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ORIGINAL ARTICLE

Assessment of heavy metal pollution of gray forest soils of agricultural lands and their phytoremediation in the cultivation of milk thistle

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The efficiency of removing heavy metals (lead, cadmium, zinc, copper) from gray forest soils in the cultivation of milk thistle has been studied. The research included field, laboratory method of atomic absorption, mathematical and statistical processing. We found that the content of lead, cadmium, zinc, and copper in the vegetative mass of milk thistle when grown on gray forest soils in the right-bank forest-steppe of Ukraine was 6.2 mg/kg, 1.25 mg/kg, 32.5 mg/kg, and 12.0 mg/kg, respectively. The high accumulation of heavy metals by milk thistle had a positive effect on the removal of lead, cadmium, zinc, and copper due to phytoremediation. Thus, 159 g and 1.12 g of lead; 31.9 g and 0.15 g of cadmium; 828.5 g and 11 g of zinc, and 306 g and 4.0 g of copper, respectively, are removed from the soil of each hectare with a vegetative mass and seeds of milk thistle with a yield of 25.5 t/ha. Thus, when growing milk thistle from gray forest soils per 1 ha of area for each growing season of this culture is made 160 g of lead, 32 g of cadmium, 839 g of zinc, and 310 g of copper.

Keywords: Lead, cadmium, zinc, copper, milk thistle, phytoremediation, concentration, vegetative mass, seeds.

Introduction

Artificial population activities have led to increased pollution of the environment, particularly agricultural soils with various toxicants, including heavy metals (Zwolak et al., 2019, Razanov et al., 2018; Razanov et al., 2020). Today, both in Ukraine and globally, the sources of agricultural soil pollution are mineral fertilizers, pesticides, herbicides, growth stimulants, the use of which, especially in intensive agriculture, is growing year by year, which is the reason for increased toxicants in soils. (Lemanowicz, 2015; Razanov et al., 2018; Kumar et al., 2019; Titarenko, 2021). Practice shows that in Ukraine, the use of mineral fertilizers and plant protection products from weeds and pests has increased dramatically over the past 30 years, their application rates have increased, especially in intensive farming conditions.

Among the heavy metals that enter the soil, the most significant dangers are lead, cadmium, zinc, and copper due to their high supply to plants (Caldasa & Machadob, 2004; Ali, 2018). Toxic metals are nondegradable and accumulated in nature. As a result, they consequently enter into the food chain (Patra et al., 2020).

It is known that with mineral fertilizers, in particular nitrogen, phosphorus and potassium fertilizers enter the soil (mg/kg): lead– 174.4; 138.1; 196.5; cadmium–1.3; 2.7; 0.6; zinc–186.4; 1230.1; 182.3; copper–201.9; 155.1; 186.4 respectively (Orlov, 1994). Organic fertilizers (humus, sugar beet lime sludge compost), 3.3 mg and 28 mg of lead, 0.2 mg and 0.18 mg of cadmium, 12.1 mg and 22 mg of zinc, and 19.8 mg and 6.3 mg of copper enter the soil with each kilogram.

Intensive receipts of heavy metals into the soil have caused some problems in agricultural production. Since the 60s of the last century, as a result of human activities, environmental pollution in some areas has exceeded the natural capacity for self-cleaning.

Once in the soil, heavy metals fill the reaction centers. It is known that the course of migration and sorption processes of heavy metals in soils depends on soil properties, in particular, humus content, mineral composition, soil pH, and metabolic bases (Zhou et al., 2016). Entering the soil, heavy metals turn into slowly movable complexes. There are some differences in the movement of heavy metals in the soil; in particular, lead and copper are more firmly fixed in organic complexes than cadmium. Soil organic matter binds heavy metals more strongly than mineral complex. Heavy metals in soil may be found in one or more of the following forms: dissolved (in soil solution), exchangeable (in organic and inorganic components), as insoluble precipitates with other soil components (Aydinalp & Marinova, 2003). Heavy metals in exchange form are the most dangerous because they are constantly moving in the soil-plant syste-their products, which threatens its use as food raw materials (Wang et al., 2003). Therefore, in the conditions of man-caused load on agricultural lands, essential measures to reduce pollution and inflow of heavy metals into plants are the use of agronomic and agrobiological measures in crop production, which include tillage methods, selection in crop rotation of crops with low ability to accumulate toxicants, removal of heavy metals from soils by plants due to phytoremediation, increase of humus content due to the use of organic and green fertilizers, lowering of soil pH (Saxena et al., 2020; Muthusaravanan et al., 2018).

Among these measures, the high efficiency of reducing the concentration of heavy metals in the soil is observed due to phytoremediation, in which the vegetative mass of plants from the soil removes a certain amount of heavy metals in exchange form (Muthusaravanan et al., 2018; Liu et al., 2020; Saxena et al., 2020; Shah Vijendra & Daverey, 2020; Nedjimi, 2021).

Phytoremediation is a low-costly, socially acceptable, and environmentally friendly technology compared to other chemical methods of HMs decontamination. This technique applied various mechanisms, which include HMs uptake (phytoextraction), breakdown and transformation of HMs (phytodegradation), emission in the atmosphere (phytovolatilization), and their stabilization in the root system (phytostabilization) (Nedjimi, 2021). Among agricultural plants, there are plants suitable for phytoremediation (Kirdey, 2017).

Recently, crop rotation in the right-bank Forest-Steppe of Ukraine also includes milk thistle, the vegetative mass, and seeds used mainly as medicinal raw materials (Devi, 2019; Bhattacharya, 2020). It is known that milk thistle actively accumulates heavy metals, which helps to reduce their concentration in soils (Razanov et al., 2021). Therefore, the research aimed to study the intensity of removal of heavy metals from the soils by milk thistle in the conditions of agricultural lands of the Forest-Steppe of Ukraine.

Materials and Methods

The research was conducted in the conditions of the right-bank Forest-Steppe of Ukraine on gray forest soils in the farms of the Vinnytsia region, using four agricultural lands. Soil selection to detect the intensity of heavy metal contamination was performed by the envelope method. The vegetative mass of milk thistle was selected by spot sampling. The concentration of heavy metals (lead, cadmium, zinc, copper) was determined by atomic absorption spectrometry. The content of heavy metals in the vegetative mass and seeds was determined based on dehydrated matter. The coefficient of accumulation (AC) was calculated as the ratio of heavy metals in the plant (vegetative mass, seeds) to their mobile contents soil forms and hazard ratio (HR), as the ratio of heavy metals in the plant (vegetative mass, seeds) to their MPC. The milk thistle's vegetative mass was 5 mg/kg for lead, 1.0 mg/kg for cadmium, 10 mg/kg for zinc, and 5 mg/kg for copper. The MPC of milk thistle seeds was lead–0.5 mg/kg, cadmium–0.1 mg/kg, zinc–50 mg/kg, and copper–10 mg/kg.

Results and Discussion

The analysis of research results (Table 1) showed that in the soils where milk thistle was grown, no exceedances of the MPC were observed. The lead content in the soils of agricultural lands where milk thistle was grown ranged from 1.0 mg/kg to 1.3 mg/kg, which averaged 1.2 mg/kg. Compared to the MPC, the lead content in the soil was 1.17 times lower than this figure. The cadmium content ranged from 0.23 mg/kg to 0.4 mg/kg, which averaged 0.32 mg/kg, 2.1 times lower than the MPC. The zinc content in the soils ranged from 3.5 mg/kg to 5.2 mg/kg, which averaged 4.7 mg/kg.

Compared to the MPC, the zinc content in soils was 4.9 times lower than this figure. The soil's copper content ranged from 1.0 mg/kg to 1.8 mg/kg, which averaged 1.35 mg/kg. Compared to the MPC, the copper content in soils was 2.2 times lower.

Agricultural land	Heavy metals									
Agricultural land	Lead	MPC	Cadmium	MPC	Zinc	MPC	Copper	MPC		
1	1.2	6.0	0.3	0.7	4.7	23	1.0	3.0		
2	1.0	6.0	0.2	0.7	3.5	23	1.2	3.0		
3	1.3	6.0	0.4	0.7	5.4	23	1.8	3.0		
4	1.2	6.0	0.37	0.7	5.2	23	1.4	3.0		
On average	1.17	6.0	0.32	0.7	4.7	23	1.35	3.0		

Table 1. Soil pollution by heavy metals, mg/kg.

Analysis of research results (Table 2) showed that even though in the soil of agricultural lands the content of heavy metals (lead, cadmium, zinc, copper) was lower than the MPC, in the vegetative mass of milk thistle revealed a significant excess of existing permissible norms.

	Lead			Cadmium			Zinc			Copper		
Agricultural land	Actual conc.	AC	HR	Actual conc.	AC	HR	Actual conc.	AC	HR	Actual conc.	AC	HR
1	6.2	5.1	1.2	1.3	4.3	1.3	32	6.8	3.2	12.5	12.5	2.5
2 3	7.1 5.4	7.1 4.1	1.4 1.3	1.2 1.1	5.2 2.7	1.2 1.1	34 34	9.7 6.3	3.4 3.4	14.5 10.5	10.4 5.8	2.9 2.0
4	6.2	5.1	1.2	1.4	3.8	1.4	30	5.7	3.0	10.5	7.5	2.0
On average	6.2	5.3	1.27	1.25	4.0	1.25	32.5	7.1	3.25	12.0	9.0	2.4

Table 2. Contamination of the vegetative mass of milk thistle spotted with heavy metals.

In particular, the lead content in the vegetative mass of milk thistle ranged from 5.4 mg/kg to 7.1 mg/kg, which averaged 6.2 mg/kg. That is, the content in the vegetative mass of milk thistle exceeded the MPC by 1.24 times.

The cadmium content in the vegetative mass of milk thistle ranged from 1.1 mg/kg to 1.4 mg/kg, which averaged 1.25. Compared with the MPC, the cadmium content exceeded this figure by 1.25 times.

The zinc content in the vegetative mass of milk thistle ranged from 30 mg/kg to 34 mg/kg, which averaged 32.5 mg/kg. Compared with the MPC, the zinc content in the vegetative mass of milk thistle was 3.25 times higher.

The copper content in the vegetative mass ranged from 10.5 mg/kg to 14.5 mg/kg, which averaged 12.0 mg/kg, and in comparison with the MPC, exceeded this figure by 2.4 times.

The average coefficient of accumulation of lead, cadmium, zinc, and copper on the studied lands was 5.3; 4.0; 7.1, and 9.0, respectively. The highest coefficient of accumulation in the vegetative mass of milk thistle was observed for copper and the lowest for cadmium.

The hazard ratio for heavy metals in the vegetative milk thistle on average for agricultural land was for lead, cadmium, zinc, and copper 1.27; 1.25; 3.25 and 2.4 respectively. The hazard ratio for heavy metals in the vegetative mass was observed for zinc and the lowest for cadmium.

Analyzing the results of the studies shown in Table 3, it should be noted that the content of heavy metals in the seeds of milk thistle on the studied lands was on average: lead 2.8 mg/kg, cadmium 0.41 mg/kg, zinc 16.8 mg/kg and copper 7.1 mg/kg. At the same time, it should be noted that the content of lead and cadmium in milk thistle seeds exceeded the MPC by 5.6 times and 4.1 times, while the content of zinc and copper was lower than the MPC by 2.9 and 1.4 times.

	Lead			Cadmium			Zinc			Copper		
Agricultural land	Actual conc.	AC	HR	Actual conc.	AC	HR	Actual conc.	AC	HR	Actual conc.	AC	HR
1	2.7	2.2	5.4	0.4	1.3	4.0	18.0	3.8	0.36	7.0	7.0	0.7
2	2.8	2.8	5.6	0.38	1.6	3.8	16.3	4.6	0.32	7.5	6.2	0.75
3	2.9	2.2	5.8	0.45	1.1	4.5	16.0	2.9	0.30	7.1	3.9	0.71
4	2.7	2.2	5.4	0.44	1.2	4.4	17.2	3.3	0.34	6.9	4.9	0.69
On average	2.8	2.35	5.5	0.41	1.3	4.2	16.8	3.6	0.33	7.1	5.5	0.71

Table 3. Contamination of milk thistle seeds spotted with heavy metals.

The accumulation coefficient in the milk thistle seeds spotted a lead, cadmium, zinc and copper averaged 2.35; 1.3; 3.6, and 5.5, respectively. The highest coefficient of accumulation of heavy metals in the seeds of milk thistle was observed for copper and the lowest–for cadmium.

The hazard ratio of heavy metals in the milk thistle seeds on the studied lands, notably lead, cadmium, zinc, and copper, averaged 5.5; 4.2; 0.33, and 0.71. The lead had the highest hazard ratio for heavy metals in the milk thistle seeds, zinc – the lowest. The high accumulation of heavy metals by milk thistle had a positive effect on the removal of lead, cadmium, zinc, and copper due to phytoremediation (Table 4).

Agricultura I land	Yield, t/ha		Lead		Cadmium		Zinc		Copper	
	Vegetativ e mass	Seed s								
1	25	0.38	155	1.14	32.5	0.16	800	10.6	312.5	4.0
2	26.5	0.37	188	1.07	31.8	0.15	901	11.1	384.2	4.0
3	24.5	0.39	132	1.13	27.0	0,15	833	10.9	257.2	4.7
4	26.0	0.38	161	1.17	36.4	0.15	780	11.7	273	3.9
On average	25.5	0.38	159	1.12	31.9	0.15	828	11.0	306	4.0

Table 4. Removal of heavy metals with vegetative mass and seeds of milk thistle (g/ha)

Thus, 159 g and 1.12 g of lead; 31.9 g and 0.15 g of cadmium; 828.5 g and 11 g of zinc, and 306 g and 4.0 g of copper, respectively, are removed from the soil of each hectare with a vegetative mass and seeds of milk thistle with a yield of 25.5 t/ha. Thus, when growing milk thistle from gray forest soils per 1 ha of area for each growing season of this culture is made 160 g of lead, 32 g of cadmium, 839 g of zinc, and 310 g of copper.

Thus, in conditions of heavy metal contamination in agricultural lands of the right-bank Forest-Steppe Ukraine, milk thistle can be grown both for obtaining seeds from this crop and for phytoremediation with subsequent removal of vegetative mass from agricultural lands and its utilization.

Conclusion

As a result of the conducted research, it is established that in the vegetative mass of milk thistle, grown in agricultural crop rotations on gray forest soils of the right-bank Forest-Steppe, the MPC is exceeded: lead-1.24 times; cadmium-1.25 times; zinc-3.25 times; copper-2.4 times. The high efficiency of removing heavy metals from the soil by milk thistle makes removing from the soil per 1 ha at a yield of 28.5 t/ha of lead-160 g, cadmium-32 g, zinc-839.5 g, and copper-310 g.

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