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# THE EFFECTS OF STRIP CROPPING AND WEED CONTROL METHODS ON YIELD AND YIELD COMPONENTS OF DENT MAIZE, COMMON BEAN AND SPRING BARLEY

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Key words: strip cropping, weed control, maize, spring barley, common bean.

Abstract

A field experiment was conducted in the years 2008–2010 at the Experimental Station of the Faculty of Agricultural Sciences, University of Life Sciences in Lublin. The experiment evaluated the effect of cropping systems (sole cropping and strip cropping) and weed control (mechanical and chemical) on the yield and yield components of maize, common beans, and spring barley. Strip cropping significantly increased the yield of maize and the percentage of ears in the total biomass. The beneficial effect of strip cropping on common bean seed yield was significant in conditions of mechanical weed control. Strip cropping increased the number of pods per plant, seed weight per plant, and 1,000 seed weight. Spring barley yield was slightly higher in the strip cropping than in the sole cropping. Strip cropping increased the number and weight of seeds per spike.

## WPŁYW UPRAWY PASOWEJ I METOD REGULACJI ZACHWASZCZENIA NA ELEMENTY STRUKTURY I PLON KUKURYDZY PASTEWNEJ, FASOLI ZWYCZAJNEJ I JĘCZMIENIA JAREGO

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Słowa kluczowe: uprawa pasowa, regulacja zachwaszczenia, kukurydza, jęczmień jary, fasola zwyczajna.

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Abstrakt

Eksperyment polowy przeprowadzono w latach 2008–2010 w Stacji Doświadczalnej Wydziału Nauk Rolniczych (50°42'N, 2316'E) Uniwersytetu Przyrodniczego w Lublinie. W doświadczeniu oceniano wpływ metod uprawy (siew czysty i uprawa pasowa) i regulacji zachwaszczenia (mechaniczna i chemiczna) na strukturę i wielkość plonów kukurydzy pastewnej, fasoli zwyczajnej i jęczmienia jarego. Uprawa pasowa zwiększała istotnie wielkość plonu kukurydzy pastewnej i udział kolb w plonie. Korzystny wpływ uprawy pasowej na wielkość plonu nasion fasoli zwyczajnej był istotny w warunkach mechanicznej metody regulacji zachwaszczenia. Uprawa pasowa zwiększała liczbę strąków i nasion z rośliny oraz masę nasion z rośliny i masę tysiąca nasion. Jęczmień jary plonował nieco wyżej w uprawie pasowej niż w uprawie jednogatunkowej. Uprawa pasowa wpływała korzystnie na elementy struktury plonu, tj. liczbę i masę ziarniaków z kłosa.

## Introduction

Intercropping, has been used in numerous parts of the world (ZHANG and LI 2003, ARLAUSKIENÉ et al. 2011, DORDAS 2012). When crops are planted together, competition and facilitation can occur simultaneously (MARIOTTI et al. 2009). According to WU et al. (2012), when we increase facilitation and decrease competition between crops, multi-cropping systems can use environmental resources more effectively and can reduce costs, which improves the sustainability of crop production. Strip cropping is a form of intercropping used in many regions of the world (ANDRADE et al. 2012, HAUGGAARD-NIELSEN et al. 2012, COLL et al. 2012). This system protects the soil from water and wind erosion and reduces nutrient and pesticides leaching (ZHANG and LI 2003, ROGOBETE and GROZAV 2011). Strip cropping can also limit the occurrence of pests, diseases, and weeds, so that the use of pesticides can be reduced (MA et al. 2007, GŁOWACKA 2013a). Placing plants in strips minimizes competition between them for water, light, and nutrients, while greater diversity increases the stability of the agro-ecosystem. Numerous studies have demonstrated that the combined yields in strip cropping exceed the sum of the component species grown alone, as a result of complementary use of available growth resources (BORGHI et al. 2012, COLL et al. 2012, GŁOWACKA 2013b). Strips of maize and soybeans or dry beans have been used by farmers in the Eastern and Midwest U.S. because of higher yields and greater economic stability of this system (HAUGGAARD-NIELSEN et al. 2012). In Poland, the most commonly used form of intercropping is the cultivation of mixed cereals or of cereals with legumes (TOBIASZ-SALACH et al. 2011). Strip cropping is an alternative offering more possibilities, as different species are sown and harvested individually and therefore may be more useful in growing plants for different purposes. This system can be regarded as the adaptation of the more traditional intercropping systems but allowing the use of modern farm machinery (HAUGGAARD-NIELSEN et al. 2012). In the few research on strip cropping conducted in Poland it has been found to reduce the number of weeds in common bean and dent maize and to increase the trade yield of common bean and the percentage of ears in the total maize biomass. This effect of strip cropping system was particularly pronounced when used in combination with mechanical weed control (GŁOWACKA 2008, 2011). The efficiency of strip cropping depends on the choice of plant species, weed control methods, and weather conditions. The aim of this study was to evaluate the impact of strip cropping and varied weed control methods on the yield and yield components of maize, common beans, and spring barley.

## Materials and Methods

A field experiment was conducted in the years 2008–2010 at the Experimental Station of the Faculty of Agricultural Sciences in Zamość, University of Life Sciences in Lublin (50°42'N, 23°16'E), on brown soil of the group Cambisols which was slightly acidic ($pH_{KCl}$ – 6.2), with average content of organic matter (19 g $kg^{-1}$), high content of available phosphorus and potassium (185 mg P $kg^{-1}$ and 216 mg K $kg^{-1}$), and average magnesium content (57 mg $kg^{-1}$). The subject of the study was the Celio variety of dent maize, the Aura variety of common bean, and the Start variety of spring barley. The experiment was carried out in a split-plot design in four replications. The factors analyzed were: I. Cropping method (CM). 1. Sole cropping of a single species, in which the size of one plot of each crop was 26.4 $m^2$ for sowing and 22.0 $m^2$ for harvesting; 2. Strip cropping, in which three crops – dent maize (*Zea mays* L. conv. *dentiformis*), common bean (*Phaseolus vulgaris* L.), and spring barley (*Hordeum vulgare* L.) – were grown side-by-side, each in separate strips 3.3 m wide. The size of the plots was 13.2 $m^2$ for sowing and 11 $m^2$ for harvesting. II. Weed control method (WC); *A* – mechanical: maize – weeding of interrows twice (first in the 5–6 leaf stage – BBCH 15/16 – and again two weeks later); common bean – weeding of interrows twice (first 4–5 weeks after sowing, then 3 weeks later); spring barley – harrowing twice (first in the one-leaf stage – BBCH 10 – and again in the 5-leaf stage – BBCH 15); *B* – chemical: maize – a.i. bromoxynil + terbuthylazine at 144 g $ha^{-1}$ + + 400 g $ha^{-1}$ at the 4–6 leaf stage (BBCH 14/16); common bean – a.i. trifluralin before sowing at 810 g $ha^{-1}$ + bentazon at 1,200 g $ha^{-1}$ after emergence, when the first pair of trifoliate leaves had unfolded in the bean plants (BBCH 13–14); spring barley – a.i. 4-chloro-2-methylphenoxyacetic acid at 500 g $ha^{-1}$ at the full tillering stage (BBCH 22–23).

Dent maize was grown for silage with spring barley as a forecrop. Maize was sown on 28$^{th}$ April and 2$^{nd}$ and 5$^{th}$ May. The sowing rate was 11 plants per m$^2$, and the spacing between rows was 65 cm. In the sole cropping 10 rows of maize were planted on each plot, while in the strip cropping 5 rows were planted. The maize was harvested at the milky-wax stage (BBCH 79/83). Common bean was grown for dry seeds with maize as a forecrop. In the successive years of the study, beans were sown on 28$^{th}$ April and 2$^{nd}$ and 5$^{th}$ May. The distance between rows was 47 cm and the density was 35 plants per m$^2$. In the sole cropping 14 rows of beans were planted on each plot, while in the strip cropping 7 rows were planted. Beans were harvested by hand in the third week of August or first week of September. Spring barley was grown on a site where the previous crop was common bean. In the successive years, barley was sown on 12$^{th}$, 15$^{th}$, and 19$^{th}$ April at a rate of 350 seeds per m$^2$, the spacing between rows was 15 cm. In strip 22 rows of barley were planted. Barley was harvested in the first or second third of August (BBCH 89).

In strip cropping system strips followed a north-south orientation, and their arrangement is shown in Figure 1. Weather conditions varied over the years of the study (Table 1). A detailed description of the agriculture procedures for each crop was given in an earlier paper (GŁOWACKA 2013a).

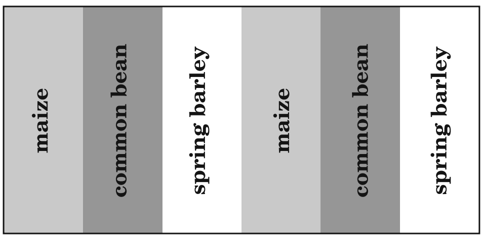


Fig. 1. The arrangement of strips in strip cropping system

Table 1

Rainfall and air temperature in months IV–IX as compared to the long-term means (1971–2010), according to the Meteorological Station in Zamość

| Years | Rainfall [mm] | | | | | | |
|---|---|---|---|---|---|---|---|
| | April | May | June | July | August | September | Sum |
| 2008 | 71.5 | 74.8 | 48.9 | 104.6 | 69.7 | 80.4 | 449.9 |
| 2009 | 15.5 | 102.6 | 124.4 | 24.2 | 48.9 | 34.5 | 350.1 |
| 2010 | 30.7 | 106.7 | 62.9 | 143.5 | 86.1 | 25.4 | 455.3 |
| Means for 1971–2010 | 41.8 | 70.7 | 72.8 | 91.2 | 65.3 | 52.1 | 393.9 |
| Temperature [°C] | | | | | | | |
| 2008 | 10.7 | 15.5 | 19.4 | 20.2 | 20.6 | 19.7 | 3031 |
| 2009 | 11.3 | 13.8 | 20.2 | 20.0 | 20.1 | 16.9 | 3122 |
| 2010 | 11.0 | 15.1 | 18.4 | 21.5 | 20.2 | 16.6 | 3141 |
| Means for 1971–2010 | 9.0 | 14.6 | 17.9 | 19.5 | 18.4 | 13.7 | 2849 |

Before the maize harvest, plant densities, plant height, and the percentage of ears, stems, and leaves in the green matter were determined. For the sole cropping, the designated test area consisted of 2 m sections from three inner rows. In the strip cropping, plants were picked from a 2 m of each row and yield and its structure were determined. After mechanical harvesting, yield of dry matter was determined. Before the bean harvest determinations were made of plant density, number of pods per plant, number and weight of seeds per pod and per plant, and 1,000 seed weight. For the sole cropping, plants were picked from two randomly designated sampling areas of 1 $m^2$ on each plot. In the strip cropping, plants were picked from a 2 m length of each row and yield and yield structure were determined. After hand harvesting, seed yield was determined at 15% moisture. In the spring barley grown in sole cropping, plants were picked by hand from two randomly designated sampling areas of 1 $m^2$ on each plot. For the strip cropping, the sampling areas were sections 2 m long from the three rows nearest the maize strip, the middle three rows, and the three rows next to the strip of beans. In the plants from the sampling areas, determinations were made of the number of spikes per unit area, culm and spike length, seed number and weight per spike, and 1,000 grain weight. After harvesting with a plot combine, barley grain yield was determined at 15% moisture content.

LER – the land equivalent ratio – was also calculated according to the formula:

$$LER = \Sigma\ (Ysi/Ymi)$$

where:
Ysi is the yield of each species in strip cropping (per 0.33 ha),
Ymi is the yield of each species in sole cropping (per ha).

This ratio was calculated for all species (i) to determine the partial LER, and the partial LERs were summed to obtain the total LER for the strip cropping. A total LER < 1 means that the strip cropping is less efficient than sole cropping, while a total LER > 1 indicates that strip cropping is more efficient than growing a single species alone.

The results were analysed by analysis of variance ANOVA using STATISTICA PL. The differences between averages were evaluated using Tukey's test, at $P < 0.05$.

## Results and Discussion

Maize is a species often chosen for cultivation in strip cropping, as it is highly responsive to edge effect, and as a tall, C4 photosynthesis plant, it efficiently utilizes the greater quantity of available sunlight (GHAFARZADEH et al. 1997). NING et al. (2012) states that intercropping using spring- and summer-sown maize presents advantages in terms of biomass yield and gross energy as compared to sole cropping. However, COLL et al. (2012) reported that maize, as a sole crop, showed the highest resource productivity (water and radiation) as compared to maize-soybean intercrop. In various experiments, a significant increase in maize yield in border rows has been noted (by 50%), and consequently overall yield in the strip was higher (CRUSE and GILLEY 1996, LESOING and FRANCIS 1999). In the present study maize yield in the strip cropping was on average 11% higher than in the sole cropping (Table 2). This resulted from a significant increase in yield in the maize border rows – by 26.0–29.6% in the row adjacent to the common beans, and by 17.0–21.5% in the row next to barley (Figure 2 and Figure 3). These differences were due to the neighboring plant species. When IRAGAVARAPU and RANDALL (1996) grew maize in strips with soy and wheat, they noted a 23% increase in maize yield in the extreme row adjacent to the wheat, and a 27% increase in the row adjacent to the soy strip. In intercropping, plant species can be complementary in chemical, spatial and temporal resource use (FOX 2005). Moreover, species can facilitate each other by creating the habitat and/or increasing nutrient availability for co-occurring species (EISENHAUER 2012). WU et al. (2012) suggested that in intercropping system two or more species differ in growth forms and physiological parameters. Thus, resources are used in a complementary fashion, in both time and space, due to niche partitioning. The effectiveness of strip cropping is also affected by how the strips are arranged. Plants in the eastern border rows produced higher yield than the rows on the western border. This is due to the faster rate of photosynthesis in the cooler mornings, when the sunlight reaches the eastern edge, than in the hot afternoons, when it falls on the western edge of the strip and may not be fully utilized by maize plants due to water stress and wilting.

Strip cropping significantly increased weight per plant, but decreased plant height by an average of 23 cm. The reduction in plant height may be due to greater access to photosynthetically active light and shortened internodes (JURIK and VAN 2004). This system also increased the percentage of ears in the total yield, while the share of stalks decreased and the share of leaves remained at a similar level (Table 3). A particularly significant increase in the percentage of ears was observed in the border rows of the maize strips (Figure 4). A similar

Table 2

Effect of cropping method and weed control method on the yield of dent maize, spring barley and common bean (dt $ha^{-1}$)

| I. Cropping method (CM) | II. Weed control (WC) | Maize biomass (d.m.) | | | | Grain of spring barley | | | | Common bean seeds | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | years | | | mean | years | | | mean | years | | | mean |
| | | 2008 | 2009 | 2010 | | 2008 | 2009 | 2010 | | 2008 | 2009 | 2010 | |
| Sole cropping (1) | *A** | 160 | 139 | 151 | 150 | 53.3 | 40.5 | 37.7 | 43.8 | 9.6 | 8.6 | 10.2 | 9.5 |
| | *B* | 186 | 166 | 178 | 177 | 61.0 | 46.6 | 45.5 | 51.0 | 17.6 | 16.4 | 16.5 | 16.8 |
| Strip cropping (2) | *A* | 177 | 156 | 168 | 167 | 57.4 | 45.1 | 38.9 | 47.1 | 13.4 | 10.4 | 11.4 | 11.9 |
| | *B* | 206 | 184 | 197 | 196 | 64.1 | 47.9 | 44.9 | 52.3 | 18.9 | 17.0 | 17.3 | 17.7 |
| $LSD_{0.05}$ for CM · WC | | n.s. | n.s. | n.s. | n.s. | n.s. | 1.3 | 1.1 | 0.81 | 1.9 | n.s. | 1.5 | 1.8 |
| Average for factors | | | | | | | | | | | | | |
| Averages CM | sole cropping | 173 | 153 | 165 | 162 | 57.1 | 43.6 | 41.6 | 47.4 | 13.6 | 12.5 | 13.4 | 13.2 |
| | strip cropping | 192 | 100 | 183 | 181 | 60.7 | 46.5 | 41.4 | 49.7 | 16.2 | 13.7 | 14.4 | 14.8 |
| $LSD_{0.05}$ for CM | | 5.0 | 6.0 | 5.0 | 16.0 | 1.7 | 1.2 | n.s. | 1.1 | 0.8 | 1.0 | 0.4 | 0.8 |
| Averages WC | *A* | 16.9 | 148 | 160 | 159 | 55.3 | 42.8 | 38.3 | 45.5 | 11.5 | 9.5 | 10.8 | 10.7 |
| | *B* | 193 | 175 | 188 | 185 | 62.5 | 47.2 | 45.2 | 51.7 | 18.2 | 16.7 | 16.9 | 17.3 |
| $LSD_{0.05}$ for WC | | 4.0 | 5.0 | 11.0 | 12.0 | 1.3 | 0.9 | 0.8 | 1.2 | 0.6 | 0.8 | 0.3 | 0.6 |
| Years | | 182 | 161 | 17.3 | – | 58.9 | 45.0 | 41.8 | – | 14.9 | 13.1 | 13.9 | – |
| $LSD_{0.05}$ for years | | 14.0 | | | | 3.6 | | | | 0.8 | | | |

* weed control: *A* – mechanical, *B* – chemical

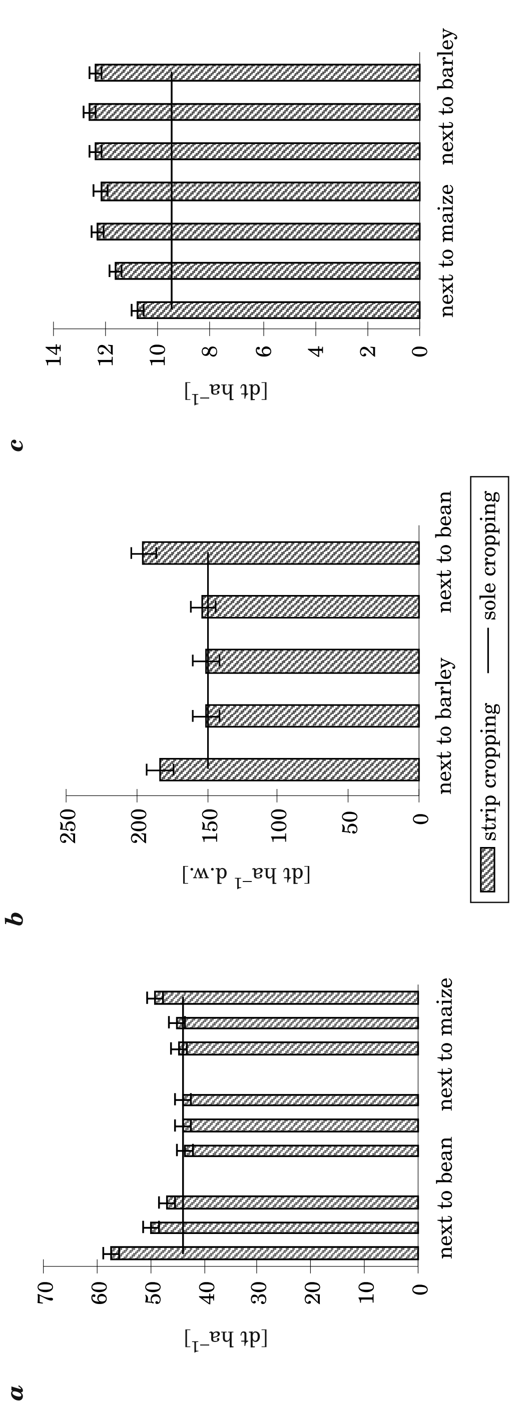


Fig. 2. The influence of row position in the strip on the yield of spring barley (*a*), maize (*b*), common bean (*c*) in conditions of mechanical weed control; note: bars represent the standard errors

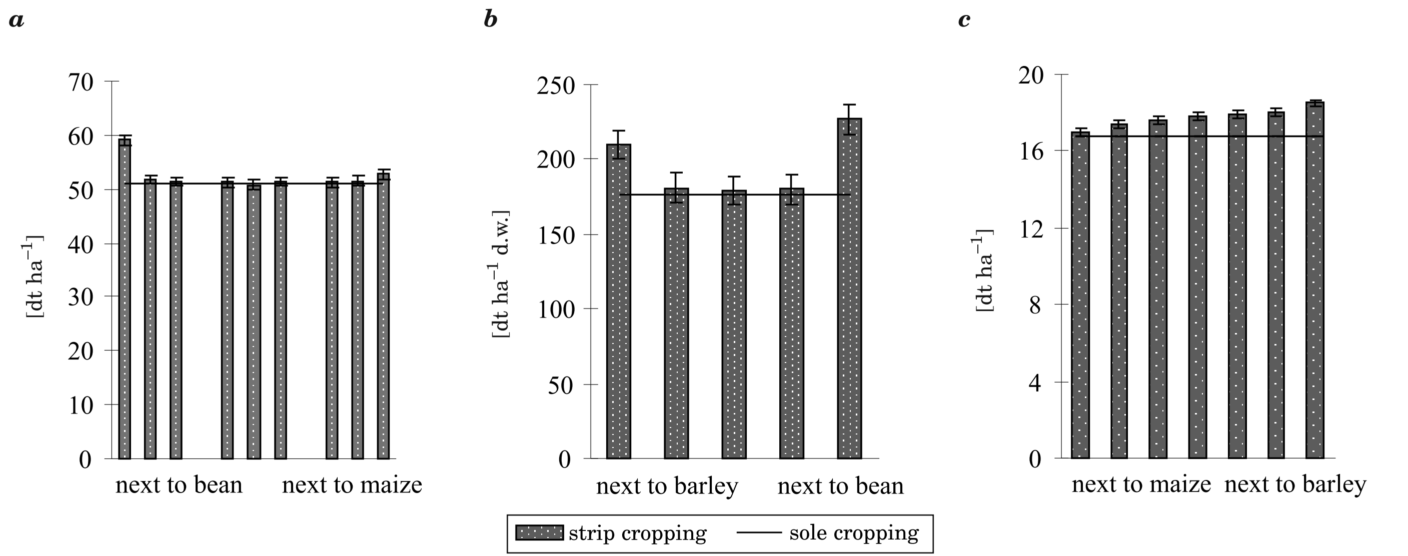


Fig. 3. The influence of row position in the strip on the yield of spring barley (*a*), maize (*b*), common bean (c) in conditions of chemical weed control; note: bars represent the standard errors

Table 3

Plant height, density and chosen yield components of maize (mean from 2008–2010)

| I. Cropping method (CM) | II. Weed control (WC) | Weight of one plant [g] | Plant densities [per 1 m$^2$] | Plant height [cm] | Percentage share in green matter [%] | | |
|---|---|---|---|---|---|---|---|
| | | | | | ears | stems | leafs |
| Sole cropping (1) | *A*<br>*B* | 517.6<br>670.3 | 10.6<br>9.8 | 236.0<br>257.0 | 36.5<br>34.9 | 46.9<br>48.2 | 16.6<br>16.9 |
| Strip cropping (2) | *A*<br>*B* | 604.1<br>718.6 | 9.8<br>9.2 | 210.0<br>238.0 | 37.1<br>37.3 | 46.1<br>45.8 | 16.8<br>17.1 |
| $LSD_{0.05}$ for CM · WC | | n.s. | n.s. | 5.0 | n.s. | 0.97 | n.s. |
| Average for factors | | | | | | | |
| Averages CM | sole cropping<br>strip cropping | 593.9<br>661.3 | 10.2<br>9.5 | 247.0<br>224.0 | 35.7<br>37.2 | 47.5<br>46.0 | 16.7<br>16.9 |
| $LSD_{0.05}$ for CM | | 48.5 | 0.6 | 4.6 | 1.2 | 0.89 | n.s. |
| Averages WC | *A*<br>*B* | 560.8<br>694.4 | 10.2<br>9.5 | 223.0<br>248.0 | 36.8<br>36.1 | 46.5<br>47.0 | 16.7<br>17.0 |
| $LSD_{0.05}$ for WC | | 37.3 | 0.6 | 3.5 | n.s. | n.s. | n.s. |
| Years | 2008<br>2009<br>2010 | 753.0<br>577.0<br>552.0 | 10.0<br>9.3<br>10.1 | 246.0<br>242.0<br>218.0 | 36.5<br>33.1<br>39.7 | 49.2<br>50.1<br>40.9 | 14.3<br>16.8<br>19.3 |
| $LSD_{0.05}$ | | 43.7 | n.s | 6.4 | 2.4 | 1.8 | 2.3 |

Explanations as in Table 2

trend of reduced plant height and increased share of ears in the yield was observed in spring wheat/maize/common bean strip cropping (GŁOWACKA 2008).

GARCIA-PRÉCHAC (1992) states that maize/soy/oats strip cropping are more efficient than the cultivation of each species separately in conditions of moderate or high humidity. In the present study, irrespective of the tested factors, the lowest yield with the smallest share of ears was obtained in the year with the least rainfall, which, moreover, was unevenly distributed over the season (Table 2). However, in this growing season the yield increase in strip cropping in comparison to sole cropping was 11.8%, which was the highest increase of all the years of the research. This may be due to the fact that barley and bean plants are less competitive in water uptake than maize. Moreover, there were significant shortages of rainfall in July, August, and September, months in which the plants accompanying the maize, especially barley, need less water.

Maize, due to the cultivation of a wide inter-row spacing and relatively slow growth in the early stages, is quite sensitive to competition from weeds. Worldwide yield losses in maize due to weeds are estimated to be around 37% (OERKE and DEHNE 2004). It was observed and discussed in other paper that weed infestation of maize was significantly higher in the case of the mechanical

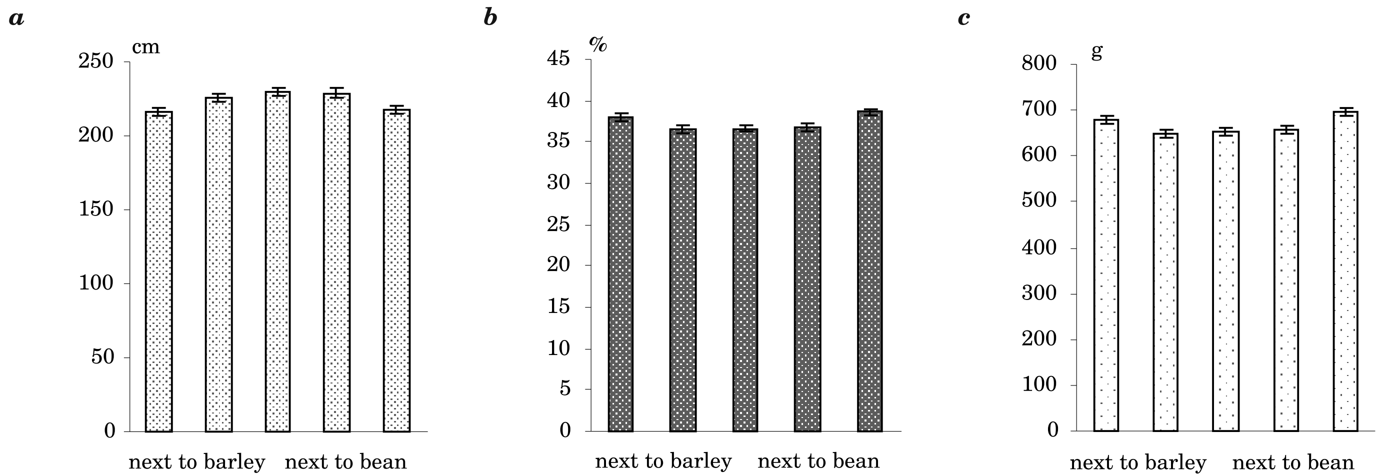


Fig. 4. The influence of row position in the strip on some elements of maize yield structure (average for weed control method): *a* – plant height, *b* – percentage of ears, *c* – weight of one plant; note: bars represent the standard errors

weed control (GŁOWACKA 2013). Mechanical method is often insufficiently effective because the weeds in the maize rows are not completely destroyed (ABDIN et al. 2000). Differences in weed infestation, significantly affected the yield and yield structure of the maize. The lowest maize biomass, with the smallest percentage of ears, was produced in conditions of mechanical weed control. The use of chemical treatments increased yield by 17.8% and the percentage of ears by 3.4%. Statistical analysis did not confirm an interaction between the cropping systems and weed control method.

Maize in strip cropping is often accompanied by soy. As a taller plant, maize can significantly reduce the access of soy to light and compete with it for water and minerals, and as a result significantly reduce soybean yield (EGLI and YU 1991, LESOING and FRANCIS 1999). For this reason, small grain plants such as wheat and oats are included in the strip cropping to minimize the negative impact of the maize on the other plant (IRAGAVARAPU and RANDALL 1996). In this study, common bean was introduced in the strip cropping because it is a leguminous plant often grown for dry seeds, especially in south-eastern Poland (ŁABUDA 2010). In a previous study by GŁOWACKA (2011), trade yield of bean increased in spring wheat/maize/common bean strip cropping, and a positive effect of strip cropping was evident in conditions of mechanical weed control. In the present study as well the seed yield was on average 13% higher in the strip cropping than in the sole cropping (Table 2). Strip cropping also significantly increased the number of pods and seeds per plant, seed weight per plant, and 1,000 seed weight. The beneficial effect of strip cropping was pronounced on plots where mechanical weed control was used (Table 2 and Table 4). This was probably due to the observed and discussed in other paper, lower weed infestation in the beans grown in strips and weeded mechanically (GŁOWACKA 2013). At these site, strip cropping reduced the number of weeds by 32% and their above-ground dry weight by 42% compared to sole cropping, while at the sites with chemical weed control the differences were only 14% and 13% for the number and biomass of weeds, respectively. Previous studies conducted in Poland have determined that strip cropping of maize, common bean and spring weed reduced both the number and dry weight of weeds in common bean and spring wheat in comparison with sole cropping (GŁOWACKA 2010). LIEBMAN and DYCK (1993) also suggest that weed infestation of crops can be reduced by the introduction of strip cropping. In addition, the adjacent strip of maize was a barrier protecting the bean plants from the wind, which may have improved water use and the temperature in the bean crop, thus favourably influencing the number of pods per plant (Table 4). Contrary, in the study by COLL et al. (2012) biomass and grain production of soybean decreased by 71–80% and by 64–77% when it was intercropped with maize and sunflower respectively. Intercrops arrangement in the cited study consisted of two rows of soybean and one row of maize or sunflower. In our experiment strip cropping consisted of 7 rows of common bean, 22 rows of barley and 5 rows of maize. Thus the negative impact of the maize on the neighbouring plant of common bean was smallest.

Table 4

Chosen yield components of common bean (mean from 2008–2010)

| I. Cropping method (CM) | II. Weed control (WC) | Number [piece] | | | Weight [g] | | | Plant densities [per 1 m$^2$] |
|---|---|---|---|---|---|---|---|---|
| | | pods per plant | seeds per | | seeds per | | 1,000 seeds | |
| | | | pod | plant | pod | plant | | |
| Sole cropping (1) | *A*<br>*B* | 11.4<br>16.9 | 2.9<br>3.2 | 35.1<br>60.5 | 1.62<br>1.99 | 19.4<br>32.1 | 540.5<br>570.7 | 43.2<br>46.5 |
| Strip cropping (2) | *A*<br>*B* | 14.0<br>18.3 | 3.1<br>3.3 | 40.0<br>65.8 | 1.85<br>2.10 | 25.6<br>36.4 | 585.0<br>610.0 | 44.8<br>47.8 |
| $LSD_{0.05}$ for CM · WC | | n.s. | n.s. | n.s. | n.s. | 2.0 | 3.7 | n.s. |
| Average for factors | | | | | | | | |
| Averages CM | sole cropping<br>strip cropping | 14.2<br>16.1 | 3.0<br>3.2 | 47.8<br>52.9 | 1.80<br>1.97 | 25.8<br>31.0 | 565.6<br>597.7 | 44.8<br>46.3 |
| $LSD_{0.05}$ for CM | | 1.0 | n.s. | 1.8 | 0.6 | 1.8 | 3.4 | n.s. |
| Averages WC | *A*<br>*B* | 12.8<br>17.6 | 3.0<br>3.3 | 37.5<br>63.2 | 1.73<br>2.04 | 22.5<br>34.3 | 562.8<br>600.6 | 44.0<br>47.1 |
| $LSD_{0.05}$ for WC | | 0.7 | 0.2 | 1.9 | 0.3 | 1.4 | 2.6 | 2.9 |
| Years | 2008<br>2009<br>2010 | 17.1<br>14.0<br>14.5 | 3.2<br>3.0<br>3.0 | 57.4<br>45.8<br>47.2 | 2.10<br>1.70<br>1.80 | 32.0<br>26.2<br>27.0 | 598.0<br>570.0<br>577.0 | 47.0<br>43.0<br>46.0 |
| $LSD_{0.05}$ for years | | 1.4 | n.s. | 2.4 | 0.3 | 1.8 | 4.6 | 3.5 |

Explanations as in Table 2

Both the seed yield and yield components varied depending on the row position in the beans strip. The fewest pods and seeds per plant were noted in the row adjacent to barley, and the most in the row next to maize. The highest seed weight per plant was observed in the row next to the barley (Figure 5). The yield of bean seeds was the lowest in the row bordering the maize strip. Differences between the rows in the strip were particularly evident under conditions of mechanical weed control (Figure 2). Although a negative impact of the maize was visible in the row directly adjacent to the maize, yield increased in successive rows and was highest in the row adjacent to the barley (Figure 2 and Figure 3). Changes in the number of pods and seeds per plant in rows of the bean strip showed that competition from maize was not as strong in the earlier stages of development (Figure 5). Maize and beans were sown at the same time, and maize is characterized by slow initial growth. During the

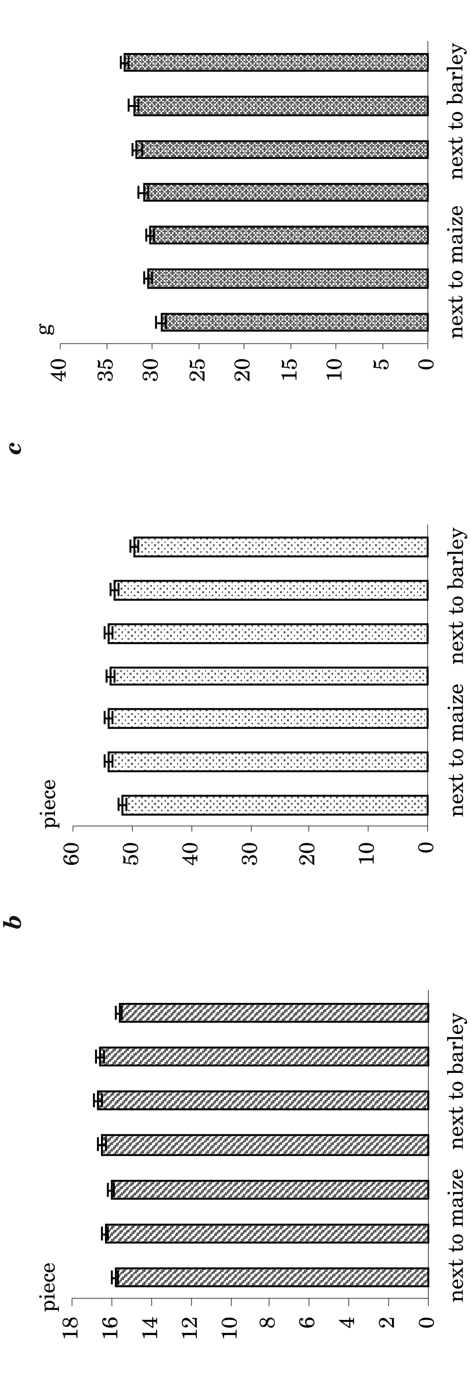


Fig. 5. The influence of row position in the strip on some elements of common beans yields structure (average for weed control method): *a* – pods per plant, *b* – seed number per plant, *c* – seed weight per plant; note: bars represent the standard errors

seed-filling period the competitiveness of the maize for the beans was greater, so that the seed weight per plant was higher in the row directly adjacent to the barley.

Beans plants are relatively small, which also increases their susceptibility to weed infestation, particularly in the initial period of growth (HEKMAT et al. 2007, SIKKEMA et al. 2008). An important element in the cultivation of common beans is to keep the plantation free from weeds during the first 3–5 weeks after sowing. Limiting weed control to mechanical treatments can significantly reduce the yield of beans (GŁOWACKA 2011). In this study, weed control limited to weeding of interrows twice decreased seed yield by an average of 38% compared to the use of herbicides (Table 2). Mechanical weed control also significantly reduced the some elements of yield structure (Table 4). This may be due to the fact that the use of herbicides significantly reduced the number and biomass of weeds compared to mechanical weed control (GŁOWACKA 2013).

The yield and yield structure of the barley was variable in different years of the study, and varied depending on the cropping system and weed control method (Table 2 and Table 5). In the first and second year, spring barley yield was significantly higher (+6.6%) in the strip cropping than in the sole cropping. In the third year of the study the impact of strip cropping was not significant. Average grain yield in the experiment was about 4.9% higher in strip cropping. Studies on strip cropping have generally found yield increases in small grains accompanying maize and soybeans (IRAGAVARAPU and RANDALL 1996, GHAFFARZADEH et al. 1998). The small grains in these experiments and the barley in the present study were sown 3–4 weeks earlier than other plants, so there was less competition in the border rows in the early stages of growth. Later, when the beans and maize can compete with the barley, it needs less water, nutrients, and light. Strip cropping significantly increasing the number of spikes per unit area, the weight and number of grain per spike and 1,000 seed weight. It did not affect the length of the culm. The higher yield in the strip cropping resulted from the reaction of barley to the edge effect, especially in the row adjacent to the common beans (Figure 2 and Figure 3). The yield advantage of the border row was mainly attributed to more solar energy, good ventilation, and less competition for nutrients, which resulted in more spikes or panicles, higher biomass production, and consequently higher grain yields (WANG et al. 2013). In a study by RUDNICKI and GAŁĘZEWSKI (2008) on the edge effect, the yield of oat grain in the first border row increased by 85%. In our study, barley yield in the first row of the bean strips was higher than in the middle rows by 27% and 16%, for the mechanical and chemical weed control. In the barley row adjacent to the maize grain yield also increased, but to a much lesser extent. Higher yield of border rows resulted from greater access to photosynthetically active light, better ventilation and less competition for nutrients and water (RUDNICKI and GAŁĘZEWSKI 2008, WANG et al. 2013). Spikes densities and the number of grains per spike were higher in the border rows of the barley strip, irrespective of the neighboring plant species. However, higher seed weight per spike was noted in the border rows adjacent to the bean strip (Figure 6). The number of spikes is determined mainly by tillering phase, which depends on natural factors such as temperature and water availability and agricultural practices, mainly of nitrogen availability for plants. The tillering phase of barley occurred at times, when the other accompanying crops had a reduced demand for resources. Avoiding the overlapping of critical periods improves complementarities in the use of resources between intercrop components with positive implications on resources use efficiency (COLL et al. 2012).

Table 5

Chosen yield components of spring barley (mean from 2008–2010)

| I. Cropping method (CM) | II. Weed control (WC) | Number of spike [per 1 m$^2$] | Length of [cm] | | Grain number in spike | Weight of [g] | |
|---|---|---|---|---|---|---|---|
| | | | culm | spike | | grain from spike | 1,000 grains |
| Sole cropping (1) | *A*<br>*B* | 476.0<br>518.0 | 79.6<br>75.7 | 7.1<br>7.0 | 18.5<br>18.7 | 0.96<br>1.02 | 50.7<br>53.0 |
| Strip cropping (2) | *A*<br>*B* | 497.0<br>536.0 | 76.1<br>70.6 | 7.4<br>7.7 | 19.4<br>19.7 | 1.06<br>1.09 | 51.9<br>54.0 |
| $LSD_{0.05}$ for CM · WC | | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. |
| Average for factors | | | | | | | |
| Averages CM | sole cropping<br>strip cropping | 497.0<br>516.0 | 77.6<br>73.4 | 7.0<br>7.6 | 18.6<br>19.5 | 0.99<br>1.08 | 51.8<br>52.9 |
| $LSD_{0.05}$ for CM | | 16.0 | n.s. | 0.3 | 0.4 | 0.03 | 0.6 |
| Averages WC | *A*<br>*B* | 487.0<br>527.0 | 77.9<br>73.2 | 7.3<br>7.3 | 19.0<br>19.2 | 1.01<br>1.06 | 51.3<br>53.5 |
| $LSD_{0.05}$ for WC | | 18.0 | 4.4 | n.s. | n.s. | 0.02 | 0.4 |
| Years | 2008<br>2009<br>2010 | 535.0<br>504.0<br>482.0 | 79.2<br>74.7<br>72.9 | 7.6<br>7.2<br>7.1 | 22.6<br>18.2<br>16.7 | 1.23<br>0.92<br>0.91 | 55.7<br>52.4<br>53.6 |
| $LSD_{0.05}$ for years | | 28.0 | 6.3 | 0.4 | 0.9 | 0.08 | 0.7 |

Explanations as in Table 2

Land equivalent ratio (LER) is often used to compare the efficiency of intercropping with sole cropping (CONNOLLY et al. 2001). On average for the experiment, the LER was 1.13 and 1.09 for mechanical and chemical weed control. This means that maize/beans/spring barley strip cropping was 9–13% more efficient than the sole cropping of a single species.

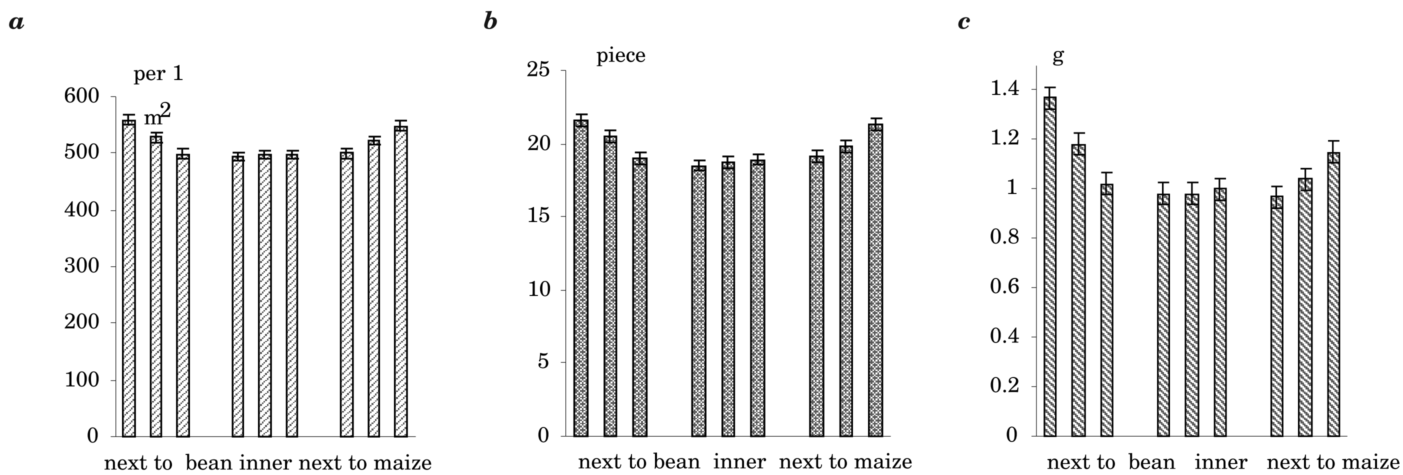


Fig. 6. The influence of row position in the strip on some elements of spring barley yield structure (average for weed control method): *a* – number of spikes, *b* – grain number per spike, *c* – grain weight per spike; note: bars represent the standard errors

## Conclusion

1. Strip cropping significantly increased the yield of dent maize, as well as the percentage of ears in the total yield.

2. The beneficial effects of strip cropping on seed yield in common beans were significant only where mechanical weed control was used. Strip cropping also significantly increased the number of pods and seeds per plant, seed weight per plant, and 1,000 seed weight.

3. Spring barley yield was slightly higher in the strip cropping than in the sole cropping. Strip cropping also positively affected yield components, such as the weight and number of grain per spike and 1,000 seed weight.

4. Yields of dent maize, spring barley, and common bean were significantly higher for the chemical weed control method than for the mechanical method.

5. A significant interaction between the cropping system and weed control method was found only for beans, with strip cropping found to be more effective in combination with mechanical weed control.

6. Both yield and yield components varied depending on the row position of the strip. The extent of the changes depended not only on the trait tested and the crop species, but also on the neighbouring plant in the strip.

7. The land equivalent ratio indicates that strip cropping was comparable to or more efficient than sole cropping. This, in combination with environmental benefits, indicates that strip cropping can be an element of sustainable agriculture.

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# THE EFFECT OF SULFATE AND ELEMENTAL SULFUR APPLICATION ON MODIFICATION OF CONCENTRATIONS OF MANGANESE AND LEAD IN SOIL

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Key words: fertilizer, sulfur, soil, heavy metals, lead, manganese, interaction.

Abstract

Soil acidification due to sulfur fertilization can produce an indirect result such as increased solubility and mobility of heavy metals in soil, thus affecting availability to plants of these elements derived from both natural and man-made resources. The purpose of this paper has been to explore the effect of incremental doses of sulfate and elemental sulfur on changes in the natural content of easily soluble forms of manganese and lead in two soil horizons: 0–40 and 40–80 cm. A three-year field experiment was set up on brown, acid soil with the texture of heavy loamy sand. Soil for chemical analyses was sampled in spring and autumn. Soluble forms were extracted from soil with 1 mol HCl $dm^{-3}$ solution and their concentrations were determined with the atomic absorption spectrophotometric method. Throughout the whole experiment, the dose of 40 kg $ha^{-1}$ $S\text{-}SO^{2-}{}_4$ induced higher concentrations of manganese in soil in the 0–40 cm layer compared to the other fertilization treatments. During the three years of the field trials, the application of sulfate sulfur and elemental sulfur to soil tended to cause a small increase in the soil content of lead soluble in 1 mol HCl $dm^{-1}$ in the 0–40 cm soil depth compared to the soil before the experiment. The concentrations of manganese and lead in soil in the 40–80 cm layer did not depend much on the form and dose of sulfur introduced to soil.

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**WPŁYW STOSOWANIA SIARKI SIARCZANOWEJ I ELEMENTARNEJ NA ZMIANY ZAWARTOŚCI MANGANU I OŁOWIU W GLEBIE**

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Słowa kluczowe: nawożenie, siarka, gleba, metale ciężkie, ołów, mangan, interakcja.

Abstrakt

Zakwaszenie gleby przez nawożenie siarką może pośrednio przyczyniać się do zwiększania rozpuszczalności i mobilności metali ciężkich w glebie, a tym samym ich dostępności dla roślin zarówno ze źródeł naturalnych, jak i antropogenicznych. Celem przedstawionej pracy było zbadanie wpływu wzrastających dawek siarki siarczanowej i elementarnej na zmiany naturalnej zawartości łatwo rozpuszczalnych form manganu i ołowiu w dwóch poziomach gleby 0–40 i 40–80 cm. Trzyletnie doświadczenie polowe założono na glebie brunatnej, kwaśnej o składzie granulometrycznym piasku gliniastego mocnego. Glebę do analiz chemicznych pobierano wiosną i jesienią. Formy rozpuszczalne ekstrahowano z gleby roztworem 1 mol HCl $dm^{-3}$, a ich zawartość oznaczono metodą absorpcyjnej spektrometrii atomowej. Przez cały okres trwania doświadczenia dawka 40 kg $ha^{-1}$ S-$SO^{2-}{}_4$ powodowała zwiększenie koncentracji manganu w glebie w poziomie 0–40 cm w odniesieniu do pozostałych obiektów nawozowych. W ciągu 3 lat badań stosowanie siarki siarczanowej i elementarnej wpłynęło na ogół na niewielkie zwiększenie zawartości ołowiu rozpuszczalnego w 1 mol HCl $dm^{-1}$ w glebie, w warstwie 0–40 cm, w porównaniu z glebą przed założeniem doświadczenia. Zawartość manganu i ołowiu w glebie w warstwie 40–80 cm nie zależała w większym stopniu od zastosowanej formy i dawki siarki.

## Introduction

Soils under arable fields in the Province of Warmia and Mazury are characterized by moderate concentrations of trace elements, much below the average amounts in whole Poland. Usually, they have the natural ($0^o$) content of heavy metals (TERELAK et al. 2001). However, predicting the extent of their potential mobilization is a complex problem, as the process is governed by soil-specific and environmental conditions as well as human activity. Soil reaction, for example, has an essential influence on the solubility and speciation of heavy metals, especially in soil solution (NAIDU et al. 1998, MÜHLBACHOVÁ et al. 2005). Soils that have an alkaline character and high pH are more likely to suffer from a deficit of microelements, which is manifested by poor crop yields, low effectiveness of fertilizers and high sensitivity of plants to diseases and pests (MALAKOUTI 2008). Soil acidification can stimulate the toxic nature of heavy metals and their phytoavailability (NEDERLOF and RIEMSOLIJK 1995, TEMMINGHOFF et al. 1997). KAYSER et al. (2000) as well as KAYSER et al.

(2001), who share the above view, demonstrated experimentally that when elemental sulfur had been incorporated into soil, the soil pH decreased while the solubility of heavy metals in soil increased. Among some disturbing effects of soil contamination with sulfur are the elevated solubility of manganese and mobilization of trace elements derived from both natural and anthropogenic pools (SCHWARZ et al. 2012).

The translocation of lead in the soil environment depends on the soil texture. Typically, strong adsorption on iron hydroxides and soil colloids inhibits the mobility of lead, which nonetheless undergoes biomagnification and can easily enter a trophic chain (KABATA-PENDIAS 1992, MARTINEZ et al. 2000). KOS et al. (2003) did an experiment which proved that soil solutions either did not contain or else had very small amounts of lead forms which were directly available to plants because lead tends to form permanent complexes with soil's organic matter. Soil amendment with chelates improves the bioavailability of lead, thus increasing the phytoextractibility of this element. The presence of organic matter in soil, soil sorption properties and soil acidification are important factors which influence the sorption and desorption of lead (MA et al. 2010).

The purpose of the experiment discussed in this paper has been to investigate the effect of increasing doses of sulfate and elemental sulfur on changes in the content of lead and manganese soluble in 1 mol HCl in the soil layers 0–40 and 40–80 cm deep.

The analyzed soil samples originated from the depths of 0–40 cm and 40–80 cm because of the underlying assumption of the experiment, which was to trace the migration of lead and magnesium downwards the soil profile.

## Materials and Methods

A three-year field experiment was conducted from 2000 to 2002, in North-East Poland. The village is distant from larger industrial plants which emit sulfur compounds and lies far from any big cities. The concentration of sulfur in the soil were not caused by human activity.

The trial was set up on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulfur 4.10, available phosphorus 34.5 and potassium 110.0 mg $kg^{-1}$ of soil. The annual rates of sulphate sulfur ($SO^{2-}_4$-S) and elemental sulfur ($S^0$-S) were: $S_1$ – 40, $S_2$ – 80 and $S_3$ – 120 kg $ha^{-1}$. Air-dry soil was passed through a 1 mm mesh sieve. The soil samples were used to determine soil pH in 1 mol KCl (the ratio between soil and extraction –1:2.5); total sulfur (Butters, Chenery 1959) and S-$SO^{2-}_4$ with the turbidimetric method (the ratio between soil and extraction 1:3); N-$NO_3^-$ by colorimetry using phenyl disulphonic acid (the ratio between soil and extraction 1:5); N-$NH_4^+$ was determined using Nessler's reagent (the ratio between soil and extraction 1:5); available phosphorus and potassium was determined with Enger Riehm's method (DL) – (the ratio between soil and extraction 1:50).

The permanent experiment was established in a random block design and consisted of eight fertilization treatments with four replications: 1) unfertilized control, 2) NPK, 3) NPK + $S_1$-$SO_4$, 4) NPK + $S_2$-$SO_4$, 5) NPK +$S_3$-$SO_4$, 6) NPK +$S_1$-$S^0$, 7) NPK +$S_2$-$S^0$, 8) NPK +$S_3$-$S^0$. The NPK rates depended on the crop species and soil fertility. The plants chosen for the trials demonstrate different degrees of sensitivity to sulfur deficit and excess in soil (Table 1). It was predicted that while testing the chosen doses of sulfur it would be possible to find which stimulated crop yields and which caused a demonstrably negative response of the crops.

Table 1

Applied doses of NPK in the experiment

| Experimental crops | Year | kg ha$^{-1}$ | | |
|---|---|---|---|---|
| | | N | P | K |
| Head cabbage *Brassica oleracea var capitata alba* | 2000 | 200.0 | 52.5 | 180.0 |
| Common onion *Allium cepa var. cepa* | 2001 | 160.0 | 60.0 | 183.0 |
| Spring barley *Hordeum sativum var nutans* | 2002 | 90.0 | 80.0 | 111.0 |

Nitrogen in the form of ammonium nitrate or ammonium sulphate, phosphorus in the form of triple superphosphate, potassium in the form of potassium salt of 60% or in the form of potassium sulphate, sulfur in the form of potassium sulphate and ammonium sulphate supplementation as well as in the form of elemental sulfur.

Soil samples were collected from each plot, at 0–40 and 40–80 cm depths, prior to the establishment of the trials, after each harvest and before sowing the consecutive crop. Air-dry soil was passed through a 1 mm mesh sieve. Analyzed soil samples originated from the depths of 0–40 cm and 40–80 cm because of the underlying assumption of the experiment, which was to trace the migration of lead and magnesium downwards the soil profile. The soil samples were used to determine the concentrations: Pb, Mn in soil (extractions with 1 mol HCl dm$^{-3}$, the ratio between soil and extraction – 1:10) according KARCZEWSKA and KABAŁA (2008), was determined by AAS method using Schimadzu AA apparatus. This method is less expensive, allows for fast, easy measuring in soil and characterized in terms of the content of micronutrients.

The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance for a two-factor experiment in a random block design, using the form of sulfur as factor a and rate of sulfur as factor b. Additional statistical analyses were performed with the software package Statistica 6.0 PL.

## Discussion of Results

The three-year field experiment compared the effect of sulfate and elemental sulfur, added to soil in the doses of 40, 80 and 120 kg ha$^{-1}$, on mobilization and changes in the natural soil content of manganese and lead. The solubility of heavy metals is markedly affected by soil reaction, hence soil acidification may increase the potential toxicity of heavy metals and their phytoavailability. In the first year of the experiment, soil was poor in sulfur, which is why the applied doses only stimulated crop yields but had negligible impact on modifications of $pH_{KCl}$ in soil (Table 2 and Table 3). Similar results of experiments were reported by RIFFALOLI et al. (2006), who observed that a mineralized dose of elemental sulfur did not cause any significant changes in properties of analyzed soil.

Table 2

Effect of different rates and forms of sulphur on soil reaction at 0–40 cm depth

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 5.30 | 4.84 | 4.89 | 4.54 | 5.51 | 5.39 |
| NPK | 5.40 | 4.93 | 4.70 | 4.37 | 5.36 | 4.50 |
| NPK+ $S_1$-$SO^{-2}_4$ | 5.50 | 4.97 | 5.03 | 4.52 | 5.08 | 4.86 |
| NPK+ $S_2$-$SO^{-2}_4$ | 5.35 | 5.13 | 4.98 | 4.67 | 4.84 | 4.39 |
| NPK+ $S_3$-$SO^{-2}_4$ | 5.38 | 4.81 | 4.39 | 4.15 | 4.46 | 4.36 |
| NPK+$S_1$-$S$-$^0$ | 5.78 | 4.92 | 5.33 | 4.92 | 5.20 | 4.43 |
| NPK+$S_2$-$S$-$^0$ | 5.46 | 4.93 | 5.15 | 4.67 | 5.00 | 4.61 |
| NPK+$S_3$-$S$-$^0$ | 5.56 | 4.99 | 5.11 | 4.36 | 4.65 | 4.37 |
| LSD-$_{0.05}$ | | | | | | |
| *a* | n.s. | n.s. | n.s. | n.s. | 0.135 | 0.202 |
| *b* | n.s. | n.s. | 0.209 | 0.211 | 0.191 | 0.285 |
| *ab* | n.s. | n.s. | 0.295 | 0.299 | 0.271 | 0.404 |

Explanations: $SO^{-2}_4$ – sulphate sulphur; $S^0$ – elementary sulphur; $S_1$ – 40 kg ha$^{-1}$, $S_2$ – 80 kg ha$^{-1}$, $S_3$ – 120 kg ha$^{-1}$; *a* – form of sulphur; *b* – dose of sulphur; *ab* – interaction; * n.s. – no significant difference

In the spring of 2001, the pH of the soil fertilized with 120 kg of sulfate sulfur, which had already decreased in the first year of the experiment, continued to decline (Table 2). Addition of elemental sulfur led to an increase in soil pH compared to the control treatments and plots fertilized with $S\text{-}SO^{2-}{}_4$.

In the autumn in the second year of the experiment (Table 2) the dose of 120 kg $S\text{-}SO_4$ $ha^{-1}$ introduced to the 0–40 cm soil horizon caused a further decrease in the soil $pH_{KCl}$, similarly to the effect observed in spring. The soil reaction tended to be higher on plots with elemental sulfur than on the other plots. This dependence was not verified in the 40–80 cm layer of soil (Table 3).

Table 3

Effect of different rates and forms of sulphur on soil reaction at 40–80 cm depth

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 5.30 | 4.82 | 4.32 | 4.29 | 4.40 | 4.47 |
| NPK | 5.01 | 4.83 | 4.66 | 4.46 | 4.47 | 4.55 |
| NPK+ $S_1\text{-}SO^{-2}{}_4$ | 5.21 | 5.21 | 4.36 | 4.50 | 4.71 | 4.58 |
| NPK+ $S_2\text{-}SO^{-2}{}_4$ | 5.61 | 5.07 | 4.89 | 4.47 | 4.72 | 4.63 |
| NPK+ $S_3\text{-}SO^{-2}{}_4$ | 4.99 | 4.70 | 4.78 | 4.43 | 4.45 | 4.59 |
| NPK+$S_1\text{-}S\text{-}^0$ | 4.89 | 5.14 | 5.02 | 4.53 | 4.56 | 4.60 |
| NPK+$S_2\text{-}S\text{-}^0$ | 5.09 | 5.04 | 4.99 | 4.51 | 4.63 | 4.66 |
| NPK+$S_3\text{-}S\text{-}^0$ | 5.06 | 5.04 | 4.89 | 4.50 | 4.58 | 4.54 |
| $LSD_{0.05}$ | | | | | | |
| *a* | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. |
| *b* | n.s. | 0.150 | n.s. | n.s. | 0.166 | n.s. |
| *ab* | n.s. | 0.212 | n.s. | n.s. | n.s. | n.s. |

Explanations see Table 2

In the third year (in spring), the $pH_{KCl}$ of soil in the 0–40 cm layer generally increased in all the treatments relative to the autumn 2001, especially on the plots without sulfur fertilization or with the dose of 40 kg $ha^{-1}$ $S\text{-}SO_4$.

However, all the plots fertilized with sulfate sulfur and elemental sulfur demonstrated a tendency towards a lower soil reaction versus the control treatments. Sulfate sulfur was noticed to produce a stronger influence on the soil reaction, which was most profoundly lowered by the dose of 120 kg S $ha^{-1}$ $S\text{-}SO_4$. Sulfate sulfur affected the soil reaction more strongly. In the experiments reported by WEI ZHOU et al. (2002), elemental sulfur did not have any significant effect on soil $pH_{KCl}$ because only between 5.58 to 14.87% of the applied elemental sulfur was oxidized. The acidifying influence of elemental sulfur became evident in the third year of the experiment. In general, soil at the depth of 40 to 80 cm was characterized by an almost uniform reaction, except for the plot which had received 120 kg S $ha^{-1}$ S-$SO_4$ (Table 3).

In the autumn 2002 (Table 2), the 40 to 80 cm deep soil layer fertilized with sulfur, especially with the dose of 120 kg $ha^{-1}$, had a much lower $pH_{KCl}$. A similar relationship emerged in the treatments without sulfur, which may have been a consequence of the leaching of base cations from soil. In the 40–80 cm deep layer, the dose or form of sulfur fertilizer had no effect on modifications of soil pH against the control or NPK treatments (Table 3).

The concentration of manganese in soil sampled prior to the experiment from the 0–40 cm soil horizon ranged from 89.00 to 109.00 mg $kg^{-1}$ of soil (Table 4). The Mn concentration in the 40–80 cm deep layer was much smaller. In the autumn, after cabbage harvest, the concentration of manganese in soil in the both layers (0–40 and 20–80 cm) did not depend significantly on the applied form or dose of sulfur (Table 4 and Table 5).

Table 4

Effect of different rates and forms of sulphur on the content of manganese soluble in 1mol HCl $dm^{-3}$ in soil at 0–40 cm depth [mg Mn $kg^{-1}$ soil]

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 89.00 | 93.00 | 85.29 | 82.50 | 108.20 | 85.75 |
| NPK | 106.25 | 108.25 | 90.17 | 86.97 | 118.54 | 88.66 |
| NPK+ $S_1$-$SO^{-2}_4$ | 109.00 | 111.00 | 109.62 | 100.69 | 129.98 | 107.41 |
| NPK+ $S_2$-$SO^{-2}_4$ | 101.74 | 100.74 | 89.23 | 92.75 | 120.78 | 91.32 |
| NPK+ $S_3$-$SO^{-2}_4$ | 106.32 | 108.31 | 87.76 | 93.36 | 119.74 | 93.44 |
| NPK+$S_1$-$S^{-0}$ | 101.89 | 102.89 | 96.15 | 80.42 | 112.16 | 93.19 |
| NPK+$S_2$-$S^{-0}$ | 101.15 | 102.15 | 87.38 | 84.07 | 115.96 | 90.16 |
| NPK+$S_3$-$S^{-0}$ | 99.74 | 98.74 | 91.00 | 83.54 | 126.94 | 91.80 |
| $LSD_{-0.05}$ | | | | | | |
| *a* | n.s. | n.s. | 3.088 | 5.341 | n.s. | n.s. |
| *b* | n.s. | n.s. | 4.367 | n.s. | 7.368 | 6.776 |
| *ab* | n.s. | n.s. | 6.176 | 10.683 | 10.4207 | 9.583 |

Explanations see Table 2

In the spring 2001, both the form and dose of sulfur produced significant effects on the content of manganese in soil in the 0–40 cm deep layer (Table 4). In the soil from the plots fertilized with sulfate sulfur, the concentration of manganese tended to be higher than in the soil nourished with elemental sulfur. As the dose of sulfate sulfur increased, the content of manganese in soil decreased. Similar results were reported by SOLIMAN et al. (1992). Doses of elemental sulfur produced less regular results. Compared to analogous

Table 5

Effect of different rates and forms of sulphur on the content of manganese soluble in 1 mol HCl $dm^{-3}$ in soil at 40–80 cm depth [mg Mn $kg^{-1}$ soil]

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 41.64 | 42.64 | – | 38.66 | 47.10 | 40.02 |
| NPK | 41.32 | 42.31 | – | 27.76 | 51.73 | 32.27 |
| NPK+ $S_1$-$SO^{-2}{}_4$ | 45.87 | 47.87 | – | 39.01 | 58.99 | 41.31 |
| NPK+ $S_2$-$SO^{-2}{}_4$ | 43.75 | 44.75 | – | 28.60 | 43.74 | 28.96 |
| NPK+ $S_3$-$SO^{-2}{}_4$ | 46.30 | 49.30 | – | 44.39 | 71.68 | 41.53 |
| NPK+$S_1$-$S^{-0}$ | 33.86 | 37.86 | – | 32.00 | 50.35 | 35.45 |
| NPK+$S_2$-$S^{-0}$ | 39.80 | 40.80 | – | 36.90 | 53.85 | 29.80 |
| NPK+$S_3$-$S^{-0}$ | 39.45 | 40.45 | – | 38.11 | 53.90 | 26.07 |
| LSD-$_{0.05}$<br>*a*<br>*b*<br>*ab* | <br>n.s.<br>n.s.<br>n.s. | <br>n.s.<br>n.s.<br>n.s. | – | <br>n.s.<br>8.2516<br>n.s. | <br>n.s.<br>n.s.<br>n.s. | <br>n.s.<br>7.992<br>n.s. |

Explanations see Table 2

treatments examined in the autumn 2000, the content of manganese in soil decreased (Table 4). In the autumn, after onion harvest, the concentration of manganese in the 0–40 cm deep soil layer was within 80.42 to 100.69 mg $kg^{-1}$ of soil (Table 4). Sulfate sulfur fertilization, in particular with the dose of 40 kg $ha^{-1}$, affected the content of magnesium in soil by raising it above the levels found in soil treated with elemental soil. Further depletion of the manganese content in soil, first demonstrated in the spring of 2000, was observed. However, two exceptions were noted, namely the treatments with 80 and 120 kg of sulfate sulfur (Table 4). FÄSSLER et al. (2012) implied a possibility of using elemental sulfur for the sake of improved phytoextraction of metals, although they warned against excessive acidification of soil and the risk of leaching heavy metals beyond the rhizosphere. In the 40–80 cm soil horizon, significant changes in the concentrations of manganese were caused only by doses of sulfur (Table 5). The highest manganese content occurred following the application of the dose of 120 kg $ha^{-1}$ S-$SO_4$. Fertilization with the increasing doses of elemental sulfur led to an increase in the soil content of manganese. No such tendency appeared when sulfate sulfur had been added to soil.

In the third year of the experiment, prior to sowing barley, the enrichment of soil (the 0–40 cm layer) with 1 mol HCl $dm^{-1}$ soluble manganese forms was observed against the soil tested in the previous years. During the three years of the research, application of sulfate sulfur and elemental sulfur significantly affected changes in the reaction of soil within 0–40 cm depth (from acid to very acid). In all probability, the soil acidification resulted in an increase in the content of the easily soluble forms of manganese. In a study described by ERDAL et al. (2004), the application of elemental sulfur in combination with nitrogen fertilizers led to a substantial increase in the availability of micronutrients, especially manganese, in soil. On the other hand, the research reported by ABDOU et al. (2011) suggests that sulfur has an insignificant effect on plant availability of manganese in soil. In the current study, the form of sulfur did not affect significantly changes in the content of Mn in soil (Table 4). Fertilization with sulfur, particularly with high doses of this element, generally raised the content of manganese against the control treatments. However, the applied forms and doses of sulfur had no effect on changing concentrations of manganese in the 40–80 cm soil layer of soil, although an increasing tendency appeared in the plot fertilized with the dose of 120 kg $ha^{-1}$ S-$SO^{2-}{}_4$, an effect which manifested itself already in the first year of the experiment. Once the experiment was terminated, the concentration of manganese in soil at the depth of 0 to 40 cm decreased versus the same soil layer sampled in the spring of 2002. A significant effect, however, was produced only by elemental sulfur, especially its dose of 40 kg $ha^{-1}$. Similar regularities were detected in the deeper soil horizon, i.e. 40–80 cm, although much smaller quantities of 1 mol HCl $dm^{-1}$ soluble manganese forms were determined (Table 5). A much higher uptake of Mn by plants induced by sulfur fertilization and its acidification has been implied by RAHMAN et al. (2011) and ISLAM (2012), who obtained similar research results. A rapid decrease of pH affects the rate at which Al and Fe are released from aluminum silicate and ferrous minerals. The harmful influence of excessive quantities of Al and Fe active forms in the environment consists in the increased bioavailability and accumulation of Mn, Cd and Pb by plants (MOTOWICKA-TERELAK, TERELAK 1998).

Concentrations of 1 mol HCl $dm^{-1}$ soluble lead in soil prior to the experiment were evenly distributed in both soil horizons (Table 6 and Table 7), although there were twice as many such bonds in the deeper, 40–80 cm layer than in the surface soil horizon. In the autumn, after cabbage harvest, it was only the form of sulfur that affected significant modifications in the content of lead in the 0–40 cm soil layer. In general, sulfur fertilization resulted in an elevated lead concentration in soil relative to the control treatments (Table 6). Compared to sulfate sulfur, the application of elemental sulfur evoked a tendency towards an increasing content of lead in soil. The doses caused insignificant differences. In the 40–80 cm layer, the applied forms of sulfur did not have any significant influence on changes in the content of lead in soil (Table 7). In the treatments with 40 and 80 kg ha S-$SO^{2-}{}_4$ as well as 120 kg $ha^{-1}$ S-$S^0$, the content of lead was higher than in the other treatments. This could have been

Table 6

Effect of different rates and forms of sulphur on the content of lead soluble in 1 mol HCl $dm^{-3}$ in soil at 0–40 cm depth [mg Pb $kg^{-1}$ soil]

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 5.26 | 5.79 | 5.84 | 5.79 | 6.39 | 5.50 |
| NPK | 5.00 | 5.79 | 5.35 | 5.02 | 6.02 | 5.59 |
| NPK+ $S_1$-$SO^{-2}{}_4$ | 5.43 | 6.14 | 6.39 | 5.63 | 7.37 | 5.99 |
| NPK+ $S_2$-$SO^{-2}{}_4$ | 5.16 | 4.77 | 5.97 | 5.32 | 6.55 | 4.66 |
| NPK+ $S_3$-$SO^{-2}{}_4$ | 5.55 | 5.95 | 6.11 | 6.29 | 6.68 | 5.95 |
| NPK+$S_1$-$S^{-0}$ | 4.78 | 6.21 | 5.39 | 6.41 | 6.59 | 6.11 |
| NPK+$S_2$-$S^{-0}$ | 4.91 | 5.91 | 5.56 | 5.55 | 6.81 | 5.81 |
| NPK+$S_3$-$S^{-0}$ | 4.29 | 6.25 | 5.32 | 5.53 | 6.72 | 6.05 |
| $LSD_{0.05}$ | | | | | | |
| *a* | n.s. | 0.2957 | n.s. | 0.4865 | n.s. | 0.295 |
| *b* | n.s. | n.s. | n.s. | n.s. | 0.5436 | n.s. |
| *ab* | n.s. | 0.5915 | 0.6793 | n.s. | n.s. | 0.591 |

Explanations see Table 2

Table 7

Effect of different rates and forms of sulphur on the content of lead soluble in 1 mol HCl $dm^{-3}$ in soil at 40–80 cm depth [mg Pb $kg^{-1}$ soil]

| Treatments | Before cabbage sowing | After cabbage harvest | Before onion sowing | After onion harvest | Before barley sowing | After barley harvest |
|---|---|---|---|---|---|---|
| 0 | 2.11 | 2.28 | – | 3.60 | 3.05 | 2.18 |
| NPK | 3.52 | 2.99 | – | 3.22 | 3.05 | 2.89 |
| NPK+ $S_1$-$SO^{-2}{}_4$ | 2.41 | 3.24 | – | 2.95 | 2.33 | 3.14 |
| NPK+ $S_2$-$SO^{-2}{}_4$ | 2.84 | 3.20 | – | 2.88 | 2.16 | 3.18 |
| NPK+ $S_3$-$SO^{-2}{}_4$ | 2.78 | 2.40 | – | 3.84 | 2.54 | 2.38 |
| NPK+$S_1$-$S^{-0}$ | 2.52 | 2.72 | – | 3.12 | 2.46 | 2.62 |
| NPK+$S_2$-$S^{-0}$ | 1.64 | 2.70 | – | 2.58 | 1.88 | 2.65 |
| NPK+$S_3$-$S^{-0}$ | 2.30 | 3.24 | – | 3.44 | 2.03 | 3.14 |
| $LSD_{0.05}$ | | | | | | |
| *a* | n.s. | n.s. | | n.s. | n.s. | n.s. |
| *b* | n.s. | 0.5725 | – | n.s. | n.s. | 0.572 |
| *ab* | n.s. | n.s. | | n.s. | n.s. | n.s. |

Explanations see Table 2

caused by the soil acidification due to sulfur and mobilization of forms of lead soluble in 1 mol HCl $dm^{-1}$. The influence of soil reaction on mobility of heavy metals is elucidated by the solubility product, where a decrease in the soil pH by one unit is associated with a 100-fold decrease in the potential solubility of heavy metals. When soil is polluted with several metals, the so-called 'salt effect' appears. The presence of one ion enhances the activity of other ions, which promotes the bioavailability of heavy metals (MOTOWICKA-TERELAK, TERELAK 1998).

In the spring of the second year, before sowing onion, the content of lead in the 0–40 cm deep soil layer did not depend significantly on either the form or the dose of sulfur (Table 6). The concentration of lead in soil from sulfate sulfur fertilized treatments was higher than in soil from analogous treatments analyzed in the first year of the experiment. In contrast, a small decline in the concentration of lead was determined in soil with added elemental sulfur. In the autumn of the second year, the form of sulfur, especially elemental sulfur, rather that its dose, had a significant effect. In general, concentrations of lead in the 0–40 cm soil layer on sulfur fertilized and control plots were on an approximately identical level (Table 6). Sulfur fertilization did not tend to have a significant effect on changes in the lead content in the 40–80 cm soil layer (Table 7). The content of lead in this soil horizon was much smaller than in the 0–40 cm layer of soil fertilized with sulfur. Similar results were obtained by ŠICHOROVÁ et al (2004), who concluded that the concentration of lead decreased with the depth of the soil profile.

In the spring of the third year, a slight increase was noticed in the content of 1 mol HCl $dm^{-1}$ soluble lead form in all the experimental treatments versus the analogous plots from the preceding years (Table 6). However, significant effects were produced only by the higher doses of sulfur, and especially 40 kg $ha^{-1}$ of sulfate sulfur. The application of sulfur to soil caused an increase in the concentration of lead in soil compared to a plot fertilized with NPK alone. The form of sulfur did not have significant impact. In the deeper soil layer, 40–80 cm, the content of lead was smaller than in the analogous plots in the autumn or in soil sampled from the topmost soil horizon.

When the experiment was terminated, the content of lead in soil from the 0–40 cm deep layer was within 4.66 to 6.11 mg kg, and depended significantly on the form of sulfur. More lead was found in soil from the treatments with elemental than sulfate sulfur. In the soil fertilized with elemental sulfur, the content of lead forms soluble in 1 mol HCl $dm^{-1}$ was higher than in the other fertilized treatments. In general, soil was slightly richer in lead than before the experiment had commenced, especially when plots were fertilized with elemental sulfur. In the autumn 2002, after harvest, the soil from the 0–4–0 cm layer contained less lead than the soil sampled before sowing barley. TERELAK et al. (1996) claim that when soils are polluted with sulfur, the bioavailability and accumulation of Mn, Cd and Pb in crops increase. Similar results were achieved by HOLAH et al. (2010), who concluded that the content and uptake of lead by plants increased significantly in response to growing doses of elemental sulfur, which led to a decreasing content of Pb in soil. In the deeper soil horizon, i.e. 40–80 cm, the concentration of lead was much smaller than in soil samples collected from the 0–40 cm layer, and depended only on the dose of sulfur (Table 6 and Table 7).

## Conclusions

1. Throughout the whole experiment, the dose of 40 kg $ha^{-1}$ $S\text{-}SO^{2-}{}_4$ caused higher concentrations of manganese in soil within the 0–40 cm layer than in the other fertilized treatments.

2. During the three years of the experiment, the application of sulfate and elemental sulfur caused small increases in the content of lead soluble in 1 mol HCl $dm^{-1}$ in soil in the 0–40 cm layer compared to soil before the experiment was set up.

3. The content of manganese and lead in soil, within the 40–80 cm layer, did not depend much on the applied form or dose of sulfur.

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# MILLING QUALITY OF SPRING TRITICALE GRAIN UNDER DIFFERENT NITROGEN FERTILIZATION

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K e y w o r d s: milling, triticale, nitrogen fertilization, specific grinding energy, particle size distribution.

A b s t r a c t

This paper presents the milling parameters of spring triticale grain fertilized with nitrogen in doses of 80 and 120 kg ha$^{-1}$. The varied nitrogen fertilization level influenced the physical properties of triticale grain of significant importance during milling such as: test weight, thousand kernel weight, vitreousness and hardness expressed by the PSI index. Increasing the fertilization dose from 80 to 120 kg N ha$^{-1}$ contributed to a decrease the energy demand for grain milling from 38.98 to 33.44 kJ kg$^{-1}$ and a decrease in ash content in the grain. The use of the higher nitrogen dose caused an increase in the mean particle size of the milling product from 242 to 352 μm. The milling products of each of the studied cereals consisted of particles with sizes from 0.5 μm to 2000 μm. Each milling product was characterized by distribution with five modes. For sizes below 30 μm, the particle size distributions of all studied materials were comparable. The nitrogen fertilization level diversified the milling products with regard to the content of the other size fractions.

## JAKOŚĆ PRZEMIAŁU ZIARNA PSZENŻYTA JAREGO NAWOŻONEGO RÓŻNYMI DAWKAMI AZOTU

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S ł o w a k l u c z o w e: przemiał, pszenżyto, nawożenie azotem, energochłonność rozdrabniania, rozkład wielkości cząstek.

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A b s t r a c t

Przedstawiono wyniki badań procesu przemiału ziarna pszenżyta jarego nawożonego azotem w dawkach 80 i 120 kg $ha^{-1}$. Zróżnicowany poziom nawożenia azotem wpłynął na cechy fizyczne ziarna pszenżyta mające istotne znaczenie podczas przemiału, takie jak: gęstość usypowa, masa tysiąca ziaren, szklistość oraz twardość technologiczna wyrażona wskaźnikiem PSI. Zwiększenie dawki nawożenia z 80 na 120 kg N $ha^{-1}$ przyczyniło się do zmniejszenia twardości ziarna, a wraz z nią do zmniejszenia zapotrzebowania na energię do przemiału ziarna z 38,98 do 33.44 kJ $kg^{-1}$. Zmniejszyła się również zawartość popiołu w ziarnie. Zastosowanie większej dawki azotu spowodowało zwiększenie średniego rozmiaru cząstek produktu przemiału z 242 do 352 μm. Produkty przemiału każdego z badanych zbóż składały się z cząstek o wielkościach od 0.5 μm do 2000 μm. Każdy z produktów przemiału charakteryzował się rozkładem o pięciu dominantach. W zakresie wielkości poniżej 30 μm rozkłady wielkości cząstek wszystkich badanych materiałów były porównywalne. Poziom nawożenia azotem różnicował produkty przemiału pod względem zawartości pozostałych frakcji rozmiarowych.

## Introduction

Triticale (*Triticale*) is an interspecific hybrid obtained by crossing wheat (*Triticum*) and rye (*Secale*). This is a cereal with lower soil requirements than wheat which is more disease-resistant than wheat or rye. It is characterized by good winter hardiness and shows higher drought resistance than wheat (AMMAR et al. 2004). The physical properties and chemical composition of triticale grain take values intermediate between the values of the properties of the parental species. Triticale grain is a good source of protein with a favorable amino acid composition (PISULEWSKA et al. 2000). Triticale grain of spring varieties characterized by higher protein content compared to winter forms (PETKOV et al. 2000).

Triticale grain is used mainly for feed, although is a potential alternative to wheat in processed flour products such as bread, flat bread, cakes or pasta. Because of the nutritional benefits of triticale grain, undertaking research on improving its quality is still needed. Breeders are attempting to obtain new *Triticale* varieties with better grain properties, which will improve the milling and baking process (ZECEVIC et al. 2005).

The basic process in grain processing is milling, whose aim is first the separation of the endosperm, the pericarp and germs and the reduction of endosperm particles to a fraction, which passes through a sieve with an aperture of not larger than about 200 μm (POSNER 2003). The result of the milling process is affected by both the milling scheme used and the grain properties and the design and settings of the equipment. Cereal grain properties depend on genetic factors and environmental conditions and on agrotechnical practices – especially nitrogen fertilization (POMERANZ et al. 1985, DZIAMBA et al. 2001, YÜCEL et al. 2009, EDWARDS et al. 2010). The most important physical properties of grain affecting milling include grain hardness and vitreousness (GREFFEUILLE et al. 2007a, GREFFEUILLE et al. 2007b, DZIKI et al. 2011). During grinding of hard endosperm wheat grain, flour with thicker granulation and partly damaged starch grains is obtained (LETANG et al. 2001). Grain hardness significantly affects the energy consumption of grinding. Hard kernels require more energy during milling into flours than soft kernels (KILBORN et al. 1982, DZIKI and LASKOWSKI 2005, DZIKI and PRZYPEK-OCHAB 2009). Grain vitreousness is often interrelated with grain hardness. Kernels with more vitreous endosperm are most often harder (GLENN and JOHNSTON 1994) and increased endosperm vitreousness for hard wheats is associated with higher flour yields (DOBRASZCZYK 1994, HADDAD et al. 1999). According to MARSHALL et al. (1986), the geometric properties of grain such as length, width, thickness, sphericity and endosperm size also affect milling directly. Grain length, width and area have been associated with a 40% variation in the milling quality of winter wheat cultivars (BERMAN et al. 1996).

The milling value of grain, besides its physical properties, can also be evaluated on the basis of experimental milling (POSNER 2003). Based on experimental grain milling, among others, the amount and granulometric composition of semi-finished products and final products of the industrial process can be determined. Granulometric composition is of importance in subsequent processing stages. Depending on the raw material size reduction ratio, the course of such processes as: mixing, dough preparation and baking is different. The quality of the obtained products is also different (PARK et al. 2006). The energy consumption of the grinding process is directly associated with the product size reduction ratio. Energy inputs for the grinding process grow with an increasing size reduction ratio (LASKOWSKI et al. 2005).

In view of the increasing acreage of triticale cultivation in the world and the introduction of new varieties into cultivation (SALMON et al. 2004), it is necessary to evaluate the effect of triticale reaction to agrotechnical factors, especially nitrogen fertilization, in the aspect of the milling value of this grain, especially since many authors (BISKUPSKI 2000, JOHANSSON et al. 2001, MUT et al. 2005, STANKOWSKI et al. 2008, SOBCZYK et al. 2009) have indicated the possibility of influencing the quality of cereal grain by nitrogen fertilization. For these reasons, the aim of this paper was to study the physical properties of spring triticale grain fertilized with different nitrogen doses, influencing the milling process for grain and its milling.

## Materials and Methods

Two modern spring triticale varieties, Andrus and Milewo, were selected for the research. A description of these cultivars can be found in the Common Catalogue of Varieties of Agricultural Plant Species (EU) in 2011. Grain came from a field experiment conducted at the Teaching and Research Centre in Tomaszkowo (53°73'N 20°41'E) in 2010–2011. The experiment was conducted using the method of random sub-blocks, in three replications. 30.2 kg P $ha^{-1}$ in the form of 46% triple superphosphate and 83 kg K $ha^{-1}$ as potash salt were applied in triticale fertilization. Nitrogen fertilization – was applied at two levels: 80 kg $ha^{-1}$ (40 kg in the tillering phase and 40 kg in the shooting phase) and 120 kg $ha^{-1}$ (40 kg pre-sowing, 40 kg in the tillering phase and 40 kg in the shooting phase). The pre-sowing fertilizer was ammonium nitrate and the fertilizer for top dressing 46% urea.

Grain samples in the quantity of 3 kg each were cleaned and the grain moisture content was then determined (ICC Standard No. 110/1). The moisture content of the grain was increased to 15%, by adding the appropriate amount of distilled water. The increase in the moisture content of grain was carried out in sealed containers during 24 h. The following physical properties of triticale grain were determined before the milling of each sample: test weight (TW), thousand kernel weight (TKW), particle size index (PSI) and grain vitreousness. TKW was measured for each sample with the use of an electronic kernel counter (Kernel Counter LN S 50A, UNITRA CEMI) and an electronic scale WPE 120. The particle size index (PSI) was determined in accordance with the AACC 55-30: 2000 method. The vitreousness of grain was evaluated on the basis of the analysis of cross-sections of kernels and expressed as the percentage of vitreous kernels in the sample of 50 elements (GREFFEUILLE et al. 2007b). The partially vitreous kernels were classified as semi-vitreous kernels and their number in the sample was multiplied by 0.5. The ash content in triticale grain and in the flours obtained after milling (*Determination of ash*... ICC Standard No. 104/1). The protein content in triticale grain was determined by the Kjeldahl method (*Determination of crude protein*... ICC Standard No. 105/2).

Grain milling (100-gram samples) was carried out in a Brabender Quadrumat Junior laboratory mill, equipped with a cylindrical sifter fitted with a 70GG sieve (PE 236 μm). Six samples of each material were ground. The yields of the obtained flours and the milling efficiency factor $K$ were determined (SITKOWSKI 2011):

$$K = \frac{Flour\ extract}{Ash\ content\ in\ flour} \tag{1}$$

The mill was connected with the power source through the system measuring the consumption of electrical energy. The grinding time ($t_r$) was measured with a stop watch to an accuracy of ± 0.1 s. The power of idle running ($P_s$) of the mill was also determined (the average value of power consumed before the measurements and immediately after the milling of the last sample of each material). The energy necessary for putting the elements of the mill into motion ($E_s$ – energy of idle running) was calculated by multiplying the active power of idle running and the time of grinding ($E_s = P_s \cdot t_r$). The work of grinding was determined assuming that the total energy consumed ($E_c$) by the mill equaled the sum of grinding energy and the energy needed for putting the elements of the mill into motion. The specific energy of grinding $E_r$ [kJ kg$^{-1}$] was calculated with the following formula:

$$E_r = \frac{E_c - E_s}{m} \tag{2}$$

where:
$m$ – mass of the milled sample [kg]

The grinding index $K_0$ (energy required to produce 1 kg of flour) [kJ kg$^{-1}$ of flour] was also determined acc. to GREFFEUILLE et al. (2007b):

$$K_0 = \frac{E_c - E_s}{m_{\mathrm{Fl}}} \tag{3}$$

where:
$m_{\mathrm{Fl}}$ – mass of flour [kg].

The particle size distribution (PSD) of ground grain particles (middlings) was determined quantitatively by the Laser Diffraction Analysis method in a Malvern Mastersizer 2000 analyzer. The measurement result was obtained as the mean of three successive replications. The analysis of the granulometric composition of the grist determined the mean particle size according to the formula (VELU et al. 2006):

$$d_p = \sum_{i=1}^{n} \varphi_i d_i \tag{4}$$

where:
$\varphi_i$ – share of the size fraction $i$ in the studied sample [kg kg$^{-1}$],
$d_i$ – mean size of fraction $i$ particles [μm].

PSD measurements were performed after mixing of undersized and oversize particles, obtained from drum sieve mounted in mill.

The mean linear dimension of grain before grinding was determined as the arithmetic mean from the sizes of equivalent diameters of a representative sample of 30 kernels. The equivalent diameter was determined as the geometric mean from grain length ($L$), width ($W$) and thickness ($T$) (MOHSENIN 1986):

$$d_z = (LWT)^{1/3} \tag{5}$$

Geometric grain measurements were taken manually with an electronic caliper ($\Delta = \pm\ 0.05$ mm). The results are presented as the mean of the two years. Value of each of the quality of research in the following seasons were at the same level. A statistical analysis of the obtained results was conducted, including an analysis of variance using the software STATISTICA® for Windows v. 10 (StatSoft Inc.). The significance of differences between means was determined using Tukey's test. Statistical hypotheses were tested at the significance level of $\alpha = 0.05$.

## Results

Significant variation in the studied physicochemical properties of grain under the influence of the applied fertilization levels was demonstrated (Table 1). The test weight ranged from 65.5 to 67.5 kg hl$^{-1}$. Fertilization with the higher nitrogen dose contributed to an increased TW as well as increased TKW. Higher TKW values were found for the Andrus variety. The studied triticale varieties were characterized by floury endosperm structure (the mean percentage of vitreous kernels was from 20% to 36%). Fertilization with a higher nitrogen dose contributed to decreased grain vitreousness.

Table 1

Selected physical and chemical properties of the triticale grains (average values from the years 2010–2011)

| Variety | TW [kg hl$^{-1}$] | TKW [g] | Vitreousness [%] | Protein content [%] | PSI [%] | Ash content [%] |
|---|---|---|---|---|---|---|
| Andrus 80 | $65.9^a \pm 0.03$ | $36.0^c \pm 0.5$ | $36^b \pm 2.1$ | $11.62^a \pm 0.04$ | $34^a \pm 0.5$ | $2.20^d \pm 0.02$ |
| Andrus 120 | $66.8^b \pm 0.20$ | $38.0^d \pm 0.3$ | $24^a \pm 2.9$ | $11.71^a \pm 0.25$ | $38^c \pm 1.0$ | $2.16^c \pm 0.03$ |
| Milewo 80 | $65.5^a \pm 0.10$ | $33.6^a \pm 0.3$ | $26^a \pm 2.3$ | $12.70^b \pm 0.14$ | $35^{a,b} \pm 2.0$ | $2.12^b \pm 0.02$ |
| Milewo 120 | $67.5^c \pm 0.40$ | $35.0^b \pm 0.7$ | $20^a \pm 2.9$ | $12.23^c \pm 0.20$ | $37^{b,c} \pm 1.0$ | $2.05^a \pm 0.02$ |
| Fertilization | | | | | | |
| 80 | $65.7^a \pm 0.20$ | $34.8^a \pm 1.3$ | $31^b \pm 6.1$ | $12.16^a \pm 0.59$ | $34.5^a \pm 1.0$ | $2.16^b \pm 0.04$ |
| 120 | $67.1^b \pm 0.40$ | $36.5^b \pm 1.6$ | $22^a \pm 3.5$ | $11.97^a \pm 0.35$ | $37.5^b \pm 1.0$ | $2.10^a \pm 0.05$ |

Explanations: data are average values ± standard deviation, *a, b, c, d* – differences of values in columns (for the given variety) marked with the same letters are insignificant at $\alpha = 0.05$

The particle size index (PSI) ranged from 34% to 38%. Increasing the nitrogen fertilization of the studied triticale varieties contributed to increases in the PSI index. Triticale grains obtained from plots fertilized with nitrogen in the amount of 80 kg N ha$^{-1}$ were classified as very soft grains and from the plot fertilized with a dose of 120 kg N ha$^{-1}$ were classified as extra soft grains. The mean ash content in grain ranged from 2.05% to 2.2%. Increased nitrogen fertilization caused decreased ash content in grain.

Results of the evaluation of triticale grain geometrical properties are shown in Table 2. Triticale fertilization with the higher nitrogen dose contributed to increased grain length and decreased width but did not affected the grain thickness and geometric mean diameter. Flour extracts obtained from grain milling ranged from 59.3 (Andrus variety) to 63.7% (Milewo variety) – Table 3. No significant effect of nitrogen fertilization on this property was found. No significant effect of nitrogen fertilization on the ash content in flours obtained from milling was demonstrated either. The different nitrogen fertilization had no effect on the ash content of the flour. This variety was also distinguished by higher milling efficiency factor $K$, with the highest value of the $K$ factor (112) recorded for fertilization with the higher nitrogen dose. The amount of energy consumed for triticale grain grinding depended on the level of applied nitrogen fertilization. The higher nitrogen dose caused a decrease in energy spent during grain milling, favorable in terms of milling into flour. The grain grinding index $K_0$, corresponding to the energy necessary to obtain the appropriate quantity of flour, similar to the energy consumed for grain grinding, depended on the applied nitrogen fertilization. The dose of 120 kg N ha$^{-1}$ contributed to decreased $K_0$ and energy used for grain grinding.

Table 2

Geometrical properties of the triticale grains (average values from the years 2010–2011)

| Variety | Length [mm] | Width [mm] | Thickness [mm] | Geometric mean diameter ($d_z$) [mm] |
|---|---|---|---|---|
| Andrus 80 | $8.28^{a,b} \pm 0.51$ | $3.26^{a} \pm 0.25$ | $3.18^{a} \pm 0.19$ | $4.41^{a} \pm 0.24$ |
| Andrus 120 | $8.23^{a,b} \pm 0.37$ | $3.08^{a} \pm 0.29$ | $3.08^{a} \pm 0.23$ | $4.27^{a} \pm 0.23$ |
| Milewo 80 | $8.09^{a} \pm 0.39$ | $3.16^{a} \pm 0.29$ | $3.06^{a} \pm 0.27$ | $4.27^{a} \pm 0.29$ |
| Milewo 120 | $8.51^{b} \pm 0.56$ | $3.14^{a} \pm 0.28$ | $3.14^{a} \pm 0.19$ | $4.37^{a} \pm 0.25$ |
| Fertilization | | | | |
| 80 | $8.18^{a} \pm 0.46$ | $3.21^{b} \pm 0.27$ | $3.12^{a} \pm 0.24$ | $4.34^{a} \pm 0.27$ |
| 120 | $8.37^{b} \pm 0.49$ | $3.11^{a} \pm 0.28$ | $3.11^{a} \pm 0.21$ | $4.32^{a} \pm 0.24$ |

Explanations as in Table 1

Table 3

Assessment of the milling value of triticale grain (average values from the years 2010–2011)

| Variety | Flour extract [%] | Ash content in flour [%] | Milling efficiency factor ($K$) [–] | Specific grinding energy ($E_r$) [kJ kg$^{-1}$] | Grinding index ($K_0$) [kJ kg$^{-1}$ flour] | Average particle size of milling product ($d_p$) [μm] |
|---|---|---|---|---|---|---|
| Andrus 80 | 59.3$^a$ ± 1.5 | 0.60$^a$ ± 0.05 | 99$^a$ ± 6.7 | 41.44$^b$ ± 2.92 | 68.32$^b$ ± 6.19 | 266$^{a,b}$ ± 37 |
| Andrus 120 | 60.9$^a$ ± 0.9 | 0.62$^a$ ± 0.04 | 98$^a$ ± 4.8 | 33.80$^a$ ± 1.78 | 54.91$^a$ ± 3.29 | 396$^c$ ± 7 |
| Milewo 80 | 63.4$^a$ ± 3.1 | 0.58$^a$ ± 0.02 | 109$^{a,b}$ ± 7.0 | 36.52$^b$ ± 1.55 | 57.76$^b$ ± 2.97 | 219$^a$ ± 10 |
| Milewo 120 | 63.7$^a$ ± 1.7 | 0.57$^a$ ± 0.03 | 112$^b$ ± 2.8 | 33.08$^a$ ± 4.84 | 51.32$^a$ ± 7.28 | 310$^b$ ± 26 |
| Fertilization | | | | | | |
| 80 | 61.3$^a$ ± 3.1 | 0.59$^a$ ± 0.03 | 104$^a$ ± 8.3 | 38.98$^b$ ± 3.4 | 63.04$^b$ ± 7.21 | 242$^a$ ± 35 |
| 120 | 62.3$^a$ ± 1.9 | 0.59$^a$ ± 0.04 | 105$^a$ ± 7.5 | 33.44$^a$ ± 3.4 | 53.11$^a$ ± 5.57 | 352$^b$ ± 50 |

Explanations as in Table 1

An important parameter of the milling value is the granulometric composition of the milling product. The analysis of particle size distribution indicates that the nitrogen fertilization level clearly diversified the milling products with regard to the content of individual size fractions. The granulometric composition of the milling product of each of the studied cereal was characterized by a very wide particle size range, from 0.5 μm to 2000 μm (Figure 1).

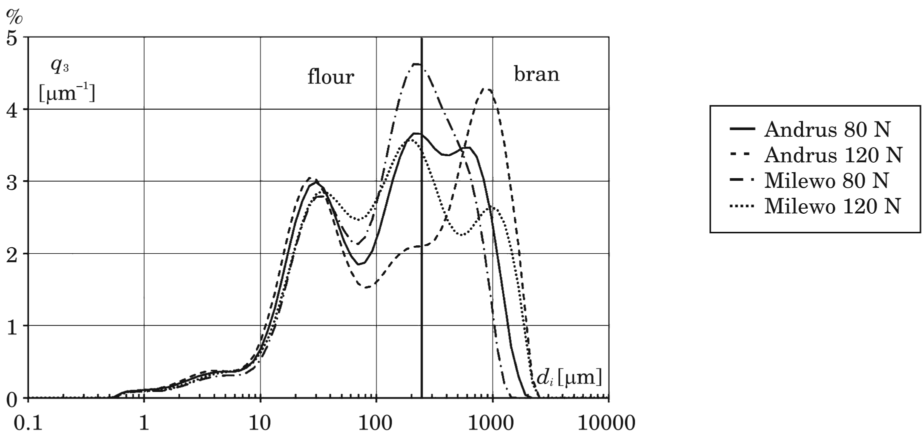


Fig. 1. Granulometric composition of middlings obtained from triticale grains (average values from the years 2010–2011)

The percentage of the fraction under 30 μm was comparable in all of the studied materials, although differences were found in thicker fractions. The percentage of the 200 μm fraction diminished noticeably with increased nitrogen fertilization in both studied varieties (from 3.6% to 2.1% for a change in the fertilization level from 80 to 120 kg N $ha^{-1}$ for the Andrus variety). A similar change in the content of the 200 μm fraction occurred in the milling product of the Milewo variety. An analogous increase in the fertilization level caused a decrease in the percentage of the 200 μm fraction from 4.6% to 3.5%. The opposite tendency found in the content of the largest size fraction. Increasing the fertilization level from 80 kg N $ha^{-1}$ to 120 kg N $ha^{-1}$ caused an increase in its percentage from 3.5% to 4.2% (Andrus) and from an almost zero to 2.7%.

Flour extract was inversely correlated with the ash content in grain ($r$ = -0.677) and the ash content in flour increased with a rising ash content in grain ($r$ = 0.769) (Table 4). The amount of energy consumed for grain milling increased with rising grain vitreousness ($r$ = 0.785) and diminished with increasing test weight ($r$ = -0.649) and the value of the PSI index ($r$ = -0.676).

Table 4

Significant value of linear correlation for physicochemical properties of grain and characteristic milling properties

| Trait | Flour extract | Ash content in flour | Milling efficiency factor | Specific grinding energy | Grinding index | Average particle size of milling product |
|---|---|---|---|---|---|---|
| TW | – | – | – | –0.649 | –0.624 | 0.587 |
| TKW | – | – | –0.593 | – | – | 0.783 |
| Ash content in grain | –0.677 | 0.769 | –0.672 | 0.612 | 0.646 | – |
| Vitreousness | – | – | – | 0.785 | 0.815 | – |
| PSI | – | – | – | –0.676 | –0.624 | 0.694 |

## Discussion

Variation of triticale nitrogen fertilization affects most of the studied qualitative grain characteristics. TKW indicating the endosperm size and its filling increased along with the increased nitrogen fertilization dose. According to SLAUGHTER et al. (1992), the higher the wheat TKW, the higher the flour extract is obtained. No such relationship for the studied triticale grain was found in own research, but it was found that higher TKW values were accompanied by a higher mean particle size in the milling product ($r$ = 0.783). Differences in the mean particle size of the milled material may result from differences in the mechanical properties of small and large caryopses.

Fertilization with the higher nitrogen dose contributed to increased test weight. A positive correlation was found between TW and the mean ground grain particle size ($r$ = 0.587). This relationship may be caused by a higher percentage of endosperm in grain (relative to bran) for grains with higher test weight (DZIKI and LASKOWSKI 2005).

The effect of milling largely depends on grain hardness. Increasing the nitrogen fertilization of the studied triticale varieties contributed to increases in the PSI index (i.e. it decreased grain hardness). Hard kernels require higher energy during grinding than soft kernels (KILBORN et al. 1982, DZIKI and LASKOWSKI 2005, DZIKI and PRZYPEK-OCHAB 2009). This relationship was also confirmed in own study. It was also found that grain with higher hardness was characterized by higher vitreousness. Positive correlations between wheat grain vitreousness and hardness and the energy consumption of the grinding process was confirmed by CACAK-PIETRZAK et al. (2009). Vitreous kernels are more resistant and require more energy input for grinding. The reason is the internal grain structure, because in a vitreous kernel starch grains are deeply embedded in the protein matrix as opposed to the structure of a floury grain, which is marked by loose endosperm structure (starch grains are set apart from each other).

The obtained amounts of ash in the grain of the studied triticale considerably exceeded the ash contents in triticale grain in the studies by SOBCZYK et al. (2009) and WARECHOWSKA and DOMSKA (2006). The high ash content in triticale grain is an unfavorable property with regard to the use of this cereal for flour. High ash content in triticale compared to wheat is due to grain morphology (PEÑA 2004). According to SOBCZYK et al. (2009), the most favorable ash level in grain for the milling value of triticale is ensured by a dose of 36 kg N ha$^{-1}$ or 98 kg N ha$^{-1}$. A dose of 120 kg N ha$^{-1}$ proved more favorable in own study.

Research conducted by CEGLIŃSKA et al. (2005) and SOBCZYK et al. (2009) indicates that flour extract obtained from milling triticale grain varies widely. In the current study, the extraction rate for flour acquired from milling triticale grain was relatively low and ranged from 59.3 to 63.7% (from 15% tempering moisture). Similar results in triticale for tempering moisture at 15% were obtained by DENNETT and TRETHOWAN (2013). Fertilization with a higher nitrogen dose contributed to a small extent to an increase in flour extract, yet this was not confirmed statistically. According to SOBCZYK et al. (2009), a rise in the nitrogen dose in triticale fertilization causes increased triticale flour extract, although according to BISKUPSKI (2000), fertilization with a higher nitrogen dose contributes to decreased triticale flour extract.

The ash content in the obtained flour is an important index of the milling value of grain. The ash content in triticale flours can vary widely depending on the obtained extract (BISKUPSKI 2000, CEGLIŃSKA et al. 2005, SOBCZYK et al. 2009). In the conducted study, the mean ash contents ranged from

0.57% to 0.62%. The varied nitrogen fertilization had no effect on the flour ash content.

In commercial milling of grain into flour, flour production takes place according to the classification of a particular flour type (with particular ash content). The milling value of grain relates to the potential possibility of obtaining the highest possible flour extract of a particular type from commercial milling in an industrial mill (SITKOWSKI 2011). The milling efficiency coefficient (*K*) applied to demonstrate the difference in the milling of the studied triticale grain. The milling efficiency coefficient includes flour extract in connection with its ash content. Nitrogen fertilization had no effect on milling efficiency coefficient. Andrus triticale showed a worse milling value than Milewo triticale.

## Conclusions

Summing up, the different nitrogen fertilization levels influenced the physical properties of triticale grain of significant importance during milling such as: test weight, thousand kernel weight, vitreousness and hardness expressed by the PSI. Increasing the fertilization dose from 80 to 120 kg N $ha^{-1}$ contributed to a subsequent decrease in energy demand for grain milling and a decrease in ash content in the grain. The use of the higher nitrogen dose caused an increase in the mean particle size of the milling product.

Further investigation is required into the role of nitrogen fertilization of triticale on milling quality. Milling quality of grain triticale with wider range at nitrogen fertilization will be the subject of our next study.

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# THE EFFECT OF SLAUGHTERING SEASON ON THE CARCASS QUALITY OF GROWING FINISHING PIGS

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K e y w o r d s: growing-finishing pigs, seasonality, lean meat percentage, carcass quality.

A b s t r a c t

The study included 83823 growing-finishing pigs of the commercial production, which were slaughtered in commercial meat factory in 2010 and 2011. The aim of the study was to assess the impact of the year and season, in which the slaughtering took place, on the carcass and meat quality traits. After slaughtering some traits were controlled using the ultrasound device Ultra Fom 300: the backfat thickness and the height of *musculus longissimus dorsi* in two points. These four measurements were used to determine the lean meat percentage and consequently the classification of carcasses according to the EUROP system. The analysis of variance showed a statistical effect of the year, season and interactions between them on all analysed features. It was shown that pigs with the highest values for lean meat percentage were obtained in autumn (55.39%) and with the lowest values were obtained in summer (55.01%) and winter (55.06%). The decline in the number of pigs slaughtered in 2011 could result from the increased share of imported meat in the total mass of processed pork.

## WPŁYW SEZONU UBOJU NA JAKOŚĆ TUSZY TUCZNIKÓW

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S ł o w a k l u c z o w e: tuczniki, sezonowość, mięsność, jakość tuszy.

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A b s t r a k t

Badaniami objęto 83 823 tuczniki populacji masowej dostarczane do jednego z zakładu przetwórstwa mięsnego w latach 2010–2011. Zasadniczym celem badań była ocena wpływu roku oraz pory roku, w których odbywały się uboje, na cechy przydatności rzeźnej. Po uboju tuczników za pomocą urządzenia ultradźwiękowego Ultra Fom 300 kontrolowano: grubość słoniny wraz ze skórą i wysokość mięśnia najdłuższego grzbietu w dwóch punktach. Wymienione cztery pomiary wykorzystano do określenia mięsności, a w konsekwencji do sklasyfikowania tusz wg systemu EUROP. W analizie wariancji wykazano statystyczny wpływ roku, pory roku i interakcji tych czynników na wszystkie analizowane cechy. Dowiedziono, że na ogół tuczniki o najwyższej mięsności były pozyskiwane jesienią (55,39%), zaś najniższej – latem (55,01%) i zimą (55,06%). Zaobserwowany spadek liczby ubijanych tuczników w roku 2011 mógł być efektem wzrostu udziału importowanych tusz / mięsa w ogólnej masie przetwarzanej wieprzowiny.

## Introduction

Poland is one of Europe's leading producers of pigs. Traditionally, pork is the main source of meat for Polish households. The production and supply of pigs in Poland are characterized by significant periodic fluctuations, which result from the profitability that is changing cyclically. Unfortunately, the tendency of declining the number of pigs in recent years has been noted (KNECHT and ŚRÓDOŃ 2011). By ensuring that the slaughter material supplied to commercial meat factory is of a high quality, it is possible to change the profitability, and therefore, reverse the downward trend in the pig population.

In Poland, the remuneration that the supplier of the slaughtering material provided for the commercial production receives depends on the body weight of slaughtered animals and lean meat percentage – the ratio of weighed lean meat versus the weight of the pig carcass (LMP). It the European Union countries the LMP is used for classifying pig carcasses (Commission Regulation – no. 3127/1994, NISSEN et al. 2006, VESTER-CHRISTIANSEN et al. 2008). LMP is determined based on a multiple regression equation, which includes four explanatory variables: backfat thickness and the height of the *musculus longissimus dorsi* at two points: 7 cm from the midline of the carcass at the last ribs and 7 cm. Between LMP and the above-mentioned explanatory (independent) variables the moderate and high dependence was found by SZYNDELER-NĘDZA and ECKERT (2008).

The diversity of carcass and meat quality, including lean meat percentage, depends of various factors such as body weight, sex and breed (BABICZ et al. 2008, SLÁDEK et al. 2004, NOWACHOWICZ 2004, SZYNDELER-NĘDZA and ECKERT 2008). In previous studies, the authors (PIWCZYŃSKI et al. 2010) have shown that the size of livestock suppliers (the production scale) affects the quality of the material. According to BABICZ et al. (2008) and MICHALSKA et al. (2006) the carcass and meat quality may varied according to the year of slaughter.

ANTOSIK et al. (2010) and RODRIGUEZ-SÁNCHEZ et al. (2009) noted that the level of the slaughter characteristics may also vary due to time of year.

The aim of this study was to assess the impact of the year and the season on the carcass and meat characteristics of growing-finishing pigs of both sexes, from a commercial production, delivered to commercial meat factory in the years 2010–2011. In addition, the aim was to examine the relationship between the carcass weight, lean meat percentage and selected measurements of backfat and *longissimus dorsi* muscle.

## Materials and Methods

The animal material consisted of 83823 growing-finishing pigs of both sexes from Kujawy and Pomorze voivodship, slaughtered in the years 2010–2011 in commercial meat factory. After slaughtering growing-finishing pigs were classified with the use of ultrasound device Ultra Fom 300 according to the EUROP system (S, E, U, R, O, P) (Commission Regulation no. 1249/2008, Commission Implementing Decision... 2011/506/UE; Rozporządzenie MRiRW Dz.U. nr 28, poz. 181). Previously, the thickness of backfat (Backfat) and the height of the *musculus longissimus dorsi* (MLD) at two points: 7 cm from the midline of the carcase at the last ribs (Backfat 1, MLD 1) and 7 cm from the midline of the carcase between the third and fourth last ribs (Backfat 2, MLD 2), were determined. These four measurements allowed to determine the lean meat percentage (LMP) (Commission Regulation no. 3127/1994).

By using a two-way analysis of variance, the authors evaluated the effect of year (2010 and 2011) and season (spring – III, IV, V, summer – VI, VII, VIII, autumn – IX, X, XI, winter – XI, I, II) on: carcass weight, lean meat percentage, backfat thickness and *longissimus dorsi* muscle. The significance of differences between compared groups (year and season), was analyzed by means of Scheffe test (SAS Institute, 2011). The $\chi^2$ test of independence, that was used subsequently, allowed to determine the type of relationship between the year and season, during which slaughtering were carried out, and the results of EUROP classification. Moreover, the Pearson correlation coefficient between carcass weight, backfat thickness, height of MLD and LMP was calculated. Statistical analyses were performed by using the SAS statistical package (SAS Institute Inc. 2011).

## Results and Discussion

Out of 83823 growing-finishing pigs, 43099 were slaughtered in 2010, and 40724 in the following year. Presumably, the decreasing number of slaughtered animals results from the decreased production profitability. The number of slaughtered animals per month, depending on the year of slaughtering, ranged as follows: in 2010 – 2467–4795 individuals, in 2011 – 2681–3924 individuals (Figure 1). In 2010 most animals were slaughtered between December and January, i.e. during the period of Christmas and New Year. The least animals were slaughtered during the peak of the holiday period in July and August. A similar trend was not observed in the following year, since the peak of slaughter fell on August and November and the decrease on May and June.

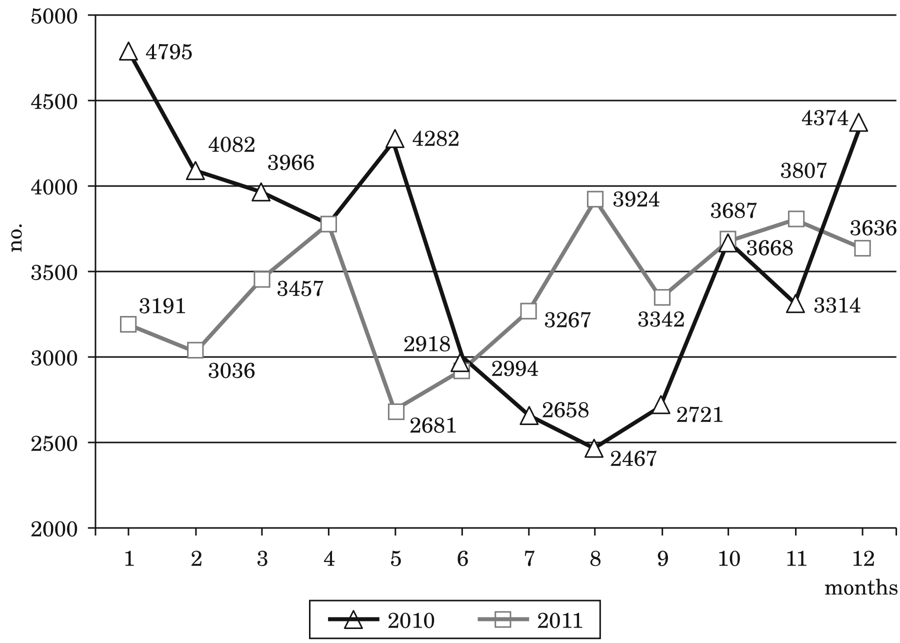



Fig. 1. The number of growing-finishing pigs slaughtered in the following months of 2010 and 2011

The average carcass weight of slaughtered pigs was 86.28 kg and the average lean meat percentage (LMP) was 55.17% (Table 1). The result of LMP was better than the one reported by BABICZ et al. (2008) in the study conducted in years 2005–2006, on 530 thousand growing-finishing pigs from the region of Lublin Voivodeship, since their result was 50.86–51.45%. The present result was also better than the one noted by KNECHT and ŚRÓDOŃ (2011) for the domestic population of pigs slaughtered in 2010 (54.8%). Moreover, similar or higher LMP values than those obtained in the present studies were obtained by ANTOSIK et al. (2010) – 57.96% and SIECZKOWSKA et al. (2009) – 57.46%.

However, it should be noted that those studies were carried out on the considerably smaller number of animals, and were additionally racially diverse.

Table 1

Descriptive characteristics of the studied traits

| | Carcass weight [kg] | MLD 1 [mm] | MLD 2 [mm] | Backfat 1 [mm] | Backfat 2 [mm] | LMP [%] |
|---|---|---|---|---|---|---|
| Mean | 86.28 | 57.34 | 54.96 | 15.06 | 17.10 | 55.17 |
| Standard deviation | 10.93 | 6.17 | 6.91 | 4.45 | 5.09 | 3.75 |
| Coefficient of variation [%] | 12.66 | 10.75 | 12.57 | 29.54 | 29.77 | 6.80 |
| Lower quartile | 78.60 | 53.10 | 50.10 | 11.80 | 13.40 | 53.00 |
| Median | 85.90 | 57.60 | 55.20 | 14.40 | 16.50 | 55.60 |
| Upper quartile | 93.40 | 61.80 | 60.00 | 17.60 | 20.00 | 57.80 |

Explantions: MLD 1 – height of *musculus longissimus dorsi* 1; MLD 2 – height of *musculus longissimus dorsi* 2; Backfat 1 – backfat thickness 1; Backfat 2 – backfat thickness; LMP – lean meat percentage.

The analysis of the designated quartiles indicates that, in terms of weight, 25% of the carcases did not exceed 78.6 kg, following 25% was in the range from 78.6 to 85.9 kg, and further 25% was in the range from 85.9 to 93.4 kg (Table 1). The remaining 25% of the carcasses was characterized by a weight higher than 93.4 kg. It was noted that the highest variability among the analyzed features characterized the backfat thickness – the coefficient of variation, depending on the point of measurement, ranged from 29.54% to 29.77%. The variability of carcass weight and the MLD height did not exceed 13%. The greatest equalization was observed in case of LMP index, 6.8%.

The analysis of variance showed a highly significant ($P < 0.0001$) effect of year, season (Table 2) and interaction (Figure 2) of both factors on all examined traits. It should be emphasized that the differences between the year 2010 and 2011, in all examined traits, were considered highly significant also according to the Scheffe test. The analysis of the calculated arithmetic means shows that in 2011, in comparison to 2010, slaughtered growing-finishing pigs had a lower carcass weight, height of MLD and backfat thickness. The lean meat percentage (LMP) of animals slaughtered in 2011 was 55.32% and was by 0.3 percentage units higher than those slaughtered in 2010.

Table 2

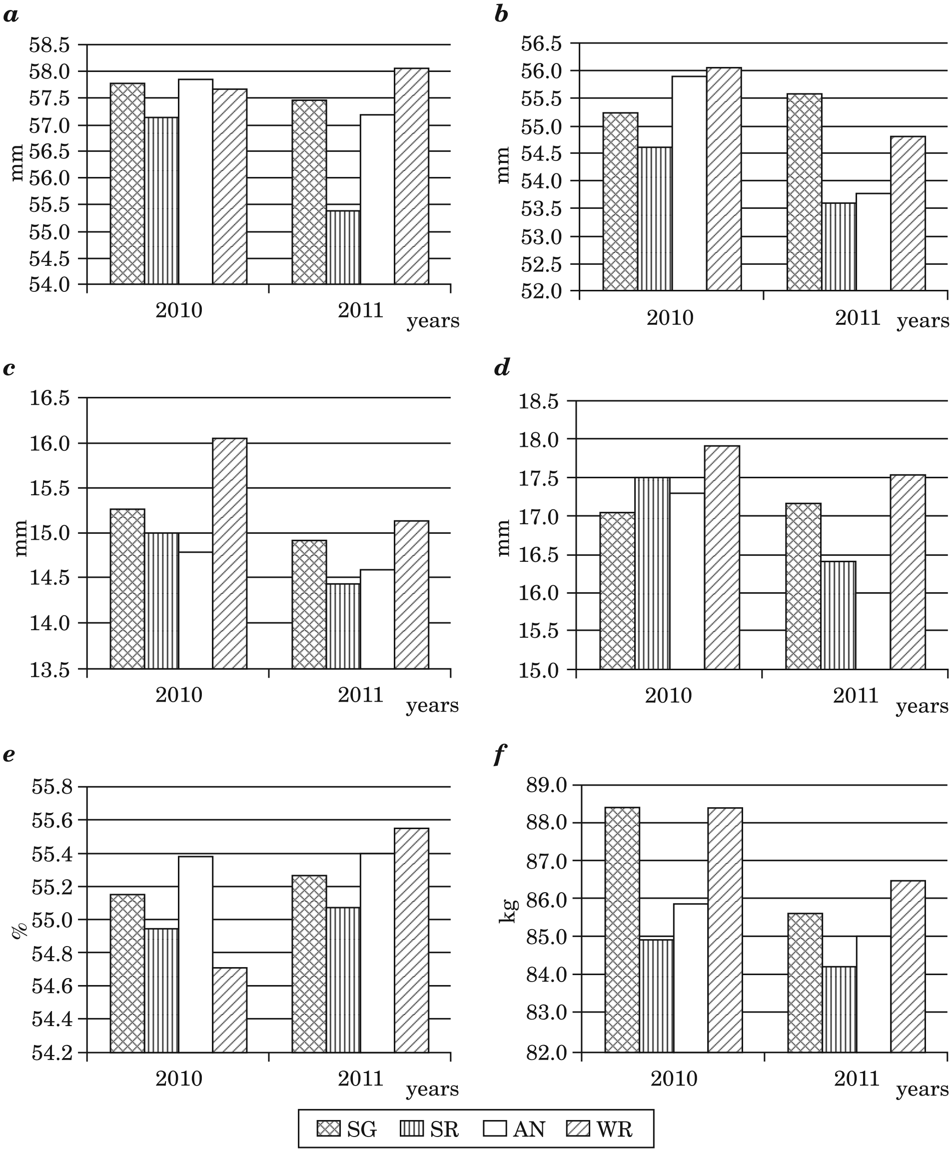
Influence of the year and slaughter season on analysed traits

| Trait | Statistic | Year | | Season of the year | | | |
|---|---|---|---|---|---|---|---|
| | | 2010 | 2011 | spring | summer | autumn | winter |
| Carcass weight [kg] | $\bar{x}$ | 87.16 A | 85.32 A | 87.12 A | 84.53 AB | 85.43 ABC | 87.58 ABC |
| | CV | 12.34 | 13.03 | 12.29 | 13.13 | 12.77 | 12.49 |
| MLD 1 [mm] | $\bar{x}$ | 57.64 A | 57.02 A | 57.64 Aa | 56.17 AB | 57.5 Bb | 57.83 Bab |
| | CV | 10.36 | 11.14 | 10.48 | 11.07 | 10.9 | 10.43 |
| MLD 2 [mm] | $\bar{x}$ | 55.5 A | 54.39 A | 55.39 A | 54.02 AB | 54.75 ABC | 55.49 BC |
| | CV | 12.23 | 12.86 | 12.7 | 12.74 | 12.52 | 12.19 |
| Backfat 1 [mm] | $\bar{x}$ | 15.35 A | 14.76 A | 15.11 A | 14.69 AB | 14.68 AC | 15.66 ABC |
| | CV | 28.96 | 30.06 | 29.99 | 30.41 | 28.77 | 28.69 |
| Backfat 2 [mm] | $\bar{x}$ | 17.44 A | 16.74 A | 17.07 A | 16.88 AB | 16.62 ABC | 17.73 ABC |
| | CV | 29.3 | 30.15 | 30.17 | 30.64 | 29.38 | 28.7 |
| LMP [%] | $\bar{x}$ | 55.02 A | 55.32 A | 55.2 A | 55.01 AB | 55.39 ABC | 55.06 AC |
| | CV | 7 | 6.69 | 6.94 | 6.95 | 6.45 | 7.04 |

Explanations: AA (aa) – averages marked with the same capital (small) letters, vary at $P \le 0.01$ ($P \le 0.05$); CV – coefficient of variation, MLD 1 – height of *musculus longissimus dorsi* 1; MLD 2 – height of *musculus longissimus dorsi* 2; Backfat 1 – backfat thickness 1; Backfat 2 – backfat thickness; LMP – lean meat percentage

BABICZ et al. (2008) indicate that year of the slaughter may differentiate the slaughter material. The difference between LMP of pigs slaughtered in two years i.e. 2005 and 2006, was 0.59 percentage units ($P \le 0.01$). Moreover, the carcass weight increased by 0.4 kg ($P < 0.05$). According to MICHALSKA et al. (2006), changes in carcass and meat quality observed over time may be caused by the successful breeding program. In Poland the effects of genetic improvement in gilts herds, having a direct mass population, are presented in the annual reports of the Polish Pig Breeders and Producers Association „POLSUS" (2012).

By analyzing the impact of the seasons on the investigated traits, it was found that growing-finishing pigs slaughtered during winter and spring had the highest carcass weight, height of MLD and backfat thickness, which was found to be highly significant (Table 2). In turn, growing-finishing pigs that had been slaughtered in summer had the lowest carcass weight and MLD




Interactions – $P < 0.0001$

Fig. 2. Slaughter traits in respect of the year of research and season: *a* – height of *musculus longissimus dorsi* 1; *b* – height of *musculus longissimus dorsi* 2; *c* – backfat thickness 1; *d* – backfat thickness 2, *e* – lean meat percentage, *f* – carcass weight

height. The animals slaughtered in autumn had the thinnest backfat. The carcass lean meat percentage (LMP), depending on the time of year ranged in a narrow interval, from 55.01% to 55.39%. The highest value of these traits characterized the carcasses of pigs slaughtered in autumn, while the lowest characterized the carcasses of pigs slaughtered in spring.

In the present studies, the results of the impact of the seasons on the value of the carcass and meat quality are in accordance with the study of ANTOSIK et al. (2010), which was conducted on 2500 growing-finishing pigs of the commercial production. Pigs slaughtered during autumn were characterized by the highest meat content, the greatest height of MLD and the lowest backfat thickness at the S1 point.

The distribution of carcass classes, depending on the year and season, is presented in the Table 3. The chi-square test showed a highly significant relationships ($P \leq 0.01$) between the year, season of year and carcass classification according to EUROP system. The impact of both factors, i.e. year and season, on lean meat percentage, which is the basis for the classification of carcasses according to the EUROP system, was previously demonstrated by means of analysis of variance (Table 2). The results presented in the table confirmed a better LMP of animals slaughtered in 2011, compared to those slaughtered in 2010 – a greater share of carcasses was classified as a class S and E. At the same time, the distributions showed that, generally, the greatest number of carcasses was classified to the S and E class during autumn and

Table 3

The distribution of lean meat percentage classes in respect of the year of research and season

| Factor | Level | Lean meat percentage class | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|
| | | – | S | E | U | R | O | P | |
| Year | 2010 | N<br>% | 3438<br>7.98 | 20216<br>46.91 | 15245<br>35.37 | 3592<br>8.33 | 573<br>1.33 | 35<br>0.08 | 43099 |
| | 2011 | N<br>% | 3338<br>8.2 | 20618<br>50.63 | 13364<br>32.82 | 2917<br>7.16 | 436<br>1.07 | 51<br>0.13 | 40724 |
| Season of the year | spring | N<br>% | 1950<br>8.89 | 10505<br>47.88 | 7463<br>34.01 | 1718<br>7.83 | 269<br>1.23 | 37<br>0.17 | 21942 |
| | summer | N<br>% | 1227<br>6.73 | 8955<br>49.13 | 6379<br>35 | 1423<br>7.81 | 221<br>1.21 | 23<br>0.13 | 18228 |
| | autumn | N<br>% | 1685<br>8.2 | 10393<br>50.6 | 6947<br>33.82 | 1329<br>6.47 | 177<br>0.86 | 8<br>0.04 | 20539 |
| | winter | N<br>% | 1914<br>8.28 | 10981<br>47.51 | 7820<br>33.83 | 2039<br>8.82 | 342<br>1.48 | 18<br>0.08 | 23114 |
| Total | – | N<br>% | 6776<br>8.08 | 40834<br>48.71 | 28609<br>34.13 | 6509<br>7.77 | 1009<br>1.20 | 86<br>0.10 | 83823 |

spring: 58.80% and 56.77% respectively (Table 3). Among the evaluated carcasses 90.93% were classified as class SEU, which indicated a good quality of carcass and meat.

SLÁDEK et al. (2004) reported positive correlations between the slaughter weight and the MLD height ($r$ = 0.327) and backfat thickness ($r$ = 0.450). The negative relationships were observed between backfat thickness and the meat content in carcasses ($r$ = 0.907). Consequently, when the warm carcass weight increased, the backfat thickness and height of MLD increased as well (ANTOSIK and KOĆWIN-PODSIADŁA 2010).

All correlation coefficients, calculated during the present studies and placed in Table 4, despite a wide range of values, were highly significant. Most of them indicated positive relationships. The negative relations were noted between backfat thickness in two points and measurement of MLD and LMP, as well as between carcass weight and LMP. It was observed that carcass weight was weakly ($r$ = 0.083–0.179) correlated with the height of MLD and low (point 2, $r$ = 0.367) and moderate (point 1, $r$ = 0.424) correlated with the backfat thickness, and low ($r$ = -0,250) correlated with meat content (Table 4). The correlation coefficients indicate moderate (0.597–0.609) relationship between the height of MLD and LMP. High (–0.872) and very high values (–0.903) of correlation coefficients were obtained for the association between backfat thickness in two points and LMP. These results are in accordance with those reported by SZYNDLER-NĘDZA and ECKERT (2008) in terms of the direction of the relationship between measurements of backfat thickness and MLD (results of performance tested gilts) and LMP. In the cited studies the

Table 4

The relationship between tested traits

| Traits | Carcass weight | MLD 1 | MLD 2 | Backfat 1 | Backfat 2 |
|---|---|---|---|---|---|
| MLD 1 [mm] | 0.179<br><.0001 | – | – | – | – |
| MLD 2 [mm] | 0.083<br><.0001 | 0.438<br><.0001 | – | – | – |
| Backfat 1 [mm] | 0.424<br><.0001 | -0.338<br><.0001 | -0.322<br><.0001 | – | – |
| Backfat 2 [mm] | 0.367<br><.0009 | -0.260<br><.0001 | -0.440<br><.0001 | 0.829<br><.0001 | – |
| LMP [%] | -0.250<br><.0001 | 0.597<br><.0001 | 0.609<br><.0001 | -0.903<br><.0001 | -0.872<br><.0001 |

Explanations: MLD 1 – height of *musculus longissimus dorsi* 1; MLD 2 – height of *musculus longissimus dorsi* 2; Backfat 1 – backfat thickness 1; Backfat 2 – backfat thickness; LMP – lean meat percentage discrepancies occurred in the strength of relationships. The correlation coefficients between the backfat thickness in two points and lean meat percentage LMP ranged from –0.753 to –0.628. On the other hand, in the case of the height of MLD, measured in point 2, the correlation coefficient was significantly lower – 0,066–0,170.

The analysis of variance showed that the interaction between year and season was highly significant in all analyzed traits. Therefore, arithmetic means for each seasons, depending on the year of slaughter, were additionally analyzed in detail (Figure 2). The analysis showed that in 2010 carcasses of the highest weight were collected during the autumn and winter season, and the lowest during spring and summer. The same trend continued in later years, however, the differences in the average carcass weight in corresponding seasons were significantly lower. The results obtained in the present studies, as well as those obtained by other authors (SLHDEK et al. 2004, SZYNDLER-NĘDZA and ECKERT 2008), demonstrated a statistical correlation between the carcass weight and the ultrasound measurements and carcass lean meat percentage. Therefore, it may be expected that in the seasons in which slaughtered animals had the highest weight, the backfat thickness in two points would be the greatest. It was fully confirmed in the case of the both thickness measurement points, but only in relation to the year 2011 (Figure 2). In 2010, the backfat thickness, measured in the point 2, was the highest during the winter months, and the thinnest during spring.

Taking into account the height of MLD, measured at both points, it was found that the height was the smallest in spring – both in 2010 and 2011. However, it was not possible to clearly identify which season resulted in achieving the maximum height of MLD, as it was additionally conditioned by the year of slaughter. It was noted that in 2010, LMP was the highest during the autumn period, and the lowest in winter. A year later, the previous ranking was different, the growing-finishing pigs slaughtered during winter had the highest meat content, and those slaughtered during summer had the lowest.

## Conclusions

The present study showed a highly significant effect of the year and season on the carcass weight and the slaughter quality of growing-finishing pigs. Growing-finishing pigs, that were slaughtered during autumn, were found to have the highest lean meat percentage (55,39%), while those slaughtered during summer (55,01%) and winter (55,06%) were found to have lower LMP. At the same time highly significant interactions indicated that the effect of seasons on the slaughter characteristics was modified by the year of slaughter.

The findings indicate high monthly and annual fluctuations in the number of slaughtered animals, which most likely was caused by changing economic situation. The statistical analysis of correlations revealed that the carcass weight was moderately, positively correlated with the backfat thickness in two points, and negatively correlated with the lean meat percentage of carcasses.

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# EFFECT OF INDUSTRIAL CONDITIONS OF HEAT TREATMENT OF RAPE, MUSTARD, FLAX AND CAMELINA SEEDS ON THE QUALITY OF OILS INTENDED FOR BIODIESEL PRODUCTION*

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Key words: rapeseed, mustard, flax, camelina, pressing, oils, quality.

Abstract

The aim of the study was to determine the effect of industrial conditions of heating rape, mustard, flax and camelina seeds on the pressing efficiency and quality of oil intended for biodiesel production. The research was conducted on rape, mustard, fibre flax and camelina seeds. Oils were pressed from seeds heated at 60, 70 and 80°C using the Kocibórz Biorefinery production line equipment. The quality of oils was assessed on the basis of the value of indicators affecting the course and the efficiency of transesterification and the stability of esters, i.e. the content of water and volatile compounds, the content of chlorophyll pigments and carotenoids, the content of phosphorus, degree of hydrolysis and oxidation and the composition of fatty acids.

It was found that the temperature of seed treatment positively affected pressing efficiency, but it had a negative effect on the quality of oils. The quality of oils deteriorated with an increase in temperature, which was indicated by a higher rate of hydrolysis and oxidation and an increased content of chlorophyll pigments and phosphorus. On the other hand, heat treatment temperature did not bring about any significant changes in the composition of fatty acids. In the case of rape and mustard seeds, the optimum pressing temperature on the production line in the Kocibórz Biorefinery for good pressing efficiency and oil quality was 70°C. For flax and camelina seeds, it was established that heat treatment of seeds under industrial conditions should be carried out at 60°C.

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**WPŁYW PRZEMYSŁOWYCH WARUNKÓW OGRZEWANIA NASION RZEPAKU, GORCZYCY, LNU I LNIANKI NA JAKOŚĆ OLEJÓW PRZEZNACZONYCH DO PRODUKCJI BIODIESLA**

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Słowa kluczowe: rzepak, gorczyca, len, lnianka, tłoczenie, oleje, jakość.

Abstrakt

Celem pracy było określenie wpływu przemysłowych warunków ogrzewania nasion rzepaku, gorczycy, lnu i lnianki na wydajność tłoczenia i jakość olejów przeznaczonych do produkcji biodiesla. Badania wykonano na nasionach rzepaku, gorczycy, lnu włóknistego i lnianki. Oleje tłoczono z nasion ogrzewanych w temperaturach 60, 70 i 80°C w urządzeniach linii technologicznej Agrorafinerii Kocibórz (UWM Olsztyn). Jakość olejów oceniono na podstawie wartości wyróżników, które mają wpływ na przebieg i wydajność przeestryfikowania oraz stabilność estrów, tj. zawartości wody i związków lotnych, zawartości barwników chlorofilowych i karotenoidów, zawartości fosforu, stopnia hydrolizy i stopnia utlenienia oraz składu kwasów tłuszczowych.

Wykazano, iż temperatury ogrzewania nasion miały korzystny wpływ na wydajność tłoczenia, natomiast negatywny na cechy olejów. Wraz ze wzrostem temperatury następowało pogorszenie jakości olejów, na co wskazał podwyższony stopień hydrolizy i utlenienia oraz zwiększona zawartość barwników chlorofilowych i fosforu. Temperatura ogrzewania nie spowodowała natomiast istotnych zmian w składzie kwasów tłuszczowych. W przypadku nasion rzepaku i gorczycy za optymalną temperaturę tłoczenia na linii technologicznej w Agrorafinerii Kocibórz, z uwagi na dobrą wydajność tłoczenia i równocześnie dobrą jakość oleju, uznano 70°C. Z kolei w przypadku nasion lnu i lnianki stwierdzono, iż ogrzewanie nasion w warunkach przemysłowych powinno być prowadzone w temperaturze 60°C.

## Introduction

Biocomponents and liquid biofuels, as an alternative for traditional fuels, have started to play an increasingly more important role in the energy policy of the European Union. The growing demand of the economy for fuels and energy, in view of the diminishing resources of fossil fuels has prompted interest in the use of biocomponents, liquid fuels and other renewable fuels. The need for such activities in our country results from legal acts adopted by the European Union and which are also applicable in Poland. They include, e.g. the Green Paper (2000), European Union directives (Directive... 2001, 2003a,b) and the Kyoto protocol (1997).

The main oil production raw material cultivated in Polish conditions is rapeseed, used both for food and for fuel purposes. The factors determining its usefulness for the production of methyl esters of higher fatty acids include its cultivar, seed yield and the fat content in seeds (HEIMANN 2002, KACHEL-

-JAKUBOWSKA and SZPRYNGIEL 2009). Seeds used in processing, both for food and for energy purposes, should originate from cultivars of double low rapeseed, characterised by a minimum oil content of 40%, a minimum percentage of oleic acid of 56%, acid value for oil ≤ 3.0 mg KOH · $g^{-1}$, erucic acid percentage < 1.0% and the content of alkenyl glucosinolates < 25 μmol · $g^{-1}$ defatted dry matter (*Rośliny przemysłowe oleiste*... PN-90/R-66151).

Own research concerning the composition of fatty acids of seeds of various rape cultivars has demonstrated that winter, open pollinated and hybrid cultivars of rapeseeds, characterised by high oil content (> 40%) and optimum composition of fatty acids (≥ 56% oleic acid ≤ 12% linolenic acid) were the best raw material for biodiesel production (AMBROSEWICZ et al. 2012).

Because of the growing demand for seeds and rapeseed oil both for fuel purposes and, to a lesser extent, for consumption purposes, it is increasingly more difficult, year-by-year, to provide the required amount of these raw materials. As results from the report presented in *Rynek Rzepaku – stan i perspektywy* (2012), the demand for rapeseed oil intended for food purposes will grow very slowly, due to the high variety of vegetable oils in the market. On the other hand, it was found that an obligation to increase the share of biocomponents in liquid fuels imposed on the fuel sector (National Index Target in 2013 – 7.10%) has contributed to the growing demand for this raw material. It was estimated, for instance, that as much as two million tonnes of rape seeds should be provided for production of esters carried out exclusively on the base of rapeseed oil only. Consequently, the use of other oil raw materials grown in Poland (e.g. flax, camelina and mustard seeds) is considered necessary.

Oils from seeds are extruded by pressing and/or extraction. Oil intended for biodiesel production is extruded by pressing, the efficiency of which depends highly on the method of seed conditioning (heat treatment) (RADZIEMSKA et al. 2009). Seed heating results in decomposition of all cell structures, thus releasing both reserve and structural fat (TAŃSKA and ROTKIEWICZ 2003). The results of own research (TAŃSKA et al. 2013a,b) showed that good pressing efficiency and a relatively good quality of oil was obtained when seeds were heated at 60°C and 80°C. A similar range of temperatures is used in domestic agricultural biorefineries. These conclusions provide a basis conducting further research under industrial conditions of Kocibórz Biorefinery (UWM in Olsztyn).

## Material and Methods

The research material included seeds of winter oilseed rape, white mustard, flax and camelina and oils pressed from those seeds. Samples of seeds harvested in 2011 were obtained from the Plant Production and Experimental

Station in Bałcyny. Samples were characterized in terms of moisture content (*Oznaczenie zawartości wody*... PN-62/R-66163), fat content (*Nasiona oleiste*... PN-EN ISO 659:2009) and content of impurities (*Rośliny przemysłowe oleiste*... PN-91/R66160) – Table 1.

Table 1

Characterization of the experimental material

| Discriminants | Rapeseed | Mustard | Flax | Camelina |
|---|---|---|---|---|
| Moisture [%] | $7.20^{a} \pm 0.45$ | $8.51^{c} \pm 0.68$ | $8.20^{b} \pm 0.42$ | $7.40^{a} \pm 0.21$ |
| Content of fat [% d.wt] | $47.52^{d} \pm 0.58$ | $31.72^{a} \pm 1.45$ | $39.15^{c} \pm 0.98$ | $36.72^{b} \pm 1.23$ |
| Total content of impurities [%] | $4.28^{b} \pm 0.51$ | $4.48^{b} \pm 0.32$ | $10.92^{c} \pm 0.59$ | $1.12^{a} \pm 0.32$ |
| – useful impurities [%] | $2.99^{c} \pm 0.21$ | $2.39^{b} \pm 0.12$ | $2.40^{b} \pm 0.14$ | $0.00^{a} \pm 0.00$ |
| – useless impurities [%] | $1.29^{a} \pm 0.21$ | $1.09^{a} \pm 0.01$ | $8.52^{b} \pm 0.52$ | $1.12^{a} \pm 0.31$ |
| The presence of mites [number of pieces · kg of seeds$^{-1}$] | | | | |
| – live | trace | trace | trace | trace |
| – dead | trace | trace | trace | trace |

Explanation: *a, b*... – mean values in lines marked with the same letter are not significantly different ($p \le 0.05$)

Oil pressing under industrial processing conditions in Kocibórz Biorefinery (UWM in Olsztyn) was preceded by heat treatment of seeds in a conditioner, at 60°C, 70°C and 80°C. Pressing was carried out in a ET 996 expeller with a capacity of about 3500–4000 kg/24h (with conditioning) and about 1.800 kg/24h with cold pressing.

Pressing efficiency [%] was calculated as the relative relation to the oil content in the oil cake and seeds, according to the following formula:

$$\frac{A - B \cdot 100}{A}$$

where:
*A* – fat content in seeds [%] determined by the Soxhlet method;
*B* – fat content in the cake [%] determined by the Soxhlet method.

The quality of oils was evaluated by assaying: the water and volatile compounds content (*Oleje i tłuszcze*... PN-EN ISO 662:2001), acid value (*Oleje i tłuszcze*... PN-ISO 660:1998), peroxide value (*Oleje i tłuszcze*... PN-ISO 3960:2005), anisidine value (*Tłuszcze roślinne jadalne*... PN-93/A-86926), content of chlorophyll pigments (BEUTNER i in. 2001), the content of carotenoid pigments (FRANKE et al. 2010), phosphorus content (*Tłuszcze roślinne* *jadalne*... PN-88/A-86930) and the fatty acids composition. The fatty acids composition was estimated acc. PN-EN-ISO-5508:1996 (*Analiza estrów*... PN-EN-ISO-5508:1996), preparing methyl esters by the method described by ZADERNOWSKI and SOSULSKI (1978). The separation of methyl esters were carried out applying GC 8000 series FISONS Instrument Gas Chromatograph equipped with a flame-ionization detector using a column type DB-225 (30 m x 0.25 mm x 0.15 μm) and helium as a carrier gas. Fatty acids were identified according to retention time determined for fatty acid standards.

## Statistical Analysis

For each sample the arithmetic mean and standard deviation were determined. Obtained results of researches were statistically analyzed using the Statictica 9.0 PL (StatSoft Poland) program. In order to indicate significance of differences between seeds and oils analysis of variance (ANOVA) with Tukey's test of $p \leq 0.05$ significance level was used.

## Results and Discussion

Heat treatment of seeds before pressing had an effect on the effectiveness and quality of oils. The highest efficiency was obtained when oil was pressed from seeds of various species heated at 80°C. For rapeseed oil, the pressing efficiency amounted to 74%, for mustard – 57%, while flax and camelina revealed a similar level of about 67%. The lowest and the similar pressing efficiency, 62–64%, was obtained at 60°C for rapeseed, flax and camelina seeds. For mustard seeds, oil pressing efficiency was only 52% (Table 2).

It was also found that the growth rate of pressing efficiency was differentiated for seeds of individual species, which was closely related to the oil content of these raw materials. Seeds with a higher fat content (rapeseed), heated at 80°C, were characterized by the highest pressing efficiency (Table 2). An increase in the temperature from 60°C to 80°C improved the pressing efficiency for seeds with the highest oil content (rapeseed) by 11 percentage points and the lowest oil content (mustard) by 5 percentage points. On the other hand, in the case of seeds of medium oil content, namely flax and camelina, a growth in pressing temperature increased oil efficiency by only 4 and 2 percentage points, respectively (Table 2).

Oil quality was closely related to the species and parameters of seed heating (Table 3, Table 4). The results of research demonstrated that the content of water and volatile substances in oils pressed at various temperatures ranged

Table 2

Efficiency of pressing and fat content in seeds and pressed pulp

| Samples | Efficiency of pressing [%] | Fat content [%] |
|---|---|---|
| Rapeseed | – | 47.52 ± 0.85 |
| preseed pulp 60°C | $63^{a}$ ± 0.57 | $17.36^{c}$ ± 0.82 |
| preseed pulp 70°C | $70^{b}$ ± 0.46 | $14.39^{b}$ ± 0.57 |
| preseed pulp 80°C | $74^{c}$ ± 0.54 | $12.42^{a}$ ± 0.76 |
| Mustard | – | 31.72 ± 0.66 |
| preseed pulp 60°C | $52^{a}$ ± 0.58 | $15.14^{c}$ ± 0.72 |
| preseed pulp 70°C | $55^{b}$ ± 0.00 | $14.20^{b}$ ± 0.60 |
| preseed pulp 80°C | $57^{b,c}$ ± 0.65 | $13.73^{a}$ ± 0.61 |
| Flax | – | 39.15 ± 0.52 |
| preseed pulp 60°C | $64^{a}$ ± 0.85 | $14.21^{c}$ ± 0.30 |
| preseed pulp 70°C | $65^{b}$ ± 0.45 | $13.64^{b}$ ± 0.33 |
| preseed pulp 80°C | $68^{c}$ ± 0.32 | $12.66^{a}$ ± 0.30 |
| Camelina | – | 36.72 ± 0.37 |
| preseed pulp 60°C | $62^{a}$ ± 0.85 | $14.06^{b}$ ± 0.37 |
| preseed pulp 70°C | $62^{a}$ ± 0.54 | $14.02^{b}$ ± 0.23 |
| preseed pulp 80°C | $64^{a,b}$ ± 0.57 | $13.11^{a}$ ± 0.25 |

Explanation as in Table 1

from 0.07 for a sample obtained from rapeseeds heated at 60°C to 0.25% for a sample of flax seeds heated at 70°C. According to BUCZEK and CZEPIRSKI (2004), as well as KOTOWSKI (2004), the threshold content of those compounds should not exceed 0.50% (Table 3). An excessive water content in oil intended for biodiesel production contributes to an undesired reaction of triacylglycerol hydrolysis, resulting in the formation of significant amounts of free fatty acids, and consequently soaps after adding an alkaline catalyst (MATHIYAZHAGAN and GANAPATHI 2011).

It was found that the chlorophyll pigment content depended on species and seed treatment temperature (Table 3). It was proven that oils pressed from seeds conditioned at the highest temperature were characterized by the highest content of chlorophyll pigments, while those heated at 60°C and 70°C contained a comparable content of those compounds (Table 3).

Generally, it was found that oils pressed from mustard seeds were characterized by the highest content of chlorophyll pigments (from 17.22 $mg \cdot kg^{-1}$ in the case of oil obtained from seeds heated at 60°C, to 26.12 $mg \cdot kg^{-1}$ for oil of seeds heated at 80°C). Rapeseed oil samples had a similar content of chlorophyll pigments, between 16.80 $mg \cdot kg^{-1}$ and 25.40 $mg \cdot kg^{-1}$. The lowest content of chlorophyll pigments was found in flax oil samples: from 5.16 $mg \cdot kg^{-1}$ (sample from seeds heated at 60°C) to 11.50 $mg \cdot kg^{-1}$ (sample from seeds heated at 70°C) – Table 3.

Table 3

Characteristics of oils obtained from seeds heated at different temperatures

| Discriminants | Rapeseed | | | Mustard | | | Flax | | | Camelina | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | temperature of heating | | | | | | | | | | | |
| | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C |
| The water and volatile compounds content [%] | 0.07$^{a}$ ± 0.07 | 0.15$^{c}$ ± 0.12 | 0.13$^{b}$ ± 0.15 | 0.20$^{b}$ ± 0.21 | 0.12$^{a}$ ± 0.20 | 0.24$^{c}$ ± 0.00 | 0.24$^{b}$ ± 0.24 | 0.25$^{b}$ ± 0.20 | 0.20$^{a}$ ± 0.25 | 0.21$^{a}$ ± 0.21 | 0.22$^{a}$ ± 0.22 | 0.23$^{a}$ ± 0.23 |
| The content of chlorophyll pigments [mg · kg$^{-1}$] | 16.80$^{a}$ ± 0.12 | 19.42$^{b}$ ± 0.12 | 25.40$^{c}$ ± 0.00 | 17.22$^{a}$ ± 0.00 | 17.85$^{b}$ ± 0.07 | 26.12$^{c}$ ± 0.00 | 5.16$^{a}$ ± 0.00 | 6.18$^{b}$ ± 0.00 | 11.50$^{c}$ ± 0.37 | 10.12$^{a}$ ± 0.24 | 10.89$^{a}$ ± 0.12 | 16.33$^{b}$ ± 0.12 |
| The content of carotenoid pigments [mg · kg$^{-1}$] | 11.7$^{b}$ ± 0.11 | 10.6$^{a}$ ± 0.04 | 10.3$^{a}$ ± 0.00 | 10.4$^{b}$ ± 0.01 | 9.0$^{a}$ ± 0.08 | 10.6$^{c}$ ± 0.01 | 18.0$^{a}$ ± 0.08 | 17.9$^{a}$ ± 0.04 | 25.7$^{b}$ ± 0.28 | 21.6$^{a}$ ± 0.08 | 25.9$^{b}$ ± 0.06 | 31.7$^{c}$ ± 0.00 |
| Phosphorus content [mg · kg$^{-1}$] | 4.22$^{b}$ ± 0.14 | 3.64$^{a}$ ± 0.18 | 5.56$^{c}$ ± 0.33 | 1.13$^{a}$ ± 0.19 | 2.33$^{b}$ ± 0.15 | 10.12$^{c}$ ± 0.14 | 11.92$^{a}$ ± 0.48 | 25.27$^{b}$ ± 0.67 | 26.18$^{b}$ ± 0.62 | 4.75$^{a}$ ± 0.42 | 7.15*b* ± 0.28 | 25.55$^{c}$ ± 0.82 |

Explanation as in Table 1

The content of carotenoid pigments in rapeseed and mustard oils was about two times lower than in flax and camelina oils, and it did not show any clear relation to the temperature of seed treatment (Table 3). On the other hand, in the case of oils obtained from flax and camelina, it was found that the higher the temperature of seed treatment, the higher was the content of these pigments (Table 3). The total growth in the content of carotenoids in flax and camelina oils, calculated on the basis of a difference between the content of carotenoid pigments in oils pressed at 60°C and 80°C, amounted to 7.7 mg · kg$^{-1}$ for flax, and 10.1 mg · kg$^{-1}$ for camelina.

Pigments of vegetable oils, including carotenoid and chlorophyll pigments, demonstrate pro-oxidant or antioxidant activity (ROTKIEWICZ et al. 2002, STROBEL et al. 2005). BEUTNER et al. (2001) found that the activity of carotenoids consisted in deactivation, i.e. chemical and physical "quenching" of singlet oxygen. It is also claimed that carotenoids can delay the process of lipid autoxidation, among others, by scavenging free radicals. In turn, chlorophyll pigments (chlorophyll a and b and their derivatives) are pro-oxidative compounds, which in the presence of light initiate reactions consisting in the generation of highly reactive singlet oxygen from triplet oxygen, strengthening autoxidation of lipids (RAWLS and VAN SANTEN 1970, MIŃKOWSKI 2008).

The phosphorus content in oil, like the pigment content, depended both on the species and the temperature of seed treatment (Table 3). Generally, it was found that flax and camelina were characterised by a significantly higher content of phosphorus than rapeseed and mustard oils. Generally, a significant growth in the phosphorus content was observed in oils pressed from seeds heated in increasing temperatures. Although the growth in the phosphorus content in flax, camelina and mustard oils was of a linear nature, for rapeseed oils a significantly higher content of this compound was found in a sample obtained from seeds heated only at 80°C. Rapeseed oils heated at 60°C and 70°C revealed comparable phosphorus content. The highest content of phosphorus in oils obtained in the research, amounting to 25.55–26.18 mg · kg$^{-1}$ (sample of camelina and flax oil from seeds heated at 80°C) does not exceed the internationally recognised threshold value of 50 mg · kg$^{-1}$ for oil intended for biodiesel production (WALISIEWICZ-NIEDBALSKA 2004).

Phosphorus compounds in oils include mainly phospholipids which impede the transesterification process. It is believed that their presence reduces the activity of catalysts, inhibits the rate of reaction and makes it difficult to separate the ester phase from the glycerine (PODKÓWKA 2004, VAN GERPEN 2005).

The degree of oil hydrolysis (determined by acid value) depended on the species and the seed heating temperature. Oils obtained from flax seeds were characterised by the highest and significantly varied acid values

(11.45–14.49 mg KOH · $g^{-1}$). Oils produced from rapeseed and mustard seeds were characterised by the lowest, comparable values (1.79–2.13 mg KOH · $g^{-1}$) (Table 4). An increase in the temperature of seed treatment before pressing affected the growth of the acid value for all oils, although this value was significant only in the case of flax and camelina oils. Differences in the acid value of oils obtained from seeds heated at extreme temperatures (60–80°C) amounted to only 0.21 mg KOH · $g^{-1}$ and 0.25 mg KOH · $g^{-1}$ for rapeseed and mustard oil and 3.04 mg KOH · $g^{-1}$ and 3.15 mg KOH · $g^{-1}$ for flax and camelina (Table 4).

The acid value of oils intended for transesterification with the use of alkaline catalyst should not be too high. Literature sources provide different values; from ≤ 1 mg KOH · $g^{-1}$ (WALISIEWICZ-NIEDBALSKA 2004) to 6 mg KOH · $g^{-1}$ (BUCZEK and CZEPIRSKI 2004, KOTOWSKI 2004, RAMADHAS et al. 2005, RADZIEMSKA et al. 2009). In the case of transesterification with the use of acid catalyst, higher values of this indicator are acceptable ≤ 10 mg KOH · $g^{-1}$ (BUCZEK and CZEPIRSKI 2004).

An increased content of free fatty acids in oils intended for basic transesterification is undesirable since this contributes to a saponification reaction, and consequently, an increase in viscosity, gel and foam formation, which hinders the course of the process, as well as the separation of phases (MA and HANNA 1999, ZHANG et al. 2003, MATHIYAZHAGAN and GANAPATHI 2011). As WALISIEWICZ-NIEDBALSKA et al. (2005) also reported, the saponification reaction of FFA involves the release of reaction water, which hydrolyses fat and creates another portion of free fatty acids. During acid catalysis, on the other hand, FFA reacts with alcohol, forming esters and also, unfortunately, water, which impedes the transesterification of glycerides (CANAKCI 2007).

The peroxide value, determining the content of primary oxidation products, ranged from 0.46 mEq $O_2$ · $kg^{-1}$ (flax oil obtained from seeds heated at 60°C) to 1.38 mEq $O_2$ · $kg^{-1}$ (flax oil obtained from seeds heated at 80°C) (Table 4). Seed treatment resulted in a significant, although small, growth in the content of peroxides in oils from all species (Table 4).

The content of secondary oxidation products, as determined by the anisidine value, did not reveal any clear relation, either to a species of seeds or the temperature of seed treatment. Generally, the values of this determinant were low and did not exceed the following levels: for rapeseed oil obtained from seeds heated at 80°C – 0.85, for mustard oil from seeds heated at 60°C – 2.67, for flax oil from seeds heated at 70°C – 2.57 and for camelina oil from seeds obtained at 60°C – 1.31 (Table 4).

The low peroxide and anisidine values observed in the study indicate a low level of oil oxidation, which indicates the good quality of seeds. Although those factors are not mentioned in the quality assessment of oils intended for

Table 4

Characteristics of oils obtained from seeds heated at different temperatures

| Discriminants | Rapeseed | | | Mustard | | | Flax | | | Camelina | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | temperature of heating | | | | | | | | | | | |
| | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C | 60°C | 70°C | 80°C |
| Acid value [mg KOH · $g^{-1}$] | $1.92^{a}$ ± 0.05 | $2.06^{b}$ ± 0.04 | $2.13^{c}$ ± 0.03 | $1.79^{a}$ ± 0.08 | $1.95^{b}$ ± 0.07 | $2.04^{c}$ ± 0.02 | $11.45^{a}$ ± 0.00 | $13.21^{b}$ ± 0.01 | $14.49^{c}$ ± 0.06 | $3.02^{a}$ ± 0.08 | $2.95^{c}$ ± 0.07 | $6.17^{b}$ ± 0.05 |
| Peroxide value [mEq $O_2$ · $kg^{-1}$] | $0.89^{a}$ ± 0.01 | $0.96^{b}$ ± 0.02 | $1.07^{c}$ ± 0.01 | $0.62^{a}$ ± 0.06 | $0.77^{b}$ ± 0.03 | $0.99^{c}$ ± 0.03 | $0.46^{a}$ ± 0.05 | $0.55^{b}$ ± 0.00 | $1.38^{c}$ ± 0.01 | $1.07^{a}$ ± 0.02 | $1.23^{b}$ ± 0.07 | $1.08^{a}$ ± 0.01 |
| Anisidine value [–] | $0.56^{a}$ ± 0.01 | $0.73^{b}$ ± 0.02 | $0.85^{c}$ ± 0.04 | $2.67^{b}$ ± 0.09 | $2.00^{a}$ ± 0.06 | $2.60^{b}$ ± 0.01 | $1.40^{a}$ ± 0.09 | $2.57^{c}$ ± 0.09 | $2.05^{b}$ ± 0.09 | $1.31^{c}$ ± 0.05 | $1.06^{b}$ ± 0.03 | $0.88^{a}$ ± 0.09 |

Explantation as in Table 1

Table 5

Fatty acids composition [%]

| Fatty acids | Rapeseed | | Mustard | | Flax | | Camelina | |
|---|---|---|---|---|---|---|---|---|
| | temperature of heating | | | | | | | |
| | 60°C | 80°C | 60°C | 80°C | 60°C | 80°C | 60°C | 80°C |
| Palmitic | $4.97^b \pm 0.02$ | $4.80^a \pm 0.04$ | $3.85^a \pm 0.67$ | $3.81^a \pm 0.43$ | $6.08^a \pm 0.23$ | $6.06^a \pm 0.21$ | $5.38^a \pm 0.21$ | $5.52^b \pm 0.33$ |
| Palmitoleic | $0.24^a \pm 0.01$ | $0.22^a \pm 0.00$ | $0.19^a \pm 0.02$ | $0.18^a \pm 0.00$ | < 0.10 | < 0.10 | $0.11^a \pm 0.00$ | $0.10^a \pm 0.02$ |
| Stearic | $1.31^a \pm 0.02$ | $1.30^a \pm 0.04$ | $2.01^a \pm 0.12$ | $2.09^b \pm 0.11$ | $4.46^a \pm 0.36$ | $4.42^a \pm 0.43$ | $2.33^a \pm 0.25$ | $2.27^a \pm 0.25$ |
| Oleic | $62.32^a \pm 1.23$ | $62.52^a \pm 0.89$ | $63.38^a \pm 0.98$ | $64.30^b \pm 0.77$ | $23.57^b \pm 0.54$ | $23.39^a \pm 0{,}21$ | $15.77^b \pm 0.76$ | $15.62^a \pm 0.69$ |
| Linoleic | $20.26^a \pm 0.78$ | $20.34^a \pm 0.65$ | $9.85^b \pm 0.67$ | $9.46^a \pm 0.98$ | $14.65^a \pm 0.54$ | $14.94^b \pm 0.32$ | $16.51^a \pm 0.11$ | $16.67^b \pm 0.24$ |
| Linolenic | $\mathbf{9.51}^a \pm 0.45$ | $\mathbf{9.40}^a \pm 0.23$ | $\mathbf{14.74}^b \pm 1.05$ | $\mathbf{14.28}^a \pm 0.78$ | $\mathbf{51.24}^a \pm 0.65$ | $\mathbf{51.19}^a \pm 0.76$ | $\mathbf{37.32}^a \pm 0.87$ | $\mathbf{37.44}^a \pm 0.99$ |
| Arachidic | $0.45^a \pm 0.00$ | $0.43^a \pm 0.05$ | $0.59^b \pm 0.03$ | $0.46^a \pm 0.01$ | < 0.10 | < 0.10 | $1.33^a \pm 0.06$ | $1.37^a \pm 0.08$ |
| Eicosenoic | $0.94^a \pm 0.08$ | $0.99^a \pm 0.04$ | $2.58^a \pm 0.00$ | $2.58^a \pm 0.04$ | < 0.10 | < 0.10 | $15.32^a \pm 0.65$ | $15.36^a \pm 0.76$ |
| Eicosadienoic | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $2.16^a \pm 0.04$ | $2.04^a \pm 0.03$ |
| Homo-γ-linolenic | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $1.74^a \pm 0.08$ | $1.64^a \pm 0.07$ |
| Behenic | < 0.10 | < 0.10 | $2.81^a \pm 0.03$ | $2.84^a \pm 0.01$ | < 0.10 | < 0.10 | $0.26^a \pm 0.04$ | $0.23^a \pm 0.00$ |
| Erucic | < 0.10 | < 0.10 | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $0.00^a \pm 0.00$ | $1.77^a \pm 0.02$ | $1.74^a \pm 0.04$ |

Explanation as in Table 1

biodiesel production, they are still important indicators of the degree of oxidative changes affecting durability.

The composition of fatty acids in all samples under examination was typical for oils obtained from seeds of those species. It was found that seed treatment at 80°C did not result in any significant changes in the share of individual fatty acids (Table 5).

According to PN-EN 14214:2012, one of the main characteristics that qualify oil for biodiesel production is the percentage of linolenic acid, which should not exceed 12% (PN-EN 14214:2012). Among the examined oils, this requirement was satisfied only by rapeseed oil (from 9.40% oil of seeds heated at 80°C to 9.51% oil from seeds heated at 60°C).

The share of linolenic acid in mustard, flax and camelina oil exceeded the threshold value by 2.5, 39.2 and 25.3 percentage points, respectively. These oils should not be used as raw materials for biodiesel production on their own, but they should be used in mixes with fats characterised by a low share of linolenic acids, e.g. palm oil or animal fats.

## Summary

The results of the research performed made it possible to claim that the optimum temperature of heating rape and mustard seeds in the Kocibórz Biorefinery was 80°C, and for flax and camelina it was 60°C. The oils extracted from seeds conditioned at the above specified temperatures were characterised by good pressing efficiency and good quality, understood as a low content of non-triacylglycerol compounds hindering transesterification and reducing the durability of esters.

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# COMPARISON OF SEDIMENTATION TESTS OF WASTEWATER SLUDGE AND AGGREGATES OF MODEL SILICA SUSPENSION

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K e y  w o r d s: flocculation, sedimentation, organic polymers.

A b s t r a c t

Results of sedimentation tests conducted on pulp and paper wastewater were compared with the results of macroscopic photographic analysis of silica aggregate suspensions. The peak effectiveness of the phase separation was achieved with the use of cationic polymer Z63 which – when used together with polyaluminium chloride (PAC) – reduced the volume of sludge by up to 38% compared to PAC alone. Used together with anionic (P2540, M1011) and cationic (Z63, Z92) polymers, PAC reduced the sludge sedimentation time by half compared to PAC alone. Aggregates formed during the process of silica flocculation with PAC and cationic flocculant Z63 are larger than those formed with an anionic one.

## PORÓWNANIE TESTÓW SEDYMENTACJI OSADU ŚCIEKOWEGO Z AGREGATAMI MODELOWEJ ZAWIESINY KRZEMIONKI

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A b s t r a k t

Porównano wyniki testów sedymentacyjnych przeprowadzonych na ściekach celulozowo-papierniczych z wynikami makroskopowej analizy fotograficznej agregatów zawiesiny krzemionki. Najwyższą skuteczność separacji faz uzyskano z udziałem polimeru kationowego Z63, który we współpracy z chlorkiem poliglinu (PAC) obniżał objętość warstwy osadu ściekowego nawet do 38% w stosunku do samego PAC. PAC zarówno we współpracy z polimerami anionowymi (P2540, M1011), jak i kationowymi (Z63, Z92), powodował skrócenie czasu sedymentacji osadu ściekowego o połowę w porównaniu z próbami z samym PAC. Agregaty utworzone w procesie flokulacji zawiesiny krzemionki za pomocą PAC i kationowego flokulantu Z63 charakteryzują się wyższym wymiarem niż te otrzymane z flokulantem anionowym.

## Introduction

There are currently a number of methods used to determine the degree of particle aggregation (GREGORY 2009, YU et al. 2006), which enable analysing the kinetics of aggregation and change of the size of floccules formed at different stages of flocculation. Kinetics of the particle aggregation can be described by either of two models. The model of perikinetic particle collisions, associated with Brownian motion, can be applied to particles smaller than 1 μm. On the other hand, orthokinetic aggregation, caused by hydrodynamic interactions (for example while suspension is being stirred) occurs for particles larger than 1 μm. According to GREGORY (2009), the number of particles decreases in a linear manner in the process of orthokinetic aggregation and it does so exponentially during the process of perikinetic flocculation. A similar degree of aggregation can probably be achieved over a slightly longer time as a result of orthokinetic flocculation compared to the perikinetic process. The process of orthokinetic flocculation results in the formation of open-structure floccules. Particle collisions according to the CCA (cluster-cluster aggregation) mode result in the formation of floccules of different sizes. The aggregation model proposed by MEAKIN and KOLBE (1983) assumes collisions of monodispersive particles, which join and form e.g. dimers which can bind with other dimers or with individual particles. Such a process leads to the formation of aggregates of different shapes and a wide range of sizes. The effectiveness of particle aggregation in the process of flocculation with the use of polyelectrolytes depends mainly on the conditions of stirring, degree of polymer adsorption on particles and re-conformation of the polymer chain.

The effectiveness of water and wastewater purification with inorganic coagulants may increase as a result of the use of organic polyelectrolytes. The most frequently used ones include acrylamide copolymers, whose chains can change their conformation and stretching during the process of hydrolysis. The degree of polymer hydrolysis largely depends on the polymer charge density and pH of the environment (BOLTO 1995). NAPPER (1983) proposed a model of polymer adsorption in three forms of contact with the adsorbing surface: trains, tails and loops. There is a great diversity of opinions on the minimum coverage of the particle surface with polymer, which is necessary for effective flocculation to take place. The results of research conducted by DAS and SOMASUNDARAN (2004) show that the degree of effective flocculation when ultra-low doses of macromolecular PAA are used is three times lower than is needed for covering them with a monolayer of the polymer.

Anionic flocculants are regarded as the most effective polymers in the process of wastewater purification because of the presence of weakly anionic carboxylic groups in them. The maximum carboxylation of 10% is achieved in processes of electrochemical carboxylation of copolymers of acrylic acid (BOLTO 1995). The use of organic polyelectrolytes brings several benefits: they reduce doses of inorganic coagulants and favour a decrease in the amount of sludge, they also ensure a lower level of Al residue in water; and they are less dependent on pH changes.

Using excessively large doses of polymers results in numerous problems, such as re-dispersion of impurities, while using insufficient doses results in ineffective coagulation, which manifests itself in a high level of suspension and colour in purified water BOLTO (1995). The aim of the study was to compare the sedimentation rate of sludge and the results of the macroscopic photographic method of aggregates from the suspension $(SiO_2)_n$ formed by coagulation of pulp and paper wastewater and a model silica system. Coagulation/flocculation was conducted with the use of PAC and organic flocculants with a diverse ionic character.

## Methods

The effect was investigated of organic polymers with various ionic features used together with PAC on the process of phase separation in the coagulation/flocculation of pulp and paper wastewater. Table 1 presented the characteristic of pulp and paper wastewater before and after coagulation by PAC.

Table 1

Characteristic of pulp and paper wastewater before and after coagulation by PAC

| Dose PAC [mg Al dm$^{-3}$] | Turbidity | COD | Suspended solid | Colour |
|---|---|---|---|---|
| | [mg dm$^{-3}$] | | | |
| 0.0 | 860 | 1754 | 680 | 4680 |
| 20 | 34 | 788 | 14 | 179 |

A comparative analysis of the effectiveness of selected organic flocculants (anionic P2540 and M1011 and cationic Z63 and Z92) was conducted. After the process of coagulation/flocculation was completed, the increase in the sludge layer over 1 hour was measured.

A macroscopic photographic method (WIERZBICKA 2000) was used in order to measure the size of floccules formed by coagulation of the model suspension of silica with inorganic coagulants with the addition of some organic flocculants. The most effective flocculants were selected: anionic P2540 and cationic Z63. Aggregates of the appropriate sludges were measured in magnification x36 and the actual distribution of floccule sizes was determined based on those values. Each of the sludges are characterised by a diagram $Z(\%) = f(R)$, $Z$ (%) – distribution of floccule sizes, $R$ – size of object.

## Results and Discussion

The effectiveness of flocculation was expressed as the volume of sludge formed over 60 minutes. Figure 1 and Figure 2 show the process of phase separation caused by orthokinetic flocculation conducted with 20 mg of Al dm$^{-3}$ with PAC used together with cationic and anionic organic flocculants.

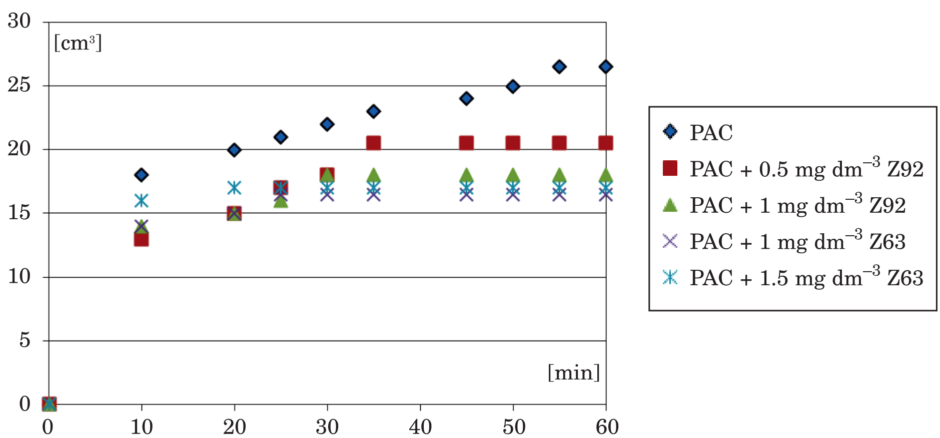


Fig. 1. Characteristics of the sludge sedimentation using PAC and cationic polymers

The diagrams show that the highest effectiveness in the phase separation process was achieved with the cationic polyelectrolyte Z63, whose dose of 1 and 1.5 mg dm$^{-3}$ reduced the solid phase by 38% and 36% compared to PAC alone. P 2540 was regarded as the optimum anionic flocculant, as its addition

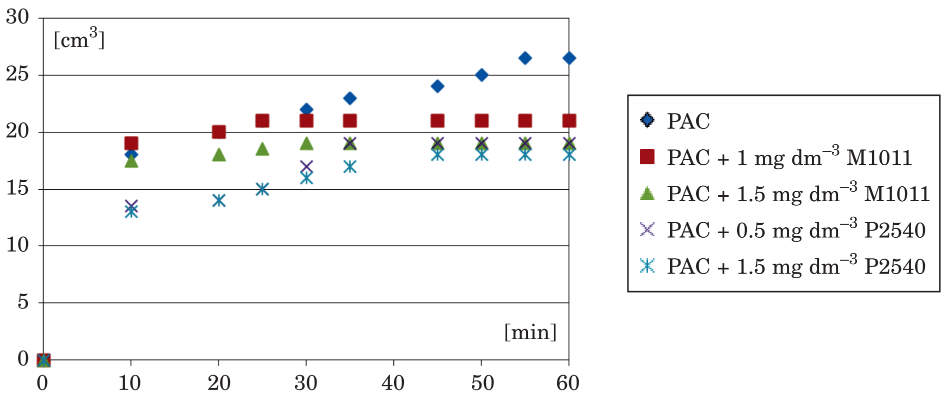


Fig. 2. Characteristics of the sludge sedimentation using PAC and anionic polymers

at 1.5 mg dm$^{-3}$ boosted the effect of PAC by 32%. This was the same as in boosting the effect of PAC with 1 mg dm$^{-3}$ of Z92. A slightly lower effectiveness of the flocculation process was observed when 0.5 mg dm$^{-3}$ of cationic polymer Z92 and anionic polymer M1011 were used. However, the result at 21–23% of reduction in the sludge volume with these flocculants is satisfactory. The values of 32–38% of the sludge volume reduction, achieved with cationic flocculants Z92 and Z63 proved better than 21–32% for anionic flocculants P2540 and M1011. Based on these data, one can claim that better separation of floccules in paper and pulp wastewater can be achieved when cationic organic flocculants Z92 and Z63 are used with an inorganic coagulant.

The enhancing effect of organic polyelectrolytes is additionally enhanced by considerable reduction in the phase separation time. The sedimentation process for cationic flocculants was completed after 30–35 minutes and for anionic flocculants after 30–45 minutes (PAC alone 55 min). It should be stressed that an addition of a small amount of organic flocculants improves the characteristics of phase separation, both in the formation of the minimum amount of sludge and in a considerable reduction of the sedimentation time.

Macromolecular polymers used in the study cause adsorption on colloidal particles to a greater extent than those with small molecules (DAS, SOMASUNDARAN 2004). The authors suggest that such high effectiveness of macromolecular polymers results from the size of their molecules, which ensure high adhesion relative to the surface of adsorption. Therefore, the effectiveness of flocculation can be controlled by adsorption of polymer. Molecules of polymer with a high molecular weight make intermolecular bridging particularly intensive when stable floccules overcome electrostatic interactions. This means that the optimum dose of a macromolecular polymer is relatively smaller than that of a polymer with small molecules (FERRETTI et al. 1997).

The supporting effect of polymers results in an increase in the size and density of floccules during the flocculation phase. Aggregates thus formed improve the effectiveness of phase separation.

Using the macroscopic photographic method allows the size, shape and structure of the aggregates to be determined. In order to optimise the flocculation conditions, measurement of the degree of aggregation and the properties of the aggregates is performed.

The process of flocculation with PAC and the anionic flocculant P2540 resulted in the formation of aggregates with the values of $R$: 0.02–0.117 mm. Distribution of the number of particles, shown in Figure 3 and Figure 4, provides grounds for determination of the percentage of particles of specific

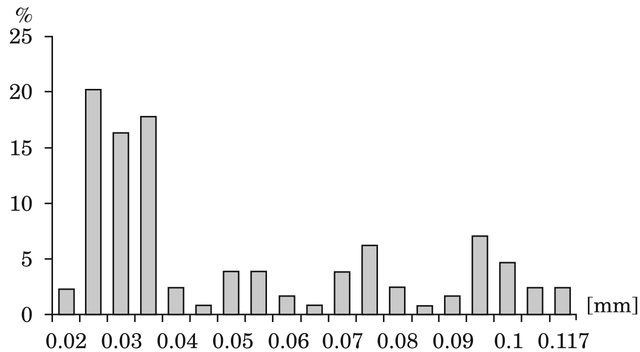


Fig. 3. Distribution of the sizes of aggregates obtained with PAC and P2540

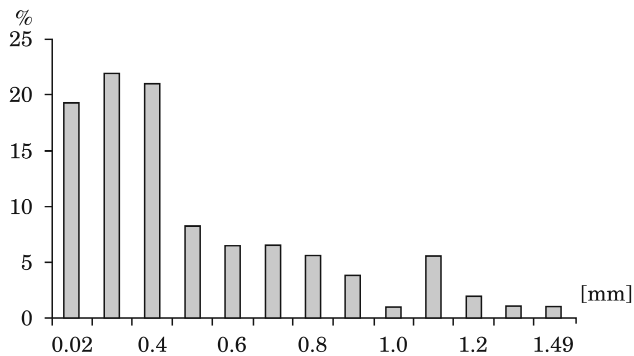


Fig. 4. Distribution of the sizes of aggregates obtained with PAC and Z63

sizes. The distribution of floccules presented in Figure 4 indicates that the highest proportion of floccules had sizes of 0.025–0.035 (53.5% calculate the average value). Floccules with the size of 0.075 and 0.095 mm accounted for approx. 15% of all samples. Figure 4 shows that the size of aggregates formed with the use of the cationic flocculant ranged from 0.02 to 1.49 mm. Such a great difference between the sizes of floccules formed with the anionic and cationic flocculant indicates that the floccules formed with the anionic polymer were less hydrated than those formed with the cationic polymer. Floccules with sizes ranging from 0.02 to 0.4 mm accounted for the largest portion of the size spectrum. The process of aggregation results in the growth of a floccule to a specific limit size, and if it grows further it disintegrates into smaller parts. The sedimentation rate for floccules formed with the anionic flocculant P2540 was equal to 0.12–1.53 mm $s^{-1}$. The value was higher for aggregates formed with PAC and the cationic – up to approx. 2.5 mm $s^{-1}$ (WIERZBICKA 2000).

Comparison of the sedimentation tests conducted on pulp and paper wastewater with the results of the macroscopic photographic method of aggregates from the suspension $(SiO_2)_n$ reveals the mechanism of action of flocculants of a different ionic character in environments with various chemical features. In pulp and paper wastewater with pH = 5 (the optimum pH value for coagulation), negatively-charged particles (accounting for a majority of impurities) are probably destabilised by polyhydroxy cations "$Al_{13}$" and cationic flocculants, in accordance with the charge neutralisation mechanism. This is probably the reason for the highest effectiveness of the cationic flocculant Z63 in sedimentation tests and for the minimum volume of the sludge formed underthose conditions. On the other hand, destabilisation of the lattice of positive charge $(SiO_2)_n$ (at pH = 7–8) with "$Al_{13}$" most probably takes place by bridging with incorporation of the $AlO_4^{5-}$ ion on the micelle surface. In that case, additional support with the anionic flocculant may consist in intensification of the bridging effect. The mechanism of flocculation differs depending on the system pH. This means that at pH = 4.5, neutralisation of the charge may result in the formation of floccules of high density, whereas the density of floccules formed at pH = 7.5 is lower due to neutralisation and intermolecular bridging.

## Conclusions

1. The highest effectiveness was achieved with the use of the cationic polymer Z63, which – when used together with PAC – reduced the volume of the sludge by 38% (1 mg $dm^{-3}$) to 36% (1.5 mg $dm^{-3}$) as compared to PAC alone.

2. When used with anionic (P2540, M1011) and cationic (Z63, Z92) polymers, PAC considerably reduced the sludge sedimentation time from 60 minutes (PAC alone) to 30–35 min.

3. Aggregates formed in the process of flocculation of silica suspension with PAC and the cationic flocculant Z63 have higher values of $R$: 0.02–1.49 mm – than those formed with the anionic flocculant P2540 – $R$: 0.02–0.117 mm.

4. The sedimentation rate of the aggregates formed in the process of flocculation with Z63 v = up to 2.5 mm $s^{-1}$ is higher than with P2540 – 0.12–1.53 mm $s^{-1}$.

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# PRELIMINARY RESULTS OF EUROPEAN GRAYLING (*THYMALLUS THYMALLUS* L.) FRY REARING TO THE AUTUMN FINGERLINGS STAGE

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Key words: fry growth, survival rate, stocking, breeding parameters, aquaculture.

Abstract

The aim of this study was to test the possibilities of rearing European grayling (*Thymallus thymallus* L.) under controlled conditions to the autumn fingerlings stage. Experimental fish originated from the farmed broodstock. Juvenile graylings were reared in plastic tanks with a bottom area of 1 $m^2$ and a depth of 0.5 m. Dan-Pel 1656 (Dana Feed) feed was used in the experiment. The mean body weight of an individual fish increased from 0.93 g to 14.60 g during the period of rearing (100 days), while the mean stock biomass increased from 0.37 to 5.15 kg $m^{-3}$. The highest values of the relative growth rate of an individual (RGR) and the relative biomass rate (RBR) were 4.36% and 3.85% a day, while the lowest values of this parameters were 0.74% and 0.61% a day, respectively. The mean value of the feed conversion ratio (FCR) increased steadily during consecutive stages of rearing, lying within the range from 0.61 to 4.11 for the initial and the last period of the experiment, respectively. The mean cumulative mortality rate was 13.23%, with the values in replications differing significantly ($P < 0.05$). The value of the length variability index ($V_L$) for the population lay within the range from 8.82% to 13.24%. The mean value of increase in total length index (ITL) were 0.15 and 0.11 for the growth period III and IV (F = 9.886; $P < 0.05$). The mean value of the protein efficiency ratio (PER) ranged from 0.39 to 2.82.

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**WSTĘPNE WYNIKI PODCHOWU LIPIENIA EUROPEJSKIEGO (*THYMALLUS THYMALLUS* L.) DO STADIUM NARYBKU JESIENNEGO**

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Słowa kluczowe: wzrost narybku, przeżywalność, materiał zarybieniowy, parametry hodowlane, akwakultura.

Abstrakt

Celem doświadczenia było sprawdzenie możliwości podchowu w warunkach kontrolowanych lipienia europejskiego (*Thymallus thymallus* L.) do stadium narybku jesiennego. Narybek pochodził od tarlaków ze stada hodowlanego. Ryby podchowywano w plastikowych basenach o powierzchni dna 1 $m^2$ i głębokości zalewu ok. 0,5 m. W doświadczeniu użyto paszy Dan-Pel 1656 (Dana Feed). W okresie trwania podchowu (100 dni) średnia masa osobnika wzrosła z 0,93 g do 14,60 g, nastąpił również wzrost średniej biomasy obsady z 0,37 do 5,15 kg $m^{-3}$. Najwyższe wartości relatywnego tempa przyrostów masy osobnika (RGR) oraz relatywnego tempa przyrostów biomasy (RBR) wyniosły odpowiednio 4,36 i 3,85% na dobę, natomiast najniższe wartości – odpowiednio 0,74% i 0,61% na dobę. Średnia wartość współczynnika pokarmowego (FCR) stale wzrastała w kolejnych etapach podchowu, wynosząc od 0,61 do 4,11 odpowiednio w pierwszym i ostatnim okresie doświadczenia. Średnia wartość śmiertelności skumulowanej wyniosła 13,23%, przy czym wartości w poszczególnych powtórzeniach istotnie się różniły ($P$ < 0,05). Wartość wskaźnika zróżnicowania wielkościowego populacji $V_L$ wynosiła od 8,82 do 13,24%. Średnie wartości wskaźnika przyrostu długości ITL wyniosły 0,15 i 0,11 odpowiednio dla III i IV okresu wzrostowego (F = 9,886; $P$ < 0,05). Średnia wartość współczynnika PER mieściła się w zakresie od 0,39 do 2,82.

## Introduction

Strengthening natural populations of endangered fish species with stocking material produced under controlled conditions is increasingly becoming the main tool used in their active protection (GORYCZKO et al. 2001). However, stocking open water bodies with farmed fish cannot be a goal in itself. In the case of the grayling (*Thymallus thymallus* L.), it should primarily make up for losses caused by intensive angling (AUGUSTYN and CIEŚLA 2000, HOLČIK 2004, WOŁOS et al. 2004, NÄSLUND et al. 2005), birds of prey (including great cormorant) and by poaching (BARTEL 2000). Ultimately, in the long term, stocking should result in the creation of stable populations, diversified both genetically and in terms of age, and – most importantly – capable of reproduction without any external stimulation. However, the ability to produce such effects depends on two fundamental factors. Firstly, the stocking practice should not violate the genetic uniqueness of local populations of the grayling (KOSKINEN et al. 2001, JANKUN et al. 2003). This is because regular stocking with foreign material, without the features of native populations, leaves a permanent genetic trace (SUŠNIK et al. 2004, DUFTNER et al. 2005) and it can considerably affect their condition (ŁUCZYŃSKI and BARTEL 1997). Secondly, constant improvement of the methods of the grayling breeding (ŁUCZYŃSKI et al. 1986, SZMYT et al. 2004, RANDÁK et al. 2009, SZMYT et al. 2012), as well as developing marking methods of juvenile stages of the species (NAGIĘĆ et al. 1995), provide an opportunity for much more successful accomplishment of stocking programmes (WITKOWSKI et al. 1994) and, consequently, improves the condition of wild fish populations supported with stocking.

Despite great scientific and technical progress, production of stocking material under controlled conditions is beset with problems. These involve – despite intensive efforts – the not-fully mastered breeding biotechniques of many species, the threats posed by pathogens (OCVIRK 1992, PYLKKÖ et al. 2005) and the fish inadvertently getting used to the presence of humans. It seems, however, that despite some reservations, the defined direction of protection of endangered fish species and modern fishery development should be pursued and expanded.

The aim of this study was to analyse the selected breeding parameters achieved in rearing of European grayling (*Thymallus thymallus* L.) to the autumn fingerlings stage.

## Materials and Methods

### Fish rearing

The experiment was conducted at the Inland Fisheries Institute, Department of Salmonid Research in Rutki. The experimental rearing was conducted for 100 days. Juvenile graylings (Table 1) obtained from the farmed broodstock were used as the study material (GORYCZKO et al. 1995); they were reared in plastic tanks with a bottom area of 1 $m^2$ and a depth of about 0.5 m.

The fish were fed every day, except on the days preceding the control weighing. The Dan-Pel 1656 feed (Dana Feed) – Table 2 was given by hand in four doses, between 7.30 a.m. and 5.00 p.m. The doses of the feed were calculated every day with the Djournal computer program (FROM and RASMUSSEN 1984). The entire experiment was performed in three replications.

Twice a week during the experiment, preventive baths in solutions of Chloramine T (9 g in 1 $m^{-3}$ of water) were conducted. The tanks were cleaned

Table 1
Number, stock biomass [g] and mean body weight [g] of fish used in the experiment

| Replication | Number of fish | Total stock biomass [g] | Mean body weight [g] |
|---|---|---|---|
| 1 | 200 | 186 | 0.93 |
| 2 | 200 | 204 | 1.02 |
| 3 | 200 | 166 | 0.83 |

every other morning, before the feeding was started. Dead fish were removed from the tanks every day and their numbers were recorded. The temperature during the experiment ranged from 11.3 to 18.9°C (Figure 1), and the dissolved oxygen from 7.2 to 10.2 mg $O_2$ $dm^{-1}$.

Table 2
Chemical composition [%] and energy value [MJ $kg^{-1}$] of the feed (Dan-Pel 1656; Dana Feed) used in the experiment, as claimed by the producer

| Component | Content in the feed [%] |
|---|---|
| Crude protein | 56.0 |
| Crude fat | 16.0 |
| N-free extractives | 11.0 |
| Crude fibre | 1.1 |
| Crude ash | 10.4 |
| Metabolizable energy [MJ $kg^{-1}$] | 17.1 |

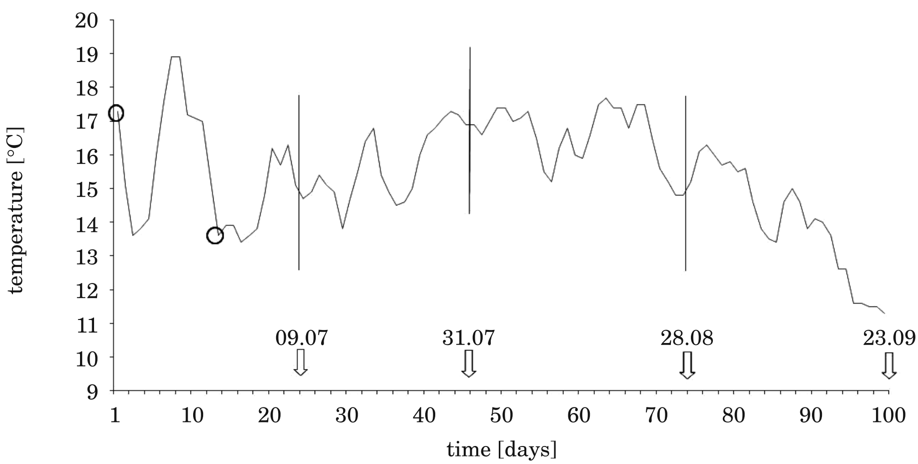


Fig. 1. Daily variability of the water temperature during the experiment. Arrows show the dates of the control measurements of the fish. The circles show the periods of rapid temperature increase.

The experiment was divided into four growth periods and control measurements of the fish were performed after each period. The period durations were: 24 (I), 22 (II), 28 (III) and 26 (IV) days. The measurements were performed after the fish were completely anaesthetised in a solution of Propiscin (IFI Olsztyn, Poland) at the concentration of 0.5 ml $dm^{-3}$. Each time the stock in the entire tank was weighed and all the fish were counted, which yielded the mean body weight per individual. Due to the small initial size of experimental fish and considerable sensitivity of graylings to all manipulations, especially at this stage, individual measurements of the body length were abandoned. Beginning with the second growth period, the *longitudo totalis* (*l.t.*) of a fish sample ($n$ = 60) was measured to assess the variability of the total length. The fish were weighed at an accuracy of 0.1 g and their lengths were measured at an accuracy of 0.1 cm.

## Data analysis

The following were calculated from the results: the SGR and SBR coefficients (BROWN 1957):

$$\mathrm{SGR} = 100 \cdot (\ln W_2 - \ln W_1) \cdot D^{-1}$$

$$\mathrm{SBR} = 100 \cdot (\ln n_2 W_2 - \ln n_1 W_1) \cdot D^{-1}$$

where:
SGR – specific growth rate; SBR – specific biomass rate; $W_1$ – average individual mass at the beginning of the rearing [g]; $W_2$ – average individual mass at the end of the rearing [g]; $n_1$ – the number of fish at the beginning of the rearing; $n_2$ – the number of fish at the end of the rearing; $D$ – time of rearing [days].

Subsequently, the relative growth rate (RGR) and the relative biomass rate (RBR) were calculated (MYSZKOWSKI 1997):

$$\mathrm{RGR} = 100 \left(e^{\frac{\mathrm{SGR}}{100}} - 1\right), \ \mathrm{RGR} = 100 \left(e^{\frac{\mathrm{SBR}}{100}} - 1\right)$$

Feed conversion ratio, FCR:

$$\mathrm{FCR} = P \cdot B^{-1}$$

where:
$P$ – amount of feed fed [g]; $B$ – fish biomass growth [g]

Protein efficiency ratio, PER:

$$PER = (FB - IB) \cdot FPS^{-1}$$

where:
IB – initial fish biomass [g]; FB – final fish biomass [g]; FPS – amount of protein feed [g].

For the growth periods III and IV, the index of increase in total length – ITL – was also calculated (PEŇÁZ et al. 1989).

$$ITL = (L_2 - L_1) \cdot D^{-1}$$

where:
$L_1$ – mean length of an individual (*l.t.*) at the beginning of the rearing period [cm];
$L_2$ – mean length of an individual (*l.t.*) at the end of the rearing period [cm];
$D$ – duration of the rearing period [days].

Moreover, the length variability index – $V_L$ (RUSZCZYC 1981) of the fish was calculated:

$$V_L = 100 \cdot SDL^{-1}$$

where:
$V_L$ – length variability index [%];
SD – standard deviation [cm];
L – mean length (*l.t.*) of an individual [cm].

## Statistical Analysis

Statistical analysis was performed at the level of $P < 0.05$ ($\alpha = 0.05$). We tested the significance of differences between the values of the rearing coefficients. The following were used: the difference significance test (t-test), the Kruskal-Wallis test (non-parametric analysis of variance), analysis of variance (ANOVA) with Tukey's post hoc test (HSD). To assess the relationship between the examined parameters, we used the method of correlation analysis. The statistical analysis of the results was performed with STATISTICA 9.0 software (Stat Soft, Inc., USA).

## Results

During the 100 days of rearing, the mean body weight of an individual fish increased from 0.93 g to 14.60 g (Table 3). A statistically significant relationship was found between the duration of rearing and the final fish body weight ($r$ = 0.990; $P < 0.05$; Figure 2). The value of body weight was found to have increased during each of the four growth periods, with the maximum on the last day of rearing. The stock biomass was found to have increased during the experiment from 0.37 to 5.15 kg $m^{-3}$.

Table 3

Rearing parameters of European grayling (*Thymallus thymallus* L.)

| Parameters | Growth periods | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| Body weight [g indiv.$^{-1}$] | 2.69 ± 0.16 | 5.99 ± 0.24 | 11.89 ± 0.43 | 14.60 ± 1.96 |
| Relative growth rate RGR [% d$^{-1}$] | 4.36 ± 0.22 | 3.71 ± 0.11 | 2.57 ± 0.01 | 0.74 ± 0.38 |
| Relative biomass rate RBR [% d$^{-1}$] | 3.85 ± 0.22 | 3.31 ± 0.25 | 2.46 ± 0.08 | 0.61 ± 0.42 |
| Protein efficiency ratio PER | 2.82 ± 0.08 | 2.22 ± 0.12 | 1.33 ± 0.04 | 0.39 ± 0.30 |
| Feed conversion ratio FCR | 0.61 ± 0.03 | 0.75 ± 0.03 | 1.11 ± 0.02 | 4.11 ± 1.82 |
| Mortality [%] | 5.83 ± 4.81 | 4.17 ± 2.92 | 1.49 ± 1.13 | 1.74 ± 1.15 |

Mean values ± SD, at the end of each growth period which lasted 24 (I), 22 (II), 28 (III) and 26 (IV) days, after which the control measurements were performed

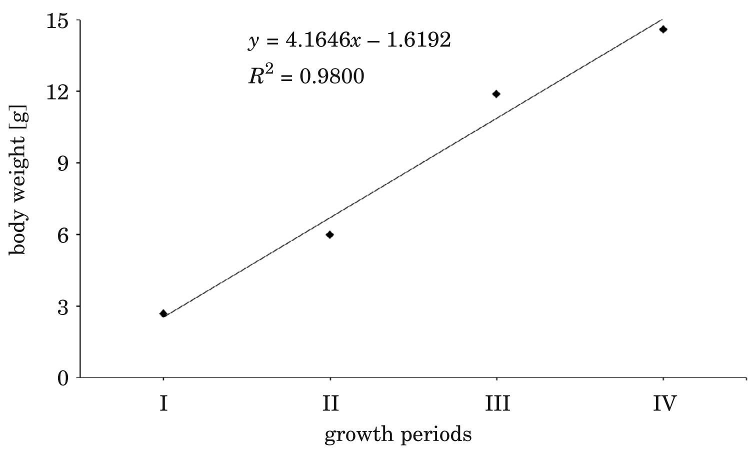


Fig. 2. Mean body weight [g] of European grayling (*Thymallus thymallus* L.) fry at the end of consecutive growth periods of the experiment. Particular growth period lasted 24 (I), 22 (II), 28 (III) and 26 (IV) days

The relative growth rates (RGR) and relative biomass rates (RBR) showed a decreasing tendency in all growth periods (Figure 3). The highest values of both parameters were recorded during the first stage of rearing and were 4.36% $d^{-1}$ (RGR) and 3.85% $d^{-1}$ (RBR), respectively. They were the lowest during the last period: 0.74% $d^{-1}$ (RGR) and 0.61% $d^{-1}$ (RBR) (Table 3; Fig. 3). Relationships between RGR and RBR, and the duration of rearing are expressed in both cases by a negative correlation coefficient, RGR ($r$ = –0.999; $P$ < 0.05; Figure 3) and RBR ($r$ = –0.997; $P$ < 0.05; Figure 3).

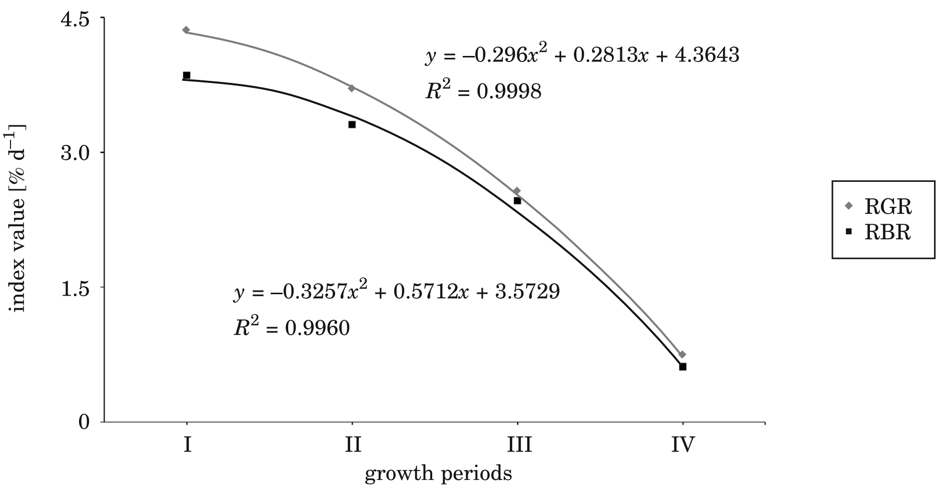


Fig. 3. Relative growth rate (RGR) and relative biomass rate (RBR) of European grayling (*Thymallus thymallus* L.) fry during the experiment. Particular growth period lasted 24 (I), 22 (II), 28 (III) and 26 (IV) days

The mean feed conversion ratio (FCR) increased during successive stages of the experiment (Table 3). There were no significant differences between the replications in growth periods I, II, and III ($P$ > 0.05). The FCR values were highly varied during the last stages of the experiment. The values of this parameter during that time were 5.71, 2.12 and 4.51 in the three replications of the experiment, respectively (Figure 4). The variation of FCR was confirmed to be statistically significant with non-parametric analysis of variance (H = 24.789; $P$ < 0.05).

The results were used as the basis for showing statistically significant differences in the mean value of protein efficiency ratio (PER) – Table 3 between subsequent growth periods ($P$ < 0.05).

The mortality of the grayling observed during different rearing periods differed and ranged from 5.83% (stage I) to 1.49% (stage III) – Table 3.

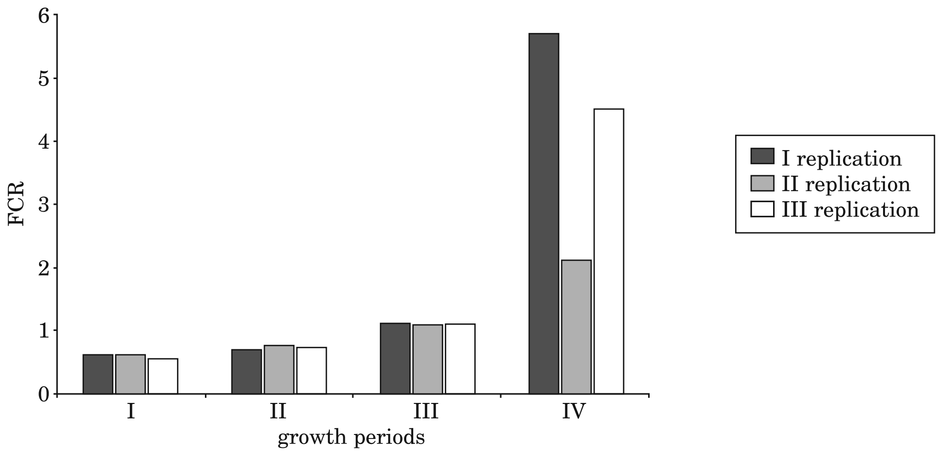


Fig. 4. Feed conversion ratio (FCR) values at the end of consecutive European grayling (*Thymallus thymallus* L.) fry growth periods with replications. Particular growth period lasted 24 (I), 22 (II), 28 (III) and 26 (IV) days. There were no significant differences between the replications in growth periods I, II, and III ($P > 0.05$). In IV growth period there are significant statistical differences between values from subsequent replications ($P < 0.05$)

The value of the cumulative mortality rate during the entire period of the experiment was 13.23%. However, statistically significant differences of 12.53%, 4.58% and 22.58% (test of significance of differences between structure indexes; $P < 0.05$) were recorded in individual replications.

The mean values of the total length increase index (ITL), calculated for the growth periods III and IV of the experiment were similar: 0.15 and 0.11. The analysis of variance showed them to be statistically significantly different ($F = 9.886$; $P < 0.05$). Tukey's test confirmed that the variability observed during the last period of rearing was responsible for the variability of ITL. The highest value of the length variability index ($V_L$) was recorded during the second growth period and was 13.24 (Table 4).

Table 4

Length of European grayling (*Thymallus thymallus* L.)

| Parameter | Growth periods | | |
|---|---|---|---|
| | II | III | IV |
| Mean fish length *l.t.*[cm] | 5.2 ± 0.69 (3.8–7.4) | 9.6 ± 0.85 (6.9–10.9) | 12.7 ± 1.14 (10.2–15.8) |
| Length variability index $V_L$ [%] | 13.24 | 8.82 | 9.00 |

Mean ± SD, range; $n = 60$ as well as the mean value of the length variability index $V_L$ , at the end of II (22 days) , III (28 days) and IV (26 days) growth period of the experiment

## Discussion

The studies of the growth of the grayling conducted so far have dealt with fish caught in the natural environment (LUSK 1975, GERTYCHOWA 1976, WITKOWSKI et al. 1989, CARLSTEIN 1997, TUREK et al. 2010). Since the biotechnique of grayling breeding has not been fully mastered (VOVK 1984, OCVIRK and VOVK 1985, CARMIE and JONARD 1988, ŠUMER 1994, KOWALEWSKI 2002, SZMYT et al. 2006), much less data have been published on the growth of the fish under controlled conditions. However, constant aquaculture development aimed at optimising the methods of stocking material production for endangered or heavily exploited species provides ample opportunities in this area of research (ŁUCZYŃSKI et al. 1986, GRUDNIEWSKA et al. 2007, WUNDERLICH et al. 2011).

As the authors expected, steady growth of each individual was observed throughout the rearing period. A similar tendency in terms of the growth, but with a smaller body weight of the graylings during the initial period of rearing, has been observed in other studies (SZMYT and GRUDNIEWSKA 2005). After 9–10 weeks from hatching, they achieved the mean body weight of an individual of 3.8 g. The completion of rearing in the cited study, which took place on 23 July, corresponds to the period of approximately one week before the end of the second growth period in present study.

According to the authors, a distinct decrease in the value of RGR and RBR in the last growth period can be attributed to the decrease in the intensity of the fish feeding at the time. As a consequence, the total fish biomass decreased and the FCR index increased. The results may suggest that it is necessary to modify the feeding strategy during the rearing of grayling, which takes place in early autumn. This may be associated with the amount of feed, frequency of feeding or the energy value of the feed. A change of the feeding procedures is indicated by a rapid increase in the mean value of FCR during the final study period and its variability in individual replications during the period. Interesting results in the last rearing period can also be observed for the protein efficiency ratio (PER). Its mean value decreased steadily and it was variable during the last stage of the rearing. In the case of the rationed feeding strategy, a decrease in intensity of fish feeding is closely related to the increase in FCR and, consequently, a decrease in PER. Similar values to those discussed in present study have been reported by WUNDERLICH et al. (2011). The authors studied the whitefish *Coregonus lavaretus* (L.) and, after 42 days of rearing, they achieved, at different levels of feeding, mean PER ranging from 1.69 to 2.06. High values of the determination coefficient $R^2$ for the RGR and RBR parameters confirm the claim of the important role played by the duration of rearing in the case of the grayling. Since the stocking requires that the material used in the process should be suited to the local environmental conditions, in some cases it may be necessary to rear the grayling fry to the autumn fingerlings stage (GORYCZKO et al. 2004). Despite the difficulties, it is extremely important to continue the efforts aimed at optimising the breeding biotechnique of this species as it will make it possible to strengthen the natural populations of the grayling and to preserve the environmental biodiversity.

The results of this study allow one to conclude that the grayling is not too sensitive to slow and steady temperature increase or decrease. However, its rapid fluctuations can have an adverse effect on the fry mortality. This may have resulted in the high mortality rate during the first period of the grayling growth: 5.83% (0.23% per day). This value was the highest of all those recorded during the experiment. Similar observations have been reported by CARLSTEIN (1993), linking the highest mean daily mortality rate of the grayling fry (0.93÷2.69% per day) with the rearing period at the most rapid temperature increase and its maximum value (17.2°C).

The decrease in the length variability index $V_L$ observed during the rearing period may have resulted from keeping the fish in controlled conditions and from their consequent gradual domestication. According to RUSZCZYC (1981), the index in excess of 10% should be regarded as significant. This may be of great importance in terms of the effect of stocking on the natural diversity of populations.

The high variability of the cumulative mortality rate in individual replications, as well as other parameters during the final phase of rearing, underlines the importance of verification of assumptions of future research projects involving the rearing of the grayling. Changes may include increasing the number of replications in the experiments, optimising the feeding parameters or the system of rearing. It may be an opportunity to solve at least some of the problems if fry could be reared in recirculating aquaculture systems.

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# CHANGES OF FAT QUALITY IN RAPESEED STORED UNDER INCREASED MOISTURE CONDITIONS

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Key words: rapeseed, storage, moulds, fat quality, fatty acid composition.

Abstract

The impact of rapeseed storing under increased moisture on the quality of fat was investigated. The studies were carried out with the samples of rapeseed with 11% and 17% moisture. The direction and rate of changes in rapeseed fat during storage at 20°C in an atmosphere of saturated solutions of sodium chlorine (NaCl) and potassium nitrate ($KNO_3$) was determined with regression equations for quality descriptors, including: acid value (AV), peroxide value (PV), anisidine value (AnV), total colour (TC) and composition of fatty acids. At the same time mouldy seed content (MSC) was determined. It was detected a rapid growth of moulds on rapeseed with 17% moisture while there was a lack of visible changes on the surface of seeds with 11% moisture. During 21-day storage, unfavourable hydrolytic and oxidative changes in fat of rapeseed were shown, which resulted in an increase of AV from 8.29 to 10.89 mg KOH $g^{-1}$ and PV from 2.04 to 10.52 mEq $O_2$ $kg^{-1}$ and 7.67 from to 13.83 mg KOH $g^{-1}$ and from 4.12 to 14.38 mEq $O_2$ $kg^{-1}$ for the seeds with 11% and 17% moisture, respectively. At the same time reduction in the nutritional value was observed, as a result of the modifications in the composition of fatty acids. During the storage of rapeseed, regardless of their moisture, a progressive reduction in the share of polyunsaturated fatty acids of n-6 and n-3 families (by 14.0% at 11% moisture and by 31.6% at 17% moisture) and an increase in the share of monounsaturated fatty acids (by 4.4% at 11% moisture and by 10.5% at 17% moisture) were recorded.

## ZMIANY W JAKOŚCI TŁUSZCZU NASION RZEPAKU PRZECHOWYWANYCH W WARUNKACH PODWYŻSZONEJ WILGOTNOŚCI

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A b s t r a k t

Badano wpływ przechowywania nasion rzepaku w warunkach podwyższonej wilgotności na jakość zawartego w nich tłuszczu. Materiał badawczy stanowiły próbki nasion rzepaku o wilgotności 11 i 17%. Kierunek i tempo zmian w tłuszczu nasion w czasie przechowywania w 20°C w atmosferze nasyconych roztworów chlorku sodu (NaCl) i azotanu potasu ($KNO_3$) określano poprzez wyznaczenie równań regresji dla wyróżników jakościowych, takich jak: liczba kwasowa (AV), liczba nadtlenkowa (PV), liczba anizydynowa (AnV), barwa ogółem (TC) oraz skład kwasów tłuszczowych. Równocześnie wyznaczano udział nasion spleśniałych (MSC). Stwierdzono szybki rozwój pleśni na nasionach rzepaku o wilgotności 17%, natomiast brak widocznych zmian na powierzchni nasion o wilgotności 11%. W trakcie 21-dniowego okresu przechowywania w tłuszczu nasion zaszły niekorzystne zmiany hydrolityczne i oksydacyjne skutkujące wzrostem wartości AV od 8,29 do 10,89 mg KOH $g^{-1}$ i PV od 2,04 do 10,52 mEq $O_2$ $kg^{-1}$ w przypadku wilgotności 11% i odpowiednio AV od 7,67 do 13,83 mg KOH $g^{-1}$ i PV od 4,12 do 14,38 mEq $O_2$ $kg^{-1}$ dla wilgotności 17%. Równocześnie nastąpiło obniżenie wartości żywieniowej tłuszczu w wyniku zmian składu kwasów tłuszczowych. Podczas przechowywania nasion rzepaku, niezależnie od ich wilgotności, zaobserwowano stopniowe zmniejszanie się udziału polienowych kwasów tłuszczowych z rodziny n-6 i n-3 (o 14,0% w wilgotności 11% oraz o 31,6% w wilgotności 17%) i zwiększanie się udziału kwasów monoenowych (o 4,4% w wilgotności 11% oraz o 10,5% w wilgotności 17%).

## Introduction

In Poland, rapeseed is the basic raw material for the oil industry and is used for only mechanical extraction of oil to produce cold pressed oil as well as mechanical and chemical extraction of crude oil to produce refined edible oil, margarine and other culinary fats. Supplying raw material with high technological quality, specified with the standard *Rośliny przemysłowe oleiste...* PN-90/R-66151, is a prerequisite for obtaining high quality rapeseed oil.

Rapeseed is a "delicate" material, which is determined by its morphology, structure and chemical composition. Agricultural procedures (timing of harvest and damages), transport, drying, cleaning and inappropriately selected storing conditions contribute to a decrease in the technological value of seeds and the quality of their lipids (TYS et al. 2003). Elevated seed temperature and moisture during storage induce biochemical changes and growth of moulds that are found on the surface of seeds. The products of oxidative and hydrolytic transformations of lipids produced by moulds decrease the palatability of oil (SATHYA et al. 2009) and are dangerous to human health (SZWED 2000). Some species of moulds are able to produce myrosinase enzyme that is responsible for degradation of glucosinolates, presented in rapeseed to compounds that can harmful to human health (WILSKA-JESZKA 2000). Moreover, fungal toxins have strong carcinogenic, mutagenic, teratogenic, cytotoxic and hallucinogenic properties (PIONTEK 1999). A safe storage period is until the signs of moulding become visible to a naked eye. After this time, the chemical composition of seeds and fat is modified to such an extent that the consumption of products manufactured from such raw material becomes dangerous to human health (SZWED 2000).

This method for determining a safe storage period of rapeseed is simple, yet it may give rise to some reservations. The human eye gets tired quickly and is incapable of noting subtle changes in a visually-inspected object, whereas biochemical changes in the seed may be substantial. The knowledge of dynamics and direction of qualitative changes in fat allow for a determination of a safe storage period for seeds, thereby limiting losses of raw material used to manufacture good quality oil (RYNIECKI 2005).

Rapeseed harvested in Poland has usually water content in a range of 7% to 17%. There is a need to decrease water content in them to a level 6–7%, which allows to store safely with no risk of seed deterioration (RUDZIŃSKA et al. 2006). However, there are few studies on the impact of storage time prior to submission of seed drying. Moreover, studies carried out previously have been based on visual analysis of the state of moulding the seeds.

The objective of the paper was to determine, in the model studies, the impact of the changes in fat of rapeseed stored under increased moisture. The direction and speed of these changes were evaluated based on the regression equations determined for quality descriptors for fat: acid value (AV), peroxide value (PV), anisidine value (AnV), total colour (TC) and the composition of fatty acids.

## Material and Methods

The study was carried out with rapeseed of the Bios cultivar without any visible mechanical and microbiological damage (inspection under a magnifying glass). The seeds contained good quality fat (AV = 0.45 mg KOH $g^{-1}$, PV = 0.87 mEq $O_2$ $kg^{-1}$ and AV = 0.52). The seeds were divided into two samples of 300 g each. The seeds were moisturized: one sample to 11% and the other sample to 17% moisture and each was then equally separated into 10 sterile glass containers (the thickness of the seed layer was 1 cm). The seeds were stored in tightly-sealed glass desiccators at 20°C in an atmosphere of saturated solutions of sodium chlorine (NaCl) and potassium(V) nitrate ($KNO_3$) for the samples with 11% and 17% moisture, respectively. The generated conditions allowed us to preserve the moisture of the seeds at the established level (TYS et al. 2003, QUIRIJNS et al. 2004). The time of moisture equalization was 2 days and from this point storage of moist rapeseed samples were started. The storage test lasted for 21 days. From each desiccator, one glass container was taken for testing every 48 or 72 hours.

The percentage of mouldy seed content (MSC) was determined in the samples of seeds with 11% and 17% moisture at the established time intervals. The seeds were then ground in an IKA Labortechnik mill. Fat was extracted from the comminuted material with Folch's method (FOLCH et al. 1957). The following parameters were determined for lipids: acid value (AV) according to *Oleje i tłuszcze*... PN-EN ISO 660: 1998, peroxide value (PV) according to *Oleje i tłuszcze*... PN-A-86934: 1995, anisidine value (AnV) according to *Oleje i tłuszcze*... PN-EN ISO 6885: 2001, total colour (TC) according to *Oleje i tłuszcze*... PN-A-86934: 1995 and composition of fatty acids according to *Oleje i tłuszcze*... PN-EN ISO 5508: 1996. Methods selected in this study are comparable to AOCS methods WARNER and ESKIN 1995).

## Statistical Analysis

An arithmetic mean and standard deviation (all analysis were conducted in triplicate) for the parameters of each sample were determined. Obtained results were statistically analyzed using the Statictica 10.0 PL (StatSoft Poland) software. In order to indicate significance of differences between stored samples analysis of variance (ANOVA) with the Duncan test of $p \leq 0.05$ significance level was used. Moreover, there were determined Pearson correlation coefficients ($r$) between selected quality factors. The direction of changes in the values of quality factors during storage were described on the basis of determined regression equations and of calculated determination coefficients $R^2$.

## Results and Discussion

The moisture of rapeseed at 11% secured its safe storage for 21 days at 20°C (Figure 1*a–c*). For the seeds with 17% moisture, a rapid increase in MSC was observed (Figure 1*d–f*). The proportion of mouldy seeds increased proportionally during storage (by app. 3% after every 5 days) – Figure 2.

An increase in rapeseed moisture favours more rapid growth of moulds, which has been confirmed by many authors (BIELECKA et al. 1994, 1995, KORNIŁŁOWICZ-KOWALSKA et al. 2000). RYNIECKI (2005) reports that rapeseed with 12% moisture stored at 20°C does not show any visible signs of moulding for 5 weeks while on seeds with 16% moisture the first moulds become visible as early as after one day of storage. The results recorded in this study are comparable to the aforementioned. Storing rapeseed with 11% moisture did not cause any visible signs of moulding for 21 days (Figure 1*a–c*), whereas on the seeds with 17% moisture the symptoms were noted on the second day

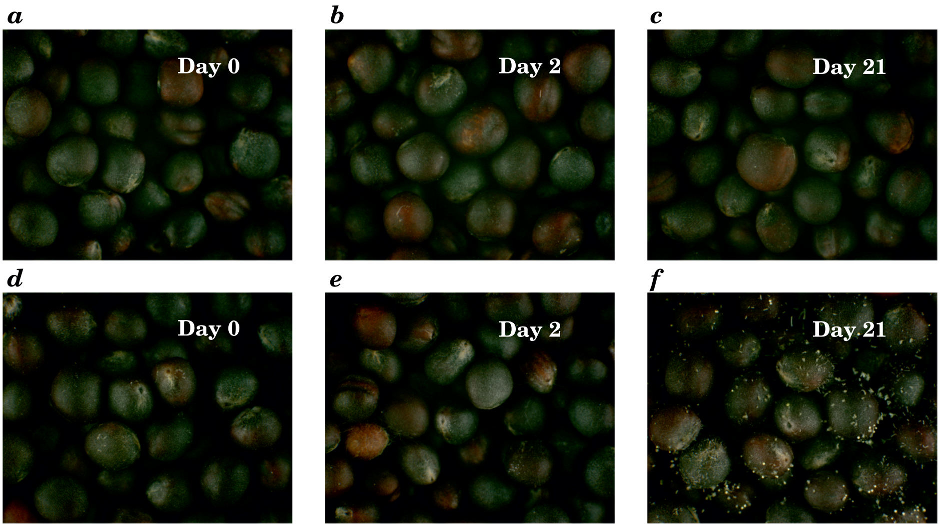


Fig. 1. Changes in moulding of rapeseed during storage: seeds with 11% moisture (*a–c*) and seeds with 17% moisture (*d–f*)

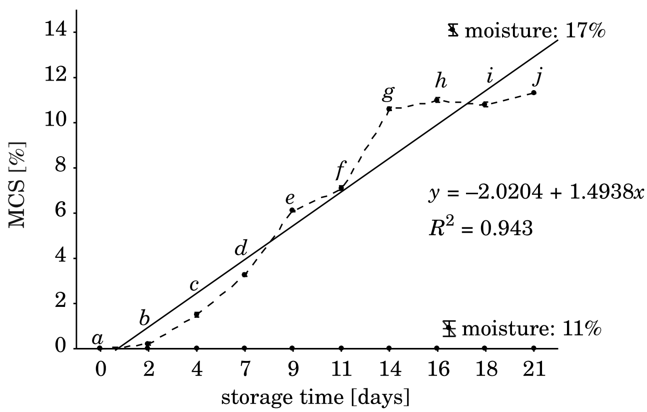


Fig. 2. Changes of mouldy seeds content (MSC) during storage seeds with 11% and 17% moisture; the different letters (*a, b, c* ...) for each moisture separately present significant differences ($p \leq 0.05$)

of storage (Figure 1*e*). Tańska et al. (2011) found that the amounts of moulds increased successively on the surface of rapeseed with 11% moisture. However, up to 15 days, the mould growth was slow and not detectable by either human eye or digital image system. The authors also demonstrated that quantity and type of moulds occurring on the rapeseed surface is connected to both the seed size and the area of rape cultivation. Burrels et al. (1980) suggest that the "clumping" is a good criterion for determining a safe storage period for moist rapeseed. In cited research seeds with 17% moisture start to agglomerate on day 4 during storage at 20°C. In order to prevent spoiling, seeds should be dried not later than on day 4.

The Polish Standard specifies the limit of mouldy seeds at not higher than 0.4%. Based on the conducted studies, it was found that moist seeds (17%) stored for up to 2 days (Figure 2) met the requirements for the proportion of mouldy seeds and might be used in production. However, until that time, some unfavourable quality changes may have taken place in fat which hinder the process of oil refinement (NIEWIADOMSKI 1993). Hydrolysis occurring in the presence of water may also provoke lipid deterioration. The growth of moulds additionally intensifies hydrolysis and causes rancidity. TYS et al. (2003, 2006) suggest that moist seeds may be stored at low temperatures. Temperatures below 10°C are appropriate for seeds with over 12% moisture. The mass of seeds stored at low temperatures showed lower biological activity and, therefore, the stability of the arrangement was preserved even at higher moisture. A long period of seeds cooling (for up to 4 weeks) is problematic and results from poor heat conductivity and, thus, there is a possibility of fat spoiling in seeds even at an early stage of storage.

An increase in AV and PV during storage was recorded for both samples of rapeseed (Figure 3, Figure 4) with the seeds of 17% moisture expressing a faster rate of these changes. The same results have been reported by other researchers (MILLS and SINHA 1980, OSEK 2000, TAŃSKA and ROTKIEWICZ 2003, SKIBA et al. 2005). The changes in AV of fat during storage of both rapeseed samples were described with a linear function (Figure 3) whereas the changes in the PV of fat were described with a square function (Figure 4). Moreover,

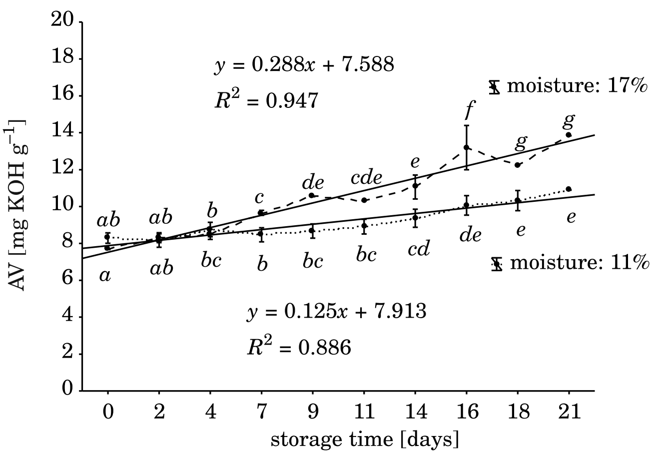


Fig. 3. Changes of acid value (AV) of fat during storage of rapeseed; the different letters (*a, b, c*, ....) for each moisture separately present significant differences ($p \leq 0.05$)

it was found that the changes in AV and PV for the seeds with 17% moisture correlated with the changes in MSC. The correlation coefficients were 0.95 and 0.93, respectively ($p \leq 0.05$, results not shown).

During the storage of biological plant material, hydrolytic and oxidative transformations of fat occur simultaneously. With higher moisture, the rate of these changes increases due to the activation of native enzymatic system and seeds respiration. Seeds are heated, which additionally potentiates hydrolysis and oxidation of fat. These conditions are favourable for mould growth and their metabolic processes also intensify hydrolysis and oxidation of fat in seeds. Furthermore, the damage caused by the penetration of moulds deep into the seed exposes fat to oxygen, facilitating auto-oxidation (SZWED 2000, SATHYA et al. 2009).

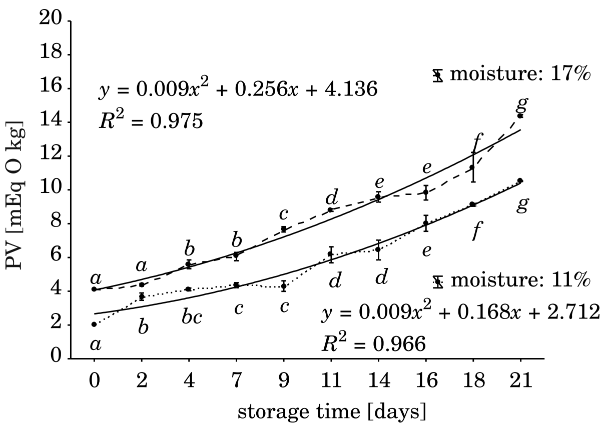


Fig. 4. Changes of peroxide value (PV) of fat during storage of rapeseed; the different letters (*a, b, c*, ...) for each moisture separately present significant differences ($p \leq 0.05$)

The Polish Standard for rapeseed sets the maximum AV at 3 mg KOH $g^{-1}$ of fat. The recorded results significantly exceeded this value as early as at the beginning of storage period and lipid spoiling probably occurred at the stage of seed moisturizing. The rapid increase in the number of acid value at the seed moisturizing may be due to the presence of microdamages that are not visible to the "naked eye", as well as the level of seed infestation and fungal characteristics. Microdamages caused by mechanical forces during harvest and transport can facilitate the distribution of moulds to the interior of the seeds through the broken coat (BIELECKA et al. 1994, MILLS 1996). NEGEDU (2012) reported differences in lipolytic activity of different mould species. The fast increasing of free fatty acid content was observed on castor oil mediums with

*Aspergillus flavus* and *Aspergillus niger*, while *Cephaliopora irregularis* and *Penicillium chrysogenum* showed low lipolytic activity.

The initial value of PV was 2.04 and 4.13 mEq $O_2$ $kg^{-1}$, respectively, for seeds with 11% and 17% moisture. It may be thus concluded that lipids in the seeds had a low initial degree of oxidation, regardless of the level of moisture. Comparable results for crude rapeseed oil have been reported by other authors (GUILLEN and CABO 2002, KOSKI et al. 2002).

The studies indicate that fat in moist seeds is not suitable for processing despite low PV. The evaluation of moulding degree is, thus, not a precise descriptor of fat quality. This is evidenced by the changes in AV and PV of fat in the seeds with 11% moisture, on which no signs of moulding were noted by means of visual inspection.

The recorded changes in AnV during storage indicate a process of secondary oxidation of lipids in the seeds with both 11% and 17% moisture (Figure 5). The AnV showed considerable fluctuations during the experiment, which hindered a determination of its changes over time and the formulation of regression equations. It may have resulted from the loss of volatile aldehydes and ketones, which are products of the secondary oxidation of fat (RICHARDS et al. 2005, WIJESUNDERA et al. 2008). It is assumed that fat of good quality should have an AnV below 2 units (SUBRAMANIAN et al. 2000). In the presented paper, the initial AnV was lower than the limits set by cited authors, but only up to day 2 of storage. However, the AnV procedure was developed to use the reaction primarily 2-alkenals with p-anisidine reaget (WARNER and ESKIN 1995). Under elevated moisture, fat in rapeseed may rapidly undergo hydrolytic rancidity. This process occurs when water is attached to double bounds of fatty acids and, as a result, hydroxy acids are formed (TYS et al. 2006, JACKOWSKA et al. 2008). When moulds grow, ketone rancidity may take place. A number of fungal bioconversions of medium chain fatty acids can occur, leading to the production of volatile methyl ketones and secondary alcohols. This process begins by $\alpha$- and $\beta$-dehydrogenation or $\beta$-oxidation on the residues of saturated fatty acids. Methyl ketones are the products of these transformations and their presence makes fat unusable for food processing (NIEWIADOMSKI 1993, TYS et al. 2006, JACKOWSKA et al. 2008). The important food spoilage fungi *Aspergillus*, *Penicillium*, *Cladosporium*, and *Fusarium* have all been shown to produce volatile methyl ketones and secondary alcohols from medium chain fatty acids (SCHNURER i in. 1999). ITO et al. (1990) reported that, for example, at the middle stage of *Aspergillus oryzae* growth the production of volatile compounds is maximum and decreases thereafter. Results of these analysis of mycelial growth and the production of volatile compounds show that the tendency of the almost volatile compounds corresponds better with the mycelial growth rate than the mycelial weight.

The tendency of 1-octen-3-ol is different from other volatile compounds; it increases with the cultivation time and does not decrease. SCHNEPF et al. (1991) reported that anisidine value shows to lack sensitivity when oil is stored for up to 20 weeks at 22°C in the dark, either with or without oxygen in the headspace.

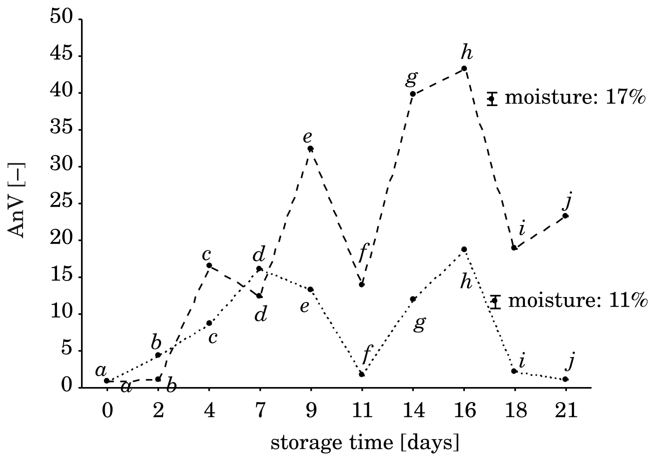


Fig. 5. Changes of anisidine value (AnV) of fat during storage of rapeseed; the different letters (*a, b, c*, ...) for each moisture separately present significant differences ($p \leq 0.05$)

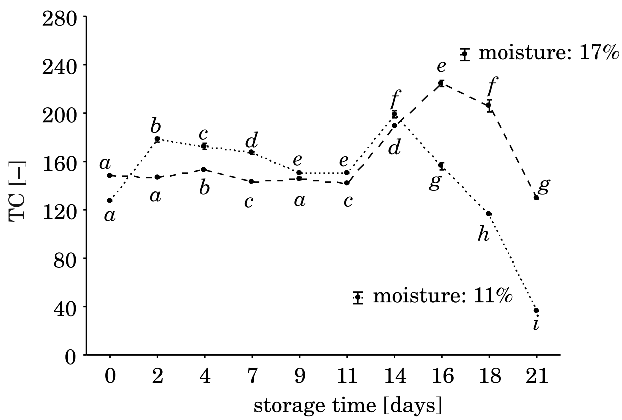


Fig. 6. Changes of TC of fat during storage of rapeseed; the different letters (*a, b, c*, ...) for each moisture separately present significant differences ($p \leq 0.05$)

It was impossible to determine the direction of TC changes in fat during storage (Figure 6). Until day 11, the TC values showed minor fluctuations and there was a subsequent increase in this descriptor followed by a decrease after day 14 and day 16 for the seeds with 11% and 17% moisture, respectively. The changes of TC during storage could be a result of two phenomena: mould growth on seeds and transformations of pigments which protect fat against oxidation.

Fungal cells multiply on the initial days of storage. Some mould species are capable of producing pigments that give them protection against sunlight. Depending on the species, moulds produce yellow, yellow-brown, brown, black and green pigments (TWARUŻEK 2006). Some species of *Aspergillus*, *Penicillium* and *Alternaria* genera are able to produce kojic acid with a yellow colour (SHIOMI et al. 2002, LI et al. 2003). Yellow phomaligols, belonging to cyclohexenone pigments, are produced by *Phoma lingam* fungus (ELBANDY et al. 2009). *Fusarium* moulds generate pink and reddish-brown pigments (VELMURUGAN et al. 2010). These compounds may absorb waves of similar lengths as carotenoids and chlorophylls, which explains an increase in TC with an expansive growth of moulds.

During the subsequent days of storage, carotenoids underwent massive oxidation. These pigments are natural antioxidants that protect rapeseed fat against the harmful impact of oxygen, light and temperature. They are oxidized more rapidly as they contain a high proportion of unsaturated bounds. Since they are transformed into short-chained, colourless compounds during this process (CAZZONELLI 2011), their transformations more significantly impacted the changes in TC.

During the experiment, there were several changes in the proportions of individual fatty acids (Figure 7). The biggest changes were noted for oleic, linoleic, linolenic and palmitic acids, the acids which constitute the major fraction of rapeseed fat. During storage, a proportion of polyunsaturated acids – linoleic (n-6 family) (Figure 7*a*) and linolenic (n-3 family) (Figure 7*b*) – decreased, whereas the proportion of saturated palmitic acid (Figure 7*c*) and monounsaturated oleic acid (Figure 7*d*) – increased. The changes in the proportion of fatty acids, independent on moisture of seeds, were presented by squared functions (Figure 7). The seeds with higher moisture showed a higher rate of changes in fatty acids.

An increase in the degree of saturation of double bounds in fatty acids is associated with providing higher oxidative stability of rapeseed oil (NEFF et al. 1997). The intensive oxidation and hydrolysis which accompany mould growth speed up the rate of double bound saturation in polyunsaturated fatty acids (VAN ETTEN and GOTTLIEB 1965). To a minor degree, some moulds may contribute to an increase in the content of saturated fatty acids because they are capable of synthesizing palmitic and stearic acids. For example, the most important fatty acids obtained from culture of *Aspergillus flavus* were palmitic acid (14.97%), stearic acid (10.82%), oleic acid (35.82%) and linoleic acid (34.26%), which represented 95% total fatty acid content (FRAGA et al. 2008). Also in *Penicillium chrysogenum*, *Penicillium citrinum* and *Penicillium*

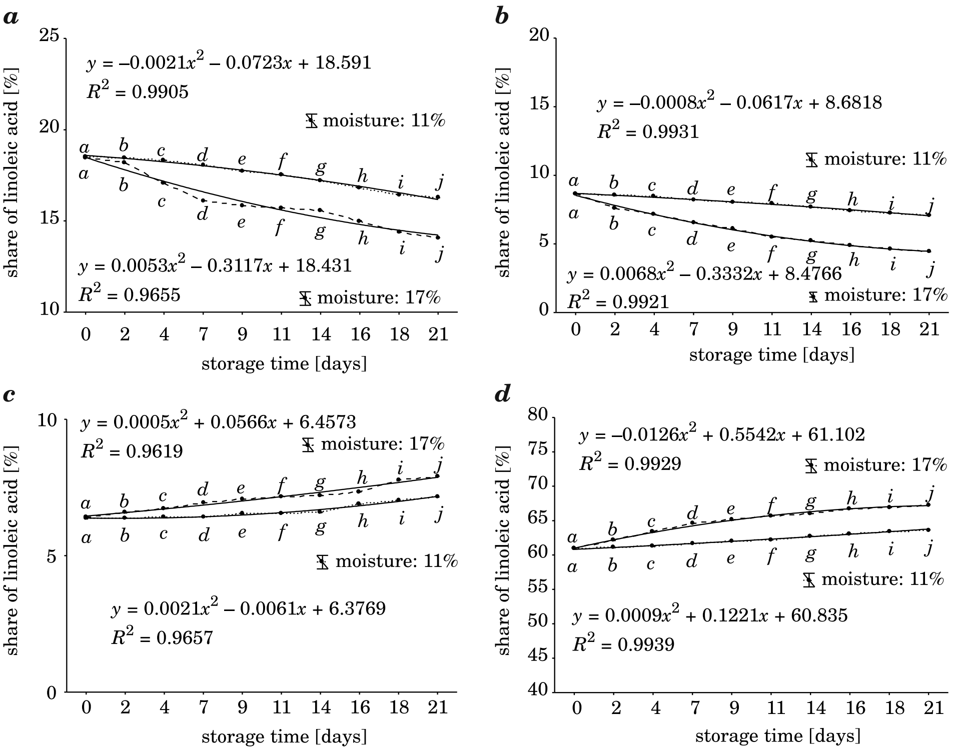


Fig. 7. Changes of fatty acid composition during storage of rapeseed: linoleic (*a*), linolenic (*b*), palmitic (*c*) and oleic (*d*) acids; the different letters (*a, b, c, ...*) for each moisture separately present significant differences ($p \leq 0.05$)

digitatum cultures, detected by KORNIŁŁOWICZ-KOWALSKA et al. (2000) on the surface of rapeseed, palmitic acid accounted for approximately 17% and stearic acid for 4–10% of the total fatty acid content (LOPES DA SILVA et al. 1998). ETTEN and GOTTLIEB (1965) found that during growth of *Penicillium antrovenetum*, share of linoleic acid decreased from 65.7 to 31.5%, whereas the percentage of palmitic and stearic acids increased from 13.9 to 19.5% and from 1.5 to 12.8%, respectively.

The changes in the proportions of individual fatty acids influenced the changes in their ratios (Table 1). A decrease in the content of n-3 and n-6 acids and a change in their ratio are unfavourable from a nutritional point of view. In the human body, eicosanoids are formed from n-3 and n-6 acids and they have the opposite action. With their regulatory role in numerous processes, it is important to supply essential fatty acids in a diet in proper amounts and in appropriate proportions (KOLANOWSKI 2007). According to FAO/WHO recommendations, fatty acids of the n-3 family should constitute 1–2% and those

Table 1

Fatty acid composition of the stored rapeseed

| Storage time [days] | 0 | 2 | 4 | 7 | 9 | 11 | 14 | 16 | 18 | 21 |
|---|---|---|---|---|---|---|---|---|---|---|
| Seeds with 11% of moisture | | | | | | | | | | |
| Share of saturated fat acids [%] | $9.89^{a*} \pm 0.00$ | $9.92^{b} \pm 0.01$ | $9.94^{c} \pm 0.01$ | $10.01^{d} \pm 0.01$ | $10.15^{e} \pm 0.01$ | $10.22^{f} \pm 0.01$ | $10.31^{g} \pm 0.01$ | $10.60^{h} \pm 0.01$ | $10.78^{i} \pm 0.01$ | $10.92^{j} \pm 0.00$ |
| Share of monounsaturated fatty acids [%] | $62.92^{a} \pm 0.01$ | $63.10^{b} \pm 0.00$ | $63.27^{c} \pm 0.01$ | $63.73^{d} \pm 0.01$ | $64.04^{e} \pm 0.00$ | $64.28^{f} \pm 0.01$ | $64.79^{g} + 0.01$ | $65.13^{h} + 0.01$ | $65.52^{i} \pm 0.01$ | $65.70^{j} \pm 0.01$ |
| Share of polyunsaturated fatty acids [%] | $27.19^{a} \pm 0.00$ | $26.98^{b} \pm 0.01$ | $26.79^{c} \pm 0.01$ | $26.26^{d} \pm 0.01$ | $25.81^{e} \pm 0.01$ | $25.50^{f} \pm 0.00$ | $24.90^{g} \pm 0.00$ | $24.27^{h} \pm 0.01$ | $23.70^{i} \pm 0.00$ | $23.38^{j} \pm 0.01$ |
| n-6/n-3 fatty acids ratio | $2.14^{a} \pm 0.00$ | $2.17^{b} \pm 0.01$ | $2.17^{b} \pm 0.01$ | $2.19^{c} \pm 0.00$ | $2.19^{c} \pm 0.01$ | $2.22^{d} \pm 0.00$ | $2.24^{e} + 0.01$ | $2.27^{f} + 0.01$ | $2.27^{f} \pm 0.01$ | $2.29^{g} \pm 0.01$ |
| Seeds with 17% of moisture | | | | | | | | | | |
| Share of saturated fatty acids [%] | $9.92^{a} \pm 0.01$ | $10.10^{b} \pm 0.01$ | $10.38^{c} \pm 0.01$ | $10.60^{d} \pm 0.00$ | $10.81^{e} \pm 0.01$ | $10.95^{f} \pm 0.01$ | $11.01^{g} \pm 0.01$ | $11.21^{h} \pm 0.01$ | $11.74^{i} \pm 0.01$ | $11.91^{j} \pm 0.00$ |
| Share of monounsaturated fatty acids [%] | $62.97^{a} \pm 0.01$ | $64.13^{b} \pm 0.01$ | $65.38^{c} \pm 0.00$ | $66.69^{d} \pm 0.01$ | $67.24^{e} \pm 0.01$ | $67.82^{f} \pm 0.00$ | $68.19^{g} \pm 0.00$ | $68.91^{h} \pm 0.01$ | $69.22^{i} \pm 0.00$ | $69.56^{j} \pm 0.01$ |
| Share of polyunsaturated fatty acids [%] | $27.11^{a} \pm 0.01$ | $25.77^{b} \pm 0.01$ | $24.24^{c} \pm 0.01$ | $22.71^{d} \pm 0.01$ | $21.95^{e} \pm 0.00$ | $21.23^{f} \pm 0.01$ | $20.80^{g} \pm 0.01$ | $19.88^{h} \pm 0.01$ | $19.04^{i} \pm 0.01$ | $18.53^{j} \pm 0.01$ |
| n-6/n-3 fatty acids ratio | $2.13^{a} \pm 0.01$ | $2.39^{b} \pm 0.00$ | $2.39^{b} \pm 0.01$ | $2.45^{c} \pm 0.00$ | $2.59^{d} \pm 0.01$ | $2.86^{e} \pm 0.01$ | $2.98^{f} \pm 0.01$ | $3.08^{g} \pm 0.01$ | $3.08^{g} \pm 0.01$ | $3.17^{h} \pm 0.01$ |

* – means in the same line followed by different letters are significantly different ($p \leq 0.05$)

of the n-6 family should constitute 5% to 8% of the energy provided with the daily diet. The n-6/n-3 ratio should thus range from 1:1 to 4:1 (DYBKOWSKA 2004). The recorded results fall within this range, yet a significant increase in the n-6/n-3 ration with a simultaneous reduction in polyunsaturated acids (by almost 10%) in fat from the seeds with 17% moisture indicates a rapid decrease in the nutritional values of these fat.

## Conclusions

Unfavourable changes in the quality of fat were recorded during the storage of rapeseed with elevated moisture at 20°C. A more intensive growth of moulds and course of qualitative changes were observed in the seeds with 17% moisture. After 4 days of storage, the degree of moulding exceeded the permissible limits. The rate of fat hydrolysis in rapeseed during storage was varied. For the first four days, the AV of lipids in the seeds with 11% and 17% moisture were at comparable levels, but in subsequent days the difference between the values of this discriminant increased. The rate of fat oxidation was similar for both samples of rapeseed with a slight advantage for the seeds with 17% moisture. Oxidation of fat in the stored samples of rapeseed resulted in an increase in the proportion of monounsaturated fatty acids and a decrease in the proportion of polyunsaturated fatty acids. These changes reduced the nutritional values of fat.

On the basis of the obtained results it can be seen that even short-term storage of moist rapeseed lead to unfavorable changes in the seeds fat. Making decision only on the basis of the participation of moldy seeds and acid value about the suitability of seeds for edible oil processing can lead to wrong conclusions. Oil obtained from the seeds stored in an increased moisture condition will require also more drastic refining conditions. In addition, mold metabolites passing into the oil may raise doubts. Therefore rapeseed with moisture of 11% should be dried no later than 4 days after harvest, and seeds with a moisture of 17% no later than 2 days after harvest.

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