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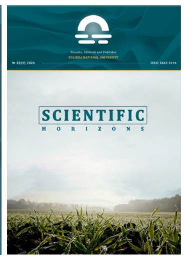

Methods for improving the ecological state of a chemically contaminated soil-plant system under the influence of military-technogenic factors on agrocoenoses

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Abstract. The purpose of the study was to investigate the effectiveness of new methods of *in situ* remediation of contaminated soils under complex military and technogenic influences on the soil-plant system in areas of atmotechnogenic emissions from an electricity and heat production facility (using the example of DTEK Kurakhiv TPP LLC in Donetsk Oblast). A systematic approach was used with the involvement of a complex of universal general scientific methods; methods of field and current methods of chemical and analytical research of soils and test plants of agrocoenoses with the determination of indicators of the elemental status of the soil-plant system, indicators of plant quality under the influence of chemical pollution and military influence; using the developed methods of chemical and biological remediation of the soil-plant system; using desk

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methods of statistical processing of the obtained data. New knowledge was obtained on the control of chemical contamination of soils and the soil-plant system under the conditions of complex influence of the military factor and chemical pollution in the zones of atmotechnogenic emissions at the electric and thermal energy production facility. New data were obtained from the analysis of the effectiveness of using the elaborated innovative methods of chemical and biological remediation of contaminated soils under new conditions of military and technogenic impacts. Priority contamination of the soil-plant system with mobile forms of lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), and nickel (Ni) compounds during shell and rocket explosions has been established. Excess of the standard values of the content of toxic metals Cd, Pb, Cu in the grain and vegetative mass of test plants *Hordeum vulgare* and *Triticum aestivum* L was found. The advantages of using the new synthesised chelate-humate preparation Smaragd and the biological product Haupsin BT for effective improvement of the ecological state of the contaminated soil-plant system were determined. The findings were the basis for further implementation of the developed methods in various farms to restore soil health in the conditions of military-technogenic impacts on the soil cover, the soil-plant system; for carrying out remediation and environmental rehabilitation of chemically contaminated soils to improve the ecological state of soils and minimise the effects of chemical pollution and military factor; in research practice – to elaborate methods and technologies for the remediation and environmental rehabilitation of chemically degraded soils in areas of pollution; to control degradation for chemical contamination of soils, promote food and environmental safety

Keywords: soil; chemical pollution; heavy metals; military-technogenic impacts; methods of soil restoration

INTRODUCTION

Researchers are developing strategies for environmental rehabilitation to restore soils and reduce the area of their chemical contamination. In particular, J. Norrman *et al.* (2020) found that pollutant removal measures have higher scores due to high scores in social and economic dimensions based on the expected increase in property values after the restoration of territories. In the critical review by P. Song *et al.* (2022) on the restoration of soils contaminated with heavy metals(HM) summarised the experience of developing new methods of *ex situ* and *in situ* physical (thermal desorption and excavation), chemical (leaching and stabilisation, electrokinetic reduction, oxidation/reduction), and biological (phytoremediation, microbial reduction) remediation and combined reduction methods. The methods are valuable for evaluating effective technologies for site remediation and rehabilitation in conditions of excessive emissions from industrial facilities.

Significant developments in physical and chemical remediation complexes were presented by researchers from China (Wu *et al.*, 2022; Mu *et al.*, 2024). To promote the protection of soil resources from pollution and land use, combined methods of restoration were proposed: physico-chemical and chemical-biological technologies, physico-biological technologies on soils contaminated with HM. It was found that the combination of phytoremediation and microbial remediation is a promising environmentally safe method. The methods are suitable in areas of mining, industrial production, wastewater irrigation, excessive fertiliser application, intensive urbanisation and growth of household waste. The studies evaluated innovative methods of physical and chemical remediation to solve the problem of soil contamination with cadmium (Cd) with the combined use of phosphate fertilisers and sepiolite, CaAl-layered double hydroxide (LDH) immobilisation and hydrotreatment. The adsorption capacity, ion exchange mechanisms, and remediation efficiency were evaluated. The combined use of phosphate fertilisers and sepiolite provided up to 72.6% removal of Cd extracted by HCl from the soil.

The international arsenal of methods for bioremediation of contaminated soils is significant. The review by M. Kumar *et al.* (2022) presented the developed methods of *in situ* remediation of chemically contaminated soils. Biological methods of controlled natural bioremediation, bioventilation (bio-spraying), nanobioremediation, bioaugmentation, and biostimulation for the degradation of soil pollutants have gained the preference *in situ*. However, bioaugmentation methods have risks of inefficiency due to the possible failure of microbial adaptations to environmental conditions. Bioventilation methods are unsuitable for low-permeable or heterogeneous soils, which narrows the possibilities of their use. According to M. Kumar *et al.* (2022), nanobioremediation methods, despite their advantages, have a risk of toxic effects on soil biota.

Based on the analysis, it is advisable to use biostimulation for the remediation of contaminated soil-plant system with ensuring possible positive effects on yield indicators, translocation of toxic metals, and environmental safety of plants due to technogenic impacts. The relevance of solving the problems of reducing pollution areas in Ukraine, scientific substantiation for the restoration of sites and their return to economic circulation, and the elaboration of remediation methods in the zones of influence of industrial facilities has increased due to the increase in military and technogenic impacts on soils due to the ongoing Russian aggression and military operations on the territory of Ukraine.

Researchers are actively developing tools to minimise military impacts and chemical pollution. C. Fernández-Lopez *et al.* (2024) established the expediency of introducing methods of chemical leaching, stabilisation photolysis, electrokinetic remediation, and bioremediation in conditions of soil contamination with explosives from military facilities, heavy metals, perfluoroalkyl and polyfluoroalkyl compounds (PFAS), polycyclic aromatic hydrocarbons (PAH) has been established. However, foreign experience does not consider the specifics of military influence and the properties of chemical soil contamination in Ukraine, which reduces the potential for using existing remediation methods. This requires updating the best practices of suitable remediation methods and their use for contaminated soils in Ukraine.

In Ukraine, such researchers as S. Baliuk *et al.* (2024), in accordance with certain priorities, developed conceptual and methodological approaches to the restoration and use of affected soils, features of their monitoring for military and technogenic impacts. The main types of military soil degradation were identified, and the impact of armed aggression and military operations on the soil cover was determined. In the context of the complex impact on the soils of Ukraine that have undergone physical, chemical and biological degradation due to military operations, the tasks of developing new and using existing methods have been updated, in particular, in the Donetsk Oblast, which is characterised by significant levels of military-technogenic impacts on agrocoenoses, especially in the areas of energy production enterprises, in particular DTEK Kurakhiv TPP LLC. Before dismantling in 2024, DTEK Kurakhiv TPP LLC (with a capacity of 1,460 MW) operated under constant shelling (Kurakhiv Thermal Power Plant, 2016).

According to the State Ecological Inspectorate of Ukraine in the Donetsk Oblast (2024), the amount of certain damage to land resources and atmospheric air around DTEK Kurakhiv TPP LLC and the city of Kurakhove was approximately UAH 1 billion. As a result of systematic Russian attacks, significant contamination of soils close to the energy production facility with organic and inorganic substances was recorded. The above determines the relevance of research aimed at finding ways to solve the important problem of reducing the military-technogenic load on agroecosystems, improving the ecological state and restoring agrocoenoses for the return of soils to agriculture.

The purpose of the study was to investigate the effectiveness of new patent-protected methods for *in situ* remediation of contaminated soils under military and technogenic influences on the soil-plant system in areas of atmotechnogenic emissions from an electricity and heat production facility (using the example of DTEK Kurakhiv TPP LLC in Donetsk Oblast) and to acquire additional insights into the controlling chemical pollution under new conditions of complex military and chemical pollution impacts.

MATERIALS AND METHODS

Research work on monitoring the effectiveness of the use of chemical and biological remedies on chemically contaminated soils due to military and technogenic impacts was carried out in 2022-2024. The study of the effectiveness of new patent-protected methods of remediation of chemically contaminated soils for monitoring their degradation due to military and technogenic impacts was carried out with the implementation of the Task 01.02.02.01.F. "To develop scientific and methodological bases for monitoring, environmental quality rationing, and remediation of chemically contaminated soils as the basis of soil and environmental management" (No. 0121U108037, NSC "ISSA named after O.N. Sokolovsky", soil protection department) in cooperation with the Donetsk State Agricultural Experimental Station of the National Academy of Agrarian Sciences of Ukraine (NAAS of Ukraine). Information, research work, and implementation of innovations provided for compliance with ethical standards, rules, and principles for the use of biological objects (in particular, plants of various species and varieties of domestic selection; test plants without genetic modifications; biologics containing microorganisms without genetic modifications) and eco- and biosafety during research, obtaining and using the results in accordance with the current Ukrainian regulatory framework on bioethics and biosafety in professional activities and the regulatory framework on soil quality and environmental protection (Convention on Biological Diversity, 1992).

In accordance with the set objective, the following were used as research objects: (1) the method of chemical remediation of contaminated soils (Patent for utility model No. 135145, 2019), which involved the use of a new synthesised chelate-humate preparation Smaragd (CHP Smaragd). The method was used under new conditions of military and technogenic impacts. (2) Method of bioremediation of the soil and soil-plant system contaminated with heavy metals (Patent for utility model No. 132724, 2019), which included the use of the biological product Haupsin BT with active strains of the bacterium of the species *Pseudomonas aureofaciens* for biostimulation *in situ*. The method was used under new conditions of military and technogenic impacts. (3) Soils (ordinary chernozems) of land plots consisting of background territories, agrocoenoses of territories of constant and periodic exposure to chemical pollution, and the potential risk of contamination of zones of influence of atmotechnogenic emissions of DTEK Kurakhiv TPP LLC. (4) Soils (mainly ordinary chernozems with low-humus light loamy composition on loessial rocks) of locally disturbed land plots of Volnovakha and Pokrovskyi districts of Donetsk Oblast, which were subjected to military influence, in particular, attacks from multiple launch rocket systems and missile strikes, as a result of Russian military operations. (5) Winter wheat (*Triticum aestivum* L.) variety «Yuzivska" and spring barley (*Hordeum vulgare*) variety "Avers" on an area of 1 ha were used as test plants in conditions of military and technogenic impacts.

The following research methods were used to conduct research in accordance with the set goal and objectives: (1) Universal general scientific methods, computational-analytical and comparative methods. (2) Field research methods according to the field experiment methodology (Dospekhov, 1985). Introduction of new CHP Smaragd into the soil was carried out before sowing test plants at a specific dose of 2.5-3 l/ha and 1.5-2 l/t – for seed treatment; at a dose of 2.5 – 3 l/ha – to optimise the growth and development of plants according to their phenophases. With the established polyelement contamination of the soil Cd, Pb, Zn, the applied doses of the drug were doubled. For *in situ* biostimulation, the biological preparation Haupsin BT with strains B – 306 and B – 111 (pH 6.7; titre 5.6 x 10^{10} viable CFU/cm^3) bacteria of the type *Pseudomonas aureofaciens*. Active agents of the biological product Haupsin BT have antifungal, entomocidal, antibacterial, and antiviral properties, the biological product contains bacteria-antagonists of soil phytopathogens. Haupsin BT is applied to the soil and used for seed treatment of test plants, their foliar treatment in the active phases of growth and development. In particular, the introduction of the biological product Haupsin BT was carried out in the spring directly into the soil during its cultivation 5-6 days before sowing plants at an air temperature above +12°C, in the form of a manufactured liquid in accordance with the current regulations TU 31. (3) Certified and standardised in Ukraine chemical and analytical methods for determining individual characteristics of the elemental status of soils: according to DSTU ISO 11047:2005 (2007) – gross forms of chemical elements in the soil; according to DSTU 4770.1:2007 (2009), in particular mobile forms of trace elements (TE) and heavy metals (HM) (manganese Mn, zinc Zn, cadmium Cd, iron Fe, cobalt Co, copper Cu, nickel Ni, chromium Cr, lead Pb) in the soil; acid-soluble forms of Cd compounds in the soil according to DSTU 7607:2014 (2014) were determined by atomic absorption spectrophotometry; Cu in the soil – according to DSTU 7831:2015 (2016); Pb in the soil – according to DSTU 7832:2015 (2016); Zn in the soil – according to DSTU 7853:2015 (2016). Soil sampling of background areas was carried out in accordance with the current DSTU 4287:2004 (2005). Soil sampling of control variants, zones of military-technogenic impacts was carried out in accordance with the standardised methods of DSTU ISO 10381-1:2004 (2006), DSTU ISO 10381-2:2004 (2006), DSTU ISO 10381-5:2009 (2011) and the international standard ISO 18400-102:2017 (2017). Plant sampling and mineralisation were carried out in accordance with DSTU 7670:2014 (2015).

Assessment of the microelement status and HM content in soils was carried out using the established background levels of their content for soils of a certain natural and climatic zone of Ukraine according to A. Fateyev and V. Samokhvalova (2019) and in accordance with the current threshold limit value of hazardous substances in soils. (4) Methods for conducting phenological observations of cultural phytocoenoses and determining indicators of productivity of test plants and crop structure (field germination, bushiness of test crops) according to method by B. Dospekhov (1985). (5) Atomic absorption method for determining the content of TE/HM (Cu, Pb, Zn, Cd) in plants according to methods of soil and plant analysis (1999). Assessment of the element status of test plants was carried out according to the threshold limit values (TLV) of toxic elements in plants in accordance with the Addendum No. 122-12/805 (1991), DSTU 3769-98 (1998), DSTU 3768:2019 (2019) regulatory documents in force in Ukraine. (6) Statistical data processing methods of the statistical analysis software suite Statistica 10 and Microsoft Excel. The Fischer's criterion was applied when performing calculations.

RESULTS

Based on studies of agrocoenosis soils in chemical pollution zones from DTEK Kurakhiv TPP LLC, the spread of pollution at distances up to 3 km, 10 km, 20 km, and 30 km from the emission centre of the energy production facility was established. A regular increase in contamination of the soil-plant system with mobile forms of Pb, Cd, Cu, and Zn compounds was determined. In particular, the background values of acid- soluble forms of Cd compounds were exceeded by 1.7-2.3 times (extractant 1N HCl) and mobile forms of Cd compounds by 2 times (extractant AAB with pH 4.8) (Table 1). An increase in the content of gross and acid-soluble forms of Pb was found, respectively, by 38% and 12% compared to the background level of the toxicant metal content in the soil. An excess of background levels of mobile forms of Cu was found by 3.8 times, and by 1.7 times for the content of acid-soluble forms of Cu compounds in the soils under study. There was also an increase in the content of gross forms of Zn by 16%, acid-soluble forms of Zn compounds by 1.5-1.8 times in ordinary chernozems.

A decrease in the levels of heavy metal contamination of grain crops with a distance from the centre of pollutant emissions of DTEK Kurakhiv TPP LLC was revealed. The normative values of the elemental composition of plants *Hordeum vulgare* and *Triticum aestivum* L. are reached at a distance of 10-15 km to 30-40 km from the centre of emissions of pollutants (Table 2). Exceedances of standard Cu levels were found in *Hordeum vulgare* test plants, amounting to 5% in grain and 11-44% in straw.

Table 1. *Content of gross and mobile forms of heavy metal compounds in ordinary chernozems in zones of technogenic impact of DTEK Kurakhiv TPP LLC*

Object of analysis	Concentration of various forms of HM in soils, mg/kg											
	Cd			Pb			Cu			Zn		
	1	2	3	1	2	3	1	2	3	1	2	3
Soil	0.3-1.0	0.5-0.7	0.14-0.2	13.9-18.0	1.74-1.89	0.4-0.9	13.5-16.0	4.8-8.6	1.7-1.9	44-64	14.6-18.3	0.9-1.7
Background content	1.0	0.30	0.10	13.0	5.0	0.8	22.0	5.0	0.5	55.0	10.0	1.6
TLV	3.0	0.7		32.0	6.0		100	3.0		300	23.0	

Note: *1 – gross forms, 2 – acid-soluble forms (extractant 1N HCl), 3 – mobile forms (extractant ammonium acetate buffer solution with pH 4.8)*
Source: *created by the authors based on the results of chemical and analytical studies*

Table 2. *HM content in plants in areas affected by different levels of technogenic impact*

Object of analysis	HM content, mg/kg											
	Cu (TLV[1] = 10)			Pb (TLV = 0.5)			Zn (TLV = 50)			Cd (TLV=0.1)		
	Distance to the source of emissions, km											
	⩽3	5-15	>30	⩽3	5-15	>30	⩽3	5-15	>30	⩽3	5-15	>30
Spring barley (*Hordeum vulgare*):												
grain straw	10.5 14.4	6.5 11.1	6.6 9.3	1.8 1.9	1.0 1.3	0.7 0.9	26.4 31.9	14.0 17.0	14.7 15.0	1.28 1.62	0.56 0.45	0.38 0.51
LSD[2]$_{05}$ grain / straw	0.94/ 0.95	0.95/ 0.69	0.86/ 0.63	0.43/ 0.37	0.19/ 0.55	0.85/ 0.83	0.64/ 0.64	0.38/ 0.06	0.69/ 0.38	0.08/ 0.05	0.16/ 0.30	0.14/ 0.24
Winter wheat (*Triticum aestivum*):												
grain straw	4.5 4.9	2.5 3.7	1.2 1.9	2.5 2.8	1.3 2.3	0.7 1.0	37.0 42.2	19.1 22.5	19.3 22.2	0.78 0.96	0.51 0.58	0.48 0.52
LSD$_{05}$ grain / straw	0.63/ 0.95	0.64/ 0.69	0.95/ 0.63	0.63/ 0.63	0.31/ 0.63	0.63/ 0.44	0.63/ 0.85	0.31/ 0.57	0.95/ 0.31	0.76/ 0.12	0.06/ 0.13	0.12/ 0.12

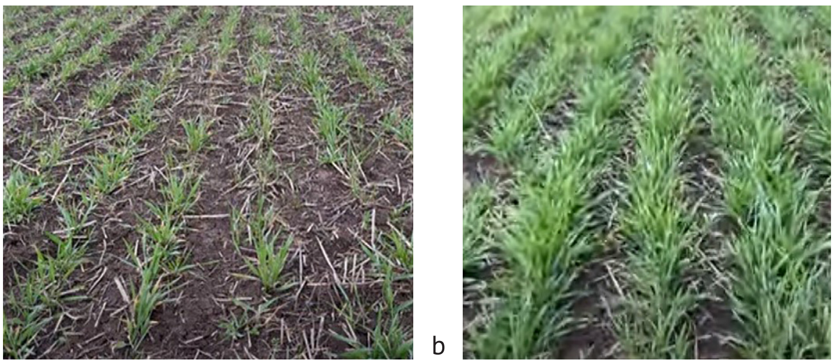
Note: *[1]TLV – threshold limit values in accordance with the current regulatory documents of Ukraine (DSTU 3769-98, DSTU 3768:2019); [2]LSD$_{05}$ – the least significant difference*
Source: *created by the authors based on the results of chemical and analytical studies*

The standard Pb content was exceeded in barley grain by 1.4-3.6 times, in straw of the test crop – by 1.8-3.8 times. The established values of Zn content in spring barley plants did not exceed the current TLV. However, the accumulation of the toxic metal Cd was recorded both in the grain and in the straw of spring barley. In comparison with the current TLV, the excess of Cd content in barley grain was 3.8-12.8 times, in barley straw – 4.5-16.2 times. Analysis of test plants of *Triticum aestivum* L. found an excess of the standard Pb content in wheat grain by 1.4-5 times, in straw of the test crop – by 2.-5.6 times. The established values of Zn and Cu content in winter wheat test plants did not exceed the current TLV. The determined levels of Cd content exceeded the standard TLV in grain by 4.8-7.8 times, in straw – by 5.2-9.6 times (Table 2). Research into areas affected by military activity has revealed destruction of the soil surface and the formation of craters of various diameters (Fig. 1), chemical contamination of the soil at the sites of shell and rocket explosions, and physical contamination with metal debris of various sizes. An increased content of toxic metals Pb, Cd, Ni, Cu was observed in the explosion locations. The results of the analysis of soil samples indicate an excess of the background levels of pollutants in the soil of shelled locations or existing craters by 7-17 times; in combat locations, the excess of the background levels of Cd and Pb in the soil was 1.1-1.3 times.

Craters formed as a result of the use of various types of weapons by the aggressor during massive attacks on the territory under study were examined. The characteristics of craters are determined and categorised based on the tactical and technical parameters of the weapons used by the aggressor. In particular, mortars with 82-mm fragmentation shells and high-explosive fragmentation mines (82 mm calibre) created craters with the smallest diameter of about 1 m. "Grad" installations and field and self-propelled howitzers (120 mm calibre) left craters with a diameter of 2.5-3.5 m. Craters from mortars with 152-mm shells, towed guns, howitzers and self-propelled howitzers (152 mm calibre) had a diameter of 4-6 m. Characteristic signs of the impact on the soil from multiple launch rocket systems "Uragan" (calibre 220 mm) were craters with a diameter of 7 m. Thus, it was determined that at the time of the surveys, the maximum number of craters in the areas under study was the result of attacks from "Grad" launcher installations, field and self-propelled howitzers of 120 mm calibre, and the use of mortars with 82 mm fragmentation shells and high-explosive fragmentation mines of the same calibre. The applied algorithm of ecological rehabilitation of chemically contaminated chernozem soils in the zones of atmo-technogenic influence of DTEK Kurakhiv TPP LLC and disturbed soils of land plots included preliminary determination of the ecological state of the soil-plant system, the use of the developed composition of the new CHP Smaragd in the soil-plant system and on soils with crater locations (diameter 1-4 m); consideration of the established laws of translocation of HM and TE in grain crops under study. Additionally, the method allowed determining the types of weapons based on individual characteristics and diameters of craters formed in areas of military and technogenic impacts.

Figure 1. *Typical craters of various diameters identified from the surveyed chemically contaminated areas in the zones of influence of technogenic emissions of pollutants of the energy facility (DTEK Kurakhiv TPP LLC)*
Source: *created by the authors based on soil research conducted in 2022-2024*

Under conditions of chemical contamination and military impact on the soil-plant system, the new preparation is used for seed treatment, fertilising plants and applying to the soil to obtain remediating and fertilising effects. Positive results of exposure to CHP Smaragd in the conditions of military-technogenic impacts are conditioned by a certain ratio of interacting agents of the drug composition. The composition of CHP Smaragd, proposed for use in chemically contaminated soil-plant systems, contains chelated compounds of TE (Fe, Mn, Zn, Cu, Co, Mo, and B), obtained based on the OEDP (oxyethylidenediphosphonic acid) complexon. The humate component of CHP Smaragd is obtained based on a preparation of known humate from organic raw materials of natural origin, followed by introduction into a chelate solution. Phenological observations were carried out to analyse the effect of CHP Smaragd on the yield of barley (*Hordeum vulgare*) and assess the quality and environmental safety of grain and straw of test plants on chemically contaminated soils. The positive effect of the Smaragd preparation was determined based on identifying an improvement in the indicators of field germination and bushiness of plants that characterise the yield structure of test plants under military and technogenic impacts (Fig. 2).



a b

Figure 2. *Phenotypic features of Hordeum vulgare in the surveyed areas of complex impacts of chemical pollution and military factor in the emission zones of DTEK Kurakhiv TPP LLC when using CHP Smaragd in chemically contaminated areas*
Note: *a – control (contaminated soil due to military and technogenic impacts); b – option of using CHP Smaragd in conditions of chemical contamination of the soil-plant system*
Source: *created by the authors based on soil research conducted in 2022-2024*

It was found that the bushiness indicator of *Hordeum vulgare* increased from 1.7 (control option) to 2.3 when using CHP Smaragd. It was recorded that the bushiness coefficient increased to 1.5-1.7; the indicator of productive bushiness in the control was 1.3. It was also established that field germination of *Hordeum vulgare* increased by 4.5% compared to the control version, where this figure was 87.5%. At the experimental sites located at a distance of 0-3 km and 3-10 km from DTEK Kurakhiv TPP LLC, the degree of technogenic impact of the power plant on the agrophytocoenosis of barley was determined in accordance with the average annual wind rose and zones of the greatest dispersion of emissions from the enterprise. In studies of the soil-plant system, the influence of chemical pollution and military factor when using CHP Smaragd was considered. The use of the proposed variants of the experiment allowed assessing the relationship between the intensity of technogenic load and the reaction of test crops. The results are presented as analytical data (Table 3).

***Table 3**. Efficiency of using CHP Smaragd considering individual test indicators of spring barley (Hordeum vulgare)*

Experiment options	Test crop yield, t/ha	Accumulation of heavy metals in plants, mg/kg		
		Zn	**Cd**	**Pb**
1. Control (contaminated soil of areas affected by pollutant emissions from Kurakhiv TPP)	2.88	50.5 60.4	0.11[1] 0.64 [2]	0.59 3.42
2. Contaminated soil of the Kurakhiv TPP pollutant emission zones + *CHP Smaragd*	3.40	40.75 45.9	0.09 0.46	0.45 2.60
3. Contaminated soil of the Kurakhiv TPP pollutant emission zones + military factor	2.73	52.9 56.9	0.13 0.69	0.65 3.8
4. Contaminated soil of the Kurakhiv TPP pollutant emission zones + military factor + *CHP Smaragd*	3.33	42.52 47.2	0.08 0.49	0.50 2.80
TLV of HM in grain/vegetative mass of plants		50.0	0.1	0.5
50.0		0.3	5.0	
		grain / straw		
LSD_{05}	0.21	0.21/ 1.32/	0.01// 0.09	0.07/ 0.23
LSD_{01}	0.32	0.31/ 2.0	0.02/ 0.13	0.11/ 0.36
Fischer's criterion		grain / straw		
Ffact. F_{05} = 4.76 F_{01} = 9.80	26.70	98.90/ 72.30	38.8/ 24.79	26.41/ 53.28

***Note:** [1]numerator – HM content in the grain; [2]denominator – HM content in the vegetative mass*
***Source:** created by the authors based on soil research conducted in 2022-2024*

The results of field studies indicate an improvement and restoration of the productivity of spring barley (*Hordeum vulgare*), as a factor for further restoration of the overall efficiency of agricultural production due to military and technogenic impacts. In particular, the positive effect of using CHP Smaragd on the yield growth indicators of test plants in comparison with the control version was confirmed. An additional barley yield of 0.52 t/ha was obtained in relation to the control using the biological product CHP Smaragd on chemically contaminated chernozem soils and an increase in the yield of 0.45 t/ha in the zones of influence of atmo-technogenic emissions of pollutants and military factor (Table 3). In the conditions of pollutant emission and military impact of the surveyed territories, the effect of CHP Smaragd on the accumulation of HM by *Hordeum vulgare* was investigated. A decrease in the Zn content was found by 16% in grain and by 22% in vegetative mass of *Hordeum vulgare* under military conditions and the use of CHP Smaragd in the soil-plant system. In the studied areas of industrial emissions of energy production, it was found that the use of CHP Smaragd provided a reduction in the Zn content in test plants. The recorded decrease in the content of toxicant metal in the grain of test plants was 19.3%, in the vegetative mass of *Hordeum vulgare* – 24%.

The use of CHP Smaragd in contaminated areas by energy company emissions contributed to a significant reduction in the Pb content in plant products. It was determined that the level of Pb accumulation in the grain and vegetative mass of the test culture decreased by 24%. Under military conditions, the Pb content decreased by 15% in grain and by 18% in vegetative mass of *Hordeum vulgare*. It was found that under the conditions of military influence and chemical contamination of the soil-plant system, the use of this method of chemical remediation helped to reduce the level of Cd in grain of *Hordeum vulgare* by 27%, in the vegetative mass – by 23%. It was determined that the use of the drug by the proposed method in the soil-plant system when exposed to pollutants in the zone of action of the Kurakhiv TPP contributed to a decrease in the Cd content in grain of *Hordeum vulgare* by 18%, in the vegetative mass – by 28%. Thus, an improvement in the ecological state of the soil-plant system has been established, which is conditioned by the detected remediation effect of CHP Smaragd with a fertilising and stimulating effect, which ensures the effectiveness of the proposed remediation method under conditions of chemical pollution and the influence of military factors.

Based on the results of comprehensive research in the soil-plant system on the effectiveness of an innovative method of activating the natural biological potential of the soil in the conditions of military-technogenic impacts, effective bioremediating cleaning of toxic pollutants has been established. The basis of the proposed method of biological remediation is the use of the biological product Haupsin BT, the detection of its remediation properties and the processes of activation of microbiological and biochemical properties of chemically contaminated soils due to the use of the biological product. The basic principle of remediation action of active agents of biologics consists in the establishment of specific microbial-plant associations that increase the effectiveness of the specified biologics, which allows neutralising the harmful effects of pollutants at established load levels and also partially restoring the productive properties of plants under military-technogenic impacts. Thus, the new method used under the new conditions ensures the restoration of test plants and an integrated increase in the biological efficiency of remediation agents and contributes to the rehabilitation of the ecological functionality of the contaminated soil-plant system.

Phenological observations on the effect of Haupsin BT biologics on the yield of winter wheat (*Triticum aestivum*) and on the indicators of grain quality and environmental safety on chemically contaminated soils, ensured the identification of the effective effect of the proposed method of bioremediation of the soil-plant system. An improvement in the structural indicators of the test crop yield was recorded using the biological product Haupsin BT on contaminated soils. In particular, ensuring increased productivity of *Triticum aestivum* (Fig. 3) contributed to the growth of the tillering coefficient to 1.6-1.8 compared to the productive bushiness of 1.4 in the control, it was determined that the bushiness indicator of *Triticum aestivum* increased from 1.9 (control variant) to 2.8 when using the biological product Haupsin BT. Field germination of the test culture under the influence of a biological product increased by 3.5% compared to the control version (86.7%). Given the current military-technogenic factors at the experimental sites used and distances of 0-3 km and 3-10 km, in accordance with the maximum dispersion of HM emissions and the average annual wind rose, the degree of influence of the Kurakhiv TPP on the agrophytocoenosis of winter wheat (*Triticum aestivum)* was determined (Table 4). The restoration of productivity of phytocoenosis crops using the proposed bioremediation method using the drug Haupsin BT was established, which was confirmed by the indicators of an increase in the yield of the test crop compared to the control. In particular, an increase in the yield of *Triticum aestivum* of 0.6 t/ha was obtained by using the biological product Haupsin BT in the case of chemical soil contamination, and an additional yield of *Triticum aestivum* of 0.52 t/ha was obtained in relation to the control of military-technogenic influences.

Table 4*. Efficiency of using the biological product Haupsin BT based on individual test indicators of winter wheat (Triticum aestivum)*

Experiment options	Test crop yield, t/ha	Accumulation of heavy metals in plants, mg/kg		
		Zn	Cd	Pb
1. Control (contaminated soil of areas affected by pollutant emissions from Kurakhiv TPP)	3.38	59.5 62.4	0.11[1] 0.9[2]	0.80 5.2
2. Contaminated soil of the Kurakhiv TPP pollutant emission zones + *CHP Smaragd*	3.98	39.75 50.9	0.07 0.52	0.55 3.22
3. Contaminated soil of the Kurakhiv TPP pollutant emission zones + military factor	3.05	60.9 67.92	0.10 0.92	0.75 5.9
4. Contaminated soil of the Kurakhiv TPP pollutant emission zones + military factor + *CHP Smaragd*	3.90	45.3 42.5	0.08 0.64	0.52 3.59
TLV of HM in grain/vegetative mass of plants 50.0		50.0 0.3	0.1 5.0	0.5
		grain / straw		
LSD_{05}	0.25	4.59/ 4.94	0.02// 0.09	0.11/ 0.26
LSD_{01}	0.38	6.96/ 7.47	0.02/ 0.13	0.17/ 0.40

Table 4. Continued

Experiment options	Test crop yield, t/ha	Accumulation of heavy metals in plants, mg/kg		
		Zn	Cd	Pb
Fischer's criterion Ffact.		grain / straw		
$F_{05} = 4.76$ $F_{01} = 9.80$	46.76	50.03/ 72.30	13.0/ 53.74	13.44/ 255.47
Significance between parameters is indicated by p <0.05 and p <0.01				

Note: *[1]numerator – HM content in grain; [2]denominator – HM content in the vegetative mass*
Source: *created by the authors based on soil research conducted in 2022-2024*

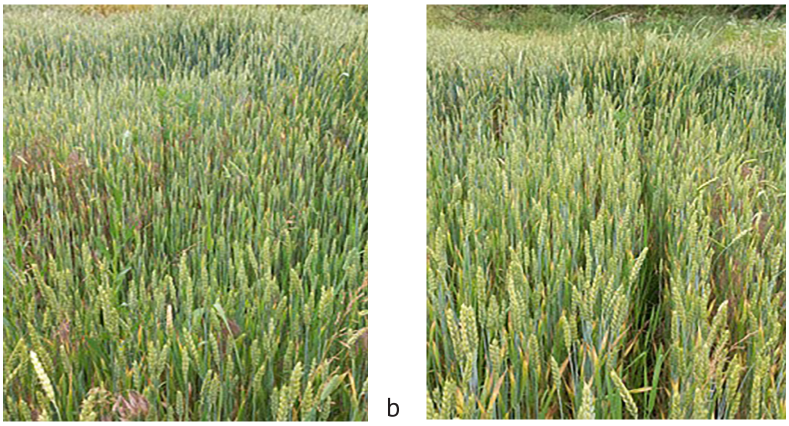


***Figure 3**. Effect of using a biological product Haupsin BT on the soil-plant system of chemically contaminated territories of the zone of influence of atmotechnogenic emissions of pollutants of DTEK Kurakhiv TPP LLC and military-technogenic impacts*
Note: *a – control (contaminated soil due to military-technogenic impacts); b – option of using a biological product Haupsin BT in conditions of soil-plant system contamination*
Source: *created by the authors based on soil research conducted in 2022-2024*

The results of the research determined that the use of the new method and biologic preparation Haupsin BT in conditions of exposure to pollutant emissions from Kurakhiv TPP provided a reduction in Cd accumulation in test plants *Triticum aestivum*. It was found that a decrease in the concentration of toxicant metal in grain of *Triticum aestivum* was 36.4%, and an even more pronounced decrease in the Cd content was noted in the vegetative mass of the grain crop, which was 42%. The results demonstrated the effectiveness of the biological product in reducing the toxic load on plants, thus contributing to improving the environmental safety of the soil-plant system.

It was determined that in the conditions of military-technogenic impacts on the soil-plant system, the use of the developed method of biological remediation contributes to a significant decrease in the concentration of toxic metals in *Triticum aestivum plants*. In particular, in the test areas where the biological product Haupsin BT was used under military conditions, a decrease in Zn content of 24% and 32% was observed in the grain and vegetative mass of the test crop, respectively. Reduction of bioaccumulation of Zn by test plants was determined *Triticum aestivum* due to the use of the biological product Haupsin BT in the areas of exposure to pollutants of the Kurakhiv TPP. A decrease in the concentration of Zn in grain and vegetative mass of plants was recorded by 33% and 18.4%, respectively. The Cd content in the grain of the grain crop decreased by 27%, in the vegetative mass of plants – by 29%. The use of the biological product Haupsin BT under military impact on agrocoenoses provided a decrease in the concentration of Pb by 35% in grain, by 31% in vegetative mass of *Triticum aestivum*. Under the conditions of technogenic impacts, it was found that the use of the developed bioremediation method led to a decrease in the Pb content by 31% and 38%, respectively, in the grain and vegetative mass of test plants *Triticum aestivum*. Thus, the use of Haupsin BT biological product based on active strains of bacteria of the genus in the soil-plant system of *Pseudomonas sp.* provided a bioremedical effect and ecological stabilisation of the contaminated soil-plant system while simultaneously neutralising negative pollution processes due to the complex action of the biological product by activating the natural biological potential of the soil.

Statistically, data processing is performed using the univariate variance analysis module. The Fischer's criterion was applied when performing calculations. Variances of options and errors are determined for calculating the least significant difference (LSD) (Tables 2-4) and for calculating the Fischer's criterion (Tables 3-4). The significance between the parameters is indicated by the levels $p < 0.05$ and $p < 0.01$. The condition $F_{fact} > F_{theor}$ is performed for all variants of the proposed experiments (Tables 3-4), which proves the correctness of the schemes and the reliability of the results obtained. Thus, an alternative hypothesis is accepted, according to which the difference between the sample averages in experiments is significant. The results of statistical analysis of the obtained data prove the significance of the influence of the studied factor of applying remediants on the effective feature – the content of toxic metals in plants and the yield indicators of test crops. Reliable remediation effects on reducing the content of toxic metals in grain crops on soils contaminated with Cd, Pb, Zn have been established; the positive impact of the proposed methods of remediation of contaminated soils on the restoration of cultural phytocoenoses under new conditions of complex military-technogenic impacts.

DISCUSSION

The results of research under the conditions of military-technogenic impacts revealed the positive effects of the application of the developed algorithms using the new synthesised CHP Smaragd and the well-known biological product Haupsin BT (Ukraine) with its established remediation property in the soil-plant system with the background of chemical contamination. Methods of remediation according to the mechanism of action of the used drugs have been developed, aimed at biostimulation in the contaminated soil-plant system, at creating favourable conditions for soil microorganisms to degrade pollutants, and ensuring environmental effects of *in situ* remediation methods. Bioremediation, as a method of restoring chemically contaminated soil *in situ*, is considered by researchers as an alternative to excavating soil contaminated with pollutants of various kinds (Wang *et al.*, 2021; Michael-Igolima *et al.*, 2022). The range of soil restoration methods *in situ* was tested with varying success in the field. The research focus for developing new methods is on identifying and eliminating factors that limit biodegradation. The identified limiting factors for the biodegradation of soil pollutants are as follows: lack of oxygen and nutrients, soil structure and moisture, soil temperature; bioavailability of pollutants, soil pH, nature of pollution, potential for decomposition of pollutants, etc. (Cavazzoli *et al.,* 2022; 2023).

The results obtained confirmed the feasibility of using the advantages of the principles and mechanism of biodegradation in biostimulation for remediation of the contaminated soil-plant system. Researchers from Finland emphasises that in order to enhance biostimulation, it is advisable to use chemical and physical methods of remediation of contaminated soils (Romantschuk *et al.*, 2023). In the current research, the method of chemical and biological remediation of soils contaminated with HM has been successfully combined and it is recommended to use algorithms for sequential involvement of the proposed methods and/or a combination of methods for remediation of chemically contaminated soils of technogenic and military impact zones.

It should be noted that the results obtained are consistent with individual scientific data of other Ukrainian researchers. In particular, the findings of L. Biliavska *et al.* (2024) and M. Galkin *et al.* (2024) developed effective practical solutions to an important problem of modernity – the restoration of disturbed soils after military operations. Based on the bioindicatory role of microorganisms in determining the ecological state of soils, comprehensive solutions for restoring soil fertility have been developed (Biliavska *et al.*, 2024). In order to accelerate the restoration of soils damaged as a result of Russian military operations, it was recommended to use microbial biotechnologies in combination with phytoremediation, which will contribute to the re-involvement of restored soils in economic circulation (Galkin *et al.,* 2024). It was proposed to use newly developed and patented methods involving the application of CHP Smaragd, the biological preparation Haupsin BT and grain crops to overcome military-technogenic impacts on the soil-plant system in areas affected by energy enterprises and military factors.

Comparison of the data obtained with the results by M. Salam *et al.* (2022) found consistency of the results with proven provisions for improving the effectiveness of phytoremediation on contaminated soils by introducing stimulating carbon compounds into the soil-plant system, which should be considered as an indirect form of biostimulation. The obtained remediation effects in the soil-plant system are obviously also associated with the phytoremediation effects of grain test crops and their rhizosphere for biodegradation of pollutants by biostimulation using humate-chelate compounds in the composition of the Smaragd preparation. The potential of grain test crops that are resistant to Cd, Pb, and Zn contamination due to the functioning of physiological barriers was used. Similar scientific results of Ukrainian researchers on the use of chemical remediants and biologics to reduce and overcome chemical pollution with soil restoration were obtained and presented in publications by S. Korsun *et al.* (2019), S. Korsun (2024). In particular, studies of HM translocation in the soil-plant system have established the ability of plants to localise pollution due to the accumulation and partial transformation of pollutants. The functioning of the root systems of test plants in contaminated areas, in addition to the accumulation of heavy metals, promotes the development of microorganisms in the soil by stimulating native microflora to accelerate the degradation of pollutants.

It is noted that the basic prerequisite for the successful implementation of bioremediation is a careful selection of plants and biologics that can optimally stimulate their growth and development (Korsun *et al.,* 2019). New bioremediation measures were used at the locations of military impacts (hotbeds of burning equipment and explosions of ammunition for reducing the biogenicity of the soil by 30%, increasing the content of HM by 3-470 times), which provided for the introduction of compositions of carbohydrate-oxidising bacteria, organic substances and certain biogenic elements (doses of 5-12% by weight of the soil) with local contamination with petroleum products. During the 90 days of the experiment, the content of petroleum products in the soil on variants using biologics decreased by 59-92%. Ecostern detox (normally 1.5 l/ha, applied in full) containing microorganisms was used. Organic fertiliser was applied (peat and soil mixed in a ratio of 1:1). A decrease in the total biogenicity of the soil, the transformation coefficient of its organic matter, and an increase in the number of soil microorganisms that are trofically associated with nitrogen of organic compounds were recorded (Korsun, 2024). The positive consequences of using the proposed remediants for agrocenoses with grain crops are the impact on the yield, quality and environmental safety of grain and vegetative mass of test plants compared to the control on chemically contaminated soils. A decrease in the content of priority toxic metals Cd, Pb, Zn, Cu was revealed in grain and vegetative mass of grain crops *Hordeum vulgare, Triticum aestivum.* Studies have confirmed the positive effect of the applied remediants on the components of the crop structure, including such important indicators as field germination and the level of bushiness of plants grown on soils contaminated with harmful substances due to military and technogenic impacts. The results indicate the restoration of productivity of cultural phytocenoses, improvement of the ecological state of the soil-plant system.

Given the low level of sorption potential of explosives and the relatively low solubility of their solid particles in water, which contributes to their longer preservation in the soil and adjacent environments, therefore, the introduction of sorbents is impractical for neutralising the remains of explosives and their components in the locations of disturbed soils. It was proposed to use a patent-protected method of chemical remediation of contaminated soils using CHP Smaragd, which also contains humic substances for binding HM to complex compounds, physical absorption of soil pollutants, and their further possible transformation through ion exchange, surface adsorption, complex formation, and coagulation in the soil. For a more complete understanding of the mechanisms of action of remediants in the soil-plant system and assessment of the benefits obtained for using the chemical preparation Smaragd, data from foreign and Ukrainian researchers on the functionality of humic components in the soil were revealed. In particular, the amphiphilic properties of the supramolecular structure of humic acids determine the activity of humic substances, which is associated with a significant content of hydrophobic and hydrophilic functional groups that make up humic components (Korotkova & Chaika, 2022).

The mechanism of soil remediation using chelated compounds and humic acids is confirmed by the above provisions on the interaction of metal cations with phenolic and carboxyl groups in the molecular structure of humic acids, which leads to the formation of spherical complexes (Chaika & Korotkova, 2023). Humic substances play a significant role in the water-retaining and ion-exchange capacity of the soil, in regulating the pH and activity of soil enzymes, macronutrients and their availability for plants. Algorithms for sequential use and combination of bioremediation methods for chemically contaminated soils (Zheng *et al.,* 2022). It was noted that the necessary conditions for positive results in the remediation of contaminated soils were the determination of the effectiveness of the proposed remediation methods in conditions similar to those of the areas where it is to be scaled up. Professional experience and qualifications of researchers are important. The focus should be on the use of native microbial pollutants and evaluation of their effectiveness. Based on the results of field research, the advantages were identified (in particular, reducing the bioavailability of pollutants, increasing the efficiency of their degradation in the soil-plant system) and the effectiveness of using the proposed methods of chemical and biological remediation of contaminated soils for chemical pollution and military impacts was confirmed, which is the basis for further scaling of the proposed patent-protected author's developments; to increase the effectiveness of management decisions and further development of remediation methods for chemical pollution and military impacts in Ukraine to ensure food and environmental safety.

CONCLUSIONS

The effectiveness of using a new method of chemical remediation of the contaminated soil-plant system by introducing a new CHP Smaragd was investigated and established. The effectiveness of using a new method for activating the biological potential of soil in the conditions of bioremediation of the soil-plant system contaminated with HM was determined and evaluated. The proposed methods were used under new conditions of complex negative military-technogenic loads on agrocoenoses in the emission zones of the electric and thermal energy production facility (on the example of DTEK Kurakhiv TPP LLC in Donetsk Oblast). Analysis of the effectiveness of the use of CHP Smaragd in the soil-plant system established growth-stimulating and remediating effects in the soil-plant system due to the use of a new effective composition of the drug, which provided an improvement in the quality and environmental safety of grain and straw test plants by reducing the intake of pollutants; improving the indicators of the crop structure and field germination, and bushiness of grain crops, restoring the productivity of agrocoenosis plants on chemically contaminated soils; reducing chemical pollution caused by military and technogenic factors, improving the ecological state of the soil-plant system.

Analysis of the effectiveness of the use of the biological product Haupsin BT determined the manifestation of the bioremediation effect in the soil-plant system that has been contaminated. This effect was observed against the background of increased processes of biological purification and restoration, which contributed to an improvement in the productivity of grain crops and was confirmed by an increase in their yield indicators. An improvement in the structural characteristics of the crop was recorded with an increase in field germination and bushiness indicators of *Hordeum vulgare, Triticum aestivum*. However, a decrease in bioaccumulation of HM by plants was found in comparison with the control variants, which indicates the effectiveness of the method used to optimise bioremediation. The suitability of the developed remediation methods for contaminated disturbed chernozem soils under complex technogenic and military impacts after bomb, rocket, and artillery strikes was established. In particular, the suitability for the soils of land plots damaged due to shelling from field and self-propelled howitzers (120 mm calibre), "Grad" launchers, mortars with fragmentation shells and high-explosive fragmentation mines (82 mm calibre) with created craters with a diameter of 1-4 m. The methods were aimed at reducing the complex impact of the military factor and chemical pollution to stabilise the soil-plant system. In order to reduce the intensity of the processes of chemical degradation of soils and their restoration and return of land plots to economic use, the methods used in the conditions of military-technogenic impacts should be recommended for use by agricultural producers for growing grain crops in areas with negative consequences of military operations and chemical exposure and increased risks of soil and plant pollution.

When establishing high levels of soil contamination due to military-technogenic impacts, it is also advisable to use algorithms for consistent application of the proposed methods and/or a combination of elaborated methods of remediation of chemically contaminated soils to enhance remediation effects in the soil-plant system. It is advisable to use new knowledge on the effectiveness of the proposed new patent-protected methods of remediation of contaminated soils in the zones of atmotechnogenic emissions of the electric and thermal energy production facility to control the chemical degradation of soils and the soil-plant system under military-technogenic impacts. Prospects for further research on the remediation of chemically contaminated soils for military-technogenic impacts is the development of scientific and methodological support (new methods, methodological approaches, techniques) for environmental rehabilitation of chemically contaminated soils, the soil-plant system considering the type of pollution to minimise the impact, improve the environmental condition and control degradation; to manage the elemental status of soils of contaminated territories considering the harmfulness of pollution and levels of soil degradation; making managerial decisions on soil restoration for military-technogenic impacts in the zones of existing and destroyed industrial facilities.

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CONFLICT OF INTEREST

None.

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Методи покращення екологічного стану хімічно забрудненої системи ґрунт-рослина за впливу мілітарно-техногенних факторів на агроценози

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Анотація. Мета роботи – дослідити ефективність нових методів ремедіації *in situ* забруднених ґрунтів при комплексних мілітарно-техногенних впливах на систему ґрунт-рослина в зонах атмотехногенних викидів об'єкту виробництва електричної та теплової енергії (на прикладі ТОВ «ДТЕК Курахівська ТЕС» Донецької області). Використано системний підхід із залученням комплексу універсальних загальнонаукових методів; методів польових і чинних методів хіміко-аналітичних досліджень ґрунтів і тест-рослин агроценозів із визначенням показників елементного статусу системи ґрунт-рослина, індикаторних показників якості рослин за впливу хімічного забруднення та мілітарного впливу; використанням розроблених методів хімічної і біологічної ремедіації системи ґрунт-рослина; застосуванням камеральних методів статистичної обробки отриманих даних. Отримано нові знання з контролю хімічного забруднення ґрунтів і системи ґрунт-рослина за умов комплексного впливу мілітарного фактору і хімічного забруднення в зонах атмотехногенних викидів об'єкту виробництва електричної та теплової енергії. Отримано нові дані з аналізу ефективності використання розроблених інноваційних методів хімічної та біологічної ремедіації забруднених ґрунтів за нових умов мілітарно-техногенних впливів. Встановлено пріоритетне забруднення системи ґрунт-рослина рухомими формами сполук свинцю (Pb), кадмію (Cd), цинку (Zn), міді (Cu) та нікелю (Ni) за вибухів снарядів і ракет. Встановлено перевищення нормативних значень вмісту металів-токсикантів Cd, Pb, Cu у зерні та вегетативній масі тест-рослин *Hordeum vulgare* і *Triticum aestivum* L. Визначено переваги використання нового синтезованого хелатно-гуматного препарату Смарагд та біопрепарату Гаупсин БТ для ефективного поліпшення екологічного стану забрудненої системи ґрунт-рослина. Результати досліджень є підставою для подальшого впровадження розроблених методів у господарствах різних форм господарювання для відновлення здоров'я ґрунтів за умов мілітарно-техногенних впливів на ґрунтовий покрив, систему ґрунт-рослина; за проведення заходів ремедіації та екологічної реабілітації хімічно забруднених ґрунтів для покращення екологічного стану ґрунтів і мінімізації впливів хімічного забруднення і мілітарного фактору; у науково-дослідній практиці – для розробки методів і технологій ремедіації та екологічної реабілітації хімічно деградованих ґрунтів територій забруднення; контролю деградації за хімічного забруднення ґрунтів, сприяння забезпеченню продовольчої та екологічної безпеки

Ключові слова: ґрунт; хімічне забруднення; важкі метали; мілітарно-техногенні впливи; методи відновлення ґрунту