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Features of the influence of copper nanoparticles and copper oxide on the formation of barley crop

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Abstract. In addition to modern methods of agricultural technology, currently the achievements of selection and genetics are widely used, as well as modern nanotechnology and nanomaterials, to improve food production. One of the forms of biologically active nanomaterials is metal nanopowders and their derivatives. The application is carried out in minimal doses that can significantly reduce costs in agricultural production. Improving the yield and quality of crops by optimizing nutrition and plant protection using nanotechnology and nanomaterials will solve not only the problems of increasing the yield and quality of farmed products, but also environmental problems. The purpose of this research was to determine the effect of copper and copper oxide nanoparticles on the formation of a barley crop. Under the conditions of a lysimetric experiment, the effect of presowing treatment of spring barley seeds by nanoparticles of copper and copper oxide on the growth and development of plants, yield, and their nutritional value was studied. The used nanoparticles have the following characteristics: Cu - 40–60 nm, phase composition: Cu - 100%; CuO - 40–60 nm, phase composition: CuO - 100%. A suspension of nanoparticles was obtained by dispersion by ultrasound in an aqueous solution. Nanopowders of copper and copper oxide in the solution contained 0.01 g per hectare seed rate. Barley seeds were soaked 30 minutes before sowing in double distilled water (control variant), as well as in a suspension of nanoparticles. Presowing treatment of barley seeds by Cu nanoparticles contributed to the intensification of growth processes, as well as an increase in green mass. The use of copper nanoparticles contributed to an increase in grain yield by 17.3% compared with the control, while there was no decrease in nutritional value: metabolic energy, feed units, digested protein. Based on the research results, it is preferable to use copper nanoparticles in comparison with copper oxide nanoparticles to obtain a higher barley yield.

Key words: copper nanoparticles, copper oxide nanoparticles, linear growth, spring barley yield, nutritional value.

INTRODUCTION

The search and development of techniques that could increase the yield of cultivated plants without increasing fertilizer application rates, as well as improve the quality of agricultural products, is a priority area of modern crop production (Churilov et al., 2013, 2018; Polischuk et al., 2018; Zakharova et al., 2018; Chernikova et al., 2019a, 2019b). One of these areas is the transition to technologies that contribute to optimizing plant nutrition with microelements and stimulators of their growth and development in accordance with the biological requirements of crops, to a strategy for the integrated and differentiated use of genetic, soil-climatic and technogenic factors (Hafeez et al., 2015; Mengmeng Rui et al., 2016; Hlisnikovský et al., 2019; Olkhovskaya et al., 2019).

Adaptive intensification of agriculture requires widespread use of methods of biological correction, which includes non-root feeding by growth stimulants.

Interest in the use of nanoparticles (NPs) in crop production and agricultural practice is associated with their unique properties. Long-term studies of dispersed NP systems have revealed the following features of their biological action:

– metal nanoparticles have low toxicity, by 7–50 times less toxicity of metals in ionic form;

– have a prolonged and multifunctional effect;

– stimulate metabolic processes;

– easily penetrate into all organs and tissues;

– their biological activity is associated with the structural features of the particles and their physicochemical characteristics, etc. (Zeyruk et al., 2019).

The biological activity of metal nanoparticles is directly related to their physicochemical characteristics: particle size, their shape, phase state of particles (Olkhovskaya et al., 2019). As the result, for the successful use of nanoparticles and nanomaterials for the crop industry, their physicochemical properties must be taken into account.

Microelements play an important role in obtaining high yields of good quality spring barley grain. The essential element copper and its oxide were selected to research the influence of NPs of metals on the formation of barley. Copper is a constituent of enzymes that play an important role in redox processes. They improve the intensity of photosynthesis, promote the formation of chlorophyll, have a positive effect on carbohydrate and nitrogen metabolism, and increase the resistance of plants against fungal and bacterial diseases. The protein content in grain increases under the influence of copper (Copper for plants, 2019).

The stimulation was revealed under the action of the dispersed solutions at extremely low concentrations of NPCu (up to 10^{-17} mg L^{-1}). The sol treatment of seeds promoted an increase in the degree of their resistance to pathogenic fungi (causing root rots in sprouts) (Maslobrod et al., 2014).

It should be noted that a number of authors (Fedorenko et al., 2020) note the toxic effect of CuO nanoparticles on plant development, which is manifested in changes in tissue and intracellular levels in barley roots. At the same time, there are practically no qualitative changes in plant leaves under the influence of copper in macroand nanodisperse forms. It is shown that the maximum concentration for safe use of copper nanopowder is 100 g ha^{-1}, and for copper oxide nanopowder - 10.0 g ha^{-1}.

Barley is a culture of versatile use, which has great feed, food, technical and agricultural value. In industrial bakery, barley is sometimes used as a component in the formulation of some varieties of wheat bread. In terms of food, barley remains only a popular cereal crop, which pearl barley and peeled barley groats are obtained from.

Barley is one of the important fodder-grain crops (1 kg of grain contains 1.1 feed units). It is introduced as the main ingredient in most animal feeds. The green mass of barley in a mixture with legumes (vetch, peas, maple pea, lathyrus) is used for green feed, silage, haylage, hay.

The purpose of this research was to determine the effect of copper and copper oxide nanoparticles on the formation of a barley crop.

MATERIALS AND METHODS

The research was carried out in the lysimeters of the NSRIHEA design with undisturbed soil profile (Fig. 1). The area of stationary field lysimeters is 1.3 m^2.

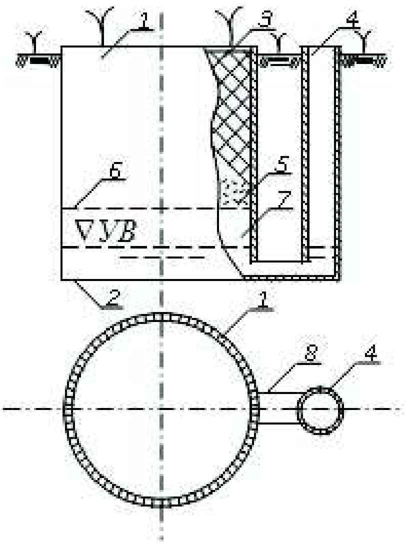

Figure 1. Diagram of a water balance lysimeter (legend: 1 – lysimeter case; 2 – lysimeter bottom; 3 – soil monolith; 4 – pocket for water extraction; 5 – gravel packing; 6 – strainer; 7 – groundwater level; 8 – communication channel).

Lysimeters are charged with gray forest soil. Taken soil samples from a depth of 0–25 cm at the beginning of the experiment characterize the soil with a low content of organic matter from 3.8% to 5.4% (on average 4.6% ± 0.6) (Fig. 2).

The acid-base reaction of the soil refers to slightly acidic, pH from 5.3 to 6.4 (on average 5.7 ± 0.1). The supply of soil with mobile nutrients on average was as follows: potassium content - 833.5 mg kg^{-1}, total nitrogen - 0.12%, mobile phosphorus - 128 mg kg^{-1} that characterizes this soil as medium provided with these elements.

Figure 2. Lysimetric experiment on gray forest soil.

According to our research plan, the effect of copper and copper oxide nanoparticles was studied with an optimal concentration of 0.01 g hectare seed rate (Table 1). The experiment was carried out in four replicates.

Table 1. The setup of the experiment

Lysimeter number	Variant name	Abbreviation
1, 5, 9, 13	Suspension of nanopowder of copper oxide at a dose of 0.01 g ha^{-1}	CuO 0.01
2, 6, 10, 14	Suspension of copper nanopowder in a dose of 0.01 g ha^{-1}	Cu 0.01 $N_{60}P_{60}K_{60}$
3, 7, 11,15	Suspension of copper nanopowder in a dose of 0.01 g ha	Cu 0.01
4, 8, 12, 16	Control	C

Nanoparticles obtained at the Moscow Institute of steel and alloys by gas-phase chemical reactions. The used nanoparticles are single crystal structures of circular regular shape and have the following characteristics: Cu - 40–60 nm, phase composition: Cu°- 100%; CuO - 40–60 nm, phase composition: CuO - 100%. A suspension of nanoparticles was obtained by dispersion by ultrasound in an aqueous solution. Nanopowders of copper and copper oxide contained 0.01 g per hectare seed rate in the solution. Barley seeds were soaked 30 minutes before sowing in double distilled water (control variant), as well as in a suspension of nanoparticles.

Barley spring variety 'Kati' was chosen as the object of research (Fig. 3). The species is nutans. The bush is intermediate. The leaf sheath of the lower leaves is without pubescence. The anthocyanin color of the flag leaf ligules is medium - strong, the wax coating on the sheath is weak - medium. The plant has short - medium length. Pyramidal spike - cylindrical, loose - medium density, with medium - strong waxy coating. The awns are longer than spike, serrated, with medium - strong anthocyanin coloration of tips. The first segment of the spike rod has short - medium length, with a slight bend. Sterile spike is from parallel to slightly deflected. The pubescence of the main setae of the weevil is long. Anthocyanin coloration of the nerves of the outer floral scales is weak.

Figure 3. Spring barley variety Kati.

The serration of the internal lateral nerves of the outer floral scales is absent or very weak. The weevil is very large, with an undescended abdominal groove and a covering lodicule. The mass of 1,000 grains is 46–56 g. Grain-fodder. The protein content is 10.9–14.5%. Susceptible to root rot.

Sowing was conducted on April 26, 2019. The technology for growing spring barley in lysimeters imitated the generally accepted one for gray forest soil in this region, but with some features of lysimetric studies.

The grooves were made in the plots with a depth of 3–4 cm; at a distance of 12 cm, the seed rate was distributed at the rate of 55 grains per 1 linear meter (Fig. 4). In the phase, the pips were pulled and 50 pieces were left per 1 linear meter. Agricultural cultivation culture is generally accepted for this zone. Harvesting barley was carried out in a phase of full ripeness. Plants were cut at a height of 1–2 cm from the root neck, placed in bags indicating the number of the variant and repetition.

Figure 4. Establishment of lysimetric experiment (sowing barley of Kati variety).

In the laboratory, the above-ground crop was dried to constant weight. After threshing the grain, the refined grain was weighed. Samples were taken from the crop by repetition, numbered, according to the registry, for shipment to the laboratory. A mass of 1,000 seeds, grain moisture, and nutritional value (metabolic energy, feed units, digestible protein) were determined using generally accepted GOST methods.

RESULTS AND DISCUSSION

Linear plant growth is an important environmental indicator that indirectly characterizes the intensity of cell division or extension. Phenological observations of the growth and development of plants were carried throughout the growing season. This season the weather conditions were unfavorable: temperatures were low for this period, as well as prolonged rains with gusty winds. This fact affected the development of plants and, as a consequence, productivity.

Phenological studies consisted of measuring the height of plants. The observations were carried out in two rows: 3 and 5. The height of the plants was determined by the highest tip, 10 plants of the counting row. The calculation was carried out on 1 plant, calculating the average value for each indicator. There were two of them on barley - 10.05 and 26.07.

The highest linear growth rates of plants on May 10, 2019 were revealed on the variant using copper nanoparticles with the joint application of mineral fertilizers (Table 2). Differences with the control variant were 1.29 cm or 18.14%. It should be noted that the growth and development of plants in the control was uneven and unstable. In variants where copper and copper oxide nanoparticles at a dose of 0.01 g ha^{-1} were used for pre-sowing seed treatment, an increase in plant height by 0.61 and 0.22 cm was also observed that amounted to 9.49% and 6.28%.

Table 2. Linear growth of barley during presowing treatment of barley seeds by copper and copper oxide nanoparticles

No.	Experiment variants	Plant Height, cm					
		10.05.2019			26.07.2019		
		mean	change		mean	change	
			cm ±	%		cm ±	%
1	CuO 0.01	6.43	+ 0.61	9.49%	69.68	+ 0.21	0.30
2	Cu 0.01 N60P60K60	7.11	+ 1.29	18.14%	70.85	+ 1.38	1.95
3	Cu 0.01	6.21	+ 0.22	6.28%	77.01	+ 5.54	9.79
4	C	5.82	-	-	69.47	-	-
$HCP_{0.95}$		0.9	-	-	3.7	-	-

The linear growth indicators on July 26, 2019 were as follows: the highest plant height was noted on the variant using copper nanoparticles at a dose of 0.01 g ha^{-1}. The increase in this indicator compared with the control variant of the experiment amounted to 7.19%. Copper nanoparticles probably contributed to an increase in the adaptive potential of plants that led to the stabilization of growth processes and increased resistance to lodging. The use of copper oxide nanoparticles had practically no effect on plant growth in the last stages of vegetation, and the difference with the control was insignificant 0.21 cm or 0.30%.

Productivity is the most important effective indicator of crop production and agricultural production in general. The yield level reflects the impact of the conditions which the plants are grown in and the quality of the measures taken.

Indicators of linear growth and productivity in our experiment were directly dependent on each other. Thus, the highest yield was noted in the variant with the use of Cu NPs - 44.8 c ha^{-1} (Table 3). The mass of 1,000 seeds (Table 4) in this variant was less, however, the number of spikelets and grains in the ear at the time of harvesting was more. Plants during using copper nanoparticles were more resistant to lodging and shedding of seeds that probably led to an increase in this indicator in comparison with the control variant, as well as other experimental variants.

Table 3. The effect of copper and copper oxide nanoparticles on barley yield

No.	Experiment variants	Harvest of main products, c ha^{-1}		
		mean	change c ha^{-1}	%
1	CuO 0.01	35.7	+ 0.4	1.12
2	Cu 0.01 N60P60K60	38.8	+ 3.5	9.02
3	Cu 0.01	44.8	+ 9.5	17.3
4	C	35.3	-	-
Research accuracy indicators		m = 5%		
		$HCP_{0.95}$ = 4.8 c ha^{-1}		

The use of copper oxide nanoparticles and copper nanoparticles together with mineral fertilizers also contributed to an increase in the yield of spring barley. When analyzing the obtained data of the options, it is seen that the yield increases in comparison with the control variant are as follows: CuO 0.01–0.4 c ha^{-1} (1.12%), Cu 0.01 N60P60K60 - 3.5 c ha^{-1} (9, 02%), Cu 0.01–9.5 c ha^{-1} (17.3%).

Table 4. Nutritional value and physical properties of barley grain

No.	Experiment variants	Weight 1,000 grains, g	Moisture, %	Nutritional value 1 kg		
				Metabolic energy E, MJ	Feed units	Digestible protein, g
1	CuO 0.01	66.2	14.2	10.79	1.1	60.0
2	Cu 0.01 N60P60K60	71.7	14.2	10.84	1.1	67.1
3	Cu 0.01	66.0	14.5	10.79	1.1	58.1
4	C	65.4	14.1	10.79	1.1	62.0

One of the most important elements of the crop structure is grain size expressed through the mass of 1,000 seeds. Of course, the mass of 1,000 seeds is the second element of spike productivity after the grain content, but at the same time (Sumina, 2010), this parameter relates to the supply of nutrients, germination ability and seed viability. This indicator is a 'grading factor', but it may vary depending on growing conditions. The mass value of 1,000 grains is an indirect indicator of the 'sufficient balance of the genetic complex', which is responsible for grain size.

The mass index of 1,000 seeds significantly exceeded the average values (46–56 g), which are characteristic for the features of the Kati variety of spring barley (Table 4). Probably, presowing soaking contributed to the increase of this indicator in all variants of the experiment.

It should be noted that the largest mass of 1,000 seeds was in the variant with the use of copper nanoparticles with the joint application of mineral fertilizers and amounted to 71.7 g that was 6.3 g (8.79%) more in comparison with the control variant of the experiment. The use of only nanoparticles of copper and copper oxide at a dose of 0.01 g per hectare seed rate also contributed to an increase in this indicator: 0.6 (0.91%) and 0.8 (1.21%) g, respectively.

Digestible protein is a crude protein that is absorbed into the bloodstream and lymph from the digestive tract of cattle. Its amount was in the same stages on all variants of the experiment and ranged from 58.1 to 67.1 g per 1 kg of fodder. Its greatest value was on the Cu 0.01 N60P60K60 variant. It is established that nanoparticles have a huge specific surface, and hence excess surface energy. Copper, as a microelement, shows a synergism with respect to the nitrogen macroelement: a sufficient level of Cu in the soil improves the absorption of N. Probably having a size of 40–60 nm, copper nanoparticles do not penetrate the membrane, while promoting the intensification of nitrogen metabolism in the cell, as a result, the use of these particles together with mineral fertilizers leads to an increase in digestible protein in barley grain and an increase in the mass of the seeds.

In all variants of the experiment, the number of feed units was 1.1 kg that corresponds to the average values that are characteristic for this crop (Table 4).

The amount of energy in the fodder is the most important indicator of its value. The value of this indicator in all variants of the experiment, with the exception of Cu0.01 N60P60K60, was at the same level and amounted to 10.79 MJ. A slight increase was observed during using copper nanoparticles with the joint application of mineral fertilizers and it amounted to 10.84 MJ that is 0.05 MJ more in 1 kg.

The moisture content of the grain is one of the most important indicators of its quality, which was determined immediately after consumption. Water has a strong effect on the grain itself and microorganisms on its surface. Microbes develop faster, the number of ticks and insects increases and also other changes occur on wet grain. Humidity is a factor that shows the proportion of grain nutrients and the duration of its storage. The higher the moisture content in the grain mass, the less it contains nutrients and the faster it spoils. Excessive moisture leads to the activation of physiological, physico-chemical processes. The grain begins to swell, germinate, high molecular weight biopolymers are broken down, the enzymes are activated. The nature and the flowability of grain decrease; it becomes vulnerable to mechanical damage. If the grain remains wet for a long time, its storage and processing become impossible. In any case, grain yield and product quality are reduced during using moist raw materials (Grain moisture, 2019).

The moisture content of the presented samples was within the base humidity, which is from 13.5 to 15%. On average, for all variants of the experiment, it amounted to 14.2%.

CONCLUSIONS

From the obtained data, it can be concluded that the pre-sowing treatment of barley seeds with copper and copper oxide nanoparticles does not have a toxic effect and contributes to an increase in yield. Pre-soaking of spring barley seeds in suspension with copper nanoparticles at a dose of 0.01 g per hectare seed sowing rate contributed to an increase in the adaptive potential of plants. This played a large role in the formation of the crop: the largest increase was obtained in this experiment variant and amounted to 44.8 kg ha^{-1} that is 17.3% more in comparison with the control variant.

Such indicators as the mass of 1,000 g of seeds, as well as nutritional value: metabolic energy and digestible protein due to the intensification of nitrogen metabolism were the best in the variant with the use of copper nanoparticles with the joint application of mineral fertilizers.

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