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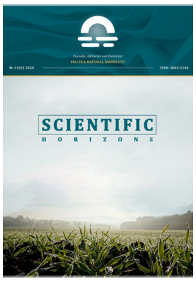

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Ecological and toxicological condition of militarily degraded chernozems: A case study of the Chkalovsk territorial community

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Abstract. This study aimed to assess the ecological and toxicological condition of militarily degraded chernozems in the Chkalovsk territorial community of the Chuhuiv District in the Kharkiv Region. This involved conducting a detailed, comprehensive survey of the ecological and toxicological condition of the chernozems in the Chkalovsk territorial community, which were affected by military actions, and determining their suitability for agricultural use. If necessary, recommendations for soil remediation measures were provided. An improved system for classifying and assessing the degree of military degradation of soils, based on indicators of chemical contamination by organic and inorganic compounds, was proposed. It was established that on recently demined areas of the de-occupied territory, there is a trend of slight increases in the content of lead (1.4 times), cobalt (1.3 times), iron (1.6 times), and zinc (2.6 times) relative to pre-war (background) levels. The observed exceedances of heavy metals in the soil, while present, are not critical for agriculture and do not necessitate land conservation or the implementation of overly complex and costly soil remediation measures. A slight decrease in mobile cadmium, lead, nickel, cobalt, and iron was recorded after demining, accompanied by an increase in plant-available chromium and zinc. The concentrations of bioavailable manganese and copper remained almost unchanged during this period. These changes may also indicate the ongoing processes of self restoration in chernozem soils, which are typically characterised by high buffering capacity against heavy metals. The results obtained demonstrate very low concentrations of all polycyclic aromatic hydrocarbons, explosive substances, and related nitroaromatic compounds in the studied soils. The findings can be used when developing a post-war soil restoration programme and the rational use of land in agricultural production

Keywords: soil contamination; ecological safety; Russian-Ukrainian war; heavy metals; petroleum products; military soil degradation; agricultural production

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INTRODUCTION

Ukraine has a unique soil cover, with more than 60% of its territory occupied by chernozem soils, which are unparalleled in their properties, fertility potential, and suitability for growing a variety of field crops. The area covered by chernozems exceeds 24 million hectares. Ukrainian chernozem is a national brand, a cornerstone of food and economic security, and a foundation for human prosperity. Chernozem is the gold standard of soils, a natural phenomenon characterised by distinctive morphological, physical, and chemical properties, and exceptionally high fertility. Thanks to the resource potential of naturally fertile chernozems, Ukraine holds a leading position in the global export of grain, sunflower, and other crops. Chernozems are classified as Black soils, considered the most valuable for food security. They are characterised by high organic carbon content (over 1.2%), a top dark-coloured horizon thickness of at least 25 cm, cation exchange capacity exceeding 25 mmol/kg, and base saturation of over 50% (FAO, 2022).

The impact of warfare on the agricultural sector and land resources has become a focal point for scientific research. Notably, J. Teixeira da Silva *et al.* (2023) investigated the effects of the Russian-Ukrainian war on agricultural production and food security at various levels of governance. V. Zhuk *et al.* (2023) substantiated the utility of accounting methods for assessing the damages inflicted upon Ukrainian agricultural businesses by the war, however, the issue of evaluating the damage to land remained unaddressed in their study. S. Baliuk *et al.* (2024) conducted a pilot assessment and mapping of the impact of warfare on Ukraine's soil resources. A. Kucher and L. Kucher (2024) undertook an economic evaluation of the harm and losses incurred by soils and lands as a result of the Russian-Ukrainian war.

The problem of soil contamination in Ukraine was pressing even before the war, but its significance has increased substantially following the Russian invasion. For instance, according to Ye. Ulko *et al.* (2022), a quantitative assessment of the impact of soil contamination by mobile forms of lead and cadmium on land use efficiency and normative monetary valuation of arable land revealed the potential for improvement if the contamination issue were addressed. As noted by H. Kireitseva *et al.* (2023), the environmental impact of war may seem secondary amidst human suffering and daily destruction, but the consequences of environmental crimes are long-lasting and their remediation can take many years.

The ecological risks associated with warfare have been exacerbated by the ongoing conflict, posing significant threats to the environment, particularly soil and water resources, as well as the quality of agricultural produce. The intense anthropogenic pressures resulting from military activities can induce processes of military degradation in soils, including chemical degradation caused by contamination with toxic substances. This has a detrimental impact on the eco-toxicological status of soils, their health, and the ecosystem services they provide. Prolonged warfare results in widespread damage to agricultural lands, especially chernozems, and intensifies chemical contamination of soils and water sources due to the detonation of explosives, destruction of heavy machinery, spills and burning of petroleum products. Moreover, as J. Hupy and

R. Schaetz (2006) noted, explosions can disrupt the soil profile and mix the fertile topsoil with underlying Quaternary deposits (bombturbation), leading to alterations in the geochemical background of the soil cover in active conflict zones. An ecological and toxicological review conducted by A. Rodríguez-Seijo *et al.* (2024) revealed that military activities are a significant source of contamination of water and soil with inorganic and organic pollutants.

These factors can lead to a range of negative consequences for public health, agricultural product quality, water resources, and the flora and fauna of Ukraine. The risk of land contamination arises not only from the destruction of industrial enterprises, processing complexes, buildings, and structures. Direct sources of contamination of agricultural land during combat operations include various calibres of munitions containing a wide range of toxic compounds, the burning of heavy machinery, and spills of fuel, lubricants, and organic solvents.

The intense fighting that took place over several months during the liberation of the Chkalovsk territorial community and the urgent need to return these lands to agricultural production to ensure the country's food security and maintain its export potential necessitates a detailed assessment of the condition of agricultural lands. This requires the development and implementation of a restoration program, including recommendations for the reclamation of disturbed lands using comprehensive soil remediation measures. Therefore, this study aims to assess the impact of warfare on the eco-toxicological condition of chernozems using the Chkalovsk territorial community of the Chuhuiv District of Kharkiv Region as a case study.

MATERIALS AND METHODS

The soil sampling network encompassed agricultural lands within the Chkalovsk territorial community. Sampling points were georeferenced using a GPS-12 satellite positioning device with the WGS 84 datum. The study employed both remote sensing and field methods, utilising modern technical equipment and geographic information systems. Soil sampling schemes are presented in Figure 1. Soil samples from suspected contaminated areas were collected between September and November 2023 following DSTU ISO 10381-1:2004 (2006), DSTU ISO 10381-2:2004 (2006), DSTU ISO 10381-5:2009 (2011), and DSTU ISO 16133:2005 (2007), considering the recommendations of the current international ISO 18400 series standards. Transportation and preparation for physicochemical analyses were conducted according to DSTU ISO 11464-2007 (2009). The selection of soil sampling points within the Chkalovsk territorial community was based on the following principles: demining, accessibility, coverage of the community's territory, and sufficiency of information.

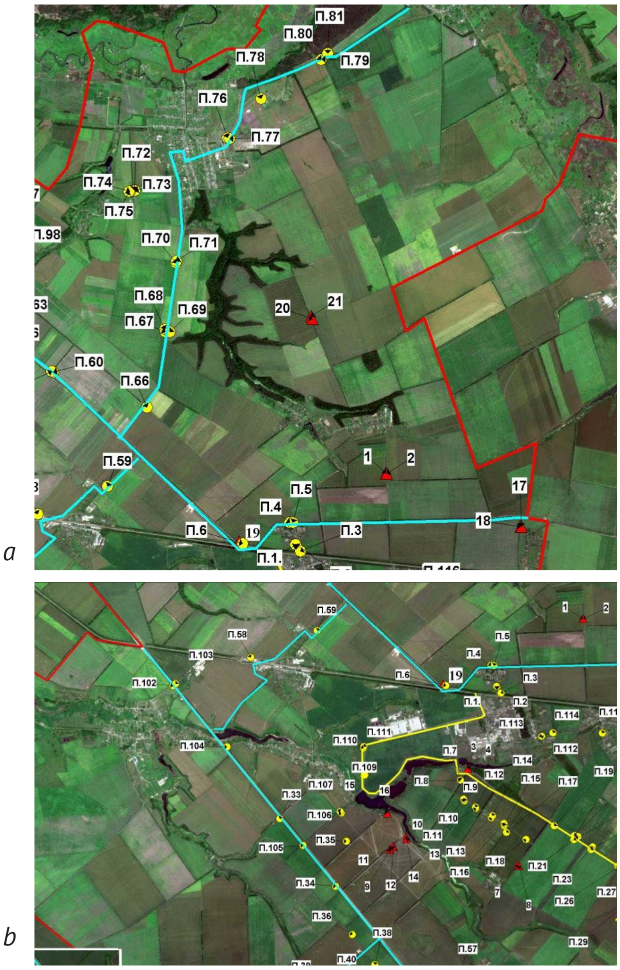

***Figure 1**. Scheme of soil sampling points in the Chkalovsk territorial community*
***Note:** a – northern part of the community, b – southern part of the community*
***Source:** developed by the authors*

While the foundational standards underlying DSTU ISO 10381-5:2009 (2011) and DSTU ISO 19258:2014 (2015) do not provide detailed guidance on the collection of background soil samples, they permit the use of other national standards for this purpose. In Ukraine, DSTU 7243:2011 (2012) serves as a reference. Moreover, the nationally approved DSTU 17.4.3.01:2019 (2019) and DSTU 17.4.4.02:2019 (2019) offer quite specific recommendations in this regard. However, despite their highly detailed requirements and ease of practical application, these standards are adaptations of older Soviet-era GOST standards, primarily focused on cases of industrial and accidental soil contamination.

An integrated approach combining systematic, structural-genetic, and comparativegeographic methods, as well as synthesis, infometry, critical analysis, and generalisation was employed to investigate the landscape and geochemical characteristics of contaminant distribution in the studied soils and their bioavailability to plants. To assess the level of soil contamination by heavy metals, benz[*a*]pyrene, and petroleum products, their MPCs were considered by Resolution of the Cabinet of Ministers of Ukraine No. 1325 (2021), and the requirements of DSTU 7243:2011 (2012). The presence of explosive residues and their toxic metabolites was evaluated as an indication of contamination with new hazardous substances (naturally absent in soils), according to the Order of the Ministry of Environmental Protection and Nuclear Safety of Ukraine No. 171 (1997).

According to DSTU 7243:2011 (2012), if the soil contains a contaminant at a level exceeding the MPC and three times the background level, the land is classified as technologically contaminated. In cases of soil contamination with multiple hazardous substances, the land is considered technologically contaminated if the total pollution index (Zc) exceeds 16.

The total pollution index is calculated using the formula:

$$Zc = \sum_{1}^{n} Cc - (n - 1), \qquad (1)$$

where $Cc = \frac{Ca}{Cb}$ (C_a is the actual content of the *i*-th element; C_b is the background content of the *i*-th element)

All parts of land plots where at least a moderately hazardous or hazardous level of technological contamination is determined must be conserved for a period determined by the persistence class of the substance, ranging from 3 to 10 years. If a smaller number of pollutants are detected but exceed the translocation hazard index, the land is considered to have limited suitability for agricultural use and requires a set of preventive measures to prevent product contamination. In such cases, if the area with a high content of toxicants is less than 50% of the land plot, only that specific part may be classified as technologically contaminated (DSTU 7243:2011, 2012).

Radial soil sampling for the determination of total petroleum hydrocarbons, PAHs (polycyclic aromatic hydrocarbons), and residual amounts of explosives was conducted in areas affected by battles involving burning machinery and fuel spills. Samples were collected following a modified scheme with distances of 1 m, 3 m, 5 m, 7 m, and 10 m from the local source of contamination. Laboratory analysis of the collected samples was performed using gas chromatography/mass spectrometry (GC/MS). The instrument used was a Hewlett Packard HP6890/5972A gas chromatograph equipped with a mass-selective detector. Component separation was carried out on an Rxi-5MS capillary column (5% diphenyl) with dimensions of 30 m×0.25 mm×0.25 µm. The chemical composition of the compounds was identified by comparing the obtained mass spectra with reference spectra from the Wiley 138 and NIST 02 electronic libraries.

During the investigation of organic pollutants in the community's soils, the content of 16 polycyclic aromatic hydrocarbons (PAHs) was determined. These included naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[*ghi*]perylene, benzo[*a*]pyrene, benzo[*a]* anthracene, dibenzo[*a,h*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno(1,2,3-*cd*)pyrene. Additionally, residues of explosives were analysed, encompassing four nitrotoluenes: 1,3-dinitrotoluene (DNT) benzene, 2methyl-1,3-dinitro-, 1,3-dinitrotoluene (DNT) benzene, 2-methyl-1,3-dinitro, 1,3,5trinitrotoluene (TNT), also known as trotyl. Furthermore, hexogen (1,3,5trinitro1,3,5*triazacyclohexane*, also known as cyclonite or RDX) and octogen (homocyclonite or HMX) were assessed.

RESULTS AND DISCUSSION

Military degradation of chernozems can manifest in various ways and degrees. Assessing the extent of military degradation was based on clearly defined parameters to avoid subjectivity. To unify approaches to determining degradation types and objectively assessing the degree caused by hostilities, scientists from the National Scientific Centre "Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky" have developed an improved system for classifying and assessing the degree of military degradation. A fragment of this system, which relates to the chemical degradation of soils, is presented in Table 1.

Table 1*. Fragment of an improved system for classifying and assessing the degree of military degradation of soils based on indicators of chemical contamination with organic and inorganic compounds*

Type of degradation	**Subtype**	**Form**	**Assessment indicator**	**Degree of degradation**				
				Absent	**Mild**	**Moderate**	**Severe**	**Catastrophic**
Chemical	Military	Pollution by toxic inorganic substances	Total Hg content*, mg/kg	⩽ 1.0	1.1-2.1	2.2-4.1	4.2-6.2	⩾ 6.3
			Mobile Zn content*, mg/kg	⩽ 11.0	11.1-23.0	23.1-46.0	46.1-69.0	⩾ 69.1
			Mobile Mn content*, mg/kg	⩽ 50.0	50.1-100.0	100.1-200.0	200.1-300.0	⩾ 300.1
			Mobile Cu content*, mg/kg	⩽ 1.5	1.6-3.0	3.1-6.0	6.1-9.0	⩾ 9.1
			Mobile Co content*, mg/kg	⩽ 2.5	2.6-5.0	5.1-10.0	10.1-15.0	⩾ 15.1
			Mobile Pb content*, mg/kg	⩽ 3.0	3.1-6.0	6.1-12.0	12.1-18.0	⩾ 18.1
			Total Cd content, mg/kg	⩽ 3.0	3.1-5.0	5.1-7.0	7.1-10.0	⩾ 10.1
			Mobile Cd content, mg/kg	⩽ 0.35	0.36-0.7	0.7-1.4	1.5-2.0	⩾ 2.1
			Mobile Cr content, mg/kg	⩽ 3.0	3.1-6.0	6.1-12.0	12.1-18.0	⩾ 18.1
			Mobile Ni content, mg/kg	⩽ 2.0	2.1-4.0	4.1-8.0	8.0-12.0	⩾ 12.1

Table 1. Continued

Type of degradation	Subtype	Form	Assessment indicator	Degree of degradation				
				Absent	Mild	Moderate	Severe	Catastrophic
Chemical	Military	Pollution by toxic inorganic substances	Mobile W content, mg/kg	⩽ 5.0	5.1-10.0	10.1-20.0	20.1-30.0	⩾ 30.1
			Mobile F content, mg/kg	⩽ 1.4	1.5-2.8	2.9-5.4	5.5-8.4	⩾ 8.5
			Total As content, mg/kg	⩽ 1.0	1.0-2.0	2.1-4.0	4.1-6.0	⩾ 6.1
			Total Sb content, mg/kg	⩽ 2.2	2.3-4.5	4.6-9.0	9.1-13.5	⩾ 13.6
		Pollution by toxic organic substances	Benzo[*a*]pyrene content, mg/kg	⩽ 0.01	0.011-0.020	0.021-0.040	0.040-0.060	⩾ 0.061
			Benzene content, mg/kg	⩽ 0.15	0.16-0.30	0.31-0.60	0.61-0.90	⩾ 0.91
			Phenol content, mg/kg	⩽ 2.0	2.1-4.0	4.1-8.0	8.0-12.0	⩾ 12.1
			Formaldehyde content, mg/kg	⩽ 3.5	3.6-7.0	7.1-14.0	14.1-21.0	⩾ 21.0
			Toluene content, mg/kg	⩽ 0.15	0.16-0.30	0.31-0.60	0.61-0.90	⩾ 0.90
			Oil and petroleum product content*, mg/kg	⩽ 2000.0	2000.1-4000.0	4000.1-8000.0	8000.1-12 000.0	⩾ 12 000.1

Note: ** – regulatory references from DSTU 7872:2015 (2016)*
Source: *developed by the authors*

The systematic analysis of experimental data on heavy metal content in the soils of the community involved comparisons with the MPCs established by the Resolution of the Cabinet of Ministers of Ukraine, No. 1325 (2021). Additionally, the degree of soil contamination was assessed according to DSTU 7243:2011 (2012). This standard requires background levels of potential contaminants to be determined from samples collected at least 20 km from the pollution source or outside the visually defined area of local technogenic contamination. However, this standard was developed during the pre-war period, and the collection of background samples in de-occupied and/or conflict-affected areas remains subject to unresolved issues requiring further scientific investigation. These include challenges in systematising and classifying areas and determining the radius of potential contamination from explosions of munitions of various calibres. Under these circumstances, the most appropriate approach appears to involve using pre-war data on soil analysis as baseline or initial reference information. This ensures the use of reliable benchmarks while addressing current limitations in background sampling in post-conflict regions. For this purpose, during the study of community lands, the available data from the Soil Conservation Department on the survey of chernozem soils within the Grakivske experimental field for the content of heavy metals and microelements were summarised. The results of pre-war field studies, which included control plots as well as variants with the application of standard doses of macro-mineral and organic fertilisers for growing legumes and cereals (soybeans, wheat, barley), were processed. In total, the quantitative characteristics of 36 background soil samples were processed to determine average values for further research. The main statistical characteristics of the studied indicators are presented in Table 2. The results of the analytical testing of soil samples collected within the Chkalovsk territorial community in 2023 indicate that one year after the de-occupation of this area, the concentrations of heavy metals and trace elements do not exceed the maximum allowable limits and show no significant deviations from background levels. Moreover, the concentrations of mobile forms of toxicants such as Cd, Cr, and Ni, as well as essential elements like Mn and Cu, remain within the "minimum-maximum" range of pre-war background data from uncontaminated areas, accounting for analytical error (Table 2).

Table 2*. Statistical characteristics of heavy metal content in soils at the studied and background sites of the Chkalovsk territorial community*

Indicator	Mean	+95% Confidence interval	-95% Confidence interval	Standard deviation	Minimum	Maximum	Median	Standard error	MPC
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Cd content (demining)	0.04867	0.02885	0.06848	0.04692	0.00500	0.18900	0.04050	0.009578	0.7
Cd content (postdemining)	0.02171	0.01465	0.02878	0.02238	0.00080	0.08900	0.01270	0.003495	0.7
Cd content (background)	0.07867	0.05803	0.09930	0.05526	0.00000	0.19000	0.06000	0.010088	0.7
Cr content (demining)	0.09863	0.02522	0.17203	0.17383	0.00500	0.76200	0.02500	0.035483	6.0
Cr content (postdemining)	0.20491	0.14570	0.26413	0.18760	0.00280	0.65120	0.14210	0.029298	6.0

Table 2. Continued

Indicator	Mean	+95% Confidence interval	-95% Confidence interval	Standard deviation	Minimum	Maximum	Median	Standard error	MPC
1	2	3	4	5	6	7	8	9	10
Cr content (background)	0.95133	0.70845	1.19421	0.65045	0.01000	2.35000	0.73000	0.118755	6.0
Ni content (demining)	0.51563	0.41636	0.61489	0.23508	0.14100	1.03700	0.46550	0.047986	4.0
Ni content (postdemining)	0.24932	0.18816	0.31048	0.19375	0.04810	0.79300	0.20520	0.030259	4.0
Ni content (background)	0.41033	0.31133	0.50933	0.26513	0.03000	1.00000	0.34500	0.048406	4.0
Pb content (demining)	1.54571	1.18340	1.90802	0.85802	0.06600	3.25000	1.61400	0.175143	6.0
Pb content (postdemining)	1.26701	1.02149	1.51253	0.77785	0.02880	2.85500	1.29200	0.121479	6.0
Pb content (background)	0.95133	0.70845	1.19421	0.65045	0.01000	2.35000	0.73000	0.118755	6.0
Co content (demining)	0.34321	0.25940	0.42702	0.19848	0.02400	0.78600	0.34550	0.040515	5.0
Co content (postdemining)	0.25129	0.18894	0.31363	0.19751	0.00300	1.02040	0.21450	0.030845	5.0
Co content (background)	0.27556	0.21799	0.33312	0.17013	0.01000	0.61000	0.25500	0.028356	5.0
Cu content (demining)	0.23333	0.16777	0.29890	0.15527	0.00200	0.61300	0.22300	0.031695	3.0
Cu content (postdemining)	0.22638	0.18296	0.26979	0.13756	0.01330	0.62200	0.20270	0.021483	3.0
Cu content (background)	0.23389	0.17844	0.28934	0.16389	0.01000	0.60000	0.23500	0.027314	3.0
Zn content (demining)	0.33825	0.19632	0.48018	0.33612	0.00400	1.58600	0.23550	0.068610	23.0
Zn content (postdemining)	0.49702	0.37159	0.62245	0.39739	0.00100	1.81250	0.47530	0.062062	23.0
Zn content (background)	0.13278	0.08616	0.17940	0.13779	0.01000	0.60000	0.08500	0.022965	23.0
Fe content (demining)	2.46000	2.14503	2.77497	0.74590	1.00800	4.58700	2.40650	0.152257	-
Fe content (postdemining)	1.82786	1.55574	2.09998	0.86212	0.83930	4.64900	1.55080	0.134641	-
Fe content (background)	0.84083	0.58559	1.09608	0.75437	0.12000	2.84000	0.55000	0.125729	-
Mn content (demining)	5.69392	4.64625	6.74159	2.48108	2.32000	12.53000	5.73800	0.506449	140.0
Mn content (postdemining)	5.56266	4.48113	6.64419	3.42647	1.19020	17.52200	4.31010	0.535124	140.0
Mn content (background)	30.56133	24.54379	36.57888	16.11529	10.51000	80.10000	26.92000	2.942235	140.0

Source: *developed by the authors*

During the research, concentration factors of elements in soil samples were determined as the ratio of actual to average background values (Table 3). Due to the absence of a threefold exceedance of background values for several heavy metals simultaneously, the overall soil pollution index Zc was not determined. For example, the concentration factors for Cd were only 0.01-2.36, Co – 0.01-3.6, Cr – 0.01-2.8; Cu – 0.01-2.7; Fe – 1.0-5.5; Mn – 0.05-0.67; Ni – 0.1-2.5; Pb – 0.033.4. Only for plant-available forms of Zn did they reach 12.0-13.9 in some cases, which is largely due to very low background concentrations of this element in the pre-war period. The low provision of soils with mobile zinc, which is often found on agricultural lands in the Kharkiv Region, is often a consequence of the presence of carbonates and increased concentrations of PO^{3-}_4 due to the application of phosphorus fertilisers.

***Table 3**. Concentration coefficients of heavy metals in the soils of the Chkalovsk territorial community, 2023*

Crop	**Concentration coefficients of heavy metals (AAB with pH 4.8)**								
	Cd	***Co***	***Cr***	***Cu***	***Fe***	***Mn***	***Ni***	***Pb***	***Zn***
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
weeds (demining)	0.61	1.84	2.8	1.2	1.9	0.1	0.8	1.2	1.3
weeds (demining)	0.06	1.02	0.1	0.3	3.2	0.2	1.1	1.0	0.4
arable land (demining)	0.06	0.3	0	1.4	3.5	0.4	0.3	1.7	2.4
barley (demining)	0.06	1.83	0.1	0.9	2.9	0.1	2.5	1.3	4.6
sunflower (demining)	0.13	2.81	0.3	0.5	2.6	0.2	0.8	0.1	3.4
weeds (demining)	0.06	1.19	0.1	1.6	3.0	0.1	0.7	2.2	3.9
sunflower (demining)	1.51	1.73	0.6	1.0	3.8	0.1	1.5	0.6	1.0
weeds (demining)	0.5	1.29	0	0.7	2.5	0.1	0.6	2.5	1.5
sunflower (demining)	0.06	1.3	0	0	4.0	0.1	2.4	2.3	2.4
arable land (demining)	0.51	2.17	0.1	2.1	2.7	0.5	1.2	1.9	1.2
arable land (demining)	0.9	1.28	0	0.4	4.0	0.4	1.4	1.9	5.0
arable land (demining)	0.19	2.08	0	1.0	3.6	0.3	1.1	2.3	1.7
arable land (demining)	1.35	0.98	0.1	0.7	2.2	0.2	1.1	2.2	3.7
sunflower (demining)	0.51	0.84	0.1	0.2	3.1	0.2	0.8	0.6	1.2
arable land (demining)	0.31	0.86	0.5	0.2	2.9	0.2	0.9	1.7	0.9
arable land (demining)	0.23	0.21	0.1	1.0	2.6	0.2	1.5	3.4	2.8
arable land (demining)	2.36	1.83	0.1	0.4	2.2	0.2	1.0	0.5	0.3
arable land (demining)	0.79	1.46	0.1	1.4	3.3	0.3	1.4	1.4	0
arable land (demining)	0.75	0.2	0.6	0.7	2.2	0.2	0.9	2.5	2.4
arable land (demining)	0.06	0.09	0.2	1.2	3	0.3	0.9	0.9	1.9
arable land (demining)	0.81	1.06	1.0	1.5	1.2	0.3	1.6	3.4	1.1
arable land (demining)	0.33	0.32	1.6	2.1	2.8	0.2	2.4	1.5	6.2
sunflower (demining)	1.21	1.88	0.1	2.7	5.5	0.3	1.6	1.9	12
arable land (demining)	1.23	0.87	0.2	1.3	1.7	0.2	1.6	0.2	0.8
sunflower (demining)	0.8	0.32	0	1.1	2.0	0.1	0.9	2.0	0
sunflower (demining)	0.11	0.01	0.1	0.7	1.5	0.2	0.9	2.0	1.1
sunflower (demining)	1.05	0.27	0	2.1	3.3	0.2	1.3	2.4	2.5
sunflower (demining)	0.58	1.83	0.8	1.1	5.5	0.7	1.7	1.4	9.8
sunflower (demining)	0.24	0.63	1.3	1.4	2.1	0.3	1.9	1.4	0.5
winter cereal (demining)	0.26	1.09	1.6	0.6	3.7	0.3	0.4	0.5	0.7
arable land (demining)	0.01	1.62	1.1	0.5	1.8	0.4	0.5	0.6	5.9
maize	1.11	1.82	0.8	2.7	3.3	0.2	0.7	3.0	2.6
maize	0.06	1.11	0.6	2.3	2.5	0.1	0.5	1.4	2.9
maize	0.76	0.45	0.5	1.1	2.7	0.2	1.7	2.6	1.3
maize	0.24	0.23	0.3	0.5	2.0	0.2	0.5	0.1	4.1
arable land after sunflower	0.37	0.78	1.5	0.4	1.7	0.3	0.5	2.7	5.7
winter cereal	0.05	1.26	0.1	0.8	1.9	0.2	0.8	0.3	0.6

Table 3. Continued

Crop	**Concentration coefficients of heavy metals (AAB with pH 4.8)**								
	Cd	***Co***	***Cr***	***Cu***	***Fe***	***Mn***	***Ni***	***Pb***	***Zn***
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
sunflower	0.3	0.77	0	1.0	3.3	0.2	0.5	1.6	2.3
maize	0.06	0.15	0.4	0.4	1.7	0.1	0.3	1.8	3.9
sunflower	0.39	1.33	0.4	0.9	1.7	0.1	0.1	0.3	6.2
arable land	0.59	0.1	0.4	0.1	2.0	0.3	0.1	2.7	5.0
arable land	0.06	1.46	0.7	0.4	1.6	0.2	0.1	0.6	4.7
arable land after sunflower	0.06	1.18	1.7	0.5	1.6	0.5	0.3	0.7	3.7
arable land after sunflower	0.35	1.25	0.5	1.4	1.8	0.3	0.5	1.5	0.4
sunflower	0.06	0.41	0.2	0.5	2.1	0.2	0.2	2.3	1.0
arable land	0.45	1.46	0.7	0.7	1.6	0.3	0.1	2.8	4.2
winter arable land	0.22	0.15	0.5	1.0	1.4	0.1	0.5	0.2	14.0
sunflower	0.06	1.55	0.2	0.4	1.4	0.2	0.3	1.1	12.0
sunflower	0.06	1.46	0.2	1.3	1.5	0.2	0.5	1.8	2.0
winter arable land	0.06	0.5	2.1	1.7	1.1	0.2	0.2	0.5	3.6
maize	0.06	0.71	0.4	1.2	1.9	0	0.9	1.3	3.9
sunflower	0.16	0.49	0	0.9	1.8	0.1	0.7	1.7	1.5
winter arable land	0.48	1.04	2.0	0.9	3.0	0.2	0.1	1.1	8.4
sunflower	0.45	0.06	1.8	1.3	3.2	0.1	0.5	1.0	4.1
sunflower	0.06	0.15	0	0.2	3.1	0.2	0.9	1.2	4.4
maize	0.06	0.76	0.1	1.4	1.7	0.1	0.1	1.5	3.1
maize	0.06	0.96	0.7	1.7	5.5	0.1	0.7	2	2.7
arable land	0.01	0.33	0	1.6	2	0.6	0.2	1.1	4.1
sunflower	0.13	0.67	1.5	0.1	1.6	0.2	0.6	1.4	0.5
sunflower	0.06	1.59	0.4	0.8	1.5	0.1	1.6	0.6	1.5
sunflower	0.25	3.64	2.2	0.1	1.6	0.1	1.1	1.3	7.0
sunflower stubble	0.06	1.47	2.4	1.3	1.2	0.3	0.7	1.4	0.5
sunflower	0.33	1.27	0.8	0.8	2.3	0.1	0.4	0	4.1
sunflower	0.06	0.33	1.4	1.6	1.0	0.1	0.3	0	5.5
arable land	0.51	0.15	0.6	0.7	1.0	0.1	0.1	0.6	5.4
Average (demining)	*0.62*	*1.25*	*0.1*	*1*	*2.9*	*0.2*	*1.3*	*1.6*	*2.5*
Average (post-demining)	*0.28*	*0.91*	*0.2*	*1*	*2.2*	*0.2*	*0.6*	*1.3*	*3.7*

Source: *developed by the authors*

A clearer understanding of the changes in the ecological and toxicological state of soils in such areas can be obtained through statistical processing of point information without prior averaging (Table 2, Fig. 2). Under these conditions, the difference between the content of mobile forms of pollutants in soils before the war and after de-occupation is significantly smaller. In particular, in recently demined areas of this de-occupied territory, there is a tendency towards a slight increase in the content of lead (by 1.4 times), cobalt (1.3 times), iron (1.6 times) and zinc (2.6 times) relative to the pre-war (background) content. Such excesses are not considered critical for agriculture and do not require land conservation or the application of overly complex and costly soil remediation measures.

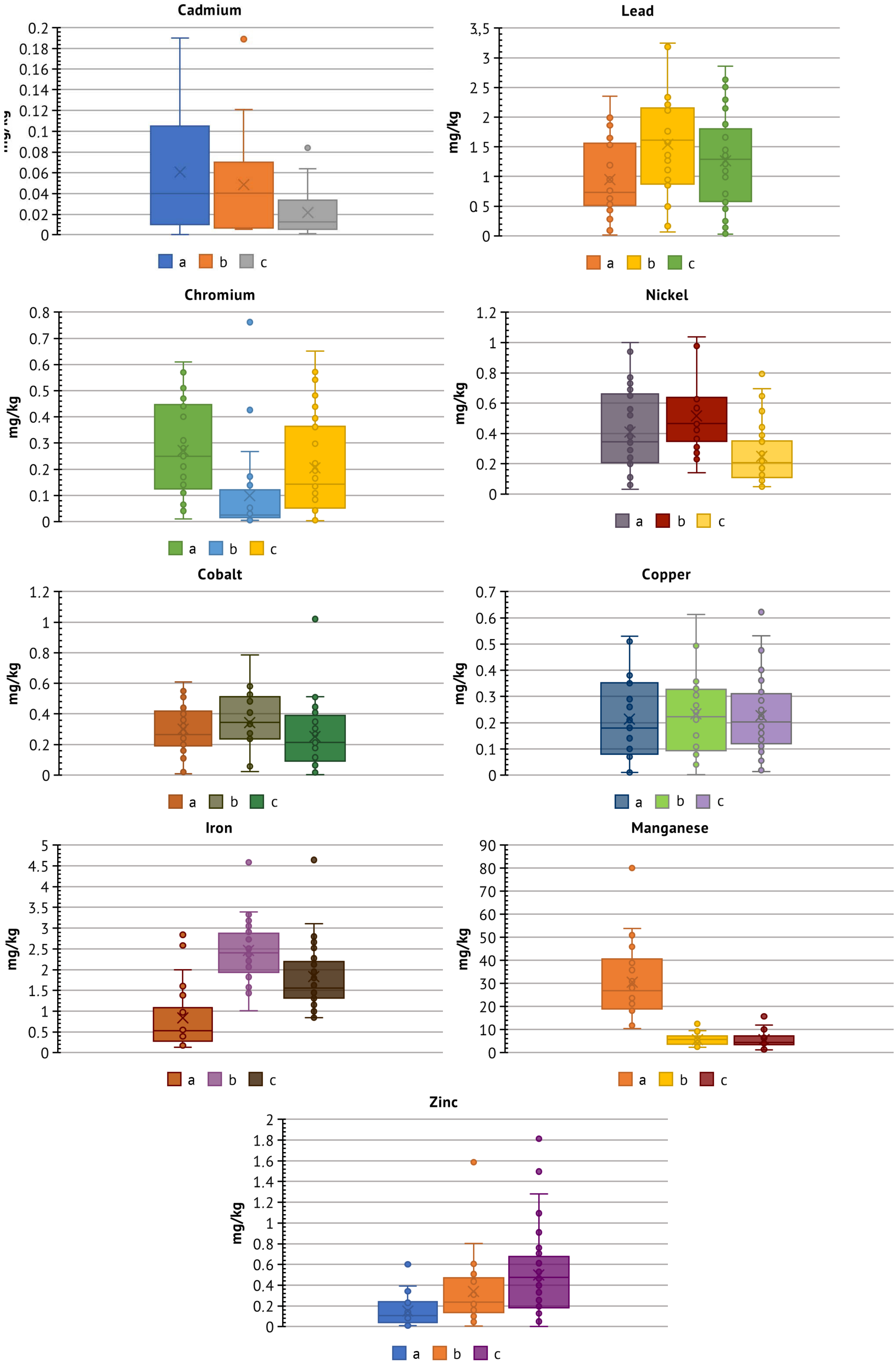

***Figure 2**. Dynamics of mobile forms of heavy metals and microelements in soils of the Chkalovsk territorial community*
***Note:** a) recent demining; b) a few months after demining (in agricultural production); c) background content (prewar data)*
***Source:** developed by the authors*

Both the statistical characteristics (Table 2) and graphical representations (Fig. 2) reveal a certain difference in the content of heavy metals and microelements between soils that were demined beforehand and are already used in agricultural production, and those where demining occurred recently. Over time, after demining, a slight decrease in the content of mobile cadmium, lead, nickel, cobalt, and iron can be observed, accompanied by an increase in the amount of plantavailable chromium and zinc. The concentrations of bioavailable forms of manganese and copper have remained almost unchanged during this time. The observed changes may also indicate ongoing processes of self-restoration of chernozem soils, which are typically characterised by high buffering capacity concerning heavy metals. It should be noted separately that the content of petroleum products in the collected soil samples a few months after the hostilities was quite low and ranged from 2.6 to 23.2 mg/kg of soil, which is significantly less than the maximum permissible concentration for agricultural land – 500 mg/kg of soil (Table 4).

***Table 4**. Content of petroleum products in soils at the site of fuel spill and tanker fire*

No.	Sampling location	Petroleum product content, mg/kg
1	Tanker, soil layer 0-30 cm	20.6
2	Tanker, soil layer 30-60 cm	20.8
3	Tanker, 1 m (azimuth 1), layer 0-30 cm	16.8
4	Tanker, 1 m (azimuth 1), layer 30-60 cm	13.2
5	Tanker, 1 m (azimuth 2), layer 0-30 cm	22.8
6	Tanker, 1 m (azimuth 2), layer 30-60 cm	2.6
7	Tanker, 3 m (azimuth 1), layer 0-30 cm	15.2
8	Tanker, 3 m (azimuth 1), layer 30-60 cm	12.0
9	Tanker, 3 m (azimuth 2), layer 0-30 cm	18.4
10	Tanker, 3 m (azimuth 2), layer 30-60 cm	23.2
11	Tanker, 5 m (azimuth 1), layer 0-30 cm	12.0
12	Tanker, 5 m (azimuth 1), layer 30-60 cm	15.4
13	Tanker, 5 m (azimuth 2), layer 0-30 cm	14.0
14	Tanker, 5 m (azimuth 2), layer 30-60 cm	12.3
15	Tanker, 7 m (azimuth 1), layer 0-30 cm	21.8
16	Tanker, 7 m (azimuth 1), layer 30-60 cm	16.2
17	Tanker, 7 m (azimuth 2), layer 0-30 cm	13.2

***Source:** developed by the authors*

The results obtained indicate very low concentrations of all polycyclic aromatic hydrocarbons, explosives, and related nitroaromatic compounds in the analysed soils (Table 4). The content of these substances in all analysed soil samples was below the method's detection limit (<0.002 for polycyclic aromatic hydrocarbons and <0.005 for explosives and their metabolites), indicating their practical absence. Considering the obtained data from 2023 in the context of providing soils of the Chkalovsk territorial community with physiologically necessary microelements, it can be noted that the soils are very low in zinc (even for low-demanding crops) and have insufficient levels of available copper and manganese for high-demanding crops. The low content of microelements indicates the need for the application of micronutrients, which not only significantly increases crop yields but also becomes an important factor in improving their micronutrient composition.

Returning to the issue of soil contamination risks in the community, it should be noted that the ranges of heavy metal content variations in soils, as well as in geological formations, are typically quite broad due to their natural variability. Narrowing the range of variability of background values to a minimum during their combination/averaging leads to obtaining significantly higher concentration factors for heavy metals than when operating with a full sample of initial background data. In general, to classify land as technogenically contaminated, the content of a substance polluting the soil must exceed the MPC and be three times higher than the background content. Since none of the soil samples analysed in 2023 contained heavy metals in the specified concentrations, it can be stated that, according to DSTU 7243:2011 (2012), the surveyed soils in the community cannot be considered technogenically contaminated. However, full conclusions about the ecological state of soils in terms of heavy metal content in the community require additional information on the content of heavy metals in soils of other land plots and test plants from various agricultural crops.

The likely reasons for such low concentrations of hydrocarbons could include the burning of petroleum products during the tanker fire, the reduction of light hydrocarbon fractions due to their high volatility (which increases with temperature), and possible leaching down the soil profile during rainfall events.

The intensity of contamination by these substances is significantly influenced by the detonation level of munitions, i.e., the amount of explosive that burns during the explosion and the amount that remains in the soil.

Furthermore, as previously noted by S. Baliuk *et al.* (2024), complex chemical compounds, such as explosives, can undergo partial decomposition on the soil surface through processes like photolysis and hydrolysis, be adsorbed by the soil, or leach into groundwater and surface water sources along with atmospheric precipitation. The rate and extent of migration and transformation of explosives are influenced by the physicochemical properties of these compounds (e.g., solubility, vapour pressure, Henry's law constant), environmental factors (weather conditions), soil characteristics (including pH, redox status), and biological factors (populations of microorganisms that degrade explosives). The processes affecting the fate of explosives in the environment can be divided into two groups: a) influence on migration and sorption (dissolution, evaporation, adsorption); b) influence on transformation (photolysis, hydrolysis, reduction, and biodegradation).

The most well-known and widely used explosives found in military munitions that remain in soils after incomplete detonation of projectiles are trinitrotoluene (TNT), hexogen (RDX), and octogen (HMX), as well as their transformation products (1,3-DNT, 2,4-DNT, 2,6-DNT, 4-DNT, MNX, DNX, TNX), which are toxic to humans and other organisms. Additionally, according to J. Pichtel (2012) and B. Heerspink *et al.* (2017), soils in combat zones are contaminated with residues of primary (initiating) explosives and propellants containing low-explosive materials that propel rockets or accelerate projectiles from guns, as well as a wide range of associated organic and mineral pollutants from munitions and equipment, with heavy metals, polycyclic aromatic hydrocarbons, and other petroleum products being the primary ones. Notably, the adsorption processes of TNT, RDX, HMX, 2,4-DNT, DNAN, and their metabolites are significantly dependent on hydro-thermal conditions (precipitation and temperature), granulometric composition (especially the content of clay minerals), the quantity and fractional composition of humus, the content of exchangeable cations (especially K^+ and NH^{4+}), and the number of functional groups in nitroaromatic compounds (Brannon & Pennington, 2002; Qin *et al.*, 2021).

According to S. Baliuk *et al.* (2022), a survey of soils conducted in spring 2022 in areas of active hostilities in the Kharkiv Region revealed elevated levels of heavy metals such as nickel (1.34.0 clarks), copper (1.4-12.8 clarks), chromium (1.2-3.4 clarks), cadmium (2-18 clarks), and lead (2.6-22 clarks) compared to background levels. A significant portion of the aforementioned toxicants, including elements like cadmium, lead, nickel, and chromium, as well as organic pollutants such as formaldehyde, nitrotoluenes, and polycyclic aromatic hydrocarbons, are classified as dangerous carcinogens for humans and animals, causing irreversible changes or damage to the parts of the genetic apparatus that control somatic cells. As land is the primary means of agricultural production, some of these substances can accumulate in commercial plant products, posing a health risk to consumers.

A particular problem is the high mobility of certain chemical elements and organic compounds (especially hexogen) and their transformation products in soils, which, according to A. Lorenz *et al.* (2013), lead to further contamination of groundwater and pose a threat to the drinking water supply for the population. Based on the results of environmental monitoring studies in the Kharkiv District of the Kharkiv Region in autumn 2022 and their comparison with data from 20182021, specialists from the National Scientific Centre "Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky" noted unusually high concentrations (above the MPC) of cadmium, chromium, and lead in groundwater and surface water in the surveyed area due to their migration from the soil environment under the influence of prolonged precipitation.

In a study by O. Datsko *et al.* (2024) analysing the impact of aerial bombings on agricultural land in Sumy and Chernihiv regions, it was found that these soils were not always contaminated with heavy metals such as barium, zirconium, rubidium, zinc, and vanadium. The content of barium, zirconium, and manganese on crater slopes did not show a clear increase compared to control areas. Strontium, rubidium, and zinc did not always demonstrate excess in craters. According to M. Solokha *et al.* (2023), an increase in the content of heavy metals (manganese, iron, cobalt, copper, cadmium, chromium, lead, and nickel) was found in soils subjected to bombing compared to areas that were not bombed. Subsequently, M. Solokha *et al.* (2024) established that fragments of destroyed military equipment, ammunition, and fuel residues lead to soil contamination, with the highest levels of contamination recorded for Pb, Zn, and Cd; the contamination distribution was as follows: Pb > Zn > Cd > Cu. According to K. Petrushka *et al.* (2024), as a result of rocket attacks, all soil samples in the Lviv Region showed a significant excess of the MPC of titanium, zinc, lead, and nickel. A cumulative assessment of the impact of all elements on the environment showed significant contamination of the study area.

However, the conclusions of the current study do not entirely align with the following research. I. Bulba *et al.* (2024) found that in Dnipropetrovsk Region, as a result of hostilities, soil contamination with lead exceeded the MPC by 3 times, and with fluorine by 1.5 times; in Mykolaiv Region, the lead content in the soil exceeded the MPC by 5 times, the content of zinc, copper, fluorine, and petroleum products by 25%; in Zaporizhzhia Region, the lead content exceeded the MPC by 11.2 times, the content of zinc, fluorine increased by 50%, petroleum products by 35%, and phosphates by

30%. According to O. Shebanina *et al.* (2023), the illegal disposal of chemical waste and active hostilities led to significant contamination of soils with heavy metals and petroleum products: in Kharkiv Region, cadmium contamination increased by 200%; in Kherson and Zaporizhzhia regions, an increase in oil spills of 139% and 156% was recorded. Differences in the results regarding soil contamination with heavy metals are likely related to different types of military impacts (bombing, rocket attacks, fragments of destroyed equipment, etc.), different soils, and other spatiotemporal factors. For example, in the study of G. Trokhymenko *et al.* (2023), it was established that loams and chernozems are more prone to the accumulation of heavy metals than sandy soils. In loam, the rate of metal release decreases from 16.7% to 69.7% compared to sandy soil; in comparison of chernozem to loam, this rate slows down from 17.85% to 32.08%. At the same time, the rate of spread of barium, cobalt, arsenic, lead, mercury, manganese, strontium, and titanium does not depend on the type and mechanical parameters of the soil.

The observed changes may also indicate the occurrence of self-recovery processes in chernozem soils, which are typically characterised by high buffering capacity, especially concerning heavy metals. The obtained results also confirm that a significant portion of chernozem soils in former combat zones may undergo restoration without the application of costly remediation measures, which has a significant positive impact on the development of agriculture in such regions and the preservation of the country's export potential.

CONCLUSIONS

This study assessed the ecological and toxicological state of militarily degraded chernozems using the Chkalovsk territorial community in the Chuhuiv District of Kharkiv Region as an example. An improved system for classifying and assessing the degree of military degradation of soils has been proposed, focusing on indicators of chemical contamination by organic and inorganic compounds. This system is recommended for comprehensive assessments of the ecological and toxicological state of soil cover.

The results of the study indicate that the military degradation of soils in the Chkalovsk territorial community is more associated with physical damage, such as bomb craters than with chemical contamination of soils. It was found that in recently demined areas of the de-occupied territory, there is a tendency for a slight increase in the content of lead (by 1.4 times), cobalt (1.3 times), iron (1.6 times), and zinc (2.6 times) relative to the pre-war (background) content. However, such excesses are not critical for agriculture, therefore, the examined chernozems in the community cannot be considered technogenically (chemically) contaminated, neither according to the comparison with the maximum permissible concentrations (MPC) established by the current Resolution of the Cabinet of Ministers of Ukraine, No. 1325 dated 15 December 2021, nor according to the requirements of DSTU 7243:2011, nor according to the gradations of the improved system for classifying and assessing the degree of military degradation of soils.

Some time after demining, a slight decrease in the content of mobile cadmium, lead, nickel, cobalt, and iron was recorded on average, with an increase in the amount of chromium and zinc available to plants. The concentrations of bioavailable forms of manganese and copper remained almost unchanged during this period. The observed changes may also indicate the occurrence of self-recovery processes in chernozem soils, which are typically characterised by high buffering capacity concerning heavy metals without the application of expensive remediation measures. The obtained data allow for a positive assessment of the future potential of agricultural production on chernozem soils in combat zones. For a comprehensive assessment of the ecological state of soils in terms of heavy metal content in the community, additional information is needed on the content of heavy metals in soils of other land plots and test plants from various crops. This could be one of the promising directions of research.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Еколого-токсикологічний стан мілітарно деградованих чорноземів: кейс Чкаловської територіальної громади

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Анотація. Метою цього дослідження було оцінювання еколого-токсикологічного стану мілітарно деградованих чорноземів на прикладі Чкаловської територіальної громади Чугуївського району Харківської області. Для цього було передбачено провести детальне комплексне обстеження еколого-токсикологічного стану чорноземних ґрунтів Чкаловської територіальної громади, постраждалих унаслідок воєнних дій і визначити придатність обстежених ґрунтів для ведення сільського господарства та, за необхідності, запропонувати заходи з ремедіації забруднених ґрунтів. Запропоновано удосконалену систему класифікації та оцінювання ступеня мілітарної деградації ґрунтів у частині показників хімічного забруднення органічними та неорганічними сполуками. Установлено, що на нещодавно розмінованих ділянках деокупованої території відмічається тенденція незначного збільшення вмісту плюмбуму (у 1,4 рази), кобальту (1,3 рази), заліза (1,6 рази) і цинку (2,6 рази) відносно довоєнного (фонового) вмісту. Однак такі перевищення не є критичними для ведення сільського господарства, і не потребують консервації земель або застосування надскладних і дороговартісних заходів з очищення ґрунтів. Через деякий час після розмінування в середньому зафіксовано незначне зменшення вмісту рухомого кадмію, плюмбуму, нікелю, кобальту і феруму за збільшення кількості доступних рослинам хрому й цинку. Концентрації біодоступних форм мангану та купруму за цей час майже не змінилися. Визначені зміни можуть також свідчити про протікання процесів самовідновлення чорноземних ґрунтів, які зазвичай характеризуються високою буферністю щодо важких металів. Одержані результати свідчать про дуже низькі концентрації усіх поліароматичних вуглеводнів і вибухонебезпечних речовин та споріднених нітроароматичних сполук у досліджених ґрунтах. Результати дослідження можуть бути використані під час розробки програми післявоєнного відновлення ґрунтів і раціонального використання земель в аграрному виробництві

Ключові слова: забруднення ґрунтів; екологічна безпека; російсько-українська війна; важкі метали; нафтопродукти; мілітарна деградація ґрунтів; аграрне виробництво