

**THE YIELD AND GRAIN QUALITY OF WINTER RYE  
(*SECALE CEREALE L.*) UNDER THE CONDITIONS  
OF FOLIAR FERTILIZATION  
WITH MICRONUTRIENTS (Cu, Zn and Mn)**

***Arkadiusz Stępień<sup>1</sup>, Katarzyna Wojtkowiak<sup>2</sup>,  
Mirosław Pietruszewicz<sup>1</sup>, Michał Skłodowski<sup>1</sup>,  
Renata Pietrzak-Fiećko<sup>3</sup>***

<sup>1</sup> Department of Agroecosystems

<sup>2</sup> Department of Safety Fundamentals

<sup>3</sup> Department of Commodities and Food Analysis  
University of Warmia and Mazury in Olsztyn

Key words: foliar fertilization, nutrients, protein, starch, yield components.

Abstract

The grain of winter rye (*Secale cereale L.*) originated from a field experiment conducted in the years 2011–2013 at the Didactic-Experimental Centre of the University of Warmia and Mazury in Tomaszkowo (53°72 N; 20°42 E) in Poland. The aim of the study was to determine the yield of winter rye and its components and the content of proteins, starch and selected mineral components (P, K, Ca, Mg, Cu, Fe, Zn, Mn) in grain under the conditions of NPK fertilization and foliar feeding with micronutrients applied separately or in combination. Fertilization with mineral fertilizers (NPK) and with mineral fertilizers with micronutrients applied separately or in combination resulted in a significant increase in grain yield, as compared to the plot with no fertilization. Fertilization with mineral fertilizers and foliar feeding with micronutrients (except for Cu) increased protein content in rye grain. Foliar application of nitrogen of basic fertilization with copper increased the concentration of starch in the grain. The mineral fertilization (NPK) with micronutrients applied in combination (NPK+Cu, Zn, Mn) increased the content of phosphorus (as compared to the plot with no fertilization and fertilized with mineral fertilizers NPK) and potassium (as compared to the NPK plot). Supplementation of basic fertilization with zinc or manganese or a combination of micronutrients resulted in an increase in Mn content in the grain as compared to the plot with no fertilization and as compared to the plot fertilized with mineral fertilizers.

**PLONOWANIE I JAKOŚĆ ZIARNA ŻYTA OZIMEGO (*SECALE CEREALE L.*)  
W WARUNKACH DOLISTNEGO NAWOŻENIA MIKROELEMENTAMI (Cu, Zn i Mn)**

**Arkadiusz Stępień<sup>1</sup>, Katarzyna Wojtkowiak<sup>2</sup>, Mirosław Pietrusewicz<sup>1</sup>,  
Michał Skłodowski<sup>1</sup>, Renata Pietrzak-Fiećko<sup>3</sup>**

<sup>1</sup> Katedra Agroekosystemów

<sup>2</sup> Katedra Podstaw Bezpieczeństwa

<sup>3</sup> Katedra Towaroznawstwa i Badań Żywności  
Uniwersytet Warmińsko-Mazurski w Olsztynie

Słowa kluczowe: nawożenie dolistne, składniki pokarmowe, białko, skrobia, składowe plonu.

Abstrakt

Ziarno żyta ozimego (*Secale cereale L.*) pochodziło z doświadczenia polowego przeprowadzonego w latach 2011–2013 w Zakładzie Dydaktyczno-Doświadczalnym UWM w Tomaszku (53°72 N; 20°42 E) Polska. Celem pracy było określenie plonu żyta ozimego i jego komponentów oraz zawartości białka, skrobi i wybranych składników mineralnych (P, K, Ca, Mg, Cu, Fe, Zn, Mn) w ziarnie pod wpływem dolistnego dokarmiania mikroelementami stosowanymi pojedynczo lub łącznie. Pod wpływem nawożenia nawozami mineralnymi (NPK) oraz mineralnie łącznie z mikroelementami stosowanymi pojedynczo lub łącznie stwierdzono istotny wzrost plonu ziarna względem obiektu bez nawożenia. Nawożenie nawozami mineralnymi oraz dolistne dokarmianie mikroelementami (za wyjątkiem Cu) zwiększyło zawartość białka w ziarnie żyta. Dolistne dokarmianie azotem i miedzią zwiększyło koncentrację skrobi w ziarnie. Wspomaganie nawożenia NPK mikroelementami stosowanymi łącznie (NPK+Cu, Zn, Mn) zwiększyło zawartość fosforu (w porównaniu z obiektem bez nawożenia i nawożonym nawozami mineralnymi NPK) oraz potasu (względem obiektu NPK). Uzupełnienie podstawowego nawożenia cynkiem lub manganem lub łącznie mikroelementami wpłynęło na wzrost zawartości Mn w ziarnie względem obiektu bez nawożenia i w porównaniu z obiektem nawożonym nawozami mineralnymi.

## Introduction

Winter rye (*Secale cereale L.*) is a cereal whose grain is used mainly for human consumption (BUSHUK 2001). Therefore, the content of micronutrients and macronutrients in the grain is as important as the yield (BEDNAREK et al. 2006, KOWIESKA et al. 2011). In the agronomical practises of cereals the main factors which allow for the achievement of high yield of plants having favourable quality properties include the level of agronomical practises, habitat conditions and genetic determinants of the varieties (JANKOWSKI et al. 2003, HANSEN et al. 2004, NEDZINSKIENE 2006, JASKULSKI and JASKULSKA 2009, CIOROMELE and CONTOMAN 2015). It is suggested that the yield and the nutritional and technological value of the grain is determined by satisfying nutritional needs by fertilization (STĘPIEŃ and WOJTKOWIAK 2015). The dose and form of fertilizer components and the method of fertilization are very

important. The treatment of intervention foliar feeding of plants with micronutrients at the time of critical demand for nutrients is applied more and more frequently (FEGARIA et al. 2009). Foliar application of fertilizers is recommended in the phase of shooting when the plant is in a period of intensive cell divisions. In practice, three most important elements considered during feeding of cereals are: Mn, Cu and Zn. These micronutrients are involved in many physiological processes, including their presence in the composition of various enzymes and their role as enzyme activators (HANSCH and MENDEL 2009). These elements also affect the effectiveness of fertilization with macronutrients and influence the yield and chemical composition of the grain. The economic and environmental reason for the foliar application of certain nutrients is also their high productive efficiency (JASKULSKI and JASKULSKA 2009).

The effect of fertilization with nitrogen fertilizers on the quality characteristics of the plants was a subject of many studies; however the effect of nitrogen together with foliar application of micronutrients is less investigated.

The aim of the study was to determine the yield and its components, the content of proteins, starch and selected mineral components (P, K, Ca, Mg, Cu, Fe, Zn, Mn) in grain of winter rye under the conditions NPK fertilization and of foliar feeding with micronutrients applied separately or in combination.

## Materials and Methods

The field experiment was conducted at the Didactic-Experimental Centre in Tomaszkowo (53°72 N; 20°42 E) in Poland. Winter rye (*Secale cereal L.*) of the Dańkowskie Diament variety was cultivated in 2011/2012 and 2012/2013 growing seasons on a lessive soil with a granulometric composition of a medium silty loam of complex 4, class IIIb. The soil characteristics presented in the Table 1. The experiment was established using a method of randomised blocks, in triplicate. The plot size was 6.25 m<sup>2</sup>, the harvested plot area was 4.0 m<sup>2</sup>. Winter rye was cultivated after winter triticale, sowing 160 kg ha<sup>-1</sup> in 2011 and 172 kg ha<sup>-1</sup> in 2012 (5.00 million grains ha<sup>-1</sup>), spacing between plant rows of 120 mm.

In the experiment, the following variants of fertilization were taken into account:

1. „Without fertilization” (control I).
2. „NPK” (control II) – At all sites, nitrogen fertilization was applied at an amount of 90.0 kg · ha<sup>-1</sup> with the doses divided as follows: in-soil application of 54.0 kg · ha<sup>-1</sup> (urea 46%) at the tillering stage (at Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie scale: BBCH 22–23), and foliar

Table 1  
Physical and chemical soil properties before the experiment started (average 2011–2012)

| Measured parameters                    | Corresponding values |
|--|----------------------|
| Soil type (WRB 2014)                   | Haplic Cambisol      |
| Soil texture                           | loam                 |
| pH in KCl                              | 6.89                 |
| Total organic C, g kg <sup>-1</sup> DM | 7.93                 |
| Total N, g kg <sup>-1</sup> DM         | 0.95                 |
| P, mg kg <sup>-1</sup>                 | 76.4                 |
| K, mg kg <sup>-1</sup>                 | 195.1                |
| Mg, mg kg <sup>-1</sup>                | 74.0                 |
| Mn, mg kg <sup>-1</sup>                | 214                  |
| Cu, mg kg <sup>-1</sup>                | 2.8                  |
| Zn, mg kg <sup>-1</sup>                | 9.0                  |
| Fe, mg kg <sup>-1</sup>                | 1700                 |

application of 36.0 kg N ha<sup>-1</sup> (10% urea solution) at the stem elongation stage (BBCH 30–31). Triple superphosphate (46%) at a dose equivalent to 30.2 kg P · ha<sup>-1</sup>, and potassium salt (56%) at a dose equivalent to 83.1 kg K ha<sup>-1</sup>, as a pre-sowing application.

3. „NPK+Cu” – Mineral fertilization as in the „NPK” variant + foliar fertilization with 0.2 kg Cu ha<sup>-1</sup> (1% solution of CuSO<sub>4</sub> – with 10% urea solution).

4. „NPK+Zn” – Mineral fertilization as in the „NPK” variant + foliar fertilization with 0.2 kg Zn ha<sup>-1</sup> (1% solution of ZnSO<sub>4</sub> – with 10% urea solution).

5. „NPK+Mn” – Mineral fertilization as in the „NPK” variant + foliar fertilization with 0.2 kg Mn ha<sup>-1</sup> (0.5% solution of MnSO<sub>4</sub> – with 10% urea solution).

6. „NPK+Cu,Zn,Mn” – Mineral fertilization as in the „NPK” variant + foliar fertilization with: 0.2 kg Cu ha<sup>-1</sup>; 0.2 kg Zn ha<sup>-1</sup>; 0.2 kg Mn ha<sup>-1</sup> – with 10% urea solution.

Cu, Zn and Mn (individually or in combination) were applied to leaves as aqueous solutions at the stem elongation stage (BBCH 30–31).

Soil tillage treatments included first ploughing performed after harvesting the forecrop. In order to cover crop residues before sowing of winter rye, a pre-sowing plough and harrowing were performed. Directly before sowing, a combined cultivator and seed drill was applied to all plots in order to mix mineral fertilizers and prepare the soil for sowing. Weeds were destroyed using herbicides in 2012 – Mustang Forte 195 SE (a.i. florasulam 5 g, aminopyralid

10 g, 2.4 D 180 g) 1.0 dm<sup>-3</sup> ha<sup>-1</sup> and Puma Universal 069 WG (a.i. fenoksaprop-P-etyl 69.0 g) 1.2 dm<sup>-3</sup> ha<sup>-1</sup>; in 2013 – Atlantis 12 OD (a.i. jodosulfuron methyl sodium 2 g; mesosulfuron methyl 10 g) 0.45 dm<sup>-3</sup> ha<sup>-1</sup> + Sekator 125 OD (a.i.: jodosulfuron methyl sodium 25 g, amidosulfuron 100 g) 0.15 dm<sup>-3</sup> ha<sup>-1</sup>, in spring after resumption of rye vegetation (BBCH 21–29). Protection against pests and diseases was not performed.

Every year, in the course of the experiment the grain was collected, dried and purified. The amount of yield was determined and the samples were collected and subjected to chemical analysis for the content of macro- and micronutrients according to the methods used in agricultural chemistry. The samples of grain were mineralised under wet conditions in a mixture of HNO<sub>3</sub> and HClO<sub>4</sub> acids at a ratio of 4:1. The content of mineral components (Ca, Mg, K, Cu, Fe, Mn, Zn) was determined by flame atomic absorption spectrometry method (flame: acetylene-air). The analyses were performed using an iCE 3000 SERIES atomic absorption spectrometer provided by THERMO, equipped with a GLITE data station, working in emission system (WHITESIDE and MINER 1984). Phosphorus was determined using a vanadium-molybdenum method, in the material previously mineralised with H<sub>2</sub>SO<sub>4</sub> with the addition of H<sub>2</sub>O<sub>2</sub> as an oxidant.

For the measurements of protein and starch content in the grain an Infratec<sup>TM</sup> 1241 grain analyser, which employs the near-infrared analysis within the wavelength range 570–1100 nm was applied.

During the entire field experiment a monitoring of temperature and precipitation amount was conducted (Table 2). The mean monthly air temperatures during the growing season of winter rye were similar and did not differ from multi-year average values. The amount of precipitation was higher by 21.8 mm and 10.6 mm in September 2011 as compared to the multi-year average. October and November 2011 were characterised by an amount of precipitation lower by 39.0 and 31.1 mm as compared to 1981–2010, and by 13.1 and 30.7 mm as compared to the multi-year period. In April 2012 a twofold excess of the multi-year precipitation amount was recorded. In the years of the study, at the beginning of heading ray phase (May) the amounts of precipitation were similar. In June 2012 the amount of precipitation significantly exceeded the amount of precipitation in the following year of the study (2013). In July 2012 and 2013 the amounts of precipitation were similar, but they exceeded by 39% on average the multi-year amount of precipitation.

The results were statistically processed with STATISTICA 10.0 software (StatSoft, Tulsa, Oklahoma, USA). The statistical calculations were performed using a one-way ANOVA. Apart from the basic parameters, standard deviation and statistically homogenous groups were determined with Duncan's test at  $\alpha = 0.05$ . Coefficients of linear correlation (Pearson's *r*) were calculated.

Table 2

Weather conditions in 2011–2013 and the multi-year average of 1981–2010

| Year               | Month |      |      |      |      |      |      |      |      |       |       |      |         |
|--------------------|-------|------|------|------|------|------|------|------|------|-------|-------|------|---------|
|                    | IX    | X    | XI   | XII  | I    | II   | III  | IV   | V    | VI    | VII   | VIII | IX–VIII |
| Temperature (°C)   |       |      |      |      |      |      |      |      |      |       |       |      | average |
| 2011/2012          | 14.1  | 8.3  | 3.1  | 2.3  | -1.7 | -7.5 | 3.0  | 7.8  | 13.4 | 15.0  | 19.0  | 17.7 | 7.9     |
| 2012/2013          | 13.5  | 7.4  | 4.9  | -3.5 | -4.6 | -1.1 | -3.5 | 5.9  | 14.8 | 17.5  | 18.0  | 17.4 | 7.2     |
| 1981/2010          | 12.8  | 8.0  | 2.9  | -0.9 | -2.4 | -1.7 | 1.8  | 7.7  | 13.5 | 16.1  | 18.7  | 17.9 | 7.9     |
| Precipitation (mm) |       |      |      |      |      |      |      |      |      |       |       |      | sum     |
| 2011/2012          | 67.5  | 29.5 | 14.1 | 25.8 | 61.8 | 27.7 | 24.1 | 73.1 | 51.7 | 103.2 | 121.0 | 45.1 | 644.6   |
| 2012/2013          | 45.7  | 68.5 | 45.2 | 11.8 | 44.1 | 22.6 | 18.1 | 28.5 | 54.5 | 61.2  | 121.9 | 37.6 | 559.7   |
| 1981/2010          | 56.9  | 42.6 | 44.8 | 38.2 | 36.4 | 24.2 | 32.9 | 33.3 | 58.5 | 80.4  | 74.2  | 59.4 | 581.8   |

## Results and Discussion

Winter rye (*Secale cereale L.*) of the Dańkowskie Diament variety belongs to the group of the highest-yield rye variety in the area of Poland. According to COBORU (2014), the yield of grain for this variety at an average level of fertilization and protection equals 6.74 t ha<sup>-1</sup> on average, while intensive fertilization and protection increased the yield to 8.39 t ha<sup>-1</sup>. In this study the average grain yield of the study variety of winter rye was 7.98 t ha<sup>-1</sup> (Table 3). In comparison to the study of NOGALSKA et al. (2012), the grain yield of winter rye for the Dańkowskie Diament variety was higher and varied in the study years. The statistical analysis confirmed the effect of years of the study on grain yield and its components. In the first year the grain yield was higher by 14.2%, the length of the ear by 28.0%, the number of grains per ear by 44.3% and the grain weight per ear by 33.0%. The 1000 grain weight was higher in the second year of the study by 8.9%. The obtained results of the impact of weather conditions in growing seasons 2011/2012 and 2012/2013 on the described parameters confirm results previously obtained by CHMIELEWSKI and KOHN (2000). The study uses data of a long-term field experiment at Berlin-Dahlem for the period between 1962 and 1996. According to them higher temperatures in the winter and an earlier start of the growing season favour the grain yield. Moderate temperatures before starting the shooting phase prolong the period of spikelet formation, which leads to an increase in the number of spikelets. High temperatures and the drought in the ripening phase have a negative impact on the 1000 grain weight. According to JASKULSKI and JASKULSKA (2009), the beneficial effect of foliar fertilization (multifertilizers SONATA ZBOŻE) on grain yield of winter wheat is the higher, the higher is the amount of precipitation in April and June.

Table 3

Grain yield and yield components of winter rye (average 2012–2013)

| Fertilisation treatments |         | Grain yield<br>[t ha <sup>-1</sup> ] | Ear length<br>[mm] | Number of grains per ear | Weight of grains per ear [g] | Weight of 1000 grains [g] |
|--------------------------|---------|--------------------------------------|--------------------|--------------------------|------------------------------|---------------------------|
| Without fertilization    | average | 7.00 <sup>b</sup>                    | 80.9 <sup>a</sup>  | 43.2 <sup>a</sup>        | 1.34 <sup>a</sup>            | 32.8 <sup>a</sup>         |
|                          | SD      | 1.08                                 | 10.9               | 11.0                     | 0.22                         | 1.61                      |
| NPK                      | average | 8.48 <sup>a</sup>                    | 82.4 <sup>a</sup>  | 47.7 <sup>a</sup>        | 1.44 <sup>a</sup>            | 32.5 <sup>a</sup>         |
|                          | SD      | 1.35                                 | 16.09              | 10.8                     | 0.30                         | 1.12                      |
| NPK+Cu                   | average | 8.08 <sup>a</sup>                    | 83.4 <sup>a</sup>  | 44.2 <sup>a</sup>        | 1.32 <sup>a</sup>            | 33.1 <sup>a</sup>         |
|                          | SD      | 0.49                                 | 10.0               | 8.3                      | 0.22                         | 1.79                      |
| NPK+Zn                   | average | 8.23 <sup>a</sup>                    | 81.2 <sup>a</sup>  | 35.7 <sup>a</sup>        | 1.21 <sup>a</sup>            | 33.4 <sup>a</sup>         |
|                          | SD      | 1.20                                 | 11.1               | 18.3                     | 0.26                         | 3.33                      |
| NPK+Mn                   | average | 7.98 <sup>a</sup>                    | 79.1 <sup>a</sup>  | 36.3 <sup>a</sup>        | 1.40 <sup>a</sup>            | 32.7 <sup>a</sup>         |
|                          | SD      | 1.00                                 | 13.3               | 16.1                     | 0.31                         | 1.40                      |
| NPK+Cu,Zn,Mn             | average | 8.11 <sup>a</sup>                    | 78.5 <sup>a</sup>  | 42.7 <sup>a</sup>        | 1.30 <sup>a</sup>            | 32.4 <sup>a</sup>         |
|                          | SD      | 0.41                                 | 13.1               | 12.2                     | 0.34                         | 1.70                      |
| Average for years        |         |                                      |                    |                          |                              |                           |
| 2012                     | average | 8.51 <sup>a</sup>                    | 90.9 <sup>a</sup>  | 49.2 <sup>a</sup>        | 1.53 <sup>a</sup>            | 31.4 <sup>b</sup>         |
|                          | SD      | 1.11                                 | 7.1                | 12.5                     | 0.22                         | 0.87                      |
| 2013                     | average | 7.45 <sup>b</sup>                    | 71.0 <sup>b</sup>  | 34.1 <sup>b</sup>        | 1.15 <sup>b</sup>            | 34.2 <sup>a</sup>         |
|                          | SD      | 0.59                                 | 5.4                | 8.5                      | 0.15                         | 1.45                      |

Note. NPK – mineral fertilizers, Cu, Zn, Mn – micronutrients

Averages in columns (separately for fertilization treatments and years) followed by the same letter are insignificant according to Duncan's test ( $\alpha < 0.05$ ), SD – standard deviation

According to JANKOWSKI et al. (2003), NEDZINSKIENE (2006), CIROMELE and CONTOMAN (2015) and WOJTKOWIAK et al. (2015), grain yield is determined by the nitrogen dose. LEWANDOWSKI and KAUTER (2003) suggest that a significant increase in the yield of all cereal species can be obtained after the application of 70 kg N ha<sup>-1</sup> (in conditions of south western Germany).

In this study, in case of mineral fertilization (NPK) and mineral fertilization combined with micronutrients applied separately (NPK+Cu, NPK+Zn, NPK+Mn) or in combination (NPK+Cu,Zn,Mn), a significant increase in grain yield was observed, as compared to the plot with no fertilization. BLECHARCZYK et al. (2004) found that the NPK fertilization (N-90 kg ha<sup>-1</sup>, P-26 kg ha<sup>-1</sup>, K-100 kg ha<sup>-1</sup>) in crop rotation and monoculture of rye resulted in an increase in the grain yield by 102.9%, in the number of ears m<sup>-2</sup> by 38.1%, in the number of grains per ear by 41.9%, in the grain weight per ear by 46.9%, and in the 1000 grain weight by 13.9%, as compared to the control plot (with no fertilization). In this study, mineral fertilizers did not significant affect the yield components. MALAKOUTI (2008), KUMAR et al. (2009), NADIM et al. (2012) suggest that micronutrients and mutual relationships between elements posi-

tively influence physiological processes of plants, which is reflected in improved yield. In this study, foliar feeding in order to supplement the basic fertilization with mineral fertilizers (NPK) did not affect grain yield and its components. According to NOGALSKA et al. (2012) fertilization with compound fertilizers, especially with AMOFOSMAG 3, in conditions of north-eastern region of Poland, has the effect on the increase in grain yield, as compared with one-component fertilizers. JASKULSKI and JASKULSKA (2009) in four out of 9 years of their research found a significant increase in the grain yield of winter wheat by 5.0–6.7% as a result of the application of SONATA ZBOŻE compound fertilizer, as compared to the yield of the wheat which was not subjected to foliar fertilization.

The content of protein and starch belongs to important criteria for the quality of cereals (RAGAEI et al. 2006, WOJTKOWIAK et al. 2015). NOWOTNA et al. (2006) showed that the average content of protein (for five test varieties of winter rye) is 9.64%. SKUODIENE and NEKROŠEINE (2009) indicate a broader range of protein content from 9 to 19% and of starch content from 49 to 66% in rye grain obtained in west Lithuania region. In this study the grain of winter rye contained from 10.1 to 10.6% of protein (Table 4). The content of protein in the grain was differentiated by weather conditions in given years and variants of fertilization. The content of protein in the second year of the study was higher by 2.9% as compared with the first year. Higher protein content corresponded to lower grain yields of rye. The year 2013 with a lower amount of precipitation and a higher mean air temperature in the spring growing season (May-June) favoured a greater concentration of protein. Similar dependencies of protein accumulation on weather conditions were confirmed by the study of LOPES-BELLIDO et al. (2000) and GARRIDO-LESTACHE et al. (2004). As a result of mineral fertilization (NPK) and supplementation with foliar feeding with manganese (NPK+Mn), zinc (NPK+Zn) and micronutrients applied in combination (NPK+Cu,Zn,Mn), protein content in grain increased by 5.0%, 4.0%, 3.0% and 2.0%, respectively, as compared to the plot with no fertilization. Supplementation of basic fertilization with copper (NPK+Cu) or micronutrients in combination (NPK+Cu,Zn,Mn) resulted in a decrease in protein content in grain by 3.8% and 2.8%, as compared to the mineral fertilization (NPK).

In this study the starch content in the grain of winter rye of the Dańkowskie Diament variety ranged from 64.4 to 64.9%. According to ZIELIŃSKI et al. (2007) starch content in three winter rye varieties (Amilo, Warka and Dańkowskie Złote – obtained from a local plant breeding station in Poland) ranged from 53.3% to 55.7%. According to NOWOTNA et al. (2007) among 6 analyzed rye varieties, only the Walet and Dańkowskie Złote varieties contained more starch than indicated in the present study.

Table 4  
The content of proteins and starch in grain of winter rye (average 2012–2013)

| Fertilisation treatments |         | Protein [%]        | Starch [%]         |
|--------------------------|---------|--------------------|--------------------|
| Without fertilization    | average | 10.1 <sup>d</sup>  | 64.7 <sup>ab</sup> |
|                          | SD      | 0.74               | 0.61               |
| NPK                      | average | 10.6 <sup>a</sup>  | 64.4 <sup>b</sup>  |
|                          | SD      | 0.10               | 0.15               |
| NPK+Cu                   | average | 10.2 <sup>cd</sup> | 64.9 <sup>a</sup>  |
|                          | SD      | 0.23               | 0.30               |
| NPK+Zn                   | average | 10.4 <sup>ab</sup> | 64.7 <sup>ab</sup> |
|                          | SD      | 0.23               | 0.30               |
| NPK+Mn                   | average | 10.5 <sup>ab</sup> | 64.5 <sup>ab</sup> |
|                          | SD      | 0.19               | 0.21               |
| NPK+Cu,Zn,Mn             | average | 10.3 <sup>c</sup>  | 64.8 <sup>ab</sup> |
|                          | SD      | 0.08               | 0.38               |
| Average for years        |         |                    |                    |
| 2012                     | average | 10.2 <sup>b</sup>  | 64.7 <sup>a</sup>  |
|                          | SD      | 0.41               | 0.40               |
| 2013                     | average | 10.5 <sup>a</sup>  | 64.6 <sup>a</sup>  |
|                          | SD      | 0.22               | 0.35               |

Note. NPK – mineral fertilizers, Cu, Zn, Mn – micronutrients

Averages in columns (separately for fertilization treatments and years) followed by the same letter are insignificant according to Duncan's test ( $\alpha < 0.05$ ), SD – standard deviation

Table 5  
Content of macronutrients in the grain of winter rye (average 2012–2013)

| Fertilisation treatments |         | Macronutrients [g kg <sup>-1</sup> DM] |                    |                   |                   |
|--------------------------|---------|--|--------------------|-------------------|-------------------|
|                          |         | P                                      | K                  | Ca                | Mg                |
| Without fertilization    | average | 3.61 <sup>b</sup>                      | 4.45 <sup>a</sup>  | 0.59 <sup>a</sup> | 0.92 <sup>a</sup> |
|                          | SD      | 0.08                                   | 0.07               | 0.03              | 0.06              |
| NPK                      | average | 3.66 <sup>b</sup>                      | 4.29 <sup>b</sup>  | 0.56 <sup>a</sup> | 0.91 <sup>a</sup> |
|                          | SD      | 0.08                                   | 0.04               | 0.06              | 0.04              |
| NPK+Cu                   | average | 3.51 <sup>b</sup>                      | 4.42 <sup>ab</sup> | 0.57 <sup>a</sup> | 0.96 <sup>a</sup> |
|                          | SD      | 0.06                                   | 0.06               | 0.02              | 0.01              |
| NPK+Zn                   | average | 3.52 <sup>b</sup>                      | 4.39 <sup>ab</sup> | 0.55 <sup>a</sup> | 0.94 <sup>a</sup> |
|                          | SD      | 0.07                                   | 0.09               | 0.06              | 0.03              |
| NPK+Mn                   | average | 3.21 <sup>c</sup>                      | 4.37 <sup>ab</sup> | 0.52 <sup>a</sup> | 0.89 <sup>a</sup> |
|                          | SD      | 0.05                                   | 0.06               | 0.05              | 0.02              |
| NPK + Cu,Zn,Mn           | average | 3.92 <sup>a</sup>                      | 4.47 <sup>a</sup>  | 0.52 <sup>a</sup> | 0.94 <sup>a</sup> |
|                          | SD      | 0.08                                   | 0.10               | 0.05              | 0.01              |
| Average for years        |         |  |                    |                   |                   |
| 2012                     | average | 3.28 <sup>b</sup>                      | 3.85 <sup>b</sup>  | 0.65 <sup>a</sup> | 0.98 <sup>a</sup> |
|                          | SD      | 0.10                                   | 0.08               | 0.07              | 0.02              |
| 2013                     | average | 3.86 <sup>a</sup>                      | 4.95 <sup>a</sup>  | 0.47 <sup>b</sup> | 0.88 <sup>b</sup> |
|                          | SD      | 0.13                                   | 0.11               | 0.03              | 0.01              |

Note. NPK – mineral fertilizers, Cu, Zn, Mn – micronutrients

Averages in columns (separately for fertilization treatments and years) followed by the same letter are insignificant according to Duncan's test ( $\alpha < 0.05$ ), SD – standard deviation

Years of the study did not influence the concentration of starch. Among the fertilized plots, only supplementation of mineral fertilization with copper (NPK+Cu) caused an increase in starch content by 0.78%, as compared to the NPK plot. Higher starch content corresponded to a lower protein content, and the correlation coefficient equalled  $r = -0,639$  (data not shown in Table 7).

The present study demonstrated that the years of the study have an impact on the content of P, K, Ca and Mg in the grain of winter rye (Table 5). In the first year of the study more Mg (by 11.4%) and Ca (by 38.3%), and in the second year more P (by 17.7%) and K (by 28.6%) was found. The study of MALAKOUTI (2008) shows that the use of combined mineral fertilization with microelements not only increases grain yield, but also improves nutritional value of cereal grain.

In this study winter rye grain contained 3.57 g P kg<sup>-1</sup>, 4.40 g K kg<sup>-1</sup>, 0.56 g Ca kg<sup>-1</sup>, 0.93g Mg kg<sup>-1</sup> on average. In comparison to studies of NOGALSKA et al. (2012), conducted at the same localization and conditions, a higher content of Mg was found in the grain of winter rye of the Dańkowskie Diament variety. The amounts of other mineral components (K, P, Ca) were similar. In the present study the combination of mineral fertilization with foliar feeding with micronutrients (NPK+Cu,Zn,Mn) contributed to a significant increase in phosphorus content in grain (from 6.6% to 18% in comparison with individual fertilizer variants).

The highest amount of potassium was found after the application of mineral fertilizers in combination with three micronutrients (NPK+Cu,Zn,Mn) and in the plot with no fertilization. In these variants the increase in K content (by 4.0% on average) was achieved only for the plot fertilized exclusively with mineral fertilizers (NPK).

In the experiment no increase in Ca and Mg content as a result of fertilization with macro- and micronutrients was achieved. Further, in a study of LEWANDOWSKI and KAUTER (2003) increasing doses of nitrogen (0, 70 and 140 kg ha<sup>-1</sup>) did not result in clear changes in calcium content in the grain of winter rye.

According to RAGAEI et al. (2006) rye grain (obtained from Experimental Farm in UAE University) is rich in iron (43.0 mg kg) and manganese (24.4 mg kg). In turn Kan (2015) indicates that rye (cultivated on sand-loam) grain has the highest content of Zn among major cereal species. In the present study the content of micronutrients in the grain of winter rye was characterised by variability in individual years of the study (Table 6). In the first year of the study more Fe (by 1.5% respectively), and in the second year more Zn and Mn (by 8.5% and 7.0%, respectively) was found. The combination of fertilization with mineral fertilizers with manganese (NPK+Mn) favoured the increase in Cu in grain by 14.2%, as compared to the plot with no fertilization. The

supplementation of mineral fertilization (NPK) with copper (NPK+Cu) or a combination of micronutrients (NPK+Cu,Zn,Mn) resulted in an increase in iron content in grain by 9.1%; 9.0% and 5.3%, respectively, as compared to the control plot (no fertilization). Foliar spraying with zinc (NPK+Zn), manganese (NPK+Mn) and a combination of micronutrients (NPK+Cu,Zn,Mn) resulted in a reduction in Fe content, as compared to the control plot fertilized with mineral fertilizers (NPK). Foliar feeding with zinc (NPK+Zn) and a combination of micronutrients (NPK+Cu,Zn,Mn) decreased the content of Zn in the grain of winter rye, as compared with fertilization with mineral fertilizers without micronutrients (NPK). Supplementation of basic fertilization with zinc (NPK+Zn), manganese (NPK+Mn) and a combination of micronutrients (NPK+Cu,Zn,Mn) resulted in an increase in Mn content in the grain (by 33.9, 30.2 and 23.1%, respectively), as compared to the plot with no fertilization and (by 25.7%, 22.2% and 15.5%, respectively), as compared with the plot fertilized with mineral fertilizers (NPK).

Table 6

Content of micronutrients in the grain of winter rye (average 2012–2013)

| Fertilisation treatments |         | Macronutrients [mg kg <sup>-1</sup> DM] |                    |                     |                     |
|--------------------------|---------|---|--------------------|---------------------|---------------------|
|                          |         | Cu                                      | Fe                 | Zn                  | Mn                  |
| Without fertilization    | average | 2.88 <sup>bc</sup>                      | 24.13 <sup>c</sup> | 29.77 <sup>ab</sup> | 10.70 <sup>c</sup>  |
|                          | SD      | 0.07                                    | 0.19               | 0.41                | 0.41                |
| NPK                      | average | 3.05 <sup>abc</sup>                     | 26.33 <sup>a</sup> | 32.57 <sup>a</sup>  | 11.40 <sup>c</sup>  |
|                          | SD      | 0.01                                    | 0.19               | 1.04                | 0.41                |
| NPK+Cu                   | average | 3.15 <sup>ab</sup>                      | 26.30 <sup>a</sup> | 32.83 <sup>a</sup>  | 11.20 <sup>c</sup>  |
|                          | SD      | 0.06                                    | 0.27               | 3.59                | 0.47                |
| NPK+Zn                   | average | 2.80 <sup>c</sup>                       | 23.83 <sup>c</sup> | 27.63 <sup>b</sup>  | 14.33 <sup>a</sup>  |
|                          | SD      | 0.03                                    | 0.14               | 0.40                | 0.68                |
| NPK+Mn                   | average | 3.29 <sup>a</sup>                       | 24.17 <sup>c</sup> | 32.10 <sup>a</sup>  | 13.93 <sup>ab</sup> |
|                          | SD      | 0.34                                    | 0.19               | 0.18                | 0.27                |
| NPK + Cu,Zn,Mn           | average | 3.12 <sup>abc</sup>                     | 25.40 <sup>b</sup> | 27.47 <sup>b</sup>  | 13.17 <sup>b</sup>  |
|                          | SD      | 0.12                                    | 0.45               | 0.27                | 0.60                |
| Average for years        |         |   |                    |                     |                     |
| 2012                     | average | 2.99 <sup>a</sup>                       | 25.21 <sup>a</sup> | 28.68 <sup>b</sup>  | 12.04 <sup>b</sup>  |
|                          | SD      | 0.08                                    | 0.22               | 2.01                | 0.39                |
| 2013                     | average | 3.11 <sup>a</sup>                       | 24.83 <sup>b</sup> | 31.12 <sup>a</sup>  | 12.88 <sup>a</sup>  |
|                          | SD      | 0.22                                    | 0.55               | 3.00                | 0.44                |

Note. NPK – mineral fertilizers, Cu, Zn, Mn – micronutrients

Averages in columns (separately for fertilization treatments and years) followed by the same letter are insignificant according to Duncan's test ( $\alpha < 0.05$ ), SD – standard deviation

Correlation analysis showed a positive correlation between Fe content and the content of Zn ( $r=0.457$ ) and a negative one with Mn content ( $r=-0.491$ ) in winter rye grain (Table 7).

Table 7  
Correlations between content of micronutrients, macronutrients, proteins and starch in grain of winter rye (average 2012–2013)

| Specification | Fe     | Zn     | Mn     | P      | K     | Proteins |
|---------------|--------|--------|--------|--------|-------|----------|
| Cu            | n.s.   | 0.405  | n.s.   | n.s.   | n.s.  | n.s.     |
| Fe            | –      | 0.457  | -0.491 | 0.390  | n.s.  | n.s.     |
| Zn            | 0.457  | –      | -0.423 | -0.427 | n.s.  | n.s.     |
| Mn            | -0.491 | -0.423 | –      | n.s.   | n.s.  | n.s.     |
| Ca            | n.s.   | n.s.   | -0.357 | n.s.   | n.s.  | n.s.     |
| Mg            | n.s.   | n.s.   | n.s.   | 0.419  | n.s.  | n.s.     |
| Starch        | n.s.   | n.s.   | n.s.   | n.s.   | 0.358 | -0.639   |

Correlations are significant at  $p < 0.05$ ,  $N = 36$

The increase in Zn content in the grain was accompanied not only by an increase in Fe content, but also by an increase in Cu content ( $r = 0.405$ ) and a decrease in Mn content ( $r = -0.423$ ). A negative correlation between Mn content and Fe, Zn and also Ca content ( $r = -0.357$ ) was observed. With the increase of P content in rye grain, the content of Fe (0.390) and Mg ( $r = 0.419$ ) increased, while the concentration of Zn decreased ( $r = -0.427$ ). Among mineral components only potassium (K) contributed to the increase in starch content in winter rye grain ( $r = 0.358$ ). The conducted correlation analysis revealed a reduction in starch content with increasing protein content ( $r = -0.639$ ).

## Conclusion

Fertilization with mineral fertilizers (NPK) and with mineral fertilizers with micronutrients applied separately or in combination resulted in a significant increase in grain yield (by  $0.98 \text{ t ha}^{-1}$  to  $1.48 \text{ t ha}^{-1}$ ), as compared to the plot with no fertilization. Fertilization with mineral fertilizers and foliar feeding with micronutrients (except for Cu) increased protein content in rye grain (NPK 5.0%, NPK+Mn 4.0%, NPK+Zn 3.0% and NPK+Cu,Zn,Mn 2.0%). Foliar application of nitrogen of basic fertilization with copper increased the concentration of starch in the grain by 0.78% as compared to the NPK plot. The mineral fertilization (NPK) with micronutrients applied in combination (NPK+Cu,Zn,Mn) increased the content of phosphorus (by 8.6% as compared to the plot with no fertilization and by 7.1% fertilized with mineral fertilizers NPK) and potassium (by 4.2% as compared to the NPK plot). Supplementation of basic fertilization with zinc or manganese or a combination of micronutrients resulted in an increase in Mn content in the grain (by 33.9, 30.2 and 23.1%, respectively) as compared to the plot with no fertilization and (by

25.7%, 22.2% and 15.5%, respectively) as compared to the plot fertilized with mineral fertilizers.

Translated by WERONIKA SZYSZKIEWICZ

Accepted for print 7.12.2015

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