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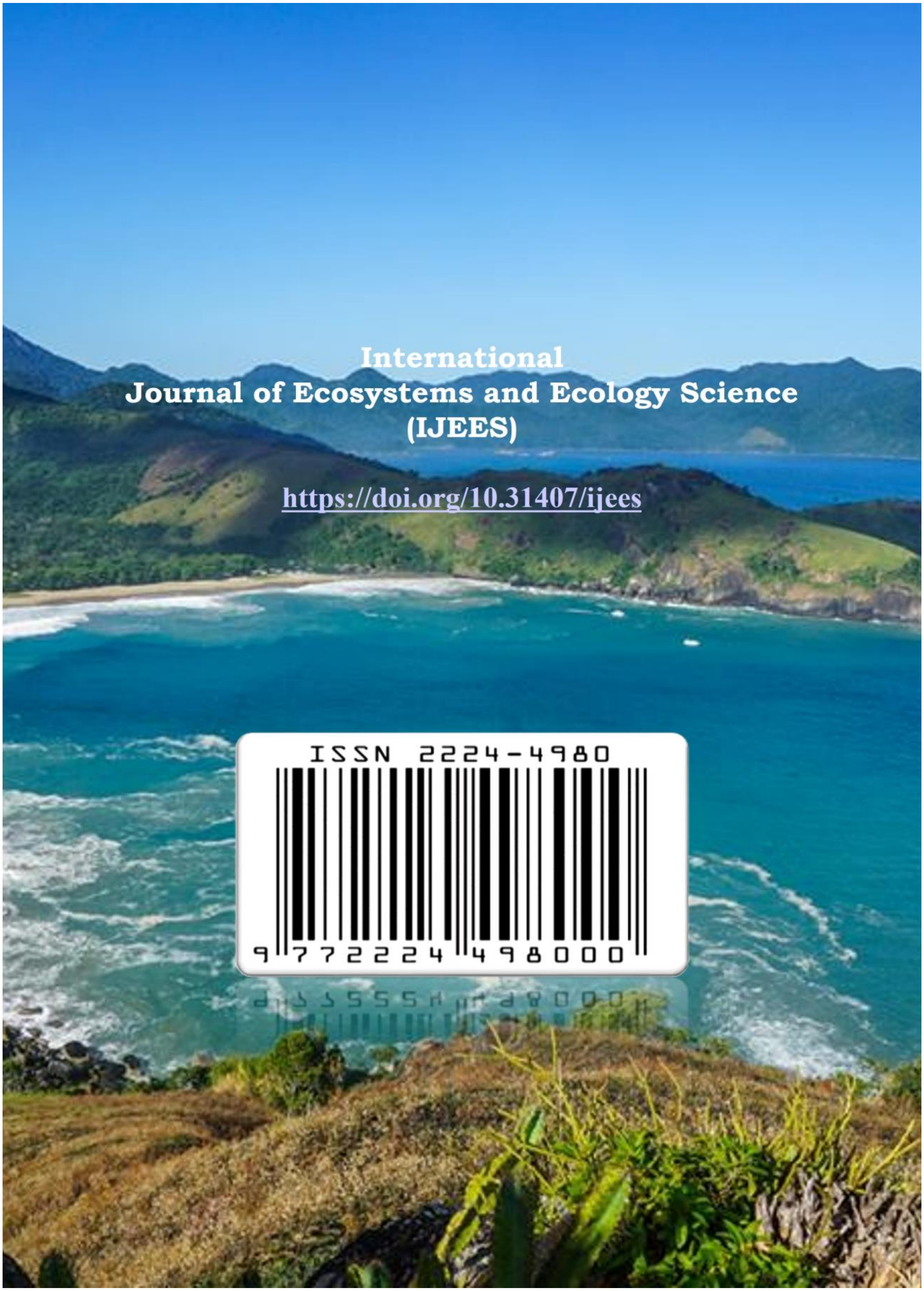
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ACCUMULATION PECULIARITIES OF HEAVY METALS IN CEREAL CROPS GRAINS OF DIFFERENT VEGETATION PERIOD IN CONDITIONS OF THE FOREST STEPPE OF THE RIGHT BANK OF UKRAINE

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ABSTRACT

Peculiarities of Cd, Zn and Cu accumulation in wheat and barley grain depending on their vegetation period have been studied. A certain influence of the vegetation period of cereals (winter, spring) in the natural and climatic conditions of the right-bank Forest-Steppe of Ukraine on the intensity of accumulation of heavy metals in grain has been established. In particular, it was found that in the grain of winter wheat and barley there is a lower concentration, accumulation coefficient, risk factor Cd, Zn and Cu compared to similar spring cereals. Some exceedances of the admissible norm of Cd according to GOST (national standart of Ukraine) 26932 in grain of spring wheat and barley are revealed. The concentration of Zn and Cu in the grain of both winter and spring wheat and barley was lower than the norm compared to the maximum allowable norm (GOST 26932). The grain of winter cereals of wheat and barley was characterized by a lower coefficient of accumulation of heavy metals, and a relatively higher coefficient of accumulation of spring cereals. The risk factor Cd exceeded the normative limit of 1.0 only in grain of spring wheat and barley. Exceedances of the normative indicator (hazard coefficient 1.0) of Zn and Cu in wheat and barley grain of both winter and spring crops were not observed.

Keywords: winter wheat, winter barley, spring wheat, spring barley, heavy metals, concentration, accumulation factor, danger factor.

INTRODUCTION

In world crop production, cereals occupy one of the leading places among agricultural plants, which are characterized by exceptionally valuable food, fodder and raw materials. In agriculture of Ukraine, cereals are also the basis of agricultural production, which meet the needs of the population in food and feed grains (Honcharuk et al., 2020; Pravdiuk et al., 2021). The most common cereals in Ukraine are winter wheat and spring barley.

These two crops occupy the largest sown areas among cereals, which play one of the main roles in improving the export potential of Ukraine (Orlovsky et al., 2019; Yakovets, 2019; Zabarna 2021). Agrarian enterprises of Ukraine pay great attention to the development of the crop industry in the direction of increasing the production of grain raw materials (Kaletnik et al., 2020).

Grain is used in the form of bread, cereals, pasta, confectionery. These products are characterized by high nutritional and taste qualities, contain sufficient amounts of proteins, carbohydrates, vitamins, amino acids and mineral salts. In addition, cereals provide livestock with feed materials (grain, straw, chaff) for the production of livestock products. All livestock industries need unlimited feed, especially industries such as pigs and poultry. They will not be able to grow without compound feeds based on cereals (Likhochvor et al., 2006; Zabarna, 2021). In addition, the grain of cereals is widely used in the manufacture of medicines, beer, alcohol, starch, cellulose, paper and more.

The country's total grain needs are determined by the amount spent on food, processing, feed, seeds, exports and the creation of state reserves. In this volume, the largest share belongs to grain consumed by the population as food and used in animal husbandry as feed material (Alexandratos et al., 2012; Muhammad Amjad Ali et al., 2019).

The grain industry in Ukraine has always been and remains the basis of the market and is traditionally strategic, as all basic needs for cereal grains are provided through its own production. Under the right economic conditions, Ukraine is able to provide itself with the necessary amount of grain and export a significant amount of it, because favorable conditions for growing grain crops, especially soil, bring Ukraine to the level of one of the world's leading grain countries (Pravdiuk et al., 2021).

An important condition for the production of grain raw materials are climatic factors, which today are quite unstable, creating certain problems in agriculture (Tkachuk, 2021).

In general, climate change is one of the most pressing global issues today. This is the beginning of a significant crisis in the relationship between man and nature. The current state of the environment is characterized by certain changes due to anthropogenic factors. Agriculture is closely linked to the use of basic natural resources such as soil, moisture, solar energy, and is therefore most vulnerable to climate change (Parry, 2019; Davydenko et al., 2021).

In Ukraine, according to the Ministry of Environmental Protection and Natural Resources and Ukrhydrometeocenter, over the past 30 years, the ambient temperature has risen by an average of 1.2° C (Ministry.., 2021). Every year there are abnormal weather phenomena (low rainfall, uneven rainfall, prolonged thaws in winter, rising temperatures during the year, stormy winds), which has some impact on vegetation and its productivity (Vdovenko et al., 2020). Such anomalous phenomena are also characterized by sharp pressure drops, which are the result of instability and significant temperature fluctuations over short periods of time. The number of anomalous phenomena on the territory of Ukraine is constantly growing, which expands the number of areas that are increasingly dependent on irrigation and soil moisture.

Ambient temperature is the most important factor determining the opportunities and timing of growing crops (Lobell, 2007). Biological and chemical processes of nutrient transformation that occur in the soil are directly dependent on temperature. Heat supply of cereal crops is characterized by the sum of average daily air temperatures above 10° C during the growing season. Both high and low temperatures disrupt the course of biochemical processes in cells and thus can cause irreversible changes in them, leading to cessation of growth, and in some cases - to the decline of cereals (Tymchuk et al., 2016).

Modern climatic temperature factors are characterized as unstable for intensive vegetation and crop formation, in particular, cereals due to high average annual temperatures, which reach + 37° C in summer and up to + 10° C in winter during thaw, low rainfall and unevenness of their loss, unstable winter periods (Peltonen-Sainio et al., 2009).

Increasing the temperature of the environment leads to increased reproduction and migration of pests of agricultural crops. Many insects, as the temperature rises, settle quickly in areas that were previously unfavorable to them due to insufficient heat. In warmer climates, insect pests begin to develop in earlier periods and damage plants that have not had time to strengthen, which leads to significant crop losses (Brabec et al., 2014). In the fields of cereals there are more and more cases of intensive development of pathogenic microorganisms, accompanied by various diseases of cereals (Li Q et al., 2011; Chakraborty et al., 2021). As a result, there is a need for increased use of chemical measures to control plant diseases, which has some impact on the quality and safety of the crop. Under such conditions, the cultivation of cereals is accompanied by contamination of the crop with residues of pesticides, nitrates, heavy metals. Among the many factors that determine the quality of cereals, the level of chemicalization in the field of crop production is important (Razanov, 2020). Mineral fertilizers are known to contain nitrogen, phosphorus and potassium, which are one of the main nutrients in plants. However, the use of mineral nitrogen, phosphorus and potassium to improve plant nutrition and increase yields contributes to the increasing removal of macro - and micronutrients from the soil, which disrupts their natural relationship in the soil environment (Korsun et al., 2018; Pelech, 2021).

At the same time, scientists emphasize that fertilizers affect the composition of trace elements in the soil and the accumulation of heavy toxic metals such as Pb, Cd, Zn and Cu and others (Razanov et al., 2017; Razanov et al., 2018; Razanov et al., 2021). Trace elements and heavy metals that enter the soil with fertilizers are mostly uncontrolled and systematic, which poses a threat to high-quality products (Yakovets, 2019; Razanov et al., 2021).
Prolonged use of mineral fertilizers in crop production over time leads to the accumulation of various toxicants in the soil, which reduces the quality of both the soil and the crop (Hossein Arfaeinia et al., 2019; Razanov et al., 2021). Excess elements such as Cd, Zn and Cu in the soil can lead to significant impairment of plant development and growth. This is clearly demonstrated by studies of heavy metal lesions of crops (Gamalero et al., 2009; Dutta et al., 2018; Dursun et al., 2020). Intensive agriculture, which is typical of most of Ukraine, harms the environment due to the growing use of chemicals in crop production, which, along with a positive factor, have a number of negative consequences (Tkachuk et al., 2021). Comparison of arable soils with virgin analogues shows that for the last 40-50 years the most characteristic negative consequences are:

- loss of arable soils of humus with an intensity of 0.42-0.51 t/ha per year;
- constant deficit of balance of nutrients in agriculture;
- acidification of chernozem soils by 0.3-0.5 pH units;
- overcompaction, especially noticeable in the western forest-steppe, destruction of structure, brittleness and crusting;
- erosional losses of the upper layer of soil, reaching several centimeters in chernozem soils and in drained soils of Polissya (Kaminskyi et al., 2018).

In addition, it is necessary to note the local contamination of soils with radionuclides (11.1% of arable land), pesticides (9.3%), heavy metals (8%), waterlogging (14%) and others. Due to the loss of humus and the extremely high level of plowing of agricultural lands, the country's soils deteriorate and the risk of water and wind erosion increases. More than 13 million hectares of agricultural land are affected by water erosion, of which almost 11 million hectares are arable land. However, despite this, today the grain economy of Ukraine is a strategic and most efficient sector of the national economy. Grain and products made from it are the basis of food security of the state. On January 1, 2016, the Association Agreement between Ukraine and the EU came into force, which allows Ukrainian business to become part of the European business community, guaranteed by the high quality and safety of food raw materials, including vegetable origin (European.., 2018). Based on this, one of the priority tasks in crop production in the current conditions of climate change and intensification of the crop industry of Ukraine is to control the quality and safety of plant raw materials, in particular, cereals.

MATERIALS AND METHODS

Studies on the accumulation of heavy metals in cereals (winter and spring wheat, winter and spring barley) were conducted in the dark gray podzolic soils of Vinnytsia, which is located in the forest-steppe zone of the central part of the Right Bank of Ukraine. The Southern Bug River divides this territory into two parts: the Left Bank, which belongs to the Dnieper Upland and the Right Bank - Podillia Plateau. The surface of Vinnytsia is an elevated plateau that descends from northwest to southeast. Most of the territory of Vinnytsia region is located within the Ukrainian Crystalline Massif. The territory of Vinnytsia is branched out by numerous river valleys, ravines and gullies, especially in the Transnistrian region. Vinnytsia region is located in the zone of temperate continental climate, for which the coldest month is January, and the warmest are July and August. The average annual rainfall in the region is 440-590 mm. May and July (130-170 mm) are characterized by the highest precipitation. The least humid are the winter months, which account for 25% of precipitation. In general, the climate of Vinnytsia region is favorable for agricultural production: long warm and fairly humid summers, early springs, dry autumns, winters with moderate frosts and heavy snow cover - all this has a positive effect on the growth of cereals, industrial and horticultural crops (Report, 2020; Zabarna, 2020). In the studied areas of the region, the most common are light gray and gray podzolic forest soils formed on loess and loess-like loams. Dark gray podzolic soils are rare in the lower parts of the slopes. Light gray podzolic forest soils are confined to narrow ridges, gray forest soils mostly occupy river slopes. According to the mechanical composition of light gray and gray forest soils are coarse-grained and medium-sawn, medium and light loam. As a rule, these are soils of unstable structure. They consist of several well-defined genetic horizons (Tsytsiura et al., 2020). In dark gray soils the reaction of the soil solution is almost neutral, in gray - slightly acidic, in light gray - acidic, due to the significant unsaturation of the absorbing complex with bases (Tsytsiura et al., 2020). Winter cereals were used in the research: winter wheat of the Akratos variety, winter barley of the Luran variety; spring cereals: spring wheat of the Xanthi variety and spring barley of the Helios variety. Winter cereals (wheat, barley) were sown on October 16, spring cereals (wheat, barley) were sown in two terms: the first on April 15 and the second on April 27. Sampling of soil to determine the content of heavy metals (cadmium, zinc, copper) was performed by the envelope method. Soil was selected with a probe to the depth of plowing - 14 cm for winter crops and 24 cm - for spring crops. Selection of grain of winter and spring cereals was carried out according to GOST 135663-83 with a manual probe from each batch separately (Pryster, 1997). Determination of heavy metals Cd, Zn and Cu in cereal grains was performed by atomic absorption method for the determination of toxic elements in food and food raw materials.

The accumulation factor (C_{acc}) was determined by the formula:

$$C_{acc} = \frac{\text{Content of heavy metals in cereal grains}}{\text{Content of heavy metals in soil}}$$

The hazard factor (C_{haz}) was determined by the formula:

$$C_{haz} = \frac{\text{Content of heavy metals in cereal grains}}{\text{Norm of heavy metals according to GOST 26932}}$$

RESULTS AND DISCUSSION

It has been proven that minerals play an important role in plant nutrition, while their entry into vegetation in high concentrations can cause a number of negative consequences, in particular, reduced crop safety. The need of plants for minerals is determined by such basic factors as: variety, yield, growth intensity and yield formation. The intensity of plant growth and formation of their harvest in turn depends on the hereditary characteristics of the variety and natural and climatic factors. Among the natural and climatic factors should be noted light, temperature, humidity, air composition. It is known that natural and climatic factors in the Forest-Steppe of Ukraine are subject to certain changes, especially with regard to air temperature and precipitation. Currently, there is an increase in ambient temperature, a significant decrease in rainfall and uneven precipitation during the year. Different varieties of cereals (winter, spring) are also used in crop production, which differ in the intensity of growth and the period of crop formation, which is characteristic of their hereditary traits. These conditions for growing cereals to some extent may affect the translocation of minerals, in particular, and heavy metals in grain products. Analysis of the intensity of accumulation of heavy metals in cereal grains (Table 1) showed exceeding the maximum allowable norms in accordance with GOST Cd. Thus, the concentration of Cd was higher in the grain of winter wheat 1.01 times, spring wheat of the first sowing period - 1.55 times and spring wheat of the second sowing period - 1.25 times compared to the maximum standards according to the existing GOST.

Table 1. Intensity of accumulation of heavy metals in cereal grains on average, mg/kg

Cereals	Terms of sowing	Heavy metals					
		Cd		Zn		Cu	
		Actual concentration, mg/kg	GOST	Actual concentration, mg/kg	GOST	Actual concentration, mg/kg	GOST
Winter wheat	16.10	0.101±0.04	0.1	8.20±0.15	50	3.21±0.23	10
Spring wheat of the first sowing period	15.04	0.155±0.02	0.1	-	50	-	10
Spring wheat of the second sowing period	27.04	0.125±0.05	0.1	10.2 ± 0.11^{xx}	50	9.79 ± 0.13^{xxx}	10
Winter barley	16.10	0.100±0.04	0.1	5.35±0.09	50	2.46±0.07	10
Spring barley of the first sowing period	15.04	0.139±0.02	0.1	12.9 ± 0.16^{xxx}	50	8.46 ± 0.12^{xxx}	10
Spring barley of the second sowing period	27.04	0.119±0.03	0.1	14.4 ± 0.14^{xxx}	50	9.71 ± 0.24^{xxx}	10

The concentration of Zn and Cu in the grain of winter wheat was 1.24 times and 3.0 times lower than in the grain of spring wheat of the second sowing period.
The concentration of Cd in the grain of winter barley did not exceed the maximum allowable norms according to the existing GOST. Whereas in barley grain of the I and II sowing period the Cd concentration exceeded 1.39 times and 1.19 times, respectively, the maximum allowable norms of the existing GOST.
The concentration of Zn and Cu was lower in the grain of winter barley, respectively, 9.3 times and 4.0 times, spring barley of the 1st sowing term - 3.8 times, 1.18 times and spring barley the 2nd sowing term - 3.4 times and 1.03 times compared to the maximum allowable norm in accordance with GOST.
There is a difference in the accumulation of heavy metals in the grain of winter and spring crops.
In particular, the concentration of Cd, Zn and Cu in winter wheat grain was 1.53 times, 1.03 times and 1.02 times lower than in spring wheat grain.
The concentration of Cd in spring wheat grain of the first sowing period was 1.24 times higher, and Zn and Cu - 1.87 times and 3.91 times lower in comparison with the grain of spring wheat of the second sowing period.
The concentration of Cd in the grain of winter barley was 1.39 times higher compared to the grain of spring barley of the first sowing period and 1.19 times - of the second sowing period.
In addition, it should be noted that the concentration of Cd in the grain of spring barley of the first sowing period was 1.16 times higher, and Zn and Cu - lower 1.11 times and 1.14 times compared to spring barley grain second sowing.
Thus, the concentration of Cd, Zn and Cu in wheat and barley grains depended on the period of cultivation of these crops.
Characterizing the coefficient of accumulation of heavy metals in cereal grains (Table 2), it should be noted that this figure also varied depending on the period of their cultivation.

Table 2. The coefficient of accumulation of heavy metals in cereal grains on average

Cereals	Terms of sowing	Heavy metals								
		Cd			Zn			Cu		
		Concentration in soil, mg/kg	Grain concentration, mg/kg	C_{acc}	Concentration in soil, mg/kg	Grain concentration, mg/kg	C_{acc}	Concentration in soil, mg/kg	Grain concentration, mg/kg	C_{acc}
Winter wheat	16.10	0.19	0.101	0.5	1.21	8.20	6.7	0.44	3.21	7.3
Spring wheat of the first sowing period	15.04	0.15	0.155	1.03	-	-	-	-	-	-
Spring wheat of the second sowing period	27.04	0.15	0.125	0.8	1.59	10.2	6.4	0.43	9.79	22.7
Winter barley	16.10	0.19	0.100	0.5	1.21	5.35	4.4	0.44	2.46	5.5
Spring barley of the first term of sowing	15.04	0.15	0.139	0.9	1.59	12.9	8.1	0.43	8.46	19.6
Spring barley of the second sowing period	27.04	0.15	0.119	0.8	1.59	14.4	9.0	0.43	9.71	22.5

The coefficient of Cd accumulation in winter wheat grain was 2.0 times and 1.6 times lower compared to similar raw materials obtained from spring wheat of I and II sowing dates. The accumulation coefficient of Zn in the grain of winter wheat was 1.4 times lower, and Cu higher 3.1 times lower compared to the grain of spring wheat of the second sowing period.

In winter barley grain, the accumulation coefficient Cd was 1.8 times lower than in spring barley grain of the first sowing period and 1.6 times lower - with the second sowing period. The accumulation coefficient of Zn and Cu in winter barley grain was also 1.8 times and 2.0 times lower compared to spring barley grain of the first sowing period and 3.5 times and 4.1 times lower compared to the second sowing period of spring barley.

The results of the studies shown in Table 3 show that the risk factor Cd in winter wheat grain was 1.53 times lower compared to spring wheat grain of the first sowing period and 1.23 times lower than the second sowing period. The hazard factor of Zn and Cu in winter wheat grain was 1.25 times and 3.03 times lower than in spring wheat of the second sowing period.

Table 3. Risk factor of heavy metals in cereal grains

Cereals	Terms of sowing	Heavy metals								
		Cd			Zn			Cu		
		Actual concentra-tion, mg/kg	GOST	$C_{haz.}$	Actual concentra-tion, mg/kg	GOST	$C_{haz.}$	Actual concentra-tion, mg/kg	GOST	$C_{haz.}$
Winter wheat	16.10	0.101	0.1	1.01	8.20	50	0.16	3.21	10	0.32
Spring wheat of the first sowing period	15.04	0.155	0.1	1.55	-	50	-	-	10	-
Spring wheat of the second sowing period	27.04	0.125	0.1	1.25	10.2	50	0.20	9.79	10	0.97
Winter barley	16.10	0.100	0.1	1.0	5.35	50	0.10	2.46	10	0.24
Spring barley of the first term of sowing	15.04	0.139	0.1	1.39	12.9	50	0.25	8.46	10	0.84
Spring barley of the second sowing period	27.04	0.119	0.1	1.19	14.4	50	0.28	9.71	10	0.97

It should be noted that the risk factor Cd in the grain of spring wheat of the first sowing period was 1.22 times higher, and Zn and Cu - lower by 1.18 times and 3.88 times, respectively, compared to the second sowing period.

The risk factor Cd in winter barley grain was 1.39 times and 1.19 times higher than in spring barley grain I and II, respectively. Whereas the danger coefficient Zn and Cu, on the contrary, was 2.5 times and 3.5 times lower in winter barley grain compared to spring barley of the first sowing period and 2.8 times and 4.04 times lower than the second sowing period. The risk factor Cd in grain of spring barley I sowing period was 1.20 times higher, and Zn and Cu - lower 1.12 times and 1.15 times, respectively, compared to spring barley grain II sowing period.

That is, the risk factor Cd in the grain of winter wheat and barley was lower compared to the grain of spring crops of these plants.
The risk factor Zn and Cu in winter wheat grain was lower in spring crops of the second sowing period, and the first period, on the contrary, higher. In winter barley grain, the danger coefficient Zn and Cu was lower compared to spring barley in both the first and second sowing periods.

Summarizing the results of research, it should be noted that the period of growing wheat and barley has a certain effect on the translocation of Cd, Zn and Cu into grain products of these cereals.

CONCLUSION

- The results of the research revealed a lower level of Cd, Zn and Cu accumulation in wheat and winter barley grain compared to similar spring cereals. Exceedances of Cd, Zn and Cu with GOST 26932 in winter wheat grain and winter barley were not detected, while in spring cereals Cd only exceeded 1.25 times and 1.19 times in barley grain.
- The accumulation coefficient of Cd and Cu in winter wheat grain was 1.6 times lower and 4.1 times lower than in spring wheat.
- The coefficient of Cd accumulation in winter barley grain was lower from 1.6 to 1.8 times, Zn - from 1.2 to 1.3 times, Cu - from 2.7 to 3.0 times compared to spring barley grain.
- The hazard factor Cd exceeded the maximum permissible level, which is 1.0 only in the grain of spring crops of wheat and barley. No exceedances of the Zn and Cu hazard coefficients were observed in wheat and barley grain samples of both winter and spring crops. The risk factor for winter barley grain was lower compared to spring grain.

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