5).

When 150 t ha^{-1} of AFAM was applied (treatment 6), the ratio of C_{HA}:C_{FA} was lowered and the conductivity increased significantly. From this viewpoint, this rate could be considered risky but only if such rates of AFAM are applied in short time intervals. The recorded conductivity of 0.24 mS cm^{-1} (treatment 6) was much below 2 mS cm^{-1}, which classifies soil as slightly salinated. Increased EC values after application of fly-ash rates over 40 t ha^{-1} are cited by several authors (Clark et al. 1999, Matsi, Keramidas 1999). Our findings prove that it is unreasonable to perceive the AFAM rate used in the experiment as "material hazardously increasing the content of salts in soil".

Table 5

The effect of ash fly-ash mixture on some pedological parameters

Treatment		Cox	CHS	CHA	CFA	C : N	$C_{HA} : C_{FA}$	CEC	EBC	BS	BD
No.	designation	(%)						(mmol kg^{-1})		(%)	(g cm^{-3})
1	0	0.954^{a}	0.369^{a}	0.164^{ab}	0.205^{a}	12.4	0.800	120.3^{ab}	109.6^{a}	91.16	1.40^{b}
2	$AFAM_1$	1.099^{a}	0.392^{a}	0.170^{bc}	0.222^{a}	14.1	0.766	119.8^{ab}	107.1^{a}	89.42	1.31^{ab}
3	NPK	0.893^{a}	0.333^{a}	0.137^{a}	0.196^{a}	11.4	0.699	115.0^{a}	104.0^{a}	90.43	1.34^{ab}
4	NPK+$AFAM_1$	1.106^{a}	0.368^{a}	0.185^{cd}	0.183^{a}	14.5	1.011	117.0^{ab}	105.8^{a}	90.44	1.28^{a}
5	NPK+$AFAM_2$	1.348^{a}	0.419^{a}	0.209^{d}	0.210^{a}	15.7	0.995	128.7^{ab}	119.4^{ab}	92.80	1.26^{a}
6	NPK+$AFAM_3$	2.057^{b}	0.716^{b}	0.210^{d}	0.506^{b}	37.7	0.415	141.2^{b}	137.0^{b}	96.98	1.23^{a}
$LSD_{0.05}$		0.596	0.160	0.026	0.077			24.28	24.64		0.117
$LSD_{0.01}$		0.805	0.216	0.035	0.105			32.78	33.27		0.158

LSD – limit of significant difference at the level = 0.05 and = 0.01.

The C:N ratios fluctuated in the range from 11.4:1 to 37.7:1 in individual treatments. The lowest value of the ratio was calculated in the treatment with NPK fertilizers application, which is in accordance with the findings of Kováčik and Wisniowska-Kielian (2009), who stated that mineral fertilizers intensify the mineralization process, causing a decline in the carbon content in soil on but increasing the content of available nutrients. This effect of mineral fertilizers is evaluated positively by farmers. However, in the long run, intense mineralization of organic matter is negative for its maintenance in the soil (Šimanský et al. 2008).

The latest findings by Rasool et al. (2008) indicate that soils poor in organic matter, when treated with mineral fertilizers in proper rates, may be enriched in carbon released through more roots growing in that soil.

The highest C:N ratio was found in treatment 6, where – beside the application of mineral fertilizers that lowered the C:N ratio – AFAM at a rate of 150 t ha^{-1} was added. This indirectly confirms that ashes produce an inhibitory effect on microflora involved in the mineralization processes.

Application of AFAM in all the treatments and combinations (treatment 2 versus 1 and treatments 4, 5, 6 versus 3) caused reduction of the N_{in} level in soil. Increasing rates of AFAM proportionally decreased the N_{in} content in soil (Table 4). These findings verify the hypothesis on possible inhibition caused of AFAM on the mineralization microflora. Nearly the same conclusions were reached by Pathan et al. (2002).

CONCLUSIONS

The results show that AFAM applied 2 weeks before barley sowing at the rate of 3 t ha^{-1} positively influenced several soil parameters. The values of pH_{KCl}, pH_{H_2O} and the content of available Ca were significantly increased. The content of total carbon (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K also increased but not significantly. The soil bulk density (BD) decreased and the cation exchange capacity (CEC) showed no change. The following characteristics were not significantly influenced: exchangeable base cations (EBC), base saturation (BS), conductivity (EC) and the content of N_{in} and Mg.

Application of AFAM in all the treatments and combinations caused reduction of the N_{in} level in soil and N_{in} content decreased proportionally with the increasing rates of AFAM.

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EVALUATION OF TITANIUM CONTENT IN MUCOSA COVERING TWO-STAGE INTRAOSSEOUS IMPLANTS*

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Abstract

Widely used biomaterials, including titanium and its alloys, manifest a range of the physicochemical properties which determine the way they are exploited. According to the literature, titanium dental implants, considered biocompatible with the human body, under certain conditions, may cause inflammatory or allergic reactions.

The aim of the study has been to evaluate the content of titanium in the mucosa covering two-stage intraosseous implants of the Osteoplant-Hex® system. The content of titanium ions in the examined samples containing segments of mucosa collected from those dental implants was determined with an inductively-coupled plasma emission spectrometer VISTA-MPX produced by VARIAN ICP. A diverse titanium content in the mucosa adjoining the implants has been revealed during their healing period. The determined concentration of titanium ranged from 0.00 to 122.59 μg g^{-1}. As the conducted research suggests, such a wide range may result from differences in the implant location, sex and age of patients. Therefore, the authors tried to find a relationship between the results and those variables.

Key words: titanium, implants, allergy.

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OCENA ZAWARTOŚCI TYTANU W BŁONIE ŚLUZOWEJ POKRYWAJĄCEJ DWUETAPOWE WSZCZEPY ŚRÓDKOSTNE

Abstrakt

Szeroko stosowane współcześnie biomateriały, w tym tytan i jego stopy, wykazują wiele cech i właściwości fizykochemicznych, które determinują sposób ich wykorzystania. Jak wynika z piśmiennictwa, wszczepy tytanowe stosowane w stomatologii, uważane za biokompatybilne z ustrojem, mogą w określonych warunkach wywoływać reakcje zapalne lub alergiczne.

Celem pracy była ocena zawartości tytanu w błonie śluzowej pokrywającej dwuetapowe wszczepy śródkostne systemu Osteoplant-Hex®. Zawartość jonów tytanu w badanych próbkach zawierających wycinki błony śluzowej pobrane nad wszczepami stomatologicznymi oznaczono na spektrometrze emisyjnym z indukcyjnie sprzężoną plazmą VISTA-MPX firmy VARIAN ICP. Wykazano zróżnicowaną zawartość tytanu w błonie śluzowej kontaktującej się z implantami w okresie ich wgajania. Oznaczono stężenia tytanu od 0,0 do 122,59 μg g^{-1}. Jak wynika z badań, duża rozpiętość wyników może być uzależniona od lokalizacji wszczepu, płci pacjentów, a także wieku, i dlatego podjęto próbę powiązania uzyskanych wyników z kilkoma potencjalnymi parametrami.

Słowa klucze: tytan, implanty, alergia.

INTRODUCTION

Titanium, a light metal of high mechanical resilience, resistant to corrosion, is commonly considered to be well-tolerated in the tissue environment. Thus it fulfills the requirements for modern metallic biomaterials applied in medicine. Owing to good osteointegration and biotolerance, titanium and its alloys are used to produce elements applied for example in dentistry and other branches of medicine (ORLICKI, KŁAPTOCZ 2003, SINGH, DAHOTRE 2007, RUSINEK et al. 2008).

To reconstruct teeth losses, present-day prosthetics more and more frequently uses titanium intraosseous implants as denture bases. Similarly to other countries, the number of implants in Poland increases proportionally to the society's affluence and the rise in the number of dentists performing implantation procedures.

In the last 40 years, descriptions of cases suggesting side effects of the use of implants, including those made of pure titanium, have appeared (UNGERSBÖCK et al. 1994, MÜLLER, THON 2006, STEJSKAL et al. 2006, PRYLIŃSKI, LIMANOWSKA-SHAW 2007, TOMIZAWA, HANAWA 2007, RUSINEK et al. 2008). They have usually comprised reactions such as metalosis or fistulas, often in the form of eczema, rash or itch surrounding the implant, thus suggesting allergy (SINGH, DAHOTRE 2007, RUSINEK et al. 2008). Most of these phenomena have been observed in the case of orthopaedic implants, and have resulted from contact with nickel, chromium and cobalt allergens, but also titanium ones, yet less frequently. Allergic reactions to metal dentures take form of bone or marrow inflammation without any changes to the skin (ŚPIEWAK, BREWCZYŃSKI 1993, POHLER 2000, MÜLLER, THON 2006, SINGH, DAHOTRE 2007). The problem also concerns, although to a lesser extent, titanium intraosseous dental implants. In these cases, allergic symptoms have caused unpleasant, long-term effects such as skin changes, receding after the removal of the allergen; however, it is believed that the reaction may sometimes be so serious that it causes complications leading even to the implant rejection (MÜLLER, THON 2006, ŚPIEWAK 2007). A strong allergic reaction in the form of eczema has been observed in a toothless patient with very good general medical examination results after the insertion of 2 dental implants. The changes on her skin and mucosa have totally vanished shortly after extraction of the titanium implants (MÜLLER, THON 2006, EGUSA et al. 2008). The suggested oversensitivity to titanium may turn out to be a reaction of the organism to trace quantities of other metals such as nickel, cobalt or palladium since implants declared to be purely titanium quite often contain minor additives (STEJSKAL et al. 1999, THON et al. 2006). The mechanism of allergic reactions related to titanium has not been scientifically proven so far (LALOR et al. 1990, RUSINEK et al. 2008) for the implanted material may be subject to various physicochemical alterations (e.g. under the influence of the environment) and, therefore, the reaction to it may also differ.

Analysing the allergy to titanium and its compounds, it is considered that the released particles/ions as haptenes merge with tissue proteins and may induce an IgE-dependent allergy. This phenomenon has not, however, been completely confirmed in literature thus far (FRIEDMANN 2006). It is thought that titanium may cause allergy in a similar way to other metals through T-lymphocyte-specific sensitivity evoking oversensitivity type IV.

The aim of the study has been to evaluate the content of titanium in the mucosa covering two-stage intraosseous implants Osteoplant-Hex® and to try to relate the release of this element to tissues to some selected factors. Attention has been paid to the purposefulness of the abovementioned study considering the potentially detrimental influence of titanium on the human organism in certain clinical situations. Most of the experimental studies into implants have been conducted on animal material. There is, nevertheless, little experimental research connected to the reactions of human tissues to titanium implants in literature.

MATERIAL AND METHODS

The research material included segments of mucosa covering two-stage screw intraosseous titanium implants Osteoplant-Hex®. The implantation procedures were carried out with the use of the closed healing method. After 4-6 months, i.e. the osteointegration period, a procedure of implant exposure was conducted through excision of the mucosa covering the implant bearing surface in order to place the healing screw in the implant. The exposure was performed with a scalpel to exclude the possibility of metal particles getting from mechanical damages into the research material. Prior to implantation, a segment of the mucosa from the area of the planned implant bed was collected. This fragment as well as the segments of mucosa taken from the alveolar ridge during other surgical procedures constituted a control group and came from patients who did not have metal restorations in their oral cavities.

The phases of the clinical studies were conducted with the consent of the Bioethics Commission of Karol Marcinkowski University of Medical Sciences in Poznan.

The content of titanium ions in the investigated samples containing the segments of mucosa from above the dental implants was determined, after previous mineralization in a microwave oven MDS – 2000, on an inductively-coupled plasma emission spectrometer VISTA-MPX produced by VARIAN ICP. The mineralization was conducted in Teflon bombs in a mixture of 65% HNO_3 + H_2O_2 (5:2), at 60 psi and a power of 40. After the mineralization, the samples were quantitatively transferred into 10ml flasks, filled up with redistilled water and then, the content of titanium was determined.

The parameters for ICP-OES determination have been compiled in Table 1.

The results of the studies were analysed statistically. Due to the fact that the variable distributions did not fulfil normality conditions, nonparametric tests were applied as they are not very sensitive to outlying observations. The Mann-Withney test was used to compare two groups, e.g. women

Table 1

The operating parameters for determinations of ICP-OES

Method parameters	Value
RF, power (kW)	1.20
Plasma flow (L min^{-1})	15.0
Nebulizer flow (L min^{-1})	0.9
Viewing height (mm)	12
Pump rate	15
Rinse time (s)	10
Auxiliary flow (L min^{-1})	1.50
Replicate read time (s)	5.0
Instrument stabilization (s)	15
Sample uptake delay (s)	30
Element – emission line (nm)	Ti - 336122

and men, maxilla-mandible. The Kruskal-Wallis test was applied to compare a larger number of groups. Spearman's rank correlation coefficient was used to assess the relationship between variables (dependence on age in the investigated group).

RESULTS AND DISCUSSION

The results have been analysed in order to evaluate the accumulation of titanium in the mucosa covering two-stage intraosseous implants during their healing period and to determine the relation between the results obtained and such parameters as the implant location (maxilla, mandible), sex and age of the patients. The comparison of the results obtained from individual patients who had had a larger number of implants inserted enabled us to identify intra-individual dependencies.

The results of titanium determination for the study group (24 samples) and the control group (21 samples) have been compared in Table 2 and Figure 1. The results of the implanted group indicate that the content of titanium in soft tissues is over 10 times greater than in the control group, which may prove translocation of titanium ions from the implant to the tissues of the human organism.

Table 2

Average Ti results of the test and control groups

Parameters	Average content of Ti ($\mu g\ g^{-1}$)
Osteoplant-Hex®	9.765
Control group	0.818

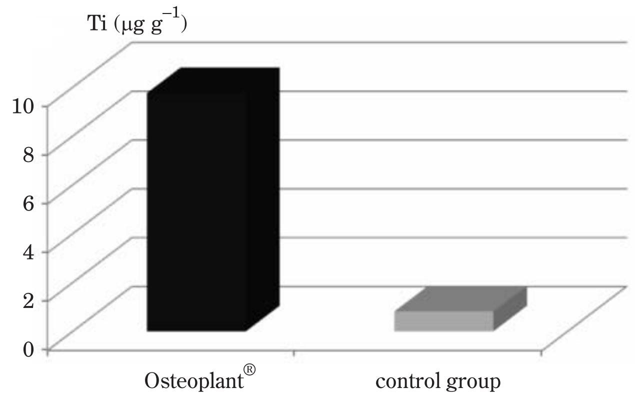

Fig. 1. Graphic presentation of the average results of the titanium content for the test and control groups

Table 3

Characteristics of the research material and results for the Osteoplant system

Patients	Sex		Average age	Implant number in a given location		Average result for group Ti ($\mu g\ g^{-1}$)
	F	M		maxilla	mandible	
24	14	10	54.166	17	35	9.765

Table 4

Results for different implant locations in patients with more than 2 implants

Patient's numbers	Maxilla			Mandible		
	1-3	4-7	average	1-3	4-7	average
1					22.4 21.6	22.00
2		6.6 12.9 28.9 20.5	17.23			
3		0.4 0.4 48.1*	16.3			
4					20.8 12.7 5.0	12.83
5					BDL 3.6	3.6
6				9.7 2.0 8.9 13.5		8.53
7	1.0 122.59	19.5	106.20		1.5 6.1 1.4	3.00
8				1.02	5.91 0.29 0.68 0.49	1.62
9				4.38 1.34	3.02 6.91 1.77	19.19
10					0.44 1.26	0.85
11					6.27 0.47 BDL	2.25
			46.58			8.21

Some of the patients participating in the study had more than two intraosseous implants inserted. Different results were obtained for the samples taken from one patient, both from distant and close locations of the implants. The results presented in Table 4 may prove intra-individual variation and a predisposition to ion migration or they may stem from heterogeneity of the inserted titanium implants.

The segments of mucosa which were subject to the study on the titanium content had been collected from patients at different age. They were divided into two representative groups: a younger one – up to the age of 60, and an older one – over the age of 60. The results of the content of titanium in the mucosa depending on the patient's age have been compared in Table 5 and Figure 2. They suggest no interdependence between the titanium ions release and age, neither among men nor women. Nonetheless, it has been noticed that the titanium content was several dozen percent lower among men than among women in both age groups. Considering the small number of the examined patients, it is difficult to draw any unambiguous conclusions, though.

Table 5

Average values obtained for groups of patients up to and over the age of 60

Age group	Sex	Quantity	Ti values		Average Ti value
			min	max	
Up to the age of 60	F	9	BDL	122.59	10.49
	M	5	0.2	20.8	4.45
Over the age of 60	F	5	BDL	48.1	10.24
	M	5	0.44	22.4	7.84

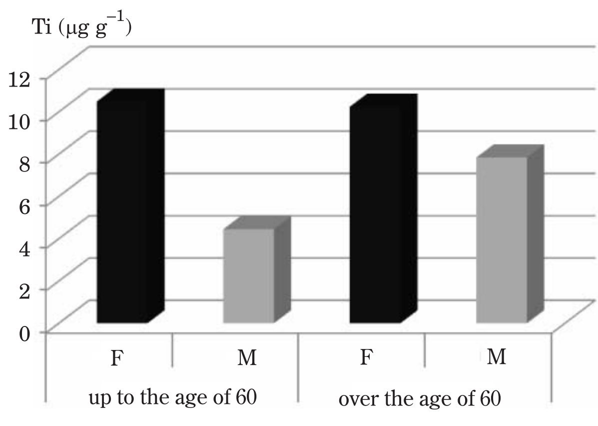

Fig. 2. Graphic presentation of the titanium content in mucosa depending on patients' age

Spearman's test suggests no correlation between age and the results obtained from the examined groups. The correlation coefficient was equal 0.003, while the relevance coefficient was close to 1.

The dependence of the results obtained on the patients' sex was another analysed factor. Women prevailed among the examined people and had a total of 30 implants inserted. The comparison of the results of the titanium content in the mucosa depending on the patient's sex has been presented in Table 6 and Figure 3.

The analysis of the results obtained in the study enables us to conclude that in both groups of patients, i.e. those up to the age of 60 as well as those over the age of 60, the titanium content is lower in men.

On the basis of the Mann-Withney test, it may be stated that there is no significant statistical difference (P=0.05) between the examined groups of women and men.

Table 6

Results for the examined groups of women and men

Sex	Number of patients	Average age	Number of implants	Average result for group ($\mu g\ g^{-1}$)
F	14	49.45	30	10.40
M	10	54.36	22	6.14

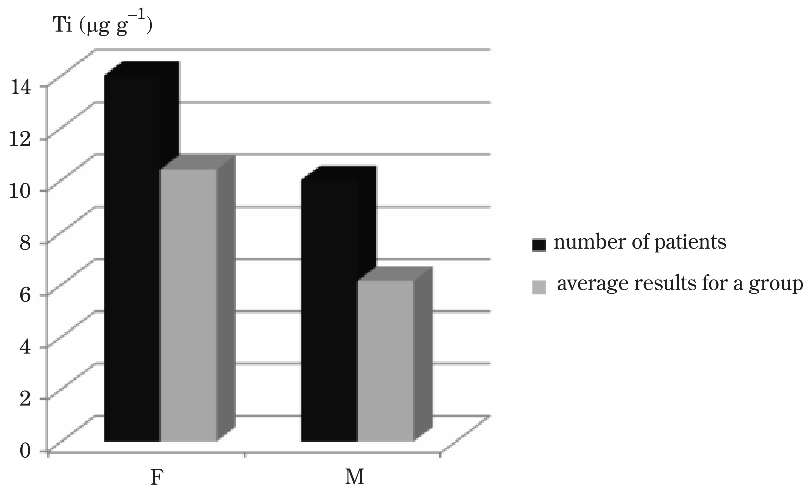

Figure 3. Graphic presentation of the titanium content in mucosa depending on patients' gender

CONCLUSIONS

1. Ions of titanium were found to migrate into the soft tissues surrounding Osteoplant-Hex dental intraosseous implants despite the biocompatibility of that metal.

2. No statistically significant correlation was observed between the amount of titanium ions released into the soft tissues and such factors as the mandibular or maxillary location of the implants, the gender or age of the patients.

3. The presence of titanium ions in the soft tissues did not cause any clinically recognizable changes in the oral cavity over a period of 4 to 6 months.

4. It is possible that the use of titanium intraosseous implants by allergic patients may lead to a negative reaction of the tissues of the masticatory organ due to the migration of various ions.

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EFFECT OF BIOELEMENTS (N, K, Mg) AND LONG-TERM STORAGE OF POTATO TUBERS ON QUANTITATIVE AND QUALITATIVE LOSSES PART II. CONTENT OF DRY MATTER AND STARCH

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Abstract

One of the top objectives of the table and food processing potato production is good tuber quality. The fact that potatoes are grown for a number of different uses makes the quality requirements high, yet also varied, both in terms of morphological traits and the chemical composition. Throughout the production cycle, potato storage is the most difficult stage of maintaining good quality of tubers. During long storage, tubers are affected by processes leading to quantitative and qualitative changes. The present three-year field experiment (2003-2005) investigated the effect of varied mineral fertilisation (N, K and Mg against a fixed P dose) applied over the plant vegetation period and the influence of storage (3 and 6 months) on the content of dry matter and starch in tubers of mid-early potato cultivars: Bila and Triada. The samples were stored in a storage chamber for 3 and 6 months (temperature +4°C, relative humidity 95%). The content of dry matter and starch was significantly affected by both the fertilisation and the storage time. With increasing N, K, Mg doses, a significant increase in the content of dry matter appeared, as compared with the control, and its highest content was reported for the fertilisation with 100 kg of nitrogen (3.5% increase), 80 kg of potassium (7.7% increase) and 100 kg of magnesium per hectare (6.2% increase). However, as for the content of starch, the doses of 100 kg of nitrogen, 160 kg of potassium and 100 kg of magnesium per hectare turned out to be the most favourable. The losses of dry matter and starch in potato tubers calculated from the balance were the highest after 6 months of storage and accounted for 8.1 and 15.4% for the magnesium experiment, 6.6 and 10.1% for the nitrogen experiment, 6.7 and 7.9% for the potassium experiment, respectively.

Key words: potato tuber, N, K, Mg fertilisation, storage, qualitative losses.

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WPŁYW BIOPIERWIASTKÓW (N, K, Mg) ORAZ DŁUGOTRWAŁEGO PRZECHOWYWANIA BULW ZIEMNIAKA NA STRATY ILOŚCIOWE JAKOŚCIOWE Cz. II. ZAWARTOŚĆ SUCHEJ MASY I SKROBI

Abstract

Jednym z nadrzędnych celów w produkcji ziemniaka jadalnego i do przetwórstwa spożywczego jest dobra jakość bulw. Wielokierunkowość użytkowania ziemniaka powoduje, że wymagania co do jego jakości są wysokie, ale też i różne, zarówno pod względem cech morfologicznych, jak i składu chemicznego. W całym cyklu produkcyjnym przechowywanie ziemniaków jest najtrudniejszym etapem utrzymania dobrej jakości bulw, ponieważ w okresie długotrwałego składowania w bulwach zachodzą procesy prowadzące do zmian ilościowych i jakościowych. W trzyletnim doświadczeniu polowym (2003-2005) badano wpływ zastosowanego w okresie wegetacji roślin zróżnicowanego nawożenia mineralnego (N, K i Mg na tle stałej dawki P) oraz przechowywania (3 i 6 miesięcy) na kształtowanie się zawartości suchej masy i skrobi w bulwach wybranych odmian ziemniaka. Do badań wybrano średnio wczesne odmiany Bila i Triada. Próby przechowywano w komorze przechowalniczej przez 3 i 6 miesięcy (temp. +4°C, wilgotność względna powietrza 95%). Na zawartość suchej masy i skrobi istotny wpływ miało zarówno zastosowane nawożenia, jak i czas składowania. Pod wpływem wzrastających dawek N, K, Mg następował istotny wzrost zawartości suchej masy w stosunku do obiektu kontrolnego, a najwyższą jej zawartość uzyskano po zastosowaniu nawożenia w ilości 100 kg azotu – wzrost o 3,5%, 80 kg potasu – wzrost o 7,7% i 100 kg magnezu – wzrost o 6,2% na 1 ha. W przypadku zawartości skrobi najkorzystniejsze okazały się dawki 100 kg azotu, 160 kg potasu i 100 kg magnezu na 1 ha. Straty suchej masy i skrobi w bulwach ziemniaka wyliczone z bilansu były najwyższe po 6 miesiącach przechowywania i wynosiły odpowiednio 8,1 i 15,4% w doświadczeniu z magnezem, 6,6 i 10,1% w doświadczeniu z azotem, 6,7 i 7,9% w doświadczeniu z potasem.

Słowa kluczowe: bulwa ziemniaka, nawożenie N, K, Mg, przechowywanie, straty jakościowe.

INTRODUCTION

One of the top objectives of the table and food processing potato production is good tuber quality. As potatoes are grown for a number of different uses, the potato quality requirements are high and varied, both in terms of morphological traits and the chemical composition. From the total annual potato produce, about 95% is stored for 1 to 9 months (October through June) for a variety of use (Gąsiorowska 2000, Leszczyński 2000, Lisińska 2006, Sowa-Niedziałkowska 2004a). Considering the entire production cycle, potato storage is the most difficult stage of maintaining good tuber quality. Throughout long-term storage, tubers are affected by processes leading to quantitative and qualitative changes (Gąsiorowska 2000, Leszczyński 2000, Sobol 2005). The extent of those changes depends on a number of factors, such as cultivars, agrotechnical factors during the vegetation period as well as storage room conditions. The tuber quality after storage is also affected by the potato handling method when preparing for storage, i.e. eliminating the tubers which are diseased, damaged and covered with soil. Mature, healthy and mechanically intact tubers are the only ones which demonstrate an adequate applicability for long-term storage (CZERKO 2001, LESZCZYŃSKI 2000, SOWA-NIEDZIAŁKOWSKA 2002, ZGÓRSKA, SOWA-NIEDZIAŁKOWSKA 2005).

The aim of the present research has been to determine the effect of a varied mineral fertilisation (N, K, Mg) and the storage period length (3 and 6 months) on the dry weight losses and starch.

MATERIAL AND METHODS

The field and storage experiment design is given in Part One.

Immediately after harvest and storage the following were determined in potato tubers: the content of dry matter with the drying method and the content of starch polarimetrically with the Evers method (KREŁOWSKA-KUŁAS 1993). The samples were stored for the period of 3 and 6 months (temperature +4°C, relative humidity 95%). After storage the amount of losses of dry matter and starch were calculated from the balance, including real natural losses.

The 3-year research results were verified with statistical calculations using Sigma Stat software (SPSS Inc., Chicago, the U.S.), and applying Tukey's test to verify the significance of differences.

RESULTS AND DISCUSSION

Potato tubers for direct consumption and for processing should demonstrate adequate morphological, chemical and organoleptic characteristics. The chemical composition of tubers, affecting their quality, is mostly cultivar-specific, although it can be modified by the environment, both during the growth and storage (ZGÓRSKA, FRYDECKA- MAZURCZYK 1996, GĄSIOROWSKA 2000, EDWARDS et al. 2002, ZGÓRSKA, SOWA-NIEDZIAŁKOWSKA 2005, ZIMOCH-GUZOWSKA, FLIS 2006).

The present research showed that, in all the trials, the content of dry matter in tubers after harvest was significantly affected by the mineral fertiliser doses applied (Figures 1, 2, 3). With the increasing N, K, Mg doses, a significant increase in the content of dry matter was observed, as compared with the control; its highest increase was reported when applying 100 kg of nitrogen, 80 kg of potassium and 100 kg of magnesium, which coincides with the results by WSZELACZYŃSKA et al. (2007), where a significant increase in the content of dry matter in tubers occurred as a result of increasing MgO doses, and following an increase in the nitrogen dose from 60 to 120 kg ha^{-1}. Contrary results were reported by BOMBIK et al. (2007),

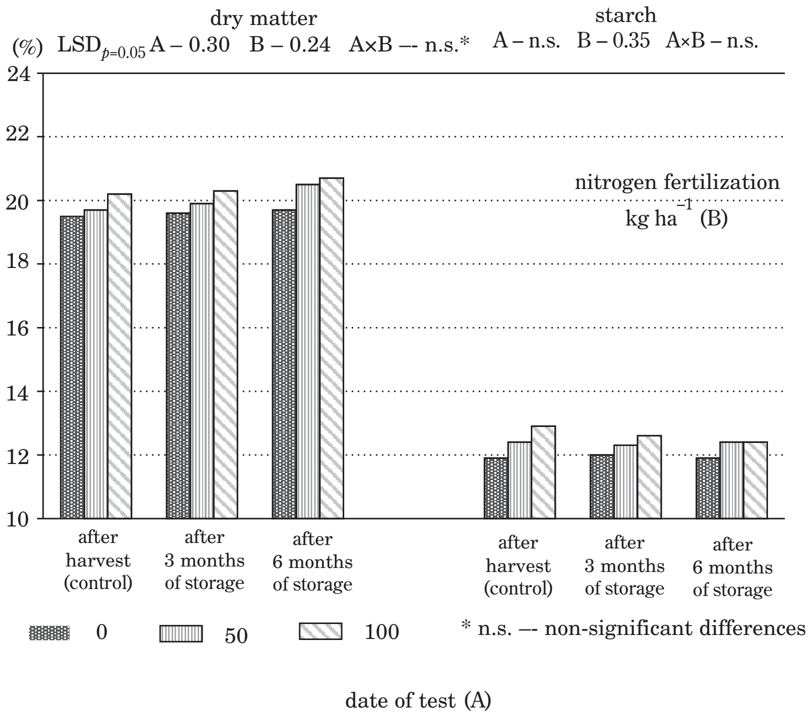

Fig. 1. The dry matter and starch content (%) in cv. Bila potato tubers depending on nitrogen fertilisation and date of test (means from 3 years)

who found out that increasing nitrogen fertilisation from 60 to 90 kg N ha^{-1} resulted in a significant decrease in the content of dry matter. According to BOMBIK et al. (2007), only very high nitrogen doses, the so-called over-fertilisation, can result in a decrease in the content of dry matter, which coincides with the results reported by WSZELACZYŃSKA et al. (2007), since a further increase in the nitrogen dose from 120 to 180 kg ha^{-1} decreased the content of dry matter. The response of cultivars with respect to the content of dry matter in tubers after storage depending on the N, K, Mg fertilisation applied is the same as after harvest.

Throughout storage, tubers are affected by biochemical processes connected with respiration and germination, causing changes in the content of dry matter and starch. The extent of changes is mostly cultivar-specific but also dependent on plant fertilisation over the vegetation period and on the storage length and temperature (BOMBIK et al. 2007, ZIMOCH-GUZOWSKA, FLIS 2006, WSZELACZYŃSKA et al. 2007). Our synthetic analysis of variance demonstrated that the content of dry matter in tubers obtained from the nitrogen and magnesium treatments (Figures 1 and 3) depended significantly on the storage duration, unlike in the potassium treatment samples (Figure 2). Interestingly, however, its significant increase, as compared with the initial

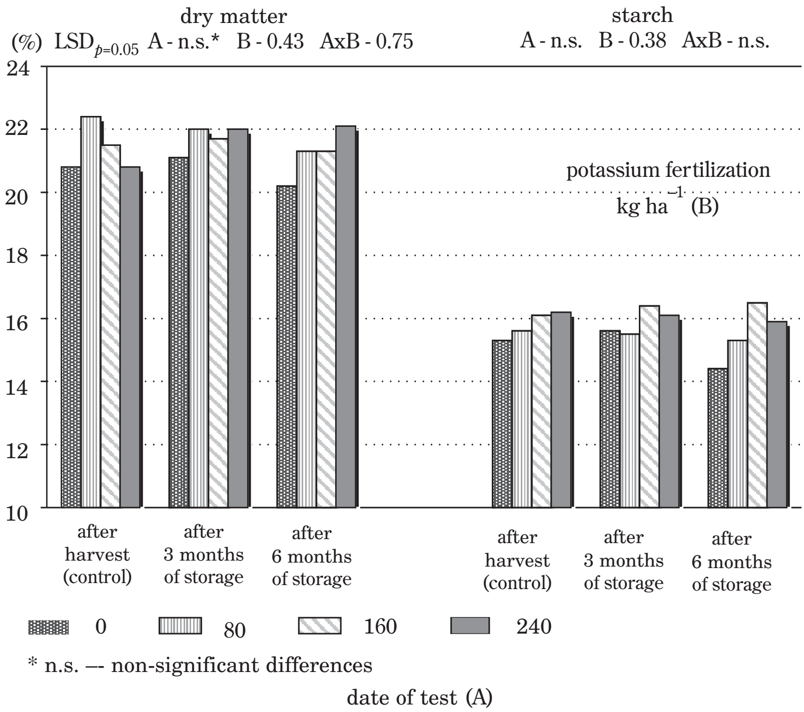

Fig. 2. The dry matter and starch content (%) in cv. Triada potato tubers depending on potassium fertilisation and date of test (means from 3 years)

period after harvest, occurred only after a longer storage (6 months) and it was, respectively, 2.5% for nitrogen experiments and 1.5% for magnesium experiments (mean for years and treatments). Different results were reported by WSZELACZYŃSKA (2002); in the experiment with varied magnesium fertilisation, a decrease in the content of dry matter in tubers was observed after 6 months of storage, as compared to its content after harvest. BOMBIK et al. (2007) report that after 6-month storage there was a significant decrease in the content of dry matter as compared with the control only in the tubers fertilised with higher nitrogen doses, namely (90 kg N ha^{-1}). Interestingly, the research reported by the above authors concerned other potato cultivars than those tested in the present research, that is table potato cultivars Mila and Irga and starch cultivar Ekra.

The most important dry matter component is starch. Its content in potato tubers depends mostly on the genetic factor so it is cultivar specific (GĄSIOROWSKA 2000, ZIMOCH-GUZOWSKA, FLIS 2006), but it is also affected by the storage temperature and time (GĄSIOROWSKA 2000, BOMBIK et al. 2007). The cultivars Bila and Triada, used in the present experiment, differed in the starch content. A higher content of starch was reported in Triada tubers (on average by 3%) – Figures 1, 2, 3. Higher quality tubers can be produced

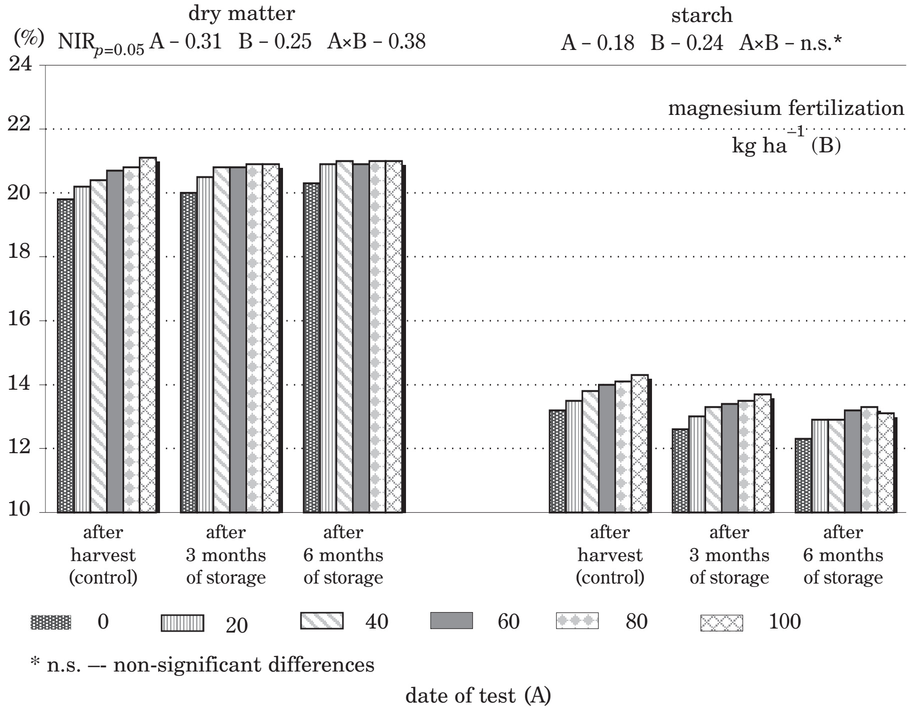

Fig. 3. The dry matter and starch content (%) in cv. Bila potato tubers, depending on magnesium fertilisation and date of test (means from 3 years)

when cultivar-specific differences are taken into account while growing potatoes (Bombik et al. 2007). In the present experiment, the content of starch depended on the storage time. After each storage period, the content of starch in tubers decreased, although its significant decrease was noted only for the magnesium treatment, both after 3 and 6 months. Bombik et al. (2007) report on a 7-month storage period resulting in a decrease in the content of starch in tubers, which occurred in a nitrogen fertilisation trial. Varied N, K and Mg fertilisation applied over the vegetation period, on the other hand, significantly increased the content of starch in tubers irrespective of the storage period. The doses of 100 kg of nitrogen, 160 kg of potassium and 100 kg of magnesium per hectare, after which the tubers contained 12.9, 16.1 and 14.3% of starch, respectively, turned out to be the most favourable. According to Gruczek et al. (2002), potassium fertilisation increases the content of starch if the doses do not exceed 160 to 180 kg K_2O ha^{-1}. The present results, as well as those reported by Rogozińska (2000), verify that conclusion. The most favourable increase in the content of starch, as compared with the control, was reported only up to the dose of 160 kg K_2O ha^{-1}, whereas any further increase in the dose, up to 240 kg K_2O ha^{-1}, did not enhance the outcome. Danilcenko et al. (2006), who fertilised potato with potassium sulphate, also reported an increase in the content of starch. In their experiment, the dose of 90 kg appeared to be the best, with a further increase in potassium fertilisation up to 150 kg causing a slight decrease in the content of starch.

The effect of nitrogen fertilisation on the content of starch in tubers was investigated by BOMBIK et al. (2007), who noticed that its content in tubers decreased as a result of increasing N doses. The relationship persisted after storage. In the present research, on the other hand, an opposite effect was observed: the higher the nitrogen dose, the higher the content of starch. The same relationship was detected after a long period of storage. JABŁOŃSKI (2002) and TRAWCZYŃSKI (2006) found that cultivars representing different earliness groups demonstrated a stable starch level, both when exposed to high and low nitrogen fertilisation. On the other hand, JABŁOŃSKI (2004), who investigated new cultivars of different earliness groups, observed their varied response to nitrogen fertilisation. High nitrogen doses in some cultivars, e.g. Danusia and Wigry, decreased the content of starch significantly, whereas in others, e.g. Wawrzyn and Wolfram, they did not cause any changes.

The interpretation of the results of losses of dry matter and starch in potato tubers after storage obtained from the balance was slightly different as it took into account the real fresh tuber weight losses during storage caused by transpiration and respiration. After each storage period, a decrease in the content of both dry matter and starch was reported, although it is always higher after a longer storage period (6 months) – Tables 1, 2, 3. The highest losses of dry matter and starch after 6 months of storage were observed in the magnesium treatment (8.1 and 15.4%), while lower losses occurred in the nitrogen treatment (6.6 and 10.1%), and the lowest – in the

Table 1

The balance of losses in dry matter and starch after storage in cv. Bila potato tubers, depending on nitrogen fertilisation and date of test (means from 3 years)

Fertilisation N (kg ha^{-1})	Dry matter				Starch			
	date of test							
	after 3 months of storage		after 6 months of storage		after 3 months of storage		after 6 months of storage	
	(%)	(g*)	(%)	(g*)	(%)	(g*)	(%)	(g*)
0	5.8	56.7	7.1	69.3	5.8	34.4	7.6	45.5
50	6.2	61.0	4.9	48.5	8.3	51.4	9.0	56.1
100	7.0	71.0	7.7	77.3	9.9	64.3	13.4	86.5
$\bar{x}$	6.3	62.5	6.6	65.2	8.0	49.7	10.1	62.8

*Actual loss of starch, calculated based on the fresh weight loss during storage of tubers in relation to the weight of the original sample – 10 kg.

Table 2

The balance of losses in dry matter and starch after storage in cv. Triada potato tubers, depending on potassium fertilisation and date of test (means from 3 years)

Fertilisation N (kg ha^{-1})	Dry matter				Starch			
	date of test							
	after 3 months of storage		after 6 months of storage		after 3 months of storage		after 6 months of storage	
	(%)	(g*)	(%)	(g*)	(%)	(g*)	(%)	(g*)
0	4.3	44.7	10.9	113.6	3.8	29.1	13.5	104.2
50	1.9	20.0	6.8	73.8	3.4	26.5	7.2	56.3
160	1.2	12.5	4.8	50.7	0.9	7.5	3.6	29.4
240	2.0	21.2	4.4	47.0	3.3	27.1	7.4	59.9
$\overline{x}$	2.3	24.6	6.7	71.3	2.9	22.6	7.9	62.5

*see Table 1

Table 3

The balance losses in dry matter and starch after storage in cv. Bila potato tubers, depending on magnesium fertilisation and date of test (means from 3 years)

Fertilisation N (kg ha^{-1})	Dry mster				Starch			
	date of test							
	after 3 months of storage		after 6 months of storage		after 3 months of storage		after 6 months of storage	
	(%)	(g*)	(%)	(g*)	(%)	(g*)	(%)	(g*)
0	6.9	68.0	7.5	74.3	11.8	77.6	16.1	106.1
20	3.6	36.3	7.8	78.4	8.7	58.7	14.8	100.3
40	3.1	31.8	7.4	75.7	8.1	56.0	15.7	107.8
60	3.6	37.5	8.5	87.7	8.1	56.2	14.6	101.7
80	4.9	51.2	7.2	74.3	9.6	67.3	13.3	93.8
100	6.2	64.9	10.4	109.4	9.5	68.2	17.6	126.3
$\overline{x}$	4.7	48.4	8.1	83.3	9.3	64.1	15.4	106.0

*see Table 1

potassium treatment (6.7 and 7.9%). The potassium and magnesium doses applied over the vegetation period limited the losses, which could be attributed to the fact that these elements improved the resistance and health of tubers, unlike nitrogen fertilisation (GĄSIOROWSKA 2000). Each nitrogen dose applied increased real losses both of dry matter and starch.

CONCLUSIONS

1. The quality of the tested potato cultivars, for direct consumption or food processing, was improved by the following treatments:
   – dry matter content was better following the application of 100 kg of nitrogen, 80 kg of potassium and 100 kg of magnesium,
   – starch content was higher following the application of 100 kg of nitrogen, 160 kg of potassium as well as 100 kg of magnesium.
2. Real losses of dry matter and starch, as compared with the initial material, were the highest after 6 months of storage, reaching, respectively:
   – 8.1 and 15.4% in the magnesium treatment,
   – 6.6 and 10.1% in the nitrogen treatment,
   – 6.7 and 7.9% in the potassium treatment.

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COMPARISON OF THE CONTENT OF SOME CHEMICAL COMPOUNDS IN TWO ENDIVE CULTIVARS GROWN ON AN OPEN FIELD (*CICHORIUM ENDIVIA* L.)

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Abstract

Compared with other European countries, Poles do not eat enough leafy vegetables, or example endive, which belongs to *Asteraceae* family. In Poland, endive is not a popular vegetable and is grown only amateur gardeners.

Endive is one of the most nutritious and healthy leafy vegetables. It contains more minerals (especially phosphorus, calcium and potassium), provitamin A and vitamins B_1, B_2 and C than lettuce, which is more popular in our country. Because of its high content of bitter compounds, endive has properties that can aid digestion.

In our experiment, the content of macro- and micronutrients and nitrates in leaves of two endive cultivars was studied. One of the cultivars was Riccia a cuor ol'oro sel blondie – a botanical variety escarole (*Cichorium endivia* var. *latifolium*), with smooth leaves and the other one was Blonda a cuor plen – from the curled endive group (*Cichorium endivia* var. *crispum)* with fringed leaves. A field experiment was conducted in 2004-2006 at the Horticultural Experimental Station in Dołuje near Szczecin.

The experiment was set in a one-factorial, randomized block design with three replications. The plot area was 2.88 m^2 (1.80×1.60 m). Cucumber grown in manure was the forecrop.

Seeds of endive were sown in a seed-bed on 20 June (in both years of the research). Transplants were planted on an open field at the phase of 4-6 leaves on 18 July (in 2006) and on 20 July (in 2007), in 40×30 cm distance. Leaf rosettes were harvested once: on 13 September (in 2006) and 8 September (in 2007). The results were statistically analysed by Tukey's test, at the significance level of 0.05.

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It was proven that the content of macro- and micronutrients in endive leaves depended significantly on a cultivar. The curled endive cultivar (var. *crispum*) was characterized by a higher content of magnesium, iron, manganese and copper, while the leaves of the escarole cultivar (var. *latifolium*) contained more phosphorus, potassium, calcium and zinc but less nitrates.

The cultivar Riccia a cuor ol'oro sel blondie (from the escarole group) contained more phosphorus, potassium and calcium, as mean values for the two years of the study. Regarding phosphorus – in the first year of the study, differences in the content of this macronutrient were not significant. However, significantly higher accumulation of phosphorus was determined in the second year in leaves of the botanical variety escarole, the fact what was also confirmed by the mean for both years of the study. This cultivar was also characterized by a significantly higher content of potassium (on average by 47.8%) and calcium (by 7.4%) in comparison with the curled endive. However, comparing the two cultivars, significantly higher amounts of magnesium (on average 187.9 mg 100 g^{-1} d.m.) and sodium (3.0 mg 100 g^{-1} d.m.) were assessed in the leaves of the endive cultivar from the curled endive group.

It was proved that tested in the experiment cultivars differed significantly according to the macroelement content (Fe, Mn, Cu and Zn) in the edible parts of the plants.

Key words: endive, cultivar, macro- and micronutrient content.

PORÓWNANIE ZAWARTOŚCI WYBRANYCH SKŁADNIKÓW CHEMICZNYCH W LIŚCIACH DWÓCH ODMIAN ENDYWII (*CICHORIUM ENDIVIA* L.)

Abstrakt

W Polsce w porównaniu z innymi krajami europejskimi obserwuje się za małe spożycie gatunków należących do grupy warzyw liściowych. Jednym z takich warzyw jest endywia – z rodziny astrowatych (*Asteraceae*), roślina mało znana, uprawiana jedynie amatorsko.

Endywia należy do cennych warzyw liściowych, które charakteryzują się wysoką wartością odżywczą i prozdrowotną. W porównaniu z bardziej popularną w naszym kraju sałatą, zawiera więcej soli mineralnych (zwłaszcza fosforu, wapnia i potasu), prowitaminy A oraz witamin B_1, B_2 i C. Dzięki zawartości substancji gorzkich ma działanie pobudzające trawienie.

Celem badań była ocena zawartości makro- i mikroelementów oraz azotanów w liściach dwóch odmian endywii: Riccia a cuor ol'oro sel blondie, należącej do odmiany botanicznej eskariola (*Cichorium endivia var. latifolium*) o gładkich liściach, i Blonda a cuor plen – z grupy endywii kędzierzawej (*Cichorium endivia var. crispum)* o liściach fryzowanych. Doświadczenie założono w latach 2004-2006, w Warzywniczej Stacji Badawczej w Dołujach k. Szczecina.

Było to doświadczenie 1-czynnikowe, założone metodą bloków losowych, w 3 powtórzeniach. Powierzchnia poletka doświadczalnego wynosiła 2,88 m^2 (1,80×1,60 m). Przedplonem dla endywii był ogórek uprawiany na oborniku. Nasiona endywii wysiewano na rozsadniku 20 czerwca (w obu latach uprawy), natomiast rozsadę w fazie 4-6 liści właściwych sadzono na miejsce stałe 18 lipca (2006 r.) i 20 lipca (2007 r.), w rozstawie 40×30 cm. Zbiór rozet liściowych wykonano jednorazowo 13 września (2006 r.) i 8 września (2007 r.).

Wyniki opracowano statystycznie z użyciem testu Tukeya na poziomie istotności α=0,05.

Stwierdzono, że zawartość makro- i mikroelementów w liściach endywii była w sposób istotny uwarunkowana zmiennością odmianową. Odmiana endywii z grupy *crispum* (kędzierzawej) odznaczała się wyższą zawartością magnezu oraz żelaza, manganu i miedzi. Liście roślin odmiany endywii z grupy *latifolium* (eskariola) zawierały więcej fosforu, potasu, wapnia i cynku, a jednocześnie mniej azotanów.

Odmiana Riccia a cuor ol'oro sel blondie (z grupy eskariola) zawierała średnio w 2 latach badań więcej fosforu, potasu i wapnia. W odniesieniu do fosforu, w 1. roku badań różnice zawartości tego makroskładnika u obu odmian okazały się nieistotne, natomiast w 2. roku stwierdzono istotnie większą koncentrację tego pierwiastka w liściach odmiany botanicznej eskariola, co potwierdziły średnie wyniki z 2 lat badań. U tej odmiany wykazano również wyższą zawartość potasu (średnio o 47,8%) i wapnia (o 7,4%) w porównaniu z endywią kędzierzawą. Natomiast istotnie więcej magnezu (średnio 187,9 mg 100 g^{-1} d.m. mg) i sodu (3,0 mg 100 g^{-1} d.m.) zawierały liście endywii z grupy endywii kędzierzawej.

Wykazano również znaczne zróżnicowanie zawartości mikroskładników (Fe, Mn, Cu i Zn) w części jadalnej badanych odmiany endywii

Słowa kluczowe: endywia, odmiany, makro- i mikroelementy.

INTRODUCTION

Among many plant products, vegetables should play an important role in human nutrition. They provide our diet with many of healthy compounds, such as: vitamins, easily digestible carbohydrates and dietary fibre. Moreover, a diet rich in vegetables and fruit is low in fat (Wolski, Dyduch 2000). The actual consumption of vegetables in Poland is 2-3-fold lower than in Greece or Spain (Cieślik 2009). Moreover, Poles eat a poor range of vegetable species. Endive is a vegetable species that is hardly recognized in our country although the nutritional value of its raw leaves is much higher than that of lettuce leaves. As demonstrated by Cieślik (2009), endive contains many valuable compounds, e.g. fructans (inulin), and a specific compound, i.e. intybin, which are said to have a beneficial effect on the digestive and cardiovascular systems.

The aim of our experiment was to assess the content of some chemical compounds in leaves of two endive cultivars grown in autumn.

MATERIAL AND METHODS

The present experiment was carried out in order to the content of macro- and micronutrients, and nitrates in leaves of two cultivars of endive: 'Riccia a cuor ol'oro sel blondie' – a botanical variety escarole (*Cichorium endivia* var. *latifolium*), with smooth leaves and 'Blonda a cuor plen' – from the curled endive group (*Cichorium endivia* var. *crispum)* with fringed leaves.

The experiment was set in a one-factorial, randomized block design with three replications. The plot area was 2.88 m^2 (1.80×1.60 m). Cucumber grown in manure was the forecrop for endive. Mineral fertilization was quantified according to the results of chemical analysis of the soil samples and supplemented to the levels recommended for lettuce (Sady 2006).

Seeds of endive were sown in a seed-bed on 20 June (in both years of the research). Transplants were planted on an open field at the phase of 4-6 leaves on 18 July (in 2006) and on 20 July (in 2007), in 40×30 cm distance. Leaf rosettes were harvested once: on 13 September (in 2006) and 8 September (in 2007).

Chemical analysis of the raw plant material (inner leaves) included the content of:

– nitrates (using the standard method, in plant extract with 2% acetic acid);
– potassium, sodium and calcium (by flame photometry);
– phosphorus (by the colorimetry);
– magnesium, zinc, manganese and iron (by atomic absorption spectrophotometry, AAS).

The results were statistically analysed by the Tukey test, at a significance level of 0.05.

RESULTS AND DISSCUSION

Statistical analysis of the results concerning the macronutrient content in endive leaves showed significant cultivar-dependent differences between the amounts of elements (except phosphorus determined in 2006) – Table 1.

The cultivar Riccia a cuor ol'oro sel blondie (the escarole group) contained more phosphorus, potassium and calcium, shown as the means for two years of the study. The differences in the content of phosphorus in the first year of the study were not significant. However, in the second year, significantly higher accumulation of phosphorus was determined in leaves of the botanical variety escarole, which was confirmed by the mean for both years of the study. This cultivar was also characterized by a significantly higher content of potassium (on average by 47.8%) and calcium (by 7.4%) in comparison with the curled endive. However, comparing these cultivars, significantly higher amounts of magnesium (on average 187.9 mg 100 g^{-1} d.m.) and sodium (3.0 mg 100 g^{-1} d.m.) were assessed for leaves of the endive from the curled endive group.

Moreover, the cultivars tested in the experiment were characterized by the a variable content of nitrates assessed in dry matter of leaves. The level of determined nitrates varied from 733.6 (for the escarole cultivar in the year 2006) to 1003.0 mg 100 g^{-1} d.m. (for the curled endive in 2007).

The results of the experiment conducted by Koudela and Ptŕikova (2007) showed a wide range of differences in the nitrate accumulation in leaves of different cultivars of endive.

The data presented in Table 2 prove that the cultivars tested in the experiment differed significantly in the micronutrient composition (Fe, Mn, Cu and Zn) of the edible parts of the plants.

Table 1

Content of $N\text{-}NO_3$ and macronutrients in endive leaves, means for 2006-2007 (mg 100^{-1} d.m.)

Botanical variety	$N\text{-}NO_3$			P			K			Ca			Mg			Na		
	2006	2007	mean	2006	2007	mean	2006	2007	mean	2006	2007	mean	2006	2007	mean	2006	2007	mean
Curled	902.4	1003.0	952.7	599.6	692.0	645.8	4357.2	3942.0	4149.6	796.2	764.0	780.1	180.6	195.1	187.9	2.7	3.2	3.0
Escarole	733.6	841.4	787.5	621.6	759.3	690.5	6121.3	6140.8	6131.1	873.9	802.2	838.1	132.5	143.3	137.9	1.9	2.3	2.1
LSD at α= 0.05	77.64	49.64	15.56	n.s.	61.19	24.86	602.8	624.3	599.2	34.37	25.46	48.20	24.37	49.64	10.20	0.14	0.22	0.19

Table 2

Content of micronutrients in endive leaves, means for 2006-2007 (mg kg^{-1} d.m.)

Botanical variety	Fe			Mn			Cu			Zn		
	2006	2007	2006-2007	2006	2007	2006-2007	2006	2007	2006-2007	2006	2007	2006-2007
Curled	198.8	250.1	224.4	34.8	39.2	37.0	13.1	12.9	13.0	29.2	37.5	33.4
Escarole	105.0	195.2	150.1	29.3	31.3	30.3	12.3	12.0	12.2	31.8	48.5	40.2
LSD at α= 0.05	63.64	18.20	20.83	0.20	0.38	0.31	0.25	0.12	0.17	n.s.	3.56	5.35

The content of iron varied from 105.0 (the botanical variety escarole in 2006) to 250.1 mg 100 g^{-1} d.m. (the curled endive cultivar in 2007). Statistical analysis of the results showed a significantly higher iron concentration in leaves of the cultivar Blonda a cuor plen, which was also characterized by a significantly higher content of manganese (on average 37 mg 100 g^{-1} d.m.) and copper (on average 13 mg 100 g^{-1} d.m.). However, leaves of Riccia a cuor ol'oro sel blondie contained significantly more zinc (on average 40.2 mg kg^{-1} d.m.).

In the Department of Horticulture of the Wroclaw University of Environmental and Life Sciences, there was a research project conducted to estimate the biological value of fourteen cultivars of endive (from the curled endive and escarole groups) grown in spring and autumn (Adamczewska-Sowińska, Uklańska 2009a, Uklańska, Adamczewska-Sowińska 2010). The authors proved a significant effect of the experimental factors on the content of macronutrients in endive leaves. Curled endive cultivars (independently of the planting date) contained higher amounts of magnesium. However, cultivars of the escarole type were characterized by a high content of calcium, what was also proved in the present study. In another experiment by the same authors (Adamczewska-Sowińska, Uklańska 2009b), it was demonstrated that, independently of nitrogen doses, plants of the cultivar Excel contained more nitrates, while cv. Cigal had more dry matter, vitamin C and chlorophyll. In the research carried out by Koudela and Ptŕikova (2007) it was found that cultivars of curled endive were characterized by a higher content of dry matter and fibre than cultivars from the escarole group.

CONCLUSIONS

1. The content of macro- and micronutrients in leaves of endive depended on a cultivar type.

2. The endive cultivar Blonda a cuor plen (from the *crispum* group) was characterized by a higher content of magnesium, iron, manganese and copper. The leaves of endive from the *latifolium* group contained more phosphorus, potassium, calcium and zinc but less nitrates.

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CONTENT OF MINERAL COMPONENTS IN ROOTS OF SELECTED CULTIVARS OF BEETROOT

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Abstract

Red beet is a very popular root vegetable in Poland. It is easily available on the market all year round, both as a fresh and processed product. Considering the level of consumption, red beet is the third most popular vegetable, after cabbage and carrot. It is easy to grow, produces high yields and is suitable for long term storage. It is also a vegetable characterized by very a high nutritional and dietetic value, rich in vitamins, minerals, proteins and organic acids. The actual quantities of these chemical compounds are mostly affected by a red beet cultivar, yield quantity and its quality.

The aim of the study has been to estimate the effect of red beet cultivars of different storage root shapes on some quality characteristics of the yield and on the content of macro- and micronutrients in the roots. The experiment was conducted at the Vegetable Experimental Station in Dołuje in 2004-2006. In mid-May each year, seeds of ten red beet cultivars in the amount of 16 kg ha^{-1} were sown in rows spaced at 30 cm. The beetroots were harvested in the third decade of September.

The results proved that the highest ratio of root to leaf mass was determined for the cultivar Rocket (on average 73.1%). In each year, the highest unit root weight was noted for the cultivars Opolski and Rocket. These two cultivars were also characterized by the highest content of dry matter (12.9 and 13.1%, respectively). In contrast, the least amount of dry matter was determined for the cultivars Bikores and Chrobry (10.5 and 10.6%). There were no significant differences assessed in the content of macronutrients (N, P, K, Ca, Mg and Na). However, there was a significant influence of the cultivars on the content of micronutrients. Among the cultivars tested in the experiment, the highest content of manganese was determined in cv. Czerwona Kula, zinc in cv. Bikores, iron in cv. Egipski and Czerwona Kula. Roots of cv. Czerwona Kula were also characterized by the highest content of copper in comparison with the other cultivars.

Key words: beetroot, macro- and microelements content.

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ZAWARTOŚĆ SKŁADNIKÓW MINERALNYCH W KORZENIACH SPICHRZOWYCH WYBRANYCH ODMIAN BURAKA ĆWIKŁOWEGO

Abstrakt

Burak ćwikłowy jest w Polsce warzywem o podstawowym znaczeniu, dostępnym na rynku przez cały rok w postaci świeżej lub przetworzonej. Pod względem wielkości spożycia zajmuje trzecie miejsce po kapuście i marchwi. Jest łatwy w uprawie, niezawodny w plonowaniu, doskonale się przechowuje. Należy jednocześnie do gatunków o wysokiej wartości odżywczej i dietetycznej. O wartości zdrowotnej, dietetycznej i odżywczej warzyw decyduje m.in. zawartość witamin, soli mineralnych, białka, kwasów organicznych. Zawartość tych składników jest w dużej mierze uzależniona od odmiany oraz wielkości i jakości plonu.

Celem pracy była ocena wpływu odmian buraka ćwikłowego o zróżnicowanych kształtach korzenia spichrzowego na wybrane cechy jakościowe plonu oraz zawartość makro- i mikroelementów. Doświadczenie założono w latach 2004-2006 w Warzywniczej Stacji Badawczej w Dołujach. Nasiona 10 odmian wysiewano w połowie maja, w ilości 16 kg ha^{-1}, w rzędy co 30 cm, korzenie zbierano w ostatniej dekadzie września.

Na podstawie badań stwierdzono największy udział masy korzeni w stosunku do masy liści w odniesieniu do odmiany Rocket (średnio 73,1%). W każdym roku badań największą masę jednostkową korzeni spichrzowych miały odmiany Opolski i Rocket. U tych odmian stwierdzono jednocześnie najwięcej suchej masy (odpowiednio: 12,9 i 13,1%). Najmniej zasobne w suchą masę były odmiany Bikores i Chrobry (10,5 i 10,6%). U badanych odmian nie wykazano istotnego zróżnicowania zawartości makroelementów (N, P, K, Ca, Mg i Na), natomiast stwierdzono istotny wpływ odmian na poziom wybranych mikroelementów w części jadalnej buraka. Spośród ocenianych odmian najwięcej manganu zawierała odmiana Czerwona Kula, a najwięcej cynku miały korzenie odmiany Bikores. Najbardziej bogate w żelazo były korzenie odmian Egipski i Czerwona Kula. U tej ostatniej odmiany wykazano również największą w porównaniu z pozostałymi odmianami zawartość miedzi.

Słowa kluczowe: burak ćwikłowy, zawartość makro- i mikroelementów.

INTRODUCTION

Red beetroot is one of the most important vegetables in Poland, available all year round, fresh or processed. It is the third vegetable, after cabbage and carrot, in respect of the amount consumed. Beetroot is easy to grow and produces stable yields. It is one of the vegetables of high nutritive value (Barański, Grzebelus 1998). Roots of beetroot contain 89.0% water, 1.5% protein, 7.58% carbohydrates, 1.0% mineral components (calcium, phosphorus, potassium, manganese, iron), vitamins (provitamin A, vitamins from B group, vitamin C) and organic acids. According to Kryńska and Martyniak (1978), the cultivar, quantity and quality of yield affect the content of these components.

The aim of our experiment has been to examine the influence of selected cultivars of beetroot on the quality traits of storage roots and the content of macro- and micronutrients.

MATERIAL AND METHODS

The experiment was carried out in 2004-2006 at the Department of Vegetable Crops, the Agricultural University in Szczecin. Ten cultivars of beetroot with flattened (Egipski and Patryk), round or oval (Bikores, Chrobry, Crosby, Czerwona Kula and Nochowski) or elongated roots (Opolski and Rocket) were tested. A single- factor experiment was conducted in a randomized block design with four replicates. Each experimental plot was 2.4 m^2 (2.0×1.2 m) in area. On 15th May, seeds of each of the ten beetroot cultivars in the amount of 16.6 kg ha^{-1} were sown in rows 30 cm apart.

Roots were harvested in the last decade of September. The content of dry matter (by drying to the stable weight at 105°C) and concentrations of mineral components (N – determined by Kjeldahl method, P – colorimetric method, K, Na and Ca – flame photometry method, Cu, Zn, Mn, Fe and Mg – flame method of atomic spectrophotometry absorption ASA), were determined in the harvested marketable yield. The results were verified statistically using Tukey's test at the significance level α=0.05.

RESULTS AND DISCUSSION

The results showed that the cultivars Opolski and Rocket were characterized by the highest mean weight of storage roots in the first year of the experiment (Table 1). In the next two years, cv. Opolski (with elongated roots) was characterized by the significantly highest weight of roots.

Table 1

Mean weight of storage root of ten cultivars of red beetroot cultivated for autumn harvest (g)

Cultivar	Years		
	2004	2005	2006
With flattened roots			
Egipski	219.4	235.8	224.6
Patryk	250.7	243.6	287.4
With round or oval roots			
Bikores	246.4	237.2	285.1
Chrobry	289.9	212.8	284.5
Crosby	213.8	236.6	220.5
Czerwona Kula	223.1	238.9	229.9
Nochowski	251.6	239.8	265.7
Pablo F1	210.4	226.3	270.5
With elongated roots			
Opolski	345.3	256.2	397.5
Rocket	305.3	302.6	296.0
LSD α=0.05	44.990	53.184	47.30

Table 2

Content of selected micronutrients in storage roots of red beetroot cultivars (in % of dry matter) – mean for 2004-2006

Cultivar	N	P	K	Mg	Ca	Na
With flatted roots						
Egipski	0.93	0.21	2.24	0.11	0.12	0.09
Patryk	1.08	0.11	2.28	0.12	0.22	0.07
With round roots						
Bikores	0.91	0.22	2.20	0.21	0.21	0.09
Chrobry	0.90	0.24	2.45	0.12	0.14	0.08
Crosby	0.95	0.24	2.54	0.14	0.14	0.11
Czerwona Kula	0.80	0.26	2.20	0.10	0.12	0.07
Nochowski	0.92	0.31	2.31	0.12	0.11	0.07
Pablo F1	0.90	0.21	2.71	0.11	0.22	0.10
With elongated roots						
Opolski	0.72	0.21	2.23	0.13	0.23	0.09
Rocket	1.15	0.20	2.80	0.14	0.22	0.11
LSD α=0.05	0.232	n.s	0.131	n.s	n.s	n.s

n.s.-non-significant differences

Concentrations of the mineral components in storage roots of the ten beetroot cultivars, expressed in dry matter of raw material, are given in Tables 2 and 3. Roots of cv. Rocket were characterized by a significantly higher content of total N in comparison with cv. Bikores, Chrobry, Pablo F_1, Czerwona Kula and Opolski. No significant differences in the content of P, Mg, Ca and Na in roots of the examined cultivars were found. However, the cultivars differed significantly in the content of the micronutrients in edible parts of beetroot (Table 3). In the years of the experiment, significantly more Mn was found in storage roots of cv. Czerwona Kula. The lowest content of Mn was determined in roots of cv. Nochowski, Patryk, Rocket and Pablo F_1 in 2005 and in roots of cv. Pablo F_1 and Crosby in 2006. The significantly highest content of Zn for the whole experiment was assessed in edible parts of cv. Pablo F_1, Rocket and Egipski. The significantly highest content of iron for the whole experiment was determined in roots of cv. Egipski. The roots of cv. Rocket were characterized by the lowest content of iron.

The red beet cultivar Czerwona Kula was characterized by the significantly highest content of copper. The other cultivars did not differ significantly in the content of this micronutrient.

The uptake of mineral components by plants depends not only on the conditions of cultivation (Jędrzejczak et al. 1999, Perucka 1999, Szura et al. 2008) but also on the species and cultivar (Kotowska, Wybieralski 1999). This observation was confirmed by the results of our experiment. Also Jadczak and Grzeszczuk (2004) described significant differences in the content of macro- and micronutrients in fruits of selected cultivars of hot pepper.

Table 3

Content of selected micronutrients in storage roots of red beetroot cultivars

Cultivar	Content of micronutrients (mg kg^{-1} d.m.)											
	Mn			Zn			Fe			Cu		
	2005	2006	mean	2005	2006	mean	2005	2006	mean	2005	2006	mean
With flatted roots												
Egipski	17.0	13.7	15.3	20.9	21.0	21.0	163.1	206.0	184.6	6.5	9.5	8.0
Patryk	13.7	16.2	14.9	26.2	31.0	28.6	164.0	140.9	152.5	5.8	7.0	6.4
With round roots												
Bikores	18.9	16.2	18.1	31.8	44.9	38.4	129.0	117.9	123.5	5.6	7.1	6.4
Chrobry	18.4	16.3	17.4	28.2	29.0	28.6	176.6	101.0	138.8	5.2	6.8	6.0
Crosby	15.4	11.2	13.3	26.4	28.1	27.3	143.0	162.2	152.6	6.2	6.8	6.5
Czerwona Kula	24.6	23.6	24.1	32.3	30.1	31.2	188.0	109.0	148.5	9.0	12.9	11.0
Nochowski	14.5	16.2	15.3	28.1	38.2	33.2	129.0	78.8	103.9	6.5	8.0	7.3
Pablo F1	12.4	12.5	12.4	23.3	24.4	23.9	164.1	148.0	156.1	5.8	8.1	7.0
With elongated roots												
Opolski	20.3	18.5	19.4	38.0	28.8	33.4	129.8	99.8	114.8	5.0	6.9	6.0
Rocket	12.9	15.0	14.0	21.5	20.6	21.1	98.8	102.0	100.4	5.7	6.6	6.2
LSD α=0.05	2.80	2.86	1.77	3.57	5.42	2.87	15.79	15.16	9.67	1.90	3.07	1.98

CONCLUSIONS

1. Roots of the examined cultivars of beetroot different significantly in the content of N, K, Mn, Zn, Fe and Cu.

2. Among the examined micronutrients, roots of beetroot contained the highest amount of iron (on the average 137.6 mg kg^{-1} d.m.).

3. The cultivars Rocket, Patryk, Crosby, Egipski and Nochowski were characterized by the highest content of total N.

4. Roots of the cultivars Rocket and Pablo F_1 were characterized by the highest content of potassium.

5. The significantly highest content of Mn and Cu was estimated in storage roots of cv. Czerwona Kula.

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EFFECT OF DIFFERENT SULFUR DOSES AND FORMS ON THE CONTENT OF SULFUR AND AVAILABLE POTASSIUM IN SOIL

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Abstract

High sulfur concentrations lead to soil acidification and, indirectly, to the mobilization of phytotoxic compounds, including aluminum and selected trace elements. On the other hand, sulfur deficiency decreases crop yield and quality. Previous studies investigating the effect of sulfur on the available potassium content of soil delivered inconclusive results.

The aim of this study has been to determine the effect of increasing doses of sulfate sulfur and elementary sulfur on the content of total sulfur, sulfate sulfur and available potassium in soil samples collected at a depth of 0-40 and 40-80 cm. A three-year field experiment was conducted on acid brown soil of the grain size distribution of heavy loamy sand. The soil was acidic in reaction ($pH_{1\ mol\ KCl\ dm^{-3}}$ of 5.30) and contained the following concentrations of mineral nutrients: mineral nitrogen – 24.0, sulfate sulfur – 4.10, available phosphorus – 34.5, available potassium – 110.0 mg kg^{-1} soil. Three sulfate sulfur ($S\text{-}SO_4$) and elementary sulfur ($S\text{-}S^0$) fertilization levels were applied each year: S_1 – 40, S_2 – 80 and S_3 – 120 kg ha^{-1}. In most cases, NPK+S fertilization, in particular the application of 120 kg S ha^{-1}, contributed to an increase in total sulfur concentrations in both sampled soil horizons compared with the NPK treatment. Sulfate accumulation in the soil increased over time, proportionally to the increasing rates of sulfur fertilizers. The effect of elementary sulfur application on an increase in the $S\text{-}SO_4$ content of the 0-40 cm soil layer was noted in the third year of the study. During the three-year experimental period, the application of both sulfur forms decreased the available potassium content of soil samples collected at the depth of 0-40 cm in comparison with the NPK treatment. The available potassium content of the 40-80 cm soil layer varied after sulfur fertilization. Sulfate sulfur exerted a stronger effect than elementary sulfur on available potassium levels in the soil.

Key words: fertilization, total sulfur, sulfate sulfur, elementary sulfur, available potassium, soil.

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WPŁYW RÓŻNYCH DAWEK I FORM SIARKI NA ZAWARTOŚĆ JEJ FORM ORAZ POTASU PRZYSWAJALNEGO W GLEBIE

Abstrakt

Wysoka zawartość siarki w glebie powoduje jej zasiarczenie i zakwaszenie oraz pośrednio uruchamia związki fitotoksyczne, szczególnie glin i niektóre pierwiastki śladowe. Niewystarczające odżywianie roślin tym pierwiastkiem obniża plon i pogarsza jego jakość. Badania dotyczące wpływu siarki na zawartość potasu przyswajalnego w glebie są rozbieżne.

Celem badań była ocena wpływu nawożenia wzrastającymi dawkami siarki w formie siarczanowej i elementarnej na zawartość siarki ogółem, siarki siarczanowej oraz potasu przyswajalnego w poziomie gleby 0-40 i 40-80 cm. Trzyletnie doświadczenie polowe przeprowadzono na glebie brunatnej kwaśnej, o składzie granulometrycznym piasku gliniastego mocnego. Gleba przed założeniem doświadczenia charakteryzowała się odczynem kwaśnym (pH $_{1\ mol\ KCl\ dm^{-3}}$ wynosiło 5,30), zawartość składników mineralnych wynosiła: azot 24,0, siarka siarczanowa 4,10, fosfor przyswajalny 34,5 i potas 110,0 mg kg^{-1} gleby. Corocznie stosowano: S_1 – 40, S_2 – 80 i S_3 – 120 kg ha^{-1} siarki siarczanowej (S-SO_4) i elementarnej (S-S^0). Nawożenie NPK + S, szczególnie 120 kg S ha^{-1}, spowodowało na ogół wzrost zawartości siarki ogółem w obu poziomach gleby, w odniesieniu do obiektu NPK. Wraz ze wzrostem dawek siarki i upływem czasu trwania doświadczenia następowało nagromadzenie siarczanów w glebie. Wpływ nawożenia siarką elementarną na zwiększenie zawartości S-SO_4 w glebie, w poziomie 0-40 cm, uwidocznił się dopiero w trzecim roku. W okresie trzech lat trwania doświadczenia dodatek obu form siarki spowodował na ogół zmniejszenie zawartości potasu przyswajalnego w poziomie gleby 0-40 cm w porównaniu z obiektem NPK. Po nawożeniu siarką, w warstwie gleby 40-80 cm, zmiany zawartości potasu przyswajanego były nieregularne. Siarka siarczanowa oddziaływała silniej na zawartość potasu przyswajalnego niż forma elementarna.

Słowa kluczowe: nawożenie, siarka ogółem, siarka siarczanowa, siarka elementarna, potas przyswajalny, gleba.

INTRODUCTION

Both sulfur deficiency and excess can be harmful to plants (TERELAK et al. 2001, KOMARNISKY et al. 2003). Recently, there has been a growing interest in sulfur fertilizers, mostly in non-industrialized areas distant from large urban agglomerations, where signs of plant sulfur deficiencies are particularly noticeable. The observed sulfur deficiency is associated with sulfur emission limits and a low sulfur content of mineral fertilizers (MECHTELD et al. 2003, WALKER, DAWSON 2003). In Europe, sulfur deficiency occurs not only in plants with high sulfur requirements but is also frequently reported in cereals (SCHUNG et al. 1993, ZHAO et al. 1996, SCHERER 2001).

Available potassium concentrations are considered to be low in nearly half of the total utilized agricultural area in Poland (BŁASZCZYK, DUDYS 2000). ŁABĘTOWICZ et al. (2005) observed negative potassium balance at 45% of the investigated farms. According to LIPIŃSKI (2005), potassium deficiency is one of the most common nutrient deficiencies in soils. Researchers differ in their opinions regarding the effect of sulfur on the available potassium content of soil. Motowicka-Terelak et al. (1995) reported that changes in available potassium levels in soil caused by excessive sulfur emissions are irregular and typical of the negative consequences of soil acidification. High sulfur concentrations in soil enhance potassium leaching (Murawska et al. 1999, Kiepul 1999). Krzywy et al. (2000) found that phosphogypsum fertilization increases the available potassium content of soil. According to Agrawal and Verma (1997), soil potassium availability reduces the adverse effect of sulfur on plant growth.

The aim of this study has been to determine the effect of increasing doses of sulfate sulfur and elementary sulfur on the content of total sulfur, sulfate sulfur and available potassium in soil samples collected at a depth of 0-40 and 40-80 cm.

MATERIALS AND METHODS

A three-year field experiment was conducted in Byszwałd near Lubawa, in 2000-2002, on acid brown soil of the grain size distribution of heavy loamy sand. The uppermost soil layer had $pH_{(KCl)}$ = 5.30 and contained the following concentrations of mineral nutrients: mineral nitrogen – 24.0, sulfate sulfur – 4.10, available phosphorus – 34.5, available potassium – 110.0 mg kg^{-1} soil. Three sulfate sulfur ($S\text{-}SO_4$) and elementary sulfur ($S\text{-}S^0$) fertilization levels were applied each year: S_1 – 40, S_2 – 80 and S_3 – 120 kg ha^{-1}. The experiment was carried out in a randomized block design and comprised eight fertilization treatments in four replications: 1) 0; 2) NPK; 3) NPK + $S_1\text{-}SO_4$; 4) NPK + $S_2\text{-}SO_4$; 5) NPK + $S_3\text{-}SO_4$; 6) NPK + $S_1\text{-}S^0$; 7) NPK + S_2 - S^0; 8) NPK + S_3 – S^0.

The following fertilizers were used: nitrogen – ammonium saltpeter or ammonium sulfate, phosphorus – triple superphosphate, potassium – 60% potash salt or potassium sulfate, sulfur – potassium sulfate + ammonium sulfate and elementary sulfur (Table 1). The tested crops were common cabbage (*Brassica oleracea var. capitata alba*) – medium late cv. Glory of Enkhuizen, onion (*Allium cepa var. cepa*) – cv. Wolska, and spring barley (*Hordeum sativum var. nutans*) – cv. Rodion.

Soil samples were collected in each plot, at a depth of 0-40 cm and 40-80 cm, before setting up the experiment, after harvest of each crop and prior to the sowing of the next crop. In the spring of 2001, soil samples were collected only from the 0-40 cm soil layer due to persistent precipitation. Air-dried soil samples were passed through a 1 mm mesh sieve. The content of total sulfur and sulfate sulfur was determined in soil samples by the turbidimetric method and available potassium concentrations were meas-

Table 1

Doses of NPK applied in the experiment

Plant	N	P	K
	(kg ha^{-1})		
Head cabbage	200.0	52.5	180.0
Common onion	160.0	60.0	183.0
Spring barley	90.0	80.0	111.0

ured by Egner-Riehm method. The results were verified statistically by an analysis of variance for two-factorial experiments in a randomized block design. Experimental factor *a* was a sulfur form and experimental factor *b* consisted of a sulfur dose. Regression analysis was performed using Statistica 6.0 PL software. The significance of differences between group means was determined by Duncan's test.

RESULTS AND DISCUSSION

Before setting up the experiment, the total sulfur content of soil was comparable across all experimental plots, in both sampled horizons (0-40 cm and 40-80 cm). Total sulfur concentrations were approximately 2.5-fold lower in the 40-80 cm soil layer than in the 0-40 cm layer. At the completion of the experiment, significant increase in the total sulfur content was noted in both soil horizons following the application of a single and triple dose of S-SO_4 and a double and triple dose of elementary sulfur, compared with the NPK treatment. In the remaining treatments, the total sulfur content of soil was similar to the values observed after NPK fertilization (Table 2). At the end of the experiment, in the treatments not fertilized with sulfur, the total sulfur content of soil decreased considerably (by around 16%) in the 0-40 cm layer but increased (from 11% to 36%) in the 40-80 cm horizon in comparison with the samples collected in the spring of 2000 (Table 2).

The S-SO_4 content of soil was affected by the dose and form of sulfur and the duration of the experiment. In most treatments, increasing sulfur doses contributed to an increase in the sulfate content of soil. Similar results were reported by KULCZYCKI (2003), who noted the highest concentrations of total sulfur and S-SO_4 in a treatment fertilized with the highest sulfur rate.

In the fall of 2000 and 2001 (after cabbage and onion harvest), following the application of single and double doses of sulfur, the S-SO_4 accumulation in both sampled soil horizons was similar to or lower than in the NPK treatment (Tables 3 and 4). The only exception was the double dose of

Table 2

Effect of different rates and forms of sulfur on the content of total sulfur in soil 0-40 cm and 40-80 cm (mg kg^{-1} soil)

Treatment	Before experiment	After experiment	cmBefore experiment	After experiment
	0 - 40 cm		40 - 80 cm	
0	54.6	45.6	19.9	24.4
NPK	54.8	45.6	20.2	22.5
NPK+ S_1-SO_4	58.2	50.3	22.8	31.6
NPK+ S_2-SO_4	57.9	45.2	20.9	20.5
NPK+ S_3-SO_4	53.6	57.6	23.2	48.6
NPK+S_1-S-^{0}	49.1	46.6	22.3	21.3
NPK+S_2-S-^{0}	58.5	51.7	24.0	25.7
NPK+S_3-S-^{0}	57.8	55.6	19.5	43.5
LSD-$_{p\text{-}0.05}$				
a	n.s.	1.59	n.s.	1.06
b	n.s.	2.25	n.s.	1.50
a x *b*	n.s.	3.18	n.s.	2.12

SO_4 – sulfate sulfur; S^0 – elementary sulfur; S_1 – 40 kg ha^{-1}, S_2 – 80 kg ha^{-1}, S_3 – 120 kg ha^{-1}, *a* – form of sulfur; *b* – dose of sulfur; *a* x *b* interaction, n.s. – no significant difference

S-SO_4 applied in 2001, which increased the S-SO_4 content of the 0–40 cm soil layer. An increase in the sulfate content of soil, caused by the application of increasing sulfur doses, was reflected in the levels of sulfate sulfur and total sulfur in plants. At the completion of the study, the sulfate content of soil samples collected at the depth of 0-40 cm (Table 3) after the application of 40 kg ha^{-1} S-SO_4 and S-S^0 was similar to the level before setting up the experiment. Increasing sulfur doses considerably increased sulfur concentrations. In the 40-80 cm soil layer, the application of 40 kg S-SO_4 did not result in any S-SO_4 accumulation in the soil. The values noted in the remaining treatments were substantially higher (Table 4). This could have been due to a relatively low sulfur uptake by spring barley, as described by Skwierawska et al. (2008), and to the migration of sulfate sulfur from the uppermost soil layer, particularly after the application of increasing S-SO_4 doses. As demonstrated in a laboratory experiment performed by Zawartka and Skwierawska (2005), S-SO_4 ions are readily translocated downward and upward in the soil profile. Sulfate accumulation in both sampled soil horizons was considerably higher in the spring than in the fall of the preceding year, particularly after the application of S–S^0.

Sulfate accumulation in both sampled soil horizons was observed in the third year of the study in NPK+S treatments. It was dependent on a sulfur

Table 3

Effect of different rates and forms of sulfur on the content of sulfate sulfur in soil 0-40 cm (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	0.9	2.3	0.9	2.1	1.60
NPK	0.0	2.3	1.1	2.0	1.10
NPK+ S_1-SO_4	0.0	5.1	1.6	2.3	5.30
NPK+ S_2-SO_4	0.0	6.3	3.2	2.6	9.70
NPK+ S_3-SO_4	9.8	6.2	3.6	4.2	12.5
NPK+S_1-S^{-0}	0.0	2.2	1.2	4.5	5.40
NPK+S_2-S^{-0}	0.0	2.6	1.5	8.4	9.60
NPK+S_3-S^{-0}	0.0	6.7	1.5	10.2	11.0
LSD-$_{p\text{-}0.05}$ *a* *b* *a* x *b*	 0.01 0.07 0.10	 0.20 0.28 0.39	 0.09 0.13 0.18	 0.35 0.49 0.69	 0.37 0.52 0.74

Explanations see Table 2

Table 4

Effect of different rates and forms of sulfur on the content of sulfate sulfur in soil 40-80 cm (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	0.9	-	1.7	2.2	2.1
NPK	0.0	-	2.0	2.3	3.0
NPK+ S_1-SO_4	0.0	-	1.2	2.0	3.5
NPK+ S_2-SO_4	0.0	-	1.6	4.3	6.9
NPK+ S_3-SO_4	5.8	-	2.7	7.5	9.2
NPK+S_1-S^{-0}	0.0	-	1.9	3.3	5.3
NPK+S_2-S^{-0}	0.0	-	2.3	3.4	5.2
NPK+S_3-S^{-0}	0.0	-	4.0	6.7	7.3
LSD-$_{p\text{-}0.05}$ *a* *b* *a* x *b*	 0.06 0.09 0.12	-	 r.n. 0.39 0.55	 0.390 0.558 0.790	 0.25 0.35 0.49

Explanations see Table 2

dose, reaching the highest level after the application of 120 kg S. The effect of elementary sulfur on an increase in the S-SO_4 content of soil was not noted in the first and second year of the study; in the third year, the S-SO_4 concentrations in soil were comparable, regardless of the type of sulfur fertilizer. The above testifies to the gradual oxidation of elementary sulfur, observed also by WEN et al. (2001). Duncan's test revealed that the application of 80 kg and 120 kg S ha^{-1} over three years caused an increase in S-SO_4 accumulation in the soil in comparison with the NPK treatment and control (Table 5).

Table 5

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

Treatment	0	NPK	I-S-SO_4	II-S-SO_4	III-S-SO_4	I-S-S0	II-S-S^0	III-S-S^0
0								
NPK	0.823871							
S_1-SO_4	0.352961	0.280555						
S_2-SO_4	0.003800*	0.002095*	0.042855*					
S_3-SO_4	0.000004*	0.000005*	0.000004*	0.000013*				
S_1-S^0	0.142091	0.104797	0.529193	0.138759	0.000004*			
S_2-S^0	0.006260*	0.003697*	0.059573	0.830541	0.000004*	0.174804		
S_3-S^0	0.000004*	0.000004*	0.000031*	0.028410*	0.010105*	0.000328*	0.021563*	
$\overline{x}$**	2.1091	1.9909	2.6023	3.7705	6.3000	2.9364	3.6568	4.9341

* significant difference,
** $\overline{x}$ – average content of sulfate sulfur in soil in particular objects for the years 2000-2003 (mg kg^{-1} soil)
SO_4 – sulfate sulfur, S^0 – elementary sulfur, S_1 – 40 kg ha^{-1}, S_2 – 80 kg ha^{-1}, S_3 – 120 kg ha^{-1}

In the fall, after cabbage harvest, the available potassium content of soil samples collected at the depth of 0-40 cm ranged from 39.1 to 73.0 mg K kg^{-1} soil (Table 6). The potassium content of soil was significantly affected by the form and dose of sulfur. The application of increasing S-SO_4 doses, in particular 80 kg and 120 kg ha^{-1}, led to a decrease in available potassium concentrations compared with the NPK treatment and the treatments fertilized with elementary sulfur. In the first year of the experiment, elementary sulfur – due to its slow oxidation – had less pronounced influence on changes in the available potassium content of soil, which is consistent with the findings of JAGGI et al. (1999) and WEI ZHOU et al. (2002). The available potassium content of the 40-80 cm soil layer was substantially lower than in the uppermost soil layer in the same treatments, ranging between 38.1 and 67.1 mg K kg^{-1} soil (Table 7). Both the form and dose of sulfur had a significant effect on changes in available potassium concentrations in soil. In most cases, the application of sulfate sulfur and elementary sulfur contributed to a significant decrease in the potassium content of soil in comparison with the NPK treatment, except in the treatment fertilized with a single dose of elementary sulfur, where available potassium levels were comparable to those noted in the NPK treatment.

Soil samples collected in the spring of 2001 at the depth of 0-40 cm were characterized by a higher available potassium content than the samples analyzed in the fall (Table 6), which could have resulted from the mobilization of potassium reserves by precipitation. The applied sulfur doses caused irregular changes in the available potassium content of soil. A considerable decrease in potassium levels was observed only in the treatment fertilized with 120 kg ha^{-1} S-S^0. The 0-40 cm soil horizon contained larger quantities of available potassium than the soil samples collected before setting up the experiment and after the first year of the study.

Table 6

Effect of different rates and forms of sulfur on the content of available potassium in soil 0-40 cm (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	39.1	40.8	33.6	44.6	14.2
NPK	73.0	67.6	117.7	92.3	102.1
NPK+ S_1-SO_4	67.6	86.2	95.8	81.8	106.6
NPK+ S_2-SO_4	52.6	68.0	68.6	75.7	107.1
NPK+ S_3-SO_4	52.6	70.0	43.6	76.9	64.1
NPK+S_1-S-^{0}	67.0	69.0	48.3	93.3	50.2
NPK+S_2-S-^{0}	69.1	74.6	55.0	59.5	99.6
NPK+S_3-S-^{0}	71.0	50.8	111.6	95.6	79.8
LSD-$_{p\text{-}0.05}$					
a	3.11	r.n.	3.52	3.28	3.98
b	4.40	4.64	4.98	4.64	5.63
a x *b*	6.23	6.56	7.04	6.56	7.96

Explanations see Table 2

In the fall, after onion harvest, the available potassium content of the 0-40 cm soil layer was in the range of 33.6-117.1 mg K kg^{-1} (Table 6). Sulfur fertilization caused a substantial decrease in potassium levels, compared with the NPK treatment, which could have been due to the leaching of potassium ions. Similar results were obtained by Zawartka and Skwierawska (2004, 2005) in laboratory experiments. In the treatment fertilized with 120 kg ha^{-1} elementary sulfur, available potassium levels were comparable with those noted in the NPK treatment. This indicates a slower release of elementary sulfur than sulfate sulfur, observed also by Kaczor, Brodowska (2008). The concentrations of available potassium in the 40-80 cm soil layer varied over a narrower range than in the 0-40 cm horizon, and they depended on the applied fertilizer (Table 7). S-SO_4 at a rate of 120 kg and elementary sulfur in all the doses decreased the available potassium content of soil in comparison with the NPK treatment. Increasing sulfur doses reduced the accumulation of available potassium in the 40-80 cm soil layer.

Table 7

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

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	46.3	-	31.1	14.7	12.7
NPK	64.0	-	49.3	41.7	54.7
NPK+ S_1-SO_4	42.5	-	48.8	24.5	40.5
NPK+ S_2-SO_4	49.0	-	48.8	28.1	27.6
NPK+ S_3-SO_4	41.3	-	43.0	29.9	11.7
NPK+S_1-S^{-0}	67.1	-	45.8	31.8	24.3
NPK+S_2-S^{-0}	43.8	-	35.6	15.7	16.8
NPK+S_3-S^{-0}	38.1	-	33.6	21.3	13.2
LSD-$_{p\text{-}0.05}$					
a	2.39	-	1.42	2.44	2.48
b	3.39		2.01	3.46	3.51
a x *b*	4.79		2.84	4.89	4.96

Explanations see Table 2

In the spring, before barley sowing, the available potassium content of the 0-40 cm soil horizon was insignificantly higher than in the previous years (Table 6). The changes in potassium levels were random. Sulfur application decreased the potassium content of soil compared with the NPK treatment, except in the treatments fertilized with 40 and 120 kg elementary sulfur. Elementary sulfur, in comparison with sulfate sulfur, caused a significant increase in potassium concentrations in soil. Potassium levels were much lower in the 40-80 cm soil layer than in the 0-40 cm horizon (Table 7). The application of both sulfate sulfur and elementary sulfur (in particular a double dose of elementary sulfur) significantly reduced available potassium concentrations in the soil in comparison with the NPK treatment.

In the fall, after barley harvest, a considerable increase in the available potassium content of the 0-40 cm soil layer was noted in the treatments fertilized with 40 and 80 kg ha^{-1} sulfate sulfur and 80 kg elementary sulfur. The application of elementary sulfur caused irregular changes in potassium

Table 8

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

Treatment	0	NPK	I-S-SO_4	II-S-SO_4	III-S-SO_4	I-S-S^0	II-S-S^0	III-S-S^0
0								
NPK	0.000005*							
I-S-SO_4	0.000004*	0.249665						
II-S-SO_4	0.000071*	0.020458*	0.202487					
III-S-SO_4	0.005104*	0.000382*	0.015615*	0.211127				
I-S-S^0	0.000354*	0.007571*	0.109835	0.653441	0.378857			
II-S-S^0	0.000830*	0.003434*	0.066570	0.486041	0.519224	0.766755		
III-S-S^0	0.000116*	0.016446*	0.178949	0.877153	0.252962	0.743474	0.560684	
$\overline{x}$**	3.182	6.601	6.009	5.354	4.623	5.106	4.954	5.275

* significant difference,
** $\overline{x}$ – average content of sulfate sulfur in soil in particular objects for the years 2000-2003 (mg kg^{-1} soil),
SO_4 – sulfate sulfur, S^0 – elementary sulfur, S_1 – 40 kg ha^{-1}, S_2 – 80 kg ha^{-1}, S_3 – 120 kg ha^{-1}

levels. Sulfate sulfur, compared with elementary sulfur, contributed to a significant increase in potassium concentrations. Soil samples collected at the depth of 40-80 cm (Table 7) were characterized by a considerably lower available potassium content than those collected at the depth of 0-40 cm (Table 6). NPK+S fertilization, in particular the application of a triple dose of sulfate sulfur and elementary sulfur, significantly decreased available potassium levels compared with the control treatment.

During the three years of the experiment, application of either sulfur form led to a significant decrease in the available potassium content of the 0-40 cm soil layer in comparison with the NPK treatment (Table 6), except the treatments fertilized with a single dose of sulfate sulfur and a triple dose of elementary sulfur. Increasing doses of sulfate sulfur tended to decrease potassium levels while the application of elementary sulfur contributed to an increase in potassium concentrations. The application of both sulfur forms caused a decrease in the available potassium content of the 40-80 cm soil layer compared with the NPK treatment (Table 7). Increasing doses of sulfate sulfur and elementary sulfur (in particular the latter) reduced potassium concentrations in soil. The fluctuations in available potassium content could have been due to the acidifying effect of sulfur, also observed in our previous study (SKWIERAWSKA et al. 2006). As shown by the results of Duncan's test, the differences noted between the treatments over the three-year experimental period were statistically significant (Table 8). The average available potassium content of soil was the lowest in the treatment fertilized with a triple dose of sulfate sulfur (a statistically significant difference).

CONCLUSIONS

1. In most cases, NPK+S fertilization, in particular the application of 120 kg S ha^{-1}, contributed to an increase in total sulfur concentrations in both sampled soil horizons (0-40 and 40-80 cm) compared with the NPK treatment.

2. The application of sulfate sulfur caused an increase in the $S\text{-}SO_4$ content of the 0-40 cm soil layer as early as the first year of the study, while the effect of elementary sulfur was not noted until the third year. The above trend was not observed with respect to the 40-80 cm soil horizon. Sulfate accumulation in soil increased over time, proportionally to the increasing rates of sulfur fertilizers.

3. During the three years of the experiment, the application of both sulfur forms decreased the available potassium content of soil samples collected at the depth of 0-40 cm in comparison with the NPK treatment, whereas the available potassium content of the 40-80 cm soil layer varied.

4. Sulfate sulfur exerted a stronger effect on available potassium levels in soil than elementary sulfur.

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PRELIMINARY EVALUATION OF THE INFLUENCE OF IODINE AND NITROGEN FERTILIZATION ON THE EFFECTIVENESS OF IODINE BIOFORTIFICATION AND MINERAL COMPOSITION OF CARROT STORAGE ROOTS

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Abstract

Biofortification of vegetables with iodine can become an alternative method to salt iodization of introducing this element to human diet. Iodine is not an essential nutrient for plants and its effect on plant growth and development has not yet been sufficiently examined. The aim of the study was to assess the influence of soil fertilization with iodine (in the form of I^- and IO_3^-) and nitrogen (applied as NO_3^- and NH_4^+) on the effectiveness of iodine biofortification as well as mineral composition of carrot storage roots. Carrot cv. Kazan F_1 was cultivated in a field experiment in 2008 and 2009. Different soil fertilization treatments with iodine as well as nitrogen were tested, including: 1 – control without N and I fertilization; 2 – KI fertilization without N application; 3 – KIO_3 fertilization without N application; 4 – KI + $Ca(NO_3)_2$ fertilization; 5 – KIO_3 + $Ca(NO_3)_2$ fertilization, 6 – KI + + $(NH_4)_2SO_4$ fertilization, 7 – KIO_3 + $(NH_4)_2SO_4$ fertilization. Iodine as KI and KIO_3 was applied pre-sowing in a dose of 2 kg I ha^{-1}. Nitrogen fertilization in the form of $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ was performed pre-sowing and as top dressing with 100 kg N ha^{-1}. In carrot storage roots, the iodine content as well as P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Mo, Al, Cd and Pb concentration were determined by the ICP-OES technique, while nitrogen – using Kjeldahl method. Better results of iodine enrichment in carrot were obtained

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after introducing this element in the form of KI, especially together with ammonium sulphate. Application of the IO_3^- form of iodine significantly improved nitrogen utilization from mineral fertilizers by carrot plants. In storage roots of carrots cultivated without N nutrition, iodine treatment (in both forms: KI and KIO_3) contributed to a significant increase in P, K and Ca content as well as a reduction in Fe accumulation. However, it had no influence on the concentration of Mg, S, Cu, Mn, Zn, Mo, Al and Pb in carrot storage roots. Application of KIO_3, in comparison to KI, resulted in a significant increase of the K, Fe and Zn content in carrot roots fertilized with $Ca(NO_3)_2$. In the case of $(NH_4)_2SO_4$ as a nitrogen source, KIO_3 contributed to significantly higher accumulation of P, K, Mg, S, Na, B, Cu, Fe, Mn, Al and Cd in carrot storage roots when compared to KI.

Key words: biofortification, iodine, nitrogen fertilization, mineral composition, carrot.

WSTĘPNA OCENA WPŁYWU NAWOŻENIA JODEM I AZOTEM NA EFEKTYWNOŚĆ BIOFORTYFIKACJI MARCHWI W JOD ORAZ NA JEJ SKŁAD MINERALNY

Abstrakt

Warzywa biofortyfikowane jodem mogą być alternatywnym, do jodowania soli, sposobem wprowadzenia tego pierwiastka do diety człowieka. Jod nie jest pierwiastkiem niezbędnym dla roślin. Jego oddziaływanie na rośliny nie zostało dostatecznie zdiagnozowane. Celem badań było określenie wpływu doglebowego nawożenia jodem (w formie I^- i IO_3^-) i azotem (w formie NO_3^- i NH_4^+) na efektywność biofortyfikacji jodem oraz na skład mineralny marchwi. Marchew odmiany Kazan F_1 uprawiano w doświadczeniu polowym w latach 2008-2009. W badaniach zastosowano zróżnicowane doglebowe nawożenie jodem (I w formie I^- lub IO_3^-) i azotem (N w formie NO_3^- lub NH_4^+): 1 – kontrola bez nawożenia N i I, 2 – nawożenie KI bez nawożenia N, 3 – nawożenie KIO_3 bez nawożenia N, 4 – nawożenie KI + $Ca(NO_3)_2$, 5 – nawożenie KIO_3 + $Ca(NO_3)_2$, 6 – nawożenie KI + $(NH_4)_2SO_4$, 7 – nawożenie KIO_3 + $(NH_4)_2SO_4$. Jod w formie KI i KIO_3 aplikowano przedsiewnie w dawce 2 kg I ha^{-1}, azot w formie $Ca(NO_3)_2$ i $(NH_4)_2SO_4$ – w dawce po 100 kg N ha^{-1} przedsiewnie i pogłównie. W marchwi oznaczono: zawartość jodu oraz P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Mo, Al, Cd i Pb techniką ICP-OES; zawartość azotu metodą Kiejdahla. Lepsze efekty wzbogacania marchwi w jod uzyskano po zastosowaniu jodu w formie KI, zwłaszcza gdy stosowano ten związek w połączeniu z siarczanem amonu. Zastosowanie jodu w formie IO_3^- istotnie poprawiało efektywność wykorzystania azotu przez rośliny z zastosowanych nawozów mineralnych. W korzeniach spichrzowych roślin nienawożonych azotem zastosowanie jodu (w formie KI i KIO_3) powodowało istotne zwiększenie zawartości P, K, Ca oraz zmniejszenie zawartości Fe; natomiast nie miało wpływu na zawartość Mg, S, Cu, Mn, Zn, Mo, Al i Pb. Zastosowanie KIO_3, w porównaniu z KI, powodowało istotne zwiększenie zawartości K, Fe i Zn w marchwi nawożonej $Ca(NO_3)_2$. W przypadku nawożenia $(NH_4)_2SO_4$ aplikacja KIO_3, w porównaniu z KI, powodowała istotne zwiększenie zawartości P, K, Mg, S, Na, B, Cu, Fe, Mn, Al i Cd w marchwi.

Słowa kluczowe: biofortyfikacja, jod, nawożenie azotem, skład mineralny, marchew.

INTRODUCTION

In Poland and many other countries around the world, iodine content in human diet is currently raised through salt iodization. Excessive salt consumption, however, has recently led to increased incidences of cardiovascular diseases. For that reason, the Global Strategy on Diet, Physical Activity and Health for the years 2008-2013 has been proposed by WHO. This program includes significant reduction of salt intake and recommends searching for alternative ways of introducing iodine to human diet. The need for global development of effective methods to enrich our diet in this element results from numerous functions that iodine plays in a human organism. Moreover, 35.2% of the global population suffers from an inadequate iodine nutrition (WINGER et al. 2008).

Iodine biofortification of vegetables can be perceived as one of the alternative ways of introducing iodine into human diet. Biofortification is defined as such a process that increases the content of biogenic elements such as Fe, Zn, Ca, Mg, Cu, I or Se in edible parts of crop plants. As a result, the consumer's health is expected to improve. Increased accumulation of biogenic elements in plants can be achieved through application of agronomic, genetic or transgenic strategies (STRZETELSKI 2005,WHITE, BROADLEY 2005, 2009, YANG et al. 2007, ZHAO, MCGRATH 2009).

Iodine is not an essential nutrient for plant growth and development and its influence on plants has not yet been diagnosed (KABATA, MUKHERJEE 2007). In general, the research on iodine neglects problems in biofortification due to the interaction of iodine with physiological and biochemical processes occurring in plants, including mineral nutrition. Evaluation of these interrelations is crucial for developing optimal agrotechniques of plant biofortification with iodine.

At present, there are no norms for an acceptable level of iodine in vegetables. In the future, results of studies on iodine biofortification can help develop these standards in order to adequately balance the content of this element in human diet.

The aim of the study has been to determine the influence of soil fertilization with iodine (in the form of I^- and IO_3^-) and nitrogen (as NO_3^- and NH_4^+) on iodine biofortification efficiency and mineral composition of carrot storage roots.

MATERIAL AND METHODS

In 2008-2009, a field experiment was conducted in Kraków (Poland), on carrot cv. Kazan F_1 grown in crop rotation on uniform soil complex. The carrot was cultivated on silt loam soil (35% sand, 28% silt and 37% clay) with the content of organic matter 2.84%-3.41% in the 0-30 cm soil layer and the following concentrations of the available forms of nutrients soluble in 0.03 M acetic acid: N (NO_3-N+NH_4-N) – 8.1-3.8 mg, P – 51.4-45.0 mg, K – 111.8-185.4 mg, Mg – 115.6-107.4 mg and Ca – 1255.8-837.9 mg in 1 dm^{-3} of soil (in 2008 and 2009, respectively). In the subsequent years, the soil

$pH_{(H_2O)}$ was 6.98-7.10 while the general concentration of salt in soil (EC) was 0.12-0.11 mS cm^{-1}. The carrot was grown on ridges, 40 cm wide and 30 cm high, where seeds were sown in one row at a rate of 37 seeds m^{-1} (approximately 550 000 seeds per 1 hectare). Seed sowing was performed on 24 April in both years of the study.

Several variants of soil fertilization with iodine (in the form of I^- or IO_3) and nitrogen (as NO_3^- or NH_4^+) were applied in the experiment: 1 – control without N and I fertilization; 2 – KI application without N fertilization; 3 – KIO_3 application without N fertilization; 4 – KI + $Ca(NO_3)_2$ fertilization; 5 – KIO_3 + $Ca(NO_3)_2$ fertilization; 6 – KI + $(NH_4)_2SO_4$ fertilization; 7 – KIO_3 + $(NH_4)_2SO_4$ fertilization. Iodine (in both forms) was applied pre-sowing in a dose of 2 kg I ha^{-1}. The iodine dose used in the experiment was chosen on the basis of our previous studies (Smoleń et. al. 2009b, Strzetelski et. al. 2010) as well as the results obtained by other authors (Borst Pauwels 1961, Smith, Middleton 1982, Altmok et al. 2003).

Nitrogen in the forms of $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ was introduced pre-sowing and as top dressing, each dose of 100 kg N ha^{-1}. The pre-sowing nitrogen fertilization (and iodine application) was conducted immediately before the ridge formation, whereas the top dressing – at canopy closure. The experiment was arranged in a split-plot design. Each experimental treatment was randomized in four replications on 2.7 m × 5 m (13.5 m^2) plots. The total area used for the experiment was 378 m^2.

The carrot was harvested on 30 and 23 September (in 2008 and 2009, respectively). During harvest, about 5 kg of carrot storage roots were taken in four replications (from each plot) for further analyses alongside soil samples from three layers (0-30 cm, 30-60 cm and 60-90 cm), which were collected using a soil drill.

In carrot storage roots, iodine content was assessed after sample incubation with 25% TMAH according to the standard project prEN 15111-R2-P5--F01, while N-total was determined using Kjeldahl method (Persson, Wennerholm 1999). The concentration of P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Mo, Al, Cd and Pb was determined after mineralization in 65% super pure HNO_3 (Merck no 100443.2500) in a CEM MARS-5 Xpress microwave oven (Pasławski, Migaszewski 2006).

In soil samples, pH was determined with a potentiometer and concentrations of I, N-NH_4, N-NO_3, P, K, Mg, Ca, S and Na were determined after extraction with 0.03 M acetic acid (Nowosielski 1988). The content of B, Cu, Fe, Mn, Zn, Mo, Al, Cd and Pb was assayed after soil extraction with 1 M HCl (Gorlach et al. 1999).

Iodine as well as P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Mo, Al, Cd and Pb in carrot and soil samples were determined with the ICP-OES technique using a Prodigy Teledyne Leeman Labs USA spectrometer. The concentration of nitrogen forms in soil samples (N-NH_4, N-NO_3) was determined with the FIA technique [PN-EN ISO 13395: 2001; PN-EN ISO 11732:2005 (U)].

The results were statistically verified using the ANOVA module of Statistica 9.0 PL programme at the significance level $P < 0.05$. Significance of changes was assessed with the use of variance analysis. For significant changes, homogenous groups were distinguished on the basis of Duncan test.

RESULTS AND DISCUSSION

In comparison to the control, significantly increased iodine content in carrot storage roots was observed in all combinations with iodine fertilization in the form of KI (Table 1). The highest amount of this element was detected in roots of plants fertilized with KI and $(NH_4)_2SO_4$ (combination 6). A slightly lower but still comparable level of iodine in carrot roots was found after fertilization with KI only (combination no.2) as well as KI together with calcium nitrate (combination no.4). It was revealed that soil application of KIO_3 (along with nitrogen fertilizers) resulted in just a slight build-up of iodine in carrot storage roots. In storage roots of plants treated with KIO_3, a tendency for increasing iodine concentration (in comparison to the control) was observed but no statistical significance was noted. It should be mentioned that in all the tested combinations, iodine content in the 0-90 cm soil layer remained at a comparable level (Table 2). In our previous studies with pot cultivation of carrot (SMOLEŃ et al. 2009a) conducted in an analogous experiment design with iodine and nitrogen fertilization (on soil characterized by similar physicochemical properties), iodine applied as KI and KIO_3 did not contribute to biofortification of carrot storage roots and leaves with this element. Exceptionally, increased concentration of iodine was found only in leaves of carrot treated with KIO_3 (without N) as well as $Ca(NO_3)_2$+KI. It should be underlined, however, that in that pot experiment iodine concentration in carrot was assayed after incubation of root and leaf samples in 2% acetic acid, not 25% solution of TMAH as in the present work. Thus, the analytical procedure applied for iodine determination (apart from different cultivation conditions) could be responsible for obtaining different results in reference to the effect of I and N fertilization on iodine biofortification of carrot.

Iodine application regarded together with differential nitrogen fertilization significantly affected the content of: N, P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Al, Cd and Pb in carrot (Table 1). However, the iodine and nitrogen treatments tested in the experiment did not influence Mo concentration in carrot storage roots.

In the aforementioned pot cultivation of carrot (SMOLEŃ 2009, SMOLEŃ et al. 2009a), application of iodine in the form of KIO_3 (in reference to KI),

Table 1

Mineral composition and the effectiveness of iodine biofortification of carrot storage roots depending on nitrogen and iodine fertilization – means from 2008-2009

Combinations	Content of iodine (mg I kg^{-1} d.w.)	Content of macroelements in % d.w. of carrot storage roots						
		N	P	K	Mg	Ca	S	Na
1. Control (without N and I)	2.0 *a*	1.42 *a*	0.350 *ab*	2.30 *b*	0.113 *a*	0.318 *ab*	0.13 *a*	0.76 *d*
2. KI (without N)	4.3 *cd*	1.46 *b*	0.380 *c*	2.46 *d*	0.111 *a*	0.345 *bc*	0.13 *a*	0.76 *d*
3. KIO_3 (without N)	2.6 *ab*	1.40 *a*	0.364 *bc*	2.38 *c*	0.112 *a*	0.348 *c*	0.13 *a*	0.81 *e*
4. $Ca(NO_3)_2$+KI	3.8 *bcd*	1.77 *c*	0.367 *bc*	2.45 *d*	0.128 *b*	0.337 *abc*	0.13 *a*	0.73 *c*
5. $Ca(NO_3)_2$+KIO_3	3.4 *abc*	2.00 *d*	0.377 *bc*	2.50 *e*	0.132 *bc*	0.351 *c*	0.14 *a*	0.72 *c*
6. $(NH_4)_2$SO4+KI	5.0 *d*	1.75 *c*	0.327 *a*	2.23 *a*	0.116 *a*	0.313 *a*	0.14 *a*	0.69 *a*
7. $(NH_4)_2SO_4$+KIO_3	3.1 *abc*	1.99 *d*	0.381 *c*	2.55 *f*	0.135 *c*	0.339 *abc*	0.15 *b*	0.70 *b*
Test *F*	*	*	*	*	*	*	*	*

Content of microelements, Al, Cd and Pb in mg kg^{-1} d.w. of carrot storage roots									
	B	Cu	Fe	Mn	Zn	Mo**	Al	Cd	Pb
1. Control (without N and I)	24.5 *c*	4.8 *a*	47.2 *c*	6.3 *ab*	24.3 *a*	0.315	44.0 *c*	1.15 *a*	0.273 *c*
2. KI (without N)	23.9 *b*	4.9 *ab*	39.5 *ab*	6.0 *a*	25.9 *a*	0.373	40.7 *bc*	1.27 *b*	0.226 *bc*
3. KIO_3 (without N)	24.2 *bc*	4.6 *a*	40.8 *ab*	6.3 *ab*	24.4 *a*	0.325	43.8 *c*	1.16 *a*	0.161 *abc*
4. $Ca(NO_3)_2$+KI	24.2 *bc*	5.3 *bc*	40.1 *ab*	6.4 *bc*	29.9 *b*	0.360	28.0 *b*	1.25 *ab*	0.230 *bc*
5. $Ca(NO_3)_2$+KIO_3	24.1 *bc*	5.6 *c*	41.8 *c*	6.6 *c*	33.2 *c*	0.385	39.8 *bc*	1.34 *b*	0.230 *bc*
6. $(NH_4)_2SO_4$+KI	23.0 *a*	5.2 *b*	33.5 *a*	11.5 *d*	30.9 *bc*	0.282	27.4 *a*	1.50 *c*	0.086 *a*
7. $(NH_4)_2SO_4$+KIO_3	25.1 *d*	6.1 *d*	42.5 *c*	16.2 *e*	37.7 *d*	0.321	38.3 *b*	1.68 *d*	0.106 *ab*
Test *F*	*	*	*	*	*	n.s.	*	*	*

Means followed by the same letters are not significantly different for $P < 0.05$.
* means are significantly different, n.s. – not significant, ** results for Mo from 2009 only

Table 2

Results of chemical analysis of soil after carrot cultivation – means for the 0-90 cm soil layer from 2008-2009

Combinations	pH_{H_2O}	(mg dm^{-3} soil)								
		I	$N-NH_4$	$N-NO_3$	P	K	Mg	Ca	S	Na
1. Control (without N and I)	7.23 *de*	1.15	0.3 *a*	1.3 *a*	16.2	23.2 *a*	75.3	998.5 *a*	7.8 *a*	4.5 *a*
2. KI (without N)	7.27 *e*	1.09	0.8 *a*	3.1 *b*	15.3	34.9 *d*	84.4	1111.5 *bc*	7.6 *a*	5.7 *bc*
3. KIO_3 (without N)	7.19 *de*	1.14	1.0 *a*	2.7 *b*	14.6	29.3 *b*	86.2	1104.5 *bc*	7.6 *a*	6.4 *c*
4. $Ca(NO_3)_2$+KI	7.14 *cd*	1.45	0.5 *a*	7.7 *c*	16.0	26.7 *ab*	82.8	1053.3 *abc*	5.9 *a*	4.7 *ab*
5. $Ca(NO_3)_2$+KIO_3	7.06 *bc*	0.52	3.0 *b*	16.0 *d*	13.9	30.8 *bc*	79.9	1008.2 *ab*	7.7 *a*	6.2 *c*
6. $(NH_4)_2$SO4+KI	7.01 *b*	0.90	0.7 *a*	8.4 *c*	16.4	35.8 *d*	89.6	1149.2 *c*	32.6 *b*	4.6 *a*
7. $(NH_4)_2SO_4$+KIO_3	6.64 *a*	0.72	7.7 *c*	18.9 *e*	13.3	35.5 *d*	86.6	1083.2 *abc*	84.8 *c*	6.4 *c*
Test *F*	*	n.s.	*	*	n.s.	*	n.s.	*	*	*
(mg kg^{-1} soil)										
	B	Cu	Fe	Mn	Zn	Mo	Al	Cd	Pb	
1. Control (without N and I)	1.3	6.63 *bc*	2073.6 *d*	239.8 *de*	38.9 *a*	1.33 *d*	1453.4 d	0.735 *ab*	39.1 *b*	
2. KI (without N)	1.3	5.99 *ab*	1920.1 *ab*	240.6 *de*	49.3 *b*	1.18 *ab*	1384.6 *a*	0.743 *abc*	74.7 *c*	
3. KIO_3 (without N)	1.9	6.82 *c*	1996.3 *c*	229.7 *b*	38.8 *a*	1.16 *a*	1406.1 *ab*	0.736 *ab*	21.7 *a*	
4. $Ca(NO_3)_2$+KI	1.2	7.09 *c*	1882.8 *a*	236.3 *c*	39.2 *a*	1.19 *abc*	1403.6 *ab*	0.729 *b*	63.4 *c*	
5. $Ca(NO_3)_2$+KIO_3	1.2	5.96 *ab*	1935.6 *b*	221.7 *a*	39.0 *a*	1.22 *bc*	1422.5 *bc*	0.727 *a*	20.9 *a*	
6. $(NH_4)_2SO_4$+KI	1.2	5.63 *a*	2035.5 *cd*	245.8 *e*	40.4 *a*	1.22 *c*	1436.3 *cd*	0.752 *bc*	21.8 *a*	
7. $(NH_4)_2SO_4$+KIO_3	1.0	6.40 *bc*	2150.1 *f*	262.1 *f*	38.9 *a*	1.38 *f*	1509.2 *f*	0.758 *c*	119.3 *d*	
Test *F*	n.s.	*	*	*	*	*	*	*	*	

Means followed by the same letters are not significantly different for $P < 0.05$.
* means are significantly different, n.s. – not significant,y

both with and without N nutrition, resulted in a higher content of N-total in storage roots but had no influence on the level of this element in leaves. In the present work, soil application of KI without nitrogen, in comparison to the control and KIO_3, contributed to a higher content of N-total in carrot (Table 1). In the case of plants fertilized with nitrogen (both as calcium nitrate and ammonium sulphate), soil application of KIO_3 (when compared to KI) significantly increased the level of N-total in carrot storage roots. The effects shown above could have been related to a higher concentration of mineral nitrogen in soil from these combinations (Table 2). The results indicate that the IO_3^- form of iodine most affected the ammonium nitrogen stabilization in soil, possibly by depressing nitrification processes – in combination with the ammonium sulphate application. Notably, the concentration of N-NO_3 in soil fertilized with $Ca(NO_3)_2$ + KIO_3 was only slightly lower when compared to the application of $(NH_4)_2SO_4$ + KIO_3. Moreover, the level of this N form in soil in the above combinations was distinctively higher when compared to KI fertilization along with the both tested nitrogen fertilizers. Iodine in the form of IO_3^- may have limited total denitrification of NO_3^- to N_2. It is worth mentioning that trace amounts of mineral nitrogen were found in soil after carrot cultivation in pots (SMOLEŃ et al. 2009a). In the available literature, no information can be on the influence of iodine (in I^- or IO_3^- form) on the conversion of mineral nitrogen in the soil environment.Therefore, it is difficult to compare our results with those reported by other authors.

In storage roots of plants grown without N, iodine application (in both forms: KI and KIO_3) led to a significant increase in the P, K and Ca content as well as a reduction in the Fe concentration. It had no influence, however, on the accumulation of Mg, S, Cu, Mn, Zn, Mo, Al and Pb in carrot (Table 1). Changes in the K, Ca and Fe concentration in carrot observed in our trials were clearly attributable to the influence of KI and KIO_3, such as an elevated content of easily soluble forms of K and Ca, as well a reduced level of Fe in soil (Table 2). It should be added that in the study conducted by SMOLEŃ (2009), fertilization with KIO_3 but without N led to higher accumulation of Al and Li as well as a reduced Cu content in carrot while the application of KI depressed the level of B, Fe, Ti and V in storage roots.

Interesting results were found with reference to iodine influence (in KI and KIO_3 forms) on mineral composition of carrot roots in dependence on the type of nitrogen fertilizer (Table 1). A significant increase in K, Fe and Zn concentration in carrot was noted after using $Ca(NO_3)_2$ + KIO_3 rather than $Ca(NO_3)_2$ + KI. In case of K and Fe, obtained results might have been related to higher level of easily soluble forms of these elements in soil (Table 2). In respect to plants fertilized with calcium nitrate, type of used iodine forms had no significant effect (when comparing KI and KIO_3) on the content of: P, Mg, Ca, S, Na, B, Cu, Mn, Mo, Al, Cd and Pb in carrot storage roots.

Soil application of KIO_3 (in comparison to KI) to plants fertilized with ammonium sulphate contributed to an increased concentration of P, K, Mg, S, Na, B, Cu, Fe, Mn, Zn, Al and Cd in carrot (Table 1). Among these elements, a significantly higher level of easily soluble forms of S, Na, Cu, Fe, Mn and Al was found in soil after cultivation of carrot fertilized with $(NH_4)_2SO_4$ + KIO_3 (when compared to $(NH_4)_2SO_4$ + KI), which could have directly affected its content in carrot roots. The concentrations of P, K, Mg, B, Zn and Cd in soil from these both combinations remained comparable.

The results of our experiment allow us to assume that an increased content of P, K, Mg, B, Zn and Cd in carrot fertilized with $(NH_4)_2SO_4$ + + KIO_3 could have been caused by the synergistic interaction of the IO_3^- form of iodine and SO_4^{2-} ions, affecting the uptake of these elements by plants. Furthermore, nitrogen fertilization in either form (calcium nitrate, ammonium sulphate) and application of iodate could have stimulated the uptake of zinc from soil. With these results, it is impossible to objectively claim whether higher accumulation of Zn in carrot was related to some synergism between IO_3^- and NO_3^-/SO_4^{2-} or with cations (Ca^{2+}, NH_4^+) introduced to soil with mineral fertilizers. Nonetheless, it is noteworthy that in the earlier pot experiment with carrot (SMOLEŃ 2009) no significant effect of KI and KIO_3 application (with different N fertilization) on the Zn content in carrot was found. In the above study, nitrogen application, both in the $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ forms, modified the influence of iodine on the uptake and accumulation of Ca, K, Mg, Na, P and S (SMOLEŃ et al. 2009a) as well as Al, B, Cd, Cr, Cu, Fe, Li, Ti and V (SMOLEŃ 2009) in comparison to the combinations without N fertilization.

In the present study, contrary results were obtained with respect to the effect of iodine application as KI and KIO_3 (with different nitrogen fertilization) on mineral composition of storage roots in comparison to our previous experiments with pot cultivation of carrot (SMOLEŃ 2009, SMOLEŃ et al. 2009a). This inconsistency could be related to the different methods of carrot cultivation, particularly resulting from the limited capacity of growth by carrot roots in the pot experiment.

CONCLUSIONS

1. In comparison to the control, a significant increase in the iodine content in carrot storage roots was found in all the combinations with iodine application in the form of KI.

2. The best effects of iodine biofortification of carrot was obtained through iodine application in the form of KI, particularly together with N fertilization with ammonium sulphate.

3. Iodine application as KIO_3 (when compared to KI) significantly improved nitrogen utilization from mineral fertilizers by carrot plants.

4. The influence of the iodine form on the N-total content in carrot roots was varied, depending on whether cultivation was carried out without N fertilization or using ammonium sulphate and calcium nitrate.

5. In the combinations without N nutrition, iodine application (both as KI and KIO_3) contributed to a significant increase in the P, K and Ca content and a reduction in the Fe concentration but had no effect on the Mg, S, Cu, Mn, Zn, Mo, Al and Pb accumulation in carrot storage roots.

6. KIO_3 application, when compared to KI, to plants fertilized with ammonium sulphate increased the concentration of: N, P, K, Mg, S, Na, B, Cu, Fe, Mn, Zn, Al and Cd in carrot. In the case of fertilization with calcium nitrate, KIO_3 treatment led to higher levels of N, K, Fe and Zn in carrot storage roots than application of KI.

7. In the combinations without N fertilization, changes in the carrot content of K, Ca and Fe were related to the influence of iodine on the availability of easily soluble forms of these elements in soil. In the case of $Ca(NO_3)_2$ application, it caused accumulation of K and Fe. When $(NH_4)_2SO_4$ was used, the concentrations of S, Na, Cu, Fe, Mn and Al in carrot roots were all affected by some interaction of iodine with these elements in soil.

8. Iodine application in the form of KI and KIO_3 together with N fertilization had a variable influence on soil pH as well as the content of N-NH_4, N-NO_3, K, S, Na, Cu, Fe, Mn, Mo, Al, Cd and Pb in soil after carrot cultivation.

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CONTENT OF Zn, Cu, Fe AND Mn IN PROCESSED FRUIT AND MIXED FRUIT AND VEGETABLE FOODSTUFFS FOR INFANTS

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Abstract

A baby's diet can be greatly varied by offering new tastes. Children tend to consume willingly fruit such as apples or bananas. The first fruit tastes may be recognized by children by enriching their menu with dessert products containing pressed fruit, delicate in taste and smooth in texture so that they are easy to swallow.

The research material consisted of fruit and vegetable desserts for infants and young children. Fifteen different types of desserts (in jars) from eight different manufacturers were tested. The content of Zn, Cu, Fe and Mn was determined by means of the AAS flame technique in a Unicam 939 (AA Spectrometer Unicam) apparatus. Although the permissible levels of Zn, Fe and Mn (Journal of Law 2007) were not exceeded in the dessert products, nearly all the products contained too much copper. The analyzed products contained the average of 282.2 mg of Zn per 100 kcal, 648.9 mg of Fe, 129.5 mg of Cu and 195.4 mg of Mn. Assuming that a baby aged 9-12 months consumes one jar of dessert daily, she/he ingests almost 0.27 mg of Zn (9% of the RDA), *ca* 0.63 mg of Fe (5.7% of the RDA), 0.12 mg of Cu (40% of the AI) and 0.21 mg of Mn from the product.

Fruit and vegetable products are an important source of mineral elements in the baby's diet. Because they usually contain less Zn and Mn in reference than demanded, they are a supplementary product rather than a staple one in infant nutrition.

Key words: baby food, infants, microelements.

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ZAWARTOŚĆ Zn, Cu, Fe I Mn W GOTOWYCH PRODUKTACH OWOCOWYCH I OWOCOWO-WARZYWNYCH PRZEZNACZONYCH DLA NIEMOWLĄT

Abstrakt

Bardzo istotną rolą urozmaicania diety jest poznawanie nowych smaków. Dzieci zazwyczaj chętnie jadają owoce o łagodnym smaku, np. jabłka lub banany. Pierwsze owocowe smaki w jadłospisie dziecko może poznać dzięki delikatnym deserkom, które zawierają przetarte owoce, mają łagodny smak i gładką konsystencję ułatwiającą przełykanie.

Materiał do badań stanowiły owocowo-warzywne desery przeznaczone dla niemowląt i małych dzieci. Badano 15 różnych typów deserów (w słoikach), wyprodukowanych przez ośmiu producentów. Zawartość Zn, Cu, Mn oraz Fe oznaczono za pomocą płomieniowej techniki AAS w aparacie Unicam 939 (AA Spektrometr Unicam). W badanych deserach dopuszczalny w polskiej normie (PN 2007) poziom Zn, Fe oraz Mn nie został przekroczony, natomiast zawartość Cu była zbyt wysoka. Badane produkty zawierały średnio 282.2 mg Zn 100 kcal^{-1}, 648.9 mg Fe, 129.5 mg Cu oraz 195.4 mg Mn. Przyjmując, że dziecko w wieku 9-12 miesięcy spożywa dziennie jeden słoik deseru, wraz z tym posiłkiem przyjmuje ok. 0.27 mg Zn (9% RDA), 0.63 mg Fe (5.7% RDA), 0.12 mg Cu (40% AI) oraz 0.21 mg Mn.

Produkty owocowo-warzywne są ważnym źródłem składników mineralnych w diecie dziecka. Ponieważ zawierają zwykle zbyt mało Zn i Mn w stosunku do zapotrzebowania, nie są produktem podstawowym w żywieniu niemowląt, a jedynie uzupełniającym.

Słowa kluczowe: żywność, niemowlęta, mikroelementy.

INTRODUCTION

Healthy nutrition during infancy is of fundamental importance to the development of children. Childhood is the time when any deficiency or excess of essential macro- or microelements may result in processes permanently affecting certain functions of an organism, also during the adulthood (KSIĄŻYK 2001). In order to attain all necessary nutritional goals, the diet of infants above six months of age should be enriched by supplementing it with adequate products (KSIĄŻYK, WEKER 2007).

A baby's diet can be greatly varied by offering new tastes. Children tend to consume willingly fruit such as apples or bananas. The first fruit tastes may be recognized by children by enriching their menu with dessert products containing pressed fruit, delicate in taste and smooth in texture so that they are easy to swallow. Moreover, fruit desserts facilitate introduction of fruit into a diet and are a valuable source of vitamin C, antioxidants and fiber in any season of the year (ČIŽKOVA et al. 2009). Fruit and vegetable products are also an important source of mineral elements in children's diet.

A mineral element may be regarded as essential for a human organism when its deficiency leads to characteristic syndromes, which recede a soon as the deficiency has been eliminated or when the function it plays in the organism has been explained. Such criteria apply to, for example, zinc, iron, copper and manganese. A serious consequence of low zinc intake, particularly in young children, is diarrhea alongside raised vulnerability to infections (HAMBIDGE, KREBS 2007). Zinc is indispensable to the synthesis of proteins and nucleic acids; it also regulates muscle contractibility and participates in the synthesis of insulin-like growth factor 1 (IGF-1) (MACDONALD 2000). Low plasma zinc concentration was associated with more severe liver disease (SCHNEIDER et al. 2009). An excessive amount of zinc may limit the absorption of copper and iron. Iron is a component of hemoglobin and myoglobin. Its lack leads to anemia, in the first place, and also to poorer concentration and mental agility (BEARD 2001). Iron overdose is rare. Copper deficiency leads to growth impairment and nervous system disorders, whereas its excess may become a cause of anemia, disorders in liver functioning and lower immunity (ZATTA, FRANK 2007). Manganese plays an important role in a number of physiologic processes in mammals and it is involved in the function of numerous organ systems (ASCHNER, ASCHNER 2005). Mn is needed for regulation of blood sugar, normal immune function, bone growth and reproduction. Too high supply of manganese is the cause of respiratory tract irritations (SOLDIN, ASCHNER 2007). Cumulative exposure to manganese causes neurotoxicity in both humans and animals. Occupational exposure to manganese by inhalation has been associated with manganism (ZAWADZKI et al. 2008). This condition occurs as a result of inhalation exposure to high levels of manganese and is not relevant to the assessment of lower levels of manganese in food. The absorption and retention of manganese from foods, low in iron, are relatively high (FINLEY, DAVIS 1999).

The aim of the study was to determine the content of selected mineral elements (zinc, copper, iron and manganese) in fruit and vegetable dessert products intended for the nutrition of babies and infants.

MATERIALS AND METHODS

Food samples

The research material consisted of fruit and vegetable desserts for infants and young children, purchased in shops in Lublin, in 2009, before their use-by date. Fifteen different types of desserts (in jars) from eight different manufacturers were tested: A-1 (ingredients: apple, pear, apple juice, wheat starch - gluten free, corn starch), A-2 (white grape juice, pear, plum, apricot, tapioca starch, rose hip), B (apple, peach, grape juice, water, sugar, corn starch), C-1 (apple, apricot), C-2 (banana, pineapple juice, orange juice, apple, corn starch, lemon juice), D (organic yoghurt, water, apple, bilberry, sugar, carrot juice), E-1 (apple, apricot, yoghurt), E-2 (apple, apricot), F-1 (apple juice, apple, cherry), F-2 (pear, apple), G-1 (apple, banana), G-2 (white grape juice, pear, plum, apricot, tapioca starch, rose hip), G-3 (apple, rose hip, grape juice, wheat starch - gluten free, corn starch), H-1 (banana, water, peach, rise flour, lemon juice, apple juice), H-2 (water, apple, banana, pear juice concentrate, rice starch, apricot, lemon juice).

The tested baby foods were made in Poland, Germany, Slovakia, the Czech Republic and Switzerland (Table 1).

Table 1

Characteristics of the analyzed fruit and mixed fruit and vegetable baby food

Trade mark	Remarks	Weight of a jar (g)	Manufactured in
A-1	food for special purposes	125	Poland
A-2	food for special purposes	125	Poland
B	food for special purposes	130	Poland
C-1	food for special purposes	130	Poland
C-2	food for special purposes	130	Poland
D	food for special purposes, organic food	125	Poland
E-1	food for special purposes	190	Slovakia
E-2	food for special purposes	190	Slovakia
F-1	organic food	190	Germany
F-2	organic food	190	Germany
G-1	food for special purposes	125	Czech Republic
G-2	food for special purposes	125	Czech Republic
G-3	food for special purposes	125	Czech Republic
H-1	food for special purposes, organic food	190	Switzerland
H-2	food for special purposes, organic food	190	Switzerland

Methods

Baby food samples were shaken manually before analysis. The content of raw ash in the samples was determined with the use of the AOAC method (1990). Approximately 10g of the analyzed material was weighed, the samples were dried at the temperature of 105°C for 48 hours and later mineralized in a zinc furnace at the temperature of 550°C for 16 hours. 10 ml of 6 N HCl was added to the mineralized samples and the solution was filtered to measuring flasks, where distilled water was added to the total volume of 50 ml. Stock solution was used in the analyses. The content of Zn, Cu, Fe and Mn was determined with the AAS flame technique in a Unicam 939 (AA Spectrometer Unicam) apparatus.

All the chemical analyses were conduced in three replications.

Calculations and statistical analysis

Referring to the energy value declared by the manufacturers (Table 2), proportions were calculated in the analyzed preparations between their particular components and energy (kcal). Additionally, the content of individual components in one jar was calculated.

Assuming that a 9-12-month-old child (who may eat all the examined products) consumes on average one jar of dessert daily, the percentage of the recommended intake of Zn, Cu and Fe was calculated. The RDA (recommended daily allowance) of zinc is 3 mg/pers./day and of iron it is 11 mg/pers./day (Jarosz, Bułhak-Jachymczyk 2008). The RDA of Cu an infant's diet has not been determined in Poland, while the AI (adequate intake) of copper is set at 0.3 mg/pers./day (Jarosz, Bułhak-Jachymczyk 2008). There is no recommended level of dietary Mn in Poland.

The results were subject to statistical analysis. The Statistica 6.0 software was used to calculate maximum, minimum and mean values, the standard deviation (SD), the standard error of the mean (SEM), and the median.

RESULTS

The standard Polish norm defining the maximum content of mineral elements in nutritional products intended for infants and young children determines proportions between particular ingredients and the energy value in kcal. The content of minerals in the analyzed products, calculated per 100 kcal, is presented in Table 2. The acceptable value of Zn, Fe and Mn was not exceeded in the dessert products (Journal of Law 2007) but nearly all the products contained too much copper. The analyzed products contained the average of 282.2 mg of Zn per 100 kcal and 129.5 mg of Cu, 648.9 mg of Fe and 195.4 mg of Mn.

Table 3 presents the content of minerals in the dessert products, calculated per 1 kg of the product, whereas Figure 1 shows the content of these minerals in one jar. The content of zinc ranged from 0.19 to 6.67 mg in 1 kg; the highest concentration of Zn was noted in the product F-2. All the desserts had a very high content of copper: on average 0.81 mg in 1 kg of the product (0.23-1.19 mg). The highest copper concentration was determined in products labeled as A-1, C-1, F-1, G-2, G-3, H-1 and H-2 (above 1 mg in 1 kg of natural mass). The highest concentration of Fe was observed in the products marked as G-2 and H-1 (*ca* 10-11 mg in 1 kg). The content of manganese ranged from 0.25-4.74 mg in 1 kg. The highest concentration was noted in the product labeled as F-1.

Table 2

Contents of Zn, Cu, Fe, Mn and energy in fruit and mixed fruit and vegetable baby food

Trade mark	Zn	Cu	Fe	Mn	Energy, kcal in 100 g **
	(μg 100 kcal^{-1})				
A-1	97.42	144.28 *	513.28	84.28	70
A-2	139.42	125.79 *	634.92	209.13	69
B	399.86	126.31 *	566.31	221.97	64
C-1	368.66	236.66 *	273.55	55.33	46
C-2	143.18	86.66 *	163.33	38.33	84
D	322.89	29.73	24.47	438.15	76
E-1	189.83	72.88 *	184.75	83.05	59
E-2	306.38	93.62 *	421.28	140.43	47
F-1	271.66	115.11 *	383.57	564.16	50
F-2	1450.86	131.52 *	448.04	65.86	51
G-1	66.67	84.13 *	757.14	169.8	63
G-2	27.54	168.12 *	1576.81	159.42	69
G-3	54.69	185.94 *	1364.06	87.50	64
H-1	241.27	185.71 *	1500.00	458.73	63
H-2	152.31	156.92 *	921.54	155.38	65
Mean value	282.18	129.5 *	648.87	195.43	62.7
Polish Norm (Jornal of Laws 2007)	2000	40	3000	600	

* excessive levels in comparison with norms
** values as declared by the manufacturer

Assuming that a baby aged 12 months consumes one jar of dessert daily, she/he takes in almost 0.27 mg of Zn (9% of the RDA), *ca* 0.63 mg of Fe (5.7% of the RDA), 0.12 mg of Cu (40 % of the AI) and 0.21 mg of Mn from the analyzed products (Table 4).

DISCUSSION

Processed foodstuffs for infants are not highly trusted by parents. Some research has shown that only 22% of the parents regularly feed their children such products (Winiarska-Mieczan, Gil 2007). A study performed by these authors revealed that the most popular products are fruit and vegetable desserts, with ready dinners served much less frequently. Among desserts and fruit and vegetable purees, the most popular are those prepared from home-grown fruit, especially apples, as well as the products containing ba-

Table 3

Contents of crude ash, Zn, Cu, Fe and Mn in fruit and mixed fruit and vegetable baby food (n=3)

Trade mark	Crude ash (%)	Zn	Cu	Fe	Mn
		(mg kg^{-1} natural mass)			
A-1	0.09	0.68	1.01	3.59	0.59
A-2	0.16	0.96	0.87	4.38	1.44
B	0.17	3.04	0.96	4.30	1.69
C-1	0.12	1.66	1.07	1.23	0.25
C-2	0.25	0.95	0.57	1.08	0.25
D	0.16	2.45	0.23	0.19	3.33
E-1	0.11	1.12	0.43	1.09	0.49
E-2	0.09	1.44	0.44	1.98	0.66
F-1	0.21	2.28	0.97	3.22	4.74
F-2	0.11	6.67	0.61	2.06	0.30
G-1	0.23	0.42	0.53	4.77	1.07
G-2	0.19	0.19	1.16	10.88	1.10
G-3	0.27	0.35	1.19	8.73	0.56
H-1	0.26	1.52	1.17	9.45	2.89
H-2	0.21	0.99	1.02	5.99	1.01
Mean value	0.18	1.65	0.81	4.20	1.36

nanas (GÓRECKA et al. 2007). Desserts are the first fruit meal in an infant's diet. They contain pressed fruit, are delicate in taste and smooth in consistency, which makes them easy to swallow. Additionally, fruit desserts facilitate introduction of fruit into babies' diet and provide a valuable source of vitamin C, as well as an important source of mineral elements.

The recommended daily allowance of zinc in infants up to 12 months of age in Poland is 3 mg/individual (JAROSZ, BUŁHAK-JACHYMCZYK 2008). Zinc deficiency is common in developed countries (BLACK 2003). It is believed that zinc deficiency inhibits children's growth and may lead to mental retardation (BHATNAGAR, NATCHU 2004). According to Norwegian studies, the content of zinc in fruit purees was 0.11 mg per 1 kg of the product (MELŘ et al. 2008). Breast milk and cereal gruel provide a good source of zinc, with the mean content of zinc in breast milk in Poland being 1.57 mg per 1 liter (STOLARCZYK 2001).

Any excess of mineral elements may also disturb the baby's development. Turkish studies revealed that food for infants may contain as much as 4 mg of copper per 1 kg of the product (SARACOGLU et al. 2007). In contrast, some analyses completed in Norway showed that fruit puree contained as much as 3.3 mg of copper per 1 kg of the product and 0.53 mg was found

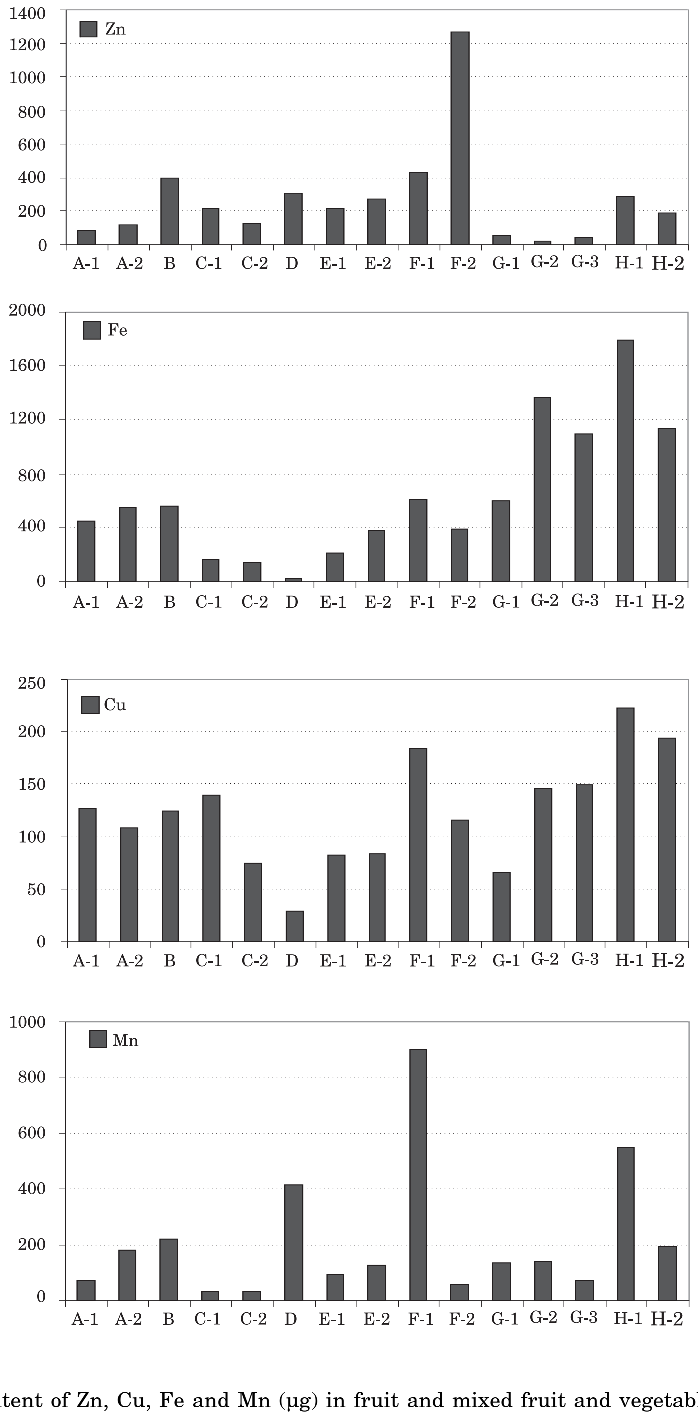

Fig. 1. Content of Zn, Cu, Fe and Mn (µg) in fruit and mixed fruit and vegetable products, in a jar (values calculated)

Table 4

Results of analyses of the fruit and vegetable baby food

Descriptive statistics	In jar			
	Zn (mg)	Cu (mg)	Fe (mg)	Mn (mg)
Maximum	1.27	0.22	1.79	0.90
Minimum	0.02	0.03	0.02	0.03
Mean	0.27	0.12	0.63	0.21
Median	0.21	0.12	0.55	0.13
SD	0.30	0.05	0.50	0.24
SEM	0.08	0.13	0.13	0.06
Mean daily intake *	0.27	0.12	0.63	0.21
Recommended level **	3	0.3	11	-
% of recommendation	9	40	5.7	-

SD – standard deviation, SEM – standard error of the means;
* Assuming that a 12-month-old child consumes on average one jar of dessert daily.
** JAROSZ, BUŁHAK-JACHYMCZYK (2008)

in 1 kg of fruit puree (MELŘ et al. 2008). A study performed by WINIARSKA-MIECZAN and NOWAK (2008) proved that in Poland the level of copper in juices for infants was high and in some products reached nearly 0.9 mg per 1 kg of the product. Excessive supply of copper leads to metabolic changes and its far-reaching consequences are related mainly to changes in the liver and, consequently, to damaging the kidneys, brain tissues, coronary vessels and the heart muscle. The most common consequences of excessive consumption of copper include mental disorders, kidney damage and hypertension (BREWER 2007, HUSTER et al. 2007). The recommended adequate intake of copper in infants up to 12 months of age in Poland is 0.3 mg/pers./day (JAROSZ, BUŁHAK-JACHYMCZYK 2008).

According to Polish studies, the average content of iron in fruit dessert and fruit juices for infants was, respectively, 2.73 mg and 1.80 mg per 1 kg of the product (MARZEC et al. 2007). Higher amounts of iron were found in baby soups (mean 3.29 mg kg^{-1}) and dinners (mean 3.83 mg kg^{-1}) (MARZEC et al. 2007). The content of iron in Turkish infant formulas has been reported in the range of 1.02-67.5 mg per 1 kg (SARACOGLU et al. 2007). The recommended daily allowance of iron in infants up to 12 months of age in Poland is 11 mg/individual (JAROSZ, BUŁHAK-JACHYMCZYK 2008). Young children are at higher risk of iron deficiency. Among children, iron deficiency is seen most often between 6 months and 2 years of age due to their rapid growth and an inadequate intake of dietary iron (HEATH et al. 2002). Iron deficiency is the most common form of nutritional deficiency and its incidence is the highest among young children (YEUNG, KWAN 2002).

A study performed by MARZEC (2003) on fruit desserts and purees and fruit and mixed fruit and vegetable juices revealed that consuming such products did not satisfy the infant's daily demand for manganese, therefore the child's daily diet must be supplemented with this element by other groups of products, e.g. vegetable and meat products or, possibly, mineral supplementation. According to MARZEC et al. (2007), the content of Mn in baby fruit desserts was 1.22 mg per 1 kg of the product. A study carried out in Spain showed that the content of Mn in fruit desserts intended for infants amounted to 0.66 mg in 1 kg of the product (VINAS et al. 2000). Milk formulas are a good source of manganese for children (IKEM et al. 2002, WINIARSKA-MIECZAN, TUPAJ 2009). There is no recommended level set in Poland for Mn but MARZEC (2003) claims that the recommended daily demand for this element by infants up to 12 months of age is 0.6-1 mg.

CONCLUSIONS

The acceptable value of Zn, Fe and Mn (Journal of Law 2007) was not exceeded in dessert products. In contrast, nearly all the products contained too much copper. The analyzed products contained the average of 282.2 mg of Zn per 100 kcal, 648.9 mg of Fe, 129.5 mg of Cu, and 195.4 mg of Mn. Assuming that a baby aged 9-12 months consumes one jar of dessert daily, she/he takes in almost 0.27 mg of Zn (9% of the RDA), 0.63 mg of Fe (5.7% of the RDA), 0.12 mg of Cu (40% of the AI) and 0.21 mg of Mn from these products.

Fruit and vegetable products are an important source of mineral elements in the baby's diet. Because they usually contain too little Zn, Fe and Mn in reference to the demand, they are only a supplementary product rather than a staple one in infant nutrition.

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REVIEW PAPERS

MAGNESIUM – FOOD AND HUMAN HEALTH

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Abstract

In the early 21^{st} century, as has been demonstrated by a number of medical reports, human health is seriously threatened by diseases and symptoms related to an insufficient intake of magnesium, independently of country, age and sex. The main causes are deeply rooted in the currently dominant eating habits, mostly based on cereals, i.e. on low concentration of minerals in grain. As it has been lately documented, edible parts of new, high-yielding varieties of cereals and also some vegetables (an important source of magnesium for people) are much poorer in minerals, including magnesium, than the old, low-yielding ones. Magnesium plays many important biochemical and physiological functions in plants, affecting both yield of their biomass and/or edible parts. Hence, fast growing plants require a high supply of magnesium, mainly via externally applied fertilizers, which will sustain their rate of growth. With the evidence of an insufficient content of magnesium in edible plant parts, food producers have now a new objective. Their aim is to increase the concentration of available magnesium in edible parts of plants, including both cereals and vegetables. The growing concern about low magnesium concentrations in plant products can be significantly mitigated through soil and/or foliar application of magnesium fertilizers. In order to produce magnesium-rich food, it is necessary to build up an effective strategy for magnesium management in arable soils, oriented towards providing adequate plant nutrition for sustaining normal human health. This target should be achieved when farmers apply a wide array of magnesium carriers, including fertilizers.

Key words: people, magnesium insufficient intake, diseases, crop plants, magnesium density, magnesium fertilizers, biofortification.

prof. Witold Grzebisz, Chair of Agricultural Chemistry and Environmental Biogeochemistry, Poznań University of Life Sciences

MAGNEZ – ŻYWNOŚĆ I ZDROWIE CZŁOWIEKA

Abstrakt

Na początku XXI w., jak wynika z wielu ostatnio publikowanych doniesień medycznych, zdrowie człowieka znajduje się w stanie dużego zagrożenia, będącego skutkiem niedostatecznego zaopatrzenia ludzi w magnez, niezależnie od kraju, wieku i płci. Główne przyczyny tego stanu są głęboko osadzone w obecnie dominujących wzorcach odżywienia, zależnych od zbóż, tzn. od koncentracji składników mineralnych w ziarnie. W ostatnim okresie wykazano, że jadalne części współczesnych, wysoko plonujących odmian zbóż, a także niektórych warzyw (ważne źródło magnezu dla ludzi), są dużo uboższe w składniki mineralne, w tym magnez, niż odmiany stare, nisko plonujące. Magnez pełni w roślinach wiele ważnych funkcji biochemicznych i fizjologicznych, istotnie kształtujących zarówno plony biomasy, jak i ich części jadalnych. Zatem współczesne odmiany roślin uprawnych wymagają bardzo dobrego zaopatrzenia w magnez, warunkującego szybkość ich wzrostu, co może być pokryte głównie przez stosowanie nawozów. W świetle faktów wskazujących na niedostateczną zawartość magnezu w żywności pochodzenia roślinnego, pojawił się nowy cel dla producentów żywności. Jest on ukierunkowany na zwiększenie koncentracji magnezu w jadalnych częściach zbóż i warzyw. Narastający problem niedoboru magnezu w produktach roślinnych można istotnie złagodzić przez doglebową lub/i dolistną aplikację nawozów magnezowych. Wyprodukowanie żywności bogatej w magnez wymaga efektywnego systemu gospodarki magnezem w glebie, aby zapewnić odpowiednie odżywienie roślin. Realizacja tego nadrzędnego celu wymaga od rolników korzystania z szerokiej gamy nośników magnezu, włącznie z nawozami.

Słowa kluczowe: człowiek, niedostateczne zaopatrzenie w magnez, choroby, rośliny uprawne, zawartość magnezu w częściach jadalnych, nawozy magnezowe, biofortyfikacja

INTRODUCTION

People's physical growth and mental well-being depend on *ca* 50 externally supplied nutrients such as vitamins, macro- and microelements (referred to as minerals by human physiologists), amino acids or essential fatty acids, which are delivered mainly in food, although some minerals are also supplied in drinking water. The list of elements recognized by physiologists as essential, i.e. vital for life processes in a human body, continues to expand. Generally, animal and human physiologists have accepted so far a much higher number of essential minerals than have more conservative plant physiologists, arriving at the present number of 22. Based on their content in a human body, all minerals are divided into two main groups, presented in the decreasing order:

– macrominerals: Na, K, Ca, Mg, S, P, Cl;
– microminerals: Fe, Zn, Cu, Mn, I, F, B, Se, and Mo, Ni, Cr, Si, As, Li, Sn, V, Co (in vitamin B_{12}).

Most of these minerals are essential both to plants and, through the food chain, to animals and humans. Hence, amounts of soil minerals taken up by plants and subsequently accumulated in plant tissue are important both as fodder for animals and/or as food for humans (WELCH, GRAHAM, 2005).

The history of mankind is closely related to development of agriculture. The first civilization revolution, which took place *ca* 10 000 years ago, changed people's lifestyle from wandering to sedentary one. However, the major change was associated with people's diet, which over millenniums has become more and more dependent on cereals as the most important source of carbohydrates, proteins and also minerals. The industrial revolution, which took place in the early 19^{th} century, was the main reason for increasing the demand of the exponentially growing human population for food. In the second part of the 20^{th} century, long-term work of farmers and plant breeders allowed selecting highly efficient crop plant varieties. However, there are also some negative consequences of both the new, high-yielding varieties and the current diet, based on cereals. The modern varieties of cereals, vegetables and oil crops can produce food in quantities sufficient to meet demands of the current human population (FAOSTAT 2010, available online, March 5, 2011). As a result of the Green Revolution, the world's human population is fairly well supported with carbohydrates and proteins produced from grain, but the content of elements is generally too low. The recognized deficiency refers mainly to an insufficient concentration of elements such as iron, zinc, selenium and also magnesium, calcium, both in edible plant parts and in final food products. The current discrepancy between a high input of carbohydrates, proteins and fat in people's daily diet and a concurrent deficiency of minerals is frequently called *micronutrient malnutrition*, but in fact it could be termed, following medical terminology, *mineral malnutrition* or *hidden hunger* (GRUSAK 2002, WELCH, GRAHAM 2002, WELCH, GRAHAM 2005, ZHAO, SHEWRY 2010).

The main objective of this review paper is best expressed by Dr. Charles Nothern's statement: "*It is simpler to cure sick soils than sick people – which shall we choose?*" (*Modern miracle men* by R. BEACH, U.S. Senate Doc. No. 264, 1936).

MAGNESIUM DECLINE IN PLANT FOOD – REASONS AND CONSEQUENCES

Magnesium recommendations and intake

The amount of magnesium in the human body rises from *ca* 760 mg at birth to 24 g in an adult. In order to keep a sufficient rate of the body growth, both at early stages and during all its life span, a human organism must be regularly supplied with this element. Therefore, any nutrient-level recommendations for humans, known as dietary reference intakes (DRIs), take into account two main factors: age and gender. Among many intake reference guidelines, the Recommended Dietary Allowance (RDA) is the one most frequently used to compare the nutritional status of different societies or groups. It is defined, accordingly to the Food and Nutrition Board of the Institute of Medicine, as “the average daily nutrient intake level sufficient to meet requirement of nearly all (97 to 98%) healthy individuals in a particular life stage and gender group” (Murrphy 2001, Usda, Usdhh 2010). Reference intake guidelines for magnesium in some European countries like Austria, Germany, Switzerland and Poland, i.e. countries characterized by very similar eating patterns, are nearly the same (Table 1). The main differences are attributed to the life stage extending from 10 to 13 years. In Poland, the recommended magnesium intake is much higher than in other countries. In the USA, just 240 mg per day is recommended during this particular life stage, irrespective of gender, whereas in Poland, the level is 300 mg for girls and 290 for boys (Vormann 2003).

Table 1

Reference intakes for magnesium (mg day^{-1})

<table>
<tr><td colspan="3">Austria, Germany, Switzerland*</td><td colspan="3">Poland**</td></tr>
<tr><td>Age</td><td>females</td><td>males</td><td>age</td><td>females</td><td>males</td></tr>
<tr><td>1-4</td><td colspan="2">80</td><td>0-1</td><td colspan="2">50-70</td></tr>
<tr><td>4-7</td><td colspan="2">120</td><td>1-3</td><td colspan="2">100-150</td></tr>
<tr><td>7-10</td><td colspan="2">170</td><td>4-6</td><td colspan="2">150</td></tr>
<tr><td>10-13</td><td>230</td><td>250</td><td>10-12</td><td>300</td><td>290</td></tr>
<tr><td>13-15</td><td>310</td><td>310</td><td>13-15</td><td>300</td><td>300</td></tr>
<tr><td>15-19</td><td>350</td><td>400</td><td>16-18</td><td>340</td><td>400</td></tr>
<tr><td>19-25</td><td>310</td><td>400</td><td>19-25</td><td>300</td><td>370</td></tr>
<tr><td>25-51</td><td rowspan="3">300</td><td rowspan="3">350</td><td>26-60</td><td rowspan="3">300</td><td rowspan="3">370</td></tr>
<tr><td>51-65</td><td rowspan="2">> 60</td></tr>
<tr><td>> 65</td></tr>
<tr><td>Pregnancy</td><td>310</td><td>-</td><td>pregnancy</td><td>350</td><td>-</td></tr>
<tr><td>Lactation</td><td>390</td><td>-</td><td>lactation</td><td>380</td><td>-</td></tr>
</table>

*D-A-CHReferenzwerte fur die Nahrstoffzufur;
**Instytut Żywności i Żywienia (Institute of Food and Nutrition)

The evaluation of an actual magnesium intake, conducted in many countries, generates a very pessimistic picture for different gender or social groups in western societies. A recent study in Poland has shown that, despite high realization of DRI norms, girls rely much more frequently than boys on diets deficient in magnesium (Figure 1). This negative trend reflects the insufficient intake of magnesium by girls more than 10 years old (Wojtasik et al. 2009). The presented pattern is significantly influenced by economic conditions of families with children and is probably seriously affected by the dominating eating habits. As reported by Ustymowicz-Fabisze-

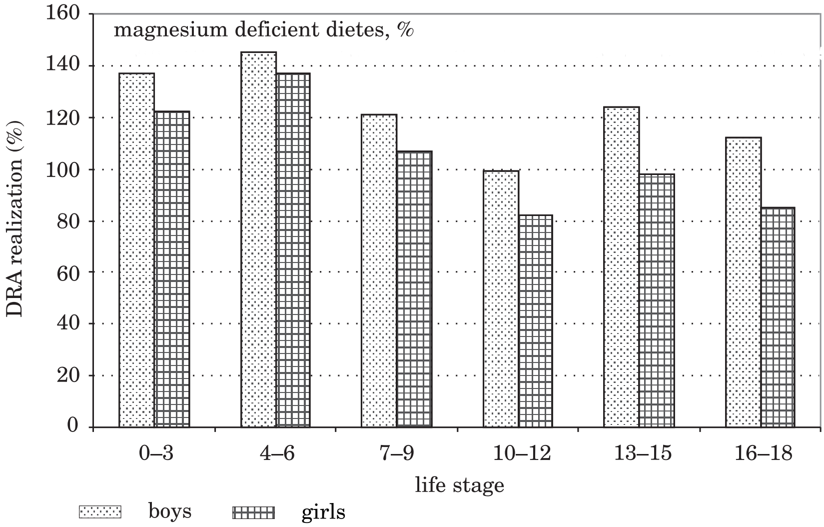

Fig. 1. Magnesium intake norms for children and adolescents in Poland (based on WOJTASIK et al. 2009)

WSKA et al. (2000), the intake of magnesium by 14-year-old children living in Białystok or in villages of the Białystok region was generally below the norms. As a rule, children living in villages made up a higher percentage of insufficient supply of magnesium, reaching 100% among 14-year-old girls. Another study, conducted on a group of 19(20)-year-old students from the same city showed an insufficient intake of magnesium by 63% of women and 60% of men (STEFAŃSKA et al. 2003).

Trends in the dietary magnesium intake in Poland are typical of western societies. In the United States, the average magnesium daily intake decreased from 475-500 mg to *ca* 200 mg day^{-1} from 1900 to 1992 (Figure 2). In the USA, the current RDA ranges for adults are fixed at 420 and 320 mg day^{-1} for men and women, respectively. However, the real magnesium intake is in the range 185-260 mg day^{-1} for men and 172-235 mg day^{-1} for women. The range-curves presented in Figure 2 show two critical timepoints, characterized by a high decline rate of magnesium intake. The first one, from *ca* 500 to 350 mg day^{-1}, took place in the 1920s and the second one, from 300 to 200 mg day^{-1}, occurred in the 1960s (ALTURA, ALTURA 1995, USDA, USDHH 2010).

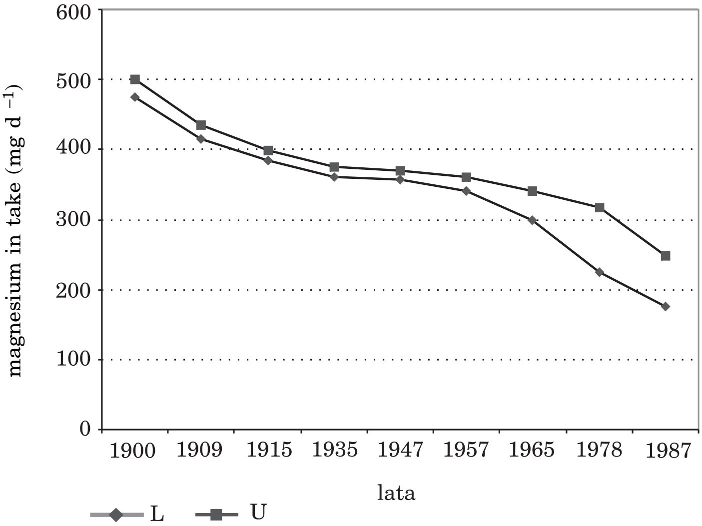

Fig. 2. Trends of magnesium intake in the USA in the 20th century:
L – low, U – upper limits (based on ALTURA, ALTURA 1995)

Evidence of decline

The consumption patterns of minerals, including magnesium, by humans show negative tendencies. In addition, they exhibit quite opposite trends to those presented for energy, fat and protein consumption. The average amount of recommended magnesium for adults in western societies is fixed at the level of *ca* 350 mg day^{-1}, i.e. 70% of its status at the beginning of the 20th century. The currently established RDA standards as compared to the pre-agrarian epoch (the Paleolithic) are 3.5-fold lower (BOYD EATON, BOYD EATON III 2000). There are some fundamental reasons for lower magnesium intake with consumed food, which can be specified in four distinct groups as follows:

1. Economic and social:
   - access to food,
   - changes in eating patterns,
2. Agronomic and technological processing:
   - depletion of soil essential nutrient contents,
   - increasing yielding potential of new varieties,
   - food processing.
3. Metabolic disturbance of magnesium availability to a human organism:
4. others: i) stage of life – fast growth of body; ii) pregnancy and lactation; iii) high physical activity; iv) intense consumption of alcohol.

As described interestingly by BOYD EATON, BOYD EATON III (2000), humans living in the Paleolithic epoch relied in consumption patterns on animal proteins, fat but rich in polyunsaturated fatty acids, and on fruit and vegetables. All these animal and plant products delivered huge amounts of minerals. Current diets in rich western societies are based on plant food, which are rich in carbohydrates and proteins from cereals. People can use magnesium from many different sources, including cereals, meat, vegetables, fruit and also water (Figure 3). Hard water is frequently considered as an important source of this element, positively affecting health of humans dwelling in some areas of the world (DELVA 2003). The intake of magnesium depends, however, on the structure of consumed products, which can be grouped in classes based on magnesium concentration in edible parts (expressed in mg kg^{-1} raw or final product) (GEBHARDT, THOMAS 2002):

1) very high, (> 1000): buckwheat grains, cocoa, almonds, pumpkin seeds, bread from wheat, rye whole grains, oat grains;
2) high (500 – 1000): spinach, soybeans boiled;
3) medium (250 – 500): artichokes, potatoes with skin, green beans;
4) low (< 250): apple, lettuce, potatoes (peeled and boiled).

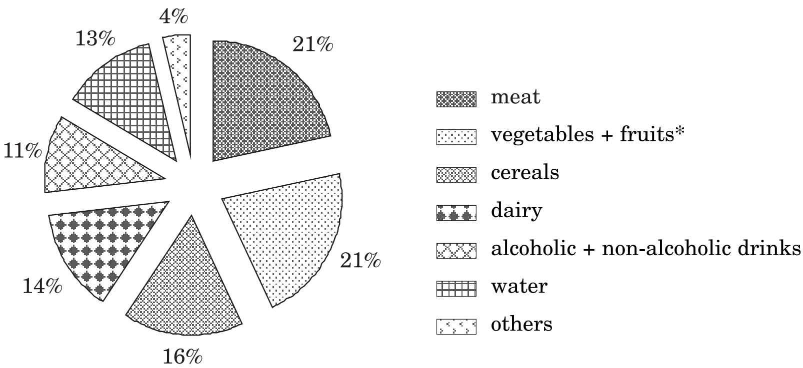

Fig. 3. Structure of magnesium delivery in food in the Spanish diet (based on JODRAL-SEGADO et al. 2003)

The second factor significantly affecting mineral levels in plant food is related to soil fertility. This view was broadly documented by the evaluation of historical data concerning basic element concentrations in five types of food products in the period extending form 1940 to the end of the 20^{th} century (Table 2). Magnesium decrease was above 20% in cheeses and vegetables and *ca* 15% in fruit and meat. These negative changes are generally related to the quality of fodder and food, relatively poor in nutrients (DAVIS 2009, THOMAS 2003, 2007). The evidence for a decline in the mineral content in plant food has been therefore termed as *soil induced dilution effect*.

The above facts and conclusions are being discussed by scientists. In many areas of intensive food production, like in Europe, no significant evidence for plant available nutrient decline has been observed. Two types

Table 2

The weighted average changes in macronutrient concentration in food products*

Elements	Food products				
	meat***	dairy***	cheeses***	fruit**	vegetables**
Sodium	-24	-47	-9	-29	-49
Potassium	-9	-7	-19	-19	-16
Phosphorus	-21	+34	-8	+2	+9
Calcium	-29	+4	-15	-16	-46
Magnesium	-14	-1	-26	-16	-24

*acc. to THOMAS (2003, 2007); **for years 1940-1991 period;
***for years 1940-2000

of investigations have been carried out to verify this hypothesis. The first one relies on the evaluation of historical food composition data. A classical example is a study performed on wheat grain from the Broadbalk Wheat Experiment, which was established in 1843 at Rothamsted (the UK). An analysis of archived grain samples showed that magnesium concentrations, irrespective of fertilization treatments, were constant over the period from 1845 to the mid-1960s. The concentration of magnesium, averaged over all fertilization treatments, was at the level of 365 mg kg^{-1}. It was, however, found that from 1968 to 2005 Mg concentrations fell significantly, mainly because of the introduction of new type of wheat short-straw cultivars (FAN et al., 2008). Another way for verifying the above hypothesis is based on the *side-by-side comparison* method, which involves comparison of high (modern) and low (old) cultivars grown under the same soil conditions. A case study conducted on broccoli allowed researchers to explain the reasons for a decrease in magnesium and calcium concentrations. It appeared that new, modern cultivars, characterized by a fast rate of growth and high yield of edible parts, are genetically unable to achieve high concentrations of minerals. The detected dilution of most minerals as found for broccoli, wheat and maize has been therefore termed a *genetic dilution effect* (DAVIES 2009).

The impact of food processing on mineral nutrients is highly important for humans, whose diet is based on cereals and potatoes (WATZKE 1998). A classical example is wheat flour, commonly used in bread production. A study on the magnesium content in food products in the USA, as presented by the USDA National Nutrient Database for Standard Reference (2011, based on GEBHARDT, THOMAS 2002) clearly shows that white wheat flour contains *ca* 18% of the original magnesium content. This striking difference is a result of the milling process, causing loss of magnesium into millfeed. The same applies to potato tuber processing. According the same source, the concentration of magnesium in potato baked with flesh and skin is *ca* 280 mg kg^{-1}, but in potatoes boiled or cooked without peelings it is 1/3 lower, i.e., at the level of 200 and 280 mg kg^{-1}, respectively.

Magnesium intake deficiency – health consequences

The above facts support an increasingly popular conclusion that while the *Green Revolution* has combated famine on the global scale, it has also created conditions for an uncontrolled decline of food quality, attributed to a decreasing intake of most minerals, in turn negatively affecting the health of consumers. Magnesium is classical exemplification of this thesis (WELCH and GRAHAM 2002, WHITE, BROADLEY 2005).

An adult human body contains 20-28 g of magnesium, which is not equally distributed in the body. It is shared between bones (60-65% of total Mg), followed by intracellular cells of muscles (27%), other cells (6-7%) and extracellular space (< 1%, serum and red blood cells). The amount of available magnesium, i.e., its potential retention in a human organism, depends on its concentration in the consumed food and on many other factors. It decreases under conditions of high dietary fiber content, excessive consumption of fat, sugar or sodium. High amounts of magnesium not retained in a body are excreted in urine (VORMANN 2003).

Within human cells, magnesium occurs mostly in bonded structures, representing 90% of its total amount. The remaining part is present in ionic forms with the prevalence of Mg^{2+}. The most important bonds are formed with nucleic acids, ATP, negatively charged phospholipids and proteins. The divalent Mg cation activates directly *ca* 350 enzymes and is indirectly involved in thousands of processes in the human body. Bio-physical functions of Mg^{2+} concern the production, storage and use of ATP molecules for any life, energy demanding processes. Other important processes regulated by magnesium are as follows: i) trans-membrane transport of calcium, sodium and potassium, ii) protein synthesis (FAWCETT et al. 1999).

Extended studies have revealed a close relationship between low magnesium consumption by humans and the major risk factors for heart diseases. It is well documented that the heart contains much more magnesium than other muscles. However, under conditions of small but negative changes of Mg^{2+} concentrations, both in the extra-cellular and/or intracellular space, its content in the heart decreases, resulting in some disturbance of its activities. Moreover, it has been reported that the rhythm of the heart depends on gentle balances occurring between Mg^{2+} and other cations (Ca^{2+}, Na^{+}, K^{+}). Magnesium deficiency induces several heart dysfunctions such as arrhythmias, high blood pressure, arteriosclerosis, formation of blood clots within blood vessels and finally myocardial infarction (DELVA 2003, DOUBAN et al. 1996, TOUYZ 2003).

MAGNESIUM IN PLANTS – FUNCTIONS AND DEFICIENCY SYMPTOMS

Uptake and redistribution within plant parts

Concentration of magnesium ions in the soil solution ranges from 125 µM to 8.5 Mm. From soil, magnesium ions are transported toward the root surface in water transpiration stream. The permeability of a root to water depends on its age. Young parts of roots consisted of rapidly growing cells, highly permeable to water and transported ions. However, in the course of growth, the anatomical structure of roots undergoes significant differentiation. The most important changes take place in the endodermis surrounding inner tissues of the root stele. In this particular tissue (relative to root maturation processes), synthesis of suberin compounds occurs progressively, creating the Casparian strip. This developing layer becomes the main biological barrier, impeding transportation of divalent cations from the apoplast into the xylem. In addition, most Mg^{2+} cations undergo binding by negatively charged chemical groups naturally present in the root cell walls Therefore, the amount of magnesium reaching the root apoplast to cover plant requirements must be 2(3)-fold higher than the real plant biological requirements. The root apoplast including the endodermis can be considered as an important, partly temporary storehouse of magnesium (CLARKSON 1985, SHAUL 2002).

Amounts of magnesium present in the root apoplast are variable due to the effect of some important factors negatively affecting magnesium supply to crop plants (CLARKSON 1985, HUNDT, KERSCHBERGER 1991, KINRAIDE et al. 2004, METSON 1974):

- low amounts of available magnesium in the soil solution;
- competition with other divalent ions; mostly Ca^{2+} due high soil pH; NH_4^+, K^+ and also by some divalent cations of micronutrients;
- elevated concentration of aluminum, Al^{3+}:
  - directly through ion competition;
  - indirectly through restricted volume of the plant root system;
- all other factors restricting the size of the root system.

The first factor can be considered as the most important one because of the dominance of mass-flow mechanisms of Mg^{2+} ions transport in the soil solution toward the root surface. The second group of factors should be considered with caution because calcium is generally responsible for the rate of root growth, in turn defining the size of the root system at any stage of crop plant growth. Relationships between magnesium and potassium ions are highly complex (HUNDT, KERSCHBERGER 1991). The actual negative effect of potassium excess on magnesium concentrations in plants can be expected only if the supply of potassium is high (WIERZBOWSKA 2006). There is strong antagonism between ammonium and magnesium ions during the uptake by plant roots (BRITTO, KRONZUCKER 2002, KUBIK-DOBOSZ 1998, METSON 1974).

Accumulation of magnesium in aerial plant biomass reaches maximum at the physiological maturity of the crop. The accumulation of phosphorus shows almost the same pattern, irrespective of crop species. The effect of phosphorus application on magnesium concentration in the plant is positive at low but negative at very high rates of fertilizer (Wierzbowska, Bowszys 2008). The illustration in Figure 4, showing the accumulation of both nutrients by a high-yielding plantation of sugar beet, indirectly indicates strong biological coherence of both elements. Final redistribution of magnesium among parts of physiologically matured seed crops shows almost the same pattern (Figure 5). Depending on the crop, *ca* 50% of the finally accumulat-

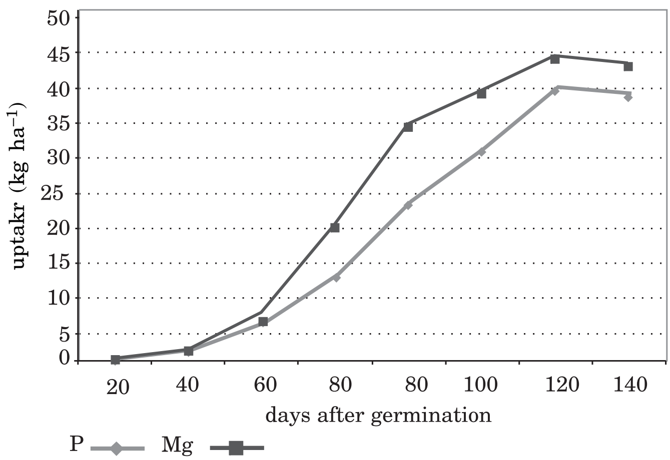

Fig. 4. Dynamics of magnesium and phosphorus accumulation by sugar beet plantation (based on Grzebisz et al. 1998)

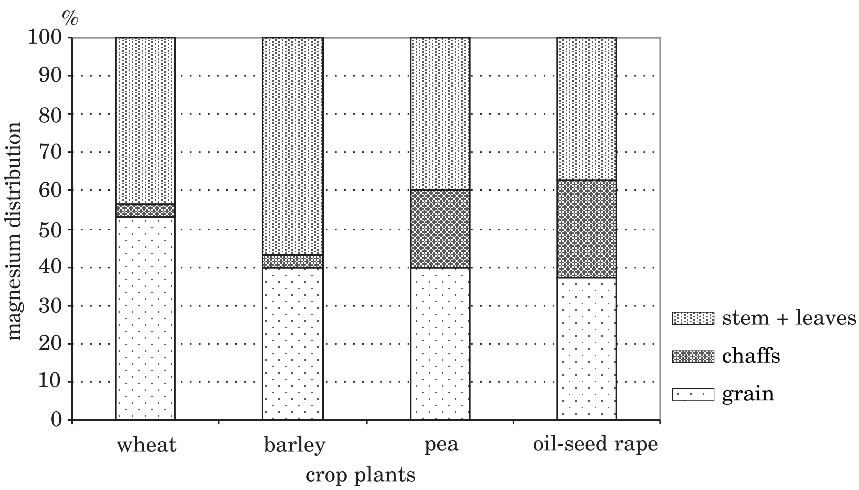

Fig. 5. Magnesium redistribution between plant parts of seeds crops at harvest (Grzebisz, non published)

ed magnesium is stored in reproductive organs such as seeds or grain. However, in seeds rich in proteins or fat, this percentage is significantly lower. The same holds true about root crops, such as sugar beets, which accumulate 25-33% of total magnesium in the taproot.

Basic biological functions

Magnesium concentrations in plants vary from 0.1% to almost 2%. Its distribution in plant cells is irregular. In leaves, the most important bonding sites for magnesium are chloroplasts, mitochondria and vacuoles. In cells of well-fed leaves, most magnesium is located in vacuoles, functioning then as the inner cellular buffer. The importance of this buffer increases under an insufficient supply of magnesium from the extracelluar leaf space. Leaf magnesium homeostasis, significantly affecting the activity of chloroplast enzymes, depends on the amounts of this element in chloroplast and its concentration in the cytosol, with optimum at 1 mM. However, free Mg^{2+} represents *ca* 10% of cytosol magnesium. The remaining part is bound by ATP (90%). Decreased concentration of magnesium in the cytosol affects of Mg^{2+} movement from both the vacuole and extracelluar leaf space (Karley, White 2009, Shaul 2002).

Magnesium affects directly or indirectly almost all biochemical and physiological processes occurring within the plant during its course of life. The hierarchy of its biological functions can be presented as follows (Maathuis, 2009, Shaul 2002):

1) photosynthesis:
   – central position in the chlorophyll molecule,
   – light reactions in the chloroplast stroma,
   – photosynthetic enzyme activation,
   – CO_2 molecule binding and reduction,
2) energy production and transformation:
   – ATP molecule synthesis, storage and release,
   – synthesis of carbohydrates, proteins and fat,
3) membrane transport:
4) distribution of carbohydrates among plant parts:
   – phloem load of photosynthetically bound sugars,
   – root system growth,
5) nucleic acids stabilization.

Deficiency symptoms development

Plant magnesium deficiency symptoms seem to be extremely classical as presented in many references. However, the newest scientific facts have revealed some complexity of the development of deficiency symptoms on the cellular level in response to magnesium homeostasis. The hierarchy of the development of deficiency symptoms is as follows:

– excessive sucrose and starch accumulation in fully expanded leaves,

– decreased sugar transport from leaves to other plant organs,
– root system growth inhibition,
– aerial plant part growth inhibition.

The first symptoms of magnesium deficiency are related to the inhibition in loading sucrose to the phloem due to insufficient synthesis of Mg-ATP. There is some scientific evidence that sugar concentration in leaves is inversely correlated with magnesium concentration (CAKMAK 1994, HERMANS et al. 2005). The first biological consequence of inhibited sucrose transportation in the phloem results in decreasing the growth rate of the newest organs such as roots (CAKMAK 1994, HERMANS et al. 2005). Therefore, inhibition of the root system size can be considered as the second symptom of magnesium deficiency. CAKMAK, KIRKBY (2008) reported that a decrease in the root growth rate took place much earlier than any symptoms detected on leaves and on a plant, i.e. related to a decreasing leaf area size, appearance of leaf chlorosis and finally a stunned rate of the plant canopy growth. The most striking symptoms of magnesium deficiency, i.e. leaf chlorosis, is a result of energy transfer disturbance. A magnesium deficient leaf, rich in sucrose and starch, is not able to transfer light energy into biological compounds such as ATP and NADPH; instead it begins to to generate reactive oxygen substances (superoxide radicals, $O_2^{\cdot -}$; hydrogen peroxide, H_2O_2, etc.). These compounds, when not inactivated into a cell, destroy enzymes and chloroplasts, impairing cell photosynthesis and finally causing degeneration of leaf surface tissues. Under low magnesium stress, these visual symptoms are weakly recognizable, but during chronic deficiency, they lead to leaf chlorosis, followed by necrosis. Due to the fact that magnesium concentration increases towards leaf veins, the first visible symptoms are observed as interveinal chlorosis (CAKMAK and KIRKBY 2008, TEWARI et al. 2006).

SOIL MAGNESIUM

Soil magnesium characteristics

The averaged content of magnesium in the lithosphere is *ca* 21 g kg^{-1}, but it is several times lower in soil, i.e. 5 g kg^{-1}. These two figures clearly indicate the high weathering potential of soil magnesium-bearing minerals. Knowledge of the mineral composition of the weathered rock, known as soil parent material, is important to make the first assessment of potential chemical characteristics of any given soil. Hence, the total magnesium content in arable soils reflects to some extent the composition of soil parent material, being the substrate during pedogenesis. Igneous basic rocks (< 66% of SiO_2 represented by basalt, gabbro, norites) show naturally greater weathering potential than acid rocks (> 66% of SiO_2 represented by granite, rhyolite) and at the same time a higher potential for releasing base cations. Therefore, based on mineral composition of soil parent material it may be concluded, that soils formed from mafic igneous rock, containing high amounts of ferromagnesian minerals, serpentine or dolomite, naturally exhibit high concentrations of total magnesium (METSON 1974, METSON, BROOKS 1975).

Naturally magnesium deficient soils are:

– sandy soils originated from granites, sandstones,
– sandy soils originated form post-glacial sandy deposits or alluvial sandy deposits,
– organic soils.

Magnesium-bearing minerals represent two basic mineral groups, known as primary and secondary minerals. The first group is represented by silicate minerals such as:

– ferromagnesian minerals: amphiboles, olivines, pyroxenes, hornblendes; important components of igneous rocks and some metamorphic rocks (serpentine, talc);
– micas (muscovite, biotite); specific by a 2:1 layer type silicate structure;

The solubility of magnesium-bearing silicates is a function of pH as presented below for two classical representatives:

1) olivine

$$Mg_{1.6}Fe(II)_{0.4}SiO_4 + 4H^+ \Leftrightarrow 1.6Mg^{2+} + 0.4Fe^{2+} + H_4SiO_4^o \qquad \log K^o = 26.18$$

2) serpentine

$$Mg_{1.6}Si_4O_{10}(OH)_8 + 12H^+ \Leftrightarrow 6Mg^{2+} + 4H_4SiO_4^o + 2H_2O \qquad \log K^o = 61.75$$

The second group is composed of minerals of different geological origin, which can be simply divided into three main sub-groups such as:

– carbonates,
– secondary clay minerals,
– soluble salts.

The carbonate family of magnesium-bearing minerals is composed mainly of dolomite and magnesite. The main factor affecting solubility is soil pH. The solubility reactions are presented below:

1) dolomite

$$CaMg(CO_3)_2 + 4H^+ \Leftrightarrow Mg^{2+} + Ca^{2+} + 2CO_{2(g)} + 2H_2O \qquad \log K^o = 18.46$$

2) magnesite

$$MgCO_3 + 2H^+ \Leftrightarrow Mg^{2+} + CO_{2(g)} + 2H_2O \qquad \log K^o = 10.69$$

In spite of its high solubility under natural conditions, dolomite is dissolved much faster than magnesite, but both are less soluble than calcite. All minerals belonging to soluble magnesium salts, for example sulfates, chlorides or nitrates are nor detectable in the soil solution. It is highly important in agronomic practice because any addition of these salts to soil results in an increase of the soil solution magnesium concentration.

Soil magnesium deficiency – reasons and assessment

The primary cause of magnesium deficiency in crop plants is the low content of its available supplies in the soil solution, thus a decreased rate of Mg^{2+} ions uptake (Hundt, Kerschberger 1991). Several methods for soil magnesium deficiency assessment can be distinguished, but three are the most important in agronomic practice:

1) available magnesium rating,
2) exchangeable magnesium content and its contribution to the soil cation-exchange capacity,
3) soil magnesium balance:
   – exchangeable magnesium balance,
   – agronomic balance.

The first method refers to the classical agro-chemical rating of plant available magnesium. Magnesium deficiency is defined by a current amount of plant available magnesium in the soil body as an indicator of a potential crop response to the applied magnesium fertilizer. Therefore, one of the most important agronomic targets is to establish a critical value of exchangeable soil magnesium (Mg_{ex}) with respect to the expected crop plants response. Schachtschabel (1954), by means of 0.0125 M $CaCl_2$ extract, defined the critical content of magnesium to *ca* 50, 70 and 1200 mg kg^{-1} soil for light, medium and heavy soils, respectively. These ranges have been generally corraborated by other researches, as reported by Metson (1974), who a year later published magnesium rating methods based on both exchangeable magnesium and reserve magnesium, i.e. hot extracted from soil by 1 M HCl test (Metson, Brooks 1975). According to the above values, the expected deficiency is related to both an exchangeable magnesium content lower than 120 mg kg^{-1} soil and its reserves below 720 mg kg^{-1} soil (Table 3). One of the most important assumptions in both approaches is the soil textural class as a factor defining the amount of Mg_{ex} in the cation exchangeable complex. It has been agreed that an ideal cation exchange complex (CEC) consists of Ca^{2+} – 65% , Mg^{2+} – 10%, K^+ – 5% and H^+ – 20% of all cations. In some studies, a 6% contribution of Mg_{ex} in the CEC is considered as sufficient to cover the crop's needs in the course of vegetation (Metson, Brooks 1975).

Table 3

Rating of exchangeable and reserve magnesium in soils* (mg kg^{-1})

Rating	Exchangeable Mg	Reserve
Very high	> 1680	> 7200
High	720-1680	3600-7200
Medium	240-720	1680-3600
Low	120-240	720-1680
Very low	< 120	< 240

*acc. to Metson, Brooks (1975)

The third method of assessing tendency towards magnesium-deficient soil relies on measuring Mg_{ex} at the beginning and at the end of three- or four-course rotation or an extended period of arable land cultivation. As presented in Table 4, long-term cultivation of rye with a constant rate of applied farmyard manure or NPK fertilizers resulted in high differentiation of the Mg_{ex} content. Plots annually fertilized with NPK become depleted of minerals, irrespective of the method of soil use (crop or fallow). This process can be mitigated by manure application, but the amount of annually produced manure even on a mixed production farm is too low to replenish losses of magnesium. An elevated content of Mg_{ex} found in the 40 to 80 cm soil layer verifies a typical feature of luvisols in temperate climates, such as accumulation of basic cations in deeper soil layers.

Table 4

Plant available magnesium distribution in the soil profiles of long-term static experiment* (mg kg^{-1} soil)

Soil layer (cm)	Black fallow		Winter rye – monoculture		Winter rye – crop rotation	
	FYM**	NPK***	FYM	NPK	FYM	NPK
0-20	52	22	55	17	58	20
21-40	49	21	46	17	58	21
41-60	99	41	72	58	81	18
61-80	66	33	85	52	90	18
81-100	52	28	52	45	56	29
100-120	36	21	40	31	44	31

*acc. to Piechota et al. (2000);
**FYM – annually applied farmyard manure at the rate of 30 t ha^{-1};
***N – 90; P – 26; K – 100 (kg ha^{-1}).

Soil balance of exchangeable magnesium can be also calculated by taking into account its available content at the beginning and the end of an observation period. However, this method does not reveal the causes of Mg_{ex} loss/gain in the investigated soil. As presented in Figure 6, Mg_{ex} balance after 8 years of study was negative despite the application of magnesium fertilizers in the total amount of 288 kg Mg ha^{-1}. The highest losses were recorded in the control treatment, i.e. without any input of NPK fertilizers. Net magnesium losses were significantly related to increasing NPK rates. Applied lime affected positively magnesium management, decreasing its losses. Maximum calculated magnesium losses, including applied magnesium fertilizer, amounted to 50 kg ha^{-1} year^{-1}.

The fourth method for assessing potential threat of magnesium deficiency to cultivated crops relies on agronomic magnesium balance, indicating current trends of magnesium soil management (Łabętowicz et al. 2004). A classical balance sheet, in accordance to the “field surface balance”, should include:

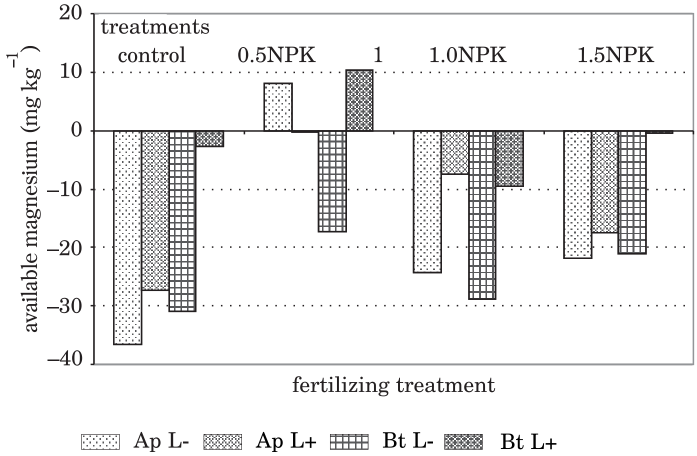

Fig. 6. Effect of liming and mineral fertilizers application on available nitrogen balance (based on KANIUCZAK 1999)

1) input: a) plant residues; b) organic fertilizers; c) mineral fertilizers; d) other sources, for example rainfalls;
2) output: a) crop removal; b) leaching; c) exchangeable Mg^{2+} fixation.

The first step in checking the soil magnesium output is to make a reliable assessment of its removal from the field. These values are mostly evaluated on the basis of utilizable part of crops. Figure 5 shows that just 40 to 60 per cent of magnesium accumulated in final biomass is in utilizable part. The rest remains in crop residues and undergoes different forms of recycling. Another indicator, known as unit nutrient uptake (in the described case: unit magnesium uptake, UMgU), helps to achieve reliable estimation of magnesium removal, as it takes into account the total magnesium in harvested crop biomass, recalculated per unit of harvestable plant part (Table 5). Indices calculated for crops are very useful in determining their sensitivity to total magnesium requirements. Therefore, this assessment must be done carefully.

The second element of a simple magnesium soil balance refers to its leaching. As shown in Figure 6, most of the magnesium lost during the investigated period was leached. SCHWEIGER, AMBERGER (1979), by lysimetric experiments, showed annual losses of Mg_{ex} at the level of 72 kg ha^{-1} for sandy soil and 92 kg ha^{-1} for medium soil during a 36-year-long period. They concluded that the majority of detected losses were due to leaching processes. However, a direct assessment of magnesium leaching by means of its concentration in water outflow from fields showed much smaller values, ranging from 18 to 25 kg Mg ha^{-1}, respectively for medium and light soils (Figure 7). These values can range from less than ten to over 40 kg ha^{-1} (SZYMCZYK et al. 2005). The highest quantitative leaching occurred in winter.

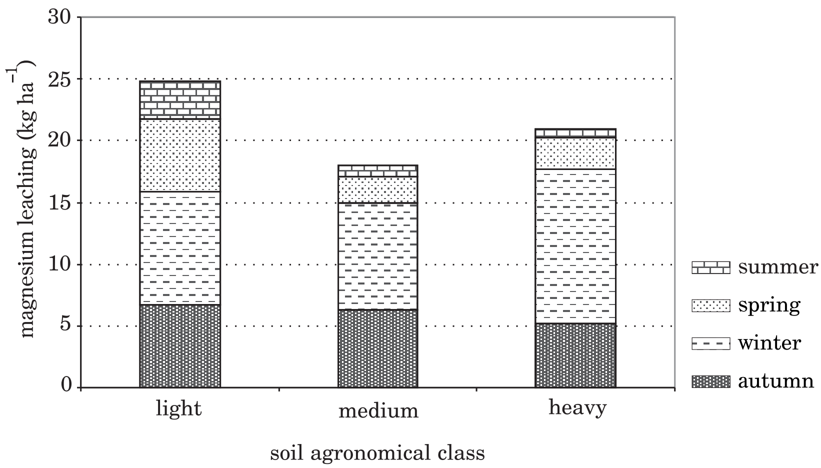

Fig. 7. Effect of soil agronomical class on magnesium leaching in main seasons of the year (based on Koc, Szymczyk 2003)

Table 5

Current and potential sources of fertilizer magnesium

Name of magnesium source or fertilizer	Chemical composition	Magnesium content (%)	Water solubility (g dm^{-3})
Water soluble salts			
Magnesium nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	10	1 250
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	25	1570
Epsom salts	$MgSO_4 \cdot 7H_2O$	10	335
Kiserite	$MgSO_4 \cdot H_2O$	18	360
Sulfate of potash magnesia	$2MgSO_4 \cdot K_2SO_4$	12	240
Schoenite	$MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$	6	330
Magnesium chelates	various	3-5	high
Oxides and carbonates			
Magnesium oxide	MgO	50-55	0.009
Dolomite	$MgCO_3CaCO_3$	8-20	0.006
Magnesite	$MgCO_3$	27	0.034
Other sources			
FCMP*		92	90% CAS**
Struvite	$MgNH_4PO_4 \cdot 6H_2O$	10	low
Magnesium ammonium phosphate	$MgNH_4PO_4$	16	0.14
Serpentine	$Mg_3SiO_5(OH)_4$	21	low

*Fused calcium magnesium phosphate; **citric acid soluble

STRATEGIES TO MITIGATE MAGNESIUM DEFICIENCY IN CROP PLANTS

Strategy set-up

The actual daily intake of magnesium from food by human individuals depends on their eating habits. Human nutritionists working out a diet take into account two basic factors: 1) food sources, i.e. food diversification, 2) concentration of minerals, such as magnesium in consumed food and drinking water. At present, there are some alternative options to increase magnesium daily intake. However, the first solution, in fact the easiest way, is to change the structure of consumed products, from low to rich in magnesium content, such as vegetables, some fruit, fish, meat, etc. Another option to cover magnesium daily requirements is to supplement food with mineral magnesium or to take it orally. The second solution is frequently applied during prevention and/or therapy of hypomagnesaemia (well defined signs or symptoms) and also during hospitalization of patients with clinical magnesium deficiency symptoms (Eby, Eby 2006, Douban et al. 1996, Fawcett et al. 1999, Wojtasik et al. 2009).

However, in this part of the review we do not aim to discuss consumption patterns, as being the objective of human nutritionists. It is much more important is to define a simple strategy of magnesium increase, achievable by plant producers, in potentially edible part of currently grown crop plants, as a primary source of food, irrespective of the way of its final consumption. At present, despite high speed of progress in biotechnology, agronomic practices are the only realistic solution for increasing magnesium concentration in plant food. The essence is to find the most effective way of magnesium management in the soil-plant continuum, taking into account three objectives: 1) adequate nutrient supply to a plant during the course of vegetation, 2) increase of its content in edible plant parts, 3) high efficiency of applied magnesium fertilizer as related to low losses via leaching.

Sources of fertilizer magnesium

There are several magnesium carriers that can meet crop plant requirements. They can be divided into different groups, based on selected criteria:

1) chemical origin: a) organic, b) mineral;
2) mineral groups: a) soluble salts, b) oxides and carbonates, c) silicates;
3) solubility: a) water soluble, b) water semi-soluble.

Despite the rate of Mg^{2+} ions release, each of the above specified magnesium-bearing fertilizer sources plays an important role in soil magnesium management. Organic sources of magnesium are of primary or secondary origin. Primary sources are plant residues, which as indicated in Figure 5, contain from 40 to 55(60)% of magnesium accumulated in aerial crop plant biomass at harvest. Plant residues of dicotyledonous crops, such as sugar beets, or oil-seed rape are naturally richer in magnesium than cereals (Hundt, Kerschberger 1991).

Therefore, such plant residues should be considered as a natural source of basic cations, including magnesium. Farmyard manure contains not only farm recycled plant residues but also other organic fodder or mineral additives used in animal nutrition. Therefore, the content of magnesium in manure is highly variable, depending on the type of farm, method of animals nutrition, type of manure. All organic sources of manure can be classified as slow-release fertilizers irrespective of the type, and the main objective of their application is to increase the total content of soil magnesium.

In practice, minerals such as soluble salts, which are easily dissolved in water, are an important source of magnesium (Table 5). This group of minerals is widely used as magnesium fertilizers in pure or processed forms. These fertilizers enrich directly the concentration of Mg^{2+} ions in the soil solution, in turn increasing the pool of nutrients directly taken up by plants. Another group of minerals, representing by carbonates and/or oxides, are poorly dissolved in water. However, they release Mg^{2+} ions when incorporated into soil. In terms of soil geochemistry, soil can be considered as weakly acid, in turn significantly affecting magnesium minerals dissolution, as presented below for dolomite:

$$(Mg\,Ca)(CO_3)_2 + 4H^+ \rightarrow Mg^{2+} + Ca^{2+} + 2CO_2 + 2H_2O$$

Some other groups of magnesium fertilizers are highly specific, for example fused calcium magnesium phosphate (FCMP), whose production is based on phosphate rock and serpentine, being fused in an electric furnace. The product contains 18-20% of P_2O_5, *ca* 12% of MgO and also silicon and lime. It is very popular in many Asian and South American countries. The main disadvantage of this fertilizer is its high cost of production, 850 kWh per 1 ton of final product (Ranawat et al. 2009). Another source of magnesium fertilizer source is serpentine ($Mg_3SiO_5(OH)_4$). Although it is not very popular, it was first used make magnesium phosphates in New Zealand 70 years ago, in the 1940s (Metson, Brooks 1975). Potential sources of magnesium are also ammonium magnesium phosphates, including mineral called struvite. This fertilizer is a product of municipal and animal manure wastewater purification. For all these groups of minerals, the particle size and their degree of crystallization are the most important factors affecting the rate of magnesium release, i.e. defining potential of Mg^{2+} cations to supply cultivated crops.

Critical stage concept – soil versus foliar application

The current nutritional status of commonly grown crop plants can be simply assessed by evaluating their sensitivity to external magnesium supply, i.e. application of magnesium containing fertilizers. The main question refers to the adequate time, amount and form of applied magnesium fertilizer. However, as discussed in chapter two, magnesium is responsible for crop plant metabolism at different stages. An adequate supply of magnesium is important for the distribution of carbohydrates assimilated by leaves, as a prerequisite of an adequate rate of the crop canopy growth (CAKMAK, KIRKBY 2008). Therefore, the first step in any reliable assessment of the nutritional status cultivated crops is to define their critical growth stage(s).

Two main strategies of magnesium fertilizer application can be considered. One relies on magnesium incorporation into soil, depending on the fertilizer solubility or the aim of the treatment. For water soluble fertilizers, the main aim is to achieve a quick increase of the available magnesium content in the soil solution (HARDTER et al. 2004). This method of magnesium application may meet crop plant requirements (GRZEBISZ et al. 2001). However, the application of soluble magnesium salts leads to concurrent leaching of much of the applied magnesium. An alternative solution is to apply slow magnesium releasing fertilizers such as dolomite or serpentine. The release of Mg^{2+} ions to a cultivated crop depends on weathering, whose intensity is controlled mainly by annual precipitation and soil pH.

Agricultural evaluation of main magnesium fertilizers is based on assumed application targets, for example defined by plant magnesium accumu-

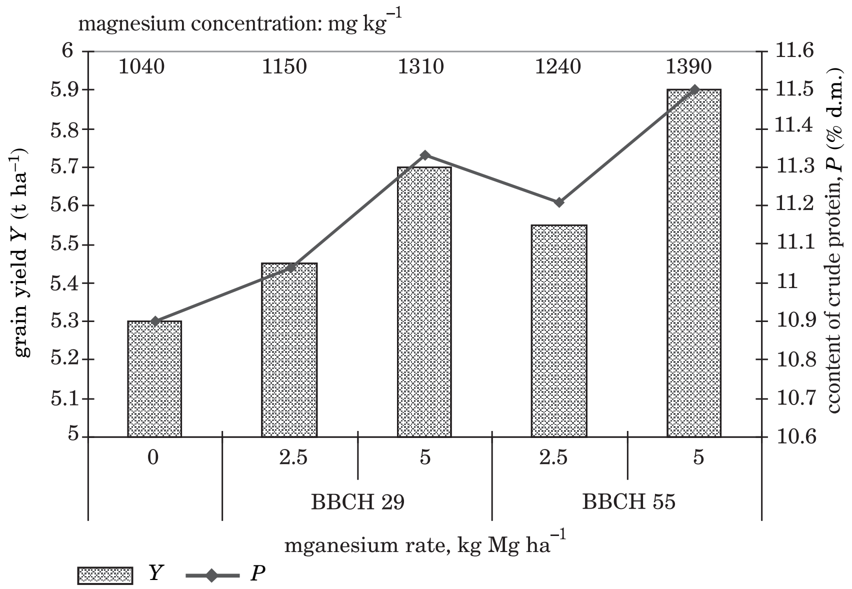

Fig. 8. Effect of timing and magnesium application rate on quantity and quality of winter wheat grain (based on MATŁOSZ 1992)

lation, leaching and crop plant yield and/or quality increase. As shown in Figure 8, in humid regions of the world, leaching of magnesium from soluble salts is high, reaching 50% of the applied Mg rates during 32 months. An effect of pure serpentine rock on both magnesium accumulation and its leaching was weak, demonstrating its low usability as Mg-fertilizer. However, the processed fertilizer called Serp-superA has fulfilled fertilizing and environmental expectations (HANLY et al. 2005, LOGANATHAN et al. 2005).

The highly probability of soil magnesium leaching from soluble salts can be easily overcome by applying lower rates or by splitting the whole rate into sub-rates applied both before and in the course of the growing season (HARDTER et al. 2004). The second option relies on foliar application of water soluble fertilizers. This strategy of magnesium supply to cultivated crops requires adequate determination of three variables affecting the production objectives: 1) time of application adequately related to plant growth and components of yield formation, 2) amount of applied magnesium, 3) salt concentration in the spraying solution. Taking into account the main objective of this review, foliar magnesium spray seems to be the simplest agronomic way of increasing magnesium concentration in edible plant parts. As presented in Figure 9, the application of 5 kg Mg ha^{-1} was able to increase the concentration of magnesium in wheat grain by 33%. This value is at the level of that reported by FAN et al. (2008) for long-stem straw, i.e. before the era of modern short-stem straw varieties.

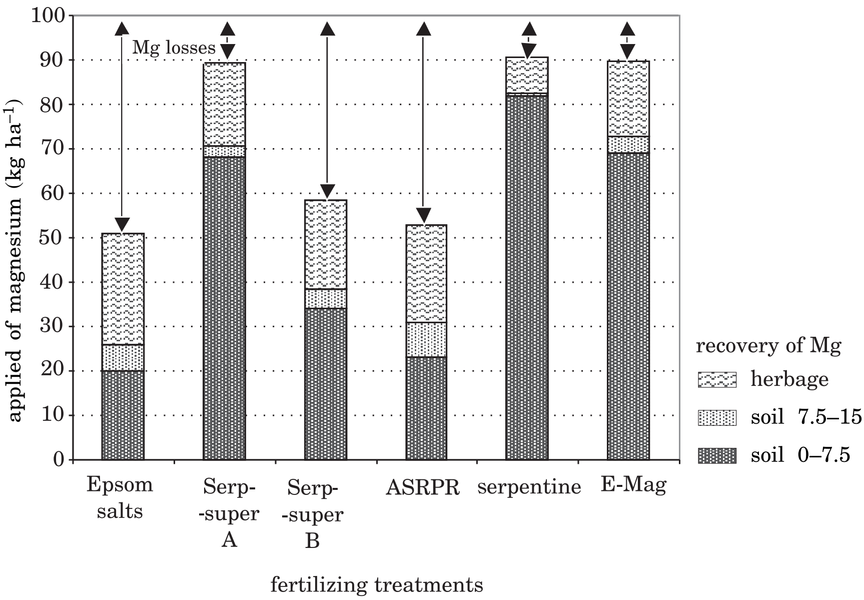

Fig. 9. Structure of fertilizer magnesium recovery (soil + herbage) and losses in soil (based on LOGANATHAN at al. 2005)

FINAL CONCLUSION

The present overview of magnesium importance for the health plants, animals and people in the whole food chain is the best described again dr Northen: "*Minerals are vital to human metabolism and health – and that no plant or animal can appropriate to itself any mineral which is not present in the soil upon which it feeds up*" (BEACH 1936). Agronomic practices consisting of well-tended soil and plant magnesium management seem the best and at the same time the cheapest way to make quick improvement of the quality of edible plant parts with respect to magnesium levels.

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EFFECTS OF MAGNESIUM ON PORK QUALITY

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Abstract

Over the recent years, there has been an increasing interest in improving pork quality, which at present often fails consumer requirements. Nutritional regime is one of the key environmental factors affecting fattening results, slaughter value and meat quality. The technological and organoleptic properties of pork can be modified through feeding. Numerous studies have been conducted to determine the effect of diet composition on meat quality.

Consumers prefer lean pork with a bright reddish-pink color, and they object to muscles that are too pale or too dark. An excess amount of meat juice in the package is also considered unacceptable.

The role of vitamins, minerals and feed additives in animal nutrition is an important consideration. Animal production efficiency is dependent upon an adequate supply of nutrients and minerals. Nutrient availability from feedstuffs is a principal factor in improving animal productivity and health as well as meat quality. Organic forms of minerals have been proven to have high bioavailability.

Since the magnesium content of standard diets satisfies the needs of animals, pigs are usually not provided with supplemental magnesium. However, research results show that magnesium compounds have a beneficial influence on selected aspects of pig production. Dietary magnesium supplementation positively affects the behavior of animals, decreases their stress sensitivity and improves pork quality by enhancing meat color, reducing drip loss and increasing acidity.

Key words: magnesium, meat quality, pigs.

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WPŁYW MAGNEZU NA JAKOŚĆ MIĘSA ŚWIŃ

Abstrakt

W ostatnich latach dużo uwagi poświęca się jakości mięsa wieprzowego, która w opinii wielu konsumentów jest niska i nie odpowiada ich wymaganiom. Żywienie zwierząt jest jednym z najważniejszych czynników środowiskowych, który ma wpływ na efektywność tuczu, wartość rzeźną i jakość mięsa. W przypadku trzody chlewnej istnieje możliwość modyfikowania zasadniczych cech jakości technologicznej i organoleptycznej mięsa poprzez żywienie. Obecnie prowadzi się wiele badań związanych z wpływem składników pokarmowych na jakość uzyskanego mięsa.

Nabywca wybierając opakowanie mięsa kulinarnego preferuje porcje z dużą zawartością chudej tkanki mięśniowej, o typowej dla wieprzowiny różowoczerwonej barwie. Nie akceptowane są porcje mięsa o barwie zbyt jasnej lub zbyt ciemnej oraz mięso z dużą ilością wycieku soku mięsnego.

Analizując wpływ żywienia na jakość mięsa, często zwraca się uwagę na rolę witamin i składników mineralnych, a także niektórych dodatków paszowych. Prawidłowe zaopatrzenie organizmu w składniki mineralne jest jednym z podstawowych czynników decydujących o efektywności produkcji zwierzęcej. Ważnym problemem jest dostępność składników mineralnych. Decyduje ona o wynikach produkcyjnych, zdrowotności zwierząt, ma również wpływ na jakość mięsa. W ostatnich latach w wielu badaniach wykazano wysoką biodostępność tzw. organicznych połączeń składników mineralnych.

Zawartość magnezu w typowych dawkach pokarmowych jest wystarczająca do pokrycia potrzeb świń. Mając na uwadze powyższe informacje, magnez nie jest zwykle dodawany do mieszanek paszowych dla świń. W piśmiennictwie naukowym znajduje się jednak wiele informacji o korzystnym wpływie dodatku związków magnezu na niektóre aspekty produkcyjne trzody chlewnej. Stosowanie dodatku magnezu w mieszankach dla świń może korzystnie oddziaływać na zachowanie świń, wrażliwość na stres i jakość mięsa, poprzez poprawę barwy, zmniejszenie wycieku soku mięsnego, podwyższenie kwasowości.

Słowa kluczowe: magnez, jakość mięsa, świnie.

INTRODUCTION

Pork consumption has a high share of total meat consumption in the EU member states including Poland. In 2008, the estimated total household consumption of meat and fish in Poland was as follows: poultry meat – 17.8 kg, pork – 16.8 kg, fish – approximately 12 kg. Quality attributes are the key factors affecting consumer purchasing decisions for pork. Over the recent years, there has been an increasing interest in improving pork quality, which often fails to meet consumer requirements. Consumers pay particular attention to the external appearance of pork portions, which is generally regarded equivalent to quality. At the moment of purchase, consumers evaluate the proportions of muscle, bone and connective tissue, meat color and the presence of meat juice in the package. Consumers prefer lean pork with a bright reddish-pink color, and they object to muscles that are too pale or too dark. An excess amount of meat juice in the package is also considered unacceptable (Aaslyng et al. 2007, Pisula, Florowski 2009).

MEAT QUALITY

Quality attributes determine the processing suitability and consumer perception of meat and meat products. They describe the sensory, nutritional, technological and sanitary quality of meat (SŁOWIŃSKI 2006). Consumers make their purchasing decisions based on an evaluation of the sensory properties of meat, including color, palatability, consistency and juiciness.

Color is one of the most important meat quality characteristics. It is a visual sensation that depends on the presence of pigments, the tissue composition and texture of meat. If consumers find the color of meat unacceptable, all other quality attributes become relatively unimportant. There is some correlation between meat color and the pH of muscles. Changes in meat color are in 50% determined by pH values measured 24 hours post mortem. The average value of color lightness L* of *m. longissimus dorsi*, measured with a Minolta colorimeter, is 44 (ranging from 38 to 48). Meat color is positively affected by nutritional factors, such as the content of vitamin C, vitamin E, selenium and magnesium (ARIHARA et al. 1993, BREWER, NOVAKOFSKI 1999, COLE, CLOSE 2005, KŁOSSOWSKA, TYSZKIEWICZ 2000, KOŁCZAK 2007a).

Palatability is a sensory attribute of meat defined as a combination of taste, aroma (flavor), consistency, temperature and acidity. Meat owes its characteristic taste mainly to a mixture of volatile compounds. Raw muscle tissue is the main source of flavor precursors and a few aroma- and taste-active compounds. Raw meat has a delicate, blood-like, slightly sweet, slightly sour, slightly salty and slightly bitter taste, depending on its biochemical composition and origin. The aroma of raw meat is weak and subtle, similar to that of commercial lactic acid. Between ten and twenty substances involved in the development of meaty, beef-like, fresh and blood-like aroma have been recently identified in raw meat. The meat of older animals has a more intense flavor than the meat of younger animals. Meat palatability is significantly affected by intramuscular fat. Different muscles from the same carcass and animal species differ with respect to the optimal levels of intramuscular fat. Neither excess nor insufficient intramuscular fat contributes to desirable flavor effects. Muscle types vary in their palatability attributes.

Meat with a high pH seems to be less salty and less palatable than meat with a low pH, most probably due to differences in the amount of free, unbound water. The palatability and flavor of meat enhance during postmortem aging (KOŁCZAK 2007b, TROY, KERRY 2010), and they change as a result of heat treatment. Flavor precursors are water- and fat-soluble compounds, including peptides, amino acids, nucleotides, reducing sugars, aliphatic hydrocarbons, fatty acids and their oxidation products. Cooked, fried, stewed and roasted meat products differ in taste and aroma. The flavor precursors present in raw meat are probably responsible for the development of palatability characteristics in heat-processed meat (KOŁCZAK 2007b, TROY, KERRY 2010).

Consistency is referred to as the sum of visual impressions regarding the color and texture of meat, determined by the quality of raw materials and the course of the technological process (ANDERSEN et al. 2005, TROY, KERRY 2010).

Juiciness is closely related to the water-holding capacity and intramuscular fat content of meat. Meat with a high water-binding capacity is more juicy and, in consequence, more palatable. Raw pork should not have any visible symptoms of water loss or become stringy and dry upon processing. Meat juiciness increases during cold storage (aging) because cell membranes lose their permeability and release cellular fluids (ANDERSEN et al. 2005, TROY, KERRY 2010).

In addition to its nutritive value, consumers are known to pay considerable attention to the palatability, tenderness and juiciness of meat (TROY, KERRY 2010).

The nutritional value of meat is a quality attribute that cannot be visually assessed, but it does affect consumer buying decisions. Meat is a valuable source of nutrients that are an important part of the human diet. Consumers generally show a distinct preference for lean, low-calorie meat with a high content of protein, vitamins and microelements (PURCHAS et al. 2009, ZULLO et al. 2003).

The chemical composition of meat can vary according to animal species, age, live weight and sex, carcass cut and postmortem changes in the muscles.

Meat is a good source of minerals. The mineral content of meat may vary widely depending on the muscle, carcass part, animal species and nutritional regime. Nutrients present in meat in larger amounts (above 0.1%), referred to as macroelements, are potassium, phosphorus, sodium, chloride, magnesium, calcium and sulfur, whereas nutrients found in smaller quantities (below 0.1%), referred to as microelements, include iron, zinc, copper, manganese and molybdenum. Mineral compounds affect the technological and sensory properties of meat. Phosphorus concentrations determine the water-holding capacity of meat, and sulfur content influences sensory attributes. Due to high levels of phosphorus and sulfur, meat and meat products belong to acid-forming foods. Meat and edible offal supply magnesium, sodium and potassium.

Inorganic compounds found in tissues are predominantly in the ionized form. They are involved in the regulation of osmotic pressure and electrolyte balance inside and outside the cells. The majority of calcium and potassium ions are bonded with proteins, mostly myosin. Calcium and magnesium ions help regulate muscle contraction. Magnesium is also an activator for many enzymatic reactions.

The content and composition of mineral salts affect the processing suitability (water-holding capacity) and organoleptic properties of meat (PURCHAS et al. 2009, ZULLO et al. 2003).

Processing suitability is determined by the technological quality attributes of raw materials, including the stage of meat aging, water-holding capacity, pH, pigment content, the proportion of muscle tissue, the method of meat preservation. The quality of raw materials influences the quality of end products. It is difficult, or even impossible, to manufacture high-quality products from poor-quality raw materials (SŁOWIŃSKI 2006).

Water-holding capacity is a key indicator of the processing suitability of meat. It is defined as the ability of muscle to retain its water (juice) and to absorb or bind extra water added to the product during the technological process. The retained (bound) water contributes to the juiciness and palatability of meat. The water-binding capacity of meat is affected by various factors, including the physical state of proteins and pH, primarily the rate of post mortem pH decline and ultimate pH values. A high water-holding capacity is observed in dry, firm and dark (DFD) meat, while meat with a low water-holding capacity tends to be pale, soft and exudative (PSE) (COLE, CLOSE 2005, VAN DE PERRE 2010).

A decrease in acidity (a rise in pH) and an increase in salt concentrations improve the water-holding capacity of meat. A high water-binding capacity is desirable if meat is to be marinated or pickled in a marinating or pickling medium. The ultimate pH of meat usually ranges from 5.65 to 5.80. The optimum pH level is 5.7-5.9. Drip loss may be effectively reduced by adding vitamin C, vitamin D, selenium, magnesium, calcium and conjugated linoleic acid (CLA) to animal diets (COLE, CLOSE 2005, D'SOUZA et al. 1999).

The sanitary quality of meat is evaluated based on microbiological contamination (total microbial counts, quantitative and qualitative composition of pathogenic microflora), the presence of residues of drugs, heavy metals, pesticides and mycotoxins, and the presence of parasites (SŁOWIŃSKI 2006, TROY, KERRY 2010). The quality characteristics of pork intended for human consumption are affected by genetic factors and environmental conditions, including nutrition (LAMMENS et al. 2007, PISULA, FLOROWSKI 2009).

The most common quality defects of fresh pork are color deviations, excessive drip loss and too high acidity. The quality attributes of meat measured most often are pH, color, water-holding capacity, tenderness and marbling.

Major research efforts are currently focused on investigating the effect of nutritional regime on meat quality and the impact of stress on production results. The role of vitamins, minerals and feed additives in animal nutrition is also an important consideration.

MAGNESIUM IN PIG NUTRITION

Macroelements and microelements are needed for the normal growth and development of all living organisms. Magnesium is a macronutrient – it is required in large quantities. Magnesium plays a vital role in numerous metabolic and enzymatic reactions as it is involved in more than 300 enzyme systems. It is also essential to build the bones. Magnesium metabolism is closely related to calcium and phosphorus metabolism. In animal organisms, around 60% magnesium is stored in the bones, 40% migrates into soft tissues and approximately 1% is found in bodily fluids.

Magnesium forms organic compounds and participates in carbohydrate and fat metabolism. Protein synthesis depends on optimal magnesium concentrations. Magnesium is essential for oxidation-reduction reactions and phosphorylation processes (formation of high-energy compounds, e.g. ATP, synthesis of H_2 and electron carriers); it is involved in the synthesis and activation of enzymes; it is the main activator of enzymatic processes in the cells and it affects the storage of catecholamines (KANIA 1998, DUGAN et al. 2004).

In monogastric animals, magnesium is absorbed primarily from the small intestine, at approximately 60%, mostly via passive transport. Potassium, calcium and ammonia are magnesium antagonists. Magnesium homeostasis is not controlled by any specific hormonal system, but the process can be indirectly regulated by the parahormone calcitonin, aldosterone, thyroxine and insulin. Magnesium levels in the body are regulated by intestinal absorption, excretion through the kidneys, excretion in feces and dietary supply. The exact magnesium requirements are difficult to determine. Plasma magnesium concentrations are not a reliable indicator of the bodily magnesium state since the extracellular fluid contains only small quantities of this element. The symptoms of magnesium deficiency are well documented, particularly in ruminants (tetany). They include a strong response of the nervous system (hypersensitivity, anxiety, fear), muscle contractions and a drop in productivity (a slower growth rate, loss of appetite). A decrease in plasma magnesium concentrations reduces the magnesium content of bones.

Toxic magnesium concentrations in pigs remain unknown, but the maximum tolerable level of magnesium has been set at 0.3% (NRC 1980). In other animal species, toxic magnesium concentrations (due to an accidental Mg oversupply) lead to a decrease in feed intake and production efficiency, drowsiness, locomotor disorders and death.

Magnesium can be found in all types of feed, including green forage, feed of animal origin and mineral feed. Concentrated feed is a richer source of magnesium than roughage. Wheat bran, dried yeast, linseed meal and cottonseed meal are good sources of magnesium. The average magnesium content (mg/kg d.m.) of cereals, oil meals and fish meals is 1.1-1.3 g, 3.0-5.8 g and 1.7-2.5 g, respectively. The magnesium content of animal meals is directly proportional to the magnesium content of bones.

Magnesium levels in roughage may vary greatly, depending on plant species, the abundance of magnesium in the soil and climatic conditions. Legumes are usually richer in magnesium than grasses. Magnesium occurs in various forms in mineral feed (Table 1).

Table 1

Magnesium content of mineral feed

Specification	Content (%)
Magnesium oxide	50.5 - 52.0
Magnesium hydroxide	36.0 - 38.0
Magnesium phosphate	24.0 - 33.0
Magnesium chloride	12.0
Magnesium sulfate	10.0

Little is known about the availability of magnesium from different sources, but it is usually higher in monogastric animals than in ruminants. In chickens, the actual absorption of dietary magnesium is as follows: maize – 55.7%, wheat – 56.8%, oat – 82.7%, barley – 54.5%, soybean meal – 60.3%, skim milk powder – 63.0% (GUNTER, SELL 1974, SELL 1979).

Diets containing the above feed components meet the magnesium requirements of monogastric animals.

The availability of magnesium from mineral feed may also vary. The availability of magnesium oxide (MgO) is determined by particle size and the temperature of the production process. Magnesium oxide is obtained by heat processing of magnesium carbonate. Large particles of MgO (>0.5 mm) and low temperature (< 800°C) during the process reduce magnesium absorption in the small intestine. The average availability of magnesium oxide, compared with magnesium phosphate, is around 20% vs 45%. The above information comes from studies on ruminants which need larger quantities of magnesium than monogastric animals. Research on the role of magnesium in poultry and pig nutrition remains scanty.

Dietary magnesium demand is relatively low in pigs. Dietary magnesium intake of 0.04% is considered sufficient, and 500-650 mg magnesium per kg complete diet is recommended for pigs and poultry. Research results show that the magnesium requirement of artificially raised piglets is 300-500 mg kg^{-1} diet (min. 325 mg kg^{-1} d.m.), and that milk provides adequate amounts of this macronutrient (NRC 1998). Dietary magnesium intake of 400-450 mg is recommended in weaned piglets for optimal growth and magnesium deficiency prevention. The demand for magnesium increases proportionally to the protein content of the ration. The magnesium requirement of weaners and growing-finishing pigs is probably similar to that of piglets. It is difficult to determine precisely the exact dietary magnesium demand in farmed animals, yet magnesium intake of 0.04-0.09% (pregnancy) and 0.015-0.065% (lactation) had no effect on production efficiency (NRC 1998).

The magnesium content of maize-soybean diets ranges from 0.14 to 0.18%, and it is sufficient to meet the needs of pigs. However, according to some authors, the availability of magnesium from natural sources reaches 50-60%. Magnesium supplements are usually not fed to pigs, although numerous literary sources point to a beneficial influence of magnesium compounds on selected aspects of pig production. Supplemental magnesium may positively affect the behavior of animals, decrease their stress sensitivity, and improve pork quality by enhancing meat color, reducing drip loss and increasing acidity (DUGAN et al. 2004).

THE EFFECTS OF MAGNESIUM ON MEAT QUALITY

As a result of stress during transport and slaughter, glycogen is converted into lactic acid and the pH of meat decreases, leading to the occurrence of PSE meat defects. Magnesium inhibits stress-induced glycolysis, thus improving meat quality (APPLE et al. 2000, OTTEN et al. 1992).

The addition of magnesium to finisher diets decreases the blood levels of cortisol and catecholamines in transported pigs, and it helps calm the excited animals (HEUGTEN, FREDERICK 2004, KUHN et al. 1981).

D'SOUZA (1998) demonstrated that magnesium contained in feed reduced the plasma levels of the stress hormones norepinephrine and epinephrine. Plasma magnesium concentrations were higher in highly stressed animals than in those subjected to minimal pre-slaughter stress.

Early post-mortem changes in the muscles include pH decline. Under natural conditions, the ultimate pH is reached upon the completion of glycogenolysis, within the first 24 hours post mortem. The ultimate pH of normal muscles is 5.3-5.7, and the critical pH value determining the suitability of meat for storage is 5.4. Fast acidification during glycogenolysis (pH decline below 5.4) contributes to the development of PSE meat characterized by a low water-holding capacity, a pale color and low protein solubility. The occurrence of PSE defects is related to the fast rate of post-mortem glycogenolysis in the muscles. Too slow glycogenolysis and glycogen depletion may produce DFD meat (VAN DE PERRE et al. 2010).

Organic magnesium supplementation (Bioplex-Mg) has been found to reduce the incidence of PSE meat from 50 to 15% carcasses. The studied animals received 1.6 g elemental magnesium daily, for only two days before slaughter (COLE, CLOSE 2005).

According to reference data, supplemental magnesium decreases drip loss and improves meat color. Various effects of magnesium on the glycogen and lactate content of meat and post-mortem pH have been reported (APPLE et al. 2000, D'SOUZA et al. 1999). In a study by COLE and CLOSE (2005), short-term administration of organic magnesium (Bioplex-Mg) to animals reduced drip loss (from 6.6 to 3.6%) and improved meat color. Magnesium may have a beneficial influence on meat quality by decreasing drip loss (-0.53%) and the incidence of PSE meat (DUGAN et al. 2004, SCHAEFER et al. 1993, D'SOUZA et al. 1998, 1999).

SCHAEFER et al. (1993) demonstrated that magnesium had no effect on the color, texture and pH_{45} of pork (the animals were supplemented daily with 40 g magnesium aspartate product containing 1.3% magnesium aspartate). The same magnesium compound applied at a 64-fold higher dose supported an improvement in meat color and water-binding capacity, and reduced the incidence of PSE meat (DUGA et al. 2004, D'SOUZA et al. 1998, 1999, SCHAEFER et al. 1993).

Similar observations were made by HAMILTON et al. (2002). Drip loss in meat from pigs fed magnesium-supplemented diets decreased in one experiment, but not in all groups. Reduced drip loss was noted when the animals were supplemented with magnesium for two or five days, but it was not observed when pigs were received the supplement for three days. Magnesium exerted a more stable effect on pork color than on drip loss (APPLE et al. 2000, 2001).

HAMILTON et al. (2003) studied the effect of magnesium propionate, magnesium sulfate and magnesium proteinate added to diets for finishing pigs on meat color stability. Meat from pigs fed magnesium propionate had higher values of color lightness, redness and yellowness, compared with meat from animals receiving magnesium sulfate and magnesium proteinate. Magnesium sulfate was found to improve color stability.

D'SOUZA et al. (1998, 1999 and 2000) reported decreased drip loss, good stability of meat color and pH when magnesium from magnesium aspartate, magnesium sulfate or magnesium chloride was supplemented at 1.6 or 3.2 g day^{-1} for two to five days before slaughter. The beneficial influence of magnesium on meat quality due to decreased drip loss and improved color has been also described by other authors (DUGAN et al. 2004).

APPLE et al. (2002) demonstrated that supplemental magnesium inhibited lipid oxidation in meat during storage. However, the benefits of magnesium supplementation are not always observed, and the positive effects of magnesium are often questioned. In an experiment by GUO et al. (2003), the inclusion of magnesium proteinate or magnesium oxide (0.5, 1.0 or 2.0 g kg^{-1} feed) in poultry diets contributed to the oxidative stability of the liver. Magnesium proteinate was found to be more effective than magnesium oxide (GUO et al. 2003).

The efficiency of magnesium absorption is significantly affected by stunning method. Electrical stunning causes the greatest stress, which is why carbon dioxide stunning is more advantageous. In the USA, heavy-weight pigs are stunned using electric current. The favorable effect of magnesium supplementation is less evident in Austria, where the slaughter weight of pigs is lower and the animals are stunned with carbon dioxide (HEUGTEN, FREDERICK 2004).

Shortening the duration of exposure to carbon dioxide or electric current and the time between stunning and bleeding prevents the released stress hormones and metabolites from reaching skeletal muscles, thus reducing the incidence of PSE meat even by 50% (KOĆWIN-PODSIADŁA, KRZĘCIO 2005).

Most of the authors cited above reported that supplemental magnesium had no effect on production results even if applied at nearly 10 g/animal/day.

Magnesium supplementation is a relatively inexpensive method of improving pork quality since magnesium supplements are economical and can be administered over short periods of time (several days). Most data point to the benefits of short-term magnesium supplementation (1-5 days) with regard to meat quality traits, whereas the information on long-term effects of magnesium use in pig nutrition is scarce. The use of selected magnesium compounds improving the quality of pelleted feed (magnesium-mica – 8% Mg) in the amount of 1.25 or 2.5% over the entire feeding period may have a beneficial influence on carcass characteristics and meat quality, with no adverse effects on productivity (APPLE et al. 2000).

The above relationships have also been observed in other studies (MAXWELL et al. 1999, WATSON et al. 1999). The findings of some authors do not confirm the benefits of magnesium-mica application during pig fattening (APPLE 1999), but it should be remembered that pigs not always respond to short-term magnesium administration, either. This suggests that the effectiveness of magnesium supplementation is determined by a variety of factors, in particular the stress sensitivity of pigs and stress levels during the experiment.

Irrespective of some inconclusive research results, it seems that both short-term and long-term magnesium supplementation has a positive effect on pork quality. Magnesium is usually applied at 2 to 4 g/animal/day or 1 to 2 g kg^{-1} feed. Animal diets can be supplemented with organic (proteinate, aspartate) or inorganic (oxide, sulfate, chloride, phosphate) magnesium. If magnesium is to be used over a long period of time, a good choice is magnesium phosphate, which provides a combination of magnesium and highly available phosphorus (13.5%). In contrast to some other magnesium sources, magnesium phosphate has no laxative effect.

The application of magnesium through feed for brief periods before slaughter may pose certain difficulties (the need to produce a special feed mix, pre-slaughter fasting). A good solution is to add magnesium to drinking water. Adding 600 mg magnesium per liter of water for two days before slaughter has been found to be most effective (FREDERICK et al. 2004, 2006). In the cited studies, the magnesium compound added to drinking water offered to animals was magnesium sulfate. Both the dose and duration of magnesium supplementation are important considerations as long-term magnesium administration through drinking water may have a prooxidative effect.

SUMMARY AND CONCLUSIONS

Many efforts are being made to improve pork products so that they meet consumer expectations regarding quality and nutritive value. Pig nutritional programs, including an adequate dietary supply of micronutrients and macronutrients, may have a significant effect on pork quality. Magnesium is a mineral involved in numerous vital functions in the body. Since the magnesium content of standard diets satisfies the needs of animals, pigs are usually not provided with supplemental magnesium. However, research results show that magnesium supplementation positively affects carcass traits and meat quality, and decreases the stress sensitivity of pigs. Therefore, application of magnesium through feed or drinking water at the final stage of fattening or several days before slaughter may contribute to improving pork quality.

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FORUM

MAGNESIUM IN EVERYDAY PRACTICE OF A PAEDIATRICIAN

Jerzy Oleszkiewicz

Facts and suggestions

Magnesium is involved in most of the physiological processes. Maintaining the right proportions between bionutrients is a prerequisite of the efficient homeostasis in a child's organism. When the balance between these proportions is disrupted, a cascade of events follows.

Colic in infants is a model example of an ailment caused by magnesium deficit. Magnesium interacts with calcium. For example, a lower level of magnesium causes an influx of calcium into cells. Simultaneously, potassium escapes from cells. As a result, the muscle tissues in the baby's digestive system contract. If this is the case, administration of an antiflatulent medicine may not bring about any therapeutic benefits.

Children up to one year of age are often administered vitamin D3, which requires the presence of magnesium to play its biological role. This vitamin stimulates the reaction of a conversion (hydroxylation) of vitamin D3 into its active form, first in the liver tissues and then in cells of the kidneys. It can be presumed that low activity of this vitamin, quite frequently observed, is due to some inhibition of this process. It manifest itself as weak growth of scalp hair, sweating, delayed teething and sometimes even fully developed rickets.

Jerzy Oleszkiewicz MD

Paediatricians and dentists are sometimes hopeless when encountering cases of first enamel and then whole deciduous teeth being destroyed. The structure of enamel is composed of dozens of elements, of which magnesium counts very high.

Magnesium deficit in children causes the so-called growing pains. The whole skeleton during the body's growth is an area where the bones are intensively built, expanded and rebuilt. Calcium, manganese, silicon, boron and especially magnesium are responsible for the metabolism in the bone system. Magnesium ensures the performance of the biological role of calcium. Magnesium deficit during the time of the body's rapid growth, i.e. between 6-7 and 12-16 years of age, may generate painful responses.

Many authors point to some disturbing findings such as raised brittleness of bones during the fast body's growth and cases of osteoporosis, which until recently was believed to be an illness of the elderly. These findings create a whole new diagnostic and therapeutic problem. The multi-facet causes of adolescent osteoporosis include, for example, deficits in mineral components, including magnesium.

Magnesium deficit triggers psychomotor hyperactivity and disturbances in concentration among children and adolescents. In the 1980s, studies were performed on the content of toxic metals in children who suffered psychosomatic disorders and were treated at the Psychosomatic Unit of the Provincial Children's Hospital in Warsaw. In nearly all the cases, the permissible levels of lead and cadmium (found in tobacco smoke) were exceeded manyfold. At the same time, drastic deficits in the natural neutralizers of these toxins, i.e. magnesium and zinc, were documented. Quantitative deficits of these neutralizers make toxic metals become involved in the metabolic processes and enter the brain. Long-term supplementations of magnesium (as a lead neutralizer) and zinc (cadmium neutralizer) most often produced positive results, such as an improved condition in terms of the psychomotor hyperactivity of children. The results of the above study were presented at the European Psychomotor Congress and the World's Toxicology Conference in New Delhi.

Determinations of the levels of magnesium and toxic metals were carried out using hair elemental assays by atomic absorption spectrophotometry at the Military University of Technology in Warsaw. In total, hair samples of 30,000 Poles from all age groups have been analyzed that way. Many authors have also reported on some positive effects of magnesium supplementation in children characterized by psychomotor hyperactivity and concentration disorders.

Other signs of magnesium deficit in children include:

– fever tremors,
– losses of consciousness, especially in maturing girls (12-16 years old),
– dream disorders,

– tics – I would include such signs as excessive winking and eyelid closing, constant clearing of the throat.
– involuntary bed wetting at night, not connected with any urological causes for such an ailment.

The recommended therapeutic dose of magnesium is 5 mg kg^{-1} of a child's body weight.

Rational considerations on the causes and results of any illness are by necessity associated with questions concerning their economic aspect. A question should be raised – what is more expensive? To prevent magnesium deficits or to bear the costs of all kinds of pathological consequences of magnesium shortage.

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