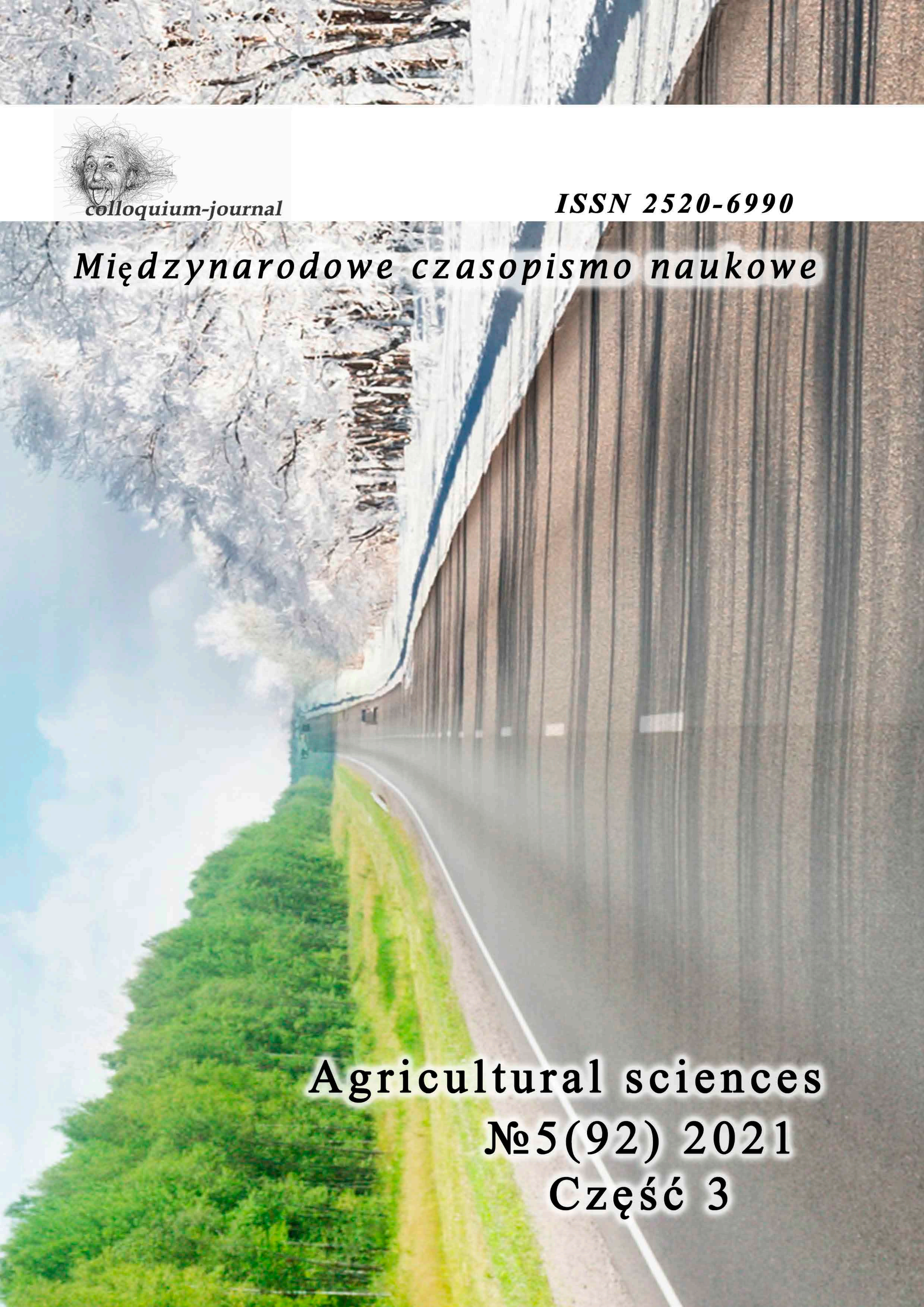

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THE INTENSITY OF ACCUMULATION OF HEAVY METALS IN THE LEAF MASS OF MILK THISTLE SEEDS WITH ITS MINERAL FERTILIZER

Abstract.

The influence of mineral fertilizer of milk thistle on the intensity of accumulation has been studied in leaf mass and seeds in conditions of local contamination of agricultural soils with heavy metals. It was found that the fertilization of milk thistle with ammonium nitrate – 60 kg/ha, potassium chloride - 60 kg/ha and simple superphosphate – 60 kg/ha increases the accumulation factor and the content of Pb, Cd, Zn and Cu in its leaf mass and seeds.

Keywords: *milk thistle, content, accumulation coefficient, danger coefficient, soil, leaf mass, seeds, heavy metals.*

I. Introduction

Possibilities of application of milk thistle are rather widespread in a national economy. Along with this, it is necessary to note the growing demand for this raw material [4, 2, 6]. However, the requirements for the quality and safety of medicinal plant raw materials are increasing [3]. It is known that the quality and safety of medicinal raw materials depends on the ecological state of the environment, the current state of which in some areas is characterized by high levels of pollution by various toxicants. Such areas include of man-made impact, highly saturated industrial production, agricultural production, especially intensive agriculture, transport, etc [1].

II. Literary review.

Recently, due to the shortage of medicinal plant raw materials, the introduction of growing medicinal plants in terms of agricultural crop rotations is practiced. However, it is known that the condition of agricultural lands as a result of chemicalization of agricultural production, use of mineral fertilizers, herbicides and pesticides in crop production is significantly deteriorating. Under such conditions, there is monitor the intensity of accumulation of heavy metals in medicinal raw materials grown in agricultural areas [5, 4].

Cultivation of milk thistle in modern field crop rotation makes it possible to increase its yield by fertilizing in particular and mineral. Agricultural lands as a result of growing different crops, especially in conditions of intensive agriculture, are under a constantly increasing level of pollution by various toxicants, including heavy metals. Growing milk thistle under such conditions requires constant monitoring of quality and safety [7].

It is known that with each mg of double superphosphate, 3.7 mg – Cd, 39mg – Pb, 48 mg – Zn and 14 mg – Cu, with potassium chloride 3.9 mg – Cd, get into the soil. 14 mg – Pb, 11 mg – Zn and 6.3 mg – Cu.

III. Research methodology.

After exploitation the intensity of accumulation of Pb, Cd Zn and Cu in leaf mass and seeds were carried out in conditions of local contamination of agricultural lands with heavy metals on gray forest soils. The research scheme included five options, the one of which provided for the cultivation of milk thistle without fertilization, the second, third, fourth and fifth provided with fertilization with mineral fertilizers, respectively, ammonium nitrate – 60 kg/ha, potassium chloride – 60 kg/ha, simple superphosphate – 60 kg/ha and a mixture of $N_{60}K_{60}P_{60}$.

The concentration of heavy metals in soils, vegetative mass and seeds of milk thistle were recognized by the atomic absorption method.

IV. Research results

As a result of research, the accumulation of lead in the leaf mass of milk thistle spotted mineral fertilizers in large quantities, significantly exceeding the maximum allowable concentration (MPC), occurs in the plant mass, which is 5.0 mg/kg of dry matter (Table 1).

Table 1

Concentration of heavy metals in the leaf mass of milk thistle (mg/kg) 2017-2019 (n = 4, m ± m)

Experi-mental fea-	Features of fertilizer	Concentration of heavy metals							
		Pb		Cd		Zn		Cu	
		Actual con-centration.	MPC	Actual con-centration.	MPC	Actual con-centration.	MPC	Actual con-centration.	MPC
I	Without fertilization	8,4±0,09	5,0	1,0±0,89	1,0	28,8±1,3	10	13,2±0,43	5,0
II	Ammonium nitrate, 60 kg /ha	12,05±0,05^{xx}	5,0	2,4±0,75^{xxx}	1,0	156,1±5,6^{xxx}	10	16,6±0,51^{xxx}	5,0
III	Potassium chloride, 60 kg/ha	12,70±0,07^{xxx}	5,0	1,7±0,083^{xxx}	1,0	33,7±1,7^{xxx}	10	15,4±0,47^{xxx}	5,0
IV	Superphosphate is simple, 60 kg ha	12,40±0,06^{xxx}	5,0	1,36±0,62^{xxx}	1,0	34,2±1.5^{xxx}	10	15,1±0,34^{xxx}	5,0
V	Ammonium nitrate, potassium chloride, simple superphos-phate, $N_{60}K_{60}P_{60}$	10,4±0,07^{xxx}	5,0	1,5±0,071^{xxx}	1,0	50,3±1.3^{xxx}	10	20,3±0,61^{xxx}	5,0

In the variant without using of fertilizers (control), the lead content in the leaf mass of milk thistle was 1.7 MPC, using a mixture of fertilizers in the active raw material $N_{60}K_{60}P_{60}$ respectively 2.1 MPC, 2.4 MPC, 2.5 MPC and 2.5 MPC.

The results of research showed a significant effect of mineral fertilizers on the intensity of accumulation in the vegetative mass of milk thistle and cadmium (Table 1), 0 mg/kg. Whereas in the vegetative mass of milk thistle spotted concentration of cadmium was higher than the MPC when feeding $N_{60}K_{60}P_{60}$ (ammonium nitrate, superphosphate simple and potassium chloride) 1.5 times, superphosphate simple – 1.36 times, potassium chloride – 1.7 times, ammonium nitrate – 2.4 times. The highest level of excess of the maximum concentration limit for cadmium in the leaf mass was observed when feeding milk thistle with ammonium nitrate.

The accumulation of zinc in the leaf mass of milk thistle with the application of mineral fertilizers, especially ammonium nitrate, in values significantly exceeding the maximum concentration limit of zinc in the leaf mass of plants - 10.0 mg / kg in dry matter.

The results of research have shown that milk thistle plants can intensively absorb zinc from the soil, even with its low content in the soil. When mineral fertilizers are applied to the soil, which may contain zinc as a ballast of substances or promote the conversion of stationary forms of zinc in the soil into mobile, there is an increase in the concentration of the element in the leaf mass of milk thistle plants. The content of zinc in ammonium nitrate according to our previous studies is 0.6 mg/kg of body weight, in superphosphate – 36.0 mg/kg, potassium chloride – 8.0 mg/kg.

In particular, in the variant without using of fertilizers, the zinc content in the leaf mass of milk thistle is 2.9 MPC, with the use of potassium chloride 3.4 MPC of simple superphosphate – 3.4 MPC of a mixture of mineral fertilizers of ammonium nitrate, superphosphate and potassium chloride – 5.0 MPC. The concentration of zinc in the leaf mass of milk thistle increased most significantly with the introduction of ammonium nitrate – 15.6 MPC (Table 1).

The results of research showed a certain effect of mineral fertilizers on the intensity of accumulation in the leaf mass of milk thistle spotted copper (Table 1). Thus, in the leaf mass of milk thistle, which was grown on gray forest soils without fertilization, the concentration of copper was 2.64 times higher than the MPC (5.0 mg/kg). Whereas for feeding $N_{60}K_{60}P_{60}$ in the vegetative mass of milk thistle, the concentration of copper was 4.06 times higher than the MPC, simple superphosphate – 3.02 times, potassium chloride – 3.08 times, ammonium nitrate – 3.32 times. The highest level of exceeding the MPC for copper was observed for complex feeding of milk thistle $N_{60}K_{60}P_{60}$ fertilizers.

In comparison, the leaf mass of milk thistle, which was grown without mineral fertilization with similar raw materials obtained using ammonium nitrate, potassium chloride, double superphosphate and a mixture of $N_{60}K_{60}P_{60}$. fertilizers, the copper concentration was 1.25 times, 1.16 times, 1.14 times and 1.53 times higher, them respectively.

Table 2

The coefficient of accumulation of heavy metals in the leaf mass of milk thistle

Experiment options	Features of fertilizer	Heavy metals			
		Pb	Cd	Zn	Cu
I	Without fertilization	3,2	10	2,9	41,2
II	Ammonium nitrate, 60 kg/ha	4,63	24,0	15,5	51,8
III	Potassium chloride, 60 kg/ha	4,88	17,0	3,4	48,1
IV	Superphosphate is simple, 60 kg/ha	4,76	13,6	3,4	47,1
V	Ammonium nitrate, potassium chloride, simple superphosphate, $N_{60}K_{60}P_{60}$	4,0	15,0	5,0	63,4

The lead content in the soil where milk thistle was grown was 2.6 mg/kg (table 2). The coefficient of accumulation of lead by the leaf mass of milk thistle without using of fertilizers was the lowest and amounted to 3.2.When using a mixture of ammonium nitrate, simple phosphate and potassium chloride, the accumulation coefficient was 4.0, when making ammonium nitrate – 4.63, simple superphosphate – 4.76, potassium chloride – 4.88. Such high indicators of the accumulation coefficient of lead indicate the intensive absorption by the leaf mass of milk thistle of lead from the soil in much higher concentrations than the content of mobile forms of lead in the soil.

Characterizing the coefficient of accumulation of cadmium in the vegetative mass of milk thistle, it should be noted that this indicator was in the range from 10 to 24. The coefficient of cadmium accumulation in the vegetative mass of milk thistle was higher than the $N_{60}K_{60}P_{60}$ fertilization fertilizers 1.5 times, simple superphosphate – 1.36 times, potassium chloride – 1.7 times, ammonium nitrate – 2.4 times compared to similar raw materials obtained without fertilization.

The coefficient of accumulation of zinc in the leaf mass of milk thistle in the variant without using of fertilizers was lower – 2.9.

Application of superphosphate simple and potassium chloride zinc accumulation coefficient – 3.4, introduction of a mixture of ammonium nitrate, superphosphate simple and potassium chloride – 5.0, use of ammonium nitrate – 15.5. Such high indicators of zinc accumulation coefficient indicate intensive absorption of leaf mass thistle of zinc spotted from the soil as microelements in higher concentrations than a large number of forms of zinc in the soil.

Characterizing the coefficient of accumulation of copper in the leaf mass of milk thistle, it should be noted that this figure was in the range from 41.2 to 63.4. The highest coefficient of copper accumulation was observed in the leaf mass of milk thistle with complex fertilization with its mineral fertilizer, and the lowest - in the variant without fertilization.

Table 3

The hazard factor of heavy metals in the leaf mass of milk thistle

Experiment options	Features of fertilizer	Heavy metals			
		Pb	Cd	Zn	Cu
I	Without fertilization	1,68	10	1,6	1,8
II	Ammonium nitrate, 60 kg/ha	2,41	2,4	2,2	2,5
III	Potassium chloride, 60 kg/ha	2,40	1,7	2,1	2,3
IV	Superphosphate is simple, 60 kg/ha	2,48	1,36	2,0	2,3
V	Ammonium nitrate, potassium chloride, simple superphosphate, $N_{60}K_{60}P_{60}$	2,08	1,5	1,9	2,0

The highest risk factor (Table 3) for lead in the leaf mass of milk thistle was set in the application of simple superphosphate – 2.48. When adding ammonium nitrate, the risk factor for lead is reduced to 2.41, when adding potassium chloride – to 2.40, and in a mixture of good ammonium nitrate, superphosphate simple and potassium chloride up to 2.08.

The risk factor for cadmium ranged from 1.0 to 2.4. The highest risk factor was characterized by the vegetative mass of milk thistle grown for fertilization with mineral fertilizers, while the lowest – without mineral fertilization. In particular, in the vegetative mass of milk thistle grown without fertilization, the risk factor for cadmium was lower compared to similar raw materials obtained for fertilization $N_{60}K_{60}P_{60}$ 1.5 times, simple superphosphate – 1.36 times, potassium chloride – 1.7 times, ammonium nitrate – 2.4 times.

The highest risk factor for zinc in the leaf mass of milk thistle was recorded in the variant with the use of ammonium nitrate – 15.6. With the introduction of a mixture of fertilizers of ammonium nitrate, simple phosphate and potassium chloride, the risk factor of zinc decreased to 5.0, with the introduction of potassium chloride and simple superphosphate – up to 3.4.

Characterizing the risk factor of copper in the leaf mass of milk thistle, it should be noted that it ranged from 2.0 to 2.5. The highest risk factor for copper in the leaf mass of milk thistle was for the use of nitrogen fertilizers. Compared with the variant without fertilization in the leaf mass of milk thistle, the risk factor for copper was 1.38 times higher than the use of ammonium nitrate, 1.27 times higher than potassium chloride, 1.27 times higher than simple superphosphate and 1.11 times higher.

Table 4

Concentration of heavy metals in the seeds of milk thistle 2017-2019
(n = 4, m ± m)

Experimental features	Features of fertilizer	Concentration of heavy metals							
		Pb		Cd		Zn		Cu	
		Actual concentration.	MPC	Actual concentration.	MPC	Actual concentration.	MPC	Actual concentration.	MPC
I	Without fertilization	330±0,04	0.5	0.40±0,017	0.1	82±3.7	50	18,3±0,39	10
II	Ammonium nitrate, 60 kg/ha	430±0,06^{xxx}	0.5	0.6±0,037^{xxx}	0.1	112±5,6^{xxx}	50	25,6±0,32^{xxx}	10
III	Potassium chloride, 60 kg/ha	4.0±0,09^{xxx}	0.5	0.52±0,032^{xxx}	0.1	107±5.4^{xxx}	50	23±0,41^{xxx}	10
IV	Superphosphate is simple, 60 kg/ha	3.95±0,05^{xxx}	0.5	0,53±0,041^{xxx}	0.1	99.0±4,5^{xxx}	50	23±0,37^{xxx}	10
V	Ammonium nitrate, potassium chloride, simple superphosphate, $N_{60}K_{60}P_{60}$	3.65±0,06^{xxx}	0.5	0.48±0,032^{xxx}	0.1	93±4,6^{xxx}	50	20,3±0,54^{xxx}	10

Our research also found a significant accumulation of lead in the seeds of milk thistle. The maximum permissible concentration of lead in plant seeds is much lower than in the leaf mass and is 0.5 mg/kg of dry matter. In the variant without fertilizers, the lead content in the seeds of milk thistle was 6.6 MPC, when fertilized with a mixture of ammonium nitrate, superphosphate and potassium chloride – 7.3 MPC, simple superphosphate – 7.9 MPC, potassium chloride – 8.0 MPC, ammonium nitrate – 8.6 MPC (Table 4).

Analysis of the results of research the effect of mineral nutrition of milk thistle on the concentration of cadmium in the seeds also showed a certain effect of potassium, nitrogen and phosphorus fertilizers on the level of accumulation of this element in the plant.

In particular, the concentration of cadmium in the seeds of milk thistle, which was grown without fertilizing with mineral fertilizers, was 4 times higher than the maximum concentration limit, while when fertilizing $N_{60}K_{60}P_{60}$ fertilizers – 4.8 times, simple superphosphate – 5.3 times, potassium chloride – 5.2 times, ammonium nitrate – 6 times.

The highest level of exceeding the MPC was found in the seeds of milk thistle for fertilizing it with nitrogen fertilizer.

Significant accumulation of zinc was also found in the seeds of milk thistle. The maximum permissible concentration of zinc in plant seeds is much higher than in the leaf mass – 50.0 mg / kg in dry matter. In the variant without using of fertilizers, the zinc content in the seeds of milk thistle is 1.6 MPC, for fertilizer with a mixture of ammonium nitrate, superphosphate and potassium chloride – 1.9, simple superphosphate – 2.0, potassium chloride – 2.1, ammonium nitrate – 2.3 MPC.

Analyzing the intensity of copper accumulation in the seeds of milk thistle, it is necessary to note a certain dependence of its concentration on the type of mineral fertilizers. Thus, the concentration of copper in the seeds of milk thistle without fertilization with mineral fertilizers was 18.3 mg/kg, while for fertilization with a mixture of $N_{60}K_{60}P_{60}$ fertilizer it was 1.1 times higher, simple superphosphate – 1.2 times, potassium chloride – 1.2 times, ammonium nitrate – 1.4 times.

Table 5

The coefficient of accumulation of heavy metals in the seeds of milk thistle

Experimental features	Features of fertilizer	Concentration of heavy metals			
		Pb	Cd	Zn	Cu
I	Without fertilization	1,36	4,0	8,1	57,1
II	Ammonium nitrate, 60 kg/ha	1,6	6,0	11,1	80
III	Potassium chloride, 60 kg/ha	1,5	5,2	10,6	72
IV	Superphosphate is simple, 60 kg/ha	1,5	5,3	9,8	71,8
V	Ammonium nitrate, potassium chloride, simple superphosphate, $N_{60}K_{60}P_{60}$	1,4	4,8	9,2	63,4

The highest coefficient of accumulation of lead by seeds of milk thistle (Table 5) was set in the variant of ammonium nitrate – 1.6. When using potassium chloride and simple superphosphate, the accumulation coefficient decreases slightly and is 1.5.

The use of a mixture of fertilizers of ammonium nitrate, superphosphate and potassium chloride further reduces the accumulation rate to 1.4. In the variant without the using of fertilizers, the coefficient of accumulation of lead by seeds of milk thistle was the lowest and was 1.3.

Detection and increase of cadmium accumulation coefficient in seeds of milk thistle with mineral fertilization, which ranged from 4.8 to 6.0.

Thus, the coefficient of accumulation of cadmium in the seeds of milk thistle for feeding a mixture of $N_{60}K_{60}P_{60}$ 1.2 times, simple superphosphate 1.3 times, potassium chloride 1.3 times ammonium nitrate 1.5 times compared to similar raw materials obtained without using of mineral fertilizers.

The highest coefficient of zinc accumulation by seeds of milk thistle was set in the variant with the introduction of ammonium nitrate – 11.1. With the use of potassium chloride, the accumulation coefficient decreases slightly – up to 10.6, and simple superphosphate – up to 9.8.

The use of a mixture of fertilizers of ammonium nitrate, superphosphate and potassium chloride further reduces the accumulation rate – up to 9.2. In the variant without using of fertilizers, the coefficient of accumulation of zinc by the seeds of milk thistle was the lowest – 8.1.

The coefficient of copper accumulation in the seeds of milk thistle was 1.4 times higher when fed with ammonium nitrate, simple superphosphate – 1.25 times, potassium chloride – 1.26 times, a mixture of $N_{60}K_{60}P_{60}$ fertilizers – 1.1 times compared to seeds obtained without fertilization.

Table 6

The coefficient of danger of heavy metals in the seeds of milk thistle

Experimental features	Features of fertilizer	Concentration of heavy metals			
		Pb	Cd	Zn	Cu
I	Without fertilization	6,6	0,40	1,6	1,8
II	Ammonium nitrate, 60 kg/ha	8,6	6,0	2,2	2,5
III	Potassium chloride, 60 kg/ha	8,0	5,2	2,1	2,3
IV	Superphosphate is simple, 60 kg/ha	7,9	5,3	2,0	2,3
V	Ammonium nitrate, potassium chloride, simple superphosphate, $N_{60}K_{60}P_{60}$	7,3	0,48	1,9	2,0

The lowest risk factor for lead (Table 6) in the seeds of milk thistle was found in the variant without using of fertilizers – 6.6. When applying a mixture of ammonium nitrate, superphosphate simple and potassium chloride, the hazard was 7.3, when using superphosphate simple – 7.9, potassium chloride – 8.0, ammonium nitrate – 8.6.

The risk factor for cadmium in the seeds of milk thistle ranged from 0.48 to 0.6. For feeding with $N_{60}K_{60}P_{60}$ mixture. In milk thistle, the risk factor for cadmium seeds was 1.2 times higher, simple superphosphate 1.3 times higher, potassium chloride 1.3 times higher, and 1.5 times higher ammonium nitrate.

The lowest risk factor for zinc in the seeds of milk thistle was found in the version without using of fertilizers – 1.6. With the introduction of a mixture of ammonium nitrate, superphosphate simple and potassium chloride, the hazard factor was 1.9, with the use of simple phosphate – 2.0, potassium chloride – 2.1, ammonium nitrate – 2.2.

The risk factor for copper ranged from 1.8 to 2.5. The highest risk factor was characterized by the seeds of milk thistle, grown for fertilization with mineral fertilizers, while the lowest - without mineral fertilization. In particular, in the seeds of milk thistle grown without fertilization, the risk factor for copper was lower compared to similar raw materials obtained for fertilization $N_{60}K_{60}P_{60}$ 1.1 times, simple superphosphate – 1.27 times, potassium chloride – 1.27 times, ammonium nitrate – 1.38 times.

V. Conclusions.

The results of the research showed that the fertilization of milk thistle, ammonium nitrate (60 kg/ha), potassium chloride (60 kg/ha) and simple superphosphate (60 kg/ha), in the conditions of local contamination of agricultural lands on gray forest soils increases the coefficient Pb,Cd,Zn and Cu, which is accompanied by an increase in these products of these toxicants to a rate exceeding the MPC.

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