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CARBON AND SILICA NANOSTRUCTURES IN THE PROTECTION OF SPRING BARLEY FROM DISEASES IN THE NORTH-WEST RUSSIA

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Abstract

Spring barley (*Hordeum vulgare* L.) is the main grain fodder crop, annually occupying about 40 % of the sown area in the North-West Russia. In recent years, there has been a clear interest in the world and domestic science to use of nanomaterials and nanotechnologies in plant protection, which is due to their unique properties and high efficiency at low concentrations. In this work, for the first time, the effect of carbon and silica sol nanocompositions on seed infection, damage to spring barley plants by root rot and leaf diseases is shown. It was determined that a stronger protective effect was manifested when using nanocompositions on the spring barley variety Ataman with a longer growing season and more susceptible to major diseases. For the first time, an additive effect has been established that enhances the protective functions of chemical or biological fungicides with the possibility of reducing their dosage when combined with nanocomposites in the treatment of seeds and vegetative plants. Our goal was to study the effectiveness of new compositions based on carbon and silica sol nanomaterials in protecting spring barley from diseases in the North-West Russia. The studies were carried out at the experimental base of the Menkovsky branch of the Agrophysical research institute (Gatchinsky District, Leningrad Province) in 2017-2018. At the first stage of research in 2017, the effectiveness of two promising nanocompositions for the protection of spring barley from root rot and leaf diseases was studied. Two experiments were carried out on Leningradsky and Ataman varieties of spring barley with different vegetation periods: on the treatment of seed material and vegetative plants with nanocompositions. The silica sol composition of NKteos was synthesized according to the original sol-gel technology based on acid hydrolysis followed by polycondensation of tetraethyl ester of orthosilicic acid or tetraethoxysilane, with the addition of macro- and microelements salts solutions and dopants — a charge of detonation nanodiamond doped with boron, or a titanium dioxide in the form of anatase to the sol. Preparation of a nanocomposition based on fullerene derivatives with methionine or threonine was carried out by dissolving microelement compounds in water and adding 0.001 % (for seed treatment) or 0.00001 % (for foliar treatment) solution of the amino acid derivative of C_{60} fullerene with threonine or with methionine. Experiment variants also included the combined use of nanocompositions with chemical and biological fungicides, as well as fungicides with silicon-containing chelated microfertilizer. Grain contamination with phytopathogens was determined using nutrient media. The development of root rot was t assessed in the phases of germination, tillering, budding and heading, leaf diseases — in the beginning of barley earing, then in 10, 20 and 30 days. At the second stage of research in 2018, the effectiveness of the technological scheme for the use of new nanocompositions in the protection of spring barley of the Leningradsky variety from diseases was evaluated. The experiment included two blocks: the treatment with nanocompositions of seeds, the treatment of seeds and vegetative plants. It is shown that the studied nanocompositions in their pure form turned out to be ineffective in protecting spring barley from root rot and leaf diseases. The decrease in the development of root rot on the early ripe variety Leningradsky did not exceed 5.3 %, on the variety Ataman it was 15.3-57.7 % ($p < 0.05$). The development of the main disease of the crop — helminthosporium spots on the two upper leaves of barley plants of the Leningradsky variety decreased by 16-22 %, of the Ataman variety — by 20-42 % ($p < 0.05$). The results of seed treatment allow us to assume that the effect of the silica sols composition is longer, since it extended to the development of helminthosporium leaf spots (decrease in damage by 7.5-15.4 %, $p < 0.05$ compared to control) and is due to the ability to activate plant metabolism and immunity. The effect of the nanocomposition based on the fullerene C_{60}-methionine derivative is more apparent due to a decrease in seed infection and primary signs of infection during the emergence of barley seedlings. The most effective for the protection of spring barley from root and leaf diseases was the combined treatment of seeds with a silica sol nanocomposition and the chemical fungicide Insure™ Perform, KS, followed by a triple treatment of vegetative plants with a nanocomposition based on a C_{60}-threonine derivative and a single treatment with the chemical fungicide Zantara, CE. Reducing the dose of a chemical preparation is advisable only if a weak manifestation of the disease is expected. High biological and economic efficiency, comparable to the result of fungicidal treatment with 100 % application rate of the preparation, was ensured by the combined use of silicon containing chelate microfertilizer SCM-G and fungicide (50 % application rate), as well as nanocomposition based of the C_{60} fullerene amino acid derivatives with methionine and fungicide (50 % application rate).

Keywords: *Hordeum vulgare* L., spring barley, root rot, leaf diseases, plant protection products, fungicides, nanomaterials, fullerene C_{60}, amino acid derivatives, C_{60} with methionine, C_{60} with threonine, silica sol, tetraethoxysilane. dopants, charge of detonation nanodiamond, titanium dioxide, anatase

In recent years, there has been a clear interest in the use of nanomaterials and nanotechnologies in agriculture, due to their unique properties and high efficiency at low concentrations [1-3]. Due to their small size and electrical neutrality, nanomaterials easily penetrate the cell membrane, and due to their large specific surface, they have a high reactivity [4-6]. Promising nanomaterials that can potentially increase plant resistance to biotic and abiotic stressors include carbon and silica nanocomposites [7-8].

Carbon nanocomposites are compositions based on water-soluble derivatives of C_{60} or C_{70} fullerene and a number of microelements, as well as physiologically active compounds [9, 10]. Recently, the number of new synthesized amino-, carboxy-, polyhydroxy- and other fullerene derivatives, which are convex closed polyhedra, composed of an even number of three-coordinated carbon atoms, has been growing [11]. Since their discovery in 1985, which was awarded the Nobel Prize in Chemistry in 1994, fullerenes and their derivatives have been increasingly used in engineering, in medicinal chemistry and in cosmetology [12-14].

Silica-based mesoporous supports, the so-called mesoporous silicate materials, have been the subject of much research since Mobil Oil (USA) synthesized mesoporous silica materials in 1992 with an ordered mesopore structure, narrow pore size distribution, high specific surface [15, 16]. In contrast to the microporous structure of zeolites already known at that time (pore diameter of about 1.5 nm), mesoporous materials have a pore size of about 3-5 nm. This class of materials served as a prototype for the further development of silica-based nanoporous structures, including silica matrices created using the original sol-gel technology [17] with the inclusion of organic molecules, nanosized particles of metals, their oxides, nanodiamonds, carbon nanotubes, which provide enhanced functional characteristics silica sols.

At the Agrophysical Research Institute (API), together with the St. Petersburg State University (SPbSU), the First St. Petersburg State Medical University (PSPbSMU), the Institute of Silicate Chemistry (ISC RAS), biologically active nanocompositions have been developed, e.g., complex microfertilizers based on water-soluble derivatives of C_{60} fullerenes [18, 19] and silica-sol nanocomposites based on tetraethoxysilane with solutions of macro- and microelements doped with a mixture of detonation nanodiamond or titanium dioxide in the form of anatase [20-22]. Aqueous suspensions of detonation nanodiamond or charge are of particular interest as precursors of composite materials or as biologically active additives, since colloidal carbon nanoparticles in an aqueous dispersion medium are the most chemically active [23]. Along with this, detonation nanodiamond and its charge doped with boron, as well as a number of metal nanoparticles (magnetized iron, aluminum, copper, gold, silver, silicon, zinc and zinc oxide, titanium dioxide, cerium oxide, etc.) have biocidal properties against bacteria, viruses and micromycetes. Their inclusion in the composition of silica sols is promising for enhancing the phytoprotective function [24-26].

The creation of preparations was based on the following principles: environmental safety, simplicity of the technological process, low cost, efficiency in small doses and availability to plants. Under controlled and field conditions, the effect of foliar treatment with nanocomposites based on fullerene derivatives on the growth, development, grain productivity of ereals and vegetable crops, their resistance to oxidative stress has been established [18, 19], and the ability to form a film (shell) around the seed under seed treatment with tetraethoxysilane-based silica sols has been shown [21, 22]. The presence of a shell with a selected qualitative and quantitative composition of components on the surface of the seeds ensured the stimulation of plant growth at the initial stages of development [21, 22].

With the presence of the properties of immunomodulators and adaptogens, there are great prospects for the use of the obtained nanocompositions in the protection of cultivated plants from phytopathogens. The first data on the positive effect of the treatment of spring barley seeds with C_{60} fullerene derivatives with methionine and threonine, as well as their nanocompositions on plant resistance to damage by the root rot pathogen Cochliobolus sativus (S. Ito & Kurib.) Drechsler ex Dastur [20], were obtained. The mechanism of their action is not associated with the regulation of the number of microorganisms on the surface of seeds. Apparently, it is due to the ability to activate the metabolism and antioxidant abilities of plants [20]. Additionally, it was found that the sol-gel composition are capable of increasing plant resistance to phytopathogens not only by activating plant immunity, but also by regulating the abundance of microorganisms, including potential pathogenes, on the surface of seeds [20].

Currently, the prospects for the use of nanopreparations in the protection of plants from harmful organisms are being extensively studied [27, 28]. In the Northwestern region of Russia, such studies are in demand for many agricultural crops, including spring barley, which annually occupies approx. 40% of the sown area [29].

In this work, for the first time, the effect of carbon and silica-sol nanocompositions on seed infection, as well as damage to spring barley plants by root rot and leaf diseases, is shown. It is shown that a stronger protective effect was manifested when using nano-compositions on the spring barley variety Ataman with a longer vegetation period and greater susceptibility to major diseases. For the first time, the presence of an additive effect was established in the combined treatment of seeds and vegetative plants with nano-compounds with chemical or biological fungicides potentially reducing the dosage of the preparations.

Our goal was to study the effectiveness of new compositions based on carbon and silica nanomaterials in the protection of spring barley from diseases in the North-West of the Russian Federation.

Materials and methods. The studies were carried out at the experimental base of the Menkovsky branch of the Agrophysical Institute (API, Gatchinsky district, Leningrad Province) in 2017-2018. The soil of the experimental fields is soddy-slightly podzolic sandy loam. The 23 cm soil layer is arable, the content of organic matter is 0.70-0.77%, mobile compounds of phosphorus and potassium (according to Kirsanov) are 266-298 and 153-167 mg/kg, respectively, pH_{KCl} 5.1-5.7.

At the first stage of work in 2017, the effectiveness of two promising nanocompositions for the protection of spring barley (*Hordeum vulgare* L.) from root rot and leaf diseases was assessed. In accordance with the methodological guidelines [30], two experiments were performed on cv. Leningradsky (64-75 days) and cv. Ataman (79-98 days) with different vegetation periods, the seeds and vegetative plants were treated with nanocomposites. To evaluate the efficiency of pre-sowing application of nanocomposites, the following treatments were used: 1 — water (control); 2 — Insure Perform, KS (Insure™ Perform, BASF, Germany; 0.4 l/t); 3 — Inshur Perform, KS (0.2 l/t); 4 — silica-ash composition based on 1 wt.% tetraethoxysilane with macro- and microelements and nanodiamond charge from detonation (NKteoa) (1.0 l/t); 5 — composition of fullerene derivative with methionine and trace elements (NFm) (1.0 l/t); 6 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 7 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 8 — NFm (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 9 — NFm (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 10 — Vitaplan, joint venture (AgroBioTechnology, Russia; 20 g/t); 11 — NKteoa (1.0 l/t) + Vitaplan, SP (20 g/t); 12 — NFm (1.0 l/t) + Vitaplan, SP (20 g/t).

The NKteoa silica-ash composition was synthesized according to the original sol-gel technology (21, 22) based on acid hydrolysis followed by polycondensation of tetraethyl ester of orthosilicic acid (TEOA), with the addition of solutions of salts of macro- and microelements and dopants (a mixture of detonation nanodiamond alloyed with boron, or titanium dioxide in the form of anatase). The composition of silica sols is 1 vol.% TEOA + microelement solution (pH 2-3) + 0.1% charge in the form of anatase with boron or 0.1% TiO_2. The solution of macro- and microelements included N, P, K, Ca, Mg, S, Fe, B, Zn, Cu, and Mn compounds [21, 22]. The mixture of detonation nanodiamond was enriched with boron directly during the in situ explosion and contained 0.96% boron, 14.7% detonation nanodiamond, 80.84% non-diamond forms of carbon, and 0.96% non-combustible impurities [25].

The preparation of a nanocomposition based on fullerene derivatives with threonine (NFtr) or methionine (NFm) was carried out by dissolving microelement compounds in water and adding 0.001% (for seed treatment) or 0.00001% (for foliar treatment) of a solution of the amino acid derivative of C_{60} fullerene with threonine or methionine [9].

Sol concentrations, as well as solutions of C_{60} fullerene amino acid derivatives with threonine or methionine (10.0 mg/l when treating seeds and 0.1 mg/l when treating vegetative plants), were selected based on the results of assessing the reactions of plants in vegetation experiments at the agro-biopolygon of the Agrophysical Institute (API) [19-21].

Inshur Perform, KS was used as a chemical fungicide for seed treatment (reference), the flow rate of the working fluid was 10 l/t. In continuation of our previous studies [31, 32], the experiment included the treatment of seed with biofungicide Vitaplan, SP.

Pre-sowing treatment of barley seeds was carried out by a previously developed method [21]. The seeds were soaked with constant stirring using a UED-20 magnetic stirrer (UED Group, Russia) in water (control) or in a silica sol solution for 10 min, after which they were dried at room temperature in air until dry and then at 30 °C for 50 min in an oven ShS-80-01 MK SPU (OAO Smolenskoye SKTB SPU, Russia). The treated seeds were stored at room temperature for 2 days before sowing. The treatment of seed material with chemical and biological preparations was carried out using a Hege 11 unit (Wintersteiger AG, Austria), designed for wet dressing of small batches of seeds.

The layout of the test plots (2 m^2) was randomized, with a 4-fold repetition. The predecessor was winter rye (*Secale cereale* L.) cv. Slavia. The seeds were sown manually.

In this and all experiments described below, tillage included autumn plowing and pre-sowing cultivation. Before sowing, ammonium nitrate was added at the rate of 60 kg/ha of active weight; in the tillering phase of barley, the herbicide Sekator, VDG (Sekator, Bayer CropScience, Germany; 0.15 kg/ha) was treated. The seeding rate is 5 million germinating seeds/ha. For spring barley yield assessment, sheaves were collected from a 1 m^2 of each plot at the phase of full ripeness. Under laboratory conditions, productive stem density, grain weight per ear and 1000-grain weight were measured.

Grain contamination with phytopathogens was determined using nutrient media [33]. Accounting for the development of root rots was carried out according to the relevant guidelines (30) on 30 plants from each plot in the phases of germination, tillering, budding and heading.

To evaluate the effectiveness of plant treatment with nanocomposites, experimental design was as follows: 1 — control (treatment of plants with water); 2 — Zantara, CE (Zantara, Bayer CropScience, Germany; 0.8 l/ha); 3 — Zantara, CE (0.4 l/ha); 4 — silicon-containing chelate microfertilizer KKhM-G (3.0 l/ha); 5 — NFm (1.0 l/ha); 6 — NFtr (1.0 l/ha); 7 — KKhM-G (3.0 l/ha) + Zantara, CE (0.8 l/ha); 8 — KKhM-G (3.0 l/ha) + Zantara, CE (0.4 l/ha); 9 — NFm (1.0 l/ha) + Zantara, CE (0.8 l/ha); 10 — NFm (1.0 l/ha) + Zantara, CE (0.4 l/ha); 11 — NFtr (1.0 l/ha) + Zantara, CE (0.8 l/ha); 12 — NFtr (1.0 l/ha) + Zantara, CE (0.4 l/ha).

Silicon-containing chelated microfertilizer KKhM-G, developed at the API (34), is an environmentally friendly biostimulant and plant resistance inductor, the main active components of which are silicon, microelements and a chelating agent (humic acids isolated from high-moor peat of a low degree of decomposition). The mass fraction for humic acids was 0.12, for Fe 9.7, B 2.07, Mn 1.66, Si 5.33, Cu 1.60, Co 1.76, Zn 1.66, Mo 3.85, S 8.17%. The working solution was applied at a rate of 300 l/ha.

As a reference, a chemical fungicide for the treatment of vegetative plants Zantara, CE, was used, the flow rate of the working solution was 300 l/ha. The repetition of treatments for microfertilizers and nano-compositions is 3-fold, starting from the tillering phase with an interval of 7 days, for a chemical fungicide - once in the phase of the beginning of barley heading.

A randomized layout of 10 m^2 plots with a 4-fold repetition was used, the predecessor was winter rye cv. Slavia. Sowing was carried out with a Lemken soliter seeder (Lemken GmbH & Co. KG, Germany), the seeding rate was 5 million germinating seeds/ha. The plants were treated using a Solo 475P knapsack sprayer (Solo Kleinmotoren GmbH, Germany).

Leaf diseases were recorded at the beginning of earing, then after 10, 20 and 30 days on 10 stems in three sites on each plot in accordance with the guidelines [30].

At the second stage of research in 2018, the effectiveness of the technological scheme for the use of new nanocompositions in protecting spring barley of the Leningradsky variety from diseases was evaluated. The experiment included two blocks, the first with the treatment of seed material with nanocomposites, the second with the treatment of seeds and vegetative plants.

Block A included treatment of seeds with preparations and vegetative plants with water: 1 — control (seed treatment with water) + water; 2 — Inshur Perform, KS (0.4 l/t) + water; 3 — Inshur Perform, KS (0.2 l/t) + water; 4 —

NKteos (1.0 l/t) + water; 5 — NKteos (1.0 l/t) + Inshur Perform, KS (0.4 l/t) + water; 6 — NKteos (1.0 l/t) + Inshur Perform, KS (0.2 l/t) + water. Block B included treatments of seeds with preparations and vegetative plants with a solution of a nanocomposition based on the amino acid derivative of C_{60} fullerene with threonine (NFtr) at a previously selected concentration of 0.1 mg/l: 7 — treatment of seeds with water + treatment of plants with NFtr (1.0 l /ha); 8 — Inshur Perform, SC (0.4 l/t) + NFtr (1.0 l/ha); 9 — Inshur Perform, SC (0.2 l/t) + NFtr (1.0 l/ha); 10 — NKteoa (1.0 l/t) + NFtr (1.0 l/ha); 11 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t) + NFtr (1.0 l/ha); 12 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t) + NFtr (1.0 l/ha).

The preparation of nanocompositions, seed and plant treatments were carried out as in previous experiments. Plants were treated 3-fold, starting from the tillering phase, with a 7-day interval. The plots (2 m^2 each, with a 4-fold repetition) were randomized. The predecessor was winter wheat cv. Moskovskaya 56. Seeding manual. The plants were treated using a Solo 475P knapsack sprayer.

Statistical processing of the obtained data was carried out using analysis of variance in the Statistica 6.0 program (StatSoft, Inc., USA). In the calculations, parametric statistics methods were used based on mean values (*M*) and standard errors of the means (±SEM), 95% confidence intervals, and the least significant difference of LSD at $p < 0.05$ (LSD_{05}).

Results. Seed infection acts as the primary focus of infection of the root system of plants. Phytoexamination of seed material showed an additive effect from the combined use of the chemical fungicide Inshur Perform, KS in full application rate with the tested carbon and silica nanocompositions against the fungus *Cochliobolus sativus* (S. Ito & Kurib.) Drechsler ex Dastur, the main causative agent of helminthosporium-fusarium root rot (Table 1). In addition, the high efficiency of the silica-sol composition against fungi of the genus Fusarium (85.7-100%) was noted. The effects of the use of the biological product Vitaplan, SP, including in combination with nanocompositions, were unstable and concerned mainly Fusarium spp. and Alternaria spp. The results obtained are consistent with previously published data on the practical absence of a biocidal effect of the studied carbon and silica compositions against *C. sativus* [20].

1. Efficiency of nanocompounds, chemical and biological fungicides and their combinations against seed infection in spring barley (*Hordeum vulgare* L.) (*n* = 10, *M*±SEM; Leningrad Province, 2017)

Variant	Cultivar	Microbiota					
		pathogenic				saprotrophic	
		Cochliobolus sativus		*Fusarium* spp.		*Alternaria* spp.	
		DI, %	BE, %	DI, %	BE, %	DI, %	BE, %
1. Control (water)	L	23.0±3.26		3.3±0.87		37.0±5.24	
	A	47.0±4.87		7.0±2.04		41.0±6.02	
2. Inshur Perform, KS (0.4 l/g)	L	8.0±2.22	65.2	0.0	100.0	4.0±0.79	89.2
	A	29.0±4.41	38.3	0.0	100.0	19.0±5.25	53.7
3. Inshur Perform, KS (0.2 l/g)	L	22.0±2.98	4.3	0.0	100.0	13.0±2.88	64.9
	A	43.0±4.68	8.5	9.0±2.54	0.0	38.0±4.54	7.3
4. NKteoa (1.0 l/g)	L	40.0±4.75	0.0	0.0	100.0	34.0±4.87	8.1
	A	45.0±5.25	4.3	1.0±0.25	85.7	48.0±5.81	0.0
5. NFm (1.0 l/g)	L	48.0±5.98	0.0	6.0±1.94	0.0	17.0±2.91	54.1
	A	43.0±4.75	8.5	5.0±1.65	28.6	47.0±5.64	0.0
6. NKteoa (1.0 l/g) + Inshur Perform, KS (0.4 l/g)	L	2.0±0.31	91.3	0.0	100.0	27.0±5.04	27.0
	A	29.0±4.47	38.3	0.0	100.0	8.0±2.34	80.5
7. NKteoa (1.0 l/g) + Inshur Perform, KS (0.2 l/g)	L	17.0±2.88	26.1	0.0	100.0	16.0±2.88	56.8
	A	52.0±5.03	0.0	2.0±0.38	71.4	18.0±3.05	56.1
8. NFm (1.0 l/g) + Inshur Perform, KS (0.4 l/g)	L	5.0±1.14	78.3	0.0	100.0	15.0±2.54	59.5
	A	22.0±3.05	53.2	4.0±0.95	42.9	6.0±1.85	85.4
9. NFm (1.0 l/g) + Inshur Perform, KS (0.2 l/g)	L	21.0±3.47	8.7	3.0±0.74	9.1	7.0±2.03	81,1
	A	57.0±5.54	0.0	10.0±3.01	0.0	4.0±0.86	90,2
10. Vitaplan, SP (20 g/t)	L	12.0±2.61	47.8	0.0	100.0	14.0±2.54	62,2
	A	54.0±5.35	0.0	9.0±2.74	0.0	25.0±4.05	39,0

Continued Table 1

11. NKteoa (1.0 l/t) + Vitaplan,	L	41.0±4.44	0.0	0.0	100.0	19.0±3.02	48,6
SP (20 g/t)	A	59.0±5.89	0.0	3.0±0.65	57.1	35.0±4.88	14,6
12. NFm (1.0 l/t) + Vitaplan, SP	L	24.0±3.35	0.0	0.0	100.0	32.0±4.45	13,5
(20 g/t)	A	85.0±8.61	0.0	4.0±0.84	42.9	4.0±0.78	90,2
LSD_{05} (cultivar)		4,44		2.10		5.25	
LSD_{05} (preparations)		5,35		3.03		7.02	
LSD_{05} (cultivar, preparations)		5,91		4.21		8.10	

N o t e. L — Leningradsky, A — Ataman; DI — disease incidence, BE — biological effectiveness. Each sample consists of 10 grains. For detailed descriptions, see the Materials and methods section.

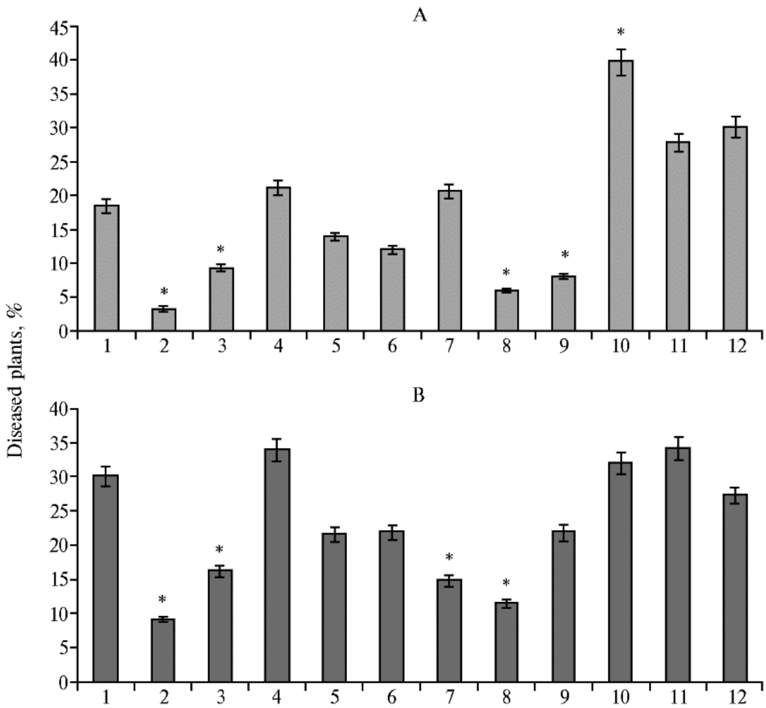

Fig. 1. Manifestation of primary root rot symptoms on plants of spring barley (*Hordeum vulgare* L.) varieties Leningradsky (A) **and Ataman** (B) **after seed treatment with nanocompounds, chemical, biological fungicides and their combinations:** 1 — control (water); 2 — Inshur Perform, KS (0.4 l/t); 3 — Inshur Perform, KS (0.2 l/t); 4 — silica composition NKteoa (1.0 l/t); 5 — composition of a fullerene derivative with methionine and NFm microelements (1.0 l/t); 6 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 7 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 8 — NFm (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 9 — NFm (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 10 — Vitaplan, SP (20 g/t); 11 — NKteoa (1.0 l/t) + Vitaplan, SP (20 g/t); 12 — NFm (1.0 l/t) + Vitaplan, SP (20 g/t) (n = 4, M±SEM; Leningrad Province, 2017). Each sample consists of 10 grains. For detailed descriptions, see the Materials and methods section.

* Differences from control are statistically significant at $p < 0.05$.

The primary symptoms of damage to seedlings of spring barley with root rot were the least manifested when seeds were treated with a chemical protectant at the full rate of application. The absence of a protective effect already at this stage was seen in the variants with the treatment of seeds with the silica-sol nanocomposition NKteos, as well as the biological preparation separately and together with the tested nanocompositions (Fig. 1). Both varieties of barley showed a decrease in the primary infection of root rot when seeds were treated with a nanocomposition based on C_{60} fullerene with methionine (24.9 and 28.2%), and even more so in combination with a chemical disinfectant (55.7 and 39.0%).

A subsequent assessment of the development of root rot showed that the most powerful and long-lasting protective effect was provided by the treatment of seeds with the chemical agent Inshur Perform, KS at 0.4 l/t. Its efficiency was

100, 76.3, 35.3% and 100, 84.6, 47.2%, respectively, for varieties Leningradsky and Ataman at tillering, stem extention and heading. A twofold decrease in the dosage led to a significant loss of the effectiveness of the chemical.

2. Efficiency of seed treatment with nanocompounds, chemical, biological fungicides and their combinations against root rot in spring barley (*Hordeum vulgare* L.) varieties at different stages of plant development (n = 4, M±SEM; Leningrad Province, 2017)

Variant	Cultivar	Stage					
		tillering		stem extention		heading	
		R, %	BE, %	R, %	BE, %	R, %	BE, %
1. Control (water)	L	1.4±0.63		3.8±0.64		6.8±2.05	
	A	1.1±0.66		2.6±0.96		7.2±1.58	
2. Inshur Perform, KS (0.4 l/g)	L	0.0	100.0	0.9±0.43	76.3	4.4±1.55	35,3
	A	0.0	100.0	0.4±0.27	84.6	3.8±2.05	47,2
3. Inshur Perform, KS (0.2 l/g)	L	1.0±0.70	28.6	1.3±0.52	65.8	7.3±1.94	0,0
	A	0.0	100.0	0.3±0.36	88.5	4.5±2.50	37,5
4. NKteoa (1.0 l/g)	L	1.9±0.20	0.0	3.6±1.24	5.3	9.5±3.55	0,0
	A	1.1±0.52	0.0	1.1±0.40	57.7	6.1±1.45	15,3
5. NFm (1.0 l/g)	L	2.0±0.67	0.0	3.6±0.78	5.3	8.6±1.53	0,0
	A	0.7±0.27	36.4	1.7±0.75	34.6	6.1±1.26	15,3
6. NKteoa (1.0 l/g) + Inshur Perform,	L	0.8±0.44	42.9	1.4±0.84	63.2	7.0±1.96	0,0
KS (0.4 l/g)	A	0.0	100.0	1.2±0.33	53.8	6.8±1.47	5,5
7. NKteoa (1.0 l/g) + Inshur Perform,	L	1.9±0.13	0.0	4.3±0.96	0.0	7.0±2.17	0,0
KS (0.2 l/g)	A	0.0	100.0	0.7±0.42	73.1	6.1±1.23	15,3
8. NFm (1.0 l/g) + Inshur Perform, KS	L	0.4±0.26	71.4	1.1±0.48	71.1	3.8±1.37	44,1
(0.4 l/g)	A	0.0	100.0	0.6±0.04	76.9	4.7±2.43	34,7
9. NFm (1.0 l/g) + Inshur Perform, KS	L	1.2±0.80	14.3	2.0±0.46	47.4	7.6±2.59	0,0
(0.2 l/g)	A	1.6±0.57	0.0	1.1±0.18	57.7	4.8±1.07	33,3
10. Vitaplan, SP (20 g/t)	L	1.9±1.48	0.0	5.5±1.53	0.0	7.8±2.23	0,0
	A	0.7±0.54	36.4	1.8±0.76	30.8	5.0±0.67	30,6
11. NKteoa (1.0 l/t) + Vitaplan, SP	L	2.7±2.01	0.0	3.2±0.92	15.8	9.0±1.55	0,0
(20 g/t)	A	0.0	100.0	1.2±0.38	53.8	7.4±1.96	0,0
12. NFm (1.0 l/t) + Vitaplan, SP	L	2.1±0.82	0.0	3.7±1.21	2.6	15.9±8.10	0,0
(20 g/t)	A	1.1±0.74	0.0	0.9±0.51	65.4	7.6±3.19	0,0
LSD_{05} (cultivar)		0,49		0.63		1.92	
LSD_{05} (preparations)		1,20		1.41		4.90	
LSD_{05} (cultivar, preparations)		1,74		2.03		7.36	

N o t e. L — Leningradsky, A — Ataman; R — disease development rate, BE — biological effectiveness. Each sample consists of 10 grains. For detailed descriptions, see the Materials and methods section.

The protective effect of seed treatment with nano-compositions was clearly expressed in the Ataman variety and, depending on the phase of development of the culture, amounted to 15.3-57.7% for the NKteoa silica-ash composition, 15.3-36.4% for NFm. An unstable, predominantly higher protective effect was noted when the biological preparation was used together with nanocomposites compared to the variant when the treatment was carried out only with the biological preparation (Table 2). However, the treatments with a biological product were less effective than the options for the combined use of nanocomposites with the fungicide Inshur Perform, KS.

The treatment of vegetative barley plants with NFm and NFtr nanocompositions turned out to be ineffective in relation to helminthosporium leaf spots: 15.6 and 21.6%for the Leningradsky variety, respectively, 20.3 and 42.2% for the Ataman variety. A weak protective effect occurred when plants were treated with microfertilizer KKhM-G, and a consistently high effect was observed in those variants where the use of microfertilizer and the above nanocompositions was supplemented by fungicidal treatment with Zantara, CE (Table 3). The weak development of powdery mildew (1.1 and 1.6%) and rhynchosporiosis (0.1 and 1.4%), observed on both varieties of spring barley in 2017, did not allow us to reliably assess the effectiveness of the studied compositions and preparations on infestation. leaf apparatus of plants with these diseases.

3. Efficiency of plant treatment with nanocompounds, microfertilizer, chemical fungicide and their combinations against helminthosporium leaf spots in spring barley (*Hordeum vulgare* L.) varieties at different stages of development (n = 4, M±SEM; Leningrad Province, 2017)

Variant	Cultivar	Stage: grain filling, R, %	grain filling, BE, %	Stage: milky ripe, R, %	milky ripe, BE, %
1. Control (water)	L	8.0±0.57		37,9±6,58	
	A	11.6±0.88		12,8±1,98	
2. Zantara, CE (0.8 l/ha)	L	4.9±1.79	38,8	11,7±1,11	69,1
	A	2.5±0.76	78,4	3,4±0,49	73,4
3. Zantara, CE (0.4 l/ha)	L	6.2±1.49	22,5	14,9±2,71	60,7
	A	3.2±0.40	72,4	4,8±0,95	62,5
4. KKhM-G (3.0 l/ha)	L	6.8±0.62	15,0	33,1±4,19	12,7
	A	12.7±1.61	0,0	8,8±1,96	31,3
5. NFm (1.0 l/ha)	L	6.5±0.73	18,8	32,0±1,30	15,6
	A	11.9±1.25	0,0	10,2±0,54	20,3
6. NFtr (1.0 l/ha)	L	7.5±1.25	6,3	29,7±4,53	21,6
	A	12.5±1.10	0,0	7,4±0,28	42,2
7. KKhM-G (3.0 l/ha) + Zantara, CE (0.8 l/ha)	L	4.8±1.19	40,0	12,4±1,52	67,3
	A	1.9±0.31	83,6	3,2±0,40	75,0
8. KKhM-G (3.0 l/ha) + Zantara, CE (0.4 l/ha)	L	5.5±0.82	31,3	15,3±1,90	59,6
	A	2.2±0.33	81,0	4,2±0,67	67,2
9. NFm (1.0 l/ha) + Zantara, CE (0.8 l/ha)	L	4.1±0.92	48,8	9,0±0,82	76,3
	A	2.5±0.60	78,4	4,4±1,62	65,6
10. NFm (1.0 l/ha) + Zantara, CE (0.4 l/ha)	L	5.6±2.92	30,0	14,4±2,05	62,0
	A	2.3±0.58	80,2	4,8±0,61	62,5
11. NFtr (1.0 l/ha) + Zantara, CE (0.8 l/ha)	L	4.4±1.11	45,0	10,3±0,87	72,8
	A	1.8±0.10	84,5	3,3±0,21	74,2
12. NFtr (1.0 l/ha) + Zantara, CE (0.4 l/ha)	L	4.4±0.62	45,0	12,6±1,53	66,8
	A	2.2±0.27	81,0	3,6±0,20	71,9
LSD_{05} (cultivar)		1,27		2,41	
LSD_{05} (preparations)		2,68		5,45	
LSD_{05} (cultivar, preparations)		2,78		5,56	

N o t e. L — Leningradsky, A — Ataman; R — disease development rate, BE — biological effectiveness. Each sample consists of 10 grains. For detailed descriptions, see the Materials and methods section.

An analysis of the elements of the structure of the spring barley yield showed that the treatment of the seed with the studied preparations had the strongest effect on the density of the productive stalk. In Leningradsky variety, the number of productive stems increased by 11% with chemicals, by 5-12% with nanocompositions, by 8-17% with their combinations, and by 10-15% with the biofungicide and its mixtures with nanocompositions.

The yield of variety Leningradsky in the control (untreated seeds) was 38.4 c/ha. Seed dressing increased the yield by 5-18% (Fig. 2). The greatest economic effect was observed when the seed material was treated with combinations of NKteoa and a chemical fungicide (an increase of 14 and 18% relative to the control at fungicide consumption rates of 0.2 and 0.4 l/t, respectively), as well as NKteoa and the biological product Vitaplan, SP (by 19%). Sufficiently high yields were recorded in the variants with the use of a biological product alone (by 112%) and in combinations with the nanocomposition of NFm and a chemical disinfectant (by 110 and 112% at fungicide consumption rates of 0.2 and 0.4 l/t, respectively).

Somewhat different data were obtained on the Ataman variety. Firstly, this variety turned out to be more productive, and secondly, the greatest and statistically significant economic effect (increase in yield) on it was shown by seed treatment with a chemical preparation (112% vs. control) and a combination of NFm and a chemical fungicide at a dose of 0.4 l/t (116% vs. control). It should be noted that there is no economic effect in the treatment of seeds only with nanocompositions.

Foliar treatment of vegetative plants with NFm and NFtr nanocompositions did not increase the yield of spring barley cv. Leningradsky. The use of microfertilizers KKhM-G followed by the use of fungicides gave a high economic effect. In this case, an excess of the individual effect of the microfertilizer or fungicide was observed. The same was noted for plant treatment of with nano-compounds and the fungicide Zantara, CE. Yields were 6% and 35% higher with NFm (0.4 l/ha) and Zantara, CE (0.8 l/ha), and 11% and 50% higher with NFtr (0.4 l/ha) and Zantara, CE (0.8 l/ha).

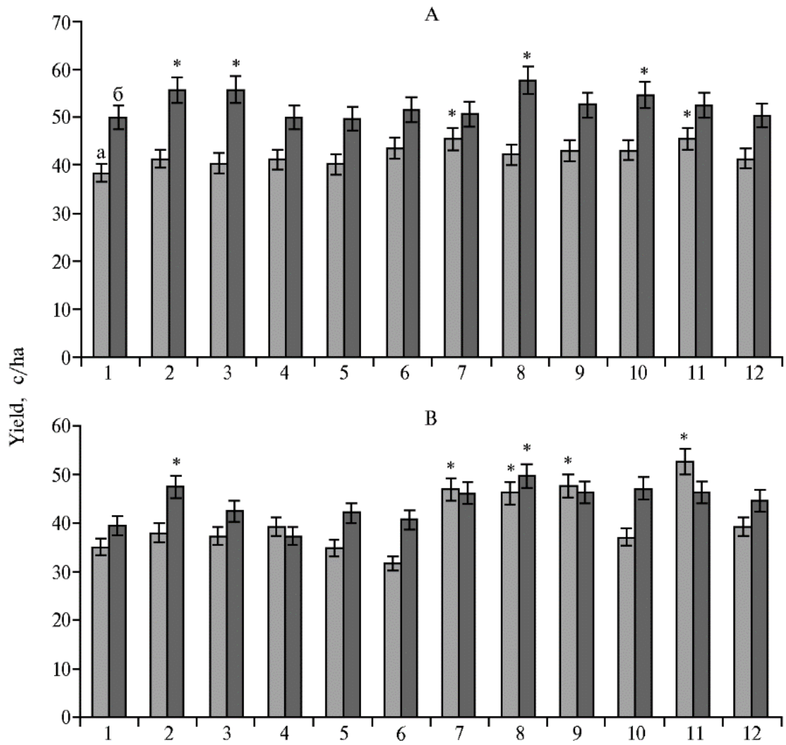

Fig. 2. Yields of spring barley (*Hordeum vulgare* L.) varieties Leningradsky (a) **and Ataman (b) after pre-sowing seed treatment** (A) **or spraying plants** (B) **with solutions of nanocompositions, KKhM-G, chemical and biological fungicides and their combinations** (n = 4, M±SEM; Leningrad Province, 2017).

A: 1 — control (water); 2 — Inshur Perform, KS (0.4 l/t); 3 — Inshur Perform, KS (0.2 l/t); 4 — silica composition NKteoa (1.0 l/t); 5 — composition of a fullerene derivative with methionine and NFm microelements (1.0 l/t); 6 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 7 — NKteoa (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 8 — NFm (1.0 l/t) + Inshur Perform, KS (0.4 l/t); 9 — NFm (1.0 l/t) + Inshur Perform, KS (0.2 l/t); 10 — Vitaplan, SP (20 g/t); 11 — NKteoa (1.0 l/t) + Vitaplan, SP (20 g/t); 12 — NFm (1.0 l/t) + Vitaplan, SP (20 g/t).

B: 1 — control (water); 2 — Zantara, CE (0.8 l/ha); 3 — Zantara, CE (0.4 l/ha); 4 — silicon-containing chelate microfertilizer KKhM-G (3.0 l/ha); 5 — NFm (1.0 l/ha); 6 — composition of fullerene derivative with threonine and microelements NFtr (1.0 l/ha); 7 — KKhM-G (3.0 l/ha) + Zantara, CE (0.8 l/ha); 8 — KKhM-G (3.0 l/ha) + Zantara, EC (0.4 l/ha); 9 — NFm (1.0 l/ha) + Zantara, CE (0.8 l/ha); 10 — NFm (1.0 l/ha) + Zantara, CE (0.4 l/ha); 11 — NFtr (1.0 l/ha) + Zantara, CE (0.8 l/ha); 12 — NFtr (1.0 l/ha) + Zantara, EC (0.4 l/ha).

Each sample was harvested from a 1 m^2 area. For detailed description, see the Materials and Methods section.

The economic effect of a single treatment of cv. Ataman with the fungicide Zantara, CE, depending on the rate of application of the drug (0.4 and 0.8 l/ha), was 8 and 20%, respectively, The treatment with KKhM-G microfertilizer and the fungicide resulted in 17 and 26% effects, with NFm and the fungicide in 17 and 19% effects, with NFtr and the fungicide in 13 and 17% effects, Thereof, the efficiency of half-dose fungicide significantly increased due to the developed silicon-containing microfertilizers KKhM-G and nanocompositions. A lower economic effect was noted in the variants where the use of only KKhM-G microfertilizer or carbon nanocomposites was envisaged.

The most objective indicator in assessing the effect of treating vegetative plants with fungicides is the 1000-grain weight. According to the obtained values, in Leningradsky variety, the combined use of KKhM-G microfertilizer and the fungicide at a dose of 0.4 and 0.8 l/ha increased this indicator by 9 and 17% vs. control. According to the effect on the 1000-grain weight in Ataman variety, foliar treatments with a fungicide were distinguished (an increase vs. control by 110 and 112% at application rates of 0.4 and 0.8 l/ha, respectively) and combined application of NFm with a fungicide (by 111 and 112%).

According to data for 2017, the most effective treatment options for protecting spring barley from diseases were identified, which in 2018 were included in the study of the effectiveness of the technological scheme for the use of nanocompositions. To enhance the protective effect during seed treatment, 0.1% titanium dioxide in the form of anatase was added to the composition of NKteoa in addition to the charge of detonation nanodiamond [22].

According to phytoexpertise, the treatment of seeds of spring barley Leningradsky variety with a silica-sol nanocomposition led to a decrease in infection with *Fusarium* fungi by 43.7% and *Alternaria* blight by 23.5%, but had no effect on the main causative agent of root rot, the fungus *C. sativus* (Table 4).

4. Efficiency of seed treatment with the nanocomposition, chemical fungicide and their combinations against seed infection in spring barley (*Hordeum vulgare* L.) cv. Leningradsky (n = 10, M±SEM; Leningrad Province, 2018)

Variant	Microbiota					
	pathogenic				saprotrophic	
	Cochliobolus sativus		*Fusarium* spp.		*Alternaria* spp.	
	DI, %	BE, %	DI, %	BE, %	DI, %	BE, %
1. Control (water)	6.0±1.35		16.0±2.05		81.0±5.41	
2. Inshur Perform, KS (0.4 l/t)	4.0±1.08	33.3	13.0±1.96	18.7	39.0±4.87	51.9
3. Inshur Perform, KS (0.2 l/t)	3.0±0.88	50.0	18.0±2.25	0.0	45.0±4.98	44.4
4. NKteoa (1.0 l/t)	17.0±2.31	0.0	9.0±1.87	43.7	62.0±5.14	23.5
5. NKteoa (1.0 l/t) + Inshur Perform, KS (0.4 l/t)	13.0±1.45	0.0	13.0±2.41	18.7	53.0±4.52	34.6
6. NKteoa (1.0 l/t) + Inshur Perform, KS (0.2 l/t)	8.0±2.06	0.0	14.0±2.87	12.5	71.0±6.42	12.3
LSD_{05}	1.51		3.53		12.46	

N o t e. DI — disease incidence, BE — biological effectiveness. Each sample consists of 10 grains. For detailed descriptions, see the Materials and methods section.

Under severe damage by root rot in 2018 caused by a long dry period during initial crop growth, there was a weak and short effect of seed treatment with the chemical fungicide Inshur Perform, KS on the disease incidence (Table 5). With the combined seed treatment with the NKteoa nanocomposition and a chemical fungicide, the effectiveness of protection against root rot increased to 10.1-21.5% vs. the control, but only at the full rate of Inshur Perform, KS. An even stronger effect (decrease in the development of root rot by 13.9-35.4% relative to the control) was observed in the variant with the treatment of seeds with a silica nanocomposition and a chemical preparation at the full rate of application, followed by a 3-fold treatment of vegetative plants with NFtr.

In 2018, a significant protective effect of seed treatment with fungicides was manifested in relation to Helminthosporium leaf spots (Table 6). In variants with inoculum dressing with Inshur Perform, KS, the development of helminthosporiasis, depending on the dose of application, decreased by 20.0-32.2% (0.4 l/t) and 17.5-32.9% (0.2 l/t) vs. control. With pre-sowing treatment with silica nanocomposition, the disease incidence rate decreased by 7.5-15.4%.

5. Efficiency of seed and plant treatments with nanocompounds, chemical fungicide and their combinations against root rot in spring barley (*Hordeum vulgare* L.) cv. Laningradsky varieties at different stages of plant development (n = 4, M±SEM; Leningrad Province, 2018)

Variant	Stage					
	tillering		stem extention		heading	
	R, %	BE, %	R, %	BE, %	R, %	BE, %
1. Control (water)	30.2±3.35		34,0±2,68		44,5±8,28	
2. Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha)	25.5±4.07	15,6	28,8±1,99	15,3	40,0±3,81	10,1
3. Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha)	30.4±6.85	0,0	32,0±4,32	5,9	42,2±4,87	5,2
4. NKteoa (seeds 1.0 l/t) + water (plants 300 l/ha)	29.4±1.83	2,6	33,6±9,09	1,2	45,0±8,11	0,0
5. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha)	24.2±6.27	19,9	26,7±7,66	21,5	40,0±3,81	10,1
6. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha)	30.8±3.49	0,0	34,3±7,04	0,0	39,8±8,67	10,6
7. Water (seeds) + NFtr (plants 1.0 l/ha)	38.5±8.15	0,0	43,9±6,51	0,0	53,5±5,93	0,0
8. Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha)	25.0±4.45	17,2	28,7±2,68	15,6	39,3±2,25	11,7
9. Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 l/ha)	29.5±8.05	2,3	29,2±2,89	14,1	44,9±2,78	0,0
10. NKteoa (seeds 1.0 l/t) + NFtr (plants 1.0 l/ha)	24.3±4.31	19,5	39,0±5,54	0,0	48,8±4,53	0,0
11. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha)	19.5±3.68	35,4	22,2±8,16	34,7	38,3±7,64	13,9
12. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 l/ha)	31.2±5.58	0,0	34,4±7,32	0,0	46,0±4,26	0,0
LSD_{05}	13.61		14,49		16,94	

N o t e. R — disease development rate, BE — biological effectiveness. Each sample consists of 30 plants. For detailed descriptions, see the Materials and methods section.

6. Efficiency of seed and plant treatment with nanocompounds, chemical fungicide and their combinations against helminthosporium leaf spots in spring barley (*Hordeum vulgare* L.) cv. Leningradsky at different stages of development (n = 4, M±SEM; Leningrad Province, 2018)

Variant	Stage			
	grain filling		milky ripe	
	R, %	BE, %	R, %	BE, %
1. Control (water)	4.0±0.34		14.3±2.42	
2. Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha)	3.2±0.16	20.0	9.7±0.33	32.2
3. Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha)	3.3±0.19	17.5	9.6±1.45	32.9
4. NKteoa (seeds 1.0 l/t) + water (plants 300 l/ha)	3.7±0.38	7.5	12.1±1.77	15.4
5. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha)	2.8±0.25	30.0	11.0±1.08	23.1
6. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha)	3.2±0.24	20.0	13.2±0.86	7.7
7. Water (seeds) + NFtr (plants 1.0 l/ha)	3.6±0.16	10.0	12.5±0.72	12.6
8. Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha)	2.9±0.35	27.5	8.5±1.02	40.6
9. Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 l/ha)	3.2±0.67	20.0	10.0±1.39	30.1
10. NKteoa (seeds 1.0 l/t) + NFtr (plants 1.0 l/ha)	2.8±0.37	30.0	11.5±1.41	19.6
11. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha)	2.9±0.23	27.5	9.9±0.35	30.8
12. NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 l/ha)	3.7±0.48	7.5	12.1±0.62	15.4
LSD_{05}	0.94		3.40	

N o t e. R — disease development rate, BE — biological effectiveness. Each sample consists of 30 plants. For detailed descriptions, see the Materials and methods section.

The icidence of helminthosporiosis decreased by 10.0-12.6% vs. control unde foliar treatment with NFtr nanocomposition and by 19.6-30.0% under seed treatment with silica-sol nanocomposition (see Table 6). A positive effect of NFtr treatment was also noted complementing the effect of seed dressing. Seed treatment with Inshur Perform, KS and 3-fold plant treatment with the NFtr nanocomposition decreased the helminthosporiosis incidence by 27.5-40.6% vs. control at 100% application rate and by 20.0-30.1% at 50% application rate.

The high productivity of spring barley plants was typical for the variants with the treatment of seeds, as well as seeds and vegetative plants with the tested nanocompositions. Exceeding the control by the mass of grain per ear in both of these options was 9%. According to the density of the productive stem stand, a variant was distinguished (15% higher than the values in the control), which provided for the sequential treatment of seeds with a silica-sol nanocomposition and the chemical preparation Inshur Perform, KS (0.4 l/t) with a further 3-fold treatment of vegetative plants with a nanocomposition of NPtr.

Analyzing the yields obtained, we can conclude that there are no significant differences between the control and the studied options for the treatment of seeds and vegetative plants of spring barley (Fig. 3).

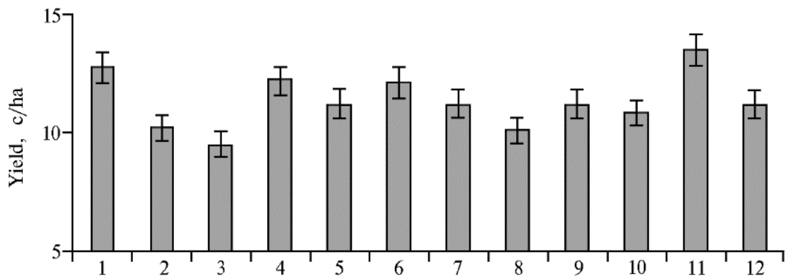

Fig. 3. Yield of spring barley (*Hordeum vulgare* L.) cv. Leningradsky after pre-sowing seed treatment and spraying plants with nanocompositions, chemical fungicide and their combinations: 1 — control (water), 2 — Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha), 3 — Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha), 4 — NKteoa (seeds 1.0 l/t) + water (plants 300 l/ha), 5 — NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + water (plants 300 l/ha), 6 — NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + water (plants 300 l/ha), 7 — water (seeds) + NFtr (plants 1.0 l/ha), 8 — Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha), 9 — Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 l/ha), 10 — NKteoa (seeds 1,0 l/t) + NFtr (plants 1.0 l/ha), 11 — NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.4 l/t) + NFtr (plants 1.0 l/ha), 12 — NKteoa (seeds 1.0 l/t) + Inshur Perform, KS (seeds 0.2 l/t) + NFtr (plants 1.0 л/га) (n = 4, M±SEM; Leningrad Province, 2018). Each sample was harvested from a 1 m^2 area. For detailed description, see the Materials and Methods section.

Initially, carbon and silica nanocomposites were considered as plant growth regulators, and their use in agriculture was aimed at increasing the quantity and quality of the crop, achieved by increasing field germination, photosynthesis intensity, and the production process [35-37]. Also, their ability to increase the resistance of plants to stressors of a biotic and abiotic nature, including the action of harmful organisms, was noted [38, 39]. The results of our studies generally indicate weak and in many cases statistically unreliable effects of treating seeds and vegetative plants with carbon and silica-ash nanocompositions to protect spring barley from root rot and leaf diseases. This can be explained by their directed action not on the pathogen attacking plant cells, but on the activation of plant metabolism and immunity, which is confirmed by the actual data of other studies [40, 41]. However, in our experiments, we have revealed a pronounced biocidal effect of silica nanocomposition against seed infection, namely the genus *Fusarium* fungi. Another important conclusion concerns the great prospects for the use of carbon and silica-sol compositions on spring barley varieties with a long growing season, which are more susceptible to the influence of phytopathogens. A possible way to enhance the protective effect is the combined use of the nanocompositions and chemicals designed to protect cultivated plants from phytopathogens. Due to the pronounced additive effect, the possibility of a significant reduction in the application of fungicides opens up, which was proved by the example of the combined use of biological and chemical preparations in the protection of spring barley from diseases [32].

The data obtained by us indicate certain prospects for the use of new carbon and silica-sol nanocompositions in the protection of spring barley from diseases in order to reduce the pesticide load during the cultivation of this crop in the North-West Russia. The co-application of chemical or biological fungicides with nanocompositions is highly effective due to enhanced protective effects and a potentially reduced dosage of chemicals and biologicals. It is necessary to continue research for scientifically based selection of the most effective combinations of nanocompositions and pesticides and improvement of technological schemes for their application.

Thus, the nanocompositions used in pure form have a weak and unreliable effect on the development of root rot on the early-ripening barley variety Leningradsky (0-5.3%), The effect on the mid-late variety Ataman is more pronounced and stable (15.3-57.7 %, $p < 0.05$). Pre-sowing seed treatment with a silica-sol nanocomposition based on 1 wt.% tetraethoxysilane (pH 2-3) with macro- and microelements and 0.1% titanium dioxide results in a decrease in the development of helminthosporium leaf spots by 7.5-15.4% ($p < 0.05$). The most prolonged and pronounced protective effect against root rots occurs under a combined treatment of seeds with a silica-sol nanocomposition and the chemical fungicide Inshur Perform, KS, followed by foliar treatment with a nanocomposition based on derivative of C_{60} fullerene with threonine. To protect spring barley from *Helminthosporium* blotches, the studied nanocompositions in their pure form were ineffective. The symptoms on the two upper leaves decreased by 16-22 and 20-42% in Leningradsky and Ataman varieties, respectively ($p < 0.05$). When seeds are treated with the silica-sol composition and vegetative plants with the nanocomposition based on the C_{60} fullerene derivative with threonine, the development of helminthosporiasis decreases by 19.6-30.0% ($p < 0.05$) which is equivalent to the treatment of seeds and plants with the chemical preparation Inshur Perform, KC at half the rate of use. Two treatments, a combined 3-fold application of the NFtr nanocomposition with a single application of the chemical fungicide Zantara, KE and the use of microfertilizer KKhM-G with the chemical fungicide Zantara, KE, provide high protective effect on both varieties. The best protocol to protect spring barley plants from root and leaf diseases compeises the combined seed treatment with a silica-sol nanocomposition and the chemical fungicide Inshur Perform, KS together with a 3-fold treatment of vegetative plants with a nanocomposition based on the threonine derivative of C_{60} fullerene and a single treatment with chemical fungicide Zantara, KE. Reducing the rate of use of a chemical preparation leads to a significant loss of efficiency and a reduction in the protective period and, thereof, is advisable only if weak manifestation of diseases is expected. High biological and economic efficiency, comparable to fungicidal treatments at 100% application rate, was ensured by the combined use of KKhM-G microfertilizer with a fungicide (50% application rate) and the combined use of a nanocomposition based on the methionine derivative of C_{60} fullerene and a fungicide (50% application rate).

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