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Peculiarities of lead, cadmium, zinc and copper accumulation in *Miscanthus × giganteus* grown on different soil types in Ukraine

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ABSTRACT

The cultivation of energy crops such as *Miscanthus × giganteus* offers dual benefits for Ukraine's bioeconomy – sustainable biomass production and environmental restoration. This study evaluates the phytoremediation potential of the *Miscanthus × giganteus* cultivar Athena by analyzing the accumulation intensity of selected heavy metals (lead, cadmium) and trace elements (zinc, copper) in its aboveground biomass grown on grey forest, chernozem, and sod-podzolic soils. Field and laboratory assessments revealed that the accumulation efficiency varied considerably with soil type. The highest uptake of copper was observed on sod-podzolic soils, while zinc peaked on grey forest soils. In contrast, lead showed maximum accumulation on chernozem soils. Despite these differences, the hazard ratio (H_R) for all studied elements remained below the critical threshold (≤ 1.0), confirming the environmental safety of the harvested biomass. These findings emphasize the potential of *Miscanthus × giganteus* not only as a renewable resource but also as an effective phytoremediation agent for heavy-metal-contaminated agroecosystems.

Keywords: phytoremediation, heavy metals, trace elements, accumulation efficiency, biomass safety, soil types.

INTRODUCTION

Intensive anthropogenic pressure on agroecosystems has heightened concerns regarding the accumulation of heavy metals in the biomass of agricultural and bioenergy crops. Elements such as Pb, Cd, Cr, Ni, and Hg increasingly build up in soils and aquatic systems due to industrial and agricultural activities, resulting in phytotoxicity and disturbances of ecological equilibrium (Zhao et al., 2022; Razanov et al., 2022; Razanov et al., 2024; Tkachuk et al., 2024). While trace elements like Zn, Cu, Fe, Mn, Mo, and Ni are essential micronutrients that support plant metabolism, their elevated concentrations may exert toxic effects (Grotz et al., 2006; Yruela, 2013; Titarenko et al., 2022). The extent of such toxicity is influenced by the specific element involved, plant species, and the physical and chemical properties of the soil (Tkachuk and Verhelis, 2021). Characteristic symptoms of heavy metal stress include impaired nitrogen metabolism, disruptions in photosynthesis and respiration, reduced enzymatic activity, inhibited root elongation, and lower biomass accumulation – often progressing to tissue necrosis in severe cases. A critical concern is the high persistence and bioaccumulative nature of heavy metals within food chains, posing risks not only to plants but also to ecosystem health and human well-being (Malinowska et al., 2017; González Henao and Ghneim-Herrera, 2021).

Numerous studies indicate that in regions subjected to intensive anthropogenic activity – particularly in proximity to mining operations – the concentrations of heavy metals such as Pb, Cd, Zn, Cu, Fe, Al, As, Cr, Ni, and Ti can far exceed environmentally acceptable thresholds (Razanov et al., 2021; Shi et al., 2023). This environmental contamination poses heightened risks to sensitive groups, including women and children, who exhibit increased vulnerability to metal-induced toxicity (Järup, 2003). Health hazards become especially critical when the internal concentrations of these elements surpass physiological limits. Overaccumulation of lead, arsenic, cadmium, nickel, mercury, and chromium has been linked to hepatotoxic effects due to the generation of reactive oxygen species (ROS), which damage cellular structures and contribute to liver pathology (Renu et al., 2021). Epidemiological evidence increasingly supports the assertion that elevated heavy metal exposure in the environment represents a substantial threat to public health (Fu and Xi, 2019).

One of the promising strategies for mitigating soil contamination involves the cultivation of plant species with a high phytoremediation potential (Barbosa et al., 2018; Osman et al., 2024). Phytoremediation is widely recognized as a sustainable and eco-friendly approach to the removal of heavy metals from polluted environments. This technology is grounded in the natural ability of plants to absorb and accumulate heavy metals from water and soil into their tissues-roots, stems, leaves, flowers, and fruits (Gavrilescu, 2022; Razanov et al., 2024b). Depending on the contamination context, various phytoremediation techniques may be employed, such as phytoextraction, phytostabilization etc. The success of these approaches is strongly influenced by the plant's biomass production and the availability of heavy metals in the soil (Shen et al., 2022; Razanov et al., 2023).

A growing body of scientific research is now devoted to identifying plant species capable of accumulating heavy metals in their aerial biomass (Mellem et al., 2009; Aveiga et al., 2023; Snitynskyi et al., 2023). These findings open up valuable opportunities for improving soil decontamination efforts and mitigating the broader environmental impacts of pollution (Kaletnik and Lutkovska, 2020; Honcharuk and Yemchyk, 2024; Honcharuk et al., 2024). Evaluating metal accumulation levels alongside ecological risk indices is key to gauging the efficiency of phytoremediation strategies and identifying the most suitable species for reclaiming degraded lands (Dydiv et al., 2023). Against this background, studying the capacity of specific plants – particularly miscanthus – to sequester heavy metals under different soil conditions remains a highly relevant objective. The utilization of such species could serve as an effective bioremediation approach and contribute to decreasing anthropogenic contamination in agricultural ecosystems (Gavrilescu, 2022; Razanov et al., 2025).

Numerous studies have explored the capacity of various plant species to accumulate toxic elements, with a particular focus on how this process is influenced by soil type (Razanov et al., 2023; Shen et al., 2022; Angon et al., 2024). Research findings confirm that anthropogenic contamination of soils is closely linked not only to land use patterns but also to the input of industrial waste, radionuclides, agrochemicals, and mineral fertilizers (Zhang et al., 2022; Shi et al., 2023). Among the most susceptible to pollution are low-humus sod-podzolic soils, which possess minimal buffering capacity and readily accumulate hazardous substances. Under acidic conditions, such pollutants tend to transform into more mobile forms, promoting their downward movement into deeper soil layers and potentially contaminating groundwater. Conversely, in neutral to alkaline environments (typical of chernozem and dark chestnut soils) most contaminants are immobilized in less bioavailable forms, thereby reducing their uptake by plants (Zhovinsky and Kuraeva, 2002; Wan et al., 2024). It is important to note, however, that the phytotoxicity of heavy metals is primarily governed not by their total soil content, but by the concentration of their mobile and plant-accessible fractions.

Previous research into heavy metal bioaccumulation in crops has identified *Miscanthus* as a highly promising energy crop with notable phytoremediation potential (Janus et al., 2017; Kaletnik et al., 2020; Pidlisnyuk et al., 2021). *Miscanthus* is a fast-growing, perennial rhizomatous grass that demonstrates exceptional adaptability and requires minimal agrochemical inputs. Its extended life cycle (up to 20 years) offers a distinct advantage over annual species in long-term cultivation systems.

One of the noteworthy anatomical features of *Miscanthus* stems is the absence of long fibers in the bast layer, unlike fiber crops such as flax or hemp, which typically necessitate additional fiber processing (Danielewicz and Surma-Slusarska, 2019). Compared to other perennials, *Miscanthus* delivers superior dry biomass yields and, once established, requires little to no fertilization or intensive management, apart from routine annual harvesting with conventional farm equipment (Feng et al., 2022).

Robust stress tolerance, and ability to grow on marginal, saline, or degraded soils position *Miscanthus* as a sustainable crop with substantial bioeconomic and environmental value (Danielewicz and Surma-Slusarska, 2019; Feng et al., 2022; Mironova et al., 2023). These characteristics also make it particularly attractive for integration into phytoremediation programs targeting contaminated agricultural lands.

Numerous studies have demonstrated that *Miscanthus* possesses the ability to actively accumulate heavy metals such as Pb, Cd, Zn, and Cu, which underpins its potential application in ecological soil remediation strategies (Novak et al., 2018; Zadel et al., 2020; Razanov et al., 2024; Razanov et al., 2025). However, the intensity of heavy metal accumulation in its aboveground biomass is influenced not only by soil type and agrochemical characteristics, but also by environmental factors and the degree of anthropogenic pressure. Given these complexities, there remains a pressing need for an in-depth assessment of how soil type affects the uptake of heavy metals by miscanthus, as well as the safety of the resulting biomass for further utilization.

The aim of this study was to assess the accumulation levels of Pb, Cd, Zn and Cu in the biomass of the *Miscanthus × giganteus* cultivar Athena, cultivated on various soil types in Ukraine. To achieve this goal, the following objectives were pursued: to examine the impact of soil type (grey forest, chernozem, and sod-podzolic) on the accumulation of Pb, Cd, Zn, and Cu in miscanthus biomass; to calculate the accumulation and hazard ratios of these elements to evaluate the ecological safety and phytoremediation potential of the crop.

MATERIALS AND METHODS

The experimental research focused on evaluating the accumulation of heavy metals (lead – Pb, cadmium – Cd) and trace elements (zinc – Zn, copper – Cu) in the aerial biomass of *Miscanthus × giganteus* cv. Athena grown on three distinct soil types: grey forest, chernozem, and sod-podzolic soils.

Field trials were conducted in two agroecological zones of Ukraine: the Forest-Steppe zone – within the territories of the Tyvrivska and Pohrebyshchenska territorial communities (Vinnytsia region); and the Polissya zone – in the Korestenska community (Zhytomyr region). The selected sites were located at a considerable distance from major sources of anthropogenic heavy metal pollution, such as industrial plants, highways, and urban centers.

Soil sampling was performed using the envelope method, which involved collecting samples from five different points within each experimental field at the depth of the arable layer (plowing depth). A composite soil sample weighing 0.5 kg was taken from each point and mixed for further analysis.

Plant material was sampled by the point-sampling method, with 3.0 kg of miscanthus aerial biomass collected from each field site.

The concentration of heavy metals (Pb and Cd) and trace elements (Zn and Cu) in both soil and plant biomass was determined using the atomic absorption spectrophotometric method, in accordance with the national standard (DSTU ISO 10381-1:2004, 2006; DSTU 4117:2007, 2007).

To assess the intensity of element uptake by *Miscanthus × giganteus* cv. Athena and the potential environmental risk associated with the resulting biomass, the following indices were calculated.

Accumulation ratio (A_R) was determined using the formula:

$$A_R = \frac{Tb}{Ts} \tag{1}$$

where: *Tb* – toxicant content in plant biomass,
Ts – toxicant content in soil

This index reflects the plant's ability to absorb and accumulate specific elements from the soil into its aboveground biomass.

Hazard ratio (H_R) was calculated as:

$$H_R = \frac{Tb}{Pb} \tag{2}$$

where: *Tb* – toxicant content in plant biomass,
Pb – permissible level of toxicant in biomass

This indicator helps evaluate the potential risk of using the biomass, particularly in energy production or other economic sectors, by comparing the detected concentration to accepted safety thresholds.

The approach to calculating A_R and H_R follows the general principles of bioconcentration and translocation factors as described by Boechat et al. (2016) and Letshwenyo et al. (2020).

Permissible levels of toxicants were determined based on the national standards of Ukraine. In particular, for the mobile forms of Pb – DSTU 4770.3:2007, for Cd – DSTU 4770.3:2007, for Zn – DSTU 4770.2:2007, and for Cu – DSTU 4770.6:2007 (DSTU, 2009).

RESULTS AND DISCUSSION

The results of the study (Table 1) indicate that the concentrations of heavy metals in the aboveground vegetative mass of *Miscanthus×giganteus* grown on grey forest soils were below the permissible levels: Pb – by 4.0 times, Cd – by 2.3 times, Zn – by 3.4 times, and Cu – by 2.6 times. The order of element concentrations in the biomass, from lowest to highest, was as follows: Cd < Pb < Cu < Zn. The accumulation ratio (A_R) values were: Pb – 1.76, Cd – 2.10, Zn – 12.8, and Cu – 30.0, indicating the following trend in increasing A_R: Cd < Pb < Zn < Cu. The hazard ratio (H_R) for all elements was below the threshold value of 1.0, suggesting no toxicological risk associated with the biomass. The H_R values were: Pb – 0.25, Cd – 0.42, Zn – 0.29, and Cu – 0.38, with the ascending order being: Cu < Pb < Zn < Cd. Among the studied elements, Zn exhibited the highest concentration in the biomass, Cu showed the highest accumulation ratio, while Cd posed the greatest potential hazard due to its relatively higher H_R value.

When *Miscanthus×giganteus* was cultivated on chernozem soils (Table 2), the concentrations of heavy metals in its aboveground biomass remained below the permissible levels: Pb – by 2.8 times, Cd – by 2.4 times, Zn – by 3.1 times, and Cu – by 2.9 times. The distribution of elements in terms of increasing concentration in the biomass followed the sequence: Cd < Pb < Cu < Zn.

The accumulation ratio (A_R) in the aboveground biomass was: Pb – 2.56, Cd – 1.34, Zn – 10.9, and Cu – 50.0. The ascending order of A_R values was: Cd < Pb < Zn < Cu. The hazard ratio (H_R) for all studied elements was below the critical value of 1.0, indicating a relatively safe level of contamination in the biomass. The H_R values were: Pb – 0.35, Cd – 0.40, Zn – 0.32, and Cu – 0.11. According to ascending H_R values, the order was: Cu < Zn < Pb < Cd. Among the studied elements, Zn showed the highest concentration in the aboveground biomass, Cu exhibited the highest accumulation ratio, while Cd presented the greatest hazard potential due to its relatively higher H_R.

Cultivation of *Miscanthus×giganteus* on sod-podzolic soils (Table 3) demonstrated that the concentrations of Pb, Cd, Zn, and Cu in the aboveground biomass were 4.1, 2.1, 3.1, and 2.2 times lower than the permissible levels, respectively. In ascending order of concentration, the distribution of these elements in the biomass followed the sequence: Cd < Pb < Cu < Zn.

The accumulation ratio (A_R) values were: Pb – 1.94, Cd – 1.41, Zn – 6.15, and Cu – 55.1. Therefore, the sequence by increasing A_R was: Cd < Pb < Zn < Cu. The hazard ratio (H_R) for all studied elements remained below the critical threshold of 1.0, confirming the safety of the resulting biomass for potential further use. The H_R values were: Pb – 0.24, Cd – 0.48, Zn – 0.33, and Cu – 0.44, with the ascending order: Pb < Zn < Cu < Cd. Among the elements analyzed, *miscanthus* biomass grown on sod-podzolic soils exhibited the highest Zn concentration, the highest A_R for Cu, and the highest H_R for Cd.

Our comparative analysis revealed that the highest Pb content in *Miscanthus × giganteus* biomass was observed when cultivated on chernozem soils, while Cd, Zn, and Cu

Table 1. Accumulation intensity of heavy metals and trace elements in the aboveground biomass of *Miscanthus×giganteus* on grey forest soils (n = 4, M ± m)

Element	Soil content (mg/kg)	Biomass content (mg/kg)	Permissible level (mg/kg)	A_R	H_R
Pb	0.713 ± 0.034	1.26 ± 0.22	5.0	1.76	0.25
Cd	0.061 ± 0.004	0.128 ± 0.012	0.3	2.1	0.42
Zn	1.15 ± 0.32	14.70 ± 1.2	50	12.8	0.29
Cu	0.127 ± 0.024	3.82 ± 0.41	10	30	0.38

Table 2. Accumulation intensity of heavy metals and trace elements in the aboveground biomass of *Miscanthus*×*giganteus* grown on chernozem soils (n = 4, M ± m)

Element	Soil content (mg/kg)	Biomass content (mg/kg)	Permissible level (mg/kg)	A_R	H_R
Pb	0.693 ± 0.024	1.78 ± 0.27	5.0	2.56	0.35
Cd	0.091 ± 0.0030	0.122 ± 0.014	0.3	1.34	0.40
Zn	1.45 ± 0.32	15.86 ± 1.21	50	10.9	0.32
Cu	0.067 ± 0.024	3.35 ± 0.57	10	50	0.11

Table 3. Accumulation intensity of heavy metals and trace elements in the aboveground biomass of *Miscanthus* × *giganteus* grown on sod-podzolic soils (n = 4, M ± m)

Element	Soil content (mg/kg)	Biomass content (mg/kg)	Permissible level (mg/kg)	A_R	H_R
Pb	0.624 ± 0.043	1.21 ± 0.14	5.0	1.94	0.24
Cd	0.102 ± 0.013	0.144 ± 0.027	0.3	1.41	0.48
Zn	2.70 ± 0.44	16.6 ± 1.7	50	6.15	0.33
Cu	0.08 ± 0.0022	4.41 ± 0.7	10	55.1	0.44

concentrations peaked in biomass from sod-podzolic soils. Specifically, the Pb content in biomass from chernozem soils exceeded that from gray forest and sod-podzolic soils by 41.2% and 47.0%, respectively. Conversely, Cd, Zn, and Cu concentrations in biomass from sod-podzolic soils were 12.5%, 12.9%, and 15.4% higher, respectively, than in plants grown on gray forest soils, and 18.0%, 4.6%, and 31.1% higher than those grown on chernozem soils. The highest A_R for Pb was recorded in miscanthus grown on chernozem soils; for Cd and Zn – on gray forest soils; and for Cu – on sod-podzolic soils. The A_R for Pb in biomass from chernozem soils exceeded that from gray forest and sod-podzolic soils by 45.4% and 32.0%, respectively. The A_R for Cd and Zn in biomass from gray forest soils was 56.7% and 17.4% higher than in chernozem soils, and 48.9% and 2.08 times higher than in sod-podzolic soils, respectively. Additionally, the A_R for Cu in miscanthus biomass from sod-podzolic soils was 1.83 times greater than in gray forest soils and 1.1 times greater than in chernozem soils.

Summarizing the results presented in Tables 1–3, it should be noted that the accumulation of Pb, Cd, Zn, and Cu in the aboveground vegetative mass of *Miscanthus* × *giganteus* varied depending on soil type. The lowest accumulation of heavy metals was observed on gray forest soils, while sod-podzolic soils contributed to the highest concentration of Cd, Zn, and Cu. In contrast, the highest Pb content was recorded when *Miscanthus* × *giganteus* was grown on chernozem soils. The accumulation ratio (A_R) of Pb reached its maximum on chernozem soils (2.56), of Cd and Zn – on gray forest soils (2.1 and 12.8, respectively), and of Cu – on sod-podzolic soils (55.1). These results highlight that *miscanthus* effectively absorbs Cu and Zn, with A_R values significantly exceeding those for Pb and Cd. The hazard ratio (H_R) remained below the critical threshold of 1.0 for all elements and soil types, confirming the relative environmental safety of using *miscanthus* biomass. The highest H_R value (0.48) was registered for Cd in *miscanthus* grown on sod-podzolic soils, while the lowest (0.11) was for Cu on chernozem soils. These findings demonstrate that *Miscanthus* × *giganteus* has a high phytoremediation potential, especially for the absorption of Zn and Cu, without exceeding toxic thresholds. Its adaptability to different soil types and capacity to accumulate heavy metals in aboveground biomass make it a promising crop for phytoremediation and the sustainable use of marginal lands.

Figure 1 illustrates the accumulation efficiency of selected heavy metals (Pb, Cd) and trace elements (Zn, Cu) in the aboveground biomass of *Miscanthus* × *giganteus* cultivated on different soil types. Cu demonstrated the highest A_R values across all soils, reaching a peak of 55.1 on sod-podzolic soils. Zn followed, with its maximum A_R value (12.8) observed on grey forest soils. In contrast, Cd and Pb exhibited relatively lower accumulation ratios, indicating a more limited phytoextraction potential. These patterns highlight the significant influence of soil properties on metal uptake, particularly the

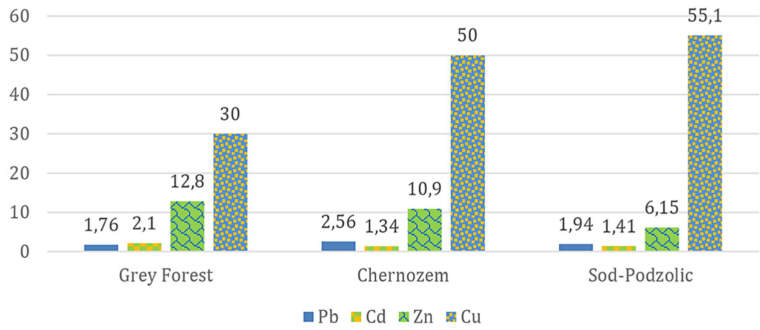

Figure 1. Accumulation ratio (A_R) of Pb, Cd, Zn, and Cu in the aerial biomass of *Miscanthus × giganteus* grown on grey forest, chernozem, and sod-podzolic soils

enhanced mobility and bioavailability of Cu in sod-podzolic soils.

Figure 2 presents a comparative analysis of the hazard ratio (H_R) for the four studied elements. The highest H_R was recorded for cadmium (0.48) in biomass from sod-podzolic soils, indicating a relatively higher potential risk despite its moderate accumulation. Pb and Zn exhibited intermediate H_R values (0.24–0.35), while Cu consistently showed the lowest H_R (0.11–0.44), confirming its lower toxicological significance in the biomass. All values remained below the threshold of 1.0, indicating that the biomass is environmentally safe for further use.

DISCUSSION

The outcomes of this research offer further confirmation that *Miscanthus × giganteus* is a highly effective species for the phytoremediation of soils contaminated with heavy metals such as Cd, Pb, Zn, and Cu. The efficiency of this plant in absorbing and redistributing these metals was found to depend on multiple factors, including the type of soil, the physicochemical characteristics of the metals, and environmental conditions.

Our observations regarding Cd accumulation are in line with earlier studies (e.g., Zgorelec et al., 2020), which demonstrated the plant's capacity to stabilize Cd in polluted soils, reducing its mobility and bioavailability. Similarly, our data corroborate previous findings on Pb uptake and highlight the pronounced accumulation of Zn and Cu in the aboveground biomass. Comparable patterns were identified by Malinowska and Kania (2024), who emphasized the role of soil pH and organic matter in enhancing the bioavailability of Zn and Cu.

Soil properties proved to be a determining factor in metal uptake efficiency. For example, Lutts et al. (2024) reported that *Miscanthus × giganteus* retains physiological activity even when grown on highly contaminated soils, exhibiting seasonal variations in metal accumulation depending on substrate characteristics. The application of organic amendments, such as sewage sludge, was shown to increase the concentration of certain elements – especially Zn and Ni – in plant tissues

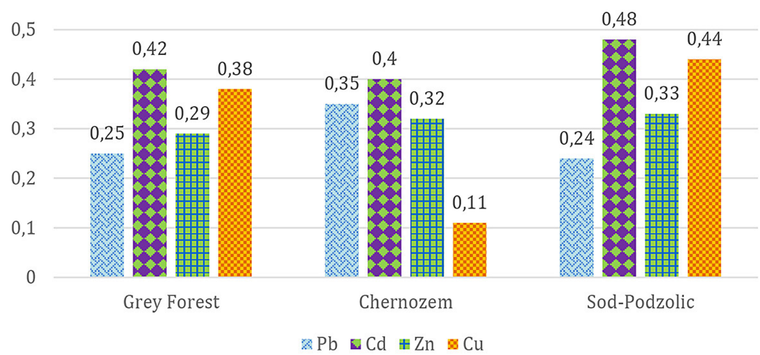

Figure 2. Hazard ratio (H_R) of Pb, Cd, Zn, and Cu in the aerial biomass of *Miscanthus × giganteus* cultivated on three soil types

(Malinowska and Kania, 2024). However, such amendments must be applied with caution due to the potential environmental side effects.

With regard to metal retention and detoxification, *Miscanthus* × *giganteus* has shown a capacity for immobilizing and compartmentalizing hazardous metals like Cd and Hg within its root tissues, supporting its role in phytostabilization (Zgorelec et al., 2020). The movement of different elements within the plant varies: for instance, Zn is often translocated to shoots, whereas Ni tends to accumulate in roots (Malinowska and Kania, 2024).

The use of *Miscanthus* biomass harvested from polluted environments represents a promising direction, particularly for renewable energy production (Myronenko et al., 2017; Pryshliak et al., 2022; Adamchuk et al., 2024). Beyond its phytoremediation capacity, the species offers distinct advantages for thermal energy applications. The obtained results are consistent with previous findings regarding the use of *Miscanthus* × *giganteus* for phytoremediation purposes. Kowalczyk-Juśko (2017) demonstrated that *Miscanthus* is capable of maintaining high biomass yields on heavy-metal-contaminated soils, confirming its suitability for phytoremediation and bioenergy production. Similarly, Pidlisnyuk et al. (2022) emphasized the high tolerance of *Miscanthus* to heavy metal stress and its potential for sustainable cultivation on marginal lands, contributing to both environmental restoration and renewable resource generation. Nevertheless, thermal utilization of biomass from contaminated areas requires careful emission control technologies to prevent secondary pollution and minimize the risk of metal reintroduction into the environment.

In conclusion, the study reinforces the suitability of *Miscanthus* × *giganteus* for use in the phytoremediation of heavy-metal-contaminated soils. However, the effectiveness and environmental safety of this approach are strongly influenced by site-specific factors, including soil characteristics and contaminant loads. Future research should aim to refine plant–soil interaction models and develop safe, integrated strategies for biomass utilization and waste management.

CONCLUSIONS

The conducted research on the accumulation intensity of heavy metals and trace elements in the aboveground biomass of *Miscanthus* × *giganteus* cultivated on different soil types in Ukraine allows us to formulate the following generalized conclusions:

- *Miscanthus* × *giganteus* demonstrated a strong ability to accumulate heavy metals, particularly Cu and Zn, across all studied soil types. The highest accumulation ratios (A_R) for Cu were recorded on sod-podzolic soils (55.1), followed by chernozem (50.0) and grey forest soils (30.0). Zn also exhibited elevated A_R values (ranging from 6.15 to 12.8), confirming the plant's efficient uptake of this element;
- Cd and Pb were accumulated to a lesser extent compared to Cu and Zn; however, their hazard ratios (H_R) were relatively higher. Among all elements, Cd showed the highest H_R value (up to 0.48 on sod-podzolic soils), indicating a potentially greater environmental concern under conditions of elevated accumulation;
- Soil type significantly affected the uptake intensity of elements. The most intensive Cu accumulation was observed on sod-podzolic soils, likely due to their low buffering capacity and the enhanced mobility of metals in acidic conditions. In contrast, chernozem soils exhibited comparatively lower A_R values, which may be attributed to their higher sorption capacity and reduced metal bioavailability;
- Importantly, the H_R values for all examined elements remained below the critical threshold of 1.0, indicating the environmental safety of the harvested biomass. The lowest H_R values were recorded for Cu (0.11–0.44), reflecting its comparatively low toxicity relative to Cd, Zn, and Pb.

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