NARDI FUNDULEA, ROMANIA
www.incda-fundulea.ro

ROMANIAN AGRICULTURAL RESEARCH, NO. 34, 2017
Print ISSN 1222-4227; Online ISSN 2067-5720

REACTION OF SPRING BARLEY TO NPK AND S FERTILIZATION. YIELD, THE CONTENT OF MACROELEMENTS AND THE VALUE OF IONIC RATIOS

Wojciech Kozera*, Bożena Barczak, Tomasz Knapowski, Ewa Spychaj-Fabisiak, Barbara Murawska

University of Science and Technology in Bydgoszcz, Department of Agricultural Chemistry, Seminaryjna 5, 85-326 Bydgoszcz, Poland

*Corresponding author. E-mail: kozera@utp.edu.pl

ABSTRACT

The sulphur balance disturbance in agro-ecosystems has resulted in an increased interest in the effect of sulphur on the crop yield size and quality. The aim of the research was to evaluate the effect of varied fertilization with nitrogen, phosphorus, potassium and sulphur on the yielding, content and ratio of mineral nutrients in the spring barley grain. Here the results from a single-factor field experiment, applying the randomised block design in Luvisols (LVa) are reported the experiment factor was made up by the NPK and S mineral fertilization applied into soil at various rates and ratios. The highest grain yields, as compared with the control, were recorded after the use of sulphur, as well as the rates of 40 and 80 kg N ha^{-1}applied with 110 and 165 kg PK ha^{-1}.The research demonstrated a significant variation in the content in the grain of the elements studied, except for sodium, as a result of the fertilization applied. The grain from the series of fertilization variants with sulphur and the rate of 165 kg ha^{-1} PK contained significantly more phosphorus (by 4.6%) and potassium (by 2.8%) than the grain where the rate of 110 kg ha^{-1} PK was applied. As a result of the fertilization in the spring barley grain there we identified excessively high mean values of K^+:Ca^{2+} as well as excessively narrow Ca^{2+}:Mg^{2+} and Ca:P ratios. The ratios K^+:Mg^{2+} (2.18), K^+:(Ca^{2+}+Mg^{2+}) (1.70) as well as (K^++Na^+):(Ca^{2+}+Mg^{2+}) (2.13) were similar to the optimal ones. Broadening the values of ionic ratios in the spring barley grain, especially K^+:Mg^{2+} as well as K^+:(Ca^{2+}+Mg^{2+}), due to sulphur application, calls for considering that nutrient for the crop managemet practices in spring barley.

Key words: chemical composition, macroelements ratios, mineral fertilization.

INTRODUCTION

To provide a high yield-forming effectiveness of fertilizers, one shall maintain the adequate ratios between the nutrients applied (Kostadinova, 2014; Hirzel and Matus, 2014). The right fertilization should be based on the balance of nutrients, considering their uptake from soil as well as from fertilizers (Staugaitis et al., 2014; Mandic et al., 2015). Over the recent years, of all the nutrients, sulphur has become the element limiting the yield and quality of crops, especially the crops used in food industry or for animal feed (Stern, 2005; Shahsavani and Gholamii, 2008; Togay et al., 2008; Jamal et al., 2010). The role of this nutrient in the cultivation of cereals, considered species with lower sulphur requirements, is less known. Sulphur deficit in soil results in a lower effectiveness of nitrogen derived from fertilizers (Hitsuda et al., 2005; Fazli et al., 2008), decreasing crop yields and deteriorating their technological applicability, which can have a negative effect on the nutrition value and digestibility of animal feeds used for the nutrition of animals, especially the monogastric ones (Barczak and Nowak, 2013). The aim of the present research was to evaluate the effect of a varied fertilization with nitrogen, phosphorus, potassium and sulphur on the content and ratios of minerals in spring barley grain.

MATERIAL AND METHODS

The field experiments were performed over 2008-2010 at the Experiment Station of the Faculty of Agriculture and Biotechnology of the University of Science and Technology in Bydgoszcz, northern Poland. The experiment was carried out in Albic Luvisol

Received 24 April 2016; accepted 7 February 2017. First online: April, 2017. DII 2067-5720 RAR 2017-68

(LVa), formed from loam, representing the agronomic category of light soil, good rye complex, IIIb soil valuation class (WRB, 2006). The soil showed a slightly acid reaction (pH_{KCl} 5.7), an average richness in available forms of phosphorus (65 mg kg^{-1} P), potassium (112 mg kg^{-1} K) and magnesium (49 mg kg^{-1} Mg). The content of sulphate (VI) form qualifies it to represent the soils with a low content of that nutrient (9.3 mg kg^{-1} $S\text{-}SO_4^{2-}$).

The field experiment was set up as a single-factor experiment, in four replications, following the randomised block design. 'Antek' spring barley was cultivated; with winter wheat as its forecrop in each research year. The experiment factor was the variation in nitrogen, phosphorus, potassium and sulphur (n=13) fertilization applied at the following rates per hectare:

A_0 – without mineral fertilization;
A_1 – 150 kg NPK (40 kg N+30 kg P+80 kg K);
A_2 – 190 kg NPK (80 kg N+30 kg P+80 kg K);
A_3 – 230 kg NPK (120 kg N+30 kg P+80 kg K);
A_4 – 173 kg NPKS (40 kg N+30 kg P+80 kg K +23 kg S);
A_5 – 213 kg NPKS (80 kg N+30 kg P+80 kg K+23 kg S);
A_6 – 253 kg NPKS (120 kg N+30 kg P+80 kg K+23 kg S);
A_7 – 205 kg NPK (40 kg N+45 kg P+120 kg K);
A_8 – 245 kg NPK (80 kg N+45 kg P+120 kg K);
A_9 – 285 kg NPK (120 kg N+45 kg P+120 kg K);
A_{10} – 228 kg NPKS (40 kg N+45 kg P+120 kg K+23 kg S);
A_{11} – 268 kg NPKS (80 kg N+45 kg P+120 kg K+23 kg S);
A_{12} – 308 kg NPKS (120 kg N+45 kg P+120 kg K+23 kg S).

In the experiment nitrogen was provided before sowing exclusively in a form of ammonium nitrate (variants: A_1, A_2, A_3 and A_7, A_8, A_9) or in a form of ammonium nitrate and ammonium sulphate (variants: A_4, A_5, A_6 as well as A_{10}, A_{11}, A_{12}, where ammonium sulphate was the source of sulphur at the rate of 23 kg ha^{-1} S) and as top dressing, fertilizer applied into soil at the shooting stage (BBCH 30), in a form of ammonium nitrate. Phosphorus and potassium were supplied pre-sowing as triple superphosphate as well as potassium salt 60%.

The average air temperature over the growing season, March through July, in respective years of the field experiment, was similar to the many-years mean (Table 1).

Table 1. Temperature and precipitation distribution throughout the field experiment

Years	Months					Total or mean
	March	April	May	June	July	
Precipitation, mm						
2008	61.2	38.7	11,5	15.5	58.7	185.6
2009	43.7	0.4	85.3	57.4	118.0	304.8
2010	28.6	33.8	92.6	18.1	107.4	280.5
Mean for 1949-2010	24.7	27.3	43.1	54.3	71.3	220.7
Air temperature, °C						
2008	3.0	7.6	13.2	17.6	19.2	12.1
2009	2.4	9.8	12.3	14.5	18.6	11.5
2010	2.4	7.8	11.5	16.7	21.6	12.0
Mean for 1949-2010	1.8	7.4	13.0	16.2	18.0	11.3

The amount of precipitation throughout the spring-summer period varied clearly in respective research years. Total precipitation was much higher over 2009 and 2010; the difference, as compared with the many-year mean was: 84.1 and 59.8 mm, respectively, which accounted for 38.1% and 27.1%. In 2008 the amount of precipitation was 35.1

mm lower than the mean for that area. In May and June 2008, April 2009 and in June 2010 the amount of precipitation was much lower than the many-years mean; the difference in the total precipitation for those four months was 31.6, 38.8, 26.9 and 36.2 mm, respectively. In March and May 2009 the amount of precipitation was almost two-fold higher than the mean for that area. In May 2010 the difference was 49.5 mm.

In the seeds from all the experiment variants, after mineralization in concentrated sulphuric acid, we assayed the content of:

– total nitrogen based on the modified Berthelot reaction; after dialysis against a buffer solution of pH 5.2 the ammonia in the sample is chlorinated to monochloramine which reacts with salicylate to 5-aminosalicylate. After oxidation and oxidative coupling a green coloured complex is formed. The absorption of the complex is measured at 660 nm (Skalar SANplus flow analyser);

– total phosphorus based on the following reaction: ammonium hepta-molybdate and potassium antimony(III) oxide tartrate react in an acidic medium with dialysed and diluted solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex by L(+) ascorbic acid – the complex is measured at 880 nm (Skalar SANplus flow analyser), potassium, calcium and sodium, with flame photometry (Varian AA 240 FS), and magnesium – with Atomic absorption spectrometry (Varian AA 240 FS).

The results facilitated the calculation of the ionic ratios: $K^+:Ca^{2+}$, $K^+:Mg^{2+}$, $K^+:(Ca^{2+}+Mg^{2+})$, Ca:P, $Ca^{2+}:Mg^{2+}$ and $(K^++Na^+):(Ca^{2+}+Mg^{2+})$.

Chemical grain analysis was performed at the Sub-Department of Agricultural Chemistry, University of Science and Technology, in the Safe Foods Production Technology Support Laboratory formed as part of the Regional Centre of Innovativeness.

The results of research were statistically verified with the analysis of variance in a single-factor experiment, applying, to evaluate the significance of differences between means, the Tukey test at the level of significance of $p \leq 0.05$.

RESULTS AND DISCUSSION

Yield of grain

Mineral fertilization showed a significant effect on the spring barley yield, the average value of which was 3.46 t ha^{-1} (Table 2). According to Klikocka et al., (2014), it is one of the key factors affecting the amount of the grain collected per area unit. The yields reported in the first and third year of research were significantly lower than the yield collected in the second year and they were: 2.62, 3.63, and 4.13 t ha^{-1}, respectively. Such considerable differences were due to uneven precipitation distribution in vegetation seasons, especially in 2008.

Table 2. Spring barley grain yield

Unit	Year	Fertilization treatments													Mean[2]
		A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}	A_{12}	
[t ha^{-1}]	2008	2.40	2.45	2.64	3.13	3.15	2.73	2.31	2.37	2.37	2.45	2.74	2.85	2.47	2.62 ^{c}
	2009	3.22	3.75	3.97	4.32	4.29	4.43	4.28	3.82	4.07	4.45	4.28	4.27	4.57	4.13 ^{a}
	2010	2.59	3.26	3.85	3.56	3.74	3.91	3.57	3.49	3.60	3.99	3.70	4.02	3.89	3.63 ^{b}
	Mean[1]	2.74 ^{f}	3.15 ^{e}	3.49 ^{c}	3.67 ^{a}	3.72 ^{a}	3.69 ^{a}	3.39 ^{d}	3.23 ^{e}	3.35 ^{d}	3.63 ^{ab}	3.57 ^{b}	3.71 ^{ab}	3.64 ^{ab}	3.46

Values in the same lines[1] and columns[2] followed by the same letter are not significantly different according to Tukey test at the level $p \leq 0.05$. A_0 – control treatment without added fertilizers, A_1 – 150 kg ha^{-1} NPK, A_2 – 190 kg ha^{-1} NPK, A_3 – 230 kg ha^{-1} NPK, A_4 – 173 kg ha^{-1} NPKS, A_5 – 213 kg ha^{-1} NPKS, A_6 – 253 kg ha^{-1} NPKS, A_7 – 205 kg ha^{-1} NPK, A_8 – 245 kg ha^{-1} NPK, A_9 – 285 kg ha^{-1} NPK, A_{10} – 228 kg ha^{-1} NPKS, A_{11} – 268 kg ha^{-1} NPKS, A_{12} – 308 kg ha^{-1} NPKS.

In the present research in all of the fertilization variants**,** the mean spring barley grain yield was significantly higher than the one collected from the control. The yield-formation effectiveness of nitrogen applied with lower and higher rates of phosphorus and potassium (110 and 165 kg PK ha^{-1}) was similar.

Nitrogen fertilization is one of the most effective yield-formation factors (Candráková et al., 2009, Jankovic et al., 2011). It demonstrates a comprehensive effect together with other crop management factors on the yield level, as well as on the quality characteristics of the grain (Liszewski, 2008, Valkama et al., 2013). A positive effect of nitrogen fertilization on the barley grain yield, according to Noworolnik et al., (2014), is most often a result of increasing the number of spikes due to a better plant tillering. The macroelement enhances the number of grains per spike, which also results in the yield increase. Excessively intensive fertilization of barley with nitrogen poses a risk of lodging, a higher intensity of diseases and, as a result, a decrease in the yield size and quality. It can also increase the losses of the nutrient, increasing the environmental pollution. With that in mind, the optimisation of the plant supply with nitrogen is essential (Muurinen et al., 2007; Peltonen-Sainio et al., 2008; Shejbalová et al., 2014).

The greatest increase in the grain yield size due to NPK rates, as compared with the control, similarly as reported by Bleidere et al. (2013) investigating same species, was due to the application of 120 kg N ha^{-1} (A_3) (the difference: 0.93 t ha^{-1} – 33.9%).

Supplementing mineral fertilization with an additional nutrient; sulphur, enhanced the barley grain yield. The highest grain yields were recorded after the use of sulphur as well as the rates of 40 and 80 kg N ha^{-1} applied with 110 (A_4) and 165 kg PK ha^{-1} (A_{11}). The differences, as compared with the control, were about 1.0 t ha^{-1} (36.0%) and, as compared with the variants without sulphur, (A_1 and A_8) 0.5 t ha^{-1} (14.0%). What is interesting, is an essential decrease in the grain yield in the variant fertilized with the highest nitrogen rate (A_6), as compared with the variants where lower rates of N were applied (A_4 and A_5). The differences accounted for 8.9 and 8.1%, respectively, which can point to an excessively high nitrogen rate, as compared with the other nutrients.

Spring barley is considered to be a species with low sulphur requirements (Lipiński et al., 2003); however some researchers (Zhao et al., 2006; Järvan et al., 2008) indicated a positive effect of sulphur fertilization on cereal crop production. As reported by Barczak (2010), the maximum barley grain yield was recorded after the application of about 40 kg S ha^{-1}. It is a relatively high rate, as compared with the one recommended for spring cereal crop management practises in the countries of Western Europe (Morris, 2007), which the author related to a low availability in available sulphur of the soil where the research was performed, and to the relatively high grain yield recorded.

In Great Britain and Germany, according to Zhao et al. (2003), the increase in the spring barley grain yield due to sulphur fertilization at the rates up to 30 kg S ha^{-1} fell within the range of 5-28% and 11-22%, respectively. In the present research, the grain yield increase as a result of sulphur application, on average, accounted for about 6%.

Content of macroelements

The fertilization resulted in, in general, a significant increase in, as compared with the non-fertilized objects, the contents of total nitrogen in spring barley grain (Table 3). Sulphur fertilization in two research years (2009 and 2010) did not result in a significant increase in the mean nitrogen content in the grain, as compared with the content of that nutrient from the variants fertilized only with NPK; although a slight positive effect of that fertilization can be observed only in 2008 with the lowest precipitation. The amount, as well as the precipitation and temperature distribution, considerably determined the production potential of barley, affecting the processes of immobilisation and mineralization, affecting the intensity of microbiological sulphur transformations due to sulphur bacteria and enhancing their availability to plants (Barczak, 2010). The above observations confirm the results reported by Järvan et al. (2008) that the less favourable to the vegetation the weather conditions, the stronger the reaction of the plant yield to sulphur fertilization. The physiological sulphur functions in the plant involve its effect on the synthesis of amino acids (Järvan et al., 2008). Applying sulphur to plant nutrition, one could thus expect an increased accumulation of nitrogen in the grain, with metabolism connected with the supply of the plants with sulphur (Barczak et al., 2014) The results coincide with the results reported by Skwierawska et al. (2008) who also noted only a trend of increasing amount of nitrogen in the grain as a result of fertilization with that macronutrient, whereas Barczak (2010) found significant increases in the content of total nitrogen in barley grain after the application of 60 kg ha^{-1} S, and Gondek and Gondek (2010) in spring wheat grain. A significantly higher nitrogen content, as compared with that reported for the year 2009, was recorded in the grain collected in 2010 and 2008 (by 14.3% and 7.6%, respectively), which points to a clear effect of weather conditions throughout research on the chemical composition of the grain yield.

Table 3. Content of macroelements in spring barley grain yield

Macroelement g kg^{-1}	Year	Fertilization treatments													Mean^{2}
		A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}	A_{12}	
Total N	2008	16.5	16.6	16.4	16.9	17.7	18.2	17.8	17.7	16.5	16.6	16.7	18.8	17.6	17.1 ^{c}
	2009	15.7	16.3	16.5	16.3	15.3	15.2	15.2	15.8	15.7	16.4	15.8	15.8	16.3	15.9 ^{b}
	2010	17.6	17.4	17.6	18.7	17.7	18.5	18.8	18.0	19.2	18.9	17.7	18.4	17.4	18.1 ^{a}
	Mean^{1}	16.6 ^{f}	16.8 ^{e}	16.8 ^{de}	17.3 ^{a}	16.9 ^{cde}	17.3 ^{a}	17.3 ^{ab}	17.2 ^{ab}	17.1 ^{abc}	17.3 ^{a}	16.7 ^{ef}	17.0 ^{bcd}	17.1 ^{bcd}	17.0
Total P	2008	3.26	3.32	3.70	3.34	3.42	3.24	3.56	3.44	3.57	3.35	3.54	3.41	3.51	3.43 ^{b}
	2009	4.11	4.44	4.60	4.37	4.42	4.32	4.11	4.30	4.59	4.48	4.33	4.69	4.25	4.38 ^{a}
	2010	3.57	3.79	3.64	3.69	3.40	3.53	3.41	3.73	3.37	3.70	3.39	4.12	3.67	3.62 ^{c}
	Mean^{1}	3.65 ^{e}	3.85 ^{bc}	3.98 ^{a}	3.80 ^{cd}	3.75 ^{cde}	3.69 ^{de}	3.69 ^{de}	3.82 ^{c}	3.85 ^{bc}	3.84 ^{c}	3.75 ^{cde}	4.07 ^{a}	3.81 ^{cd}	3.81
K	2008	4.60	4.78	5.71	5.01	5.21	4.85	5.55	5.46	5.77	5.38	5.31	5.61	5.17	5.26 ^{a}
	2009	5.24	5.27	5.24	4.92	5.27	5.24	5.21	5.68	6.88	4.57	5.24	5.68	5.89	5.41 ^{a}
	2010	3.34	3.34	3.38	3.34	3.16	3.55	3.30	3.02	3.09	3.21	3.17	3.23	3.32	3.27 ^{b}
	Mean^{1}	4.39 ^{f}	4.47 ^{ef}	4.78 ^{bc}	4.42 ^{f}	4.55 ^{e}	4.55 ^{e}	4.69 ^{c}	4.72 ^{bc}	5.25 ^{a}	4.38 ^{f}	4.57 ^{de}	4.84 ^{b}	4.79 ^{bc}	4.65
Ca	2008	0.69	0.91	0.95	0.74	0.77	0.77	0.74	0.74	0.80	0.80	0.74	0.74	0.77	0.78 ^{a}
	2009	0.40	0.41	0.40	0.42	0.39	0.39	0.41	0.42	0.38	0.42	0.41	0.38	0.42	0.40 ^{b}
	2010	0.33	0.35	0.36	0.36	0.39	0.36	0.36	0.36	0.38	0.43	0.36	0.35	0.37	0.28 ^{c}
	Mean^{1}	0.47 ^{f}	0.56 ^{ab}	0.57 ^{a}	0.51 ^{cd}	0.52 ^{c}	0.51 ^{cd}	0.51 ^{cd}	0.51 ^{cd}	0.52 ^{c}	0.55 ^{b}	0.50 ^{de}	0.49 ^{e}	0.51 ^{cd}	0.52
Mg	2008	1.01	1.01	1.03	1.05	0.99	1.00	1.01	0.99	1.05	1.03	0.99	0.99	1.02	1.01 ^{c}
	2009	1.12	1.39	1.79	1.86	1.48	1.59	1.46	1.57	1.40	1.45	1.41	1.68	1.34	1.50 ^{b}
	2010	1.86	1.96	2.06	1.91	1.88	1.89	1.99	1.97	2.09	2.03	2.01	2.06	1.94	1.97 ^{a}
	Mean^{1}	1.33 ^{e}	1.45 ^{cd}	1.62 ^{a}	1.61 ^{a}	1.45 ^{cd}	1.49 ^{bc}	1.49 ^{bc}	1.51 ^{b}	1.52 ^{b}	1.50 ^{bc}	1.47 ^{cd}	1.58 ^{a}	1.43 ^{d}	1.50
Na	2008	0.75	0.88	0.88	0.82	0.83	0.81	0.78	0.78	0.84	0.89	0.91	0.83	0.85	0.83 ^{a}
	2009	0.64	0.64	0.66	0.65	0.65	0.68	0.63	0.69	0.64	0.67	0.63	0.62	0.65	0.65 ^{b}
	2010	0.53	0.60	0.55	0.70	0.60	0.62	0.60	0.67	0.60	0.69	0.60	0.67	0.62	0.62 ^{c}
	Mean^{1}	0.64 ^{a}	0.71 ^{a}	0.70 ^{a}	0.72 ^{a}	0.69 ^{a}	0.70 ^{a}	0.67 ^{a}	0.71 ^{a}	0.69 ^{a}	0.75 ^{a}	0.71 ^{a}	0.70 ^{a}	0.71 ^{a}	0.70

Values in the same lines[1] and columns[2] followed by the same letter are not significantly different according to Tukey test at the level $p \le 0.05$. A_0 – control treatment without added fertilizers, A_1 – 150 kg ha^{-1} NPK, A_2 – 190 kg ha^{-1} NPK, A_3 – 230 kg ha^{-1} NPK, A_4 – 173 kg ha^{-1} NPKS, A_5 – 213 kg ha^{-1} NPKS, A_6 – 253 kg ha^{-1} NPKS, A_7 – 205 kg ha^{-1} NPK, A_8 – 245 kg ha^{-1} NPK, A_9 – 285 kg ha^{-1} NPK, A_{10} – 228 kg ha^{-1} NPKS, A_{11} – 268 kg ha^{-1} NPKS, A_{12} – 308 kg ha^{-1} NPKS.

Phosphorus is an element which is part of many organic compounds building cell structures as well as stimulating metabolic transformations (White and Veneklaas, 2012). The optimal nutrition with that element enhances the physiological condition of the plants, facilitates a good development of the root system, stimulates the process of grain filing and shortens the vegetation period (Bednarek and Reszka, 2007). Phosphorus in the plant is part of, e.g., nucleic acids and plays the key role in the reactions of transferring and accumulating energy as well as phosphorylation.

Irrespective of the fertilization applied, the mean content of phosphorus in the grain from the variants under study was higher than the one assayed for the grain from the control and ranged from 3.65 to 4.07 g kg^{-1}. Significant differences in the concentration of that nutrient were identified across the research years. Significantly more phosphorus got accumulated in the grain collected over 2009 and 2010, by 27.7% and 5.5%, respectively, as compared with the grain from 2008. As compared with the variants fertilized with nitrogen, against lower rates of phosphorus and potassium (A_1-A_3), increasing the rate of those nutrients to 165 kg ha^{-1} PK (A_7-A_9) did not have a significant effect on the content of total phosphorus in the grain. Significant differences were found, however, between the content of phosphorus in the grain of barley fertilized with nitrogen, sulphur and higher PK rates (A_{10}-A_{12}) and its content in the grain from the variants with nitrogen and sulphur accompanied by a lower PK fertilization (A_4-A_6). The difference was, on average, 4.6%. In the series of variants with a lower rate of PK (A_4-A_6), sulphur fertilization significantly decreased the content of phosphorus in the grain by an average of 0.17 g kg^{-1} (4.4%), as compared with the variants non-fertilized with that nutrient (A_1-A_3). The relationships demonstrate that the plants must have more effectively used the nutrients the ratios of which were more adjusted to their nutrition requirements. As reported by Barczak and Nowak (2013), the sulphur applied to barley fertilization, in general, resulted in a slight decrease, as compared with the non-fertilized variants, the content of phosphorus as well as potassium and calcium.

Potassium is an activator of about 50 enzymes, it participates in e.g. osmoregulation, transpiration (Fanaeia et al., 2009), maintaining the ionic balance (Anschütz, 2014) as well as playing an essential role in the biosynthesis of carbohydrates, mostly starch, in the grain (Motaghi and Nejad, 2014). The three-year-cycle-mean content of potassium in the spring barley grain was 4.65 g kg^{-1} (Table 2). A significant increase in the content of potassium in the grain was demonstrated, in general, in all the fertilization objects as compared with the control. A significant difference in the content of potassium was recorded between the series of variants fertilized with varied rates of nitrogen with the rates (110 and 165 kg ha^{-1} PK) which was, on average 0.22 g kg^{-1} (4.8%). Similar relationships occurred after the application of sulphur, however the difference was lower – 0.13 g kg^{-1} (2.8%). The potassium content in the plants can range from 0.30 to 80 g kg^{-1} and it is plant-species-specific, depending also on the amount of available forms of that element in soil, as well as on the presence of other cations in soil. With a higher PK rate, 40 kg ha^{-1} K and 15 kg ha^{-1} P more were introduced into soil, which increased the content of available forms of those nutrients in soil and, as a consequence, in the grain. Skwierawska et al. (2008) reported that mineral fertilization which included sulphur did not differentiate the content of phosphorus and potassium in the grain of spring barley.

In the present research the mean content of calcium in the spring barley grain was 0.52 g kg^{-1} and it was significantly higher in all the fertilization variants than the one recorded in the control. The grain from the sulphur-non-fertilized variants contained significantly more calcium, as compared with the ones with sulphur applied and significant differences in the series fertilized with the rates of 110 and 165 kg ha^{-1} PK were, on average: 0.04 g kg^{-1} (7.3%) and 0.03 g kg^{-1} (5.7%), respectively. Most calcium (an average of 0.78 g kg^{-1}) was accumulated in the grain in the first research year.

In all the fertilization variants the magnesium content in the grain of barley was significantly higher, as compared to the control, and it fell within the range of 1.33-1.62 g kg^{-1}. A significant decrease (by an average of 5.1%) was identified in the content of that element in the grain from the series of the variants fertilized with sulphur applied at lower PK rates, as compared with the ones where this element was not supplied. As reported by Barczak and Nowak (2013), after the application of fertilizers containing sulphur, the magnesium content in the oats grain, in general, increased, while Gondek and Gondek (2010), did not identify significant differences in the content of magnesium in the grain of wheat due to fertilization with NPK and S.

The content of magnesium in plants shows a high variation which depends on the species of the crop and the growing conditions. The role of that element in the plant is connected with its presence in the molecule of chlorophyll (Bose et al., 2011) as well as with participating in physiological processes connected with photosynthesis, transformation of proteins, fats and carbohydrates. This element also takes an active part in maintaining the right ionic equilibrium in the plant which, in turn, determines the yield quality; hence such an importance of monitoring its content in the biomass.

The mineral fertilization combinations did not differentiate significantly the mean contents of sodium in the grain of spring barley, although they were higher than in the control. Clear differences in the content of this element in the grain were identified in successive research years. Significantly more sodium was contained in the grain collected in 2008 as compared with the grain in successive years. Sodium is an element indispensable as a nutrient only for few plant species. Its absorbed amounts as well as the concentration in plant tissues depend, similarly to potassium, mostly on the plant species, the content of available forms of that macroelement, as well as the presence of ions of other elements in soil. As compared with the amount of other macroelements, the content of sodium in the plants is not high and usually ranges from 0.1 to 5 g kg^{-1}.

Of all the nitrogen rates applied (40, 80, 120 kg ha^{-1} N), irrespective of the other fertilizer components, the rate of 80 kg ha^{-1} N, modified the mineral composition of the spring barley grain, especially the content of K, P and Mg in general most favourably, as compared with the control. In the literature there is no agreement in terms of the direction of the effect of nitrogen fertilization on the content of macronutrients in cereals grains. Brzozowska (2008) did not observe a significant effect of fertilization with nitrogen on the content of other macronutrients in the winter wheat grain, except for nitrogen and potassium. According to Nogalska et al. (2012), the variation in the amount of the elements up taken with the yield results from the size of the grain yield.

The physiological role of macronutrients is relatively well-known, however, there is less data on the evaluation of the ionic ratios between those elements, especially the effect of sulphur fertilization on their value in the cereals grain used as an ingredient of the human diet or allocated for animal feed. The ratios of macronutrients, determining the ionic equilibrium, can affect the nutritive value of yields (Barczak and Nowak, 2013).

Ratios of macronutrients

Irrespective of the fertilization applied, the quantitative ratio of potassium to calcium as well as potassium to magnesium in kernels was; in general, lower than in the control (Table 4). In the grain from the series of variants where sulphur was applied, the ratios discussed were usually higher than from the variants non-fertilized with that nutrient, and the differences, depending on the level of PK fertilization (110 and 165 kg ha^{-1} PK) were, on average: for ratios K^+:Ca^{2+} 3.5 and 3%, and 5.9% each, for ratio K^+:Mg^{2+}.

The fertilization applied, in general, significantly narrowed the ratio K^+:(Ca^{2+}+ Mg^{2+}), as compared with the non-fertilized variants and its mean values for the years fell within 1.50-1.93. In the variants with lower PK rates, sulphur application significantly increased the ratio, as compared with the series of variants non-fertilized with sulphur, by an average of 7.0%.

The values of ratios K^+:Ca^{2+} and K^+:Mg^{2+} were related to the amount of the total potassium and sodium to the total calcium and magnesium (K^++Na^+): (Ca^{2+}+Mg^{2+}). The ratio reached the highest values for A_8 (2.35) where 80 kg ha^{-1} N was applied with a higher rate of PK; widening, as compared with the control, accounted for 4.4%. The present research did not identify a significant effect of sulphur fertilization on the value of that ratio, unlike in the report by Barczak (2010) where increasing sulphur rates widened the ratio significantly in the barley grain.

There No significant effect of the fertilization applied was noted on ratios (Ca^{2+}:Mg^{2+}) as well as (Ca:P), the mean values of which were: 0.25 and 0.14, respectively, and they were influenced by a low content of calcium in the grain.

The content of magnesium, potassium, sodium and calcium as well as the quantitative ratios between them make it possible to determine the nutrition applicability of the plants grown for animal feed, as well as the nutritional value of the yield allocated to human consumption. An excessive uptake of specific cations or anions limits the content of other, sometimes very important, macro- and microelements. High potassium contents deteriorate, whereas high calcium and magnesium contents improve the quality of animal feed (Murawska et al., 2013). Interestingly, as a result of the application of sulphur in the grain of spring barley, there was a slight widening of the ratio K^{+}:Ca^{2+} and a significant widening for K^{+}:Mg^{2+}. A similar direction of changes in the ratio of the content of potassium to the content of bivalent cations (Ca^{2+} and Mg^{2+}) due to fertilization with sulphur in the seeds not only in spring barley but also narrow-leafed lupine and white mustard, was identified by Barczak (2010). Of all crop species studied, it was the spring barley which most reacted with a change in the ionic ratios to sulphur fertilization. According to Jankowska-Huflejt (2009), in animal feeds usually much more often a potassium excess is reported than a deficit. The author highlights especially the unwanted big discrepancy (K^{+}+Na^{+}):(Ca^{2+}+Mg^{2+}) in the animal feeds of ruminants, which can result in grass tetany in cattle. Maintaining the equilibrium between uni-and bivalent ions is facilitated by the content of calcium which, similarly as magnesium, can be antagonist towards potassium (Jarnuszewski and Meller, 2013).

Table 4. Proportions of macroelements in grain of spring barley

Fertlization treatments	Proportions					
	K:Ca	K:Mg	K:(Ca+Mg)	(K+Na):(Ca+Mg)	Ca:Mg	Ca:P
A_0	10.21 cd ±2.82	2.30 bc ±0.87	1.81 b ±0.61	2.25 b ±0.73	0.25 a ±0.13	0.13 a ±0.06
A_1	9.47 g ±3.31	2.13 defg ±0.83	1.63 d ±0.90	2.06 d ±0.61	0.28 a ±0.20	0.15 a ±0.09
A_2	9.74 efg ± 3.14	2.10 fg ±1.06	1.59 d ±0.55	1.98 e ±0.69	0.27 a ±0.22	0.15 a ±0.08
A_3	9.52 g ±2.30	1.90 h ±0.83	1.50 e ±0.48	1.92 e ±0.59	0.23 a ±0.15	0.14 a ±0.06
A_4	9.62 fg ±3.08	2.18 def ±0.95	1.69 c ±`0.58	2.12 cd ±0.70	0.25 a ±0.16	0.15 a ±0.06
A_5	10.16 cde ±3.20	2.08 g ±0.79	1.63 d ±0.45	2.06 d ±0.55	0.24 a ±0.17	0.14 a ±0.07
A_6	9.99 cdef ±2.29	2.22 cd ± 1.02	1.73 c ±0.63	2.14 c ±0.74	0.24 a ±0.15	0.14 a ±0.05
A7	10.01 cdef ±2.89	2.22 cd ±1.07	1.73 c ±0.66	2.16 c ±0.76	0.24 a ±0.16	0.14 a ±0.06
A8	11.50 a ±5.36	2.45 a ±1.16	1.93 a ±0.83	2.35 a ±0.93	0.25 a ±0.16	0.14 a ±0.06
A9	8.59 h ±1.98	2.07 g ±0.98	1.59 d ±0.58	2.14 c ±0.70	0.26 a ±0.16	0.15 a ±0.07
A10	9.84 defg ±2.61	2.20 de ±1.01	1.71 c ±0.63	2.17 c ±0.78	0.25 a ±0.16	0.14 a ±0.05
A11	10.76 b ±3.51	2.21 de ±1.10	1.72 c ±0.67	2.14 c ±0.79	0.23 a ±0.16	0.13 a ±0.07
A12	10.39 bc ±3.30	2.33 b ±0.96	1.81 b ±0.64	2.26 b ±0.74	0.25 a ±0.16	0.14 a ±0.06
Mean	9.98	2.18	1.70	2.13	0.25	0.14

Means of four trials followed by ± standard deviation. Values in the same columns followed by the same letter are not significantly different according to Tukey test at the level p≤0.05. Explanations of fertilization treatments under Table 3.

The analysis of the values of the ionic ratios, in general, points to a favourable direction of changes in the chemical composition of the spring barley grain for its feed value due to NPK and S fertilization. A comparison of the results with the data reported by Wołoszyk and Iżewska (2015), as well as by Jarnuszewski and Meller (2013) for the spring barley grain suggests that, for the N P K and S fertilization applied, the mean values of K^+:Ca^{2+} in the grain were too high, Ca^{2+}:Mg^{2+} and Ca:P – too low, whereas the ratios K^+:Mg^{2+}, K^+:(Ca^{2+}+Mg^{2+}), and (K^++Na^+):(Ca^{2+}:Mg^{2+}) can be considered similar to the optimal ones. Interestingly, a significant widening of the values of the ionic ratios, especially K^+:Mg^{2+}, but also K^+:(Ca^{2+}+Mg^{2+}), occurred as a result of sulphur application.

CONCLUSIONS

The greatest increase in the grain yield size due to NPK rates, as compared with the control, was due to the application of 120 kg N ha^{-1}. As a result of sulphur application the highest grain yields were recorded after the use of that nutrient together with the rates of 40 and 80 kg N ha^{-1}applied with 110 and 165 kg PK ha^{-1}.

The mean content of the elements in the spring barley grain, except for sodium, varied significantly due to the fertilization applied, irrespective of the rate of P and K. In general, the highest contents of the macronutrients were reported after the applications of 80 kg ha^{-1} N.

The contents of phosphorus and potassium in the grain from the series of variants fertilized with sulphur and the rate of 165 kg ha^{-1} PK were significantly higher than the ones reported for the ones where that nutrient was applied with the rate of 110 kg ha^{-1} PK.

As a result of the fertilization applied in the spring barley grain, the mean values of ratio K^+:Ca^{2+} were excessively high, Ca^{2+}:$Mg^{2+}$and Ca:P – too narrow, while the ratios K^+:Mg^{2+}, K^+:(Ca^{2+}+Mg^{2+}) as well as (K^++Na^+):(Ca^{2+}:Mg^{2+}) can be considered similar to the optimal ones.

As a result of the application of sulphur in the spring barley grain, it was found that widening the values of ionic ratios, especially K^+:Mg^{2+} and K^+:(Ca^{2+}+Mg^{2+}) points to the need of considering this nutrient in the crop management practise for spring barley.

REFERENCES

Anschütz, U., Becker, D., Shabala, S., 2014. *Going beyond nutrition: regulation of potassium homoeostasis as a common denominator of plant adaptive responses to environment.* J. Plant Physiol., 171: 670-687. DOI: 10.1016/j.jplph. 2014.01.009.

Barczak, B., 2010. *Sulphur as a nutrient determining the yield size and quality of selected crop species.* Dissertations and Monographs, 144: 131 p. University of Science and Technology in Bydgoszcz. (In Polish)

Barczak, B., Knapowski, T., Kozera, W., Ralcewicz, M., 2014. *Effects of sulphur fertilization on the content and uptake of macroelements in narrow-leaf lupin.* Rom. Agric. Res., 31: 245-251.

Barczak, B., Nowak, K., 2013. *Content of macroelements and their ionic ratios in oat grain depending on the sulphur form and dose.* J. Centr. Europ. Agricult., 14(1): 114-123.

Bednarek, W., Reszka, R., 2007. *The influence of liming and fertilization with various nitrogen forms on yielding and utilization of phosphorus by spring barley.* Ann. UMCS, E, LXII(1): 23-25.

Bleidere, M., Zute, S., Brunava, L., Bobere, N., Jākobsone, I., 2013. *Yield and grain quality of hulless spring barley in field trials under different nitrogen management conditions.* Proc. Latvian Acad. Sci., B, 67(3)**:** 229-235. DOI: 10.2478/ prolas-2013-0040.

Bose, J., Babourina, O., Rengel, Z., 2011: *Role of magnesium in alleviation of aluminium toxicity in plants.* J. Exp. Bot., 62: 2251-2264. DOI: 10.1093/jxb/erq456.

Brzozowska, I., 2008. *Macroelement content in winter wheat grain as affected by cultivation and nitrogen application methods.* Acta Agroph., 11(1): 23-32.

Candráková, E, Szombathová, N., Smatana, J., 2009. *The yield and quality of spring barley affected by nitrogen fertilization during growing period.* Res. J. Agric. Sci., 41(1): 16-21.

Fanaeia, H.R., Galavia, M., Kafi, M, Ghanbari, Bonjar, A., 2009. *Amelioration of water stress by potassium fertilizer in two oilseed species.* Int. J. Plant Prod., 3(2): 41-54.

Fazli, I.S., Jamal, A., Ahmad, S., Masoodi, M., Khan, J.S., Abdin, M.Z., 2008. *Interactive effect of sulphur and nitrogen on nitrogen accumulation and harvest in oilseed crops differing in nitrogen assimilation potential.* J. Plant Nutr., 31: 1203-1220. DOI:10.1080/01904160802134905.

Gondek, K., Gondek, A., 2010. *The influence of mineral fertilization on the yield and content of selected macro and microelements in spring wheat.* J. Res. Appl. Agric. Eng., 55(1): 30-36.

Hirzel, J., Matus, I., 2013. *Effect of soil depth and increasing fertilization rate on yield and its components of two durum wheat varieties.* Chil. J. Agr. Res., 73(1): 55-59.

Hitsuda, K., Tamada, M., Klepker, D., 2005. *Sulphur requirement of eight crops at early stages of growth.* Agron. J., 97: 155-159.

Jamal, A., Moon, Y.S., Abdin, M.Z., 2010. *Sulphur – a general overview and interaction with nitrogen.* Aust. J. Crop Sci., 4(7): 523-529.

Jankovic, S., Glamoclija, D., Maletic, R., Rakic, S., Hristov, N., Ikanovic, J., 2011. *Effect of nitrogen on yield and grain quality in malting barley.* Afr. J. Biotechnol., 10(84): 534-541.

Jankowska-Huflejt, H, Wróbel, B, Barszczewski, J., 2009. *Evaluation of nutritive value of forages from grass Lands on the background of soil richness and N, P, K balances in chosen organic farms.* J. Res. Appl. Agric. Engng., 54(3): 95-102.

Jarnuszewski, G., Meller, E., 2013. *Mineral element ratios in plants grown on post bog soils fertilized with zinc and copper.* Folia Pomer. Univ. Technol. Stetin., Agric., Aliment., Pisc., Zootech., 304(26): 25-32.

Järvan, M., Edesi, L., Adamson, A., Lukme, L., Akk, A., 2008. *The effect of sulphur fertilization on yield, quality of protein and baking properties of winter wheat.* Agronomy Res., 6(2): 459-469.

Klikocka, H., Narolski, G., Michałkiewicz, G., 2014. *The effects of tillage and soil mineral fertilizationon the yield and yield components of spring barley.* Plant Soil Environ., 60(6): 255-261.

Kostadinova, S., 2014. *Grain yield and protein of barley in dependence of phosphorus and potassium nutrition*. Scientific Papers, A. Agronomy, LVII: 232-235.

Lipiński, W., Terelak, H., Motowicka-Terelak, T., 2003. *Proposal of boundary numbers of the content of sulphate sulphur in mineral soils for the purpose of fertilizer counselling services.* Rocz. Gleb., LIV(3): 79-84. (In Polish)

Liszewski, M., 2008. *The response of two forms of feed spring barley to different cultivation systems.* Dissertations and Monographs, 254: 108 p. Wroclaw University of Environmental and Life Sciences. (In Polish)

Mandic, V., Krnjaja, V., Tomic, Z., Bijelic, T., Simic, A., Muslic, D., Gogic, M., 2015. *Nitrogen fertilizer influence on wheat yield and use efficiency under different environmental conditions.* Chil. J. Agr. Res., 75(1): 92-97. DOI:10.4067/S0718-58392015000100013.

Motaghi, S., Nejad, T.S., 2014. *The effect of different levels of humic acid and potassium fertilizer on physiological indices of growth.* Int. J. Biosci., 5(2): 99-105.

Murawska, B., Spychaj-Fabisiak, E., Knapowski, T., Głowacki, B., 2013. *Ionic equilibrium in maize grain depending on the fertilization and soil type.* J. Centr. Europ. Agricult., 14(4): 1535-1546.

Muurinen, S., Kleemola, J. Peltonen-Sainio, P., 2007. *Accumulation and translocation of N in spring cereal cultivars differing in NUE.* Agron. J., 99: 441-449.

Nogalska, A., Sienkiewicz, S., Czapla, J., Skwierawska, M., 2012. *The effect of multi-component fertilizers on the yield and mineral composition of winter wheat and macronutrient uptake.* J. Elementol., 17(4): 629-638. DOI: 105601/jelem.2012.17.4.06.

Noworolnik, K., Wirkijowska, A., Mikos-Szymanska, M., 2014. *Effect of genotype and nitrogen fertilization on grain yield and quality of spring barley intended for health food use.* Bulg. J. Agric. Sci., 20(3): 576-580.

Peltonen-Sainio, P., Muurinen, S., Rajala, A., Jauhiainen, L., 2008. *Variation in harvest index of modern spring barley, oat and wheat cultivars adapted to northern growing conditions.* J. Agric. Sci., 146: 35-47.

Shahsavani, S., Gholamii, A., 2008. *Effect of sulphur fertilization on breadmaking quality of three winter wheat varieties.* Pak. J. Biol. Sci., 11: 2134-2138.

Shejbalová, Š., Černý, J., Vašák, F., Kulhánek, M., Balík J., 2014. *Nitrogen efficiency of spring barley in long-term experiment.* Plant Soil Environ., 60(7): 291-296.

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

Staugaitis, G., Brazienė, Z., Marcinkevičius, A., Mažeika, R., Antanaitis, S., Staugaitienė, R., 2014. *Spring barley as affected by nitrogen and sulphur fertilizer rates calculated using different diagnostic methods.* Zemdirbyste-Agriculture, 101(4): 373-380. DOI: 10.13080/z-a.2014.101.047.

Stern, D., 2005. *Global sulphur emissions from 1850 to 2000*. Chemosphere, 58: 163-175.

Togay, Y., Togay, N., Cig, F., Erman, M., Celen, A., 2008. *The effect of sulphur applications on nutrient composition, yield and some yield components of barley (Hordeum vulgare L.).* Afr. J. Biotechnol., 7(18): 3255-3260. DOI: 10.5897/AJB08.172.

Valkama, E., Salo, T., Esala, M., Turtola, E., 2013. *Grain quality and N uptake of spring cereals as affected by nitrogen fertilization under Nordic conditions a meta-analysis.* Agr. Food Sci., 22: 208-222.

White, P.J., Veneklaas, E.J. 2012. *Nature and nurture: the importance of seed phosphorus content.* Plant Soil, 357: 1-8.

Wołoszyk, Cz., Iżewska, A., 2015. *Yields of grain and straw, their content and ionic proportions of macroelements in maize fertilized with ash from municipal sewage sludge combustion.* J. Elementol., 20(2): 319-329. DOI: 10.5601/jelem.2014.19.3.765.

WRB, 2006. *World Reference Base for Soil Resources. A framework for international classification, correlation and communication.* World Soil

Resources Report, 103. Food and Agriculture Organization of the United Nations, Rome, 116 p.
Zhao, F. J., Fortune, S., Barbosa, V. L., McGrath, S. P., Stobart, R., Bilsborrow, P. E., Booth, E. J., Brown, A., Robson, P., 2006. *Effects of sulphur on yield and malting quality of barley.* J. Cereal Sci., 43(3): 369-377. DOI:10.1016/j.jcs.2005.12.003.
Zhao, F. J., McGrath, S.P., Blake-Kalff, M.M, Link, A., Tucker, M., 2003. *Crop responses to sulphur fertilization in Europe*. Fert. Fertil., 3(16): 26-47.