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The Models of the Heavy Metal Accumulation of the Multiple Grain Energy Cultures for Wastewater Deposition on Oil-Polluted Degraded Soils

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ABSTRACT

The research was conducted on the territory of Nadvirna oil and gas district of South-Hvizdetsky oil field of Ivano-Frankivsk region during 2016-2020. The production activity at the research site was stopped 45 years ago. Energy crops the Miscanthus (Miscanthus giganteus) and switchgrass (Panicum virgatum) were planted and sown on model research plots with an estimated area of 25 m² in triplicate. The miscanthus was planted manually according to the scheme 0.50×0.70 m. According to studies on the oil-contaminated soils, with the introduction of different sedimentation rates wastewater, the content of the Lead when growing the miscanthus increases with the introduction of SS 40 t/ha and $N_{10}P_{14}K_{58}$ (option 6) and is 4.30 mg/kg of soil. However, when growing the switchgrass with the same fertilizer application, the Lead content is 3.97 mg/kg of soil, which is 0.33 mg/kg of soil less than growing the miscanthus. The concentration coefficients of the gross forms of the Lead vary in the range of 1.01-1.09during the cultivation of the miscanthus. The concentration coefficient of the gross forms of the Cadmium varies in the range of 1.09-1.56, the maximum remains in the options for the introduction of the sewage sludge at a rate of 40 t/ha and $N_{10}P_{14}K_{58}$. The concentration coefficients of the gross forms of the Lead for growing the switchgrass 20-40 t/ha (option 4-6) are equal to 1.02-1.15. The concentration coefficient of the gross forms of the Cadmium varies between 1.18 and 1.49.

Keywords: heavy metals, switchgrass, miscanthus, energy plants, oil-contaminated soil, sewage sludge, phytorecultivation.

INTRODUCTION

Formulation of the problem. Soil degradation due to the human anthropogenic activities and depletion of the plant biodiversity is one of the most pressing environmental problems today. One of the extremely dangerous factors of the soil degradation is oil pollution due to the production activities of oil and gas and oil refining industries, as well as the functioning of oil and gas transportation infrastructure. When assessing the consequences of this type of pollution, it is not always possible to reliably predict whether the landscape environment of the ecosystem will be able to acquire a stable state, or whether degradation processes will progress irreversibly [Lopushniak 2020a, Lopushnyak 2016b]. Petrochemical pollution of the soil environment has its own characteristics, differs from many other anthropogenic influences in that it is characterized by radical changes in physicochemical, microbiological, ecological properties of the soil, is not gradual, but contributes to a sharp increase in anthropogenic pressure on ecosystems. Large areas are contaminated to varying degrees with petroleum products. Annually, tens of thousands of tons of oil pollute large areas of land, reducing its fertility, disrupting the ecological balance of the bioecosystems [Korsun 2019, Lopushnyak 2016b]. The development of the measures related to the stabilization of the ecological environment and minimization of the consequences of oil and gas pollution is associated with the assessment of their impact on the soil environment over time and the study of the biological recovery of man-made ecosystems, ie creating appropriate conditions for ecosystem restoration. Therefore, the study of the effectiveness of various methods of the environment cleaning from hydrocarbon pollution is one of the most important tasks in solving the problem of reducing the negative anthropogenic impact on the environment [Bernal-Vicente 2008, Lopushniak 2020a, Manios 2004, Grigoriy Kaletnik 2021].

One of the ways to restore technogenic affected areas is to create agrophytocenoses of the energy crops that are adapted to the growing conditions and are able to form a large amount of the biomass that is not involved in the food chain. The biomass of cultivated energy plants makes it possible to partially meet the needs for renewable energy resources, increases the intensity of carbon biosequestration. The use of the biomass for energy purposes is a priority for climate stabilization, contributes to plant biodiversity [Moroz 2018, Lemus 2002, Lopushnyak 2016b]. A number of the cultivated plants are grown for energy purposes, including energy willow and poplar, miscanthus, switchgrass, sylphia, etc. [Bouton 2007, Desjardins 2018, Elbersen 2001].

The biomass of energy crops accumulates most of the heavy metals and radionuclides, and due to its binding and accumulation in large quantities – removes a significant amount of pollutants from the soil. Most heavy metals are concentrated in the root system, which can be easily disposed of [Lemus 2002, Lewandowski 2003].

The use of organic fertilizers (straw, green manure, etc.) promotes the activation of the biological processes in the soil and increases the productivity of the energy crops [Casler 2012, Bouton 2007]. The analysis of the literature sources shows that fertilizers that contain nitrogen significantly increase the yield of the dry biomass (switchgrass and miscanthus) – by 30% and above [Kurylo 2015]. Co-application of the straw with green manure enhances the accumulation of the humus in the soil due to additional organic matter and intensification of microorganisms that accelerate the mineralization of the organic compounds, which in turn helps to increase the productivity of the agrophytocenoses [Zasidko

2017, Grigoriy 2021]. Growing switchgrass on degraded soils for several years helps to increase their fertility, and with excessive moisture – prevents waterlogging [Lopushnyak 2016b, Grigoriy Kaletnik 2021, Skachok 2016]. On the other hand, the use of the organic fertilizers significantly increases the biomass productivity of the grass energy crops. It is known that the application of the organic fertilizers (straw + green manure) contributed to the growth of green mass by 26–45%, which was the highest biomass yield of 12.3 t/ha of the miscanthus and 9.6 t/ha of the switchgrass [Skachok 2016, Kurylo 2010].

Given the significant shortage of the organic fertilizers in Ukraine, their use in energy crops is very limited, so in such conditions it is promising to use sewage sludge as a source of the organic matter for application to the soil [Lopushnyak 2016b, Lopushniak 2021c]. The largest share of the sewage sludge in agriculture is accounted for by Portugal – 87%, Spain – 65, Great Britain – 69 and the United States – 47%. In Germany and the Netherlands, most of the formed sludge is incinerated, which is 51 and 68%, respectively. In Japan, more than 52% of the sewage sludge is used for the production of the building materials [Fike 2006, Kurylo 2015, Lopushnyak 2016b, Shepelyuk 2019, Karbivska 2020].

Up to 3 million tons of new sediments are formed in Ukraine every year, of which only 3-5% are used as secondary raw materials, mainly for the production of the organo-mineral fertilizers. For example, in Ivano-Frankivsk Municipal Enterprise "Vodoekotechprom" processes about 225-275 thousand cubic meters of the raw sewage sludge per day, of which almost 140 thousand are sludge particles [Lemus 2002, Zhen 2017, Korets'kyy 2020, Lopushnyak 2016b]. According to statistics, there are up to 10 million hectares of the low-productivity land in Ukraine. According to experts, if most of these lands are used for energy plantations, you can get an average of 378 billion kWh. electricity per year, which is more than twice the production of electricity at all thermal power plant in Ukraine [Kurylo 2015, Kaletnik 2021]. The area of the soils contaminated with oil products in Ukraine exceeds 30 thousand hectares [Koval'ova 2020]. These areas also need measures to restore the ecological functions of the soil cover. The problem of the remediation of the oil-contaminated areas requires due attention and consolidation of the efforts to solve it [Franchuk 2009]. The most common energy grass

crops are the switchgrass and miscanthus. However, in Ukraine, the cultivation of the switchgrass has not yet become widespread due to the lack of the economic justification of its agricultural technologies. To date, the technology of growing the switchgrass in the soil and climatic zones of the state has not been studied enough [Korsun 2019]. It is advisable to grow the switchgrass and miscanthus not only to obtain the biomass that can be used for energy purposes, but also to protect soils from degradation and improve the ecological condition of the soil cover.

Most researchers believe that the switchgrass has great prospects for growing in Ukraine [Casler 2012, Lopushniak 2020a, Murphy 2011]. The switchgrass plant has a well-developed fibrous rhizome, which is able to penetrate into the soil up to 2–2.5 m and thus absorb heavy metals from contaminated soils at considerable depths [Monti 2001, Lopushnyak 2016b].

The miscanthus already in the first year of the growing season forms a strong root system [Gri-gliatti 2007, Lewandowski 2003, Pandey 2016]. The plant is resistant to frost, so next year, due to a significant increase in rhizome and the number of aboveground shoots, forms a continuous herbage. During this period, the miscanthus is very competitive with weeds and does not require row spacing [Alexopoulou 2008, Kurylo 2015, Skachok 2016].

According to the literature, herbaceous energy plants, such as the switchgrass and miscanthus, are ideal for planting radioactively contaminated and disturbed lands after extraction of the petroleum products, unproductive or decommissioned; are natural filters for waste removal of the agro-industrial production, are used as buffer zones in places of the biological waste accumulation of the farms [Kurylo 2015, Lopushnyak 2016b, Grigoriy 2021].

The purpose of our research is to develop and study the effectiveness of the elements of technologies for reclamation and revitalization of the oil-contaminated areas with the help of the phytoremediate plants, including energy crops – the switchgrass and miscanthus.

MATERIALS AND METHODS

The research was conducted on the territory of Nadvirna oil and gas district of South-Hvizdetsky oil field of Ivano-Frankivsk region during 2016– 2020. The production activity at the research site was stopped 45 years ago. Energy crops the Miscanthus (Miscanthus giganteus) and switchgrass (Panicum virgatum) were planted and sown on model research plots with an estimated area of 25 m² in triplicate. The miscanthus was planted manually according to the scheme 0.50×0.70 m. For planting there used rhizomes with 5–6 growth buds for better rooting. The depth of the earnings is from 12 cm. The switchgrass was sown by hand from a distance of 50 cm in a row to a depth of 5–7 cm. As a control area (background area) it was selected the area of the experimental field within 300 m from laying 2–8 options (contaminated with petroleum products).

The soil of the experimental site is sod-slightly podzolic sandy, where some oil spill remnants are found. The signs of its redistribution by genetic horizons are clearly expressed: humus-eluvial (HE) horizon - up to 24 cm, gray with powders of silicic acid, eluvial horizon (E) – up to 45 cm in the form of large spots, whitish, illuvial (I) horizon – loamy -brown layers up to 13 cm thick. The experimental area is characterized by the following agrochemical parameters: pH salt - 4.4, hydrolytic acidity - 1.8 mmol/100 g of soil, humus content – 0.6% (according to Tyurin – Kononova), nitrogen easily hydrolyzed compounds - 75 mg/kg of soil (according to Cornfield), mobile phosphorus compounds and metabolic compounds of potassium – respectively 38 and 41 mg/ kg of soil (according to Kirsanov).

Experiment options

The scheme of the application of the fertilizers for the miscanthus and switchgrass in the experimental area included the following options: 1 – control (without fertilizers); 2 – $N_{60}P_{60}K_{60}$; $3 - N_{90} P_{90} K_{90}; 4 - SS \ 20 \ t/ha + N_{50} P_{52} K_{74}; 5 - SS$ 30 t/ha + $N_{30}P_{33}K_{66}$; 6 - SS 40 t/ha + $N_{10}P_{14}K_{58}$; 7 - compost (SS + straw in the ratio (3: 1) 20 $t/ha + N_{50}P_{16}K_{67}$; 8 - compost (SS + straw in the ratio (3: 1)) 30 t/ha + $N_{30}K_{55}$. All options, except control and option 2, balanced by the introduction of the main elements of the mineral nutrition – the application rate was $N_{q_0}P_{q_0}K_{q_0}$.), as well as in the vegetative mass (aboveground and underground parts) of the switchgrass and miscanthus in accordance with DSTU 4770.3, DSTU 4770.9, atomic adsorption method [Yakist' gruntu 2009a, Yakist' gruntu 2009b] in the laboratory of Ivano-Frankivsk branch of the State Institution "State Soil Protection".

RESULTS AND DISCUSSION

For characteristics of the biogenic migration of the heavy metals and biogeochemical characteristics of the plants determined the coefficient of the biological absorption, the coefficient of the accumulation and concentration of the elements in plants. The coefficient of the biological absorption was calculated according to the methods of the formula Avessalomova [Voytyuk 2016], namely the ratio of the content of a chemical element in the plant ash to its gross content in the soil [Alexopoulou 2008, Bernal-Vicente 2008]. The coefficient of the biological accumulation was determined by the ratio of the amount of the accumulated metals contained in the plant to their content in the soil [Zhen 2017, Koval'ova 2020, Franchuk 2009]. To assess the level of the contamination with chemical elements of the soil of the experimental plots, the coefficients of the concentration of the elements were determined, which characterize the excess of each element in the soil at the pilot (experimental) site compared to the control. The concentration coefficients of the heavy metals (Cd, Pb) were determined by the ratio of the element content in the soil to its content in the soil of the background area (option No 1-control) [Grigliatti 2007, Lopushnyak 2016b].

The maximum allowable concentration of the mobile forms in the soil for Lead – 6.0 mg/ kg of soil, for Cadmium 0.7 mg/kg of soil [Shepelyuk 2019]. The Lead content in the control option (background option) was 3.05 mg/kg of soil, the Cadmium content was 0.19 mg/kg of soil for growing the miscanthus. With the application of $N_{60-90}P_{60-90}K_{60-90}$ (options 2 and 3) the content of the Lead and Cadmium increased in the range of 3.21–3.84 and 0.32–0.57 mg/kg of the soil,

respectively. The highest content of the mobile forms of the Lead was observed in the soil with the application of SS 40 t/ha and $N_{10}P_{14}K_{58}$ (option 6) and compost at the rate of 30 t/ha and $N_{30}P_{33}K_{66}$ (option 8), which was 4.30 and 3.90 mg/kg of soil, respectively (Table 1).

The Cadmium content fluctuated according to the fertilizer application rates, but reached a maximum in option 4 (SS 20 t/ha + $N_{50}P_{52}K_{74}$) and amounted to 0.44 mg/kg of soil, which is 0.25 mg/kg of soil higher than the control option. The highest content of the mobile forms of the Lead was noted in the soil for the application of SS 40 t/ha and $N_{10}P_{14}K_{58}$ (option 6) and compost at the rate of 30 t/ha and $N_{30}P_{33}K_{66}$ (option 8), as well as for the application of SS $- 30 \text{ t/ha} + N_{30}P_{33}K_{66}$ which was 3.97 and 3.69 mg/kg of soil, respectively (Fig. 1) for growing the switchgrass. The Cadmium content varied from the norms and forms of the fertilizer application and reached a maximum of 0.33 mg/kg of soil with the application of SS at the rate of 20 t/ha and $N_{50}P_{52}K_{74}$ (option 4), or 0.15 mg/kg of soil prevailed over the control option 1. The content of the gross forms of the Lead in the soil was 12.46 mg/kg of soil under control and 13.01 mg/kg of soil in option 8 (compost (SS + straw (3: 1) 30 t/ha + $N_{30}K_{55}$), which 0.55 mg/kg of soil, more compared to the control option. The content of the gross forms of the Lead when applying SS at the rate of 20-40 t/ha was 12.62-13.27 mg/kg of soil, which is 0.16-0. 81 mg/kg of soil exceeded the control over the cultivation of the miscanthus (Table 2). Which is 0.17–0.31 mg/kg of soil exceeded the control for growing the miscanthus.

The content of the gross forms of the Lead in the soil was 12.41 mg/kg of soil under control and 14.21 mg/kg of soil in the option 6 (SS - 40 t/ha +

	Content in the soil for growing miscanthus		Content in the soil for growing switchgrass		
Options	mg/kg				
	Pb	Cd	Pb	Cd	
Control (without fertilizers)	3.15	0.23	3.01	0.18	
$N_{60}P_{60}K_{60}$	3.31	0.32	3.26	0.21	
N ₉₀ P ₉₀ K ₉₀	3.94	0.57	3.79	0.26	
SS – 20 t/ha + N ₅₀ P ₅₂ K ₇₄	3.69	0.49	3.31	0.25	
SS – 30 t/ha + N ₃₀ P ₃₃ K ₆₆	3.99	0.39	3.78	0.27	
SS – 40 t/ha + N ₁₀ P ₁₄ K ₅₈	4.4	0.44	4.1	0.33	
Compost (SS + straw in the ratio (3: 1) – 20 t/ha + $N_{50}P_{16}K_{67}$	3.68	0.33	3.51	0.24	
Compost (SS + straw in the ratio (3: 1) – 30 t/ha + $N_{30}K_{55}$	4.1	0.4	3.69	0.26	

Table 1. The content of the mobile forms of the heavy metals in oil-contaminated soil for growing plants

 $N_{10}P_{14}K_{58}$) for growing the switchgrass. The content of the gross forms of the Lead when applying SS at the rate of 20–40 t/ha was 12.83–14.21 mg/kg of soil, respectively, which is 0.42–1.8 mg/kg of soil, exceeded the control option. However, the content of the gross forms of Cadmium varies within 0.61 mg/kg of soil under control and 0.87 mg/kg of soil in option 6 (SS – 40 t/ha + $N_{10}P_{14}K_{58}$) for growing the switchgrass. The content of the gross forms of Cadmium for the application of SS at the rate of 20–40 t/ha was 0.70–0.87 mg/kg of soil, which is 0.09–0.26 mg/kg of soil higher than in the control. However, in options 7 and 8, the content of the mobile forms of Cadmium was 0.81–0.83 mg/kg of soil, respectively.

The value of the concentration coefficients of the mobile forms of the Lead in the oil-contaminated soil according to the options of the experiment varied in the range of 1.05–1.51 during the cultivation of the miscanthus. The application of the sewage sludge at the rate of 20–40 t/ha (options 4–6) determined the value of the concentration coefficient at the level of 1.24-1.51, which exceeded the control (option 1) by 0.19-0.46 respectively. The value of the concentration coefficients of the mobile forms of Cadmium varied in the range of 1.68-2.62. With the introduction of the sewage sludge at the rate of 20-40 t/ha (options 4–6) the value of the concentration coefficients reached 2.38-2.62 (Table 3).

During the cultivation of the switchgrass indicator of the concentration coefficients of the mobile forms of the Lead in the oil-contaminated soil varied between 1.12 and 1.42. With the introduction of the sewage sludge at the rate of 20-40 t/ ha (option 4–6), these figures were 1.16-1.42 and exceeded the control by 0.04-0.30, respectively. The value of the concentration coefficients of the mobile forms of Cadmium in the soil varied in the range of 1.17-1.93, and with the introduction of the sewage sludge at the rate of 20-40 t/ha (options 4–6) reached 2.38-2.62.

 Table 2. The content of the gross forms of the heavy metals in oil-contaminated soil for growing the miscanthus and switchgrass

	Content in the soil for growing miscanthus		Content in the soil for growing switchgrass.		
Options	mg/kg				
	Pb	Cd	Pb	Cd	
Control (without fertilizers)	12.46	0.57	12.27	0.71	
N ₆₀ P ₆₀ K ₆₀	12.63	0.99	12.79	0.85	
$N_{90}P_{90}K_{90}$	12.67	1.2	12.91	1.1	
SS – 20 t/ha + N ₅₀ P ₅₂ K ₇₄	12.62	0.94	12.83	0.83	
SS – 30 t/ha + N ₃₀ P ₃₃ K ₆₆	13.21	1.2	13.48	0.96	
SS – 40 t/ha + N ₁₀ P ₁₄ K ₅₈	13.27	1.38	14.21	1.17	
Compost (SS + straw in the ratio (3: 1) – 20 t/ha + $N_{50}P_{16}K_{67}$	12.92	1.0	13.61	0.91	
Compost (SS + straw in the ratio (3: 1) – 30 t/ha + $N_{_{30}}K_{_{55}}$	13.11	0.94	13.85	0.83	

Table 3. The concentration coefficients of the heavy metals in the oil-contaminated soil for growing the miscanthus and switchgrass

Option	Pb	Cd	Pb*	Cd*	Pb	Cd	Pb*	Cd*
No.		Movable forms			Gross forms			
2	1.05	1.68	1.12	1.17	1.01	1.09	1.02	1.18
3	1.19	1.71	1.22	1.44	1.02	1.43	1.04	1.36
4	1.24	2.38	1.16	1.39	1.03	1.25	1.03	1.15
5	1.30	2.55	1.38	1.57	1.03	1.34	1.09	1.25
6	1.51	2.62	1.42	1.93	1.09	1.56	1.15	1.49
7	1.14	1.73	1.17	1.63	1.04	1.22	1.13	1.33
8	1.28	2.11	1.23	1.79	1.07	1.40	1.14	1.36

Note: Cd, Pb – content in the soil for growing the miscanthus; Cd^* , Pb^* – content in the soil for growing the switchgrass.

		in the green iscanthus	Content in the green mass of switchgrass		
Options	mg/kg of plant				
	Pb	Cd	Pb	Cd	
Control (without fertilizers)	0.44	1.18	0.49	1.27	
N ₆₀ P ₆₀ K ₆₀	0.54	1.31	0.67	1.43	
N ₉₀ P ₉₀ K ₉₀	0.68	1.4	0.71	1.59	
SS – 20 t/ha + N ₅₀ P ₅₂ K ₇₄	0.74	1.45	0.89	1.55	
SS – 30 t/ha + N ₃₀ P ₃₃ K ₆₆	0.82	1.54	0.94	1.69	
SS – 40 t/ha + N ₁₀ P ₁₄ K ₅₈	0.96	1.6	1.17	1.77	
Compost (SS + straw in the ratio (3: 1) – 20 t/ha + $N_{50}P_{16}K_{67}$	0.86	1.5	1	1.63	
Compost (SS + straw in the ratio (3: 1) – 30 t/ha + $N_{_{30}}K_{_{55}}$	0.9	1.59	0.92	1.51	

Table 4. The gross content of the heavy metals in the green mass of the miscanthus and switchgrass for the fertilizer based on the sewage sludge

The values of the concentration coefficients of the gross forms of the Lead in the options ranged from 1.01 to 1.09 during the cultivation of the miscanthus. With the introduction of the sewage sludge at a rate of 20-40 t/ha (options 4-6), the concentration ratio was 1.03-1.09. The values of the concentration coefficients of the gross forms of Cadmium varied in the range of 1.09-1.56, the maximum value of this indicator was in the options for the introduction of the sewage sludge at a rate of 40 t/ha using $N_{10}P_{14}K_{58}$. The value of the concentration coefficients of the gross forms of the Lead for growing the switchgrass in the oil-contaminated soil with the introduction of the sewage sludge at a rate of 20-40 t/ha (options 4-6) was equal to 1.02-1.15. The concentration coefficient of the gross forms of Cadmium varied in the range of 1.18– 1.49, the maximum remained in the options for

the introduction of the sewage sludge at a rate of 40 t/ha and $N_{10}P_{14}K_{58}$ and was 1.49. However, in options 7 and 8, the content of the concentration coefficients of the gross forms of Cadmium was equal to 1.33–1.36 mg/kg of soil, respectively, for the cultivation of the switchgrass.

The concentration of the Lead in the green mass of the miscanthus reached maximum values with the introduction of SS at the rate of 40 t/ha and $N_{10}P_{14}K_{58}$ (option 6) and was 0.96 mg/kg of the plant and thus exceeded the control (option 1) by 0, 52 mg/kg of the plant. With the introduction of SS at the rate of 20–40 t/ha (option 4–6), the Cadmium content was 1.45 – 1.6 mg/kg of plant, respectively, and exceeded the control by 0.28–0.43 mg/kg of plant. The content of the Lead in the green mass of the switchgrass varied in the range of 0.49–1.17 mg/kg of plant, with the introduction of SS in

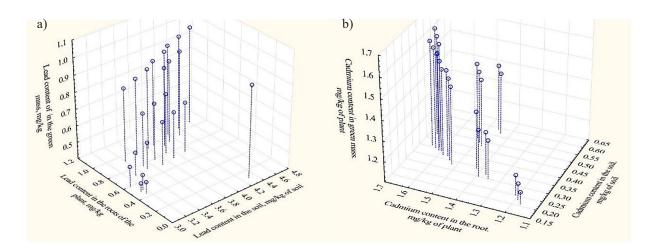


Fig. 1. The dependence of the content of the Lead (a) and Cadmium (b) in the green mass (z) on its content in the soil (x) and y roots of the miscanthus (y)

the norm – 40 t/ha and $N_{10}P_{14}K_{58}$ was 1.17 mg/ kg of plant (option 6), which by 0.68 mg/kg of plant exceeded the control rate (option 1). When applying the compost based on SS at the rate of 20 t/ha and $N_{50}P_{16}K_{67}$ and at the rate of 30 t/ha + $N_{30}K_{55}$, the content of the Lead in the green mass of the switchgrass was equal to 1.0–0.92 mg/kg of plant. The Cadmium content varied in the range of 1.27–1.77 mg/kg of plant (Table 4).

It is noted that the relationship between the content of the Lead in the green mass from its content in the underground mass of the miscanthus and in the studied soil (Fig. 1a).

Application of the sewage sludge at the rate of 20–40 t/ha (options 4 - 6) the content of the Lead in the green mass was equal to 0.74 - 0.96 mg/kg of plant, the content of the Lead in the root system, respectively, was 0.89-1.05 mg/kg of plant, and in the soil – 3.69-4.41 mg/kg of soil. When applying the compost at the rate of 20–30 t/ha (options 7–8) the content of Lead in the green mass was equal to 0.86-0.93 mg/kg of plant, in the root system, respectively, was 0.94 - 0.99 mg/kg plants, and in the soil – 3.68-4.10 mg/kg of soil.

$$z = 0.6275 - 0.0508x + 0.0508y \tag{1}$$

where: z is the content of the Lead in the green mass, mg/kg of plant, x - content of the Lead in the investigated soil, mg/kg of plant, y content of the Lead in root, mg/kg of soil.

The multiple coefficient of determination $(R^2 = 0.71)$ indicates a close correlation between these indicators. and in the studied soil (Fig. 1b).

With the introduction of the sewage sludge at the rate of 20–40 t/ha (options 4–6) the Cadmium content in the green mass of the miscanthus was 1.45-1.60 mg/kg of plant, the content of Cadmium in the root system, respectively, was 1.49-1.60 mg/kg of plant, and in the soil -0.41-0.50 mg/kg of soil. When applying the compost at the rate of 20–30 t/ha (options 7–8), the Cadmium content in the green mass was equal to 1.51-1.59 mg/kg, the Cadmium content in the root system of the miscanthus, respectively, was 1.54-1.63 mg/kg of plant, and in the soil -0.33-0.43 mg/kg of soil.

$$z = -1.1635 + 0.5536x + 2.2951y \tag{2}$$

where: z is the Cadmium content in the green mass, mg/kg of plant, x is the Cadmium content in the studied soil, mg/kg of plant, y is the Cadmium content in the root, mg/kg of soil.

The multiple coefficient of determination ($R^2 = 0.79$) indicates a high correlation between these indicators. of (Fig. 2a).

Application of the sewage sludge at the rate of 20–40 t/ha (options 4–6) the content of the Lead in the green mass of the switchgrass was 0.69-0.87 mg/kg of plant, the content of the Lead in the root, respectively, was 0.64-0.84 mg/kg of plant, and in the soil – 3.31-4.10 mg/kg of soil. When applying the composts at the rate of 20–30 t/ha (options 7–8) the content of the Lead in the green mass was 0.70-0.79 mg/kg, the content of the Lead in the root of the switchgrass was respectively 0.61-0.67 mg/kg of plant, and in the soil – 3.51-3.69 mg/kg of soil.

z = -1.5692 + 0.1227x + 1.2354y (3) where: z - content of the Lead in the green mass, mg/kg of plant, x - content of the Lead in the studied soil, mg/kg of plant, y - content of the Lead in the root, mg/kg of soil.

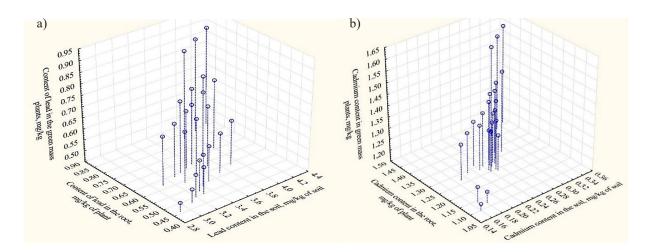


Fig. 2. The dependence of the content of the Lead (a) and Cadmium (b) in the green mass (z) on its content in the soil (x) and y roots of the switchgrass (y)

The multiple coefficient of determination ($R^2 = 0.78$) indicates a high correlation between these indicators. shown in (Fig. 2b).

For the introduction of the sewage sludge at a rate of 20–40 t/ha (options 4–6) the Cadmium content in the green mass of the switchgrass was equal to 1.35-1.57 mg/kg of plant, the content of Cadmium in the root, respectively, was 1.27-1.44 mg/kg of plant, and in the soil – 0.25-0.37 mg/kg of soil. When applying the compost at the rate of 20–30 t/ha (options 7–8), the Cadmium content in the green mass was 1.33-1.41 mg/kg, the Cadmium content in the root of the switchgrass, respectively, was 1.26-1.31 mg/kg of plant, and in the soil – 0.24-0.29 mg/kg of soil.

z = -0.0159 + 0.3591x + 0.9655y (4) where: z - content of the Lead in the green mass, mg/kg of plant, x - content of the Lead in the studied soil, mg/kg of plant, y - content of the Lead in the root, mg/kg of soil.

The multiple coefficient of determination ($R^2 = 0.74$) indicates a high correlation between these indicators (Fig. 3).

The lowest coefficients of the biological absorption of Cadmium by the miscanthus were noted for the application of the fertilizer $N_{90}P_{90}K_{90}$ (option 3) experience. In all options of the experiment, the Lead and Cadmium belong to the elements of strong accumulation.

The maximum coefficients of the biological absorption of the Lead are characteristic of the miscanthus, for the introduction of SS in the norm of SS – 40 t/ha + $N_{10}P_{14}K_{58}$, Cadmium – for the compost based on the sewage sludge water and straw (3: 1)) – 20 t/ha + $N_{50}P_{16}K_{67}$.

The lowest biological absorption coefficients of Cadmium were observed in the cultivation of the switchgrass for the application of the mineral fertilizers $N_{90}P_{90}K_{90}$ (option 3), Lead – for the application of soil $N_{60}P_{60}K_{60}$. According to the groupings of the heavy metals in the series by intensity of the biological absorption, the elements: Lead and Cadmium belong to group I and are the elements of the energy accumulation. The maximum coefficients of the biological absorption of the Lead are typical for the switchgrass, for the introduction of SS in the norm of SS – 20 t/ha + $N_{50}P_{52}K_{74}$, Cadmium – for the introduction of the swage sludge and straw (3: 1)) – 30 t/ha + $N_{30}P_{33}K_{66}$.

The lowest coefficient of the biological accumulation of Cadmium by the switchgrass was recorded for the introduction into the soil of SS at the rate of 40 t/ha and $N_{10}P_{14}K_{58}$, Lead – in the control version. (see Fig. 3 and 4).

The lowest coefficients of the biological accumulation of Cadmium by the miscanthus are recorded during the plant growth on the soil treated with the fertilizer $-N_{90}P_{90}K_{90}$ for the application of the compost at the rate of 30 t/ha and fertilizer $N_{30}K_{55}$. In the cultivation of the switchgrass and miscanthus, the elements of the intensive absorption include the Lead, the elements of very intensive absorption include the Cadmium.

Using the method of the correlation analysis, the dependence of the content of the Lead and Cadmium in the green mass on the content of the heavy metals in the ash of the miscanthus plants was established (Fig. 5).

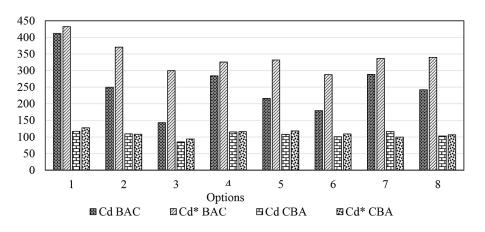


Fig. 3. Coefficients of the biological absorption and accumulation of Cadmium by the miscanthus and switchgrass for the application of the fertilizers to the soil. Note: Cd – content in soil for growing the miscanthus, Cd * – content in soil for growing the switchgrass, BAC – biological absorption coefficient, CBA – coefficient of biological accumulation

The content of the Lead in the vegetative mass of the plant in the control option is 0.47 mg/kg of plant, and its ash content – 41.8 mg/ kg of the plant. With the application of the mineral fertilizers in the norm $N_{60-90}P_{60-90}K_{60-90}$ (options 2 and 3) the content of the Lead in the green mass increased by 0.54 - 0.68 mg/kgof plant, respectively, the content of the investigated metal in the ash - by 0.85-2.0 mg/kgof plant. When applying the fertilizer based on the sewage sludge at a rate of 20-40 t/ha (options 4-6) the content of the Lead was 0.74-0.96 mg/kg of plant in the green mass, and the content in the ash, respectively, 46.90-51.6 mg/kg of plant. However, when applying the compost based on the sewage sludge at the rate of 20–30 t/ha (options 7 and 8), the content of the Lead in the green mass of the miscanthus is

0.86-0.93 mg/kg of plant, which is 0.39-0.46 mg/kg of plant more than the content in the control version. However, the content in the Lead ash in options 7–8, respectively 45.1-47.7 mg/kg of plant.

The correlation dependence of the Lead content in the green mass on the content of the Lead in the ash of the miscanthus plants can be described by the following multiple regression equation:

$$y = 33.7492 + 16.4097x \tag{5}$$

where: *y* is the content of the Lead in the ash, mg/ kg of plant, *x* is the content of the Lead in

the vegetative mass, mg/kg of plant.

According to the results of the correlationregression analysis, this dependence can be considered high, because the coefficient of determination is $R^2 = 0.70$, and the correlation coefficient r = 0.73.

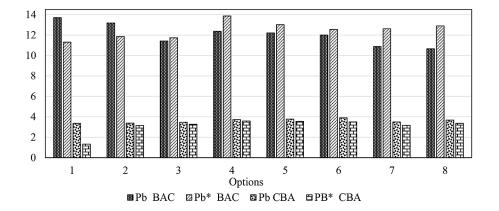


Fig. 4. Coefficients of the biological absorption and accumulation of the Lead miscanthus and switchgrass for the application of the fertilizers to the soil. Note: Pb – content in the soil for growing the miscanthus, Pb * – content in the soil for growing the switchgrass, BAC – biological absorption coefficient, CBA – coefficient of biological accumulation

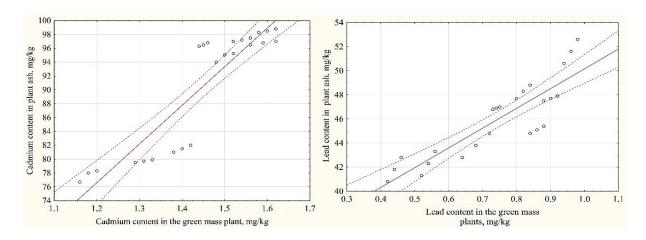


Fig. 5. The correlation between the content of the heavy metals (Pb, Cd) in the green mass and in the ash of the miscanthus

The Cadmium content in the vegetative mass of the plant in the control option was 1.18 mg/kg of plant, and the metal content in the ash - 78.24mg/kg of plant. With the application of the mineral fertilizers in the norm $N_{60-90}P_{60-90}K_{60-90}$ (options 2 and 3) the Cadmium content in the green mass increased by 0.13-0.22 mg/kg of plant, respectively, the content of the investigated metal in the ash - by 1.62 - 3.30 mg/kg of plant. When applying the fertilizer based on the sewage sludge at a rate of 20-40 t/ha (options 4-6) the Cadmium content was equal to 1.45-1.60 mg/kg of plant in the green mass, and the content in the ash, respectively, 96.56 – 98.57 mg/kg of the plant (Fig. 6).1.50–1.59 mg/kg of plant, which is 0.32–0.41 mg/kg of plant more than the content in the control version. However, the Cadmium content in the Cadmium ash in options 7-8, respectively 95.15-96.78 mg/kg of plant.

The correlation dependence of the Cadmium content in the green mass on the admium content in the ash of the miscanthus plants can be described by the following multiple regression equation:

$$y = 9.6105 + 55.8176x \tag{6}$$

where: *y* is the content of the Cadmium in the ash, mg/kg of plant, x is the content of the Cadmium in the vegetative mass, mg/kg of plant considered high because the coefficient of determination is $R^2 = 0.73$, and the correlation coefficient r = 0.79.

The content of the Lead in the vegetative mass of the plant in the control option is 0.49 mg/kg of plant, and the metal content in the ash - 30.91 mg/kg of plant. With the application of mineral fertilizers in the norm $N_{60-90}P_{60-90}K_{60-90}$ (options 2

and 3) the content of the Lead in the green mass increased by 0.57 - 0.61 mg/kg of plant, respectively, the content of the investigated metal in the ash – by 8.89–11.19 mg/kg of plant. When applying the fertilizer based on the sewage sludge at a rate of 20–40 t/ha (options 4–6), the content of the Lead was 0.69–0.87 mg/kg of plant in the green mass, and the content in the ash, respectively, 45.90–49.80 mg/kg of plant.

However, for the application of the composts based on the sewage sludge at the rate of 20–30 t/ha (options 7 and 8), the content of the Lead in the green mass of the switchgrass was 0.70–0.79 mg/kg of plant, which is 0.20–0.3 mg/kg of plant more than the content in the control version. However, the content in the Lead ash in options 7–8, respectively 44.30–47.60 mg/kg of plant.

The correlation dependence of the Lead content in the green mass on the content of the Lead in ash of the switchgrass plants can be described by the following multiple regression equation:

$$y = 35.3968 + 11.8039x$$
 (7)
where: y is the content of the Lead in the ash, mg/
kg of plant, x is the content of the Lead in
the vegetative mass, mg/kg of plant. Ac-
cording to the results of the correlation-
regression analysis, this dependence can
be considered high, because the coeffi-
cient of determination was $R^2 = 0.71$, and
the correlation coefficient $r = 0.75$.
The Cadmium content in the vegetative mass

The Cadmium content in the vegetative mass of the plant in the control option is 1.20 mg/kg of plant, and the metal content in the ash – 77.81 mg/ kg of plant.With the introduction of the mineral fertilizers in the norm $N_{60-90}P_{60-90}K_{60-90}$ (options 2

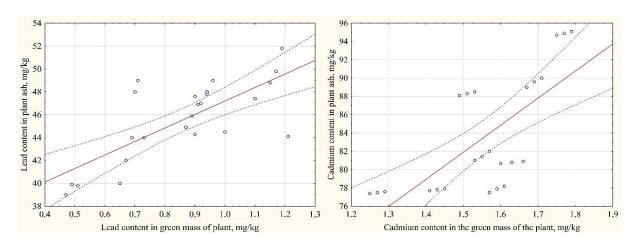


Fig. 6. The correlation between the content of the heavy metals (Pb, Cd) in the green mass and in the ash of the switchgrass

and 3) the Cadmium content in the green mass increased by 0.13-0.19 mg/kg of plant, respectively, the content of the investigated metal in the ash – by 0.03-0.09 mg/kg of plant. When applying fertilizer based on the sewage sludge at a rate of 20–40 t/ha (options 4–6), the Cadmium content was 1.35-1.57 mg/kg of plant in the green mass, and the content in the ash, respectively, 81.40 - 94.90 mg/kg of plant (Fig. 6).

However, when applying the compost based on the sewage sludge at a rate of 20–30 t/ha (options 7 and 8), the Cadmium content in the green mass of the switchgrass was 1, 33–1.41 mg/kg of plant, which is 0.13–0.21 mg/kg of plant more than the content in the control version. However, the Cadmium content in the Cadmium ash in options 7–8, respectively 80.81–88.30 mg/kg of plant.

The correlation dependence of the Cadmium content in the green mass on the Cadmium content in the ash of the switchgrass plants can be described by the following multiple regression equation:

$$y = 37.4967 + 29.5975x \tag{8}$$

where: *y* is the Cadmium content in the ash, mg/ kg of plant, *x* is the Cadmium content in the vegetative mass, mg/kg of plant.

According to the results of the correlation-regression analysis, this dependence can considered high, because the coefficient of determination is $R^2 = 0.75$, and the correlation coefficient r = 0.80.

CONCLUSIONS

According to studies on the oil-contaminated soils, with the introduction of different sedimentation rates wastewater, the content of the Lead when growing the miscanthus increases with the introduction of SS 40 t/ha and $N_{10}P_{14}K_{58}$ (option 6) and is 4.30 mg/kg of soil. However, when growing the switchgrass with the same fertilizer application, the Lead content is 3.97 mg/kg of soil, which is 0.33 mg/kg of soil less than growing the miscanthus.

The concentration coefficients of the gross forms of the Lead vary in the range of 1.01-1.09 during the cultivation of the miscanthus. The concentration coefficient of the gross forms of the Cadmium varies in the range of 1.09-1.56, the maximum remains in the options for the introduction of the sewage sludge at a rate of 40 t/ha and $N_{10}P_{14}K_{58}$. The concentration coefficients of the gross forms of the Lead for growing the switchgrass 20–40 t/ha (option 4–6) are equal to 1.02-1.15. The

concentration coefficient of the gross forms of the Cadmium varies between 1.18 and 1.49.

The dependence of the content of the Cadmium and Lead in the green mass on the content of the investigated metals in the roots of the switchgrass and miscanthus and in the studied soil indicates a high correlation between these indicators, the multiple coefficient of determination is $R^2 =$ 0.71-0.79. The analysis of the concentration dependences of the content of the heavy metals in the soil-plant system makes it possible to use the switchgrass and miscanthus plants as the bioindicators of the environmental pollution by petroleum products. The coefficients of the biological absorption of the Lead when growing the miscanthus are lower by 0.5 compared to the cultivation of the switchgrass for the introduction of SS at the rate of 20 t/ha and $N_{50}P_{52}K_{74}$, but the coefficients of the biological accumulation of the Lead for growing the miscanthus are higher by 0.14. However, the biological absorption coefficient of the Cadmium for the switchgrass and miscanthus is 336.67 and 288.33, respectively (option 7).

According to the division of the heavy metals into groups, the Cadmium and Lead according to the intensity of the biological absorption belong to group I and are elements of the energy accumulation. This feature of the energy crops (the switchgrass and miscanthus) is of great importance for the reproduction of the ecological stability of the soil, used for reclamation and revitalization of the oil-contaminated soils.

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