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Research Article

Estimation of the content of trace metals in Ukrainian military-affected soils

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Abstract

The study assessed the impact of military activities on Ukraine's soil resources, particularly heavy metal contamination. As a primary resource for agricultural production, soil undergoes significant influence from military activities, posing environmental challenges for the rational use of land. Special attention was paid to evaluating the content of chemical elements in combat zones. The research methodology included soil sampling from ten locations in the Sumy, Kharkiv, and Chernihiv regions. Samples were collected from craters, slopes, and control areas located 20 meters away. The analysis was performed using a portable X-ray fluorescence analyzer (pXRF), enabling the determination of 27 chemical elements. The results showed significant variability in the concentrations of heavy metals such as barium, zirconium, manganese, strontium, rubidium, and zinc. In many cases, the concentration of metals in crater samples was lower or comparable to control areas, indicating the influence of local anthropogenic factors, such as the application of mineral fertilizers, but not always military actions. This indicates that while military activities contribute to environmental disruption, non-military factors also play a role in shaping soil composition. Therefore, a comprehensive approach to land restoration should consider both the direct impacts of military actions and broader environmental influences, with strategies tailored to the specific conditions of each affected region.

Keywords: contamination; heavy metals; pXRF; reclamation; soil

Introduction

Soil is the primary resource that underpins all life, from the simplest microorganisms to the most advanced beings on the planet—humans. Humanity's greatest challenge remains the fact that this resource is non-renewable. This means that if agricultural soil is contaminated with toxic substances, it is impossible to exclude the affected area from use for a certain period, depending on the level of contamination. This is driven

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by the ongoing population growth. As of the second decade of December 2024, the global population exceeds 8.1 billion (World Population, 2024). According to forecasts by the UN Population Division, this figure will rise to 10 billion by 2050 (United Nations, 2024). Thus, every parcel of land must be used efficiently to support global food security. However, there are still lands in the world that remain preserved due to past military activities. These areas were formed not only during World Wars I and II, such as in France (Pearson, 2017), but also at former military bases that are no longer used for training (Jentsch *et al.*, 2009). A lot of research has shown that warfare in Croatia has significantly impacted soil quality, with military activities leading to increased concentrations of heavy metals such as zinc, cadmium, chromium, arsenic, and lead. For instance, studies in the Prasnik rainforest and combat sites in Slavonia and Baranja revealed elevated levels of toxic elements compared to control regions and ecological agricultural standards. These findings highlight the long-term environmental consequences of military operations and emphasize the need for ongoing soil monitoring and remediation efforts to restore affected areas (Mesić Kiš *et al.*, 2016; Vidosavljević *et al.*, 2014).

It is important to emphasize that land withdrawal from agricultural use does not occur arbitrarily. The primary factor is contamination with heavy metals, petroleum products, and explosive residues from military actions, which accumulate in soils, primarily threatening plant nutrition. These substances are absorbed by plants, reducing soil fertility (Broomandi *et al.*, 2020). Soil fertility declines due to degradation caused by imbalances in carbon, nutrients, and water, as well as compaction and other factors (Pichtel, 2012; Sakin *et al.*, 2024). As a result, contaminated soils become a significant barrier to the rational use of land resources and the ecological sustainability of agricultural production.

Soils impacted by military actions often cannot meet agricultural production needs due to reduced fertility and deteriorated physicochemical properties. Even if no chemical contamination is detected, the soil may exhibit poor physical properties due to compaction from heavy military equipment. For instance, studies by Barbosa *et al*. (2022) revealed that the intensity of M113 BR military vehicle movements, both in straight lines and turns, affects the physical properties of Abruptic Alisol soil. Soil previously compacted by prolonged military training withstood loads effectively during straight-line movements but showed significant deterioration in the top layer during turns. Consequently, farmers would need to invest significantly in soil treatment to reduce compaction before such land could be returned to agricultural use.

From an ecosystem perspective, soil contamination triggers a chain of negative consequences. Toxic substances can infiltrate groundwater, poison natural reservoirs and cause the death of flora and fauna. This, in turn, disrupts natural food chains and the balance of ecosystems (Dehtiar'ov *et al.*, 2024).

Today, numerous wars are ongoing in countries such as Syria, Ethiopia, Ukraine, and others. Researchers worldwide continue to study the effects of military activities on soils despite the dangers involved. For instance, Rodríguez-Seijo *et al*. (2024) investigated the impact of civilian and military shooting activities, including combat zones, on soil organisms such as microbial communities and terrestrial animals. Results show that the ecotoxicological effects of lead and explosives on earthworms and enchytraeids are well-researched, whereas information on other soil organisms like mites, ants, or gastropods remains insufficient.

Regarding research in Ukraine, results obtained by a team led by Solokha *et al*. (2023) indicate that shelling increases heavy metal content (e.g., Mn, Fe, Co, Cu, Cd, Cr, Pb, Ni) in soils and leads to vegetation degradation in combat zones. Remote sensing analysis confirmed a reduction in vegetation greenness in conflict areas (Luhansk and Donetsk regions) and an increase in southern regions due to the cessation of agricultural activities. Studies conducted in Kharkiv Oblast showed that military actions caused mechanical, chemical, and physical soil degradation, including changes in particle size distribution, significant contamination with heavy metals (Pb, Zn, Cd), and suppression of microbiological processes. Soils exhibited a 2.1-fold decrease in microbial biomass, a 20.5-fold increase in the share of mycelial organisms, and high toxicity (99.8%), negatively impacting mesobiota and vegetation (Solokha *et al.,* 2024).

Dmytruk *et al.* (2023) proposed creating a predictive soil map of Ukraine at a 1:10,000 scale to assess the impact of war on soils and lost ecosystems. This approach would account for features identified during soil recovery.

The aim of this article is to assess the impact of military actions on soil resources, particularly heavy metal contamination.

Materials and Methods

Soil sampling sites

The soil samples were taken at ten craters from the fields in the Sumy, Kharkiv and Chernihiv regions (Table 1).

Table 1. The location of the fields and their soil properties

№	Soil sample	Location	Crater size	Crater depth	Soil type	pH_{KCl}	OM, %	CEC, meq/ 100 g
Sumy region								
1.	1 crater (a); 1 slope (b); 1 intact (c).	50.2420961 35.0070679	Diameter 3.0 m	2.0 m	Deep medium-humus leached Chernozem	6.1	5.2	29.1
2.	1 crater (a); 1 slope (b); 1 intact (c).	50.2420961 35.0070679	3.2*2.1 m	2.0 m	Deep medium-humus leached Chernozem	6.1	5.2	29.1
3.	1 crater (a); 1 slope (b); 1 intact (c).	52.26223749 33.4844972	Diameter 4.7 m	0.9 m	Sod-podzolic clay loamy sandy soil	5.3	2.8	14.8
4.	1 crater (a); 1 slope (b); 1 intact (c).	50.538922 34.888243	4.0*4.1 m	1.1 m	Deep low-humus leached Chernozem	6.3	3.8	32.4
Chernihiv region								
5.	1 crater (a); 1 slope (b); 1 intact (c).	51.38348007 31.16242409	Diameter 1.5 m	0.5 m	Meadow Podzolic Soil	5.3	2.6	18.5
6.	1 crater (a); 1 slope (b); 1 intact (c).	51.39170074 31.12952423	Diameter 1.8 m	0.5 m	Sod-podzolic clay loamy sandy soil	5.4	2.9	15.6
7.	1 crater (a); 1 slope (b); 1 intact (c).	51.39578247 31.39955711	Diameter 1 m	0.4 m	Albic Luvisols	5.0	2.3	14.7
8.	1 crater (a); 1 slope (b); 1 intact (c).	51.29509735 31.280603415	Diameter 3.2 m	0.7 m	Histosols	4.7	9.0	85.2
Kharkiv region								
9.	1 crater (a); 1 slope (b); 1 intact (c).	50.00958633 37.53458023	Diameter 1.6 m	0.3 m	Deep Chernozems with Medium Humus Content	6.7	5.2	48.6

Soil sampling method

Three soil samples were gathered from each of the following locations: the crater's center, its slope from three sides, and an intact region located 20 meters away from the crater (Figure 1). The background soil samples are collected at the same crater depths as the primary samples. Following the individual bagging and labeling of each soil sample with its GPS coordinates, the soil samples were transported to the laboratory.

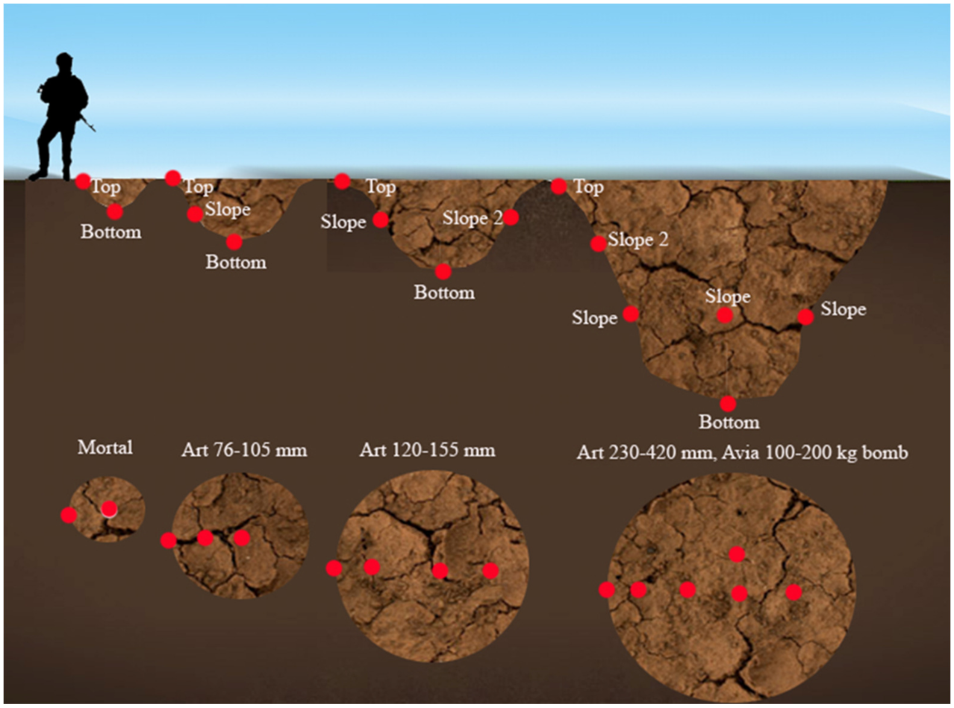

Figure 1. Soil sampling points

Soil analysis

To prepare the soil samples for examination, they were dried for six hours at 100 °C. Following this process, all plant remains were carefully removed and soil was grinded to a diameter of 1 mm. After placing the soil into the weighing bottle, each range triplicate's pXRF analysis (Thermo Scientific Niton XL 2) took 90 seconds (Datsko *et al.*, 2024; Yatsenko *et al.,* 2025).

Statistical analysis

Using Statistica 10.0 (StatSoft Inc., Tulsa, USA), descriptive statistics had emerged.

Results and Discussion

As a result of the analysis of soil samples, the content of twenty-seven chemical elements in the studied soils was revealed. Figure 2 shows the concentrations of six elements: barium (Ba), zirconium (Zr), strontium (Sr), rubidium (Rb), zinc (Zn), and manganese (Mn).

Concentrations of Zr, even though the soil samples were taken in different areas, have the most stable indicators among those studied, varying within 400-600 ppm. The highest concentration of Zr is observed in samples from farm 6.

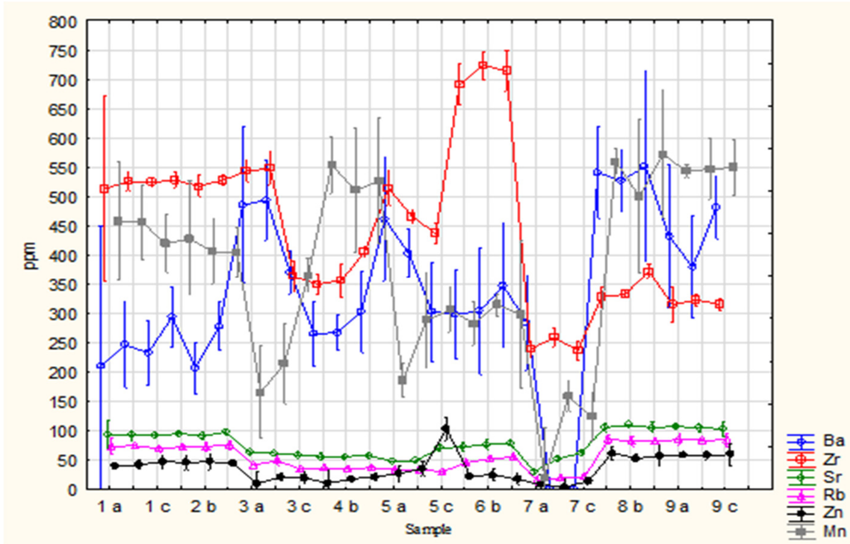

Figure 2. The mean value of the researched heavy metals

Manganese concentrations show considerable variability between samples, showing both peak values and low concentrations in a few samples. Mn concentrations have the highest peak values in samples 4b and 7b, reaching levels above 500 ppm.

Barium shows less variation compared to the other elements, but both peak values above 300 ppm and significant dips are observed. Ba concentrations tend to remain at an average level of 200 to 400 ppm, except for some samples (e.g., 5b and 9b) where an increase is observed.

Most of the samples show a significant difference in the concentrations between the elements, which indicates the heterogeneity of the chemical composition of the soils.

The presence of significant errors for certain samples, such as 3a, 6a and 7c, indicates a high variability of the concentration values and the need for additional measurements to clarify the results.

There is a certain correlation between the concentrations of Ba and Zr in several samples, which may indicate similar conditions of their accumulation.

Mn concentrations do not have an obvious correlation with other elements, which is probably due to differences in the geochemical behavior of this element.

Strontium consistently displays the highest concentration among the three elements, with values in measures from 25 to 110 ppm. The peak concentration of Sr occurs in sample 8b, surpassing 110 ppm. Rubidium maintains intermediate concentrations, ranging between 18 and 84 ppm, while Zinc generally shows the lowest levels, fluctuating between 10 and 60 ppm. However, a notable exception is observed at sample 5c, where Zn experiences a significant spike.

Sr and Rb show relatively stable trends with consistent error margins, Zn exhibits greater variability, especially around sample 5c. Interestingly, such a peak was observed in the control variant, meaning that the increased zinc concentration in the soil is most likely associated with the farm's agricultural activities.

A closer examination of sample 5c reveals simultaneous peaks in two of examined elements (Zn, Sr), indicating that a shared influencing factor is possible. This anomaly could be attributed also to the unique geochemical composition of the sampled material, such as the presence of carbonate-rich layers (affecting Sr) or sulfide minerals and organic matter (enriching Zn).

Table 2 presents the least significant differences in heavy metal concentrations in soil samples compared to an intact area. For Ba, most samples exhibit no significant difference in its content. Exceptions include 2b, 3a, 3b, 5a, and 5b, which show significantly lower values compared to the control site. Zr levels are generally similar to the intact area, except in some samples (e.g., 3a, 3b, 5a, and 8a), where significantly lower concentrations are observed. Manganese concentrations are predominantly consistent with the intact site, with notable reductions in samples 3a, 3b, 5a, and 7a. For Sr, most samples have comparable Sr levels, though 3a, 5a, 5b, and 7a exhibit significantly lower concentrations. Rubidium levels are generally unaffected, with occasional significant decreases (e.g., 3a, 3b, and 7a). Zn concentrations show higher variability. Samples 1a, 4a, and 5a consistently have significantly lower levels, while others like 1b, 2a, and 9a exhibit significantly higher values.

Table 2. The least significant difference in the content of heavy metals in the investigated soils compared to the intact area

Sample	Ba	Zr	Mn	Sr	Rb	Zn
1 a	0.379[a]	0.232[a]	0.101[a]	0.509[a]	0.667[a]	0.044[c]
1 b	0.561[a]	0.822[a]	0.091[a]	0.624[a]	0.016[c]	0.115[a]
2 a	0.354[a]	0.960[a]	0.347[a]	0.165[a]	0.244[a]	0.670[a]
2 b	0.003[b]	0.068[a]	0.974[a]	0.007[c]	0.327[a]	0.397[a]
3 a	0.007[c]	0.000[c]	0.000[b]	0.003[b]	0.004[b]	0.088[a]
3 b	0.005[c]	0.000[c]	0.000[b]	0.014[b]	0.000[b]	0.718[a]
4 a	0.078[a]	0.000[b]	0.393[a]	0.461[a]	0.695[a]	0.035[c]
4 b	0.091[a]	0.000[b]	0.641[a]	0.463[a]	0.078[a]	0.422[a]
5 a	0.000[c]	0.000[c]	0.000[b]	0.000[c]	0.062[a]	0.000[c]
5 b	0.000[c]	0.005[c]	0.382[a]	0.000[c]	0.115[a]	0.000[c]
6 a	0.191[a]	0.056[a]	0.563[a]	0.061[a]	0.000[c]	0.065[a]
6 b	0.237[a]	0.398[a]	0.550[a]	0.453[a]	0.096[a]	0.031[b]
7 a	0.000[c]	0.706[a]	0.001[b]	0.000[c]	0.006[c]	0.232[a]
7 b	1.0[a]	0.004[c]	0.115[a]	0.000[c]	0.196[a]	0.059[a]
8 a	0.768[a]	0.000[b]	0.727[a]	0.931[a]	0.095[a]	0.227[a]
8 b	0.502[a]	0.000[b]	0.069[a]	0.139[a]	0.915[a]	0.472[a]
9 a	0.161[a]	0.905[a]	0.666[a]	0.199[a]	0.784[a]	0.909[a]
9 b	0.015[b]	0.274[a]	0.857[a]	0.631[a]	0.865[a]	0.702[a]
F	58.95	809.07	283.22	331.70	61.95	92.98
p	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Note: index a reflects no significant difference comparing to intact site, b – significantly higher value, c – significantly lower value

The obtained results indicate significant variability in the behavior of heavy metals studied in soil samples. Notably, some control areas exhibited substantially higher concentrations of heavy metals compared to samples taken from craters. These results could be attributed to active anthropogenic influences on the control areas. such as the application of mineral fertilizers or pesticides at doses exceeding recommended levels or natural geochemical conditions that led to the observed distribution of the studied elements in their total form.

Regarding soil contamination caused by multiple launch rocket system (MLRS) shelling, the majority of studied elements in the crater and its slopes showed lower or comparable total concentrations of heavy metals to those in the control points.

To determine whether such localized field damage poses a threat to food security, it is essential to understand the scale of these impacts. For example, a study by Bonchkovskyi *et al.* (2024) reported that remote sensing identified 420.615 craters in the Kharkiv region with 3.411 hectares of soil damaged by heavy machinery. Craters induce secondary geomorphological processes and exhibit elevated levels of cadmium, copper, lead and other heavy metals, although these levels do not exceed permissible limits.

Research by Krainiuk *et al.* (2023) shows that substances found in ammunition and explosives, including heavy metals, form hydroxides and hydroxycomplexes upon entering ecosystems. The form and solubility of these substances depend on soil acidity. Most metals remain in a soluble form in acidic environments. promoting their migration and accumulation in plants. Many metals, such as Cd, Co, Mg, Fe, Mn, Ni and Hg, become fixed in alkaline conditions. This suggests that controlling soil pH is crucial for reducing toxicity and improving the chances of restoring contaminated areas.

Moreover, studies by global scientists indicate that heavy metal contamination of soil is not solely caused by ammunition impact. For instance, research by Ji *et al.* (2023) found that in Lianhuapao, China, where Japanese chemical weapons (JACWs) were abandoned, the concentrations of As, Cr and Ni in soils significantly exceeded permissible levels for agricultural land. An analysis of contamination sources revealed that As, Pb, Cu, Cd, and Zn were linked to JACWs, while Cr and Ni were associated with natural weathering processes.

A study by Williams and Rintoul-Hynes (2022) found that artillery shelling during World War I in the Pas-de-Calais region of France caused physical landscape changes and soil development in craters. These craters exhibited higher organic matter content and electrical conductivity, though with no significant changes in soil pH levels. Heavy metal concentrations (Cu and Pb) exceeded regional baseline values but remained within permissible limits for EU and UK soils.

Moreover, heavy metal contamination disrupts soil microbiology by reducing microbial diversity and activity, leading to imbalances in nutrient cycling (Naz *et al*., 2022). Toxic metals, such as lead, cadmium, and mercury, inhibit beneficial bacteria and fungi, affecting soil fertility and organic matter decomposition (Xu *et al*., 2021). This results in decreased nitrogen fixation and impaired phosphorus availability, further limiting plant growth. As a consequence, plants experience nutrient deficiencies, root damage, and oxidative stress, which weaken their resistance to diseases and environmental stressors. Ultimately, heavy metal pollution lowers crop yield and quality, posing risks to food security and ecosystem stability (Angong, *et al.,* 2024).

Conclusions

The study revealed significant variability in the concentrations of heavy metals in soil depending on the sampling location. In most cases, the metal content in craters was lower or comparable to that in control areas. Higher metal concentrations in control points may be associated with anthropogenic influences, such as the application of mineral fertilizers or intensive agricultural activities. Geochemical characteristics, including correlations between certain elements, suggest shared conditions of accumulation, while other elements exhibit independent behavior. The soil acidity level (pH) plays a key role in the mobility and accumulation of metals emphasizing the need for its control to reduce toxic impacts and improve the restoration of contaminated soils.

Authors' Contributions

OD, AB – study conception and design, drafting of the manuscript; EZ – performed the literature data analysis and discussion of the results; OM – analysis and interpretation of data, funding acquisition; AB - is the corresponding author; IK – author of the idea, guided the research; VI, MS – acquisition of data, drafting of the manuscript; VO – critical revision and approval of the final manuscript. All authors read and approved the final manuscript.

Ethical approval (for researches involving animals or humans)

Not applicable.

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Conflict of Interests

The authors declare that there are no conflicts of interest related to this article.

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