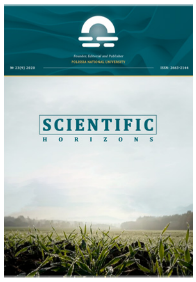
SCIENTIFIC HORIZONS

Journal homepage: https://sciencehorizon.com.ua
Scientific Horizons, 28(6), 89-99



UDC 631.4:546.3
DOI: 10.48077/scihor6.2025.89

Mechanisms for reducing heavy metal toxicity in fertiliser and agrotechnological soil protection systems

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Article's History:
Received: 23.10.2024
Revised: 12.04.2025
Accepted: 28.05.2025

Abstract. Pollution of agricultural soils with heavy metals caused by the activities of industrial enterprises, transport, and intensive use of agrochemicals poses a threat to environmental safety and productivity of agricultural systems. In this regard, the purpose of the study was to evaluate the effectiveness of combined use of green manure and organo-mineral stabilisers (zeolite and biochar) to reduce the bioavailability of heavy metals and phytotoxicity of the soil environment. The research methods included a field block experiment on chernozems southern of Southern Steppe of Ukraine contaminated with cadmium (0.7 mg/kg), using four treatment options (control, zeolite, zeolite + green manure, green manure). The results showed that the most effective option for reducing the bioavailability of cadmium was the option with the introduction of zeolite, which provided a decrease in available cadmium by 58% and a decrease in its total content by 22%. The introduction of green manure alone reduced the bioavailability of cadmium by

Suggested Citation:
Markova, N., Nikonchuk, N., Prystash, S., & Bondar, A. (2025). Mechanisms for reducing heavy metal toxicity in fertiliser and agrotechnological soil protection systems. *Scientific Horizons*, 28(6), 89-99 doi: 10.48077/scihor6.2025.89.

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31% compared to the control. Biochar in combination with phytoremediation reduced the availability of cadmium and zinc by 50%, and soil removal increased by 40% compared to phytoremediation without biochar. The biomass of the aboveground part of sunflower increased by 24% (up to 35.2 g/plant), the chlorophyll content – by 25%, and the activity of antioxidant enzymes – by 32% and 41%. Mustard and phacelia sideration helped to increase the organic carbon content in the soil by 18%, improve the cation exchange capacity by 11%, and reduce metal leaching by 30%, which indicates an improvement in the overall fixation of toxic elements. All results confirmed a significant reduction in the phytotoxicity of the soil environment and an improvement in the physiological and biochemical state of plants. The practical significance of the results lies in the possibility of using biochar, zeolite, and green manure for reclamation of contaminated soils and reducing the risk of heavy metals entering the food chain

Keywords: bioavailability; phytoremediation; sorbents; microorganisms; chelates; stabilisation; rhizosphere

INTRODUCTION

Soil contamination with heavy metals is one of the most pressing problems of modern ecology and agronomy. Heavy metals enter the soil through industrial emissions, agricultural use of chemical fertilisers and pesticides, and through household and industrial waste. They accumulate in the soil, have a high level of toxicity and are able to penetrate vegetation, which, in turn, can negatively affect human and animal health and reduce soil fertility. Reducing the bioavailability of heavy metals and neutralising their toxic effects on the environment are important tasks for researchers in the field of ecology, agrochemistry, and agronomy.

The study by Y. Wan *et al*. (2024) indicated that the sources of heavy metals entering the soil can have both natural and anthropogenic origin, but human activity remains the main factor. The greatest contribution is made by metallurgical enterprises, thermal power plants, transport infrastructure, intensive agriculture, and the use of contaminated water for irrigation, as described in detail by S. Sharafi and F. Salehi (2025). High concentrations of cadmium, lead, zinc, and copper not only alter the physical and chemical properties of soils, but also increase the risk of toxicants entering the food chain. As noted by A.K. Priya *et al*. (2023), this poses a potential threat to human health and ecosystem functioning. In this context, phytoremediation is considered as a promising biological alternative to conventional methods of reclamation, which are often expensive and energy-intensive. According to S. Gatla *et al*. (2024), phytoremediation strategies – phytoextraction, phytovolatilation, phytostabilitation and rhizofiltration – can reduce environmental pollution due to the biological potential of plants.

Special attention was drawn to the experience of using legumes (for example, *Albizia lebbeck*, *Dalbergia sissoo*, *Pongamia pinnata*), which, according to S. Gatla *et al*. (2024), can actively accumulate heavy metals and enrich the soil with nitrogen, improving its fertility. The study by K. Reyes Pinto *et al*. (2020) proved that it is not the total content of metals in the soil, but their bioavailability, that determines the real ecotoxicity and effectiveness of phytoremediation technologies. This is especially true in cases of using organic and mineral stabilisers, which contribute to the transition of metals to sedentary forms. As proved by L. Wang *et al*. (2022), the introduction of compost, biochar, and biostimulants to the soil can significantly reduce the bioavailability of Cd, Pb, and Zn. For example, when using biochar, Cd availability decreased by 30-40%, which was explained by the high sorption capacity of its carbon matrix. Composting using effective microorganisms, according to K. Reyes Pinto *et al*. (2020), provides the development of more stable organo-mineral metal complexes, especially for Cu, Pb, and Zn. The study by L. Wang *et al*. (2022) also noted that droppings and plant residues as a source of organic matter can reduce the extracted form of Cd to 28.5% and simultaneously increase the residual form to 65.8%.

In addition to chemical and biological methods of remediation, agrotechnological approaches, in particular sideration, are of considerable interest. As shown by S. Portiannyk (2024), the cultivation of cover crops such as mustard and clover promotes the accumulation of organic matter, the development of humic acids and chelates that fix heavy metals. There is also an improvement in the soil structure and a reduction in its compaction, which reduces the risk of vertical migration of metals to ground water. Reducing the toxicity of metals in phytosystems is provided by physiological and biochemical mechanisms of detoxification, in particular, the synthesis of phytochelatins, metallothioneins, activation of antioxidant enzymes, and metal sequestration in vacuoles (Pavlenko *et al*., 2025). These mechanisms, as emphasised by V. Ejaz *et al*. (2023), allow plants to effectively resist oxidative stress caused by the presence of metal ions in tissues. In addition, symbiotic interactions with arbuscular mycorrhizal fungi, such as *Glomus intraradices*, play a key role in improving nutrient absorption, detoxifying the soil environment, and increasing yields.

Despite significant progress in the development of bioremediation technologies, there are still unresolved issues regarding the interaction between different types of stabilisers and plants, the effectiveness of such measures in different agroclimatic conditions, the long-term effect of compost and green manure, and the impact of treatments on the migration of metals in the soil profile. Most studies focus on short-term effects and do not consider seasonal dynamics, microbiological activity, or soil physical properties that affect the bioavailability of metals. In this regard, the purpose of this study was to determine the effectiveness of using zeolite, biochar, and green manure in reducing the total content and bioavailability of heavy metals, and to assess changes in the agrochemical properties of the soil.

MATERIALS AND METHODS

The study was conducted in Ukraine during 2022-2024 at an experimental base in the south-eastern region of the country. The study area was characterised by a temperate continental climate with an average temperature of +23.5°C and an average precipitation level of about 35 mm/month. Field research was conducted by scientists from Mykolaiv National Agrarian University, while laboratory analyses, interpretation of results, and statistical data processing were carried out at the National University of Life and Environmental Sciences of Ukraine, which provided a comprehensive inter-agency approach to evaluating the effectiveness of the technologies under study. The pilot sites were located in the zone of pollution created by the anthropogenic impact of industrial enterprises, motor transport corridors, and local thermal power plants. The soil of the experimental plots is represented by southern black soil, thin heavy loam on loess. The reaction of the soil solution on the experimental plot was slightly acidic (pH 5.6), the humus content was 2.8%, and an average level of contamination with cadmium, lead, and zinc. The decrease in pH of southern black soils in the experimental area to 5.6 is due to the application of acidic nitrogen fertilisers and phosphorus deficiency, which disrupts the buffering capacity of the soil. Four experimental soil options were established in triplicate according to a block design:

1. Option 1 – control (contaminated with $CdCl_2$, without processing).
2. Option 2 – $CdCl_2$ + zeolite (10 t/ha) + green manure (oats, 120 kg/ha).
3. Option 3 – $CdCl_2$ + zeolite (10 t/ha).
4. Option 4 – $CdCl_2$ + green manure (oats, 120 kg/ha).

Separately from the main block experiment, an additional treatment option was implemented using biochar (15 t/ha) in combination with phytoremediation crops (sunflower *Helianthus annuus* and white mustard *Sinapis alba*). The purpose of this option was to evaluate the effectiveness of combining organic sorbent and accumulator plants in reducing the bioavailability of cadmium and zinc and improving the physiological and biochemical state of plants. The data obtained were considered separately from the main four options and were not included in the ANOVA general statistical model, but were used to compare the effectiveness of technological approaches. All test sites were equally contaminated by applying an aqueous solution of $CdCl_2$ up to a concentration of 0.7 mg/kg of dry soil mass. Sorbents were applied manually and mixed with the top layer of soil (0-20 cm). Natural sorbents (bentonite, zeolite) and organic materials (biochar from wood raw materials, 15 t/ha) were used for chemical remediation.

Green manure (white mustard – *Sinapis alba*, phacelia tansy – *Phacelia tanacetifolia*) were sown manually after initial tillage and embedded in the soil in the milky ripeness phase. The effect of sideration on the organic carbon content was evaluated, the cation exchange capacity, acid-base balance, and soil structure were analysed. Monitoring was carried out in two types of sites: control (without agrotechnical intervention) and experimental (with regular application of green manure biomass). Biological remediation included sowing of phytoremediant plants: sunflower (*Helianthus annuus*), white mustard, and yellow lupine (*Lupinus luteus*). Rhizospheric bacteria (*Pseudomonas fluorescens*, *Bacillus subtilis*) and mycorrhizal fungi (*Glomus intraradices*) were used to enhance the effect of biological fixation of metals, which were introduced as inoculants at a dose of 1×10^8 CFU/g before sowing. Observations covered the morphological characteristics of plants, determination of metal accumulation in the aboveground and underground mass, and signs of phytotoxicity.

Heavy metal contamination and dynamics were estimated by the concentrations of Pb, Cd, Zn, and Cu in the soil solution determined by atomic absorption spectrophotometry after acid decomposition. The bioavailability of metals was calculated by extraction with the chelating agent diethylentriaminpentaacetic acid (DTPA), followed by analysis of the metal content in the extract. Fractional analysis was also performed using distilled water, weak acids, and chelating agents to separate metals into mobile and bound forms. The mechanical composition of the soil, the content of organic matter and the electrical conductivity of the soil solution were determined using standard methods. To assess phytotoxicity, morphophysiological parameters of plants were analysed: biomass of the aboveground part (dry mass, g/plant), chlorophyll content (extraction of 80% with acetone, spectrophotometry at 645 and 663 Nm), concentration of malonic dialaldehyde (thiobarbiturate acid), activity of antioxidant enzymes catalase and superoxide dismutase by colourimetric methods. Additionally, the residual content of heavy metals in plant seeds (sunflower, mustard) was analysed to assess the potential risk to the food chain.

The data obtained were processed statistically using the Statistica 13.5 and OriginPro 2023 programmes. Analysis of variance (ANOVA) with Tukey's post-hoc test was used to test the reliability ($p < 0.05$). Correlation analysis was carried out with the calculation of Pearson's coefficients to establish the relationship between the concentration of metals in the soil and the degree of their accumulation by plants. All values were presented as mean standard deviations based on three independent biological repeats. The authors adhered to the standards of the Law of Ukraine No. 1264-XII "On Environmental Protection" (1991).

RESULTS

The results of chemical analysis showed that the applied tillage options significantly affected the total content and bioavailability of cadmium Cd, lead Pb, zinc Zn and copper Cu, which are critical parameters in evaluating the effectiveness of remediation technologies. The total element content was estimated after acid decomposition, and the bioavailable fraction was determined by chelated extraction using DTPA, which allows simulating the availability of metals in the rhizosphere medium. The control variant (option 1), which modelled soil contamination without any stabilisation measures, had the highest levels of cadmium: 0.68 ± 0.02 mg/kg (total) and 0.26 ± 0.01 mg/kg (DTPA-extracted) (Table 1). These indicators confirm the high mobility of cadmium and its potential ecotoxicity, which is consistent with the literature data on Cd behaviour under slightly acidic conditions of southern chernozems at pH ≈ 5.6.

***Table 1**. Content of total and bioavailable cadmium in the soil after applying various remediation options*

Option	Description	Total Cd (mg/kg)	Bioavailable Cd (mg/kg, DTPA)
1	Control ($CdCl_2$, without remediation)	0.68 ± 0.02	0.26 ± 0.01
2	Zeolite + green manure	0.59 ± 0.03	0.16 ± 0.02
3	Zeolite	0.53 ± 0.01	0.11 ± 0.01
4	Green manure	0.64 ± 0.02	0.18 ± 0.02

***Note:** total Cd content was determined after acid decomposition of samples, bioavailable – by DTPA extraction, followed by analysis using atomic absorption spectrophotometry. The values are given as the mean ± standard deviation (n = 3)*
***Source:** created by the authors based on the results of a field block experiment conducted in 2022-2024 on southern chernozems in the Southern Steppe of Ukraine*

Among the stabilising materials used, zeolite demonstrated the highest efficiency (option 3). The introduction of zeolite resulted in a decrease in the total Cd content to 0.53 ± 0.01 mg/kg, and bioavailability to 0.11 ± 0.01 mg/kg, which corresponds to a 22% and 58% decrease, respectively, compared to the control ($p < 0.05$). This decrease is explained by the high cation exchange capacity of zeolite, which can bind divalent cadmium ions by the mechanism of ion substitution in the crystal lattice, forming poorly soluble or fixed complexes. The combination of zeolite with green manure biomass (option 2) provided a slightly smaller, but still pronounced effect. In this variant, bioavailable Cd decreased to 0.16 ± 0.02 mg/kg, and total Cd decreased to 0.59 ± 0.03 mg/kg. The decrease in efficiency compared to option 3 is probably conditioned by the biological activity of plants, accompanied by the release of low-molecular organic acids that can complex heavy metals, partially restoring their mobility. However, the synergy between the chemical sorbent and the biological agent provided consistently lower metal content than in the control sample.

The green manure-only variant (option 4) resulted in a decrease in bioavailable cadmium to 0.18 ± 0.02 mg/kg and total content to 0.64 ± 0.02 mg/kg. The effect was less pronounced, but still statistically significant ($p < 0.05$). This effect can be explained by the ability of organic biomass to form organometallic complexes in the soil, and the fact that green manure enriches the soil with organic matter, which increases its sorption capacity. Similar patterns were found for other heavy metals. In particular, for lead Pb, the highest efficiency was demonstrated by the use of phosphate fertilisers, which contributed to the development of poorly soluble compounds, in particular $Pb_3(PO_4)_2$. This allowed reducing the bioavailability of lead by 55% compared to the control option, which indicates an effective chemical fixation of the element in the soil phase. In the case of zinc Zn, the introduction of biochar also showed high efficiency: the bioavailability of Zn was reduced to 50%. This effect is explained by a combination of physical and chemical mechanisms, in particular the ability of biochar to adsorb metal ions due to its high specific surface area, and the presence of active functional groups (carboxyl, phenolic) that can form stable complexes with Zn ions.

Continuing the analysis, it is important to note that the effect of remediation strategies used was not limited to reducing the total and bioavailable content of toxic elements. The identified changes also covered the key physical and chemical properties of the soil, which determine the mobility of metals, the degree of their fixation, and the long-term stability of the soil system under anthropogenic load. One of the most important indicators that experienced positive dynamics was the acid-base balance of the soil (Shebanina *et al.*, 2024). As a result of the introduction of limestone materials $CaCO_3$ and zeolite, the pH of the soil environment increased from 5.6 to 6.8, indicating effective neutralisation of acidity. This increase is significant, since in a neutral environment heavy metal ions tend to precipitate in the form of hydroxides, phosphates and carbonates, which significantly reduces their solubility and, accordingly, bioavailability. In addition, increasing the pH reduces the activity of hydrogen ions, which in an acidic environment compete with metals for binding to the surface of soil colloids. As a result, there was an improvement in the sorption capacity of the soil and the stabilisation of metals in its solid phase.

Another important indicator of the agrochemical state of the soil is the cation exchange capacity, which determines the ability of the soil matrix to retain cations, in particular, toxic elements. As a result of the use of green manure crops, in particular, *Sinapis alba* (white mustard) and *Phacelia tanacetifolia* (phacelia tansy), the cation exchange capacity increased by an average of 11%. This is conditioned by the enrichment of the soil with decomposition products of organic biomass, the development of humic and fulvic acids, which have a high ability to complex with metal ions. There was also a significant increase in the organic carbon content after sideration – at the level of 18% compared to the control samples. The accumulation of organic matter in the soil contributes to the development of stable organo-metal complexes, which are poorly soluble and much less accessible to plants, and also contributes to the activation of the soil microbiota, which is involved in the transformation of metal forms (Filss *et al.*, 1998). Assessment of the structural and physical characteristics of the soil also revealed an improvement in its aeration regime in variants with the introduction of green manure. This was conditioned by loosening of the soil due to the development of the root system of green manure crops and an increase in the amount of humus aggregates after their mineralisation. As a result, more favourable conditions were created for gas exchange, water penetration, and the development of the root system of phytoremediant crops. Such positive changes in the soil structure correlate with an increase in its biological activity and overall phytosanitary condition (Gamayunova *et al.*, 2025).

The improvement of the soil structure due to the action of green manure also played an important role in the processes of chemical binding of heavy metals and the development of their stable forms in the soil environment. In this context, special attention was paid to the assessment of the forms of stay of toxic elements, which is a key factor for understanding the mechanisms of stabilisation and the long-term effectiveness of remediation measures. One of the important aspects of evaluating the effectiveness of stabilisation measures was the determination of the forms of heavy metals in the soil. The fractional analysis showed that after the introduction of biochar, the proportion of cadmium in an easily accessible exchange form decreased from 38% to 17%, while the proportion of organically bound and residual forms increased. A similar transformation was also characteristic of zinc and lead. In particular, the variants with zeolite and phosphate additives were dominated by the precipitated phosphate form of Pb, which has low solubility and bioavailability. This indicates the effective transfer of metals to stable states, which significantly reduces the risks of their migration in the ecosystem.

Additionally, the dynamics of changes in metal concentrations during the growing season was investigated. In particular, the bioavailability of cadmium in soil solution in the biochar variant decreased gradually: on Day 30 it was 0.19 mg/kg, on Day 60 – 0.14 mg/kg, and on Day 90 – 0.11 mg/kg. This trend indicates an increase in the stabilisation effect over time, which is probably conditioned by the gradual activation of the sorption potential of biochar, humus formation, and the development of microbial activity in the rhizosphere. In addition to cadmium, other metals showed similar dynamics. In particular, in variants with phosphates, the content of bioavailable Pb decreased by 55% already on Day 60 after application, which is explained by the development of poorly soluble $Pb_3(PO_4)_2$. In the case of copper and zinc, the greatest changes were recorded in variants with liming and biochar, which confirms the universality of the adsorption mechanism of action of the organic stabiliser. The effectiveness of green manure crops was also analysed separately. White mustard (*Sinapis alba*) demonstrated the ability to reduce the concentration of mobile Cd forms in the upper soil horizon by 25%, while phacelia tansy (*Phacelia tanacetifolia*) – by 18%. This difference can be explained by different levels of biomass, the degree of microbiological activity in the rhizosphere, and the features of the release of organic acids that form chelate complexes with heavy metals. In addition, sideration contributed to an increase in organic carbon content, improved soil structure, and activated humus formation, which further affected the fixation of metals in hard-to-reach forms.

Further analysis of morphophysiological and biochemical parameters of model phytoremediant crops allowed assessing not only the influence of the considered remediation methods on the soil environment, but also the degree of phytotoxicity and the general physiological state of plants under the influence of heavy metal contamination. The results obtained indicate a clear positive effect of the use of biochar and mineral sorbents on biomass, photosynthetic activity, and antioxidant status of plants. In particular, the highest biomass of the aboveground part was demonstrated by plants grown on sites with the introduction of biochar. The average value was 35.2 ± 1.4 g/plant, which was 24% higher than the same value in the control variant (28.4 ± 1.1 g/plant). The obtained indicator shows a reduction in the phytotoxic effect of heavy metals due to their fixation in inaccessible forms, improvement of the soil structure, moisture retention capacity, and creation of favourable conditions for the development of the root system.

Photosynthetic activity also increased in the treated variants. The total chlorophyll content measured spectrophotometrically at wavelengths of 645 and 663 nm was 25% higher in plants grown in the presence of biochar or zeolite compared to control plants. An increase in the level of chlorophyll indicates the preservation of the integrity of the photosynthetic apparatus and a decrease in the degree of chlorosis, which is a typical symptom of heavy metal stress. An important biomarker of pollution – induced stress is the content of malonic dialaldehyde, the final product of lipid peroxidation that accumulates when cell membranes are damaged (Ahmadi *et al.*, 2023). In the variants using stabilisers, the concentration of malon dialaldehyde decreased by 30% compared to the control, which indicates a reduction in oxidative stress and effective adaptation of plants to pollution conditions. This is confirmed by the increased activity of antioxidant enzymes, which play a key role in neutralising reactive oxygen species in plant cells. In particular, catalase activity increased by 32% and superoxide dismutase – by 41% compared to plants in the control areas. The observed activity indicates the activation of protective mechanisms aimed at maintaining cellular homeostasis and preventing damage caused by heavy metals.

In addition to the overall improvement in the physiological and biochemical state of plants, the results of the study showed a significant difference in the ability of model crops to phytoremediate, in particular, with respect to the accumulation of heavy metals in aboveground and underground organs. The data confirm that the use of biological and chemical stimulants can significantly affect the effectiveness of phytoextraction and phytostabilisation. Thus, sunflower (*Helianthus annuus*) and white mustard (*Sinapis alba*) showed a high potential for the accumulation of cadmium Cd and zinc Zn in aboveground biomass. In the biochar variants, the Cd concentration in sunflower leaves and stems reached 3.5 mg/kg of dry weight, which is 66% higher than in the non-biochar variants (2.1 mg/kg). The data indicate the ability of biochars not only to reduce the bioavailability of toxic metals, but also to optimise plant growth conditions, so that they more actively absorb and translocate metals to aboveground parts (Harbar *et al.*, 2025). Moreover, lupine yellow (*Lupinus luteus*) showed another, no less important strategy – phytostabilisation, due to the accumulation of lead mainly in the root system. This feature limited the transfer of metal to photosynthetic organs, which reduces the risk of its entry into the trophic chain and helps to more effectively stabilise contaminated areas without the need to collect aboveground mass.

An additional factor that increased the effectiveness of phytoremediation was the use of rhizospheric bacteria, in particular, *Pseudomonas fluorescens* and *Bacillus subtilis*. Their inoculation contributed to an increase in the accumulation of heavy metals in plants by 20-30%. This effect is probably associated with the synthesis of siderophores and organic acids by bacteria, which increase the solubility of metals and stimulate their absorption. Equally important was the effect of mycorrhizal inoculation by the fungus *Glomus intraradices*. In plants that formed a symbiosis with arbuscular mycorrhizae, the biomass of the aboveground part was on average 15% higher compared to non-inoculated plants. Such indicators indicate an improvement in mineral nutrition, water supply, and an increase in non-specific immunity of plants to environmental stressors. Consequently, biological stimulation with the help of microorganisms not only improved the overall physiological state of plants, but also enhanced the effect of chemical stabilisers and agrotechnical measures applied (Shahini *et al.*, 2023). Against the background of such positive changes, further comparison of the effectiveness of individual and combined remediation strategies became reasonable. A comparative analysis of the effectiveness of the applied approaches helped to determine that combined strategies, in particular, the combination of zeolite or biochar with phytoremediation crops, provided the highest effectiveness in reducing soil pollution with heavy metals. These combinations demonstrated a synergistic effect when chemical stabilisation of metals in the soil matrix was combined with active phytonaccumulation, which significantly exceeded the effectiveness of each method separately. In particular, in the "biochar+plants" option, the total removal of Cd and Zn from the soil was 40% higher than in the variants using phytoremediation alone. This effectiveness is associated not only with a decrease in bioavailability due to the adsorption capacity of biochar, but also with improved conditions for the growth and development of phytoremediants, which, in turn, more actively absorbed metals. Generalised quantitative results on the content of total and bioavailable cadmium in the soil after applying various remediation options are shown in Figure 1. The histogram illustrates the degree of effectiveness of each approach – chemical, biological, and combinations thereof – in the context of Cd reduction.

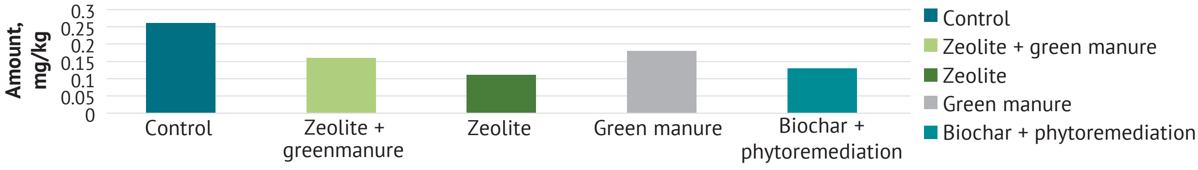

***Figure 1**. Comparative analysis of cadmium content in soil*

***Note:** total Cd content was determined after acid decomposition of samples, bioavailable – by DTPA extraction, followed by analysis using atomic absorption spectrophotometry*

***Source:** created by the authors based on the results of a field block experiment conducted in 2022-2024 on southern chernozems in the Southern Steppe of Ukraine*

In addition, the results of correlation analysis confirmed a close relationship between the bioavailability of heavy metals in the soil and the degree of their accumulation in the aboveground mass of plants. For cadmium, a high positive ratio was found – the Pearson's coefficient $r = 0.88$ at $p < 0.01$, which indicates a significant relationship between the level of availability of the element in the soil solution and its phytoextraction. The link indicates that the bioavailable fraction is the most informative parameter for predicting the effectiveness of phytoremediation, and should be considered when assessing environmental risk and planning further measures for the reclamation of contaminated land.

DISCUSSION

The results obtained confirm the high efficiency of using zeolite and green manure to reduce the bioavailability of heavy metals in agricultural soils contaminated by anthropogenic impacts. This demonstrates the potential of these materials as key elements in phytoremediation and agrotechnical strategies aimed at restoring degraded land. The use of zeolite and green manure not only reduced the concentration of mobile forms of metals (primarily Cd and Pb), but also had a positive effect on the physico-chemical and biological parameters of the soil, which creates favourable conditions for plant growth. It was observed that the introduction of zeolite led to a decrease in the fractions of heavy metals associated with the exchange and carbonate forms, which are the most mobile and bioavailable. Such changes can be explained by several mechanisms, including an increase in pH, an increase in cation exchange capacity, and the development of stable complexes between metals and active zeolite surface centres. These data are quite consistent with the findings of K.N. Palansooriya *et al.* (2022), which emphasise the sorption capacity of sorbents due to their porous structure and richness of functional groups. In addition, as noted by P. Viotti *et al.* (2024), natural minerals may contribute to the development of organo-mineral structures that further reduce the risk of toxicant migration in the soil profile.

Extraction analysis data confirmed that the use of zeolite reduces the proportion of potentially mobile forms of Cd and Pb. Similar effects were recorded in the study by K.M. Malik *et al.* (2021), where organic changes led to a shift in the balance of metals in the soil towards less bioavailable forms. This similarity allows concluding that not only the total content, but also the form of metal presence determines the environmental risk. The reduction in phytotoxicity found in this study is also consistent with the findings of A. Emamverdian *et al.* (2023), which indicate that heavy metals can cause oxidative stress and inhibit photosynthetic activity. In another study, M. Adrees *et al.* (2015) described the mechanisms by which silicon reduces the toxic effects of metals by enhancing the antioxidant response – a similar effect was observed with the use of stabilisers in the current study, which provided better conditions for plant growth and development.

Significant changes were also recorded in the biological activity of the soil. Stabilisers had a positive effect on the development of the rhizosphere microbiota, which was reflected in better plant growth. This was confirmed by A. Rashid *et al.* (2023), who described the restoration of microbial diversity after the introduction of organic and mineral amendments. In particular, W. Xu *et al.* (2024) noted an increase in the activity of enzymes and microbial biomass as a result of improved soil structure. S. Jayaram (2022) described in detail the mechanisms of metal bioimobilisation associated with microbial transformation and redox processes. The results are also consistent with the above conclusions: the use of zeolite and green manure contributed to an increase in plant biomass, a decrease in signs of phytotoxicity, and an increase in the activity of antioxidant enzymes, which may indirectly indicate an improvement in the microbial environment. Although no direct assessment of microbial composition has been carried out, the growth of physiological and biochemical parameters of plants, such as chlorophyll, catalase and superoxide dismutase, and improvements in soil structure, suggest activation of rhizospheric microflora (Romanchuck *et al.*, 2017).

S. Li *et al.* (2021) reported that natural amendments promote selective enrichment of rhizobiomes with beneficial microbes, which not only stabilises metals, but also improves plant nutrition. G.P. Sidhu (2016) further emphasised that heavy metals disrupt microbial processes, which negatively affects fertility, so restoring the microbial environment is a critical remediation task. The results of the current study indirectly confirm these mechanisms: in options with the introduction of zeolite, an increase in plant biomass, an improvement in the physico-chemical properties of the soil, and a decrease in the level of markers of oxidative stress were recorded, which may be the result of activation of positive microbial processes in the rhizosphere.

From the standpoint of environmental safety, reducing the mobility of heavy metals is an important measure to prevent them from entering the food chain (Ilderbayeva *et al.*, 2024). As stated by S.J. Melebary (2023), in many regions of the world, agricultural products exceed the permissible Cd and Pb levels, which poses a potential threat to public health. Thus, the results showed positive dynamics – the use of zeolite allowed reducing the bioavailability of Cd to 0.11 mg/kg, which is a significant decrease compared to the control, and therefore reduces the risk of metals entering phytomass and further into food products. However, the effectiveness of remediation with stabilisers varies depending on the properties of the soil. D. Yu *et al.* (2024) emphasised that parameters such as acidity, mechanical composition, and organic matter content determine how effectively stabilisers can fix metals. In this study, the maximum effectiveness of reducing the bioavailability of Cd, Zn, and Pb was observed in soils with a low organic content (2.8%) and an initial pH of 5.6. The introduction of stabilisers contributed to the neutralisation of soil acidity (up to pH 6.8) and, accordingly, the transfer of metals to less soluble and less toxic forms. This allows concluding that it is advisable to use stabilisation approaches on slightly acidic soils with an increased anthropogenic load.

In addition to stabilising metals, the use of zeolite and green manure has demonstrated additional benefits associated with improving the physical characteristics of the soil. The study found that the introduction of green manure helped to improve the water retention capacity and soil structure, which, in turn, created favourable conditions for the development of the root system and reduced the risk of compaction. This was consistent with the conclusions obtained by S. Mansoor *et al*. (2021), who pointed to the role of agrotechnical measures as soil improvers that can affect not only the chemical, but also the physical and mechanical properties of the soil. Thus, the applied approaches perform not only the function of stabilisers of toxic elements, but also improve the agrophysical state of the soil environment, contribute to increasing the efficiency of nutrient use, and also provide conditions for the formation of stable plant phytocenoses. In the context of practical farming, this makes them promising components of technologies aimed at rehabilitating degraded soils (Manushkina & Drobitko, 2025). The overall results of the study fit well with the concept of sustainable agriculture highlighted by J. Hu *et al*. (2024). According to these researchers, the use of natural, locally available materials, such as zeolite, minimises the use of chemical fertilisers and pesticides, improves soil quality, and reduces the environmental burden on agroecosystems. This approach contributes to the development of adaptive agriculture focused on preserving the soil resource and improving its ecosystem functions.

Consequently, the results of this study confirmed that the use of zeolite and green manure can be an effective multi-purpose agrotechnical practice that combines environmental safety, economic feasibility, and agronomic efficiency. The complex effect of these materials on chemical (increasing pH, reducing bioavailability of heavy metals, increasing cation exchange capacity), biological (activating rhizosphere microbiota) and physical (improving structure and water permeability) soil parameters indicates their multifunctional role in remediation strategies. To achieve maximum effect, the use of these materials requires adaptation to specific conditions: soil type, type of pollution, stabiliser characteristics, and local climate. Such an individualised approach will ensure long-term stability of the phytosystem and increase the efficiency of ecological restoration of degraded land.

CONCLUSIONS

As a result of the study, it was found that the use of natural mineral sorbents (zeolite), organic stabilisers (biochar), green manure (mustard, phacelia tansy), and their combinations can effectively reduce both the total content and bioavailability of cadmium, lead, and zinc in anthropogenically contaminated soils. The highest efficiency was demonstrated by the variant with the introduction of zeolite, which provided a 58% reduction in the bioavailability of cadmium compared to the control. In addition, this option showed a 22% decrease in the total cadmium content, which indicates the ability of the mineral not only to fix ions but also to convert them into stable forms. The combined use of zeolite with green manure contributed to an additional reduction in metal toxicity, in particular, by improving the physical and chemical properties of the soil.

The use of biochar in combination with phytoremediation crops (sunflower, mustard) provided a 40% increase in the efficiency of extracting heavy metals from the soil, in particular Cd and Zn, compared to the use of phytoremediation alone. The availability of cadmium and zinc in the soil solution decreased by 50%, which confirms the stabilisation potential of biochar in the rhizosphere. In addition, there was an improvement in the physiological and biochemical parameters of sunflower: the biomass of the aboveground part increased by 24%, the chlorophyll content increased by 25%, and the activity of antioxidant enzymes (catalase and superoxide dismutase) – by 32% and 41%, respectively. In addition, the use of green manure crops of white mustard and phacelia tansy contributed to the restoration of soil properties. Sideration increased the organic carbon content by 18% and the cation exchange capacity by 11%, which, in turn, contributed to the fixation of heavy metals and reduced their leaching by 30%.

Practical recommendations include the use of zeolite (10 t/ha) and biochar (5 t/ha) in combination with green manure and phytoremediation as an effective strategy for reducing heavy metal toxicity. However, the study had a number of limitations that should be considered. The limitations included the short duration of the experiment (one growing season) and the research on one type of soil. In addition, changes in the structure of the soil microbiota that may have implications for the long-term stability of the system have not been investigated. Prospects for further research should include long-term field trials, analysis of residual metal concentrations in products, and the investigation of the environmental impact on microbial communities.

ACKNOWLEDGEMENTS

None.

FUNDING

None.

CONFLICT OF INTEREST

None.

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Механізми зменшення токсичності важких металів в системах удобрення та агротехнологічного захисту ґрунту

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Анотація. Забруднення сільськогосподарських ґрунтів важкими металами, спричинене діяльністю промислових підприємств, транспорту та інтенсивним використанням агрохімікатів, становить загрозу екологічній безпеці та продуктивності сільськогосподарських систем. У зв'язку з цим метою дослідження була оцінка ефективності спільного використання сидератів та органо-мінеральних стабілізаторів (цеоліту та біовугілля) для зниження біодоступності важких металів та фітотоксичності ґрунтового середовища. Методи дослідження включали польовий блок-дослід на чорноземах півдня Південного Степу України, забруднених кадмієм (0,7 мг/кг), з використанням чотирьох варіантів обробки (контроль, цеоліт, цеоліт + сидерати, сидерати). Результати показали, що найефективнішим варіантом для зниження біодоступності кадмію був варіант з внесенням цеоліту, який забезпечив зниження доступного кадмію на 58 % та зниження його загального вмісту на 22 %. Внесення лише сидератів знизило біодоступність кадмію на 31 % порівняно з контролем. Біовугілля у поєднанні з фіторемедіацією зменшило доступність кадмію та цинку на 50 %, а видалення ґрунту збільшилося на 40 % порівняно з фіторемедіацією без біовугілля. Біомаса надземної частини соняшнику збільшилася на 24 % (до 35,2 г/рослину), вміст хлорофілу – на 25 %, а активність антиоксидантних ферментів – на 32 % та 41 %. Сидерація гірчицею та фацелією сприяла збільшенню вмісту органічного вуглецю в ґрунті на 18 %, покращенню ємності катіонного обміну на 11 % та зменшенню вимивання металів на 30 %, що свідчить про покращення загальної фіксації токсичних елементів. Усі результати підтверджують значне зниження фітотоксичності ґрунтового середовища та покращення фізіологічного та біохімічного стану рослин. Практичне значення результатів полягає в можливості використання біовугілля, цеоліту та сидератів для рекультивації забруднених ґрунтів та зниження ризику потрапляння важких металів у харчовий ланцюг

Ключові слова: біодоступність; фіторемедіація; сорбенти; мікроорганізми; хелати; стабілізація; ризосфера