

Content of macroelements and their ionic ratios in oat grain depending on the sulphur form and dose

Zawartość makroskładników oraz ich stosunki jonowe w ziarnie owsa w zależności od formy i dawki siarki

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ABSTRACT

The research was based on the 2001-03 field experiment set up on Luvisol, of a very good rye soil complex, IIIb soil valuation class. The soil was slightly acidic in reaction, average richness in available forms of phosphorus, potassium and magnesium as well as low richness in the content of sulphates (VI). The research demonstrated that the sulphur fertilisation applied showed, in general, a slight effect on the content and equivalent proportions of macroelements in oat grain. The fertilizers (ammonium sulphate (VI), potassium sulphate (VI) and Wigor S) applied, irrespective of the sulphur form and dose, in some of the research years there was shown a slight decrease as compared with the non-fertilisation treatment, the contents of phosphorus, potassium and calcium. The content of magnesium, especially sulphate sulphur (VI) in oat grain, as affected by fertilizers containing sulphur, in general, gets increased. The elementary sulphur form found in Wigor S made it possible to reach slightly higher contents of phosphorus, calcium and magnesium than its sulphate (VI) form than the one used in a form of K_2SO_4 and $(NH_4)_2SO_4$ however, in general, these differences were not significant. Neither were there identified any differences between the effect of the 20 and 40 kg S·ha⁻¹ doses on the content of the macroelements.

Of all the ionic ratios assayed in the oat grain, sulphur fertilisation demonstrated a significant effect on the values of $K^+ : Mg^{+2}$ and $K^+ : (Ca^{+2} + Mg^{+2})$ only.

Keywords: ionic ratios, macroelements, oat, sulphur, sulphur fertilization

STRESZCZENIE

Badania przeprowadzono na podstawie realizowanego w latach 2001-03 doświadczenia polowego, które założono na glebie płowej, kompleksu bardzo dobrego żytniego, klasy bonitacyjnej IIIb. Gleba charakteryzowała się lekko kwaśnym odczynem, średnią zasobnością w przyswajalne formy fosforu, potasu i magnezu oraz niską zasobnością pod względem zawartości siarki. Badania wykazały, że zastosowane nawożenie siarką wywierało na ogół niewielki wpływ na zawartość i równoważnikowe proporcje makroskładników w ziarnie owsa. Pod wpływem zastosowanych nawozów ($(NH_4)_2SO_4$, K_2SO_4 i Wigor S), niezależnie od formy i dawki siarki, w niektórych z lat badań wykazano niewielkie obniżenie w porównaniu z obiektem nienawożonym zawartości fosforu, potasu i wapnia. Zawartości magnezu, a

zwłaszcza siarczanów (VI) w ziarnie owsa, pod wpływem nawozów zawierających siarkę na ogół ulegały podwyższeniu. Zastosowanie Wigoru S, zawierającego elementarną formę tego składnika, pozwoliło osiągnąć nieco wyższe zawartości fosforu, wapnia i magnezu niż zastosowanie K_2SO_4 oraz $(NH_4)_2SO_4$; nie były to jednak na ogół różnice potwierdzone statystycznie. Nie stwierdzono również istotnych różnic pomiędzy działaniem dawek 20 i 40 kg S·ha⁻¹ na zawartość badanych makroskładników. Spośród oznaczanych stosunków jonowych w ziarnie owsa, badane nawozy istotnie kształtowały wartości $K^+ : Mg^{+2}$ i $K^+ : (Ca^{+2} + Mg^{+2})$.

Słowa kluczowe: makroelementy, nawożenie siarką, owies, siarka, stosunki jonowe

DETAILED ABSTRACT

Podstawą badań było trzyletnie doświadczenie polowe prowadzone na terenie Stacji Badawczej Uniwersytetu Technologiczno-Przyrodniczego w Wierchucinku (53°26' N, 17°79' E, woj. kujawsko-pomorskie). Ścisłe doświadczenie polowe założono w trzech replikacjach, na glebie płowej typowej, według międzynarodowej klasyfikacji FAO-UNESCO była to Albic Luvisols. Gleba ta zaliczana do kompleksu żyniego bardzo dobrego (klasa bonitacyjna III a), charakteryzowała się odczynem lekko kwaśnym, a pod względem zasobności cechowała ją średnią zasobność w przyswajalne formy fosforu, potasu, magnezu oraz niska - w siarkę. Doświadczenie założono metodą losowanych bloków. Badanym czynnikiem był rodzaj nawożenia mineralnego (postać jonowa siarki – $(NH_4)_2SO_4$ i K_2SO_4 lub elementarna - Wigor S), zastosowanego w dawkach 20 lub 40 kg S·ha⁻¹. W doświadczeniu przewidziano jednolite nawożenie fosforem (20 kg P·ha⁻¹ w formie superfosfatu potrójnego) i potasem (90 kg K·ha⁻¹ w formie soli potasowej 50%), uwzględniając zasobność gleby w te składniki oraz pobranie ich z przewidywanymi plonami roślin. Uzyskane wyniki badań opracowano statystycznie przy zastosowaniu analizy wariancji w układzie zależnym według modelu zgodnego ze schematem doświadczenia. Do oceny istotności różnic zastosowano test Tukey'a na poziomie istotności p=0,05.

Jak wykazały przeprowadzone badania, najwyższą zawartość w ziarnie owsa posiadał potas, nieco niższą - fosfor i znacznie niższą - magnez, wapń oraz sód. Zastosowane nawożenie siarką wywierało na ogół niewielki wpływ na zawartość badanych makroelementów. Dla niektórych z lat badań wykazano, że pod wpływem zastosowanych nawozów, niezależnie od formy i dawki siarki, nastąpiło niewielkie obniżenie w porównaniu z obiektem nienawożonym, zawartości fosforu, potasu i wapnia. Natomiast zawartości magnezu, a zwłaszcza siarki siarczanowej(VI) w ziarnie owsa, pod wpływem nawozów zawierających siarkę, na ogół ulegały podwyższeniu. Zastosowanie Wigoru S pozwoliło osiągnąć nieco wyższe zawartości fosforu, wapnia i magnezu niż zastosowanie K_2SO_4 oraz $(NH_4)_2SO_4$ – na ogół nie były to jednak różnice potwierdzone statystycznie. Nie wykazano również istotnych różnic pomiędzy działaniem dawek 20 i 40 kg S·ha⁻¹ na zawartość badanych makroskładników.

Spośród oznaczanych stosunków jonowych w ziarnie owsa, badane nawozy istotnie kształtowały tylko wartości $K^+ : Mg^{+2}$ i $K^+ : (Ca^{+2} + Mg^{+2})$. Stosunki te w wyniku stosowania nawozów na ogół zawężyły się w porównaniu z obiektem kontrolnym, co należy uznać za korzystny kierunek zmian dla wartości paszowej ziarna owsa.

INTRODUCTION

The nutritive value of cereal grain depends on the content of minerals and their proportions. The chemical composition of plants depends on the adequate mineral fertilisation, especially nitrogen fertilisation significantly. Plant nutrition with nitrogen is closely connected with sulphur requirements since nitrogen metabolism depends on the state of the supply of plants with that nutrient (Eriksen and Mortensen, 2002, Inal, et al., 2003, Zhao, et al., 1995). Since mid 1990s there is observed a growing sulphur deficit in agrosystems due to (Morris, 2007, Stern, 2000, Szulc, 2008, Terelak, et al., 1995), taken up in many European countries, also in Poland, pro-ecological measures as well as changes in the assortment of mineral fertilizers without limiting FYM fertilisation (Haneklaus, et. al., 2000, Walker and Dawson, 2003). Interestingly, as much as 71% of soils of the Kujawy and Pomorze Province show its deficit, which has attracted more interest in sulphur as a fertiliser component, affecting not only the plant yield size but also the yield quality (Terelak, et al., 1995). Due to regular limiting sulphur emissions into soils and its high importance in plant physiology and due to the current knowledge, in general limited to winter rape, a field experiment which aimed at determining the effect of various sulphur forms and doses on the content of selected macroelements and their equivalent proportions in 'Komes' oat grain.

MATERIAL AND METHODS

The field experiments were made over 2001–2003 at the Experiment Station of the University of Technology and Life Sciences at Wierzychucinek (53°26' N, 17°79' E). The station is located about 25 km away north-west from Bydgoszcz, in the catchment area of the Brda River, on the south-eastern edge of the Krajeńskie Lakes, on the area of the Krajeńska Plateau. The experiment was performed on the Luvisol, made from heavy sandy marl loam, composed of sandy loam, deposited on the light clay. The soil water relations were controlled water relations, and as for the agricultural applicability, it represented very good rye complex, of the IIIb soil valuation class, with a slightly acidic reaction and average abundance in available forms of phosphorus, potassium and magnesium. The content of sulphate form (VI) S-SO₄²⁻ qualified it to soils of low abundance in that nutrient (Lipiński, et. al. 2003).

The field experiment was set up as a strict, single-factor experiment, following the randomized blocks design method in three reps. The plot was 20 m² in size and the plot for harvest - 16 m² in size. 'Komes' oat was grown. The experiment factor involved the type of mineral fertilisation containing sulphur in a ionic or elementary form. The following fertilisation treatments were considered:

K₁ - 0 kg S·ha⁻¹

K₂ - 20 kg S·ha⁻¹ in a form of ammonium sulphate (VI)

K₃ - 40 kg S·ha⁻¹ in a form of ammonium sulphate (VI)

K₄ - 20 kg S·ha⁻¹ in a form of potassium sulphate (VI)

K₅ - 40 kg S·ha⁻¹ in a form of potassium sulphate (VI)

K₆ - 20 kg S·ha⁻¹ in a form of Wigor S fertiliser

K₇ - 40 kg S·ha⁻¹ in a form of Wigor S fertiliser

Wigor S is a mineral fertiliser, containing 90% of elementary sulphur and 10% of bentonite. The fertilisation treatments and fertilisation were made following the

agrotechnical recommendations for oat. Pre-sowing homogenous mineral fertilisation was applied. Nitrogen was sown at the dose of $80 \text{ kg N}\cdot\text{ha}^{-1}$ in a form of ammonium sulphate (for the treatments with ammonium sulphate (VI) the dose of sulphate was adequately decreased, considering nitrogen introduced with sulphate), phosphorus ($20 \text{ kg P}\cdot\text{ha}^{-1}$) was sown in a form of triple superphosphate and potassium ($90 \text{ kg K}\cdot\text{ha}^{-1}$) as 50% potassium salt.

After oat harvest the following contents were assayed:

- phosphorus – with the colorimetric method with the use of ammonium molybdate, applying colorimeter type DR- 2000,
- magnesium – with the atomic absorption spectrometry (AAS) method,
- calcium, potassium, sodium – with the atomic emission spectrometry method with the use of flame photometer Flapho-4.

The present research results were statistically verified with the analysis of variance according to the model compliant with the experiment design. To evaluate the significance of differences in treatment means, Tukey's range test was used at the probability of $p = 0.05$.

RESULTS AND DISCUSSION

The present research showed that of all the macroelements determined, the oat grain contained most potassium (on average $5.26 \text{ g}\cdot\text{kg}^{-1}$), slightly less phosphorus ($3.29 \text{ g}\cdot\text{kg}^{-1}$) and much less magnesium ($1.37 \text{ g}\cdot\text{kg}^{-1}$), calcium ($1.16 \text{ g}\cdot\text{kg}^{-1}$) and sodium ($0.79 \text{ g}\cdot\text{kg}^{-1}$) (Table 1).

The sulphur fertilisation applied demonstrated, in general, a slight affect the content of the macroelements in the oat grain. As for phosphorus, it was only in 2002 and 2003 that there was recorded, in general, significant decrease in its content as compared with the control (K_1) as affected by ammonium sulphate (VI) (treatments K_2 and K_3). The mean differences for those years following the application in that form $20 \text{ kg S}\cdot\text{ha}^{-1}$ were respectively: 9.8% and 10.3%, as affected by $40 \text{ kg S}\cdot\text{ha}^{-1}$: 7.6% and 13.4%. Wigor S containing elementary form of sulphur (treatments K_6 and K_7) affected the content of phosphorus in oat grain less considerably: significant differences, as compared with the control, were recorded only in 2003 and they were as follows: for the dose of $20 \text{ kg S}\cdot\text{ha}^{-1}$ - 8.4%, and for $40 \text{ kg S}\cdot\text{ha}^{-1}$ – 8.1%. Potassium sulphate (VI) did not differentiate the content of the nutrient in any research year significantly.

The year 2001 was the only one in which there was shown a negative effect of fertilizers containing the ionic form of sulphur on the content of potassium in oat grain. It was found that the application of $20 \text{ kg S}\cdot\text{ha}^{-1}$ in a form of ammonium sulphate (VI) (K_2), as well as potassium (K_4) sulphate (VI) in that year significantly decreased the amount of that element; the differences were 10.4% and 11.0%, respectively. In the other years there was found no significant effect of the form and doses of sulphur investigated on the content of that nutrient in oat grain.

There was demonstrated a significantly negative effect of the application of potassium sulphate (VI) on the content of calcium in oat grain. The three-research-year average difference between the sulphur non-fertilised treatment and the treatments fertilised with K_2SO_4 for doses of $20 \text{ kg S}\cdot\text{ha}^{-1}$ (K_4) was 9.0%, and for the dose of $40 \text{ kg S}\cdot\text{ha}^{-1}$ (K_5) – 9.8%. The negative effect of sulphur fertilizers on the

content of calcium in oat grain was especially clear in 2003 when in all the sulphur-fertilised treatments there was observed a significant decrease in the content of the nutrient as compared with the control.

Table 1. The content of macroelements in the oat grain ($\text{g}\cdot\text{kg}^{-1}$)
Tabela 1. Zawartość makroskładników w ziarnie owsa ($\text{g}\cdot\text{kg}^{-1}$)

| Years Lata | Controle Obiekt kontrolny K ₁ | Form of fertilizer - Forma nawozu | | | | | | Mean Średnio |
|--|---|--|----------------|--------------------------------|----------------|----------------|----------------|-----------------|
| | | (NH ₄) ₂ SO ₄ | | K ₂ SO ₄ | | Wigor S | | |
| | | Dose of sulphur- Dawka siarki ($\text{kg S}\cdot\text{ha}^{-1}$) | | | | | | |
| | | 20 | 40 | 20 | 40 | 20 | 40 | |
| | | K ₂ | K ₃ | K ₄ | K ₅ | K ₆ | K ₇ | |
| The content of phosphorus - Zawartość fosforu | | | | | | | | |
| 2001 | 3.37 | 3.57 | 3.53 | 3.57 | 3.30 | 3.67 | 3.50 | 3.50 |
| 2002 | 3.57 | 3.22 | 3.30 | 3.50 | 3.34 | 3.55 | 3.38 | 3.41 |
| 2003 | 3.20 | 2.87 | 2.77 | 3.10 | 2.97 | 2.93 | 2.94 | 2.97 |
| x | 3.38 | 3.22 | 3.20 | 3.39 | 3.20 | 3.38 | 3.27 | 3.29 |
| LSD _{0.05} /NIR _{0.05} -0.254 | | | | | | | | |
| The content of potassium - Zawartość potasu | | | | | | | | |
| 2001 | 7.00 | 6.27 | 6.60 | 6.23 | 7.03 | 6.90 | 6.90 | 6.79 |
| 2002 | 4.50 | 4.58 | 4.33 | 4.20 | 4.33 | 4.62 | 4.65 | 4.37 |
| 2003 | 4.60 | 4.57 | 4.63 | 4.57 | 4.63 | 4.37 | 4.84 | 4.63 |
| x | 5.37 | 5.14 | 5.19 | 5.00 | 5.33 | 5.29 | 5.46 | 5.26 |
| LSD _{0.05} /NIR _{0.05} -0.406 | | | | | | | | |
| The content of calcium - Zawartość wapnia | | | | | | | | |
| 2001 | 1.13 | 1.06 | 1.20 | 1.13 | 1.09 | 1.13 | 1.34 | 1.15 |
| 2002 | 1.04 | 1.09 | 0.98 | 0.93 | 0.98 | 0.98 | 0.93 | 0.99 |
| 2003 | 1.49 | 1.34 | 1.35 | 1.28 | 1.23 | 1.34 | 1.39 | 1.35 |
| x | 1.22 | 1.16 | 1.18 | 1.11 | 1.10 | 1.15 | 1.22 | 1.16 |
| LSD _{0.05} /NIR _{0.05} -0.074 | | | | | | | | |
| The content of magnesium - Zawartość magnezu | | | | | | | | |
| 2001 | 1.38 | 1.47 | 1.42 | 1.34 | 1.45 | 1.45 | 1.39 | 1.41 |
| 2002 | 1.25 | 1.34 | 1.30 | 1.38 | 1.39 | 1.27 | 1.27 | 1.31 |
| 2003 | 1.30 | 1.46 | 1.52 | 1.34 | 1.41 | 1.36 | 1.33 | 1.39 |
| x | 1.31 | 1.42 | 1.41 | 1.35 | 1.42 | 1.36 | 1.33 | 1.37 |
| LSD _{0.05} /NIR _{0.05} -0.071 | | | | | | | | |
| The content of sodium - Zawartość sodu | | | | | | | | |
| 2001 | 0.73 | 0.80 | 0.67 | 0.67 | 0.70 | 0.70 | 0.53 | 0.69 |
| 2002 | 0.70 | 0.77 | 0.70 | 0.80 | 0.77 | 0.77 | 0.73 | 0.75 |
| 2003 | 0.93 | 0.93 | 0.96 | 0.96 | 0.94 | 0.93 | 0.93 | 0.94 |
| x | 0.79 | 0.83 | 0.77 | 0.81 | 0.80 | 0.80 | 0.73 | 0.79 |
| LSD _{0.05} /NIR _{0.05} -n.s./n.i. | | | | | | | | |
| The content of S-SO ₄ - Zawartość S-SO ₄ | | | | | | | | |
| 2001 | 0.67 | 0.82 | 0.83 | 0.83 | 0.89 | 0.77 | 0.95 | 0.82 |
| 2002 | 0.83 | 0.73 | 0.80 | 1.00 | 0.77 | 0.87 | 0.80 | 0.83 |
| 2003 | 0.48 | 0.60 | 0.80 | 0.68 | 0.77 | 0.67 | 0.80 | 0.69 |
| x | 0.66 | 0.72 | 0.81 | 0.84 | 0.81 | 0.77 | 0.85 | 0.78 |
| LSD _{0.05} /NIR _{0.05} -0.071 | | | | | | | | |

Interestingly, as for potassium and calcium, the dose of 20 $\text{kg S}\cdot\text{ha}^{-1}$, irrespective of the sulphur form, modified their content more considerably than the dose of 40 $\text{kg S}\cdot\text{ha}^{-1}$.

The only nutrient, except for sulphur, the content of which in oat grain as affected by the fertilizers applied, in general, was increasing, was magnesium. Significant

differences, as compared with the control, occurred after the application of ionic sulphur forms in a form of $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 , whereas Wigor S containing elementary sulphur did not differentiate the content of the element in the oat grain considerably. Thereby the antagonistic effect of potassium present in the fertilizer on the accumulation of magnesium was not confirmed. It must be noticed, that in years 2001, 2003 objects which were fertilized with $20 \text{ kg S} \cdot \text{ha}^{-1}$ in a form of K_2SO_4 in comparison with objects on which this dose was applied in a form of $(\text{NH}_4)_2\text{SO}_4$, significantly lower content of this component appeared. The comparison of the effect of the elementary and ionic sulphur forms on the content of macroelements in oat grain demonstrates a greater effect of the sulphate (VI) form. Sulphur in elementary form is water-insoluble, which can be its advantage due to a lower risk of nutrient losses as a result of leaching. On the other hand, there is a need of its biological oxidation with the *Thiobacillus* genus bacteria to sulphate (VI) form, available to plants, which makes sulphur in elementary form act slower than in the ionic form (Withers, et. al., 1995). The process of that microbiological transformation depends on many factors, e.g. on the activity of the population of microorganisms in soil, the degree of fertilisation sulphur fragmentation and on the moisture and thermal conditions [4]. The field experiment, being the springboard for the present research, was performed as exposed to generally low rainfall, which can account for lower effectiveness of the elementary form of sulphur than the ionic form.

Sodium is an element showed to be indispensable as a nutrient only for few plant species. Its physiological role is less known than that of potassium. In nine of the research years did the present research demonstrate a significant effect of the sulphur fertilizers applied on the content of sodium in oat grain (Table 1). The applicable literature offers very few reports on the affect of sulphur fertilisation on the content of that nutrient in plant yields. The research reported by Kozłowska (2000), which showed a clear increase in the share of that element in the cations of the spring rape biomass in total after the sulphur application, seems an exception.

The results of the present research showed that sulphur fertilisation, enhancing the supply of plants with that nutrient, increased the content of its ionic form in oat grain significantly (Table 1). There was noted a more favourable effect of K_2SO_4 than $(\text{NH}_4)_2\text{SO}_4$ as well as Wigor S on the accumulation of S-SO_4^{2-} . Respective differences, irrespective of the sulphur dose, as compared with the control were, on average, 16.7%, 25.8% and 22.7%. The content of sulphur in crop yields is, to much extent, conditioned by its availability from soil and so, in most cases, better effects are brought by the application of the sulphate (VI) form than the elementary form, acting slower due to the need to oxidation to S-SO_4^{2-} , which is reported by Nad et al. (2001) who, demonstrated clearly lower contents of S-SO_4^{2-} in white and rice fertilised with elementary sulphur than with ammonium sulphate (VI) and calcium sulphate (VI) (gypsum), while Withers et al. (1995) noted no differences in the content of S-SO_4^{2-} in cereal grain after foliar application of elementary sulphur in a form of gypsum with the dose of $10 \text{ kg S} \cdot \text{ha}^{-1}$. Only the application of those fertilizers at the doses higher than $30 \text{ kg S} \cdot \text{ha}^{-1}$ showed that calcium sulphate provides the most effective source of sulphur for cereals.

The applicable literature shows that, in general, the sulphur dose affects the content of sulphates (VI) in crop seeds more considerably than its application method (Barczak, 2010), the sowing date (Eriksen and Mortensen, 2002) or the form (Grant, et al., 2003). In 2001 and in 2003 for all the treatments there was demonstrated a significant increase in the content of S-SO_4^{2-} in oat grain as affected by the sulphur

fertilisation as compared with the control. The greatest differences occurred for treatments K₄ and K₇ and were on average for three years: 27.3% and 28.8%.

The physiological role of macroelements in the plant is, in fact, well known (Kotlarz, 2000), however, there are many fewer reports on the evaluation of equivalent ratios between those elements, especially the effect of sulphur fertilisation on their value. The quantitative proportions of macroelements, determining the ionic equilibrium in seeds used as a human diet component or used for animal feed, can determine their nutritive value. As reported by Podleśna (2004), maintaining the cation-anion equilibrium is one of the basic factors determining the adequate metabolism pattern and, finally, the yield size and its quality. Based on the determinations of macroelements the contents of which were expressed in gamma equivalent, there were calculated values of the following ionic ratios were: K⁺:Ca⁺², K⁺:Mg⁺² and K⁺:(Ca⁺²+Mg⁺²) and Ca⁺²/P (Table 2).

Tabela 2. Stosunki jonowe w ziarnie owsa

Table 2. Ionic ratios in the oat grain

| Years Lata | Controle Obiekt kontrolny K ₁ | Form of fertilizer - Forma nawozu | | | | | | Mean Średnio |
|---|---|---|----------------------|--------------------------------|----------------------|----------------------|----------------------|-----------------|
| | | (NH ₄) ₂ SO ₄ | | K ₂ SO ₄ | | Wigor S | | |
| | | Dose of sulphur - Dawka siarki (kg S·ha ⁻¹) | | | | | | |
| | | 20 K ₂ | 40 K ₃ | 20 K ₄ | 40 K ₅ | 20 K ₆ | 40 K ₇ | |
| K ⁺ :Ca ²⁺ | | | | | | | | |
| 2001 | 3.18 | 3.03 | 2.82 | 2.84 | 3.31 | 3.17 | 2.66 | 3.00 |
| 2002 | 2.23 | 2.21 | 2.26 | 2.32 | 2.26 | 2.42 | 2.56 | 2.32 |
| 2003 | 1.59 | 1.75 | 1.76 | 1.83 | 1.93 | 1.68 | 1.79 | 1.76 |
| x | 2.33 | 2.33 | 2.28 | 2.33 | 2.50 | 2.42 | 2.34 | 2.36 |
| LSD _{0.05} /NIR _{0.05} -n.s./n.i. | | | | | | | | |
| K ⁺ :Mg ²⁺ | | | | | | | | |
| 2001 | 1.57 | 1.31 | 1.65 | 1.43 | 1.49 | 1.47 | 1.52 | 1.49 |
| 2002 | 1.11 | 1.05 | 1.03 | 0.94 | 0.96 | 1.13 | 1.13 | 1.05 |
| 2003 | 1.11 | 0.96 | 0.94 | 1.05 | 1.01 | 1.00 | 1.12 | 1.03 |
| x | 1.26 | 1.11 | 1.21 | 1.14 | 1.12 | 1.20 | 1.26 | 1.19 |
| LSD _{0.05} /NIR _{0.05} -0.114 | | | | | | | | |
| K ⁺ :(Ca ²⁺ +Mg ²⁺) | | | | | | | | |
| 2001 | 1.05 | 0.92 | 0.95 | 0.95 | 1.01 | 1.01 | 0.97 | 0.98 |
| 2002 | 0.74 | 0.71 | 0.71 | 0.67 | 0.67 | 0.77 | 0.78 | 0.72 |
| 2003 | 0.65 | 0.62 | 0.61 | 0.67 | 0.66 | 0.62 | 0.69 | 0.65 |
| x | 0.81 | 0.75 | 0.76 | 0.76 | 0.78 | 0.81 | 0.79 | 0.78 |
| LSD _{0.05} /NIR _{0.05} -0.076 | | | | | | | | |
| Ca ²⁺ :P | | | | | | | | |
| 2001 | 0.52 | 0.46 | 0.53 | 0.49 | 0.51 | 0.48 | 0.60 | 0.51 |
| 2002 | 0.45 | 0.52 | 0.46 | 0.41 | 0.45 | 0.43 | 0.43 | 0.45 |
| 2003 | 0.73 | 0.73 | 0.76 | 0.64 | 0.65 | 0.71 | 0.72 | 0.71 |
| x | 0.57 | 0.57 | 0.58 | 0.51 | 0.54 | 0.54 | 0.58 | 0.55 |
| LSD _{0.05} /NIR _{0.05} - n.s./n.i. | | | | | | | | |

Of the ionic ratios calculated for the oat grain, sulphur fertilisation had a significant effect on proportions K⁺:Mg⁺² and K⁺:(Ca⁺²+Mg⁺²) only. Their values as a result of the application of sulphur, in general, decreased as compared with the control. Greater

differences concerned $K^+ : Mg^{+2}$, which was due to a clear increase in the content of magnesium in oat grain as a result of the sulphur fertilizers applied. The effect of sulphur fertilisation on the value of $K^+ : (Ca^{+2} + Mg^{+2})$ was most clear in 2001 when for most treatments, except for K_5 and K_6 , the fertilizers applied decreased the proportion significantly.

The content of macrelements, e.g. potassium, calcium, magnesium and sodium, and the quantitative ratios between them, are a measure of the nutrition applicability of animal feed produced from crops grown for animal-feed purposes as well as the nutritive value of the yield of crops allocated for consumption. The state of ionic equilibrium in the plant is an important factor determining the animal feed quality since excessive uptake of specific cations or anions limit the content of other, frequently valuable macro- and microelements. It is commonly believed that high contents of potassium deteriorate, and high contents of calcium and magnesium enhance the animal feed quality (Krzywy, et al., 2002). In practice, in animal feeds potassium excess is much more common than its deficit. What is especially undesirable is an excessively high range of the quantitative ratio of univalent cations to bivalent in ruminant feeds which can, due to magnesium deficiency, lead to hypomagnesemic tetany in cattle (Kopcewicz and Lewak, 2005). The direction of changes in the values $K^+ : Mg^{+2}$ and $K^+ : (Ca^{+2} + Mg^{+2})$ demonstrated in this study is thus favourable since it comes from a decreased content of potassium and an increase in the amount of magnesium in oat grain when exposed to sulphur fertilisation. An important role in maintaining the equilibrium between univalent and bivalent ions is attributed to an adequate content of calcium which, similarly as magnesium, can have an antagonistic effect on potassium (Kotlarz, 2000). Based on the present research one can assume that sulphur fertilisation, in general, enhances the content and quantitative proportions of macroelements in oat grain, however, formulating definite conclusions is not easy due to frequently missing significance of the differences discussed.

CONCLUSIONS

1. Sulphur fertilisation affected the amount and equivalent proportions of macroelements in oat grain inconsiderably. In some research years it was demonstrated that the fertilizers applied (ammonium sulphate (VI), potassium sulphate (VI) and Wigor S), irrespective of the sulphur form and dose, a slight decrease in the content of phosphorus, potassium and calcium, as compared with the non-fertilised treatment. The content of magnesium, especially sulphate sulphur (VI) in oat grain, as affected by fertilizers containing sulphur, in general, increased.
2. The ionic sulphur form contained in $(NH_4)_2SO_4$ and K_2SO_4 , more than the elementary form contained in Wigor S, determined the content of macroelements in oat grain. The variation in the sulphur doses (20 and 40 kg $S \cdot ha^{-1}$), in general, did not trigger significant changes in the content of macroelements.
3. The values in the ratios $K^+ : Mg^{+2}$ and $K^+ : (Ca^{+2} + Mg^{+2})$ as a result of the application tested sulphur's fertilizers, in general, decreased, as compared

with the control, which must be considered to be a favourable direction of changes for the fodder value of oat grain.

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