



Top-dressing treatment of spring barley to modify its quality

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Abstract:

New barley products can be developed by modifying the content of bioactive components in the grain through breeding, as well as improving its quality at lower fertilizer costs. We aimed to study the effects of the genotype, growth conditions, and top-dressing application of nitrogen and organo-mineral fertilizers on the chemical composition of barley grain.

The barley varieties Novichok, Rodnik Prikamya, and Pamyaty Rodinoy were grown under normal (2020) and dry (2021) field conditions. The plants were top-dressed with mineral (CAS; SpetsKhimAgro, Kirovo-Chepetsk, Russia) or organo-mineral (Amino Start and Alfastim; Polydon® Agro, Moscow, Russia) fertilizers in the tillering or heading phases. The contents of protein, starch, fat, and crude fiber in the grain were analyzed with an INFRAMATIC 8620 instrument (Perten Instruments, Stockholm, Sweden).

The CAS fertilizer reduced protein, fat, and fiber by 4.5–8.3% (Novichok) during the drought and increased starch by 2.1% (Novichok), fiber by 14.2% (Rodnik Prikamya), and fat by 18.9% (Pamyaty Rodinoy) under normal humidity. Amino Start applied under normal conditions increased starch by 2.9% and reduced protein and fat by 7.8–8.9% in Rodnik Prikamya, as well as increased protein and fat by 14.4 and 6.3%, respectively, but reduced starch by 5.1% in Pamyaty Rodinoy. Alfastim applied under normal conditions reduced the content of protein by 10.7% (Rodnik Prikamya), but increased it by 3.6–7.2% in the other cultivars. It also increased fiber by 22.8% in Rodnik Prikamya, but decreased it by 18.6% in Pamyaty Rodinoy. Finally, this fertilizer decreased fat by 12.7% in Rodnik Prikamya, but increased it by 9.8% in Pamyaty Rodinoy. In the drought, the fertilizers Alfastim and Amino Start increased the protein content by 5.2–12.2% in Rodnik Prikamya and Pamyaty Rodinoy.

Top-dressing barley plants with mineral or organo-mineral fertilizers can modify the grain composition (up to 10.4% of fiber, 3.6% of starch, and 7.5% of protein and fat), depending on the consumer's requirements.

Keywords: *Hordeum vulgare*, cultivar, protein, fiber, starch, fat, yield

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INTRODUCTION

The barley (*Hordeum vulgare* L.) is one of the oldest cereals in the world that was first cultivated in the eighth millennium BC [1]. Currently, it ranks fourth by yield and crop area globally. First used as human food, barley began to be mainly used as animal feed and brewing grain, partly due to the increased importance

of wheat and rice [2, 3]. Due to its ability to grow in a wide range of climatic conditions, barley is widely cultivated in those countries where the production of other cereals is difficult [4]. Today, barley is grown in more than 100 countries around the world. In 2020, its world production amounted to 152 Mt, following rice (508.7 Mt), wheat (758.3 Mt), and corn (1207.1 Mt).

In 2019, Europe accounted for over 94.2 Mt (60%) of global barley production, followed by Asia (22.6 Mt, 16%) and North and Central America (14.5 Mt, 9%). Russia, France, and Germany have produced over 10% of the world barley production each over the past ten years [5]. In 2020, the total barley area was 51 Mha, following rice (164 Mha), corn (201 Mha), and wheat (219 Mha) [6]. Barley yield averaged 1.8 t/ha in the 1960–1970s, 2.2 t/ha in the 1980–1990s, and 2.7 t/ha since the 2000s. In 2016, it broke the barrier of 3 t/ha, with the highest yield of 3.1 t/ha in 2019.

In 2020, per capita barley consumption was highest in North Africa, with 19.5 kg in Morocco, 17.2 kg in Ethiopia, and 16.0 kg in Syria, according to FAO. This indicator is much lower in the developed countries, with 0.8 kg in the European Union, 0.6 kg in the USA, and 0.3 kg in Canada. Globally, per capita barley consumption in 2020 was 1 kg compared to 18.4 kg for corn, 53.9 kg for rice, and 67.4 kg for wheat [5].

Barley is commonly used as feed, food, and brewing grain, accounting for 65–75, 15, and 8%, respectively [7–9]. The last decade has seen an increased interest in using barley as food for humans [10]. Human health and well-being are often associated with a balanced diet. Therefore, consumers look for functional foods that have a preventative effect on chronic diseases in addition to replenishing essential nutrients [11, 12].

Chemically, barley has a high content of protein, fiber, and vitamins, as well as a low content of fat and sugar [13]. It is rich in natural antioxidants and beta-glucan, a unique soluble fiber, as well as bioactive compounds including health-benefitting phenols and lipids [14–16].

The rising interest in barley has coincided with increased obesity and chronic diseases, such as cancer and heart disease. According to medical studies, a prolonged intake of food rich in barley flour may protect the body against hyperlipidemia, diabetes, atherosclerosis, and cancer [17, 18]. Cereals such as barley and oats have been shown to reduce the risk of developing type 2 diabetes [19].

The positive characteristics of barley suggest growing possibilities for its use in food products [20, 21]. Currently, the use of barley grain is determined by various factors. The first factor is its content of protein, beta-glucans, starch, and non-starchy polysaccharides [8]. Foreign breeders, selecting new barley varieties to be used as feed, food, and brewing grain, commonly evaluate only two parameters: the hull content (chaffy or hullless grains) and the beta-glucan content. Malt barleys are almost always chaffy and low in beta-glucan. Food barleys are usually hullless and have an average content of beta-glucan. Feed barleys can be both chaffy and hullless, with a low content of beta-glucan. It is common practice that if barley grain grown for brewing does not meet certain standards, it is redirected to the feed market at a substantially lower price [22]. Food barley can also be used as feed if it is of poor quality.

Unlike foreign breeders, the Russian State Standards (R 53900-2010 for feed barley and 5060-86 for brewing barley) take into account the contents of protein, crude fiber, and ash to assess the quality of barley grain and its uses. The quality of feed barley is also determined by its fat content [23]. These components are largely dependent on the weather conditions during the growing season. For example, Bindereif *et al.* showed significant changes in protein and fat contents in climatically contrasting years [24]. Yusov *et al.* reported the effect of weather conditions on the contents of protein, starch, and fat [25]. Bohačenko *et al.* established the effect of humidity in greenhouses and phytotrons on the contents of protein and starch in barley grain [26].

On the other hand, agronomists have practiced split nitrogen application over the last decade. In particular, they first apply nitrogen during sowing and then use it as a top dressing during the critical phase of its consumption by the plants [27]. The effect of top dressing is commonly evaluated by two main indicators, the yield and the protein content in the grain. Therefore, it is of practical significance to study the effect of top-dressing application of nitrogen fertilizers on the contents of nutrients (starch, crude fiber, and fat) in barley grain grown under different humidity conditions. In addition, barley's high genotype diversity provides ample opportunities for identifying and breeding cultivars for specific uses [28, 29]. One of the key priorities in breeding is to identify the grain's genetic ability for more efficient nitrogen use and high yields, as well as to ensure its quality at lower nitrogen costs [30, 31].

To develop new products and breed new cultivars, we need to be aware of variations in the contents of bioactive components in barley grain and their mutual relations [30]. Therefore, we aimed to study the effect of the genotype, growing conditions and top-dress application of nitrogen and organo-mineral fertilizers on the chemical composition of barley grain.

STUDY OBJECTS AND METHODS

Our experiments were carried out in 2020–2021 in the field crop rotation of the Department of Agrochemistry and Crop Farming at the Federal Agricultural Research Center of the North-East (Kirov, Russia). The experimental site had a sod-podzolic, medium loam soil formed on the eluvium of Perm clays. Its arable layer had the following agrochemical parameters: $\text{pH}_{\text{KCl}} = 4.59\text{--}5.00$ units, mobile phosphorus – 148.0–157.0 mg/kg of soil, mobile potassium – 127.0–140.0 mg/kg of soil, and humus – 1.74–2.00%. The site's area was 10 m², with the plots systematically placed with an offset. The experiments were conducted in quadruple. Pre-sowing mineral fertilizers NPKS (25:4:4:2) were applied at an amount of 0.3 t/ha, which ensured at least 3.5–4.5 t/ha of spring barley grain, according to previous studies.

Our study objects were spring barley cultivars named Novichok, Rodnik Prikamya, and Pamyaty

Rodinoy. The cultivars were created for grain-fodder use by I.N. Shchennikova, a Corresponding Member of the Russian Academy of Sciences, in the Federal Agricultural Research Center of the North-East. Rodnik Prikamya and Pamyaty Rodinoy are on the list of the most valuable barley varieties in the Russian Federation.

Polydon® Amino Start and Alfastim® (Polidon® Agro Company, Moscow, Russia) were used as organo-mineral fertilizers. They contain macro-, meso-, and microelements in combination with amino acids and low-molecular-weight peptides to increase the intake of mineral fertilizers at the initial stages of vegetation. Top-dressing application of Alfastim in the second half of the growing season is recommended to increase the yield and quality of the crop. These liquid organo-mineral fertilizers of a new generation are based on humic and fulvic acids, natural growth agents, microelements, amino acids, and polysaccharides. They are widely used in the cultivation of grain crops, winter rapeseed, corn, and soybeans [32].

Polydon® Amino Start contains 200 g/L of L-amino acids, 130 g/L of nitrogen (total N), 75 g/L of phosphorus (P₂O₅), 25 g/L of potassium (K₂O), 15 g/L of magnesium (MgO), 6 g/L of iron (Fe), 3 g/L of manganese (Mn), 3 g/L of zinc (Zn), 3 g/L of copper (Cu), 3 g/L of boron (B), 1 g/L of molybdenum (Mo), and 0.05 g/L of cobalt (Co). It is used to stimulate the growth of the root system and increase the plant's productive tillering, stress resistance, and yield.

Alfastim® contains triterpene acids (100 g/L), L-amino acids (50 g/L), carbohydrates (50 g/L), auxin-cytokinin complex (10 g/L), membrane-active substances (10 g/L), and vitamins B₁, B₇, PP (5 g/L). The fertilizer activates the most important metabolic reactions, regulates the absorption of nutrients, stimulates the excretion of the root system, and increases the permeability its cell walls. In addition, it has immune-stimulating, antioxidant, and adaptogenic effects, increasing resistance to water scarcity, salt and chemical stress, as well as pathogen and pest attacks.

The liquid mineral fertilizer CAS 28 (carbamide-ammonium saltpeter mixture, or urea ammonium nitrate in English literature) (SpetsKhimAgro, Kirovo-Chepetsk, Russia) is the only nitrogen fertilizer that

contains nitrate, ammonium, and amide nitrogen and does not contain free ammonia, which can significantly reduce unproductive losses of nitrogen [33, 34]. It is used to activate the growth of the plant during the intensive development of its above-ground part and the formation of flower buds, the key to the harvest.

The experiment's scheme was as follows:

- control (without treatment of vegetative plants with mineral and organo-mineral fertilizers);
- top-dressing with Polidon® Amino Start (1 L/ha) in the tillering phase;
- top-dressing with CAS 28 (30 L/ha) in the tillering phase; and
- top-dressing with Alfastim® (1 L/ha) in the heading phase.

Harvesting was carried out with a Wintersteiger combine (Wintersteiger Seedmech, Ried im Innkreis, Austria) in the phase of full wax ripeness. The contents of crude protein, starch, crude fiber, and fat in barley grain were measured with an INFRAMATIC 8620 analyzer (Pertin Instruments, Stockholm, Sweden) according to the manufacturer's guidelines. The data were expressed as a percentage of the grain's dry weight.

Statistical processing of the data was carried out using descriptive statistics, correlation and variance analyzes in Microsoft Office Excel 2013 (Microsoft, Redmond, WA, USA).

In May, June, and the first half of July 2020, the weather was unstable in temperature and rainfall – dry in the first ten days of a month, with light, sometimes heavy rains in the second or third ten-day periods (Table 1). The second half of July was moderately warm, with frequent, sometimes heavy rains. August was warm to moderately warm, mostly dry or with little rainfall. On the whole, the prevailing weather conditions in the 2020 growing season were favorable for the cultivation of spring barley.

In May 2021, the weather was predominantly warm and hot, with both dry and rainy periods. June and July were moderately warm to hot, as well as dry with occasional rain. Some places had soil drought. August was warm to hot with local rains. On the whole, the vegetation conditions in 2021 can be described as moderately dry.

Table 1 Weather conditions during the growing season (Kirov weather station)

Month	Average t, °C	Deviation from the norm, °C	Rainfall, mm	% of the norm	Sum of effective temperatures, °C
2020					
May	12.2	+0.9	89	154	226.6
June	15.3	–1.2	41	47	535.0
July	20.5	+1.6	100	110	1016.0
August	15.1	–0.5	61	73	1327.9
2021					
May	15.0	+3.1	58	107	320.4
June	19.9	+3.5	63	78	767.3
July	19.2	+0.3	92	113	1207.2
August	18.8	+2.9	38	51	1634.8

Table 2 Effect of top-dressing fertilization on spring barley yield, t/ha

Cultivar	Mineral fertilizers			
	Control	CAS	Amino Start	Alfastim
2020				
Novichok	2.95 ^a	3.38 ^b	4.22 ^c	4.39 ^c
Rodnik Prikamya	5.03 ^a	5.37 ^b	5.01 ^a	4.86 ^a
Pamyaty Rodinoy	5.17 ^a	5.48 ^b	5.99 ^c	4.94 ^a
2021				
Novichok	1.25 ^a	2.22 ^b	2.24 ^b	2.02 ^b
Rodnik Prikamya	2.19 ^a	2.76 ^c	2.31 ^{ab}	2.45 ^b
Pamyaty Rodinoy	1.75 ^b	1.55 ^{ab}	1.75 ^b	1.29 ^a

^{a, b, c} – The parameter values accompanied by the same letters do not differ statistically according to the Duncan criterion at $p > 0.05$

RESULTS AND DISCUSSION

Under normal humidity conditions of the 2020 growing season, Pamyaty Rodinoy was the most productive cultivar, with an average grain yield of 5.40 t/ha, compared to 3.74 t/ha for Novichok (Table 2).

The top-dressing fertilization with CAS 28, Polidon® Amino Start, and Alfastim® increased the barley yield by an average of 8.3, 15.8, and 8.2%, respectively. The pre-sowing application of nitrogen fertilizers is insufficient for barley, since it has low needs in this element in the early stages of growth, and precipitation leads to its unproductive loss from the soil [27].

In a study by Plaza-Bonilla *et al.*, the top-dressing application of CAS 28 resulted in an 18% increase in barley yield compared to the control [35]. The authors recommended top-dressing to increase barley yield in the Mediterranean countries in the years with normal humidity. Glukhovtsev *et al.* reported an 8.4–17.8% increase in barley yield from the top-dressing of four spring barley cultivars with mineral and organo-mineral fertilizers [36]. In contrast to our study and those by the above authors [35, 36], Tanaka and Nakano found no effect from the top-dressing of barley with nitrogen fertilizers at normal air temperatures but they reported a positive effect at high temperatures [37]. This might be due to the fact that the Japanese researchers worked with winter barley, rather than spring barley, which grows predominantly at low air temperatures, with only a 2–3°C difference between the average temperatures during the study years and the average annual data.

The cultivars under study reacted to top-dressing differently. Particularly, Novichok was the most responsive to improved nutrition, showing a statistically significant increase of 14.6–48.8% in barley yield. Rodnik Prikamya and Pamyaty Rodinoy had a significant increase of 6.0–6.7% with the application of CAS 28 in the tillering phase. Pamyaty Rodinoy also showed a significant yield increase of 15.9% when top-dressed with Polidon® Amino Start. The treatment with Alfastim® in the heading phase was effective only for the Novichok cultivar (48.8% increase). Rodnik Prikamya was the least responsive to the application of

the fertilizers. Our findings were consistent with those in the previous studies [36, 38].

Under the dry conditions of 2021, top-dressing proved significantly more effective than in normal humidity conditions, which was consistent with the conclusions made by Glukhovtsev *et al.*, Tanaka and Nakano, and Kastury *et al.* [36, 37, 39]. In particular, the application of CAS 28, Polidon® Amino Start, and Alfastim® increased the barley yield by 25.8, 21.4, and 11.0%, respectively, compared to the control. Rodnik Prikamya showed a significantly higher yield (25–52%) than the other cultivars. The top-dressing of this cultivar with Polidon® Amino Start did not lead to higher yield, while the other two fertilizers (CAS 28 and Alfastim®) increased its yield by 12–26%. The Novichok cultivar, just like in 2020, responded positively to all the fertilizers, with an increase in grain yield of 62–79%. The Pamyaty Rodinoy cultivar showed no response to the treatment with CAS 28 and Polidon® Amino Start, and had a 26% decrease in yield when top-dressed with Alfastim®.

According to the two-factor ANOVA, under the normal humidity conditions of 2020, the effects of the cultivar's genotype, top-dressing fertilization, and interaction of factors on yield variability were 64.8, 7.3, and 15.1%, respectively. Under the dry conditions of 2021, these indicators amounted to 47.9, 12.0, and 21.1%, respectively.

Over 90% of barley grain's dry matter consists of three main components: starch (59.1–61.6%), fiber (18.16–21.46%), and crude protein (11.74–13.64%) [40]. Therefore, while increasing the productivity of spring barley cultivars, we should maintain their quality indicators. According to State Standard R53900-2010, the content of crude protein in feed barley of classes 1, 2, and 3 must be at least 130 g/kg (13%), 120–130 g/kg (12–13%), and 120 g/kg (12%), respectively.

Table 3 shows a significant effect of genotypic differences and top-dressing fertilization on the protein content in barley grain, which is consistent with the previous studies [30, 41].

As can be seen, the protein contents in our study were within the typical protein contents for spring barley of 9–13% according to Sterna *et al.*, Ortiz *et al.*, and Filippov *et al.* or 7–30% according to Jaeger *et al.* and Gong [30, 42–45].

According to Table 3, the Polidon® Amino Start and Alfastim® fertilizers raised the quality of the Rodnik Prikamya cultivar from class 3 to class 2 under the dry conditions of 2021. We also found that Polidon® Amino Start raised the quality of the Pamyaty Rodinoy cultivar from class 3 to class 1 under the normal humidity conditions of 2020. In the other cases, the barley grain corresponded to class 3.

Published data indicate that the protein content in barley grain is determined by a combination of genetic, environmental, and agronomic factors [46]. Large amounts of nitrogen and abiotic stress (drought and high temperatures) increase the protein content in

Table 3 Effect of top-dressings on protein content in barley grain, %

Treatment	Barley cultivars		
	Novichok	Rodnik Prikamya	Pamyaty Rodinoy
	2020		
Control	10.92 ^a	11.96 ^c	11.46 ^a
CAS 28	10.87 ^a	11.93 ^c	11.61 ^a
Polidon® Amino Start	10.84 ^a	11.03 ^b	13.11 ^b
Alfastim®	11.32 ^b	10.68 ^a	11.46 ^a
	2021		
Control	11.92 ^b	11.27 ^a	10.82 ^a
CAS 28	11.38 ^a	11.72 ^a	10.98 ^{ab}
Polidon® Amino Start	11.59 ^{ab}	12.48 ^b	11.72 ^b
Alfastim®	11.40 ^a	12.65 ^b	11.71 ^b

^{a, b, c} – The parameter values accompanied by the same letters do not differ statistically according to the Duncan criterion at $p > 0.05$

Table 4 Effect of top-dressings on fiber content in barley grain, %

Treatment	Barley cultivars		
	Novichok	Rodnik Prikamya	Pamyaty Rodinoy
	2020		
Control	3.49 ^{ab}	2.81 ^a	3.45 ^b
CAS 28	3.95 ^b	3.21 ^b	3.06 ^b
Polidon® Amino Start	3.64 ^b	2.81 ^a	2.92 ^a
Alfastim®	3.33 ^a	3.45 ^b	2.81 ^a
	2021		
Control	5.52 ^c	4.83 ^a	4.78 ^a
CAS 28	5.06 ^{ab}	4.92 ^a	4.73 ^a
Polidon® Amino Start	5.00 ^a	5.03 ^a	4.63 ^a
Alfastim®	5.31 ^b	4.98 ^a	4.77 ^a

^{a, b, c} – The parameter values accompanied by the same letters do not differ statistically according to the Duncan criterion at $p > 0.05$

grain [18, 47]. In our study, we found varietal differences in the cultivars' response to the same fertilizers in the years with contrasting humidity. In 2020 (normal humidity), the Alfastim® fertilizer increased the protein content in the Novichok cultivar and reduced it in the Rodnik Prikamya cultivar. In 2021 (drought), however, this fertilizer had the opposite effect on these cultivars. The Pamyaty Rodinoy cultivar benefited from all the fertilizers in dry conditions. Polidon® Amino Start had a positive effect on Pamyaty Rodinoy in both years, while for Rodnik Prikamya, its effect was positive in dry conditions and negative under normal humidity. Novichok was not affected by this fertilizer in both years. In dry conditions, it had a protein decrease of 4.5% after being treated with the CAS 28 fertilizer.

The dry conditions of 2021 halved the effect of the cultivar's genotype on the protein variability (23.3 and 12.2% for 2020 and 2021, respectively) and doubled the effect of top-dressings (5.4 and 11.4% for 2020 and 2021, respectively). The protein content correlated with barley yield in 2020 ($r = 0.701$), but their relationship became statistically insignificant under dry conditions.

Crude fiber is a coarse, indigestible component of plants. The higher its content in farm animal feed, the lower is the feed's nutritional value. At the same time, all animals need fiber in moderation to stimulate their intestinal tract [18]. We found that in all the variants of treatment, the resulting grain belonged to class 1, with a content of crude fiber under 70 g/kg (7%), varying within 2.81–5.52% (Table 4).

In our work, fiber contents (Table 4) were significantly lower than those obtained in the studies by Šterna *et al.*, Biel and Jacyno, and Prasadi and Joye, where total fiber in barley ranged within 11–34% [30, 40, 48]. However, our findings were consistent with the data of Ul Ain *et al.* and Sumina and Polonsky, who reported the content of non-starch cell wall polysaccharides of 3–8% [47, 49]. These discrepancies can be partly explained by different expressions of fiber

content, i.e., in relation to absolutely dry grain mass (in the above studies) and air-dry grain mass (in our study).

In scientific literature, the term “fiber” often refers to several different, although chemically close, substances. For example, Li and Komarek differentiate between insoluble, soluble, and total fiber [50]. Insoluble fiber includes cellulose, water-insoluble hemicellulose, and lignin, i.e., structural components of the cell wall. Soluble fiber is composed of a variety of non-cellulose poly- and oligosaccharides.

In the study by Prasadi and Joye, the contents of soluble, insoluble (cellulose, arabinoxylan and lignin), and total fiber in barley grain were 2.6–5.0, 12.0–22.1, and 10.1–27.9%, respectively [48]. According to State Standard R 53900-2010, feed barley of class 1 must contain no more than 7% of crude fiber, while that of class 3, at least 9%. Since we studied feed cultivars, rather than brewing grain, they were low in crude fiber. Crude fiber was determined by treating crushed grain samples with concentrated solutions of sulfuric acid (removing starch and hemicellulose) and then with caustic potassium (removing lignin). As a result, only cellulose remained in the sample. With this approach, our fiber contents coincided with the cellulose content (4.3–4.6%) reported by Biel and Jacyno [40].

Under the dry conditions of 2021, the top-dressings did not significantly affect the fiber content in the Rodnik Prikamya and Pamyaty Rodinoy cultivars, while significantly reducing it in the Novichok cultivar (by 3.8–9.4%). Under the normal humidity conditions of 2020, Novichok did not show any statistically significant response to the fertilization. Pamyaty Rodinoy had a reduced fiber content when treated with Polidon® Amino Start and Alfastim® (by 15.3–18.7%), while Rodnik Prikamya, on the contrary, had a higher content when treated with CAS 28 and Alfastim® (by 14.2–22.8%).

The effect of the top dressings on fiber variability was 4.9% in 2020. However, under the dry conditions of 2021, it was statistically insignificant. Yet, the effect

Table 5 Effect of top-dressings on starch content in barley grain, %

Treatment	Barley cultivars		
	Novichok	Rodnik Prikamya	Pamyaty Rodinoy
	2020		
Control	52.51 ^a	48.47 ^a	50.21 ^b
CAS 28	53.59 ^b	49.38 ^{ab}	50.63 ^c
Polidon® Amino Start	53.91 ^b	49.89 ^b	47.66 ^a
Alfastim®	53.68 ^{ab}	50.62 ^b	50.43 ^{bc}
	2021		
Control	51.00 ^{ab}	48.87 ^a	50.78 ^b
CAS 28	50.20 ^a	49.05 ^a	52.04 ^c
Polidon® Amino Start	50.95 ^{ab}	48.64 ^a	48.76 ^a
Alfastim®	51.31 ^b	48.51 ^a	49.09 ^a

^{a, b, c} – The parameter values accompanied by the same letters do not differ statistically according to the Duncan criterion at $p > 0.05$

of the cultivar's genotype remained almost unchanged, regardless of humidity (28.8 and 27.2% for 2020 and 2021, respectively).

We found no statistically significant correlations between the contents of fiber and protein in the cultivars ($p \leq 0.05$) in both years. There is no consensus in literature on these two indicators. For example, Biel and Jacyno and Filippov *et al.* reported higher contents of crude protein in barley with lower contents of starch and fiber [40, 43]. However, Šterna *et al.* revealed close positive relationships between these indicators [30]. This might be due to differences in the plant growth conditions and in the specific genotypes selected for study.

Starch is the third dominant component of spring barley grain that has a significant impact on its nutritional quality. Whole grain barley may contain 58–77% of starch [51]. In our study, the content of starch was somewhat lower (Table 5), but it was within the range reported by Doroshenko *et al.* and Izydorczyk *et al.* [15, 18].

The Rodnik Prikamya cultivar reacted to top-dressing fertilization by changing its starch content. With no significant effect observed in 2021 (drought), Polidon® Amino Start and Alfastim® had a slight positive effect (2.9–4.4%) in 2020 (normal humidity). Pamyaty Rodinoy reacted to the top-dressings more strongly, compared to the other cultivars. In both years, the CAS 28 fertilizer significantly increased the starch content in this cultivar (by 0.8–2.4%), while Polidon® Amino Start, on the contrary, decreased this indicator (by 5.1–4.0%). Alfastim® slightly reduced the starch content (by 3.3%) in dry conditions. Novichok's starch content was not significantly affected by the fertilizers in 2021. However, under normal humidity, it increased (by 2.1–2.6%) under the influence of CAS 28 and Polydon® Amino Start. Thus, we observed a significant effect of genotypic differences and growth conditions on the starch content.

Table 6 Effect of top-dressings on fat content in barley grain, %

Treatment	Barley cultivars		
	Novichok	Rodnik Prikamya	Pamyaty Rodinoy
	2020		
Control	1.82 ^a	1.57 ^b	1.43 ^a
CAS 28	1.85 ^a	1.58 ^b	1.70 ^c
Polidon® Amino Start	1.92 ^a	1.43 ^a	1.52 ^b
Alfastim®	1.82 ^a	1.37 ^a	1.57 ^b
	2021		
Control	2.44 ^b	2.20 ^a	2.17 ^a
CAS 28	2.29 ^a	2.15 ^a	2.31 ^{ab}
Polidon® Amino Start	2.30 ^a	2.16 ^a	2.28 ^{ab}
Alfastim®	2.43 ^b	2.20 ^a	2.34 ^b

^{a, b, c} – The parameter values accompanied by the same letters do not differ statistically according to the Duncan criterion at $p > 0.05$

According to ANOVA, the top-dressing fertilization had no effect on starch variability under drought conditions and a weak effect under normal humidity (4.7%). The effect of genotypic differences decreased by half in dry conditions (from 60.9 to 24.2%).

As for relationships between starch, protein, and fiber, we found statistically significant negative correlations between protein and starch contents ($r = -0.737$ in 2020 and $r = -0.623$ in 2021), as well as a close positive relationship between starch and fiber contents in 2020 ($r = 0.751$). The negative correlation between protein and starch was confirmed by the studies of Biel and Jacyno and Filippov *et al.*, although it was not always manifested in the works by Yu *et al.* and Zhou *et al.* [40, 43, 52, 53]. On the other hand, in contrast to our data, Memon *et al.* reported a negative relationship between starch and fiber contents [54].

Fat is another important component of barley grain, which affects its nutritional value. According to literature, its content in barley is 1–3% [55, 56]. Our data were consistent with this content (Table 6).

Similarly to the parameters above, the top-dressings had different effects on the fat content in barley grain depending on its genotype (cultivar) and growth conditions. In particular, the fat content in Novichok was not affected in 2020 (normal humidity), but in 2021 (drought), it decreased by 5.8–6.0% under the influence of CAS 28 and Polidon® Amino Start. Rodnik Prikamya, however, had the opposite reaction. Its fat content reduced by 8.9–12.7% when treated with Polidon® Amino Start and Alfastim® in 2020, with no effect in 2021. Pamyaty Rodinoy was affected positively by all the three fertilizers in 2020, with an increase in fat of 6.2–18.9%. However, under the dry conditions of 2021, only Alfastim® had a statistically significant effect on this cultivar, increasing its fat by 7.8%.

According to ANOVA, the effect of the cultivar on fat variability was twice as high under normal humidity compared to dry conditions (69.8 and 35.3%, respectively), with almost the same effect of top-

dressing fertilization (6.1 and 5.6%). Thus, it was the genotypic differences in responding to the drought that had the most significant effect on the fat content. This parameter correlated positively with the starch content ($r = 0.576\text{--}0.781$) and negatively with the yield ($r = -0.630\text{--}0.662$) in both years of the study. Our data were consistent with those of other researchers, who found that the weather conditions can significantly change the effectiveness of top-dressings [35, 57].

Our study revealed significant differences in the effect of the top-dressings on different cultivars of spring barley. In particular, all of the three fertilizers increased the yield of Novichok in both years. Under normal humidity, this increase amounted to 14.5% from CAS 28 and 43–49% from the other two fertilizers. In dry conditions, however, all the fertilizers were equally efficient, increasing the yield by 62–79%. The Rodnik Prikamya cultivar had its yield increased under normal humidity by CAS 28 (6.8%) and in dry conditions by CAS 28 (26.0%) and Alfastim® (13.2%). The Pamyaty Rodinoy was positively affected only under normal humidity by CAS 28 and Polidon® Amino Start, with a yield increase of 6.0 and 15.9%, respectively. In dry conditions, Alfastim® had a negative effect, decreasing the yield by 26.3%. Similar differences were observed in the effect of the fertilizers on the grain quality.

CAS 28 significantly reduced the contents of protein (4.5%), fat (6.1%), and fiber (8.3%) in the Novichok cultivar in dry conditions and increased its starch content (2.1%) under normal humidity. The other two cultivars were positively affected by this fertilizer. Rodnik Prikamya had its fiber increased by 14.2% under normal conditions. Pamyaty Rodinoy had its fat increased by 18.9% under normal humidity and starch increased by 0.8–2.5% in both years.

Polidon® Amino Start decreased the contents of fat and fiber in the Novichok cultivar by 5.7–9.4% in dry conditions and increased its starch by 2.7% under normal humidity. However, this fertilizer had the opposite effect on the contents of protein, fat, and fiber in the other two cultivars under normal humidity. It increased starch (2.9%) and decreased protein (7.8%) and fat (8.9%) in Rodnik Prikamya. In Pamyaty Rodinoy, on the contrary, it increased protein (14.4%) and fat (6.3%) and reduced starch (5.1%). Yet, in dry conditions, both cultivars had a higher protein content (by 8.3–10.7%).

Alfastim® increased the protein content (3.6%) in Novichok under normal conditions but decreased it during the drought (4.4%). It had the opposite effect on Rodnik Prikamya, reducing its protein (10.7%) under normal humidity and increasing it (12.2%) in dry conditions. As for Pamyaty Rodinoy, Alfastim® increased its protein (7.2%) under dry conditions but had no effect on this parameter under normal humidity. We also found that under normal conditions, this fertilizer

increased the fiber content in Rodnik Prikamya (22.8%), but decreased it in Pamyaty Rodinoy (18.6%). However, it had the opposite effect on the fat content, decreasing it in Rodnik Prikamya (12.7%) and increasing it in Pamyaty Rodinoy (9.8%). In addition, Alfastim® increased fat in Pamyaty Rodinoy in the drought (7.8%) and starch in Rodnik Prikamya under normal humidity (4.4%), as well as decreased fiber in Novichok in dry conditions (3.8%).

CONCLUSION

According to our results, the top-dressing of spring barley plants with various fertilizers led to a statistically significant increase in grain yield, especially in dry conditions (an average of 10–15%, with a maximum increase of 50–80% for the Novichok cultivar, compared to the control). However, the vegetation conditions (year) and top-dressings (specific fertilizer) can also change the chemical composition of grain, especially its fiber content (the coefficients of variation for Novichok, Rodnik Prikamya, and Pamyaty Rodinoy being 7.37, 10.38, and 9.08%, respectively, in 2020 with normal humidity). The starch content was the least variable: from 0.49% for Rodnik Prikamya to 3.65% for Pamyaty Rodinoy in the dry year of 2021. The variability in protein and fat was the highest for Pamyaty Rodinoy (6.73 and 7.47% under normal humidity; 4.18 and 3.38% in the drought). The lowest variability for all the parameters was found in Novichok.

These data indicate a possibility of both genetic (through traditional breeding) and agronomic (top-dressing treatment) changes in the chemical composition of spring barley grain grown for food or feed. The highest increase in fiber was observed in the Rodnik Prikamya cultivar treated with the fertilizers CAS 28 (14.2%) and Alfastim® (22.8%) under normal conditions of 2020. The protein content can be increased by treating Rodnik Prikamya and Pamyaty Rodinoy with Alfastim® and Polidon® Amino Start in dry conditions (5.2–12.2%), as well as by applying Polidon® Amino Start to Pamyaty Rodinoy under normal conditions (14.4%). Polidon® Amino Star and Alfastim® can also be used to change the fat content in barley grain, namely to increase it (by 8.2–8.3% in Pamyaty Rodinoy) or decrease it (8.9–12.7% in Rodnik Prikamya), depending on the consumer's requirements.

Thus, the top-dressing treatment of particular spring barley cultivars with specific fertilizers can significantly affect their use in the production of functional feeds and foods.

CONTRIBUTION

The authors were equally involved in writing the manuscript and are equally responsible for plagiarism.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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