

ГІДРОГЕОЛОГІЯ, ІНЖЕНЕРНА ТА ЕКОЛОГІЧНА ГЕОЛОГІЯ

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WAR-INDUCED SOIL CONTAMINATION WITH HEAVY METALS: RESULTS FROM A TEST SITE IN MYKOLAIV REGION

(Представлено членом редакційної колегії д-ром геол. наук Ксенією БОНДАР)

Background. The war in Ukraine is having a serious impact on the physical, chemical and biological properties of soils. Chemical contamination of soil in combat zones is the most discussed issue, as the detonation of various types of weapons releases a range of pollutants into the soil, among which heavy metals are one of the most toxic. Despite the fact that heavy metals are not the main pollutants, they are most often discussed in the literature. Based on a large number of publications, opposing opinions have been formed regarding the level of heavy metal contamination.

Methods. The content of heavy metals within a study site of 2000 m² (Stepova Dolyna village) was measured by portable X-ray fluorescence system. In order to identify the precision of XRF analysis, the heavy metals content (Cd, Zn, Pb, Cu, As) was determined using atomic-absorption spectrometry (Contra 800 D).

Results. A study of the lateral variability of the content of various heavy metals at a test site in Mykolaiv region, which was heavily damaged by artillery shelling in 2022, found virtually no heavy metal contamination in the soil (except for cadmium in one sample). In most cases, the content of the heavy metals is not mostly related to the location of craters, except for lead, which showed increased concentrations near craters. The very good agreement between portable XRF analyser and atomic-absorption spectrometry was found for lead content. Due to low concentrations of copper, cadmium and arsenic in the soil, the XRF analyser could not measure them.

Conclusions. At the study site, the soil contamination with heavy metals due to explosion of artillery shells, MLRS and mortar is slight. There is no traceable enrichment with heavy metals near craters that can indicate drawbacks of taking incremental samples in case of high-resolution studies. The use of a portable XRF analyser allows for rapid screening of the war-damaged soils for heavy metals and the identification of heavy metal contamination sites. However, accurate data on heavy metals contamination require more precise laboratory methods.

Keywords: Russia-Ukraine war, soil, heavy metals, contamination, portable X-ray fluorescence system, atomic-absorption spectrometry.

Background

Warfare impacts the physical, chemical and biological soil properties (Pereira et al., 2022). The detonation of ammunition leads to soil contamination with various substances: explosives and their derivatives, heavy metals,

polycyclic aromatic hydrocarbons, propellants etc. (Broomandi et al., 2020). The effect of this pollution tends to be the long-lasting as evidenced by results from the battlefields of the World Wars (Bausinger, Bonnaire, & Preuss, 2007; Meerschman et al., 2011; Williams, & Rintoul-

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Hynes, 2022). As a result, the need for specific management of the affected areas arises (Meaza et al., 2024).

Since 24th February 2022, the Russian invasion of Ukraine has already resulted in widespread soil damage (Baliuk et al., 2024; Solokha et al., 2023;), contributing to the problem of global food security (Dent et al., 2022). The war-induced soil disturbances in Ukraine has been discussed in many publications, with military-associated soil contamination being the most highlighted issue (Biyashev et al., 2024; Bonchkovskiy et al., 2025; Bondar et al., 2025; Datsko et al., 2025; Dmytrenko et al., 2023; Korsun et al., 2024; Menshov et al., 2024; Shebanina et al., 2024; Smirnova et al., 2024; Solokha et al., 2022, 2024; Splodytel et al., 2023; Tonkha et al., 2025; Zaitsev et al., 2022). However, despite the numerous publications, the war-induced soil contamination remains insufficiently discussed. Furthermore, the findings of different research groups contradict each other, as some report critical levels of contamination, whereas others claim minimal contamination. The main focus of Ukrainian research groups today is on heavy metals, since there are almost no facilities in Ukraine to study explosives, which are assumed to be the main contaminants.

Compared to other regions of Ukraine, southern Ukraine is rather poorly studied in terms of war-related soil contamination. Particularly, Splodytel (2023) reported high concentrations of trace metals in craters, suggesting critical contamination with heavy metals of the soil. Tonkha et al. (2025) demonstrated heavy metal contamination in fighting positions, notably in those containing metal fragments. Bulba et al. (2024) showed significant soil pollution with heavy metals in three southern Ukrainian regions.

Thus, this paper aims: 1) to present new results on soil contamination with heavy metals at a test site of the war-affected soils in the Mykolaiv region; 2) to discuss the possibility of using a portable X-ray fluorescence (XRF) analyser for rapid investigation of contaminated soils by comparing the results obtained by the analyser and an atomic-absorption spectrometer (AAS).

Methods

Study site. In January 2025, a test site was established at the Stepova Dolyna village of the Halytsynivska territorial hromada in Mykolaiv Oblast (Fig. 1) to collect samples for geochemical analyses and for subsequent monitoring of the recovery of the damaged soil's physical and chemical state.

The test site of 2000 m² is situated on a household plot in the Stepova Dolyna village, which has not been cultivated since 2022. The study area is characterised by considerable soil physical disturbance, since the frontline was located here in 2022, and the fighting was particularly intense. Furthermore, this area is supposed to contain landmines and unexploded ordnance (UXO).

The study site is in the dry steppe zone with xerophytic and ruderal vegetation. The test site is on a very gentle slope of the enclosed depression (Stepova Dolyna pod). Here, Endogleyic Kastanozems (dark chestnut gleyic soils) occur having clay loam texture and slight signs of salinization. The climate is rather dry with hot summers and mild winters. The average temperature in January is -1.6°C , and in July $+22.9^{\circ}\text{C}$. The average annual precipitation is 430–450 mm (Osadchyi et al., 2022).

Soil sampling. The study site was split into 20 small square plots of 100 m² each (Fig. 2). Incremental (mixed) samples were taken from each cell (small plot), which included at least 5 smaller samples from different parts of the cell. They were taken regardless of their location relative to craters or bombturbated soils in order to test the validity and applicability of the incremental sampling technique. The incremental sampling protocol is widely recognized as the opposite of discrete soil sampling (Brewer, Peard, & Heskett, 2017).

Samples were collected from the topsoil (upper 20 cm). The sampling depth was justified by (1) the concentration of the most contaminants in the topsoil in the first years after the warfare (Bonchkovskiy et al., 2025; Solokha et al., 2024); (2) the short period of time after the war damage to the soil – two years, which is not enough for the downward migration of contaminants; (3) the loamy clay texture of the soils impedes downward migration of contaminants, especially heavy metals.

Two experts participated in the sampling process – the first one took notes and the second one collected samples in the zip-lock bags. Each sample weighed about 500 g and was duplicated and homogenized to avoid errors in laboratory measurements. The background sample was collected 5 km away from the test site with the same landform and soil. Due to the dense soil cratering, it was almost impossible to take a background sample closer.



Fig. 1. Test site location

X-ray fluorescence analysis. The first step in the laboratory phase of the research was to homogenise the samples in order to reduce the degree of heterogeneity in the distribution of different fractions of the soil's solid phase. The next step was to dry the samples in ovens at a temperature of 40°C for 6 hours. Bringing the sample to a completely dry state was not possible due to the specifics of XRF analysis and the risk of destruction of some elements due to the high temperatures. Homogenisation ensured a uniform drying process. An agate mortar was used to grind the samples with purpose to avoid the contamination of the analysis. The sample was then sieved through a 1 mm laboratory sieve. The resulting fraction was pressed into 25 ml cylindrical plastic cuvettes and sealed with a polymer film. This was the end of the laboratory preparation of the samples.

For XRF analysis, we used ElvaX ProSpector 3 Advanced with the following specifications: X-ray tube – Rh, 40 kV; primary filter – automatic 8-position; the collimator – automatic 2-position; detector window – graphene, 1 µm; spectral range: Mg-U. The sample was measured three times.

XRF analysis and XRF spectrometry itself is based (Neikov, Naboychenko, & Yefimov, 2022) on the excitation of atoms of material under by a beam of X-rays, which leads to secondary fluorescence emission. The intensity of X-ray fluorescence directly depends on the concentration of each element in the sample. Analysis of the spectra allows determining the elemental composition of the sample. We used an X-ray tube with an Rh anode, which is the most common device in this field of technology. Typically, XRF analysis is used to determine the concentrations of elements from beryllium (Z=4) to uranium (Z=92) in the range from ppm to 100 % with an accuracy of 10^{-7} – 10^{-6} g. Heavier elements (with a higher Z) tend to emit X-rays with higher energy because they have more tightly bound electrons in their inner shells. The resulting spectrum is mathematically processed to allow for quantitative and qualitative (semi-quantitative) analysis. In modern XRF spectrometers, amplifiers and pulse analysers allow for the measurement of the elemental composition of a sample in less than 2 seconds with a satisfactory statistical error.

Atomic-absorption analysis.

The microwave oven (Ethos Easy Microwave Sample Preparation System, Milestone, USA) was applied for sample preparation. The system was equipped with high-pressure TFM vessels (Maxi-44 high – throughput rotor, T2 infrared temperature control, option P2 pressure control). The microwave program BCS 300 was previously changed to run with a maximum power of 1800 W. Microwave decomposition of samples was carried out with the addition of 5 ml of 65 % concentrated nitric acid (analytical grade) and of 1 ml of 35% peroxide. The wet digestion of 250 mg of each sample was conducted in closed TFM vessels during 35 minutes, max temperature was +200 °C.

The content of Cd, Pb, Zn, Cu was measured in 6 random samples using the atomic-absorption spectrometry (AAS) Contra 800D (Analytik Jena, Germany). Measurements were performed in triplicate. The content of As was measured in 6 random samples using the hydride attachment HS60A/HS (Analytik Jena, Germany) according to the instructions for the device with the use of NaBH₄, KJ, Ascorbic Acid (analytical grade). Measurements were performed in triplicate.

The following standards were used to determine concentrations and construct calibration graphs: Standart solution IV-Stock-4 1000 µg/mL in 5 % v/v Nitric Acid (Inorganic ventures, USA). Standart solution (CGAS1) of As 1000 µg/mL in 2 % v/v Nitric Acid (Inorganic ventures, USA).

Results

Soil disturbance. The study site is characterised by the significant soil disturbance: 7 craters with a diameter of 1.7–4.4 m and a depth of 0.2–0.7 m were identified. The craters were caused mainly by 120 mm mortars or 122 mm multiple launch rocket system (MLRS) BM-21 'Grad'. The largest one was caused by the detonation of a 152 mm artillery shell. Thus, the crater density on the test site is 35 craters per hectare, and the total volume of displaced soil is 11.0 m³. More detailed parameters of the surveyed craters are presented in (Tab. 1).

Table 1

Parameters of craters within the study site

№	Diameter, m	Depth, m	Volume of displaced soils, m ³	Projectile type	Soil disturbance	Crater state
1	4.4	0.6	4.1	152 mm	Ah and B soil horizons	Overgrown with vegetation
2	3.2	0.7	2.5	152 / 155 mm	Ah and B soil horizons	Partially overgrown with vegetation
3	2.1	0.4	0.6	120 / 122 mm	Ah soil horizon	Overgrown with vegetation
4	2.6	0.5	1.2	120 / 122 mm	Ah and B soil horizons	
5	2.2	0.5	0.9	120 / 122 mm	Ah and B soil horizons	
6	2.5	0.5	1.1	120 / 122 mm	Ah and B soil horizons	
7	1.9	0.3	0.4	120 / 122 mm	Ah soil horizon	

Craters destroy mostly Ah and B/Bk horizons of the Kastanozem (Fig. 2). The crater slopes are overgrown with ruderal vegetation, which restrains the erosion and the crater's filling with soil deposits. This resulted in good preservation of the craters in their primary hemisphere form. No signs of ramparts around the craters were found (except for crater No. 1), given their small size and depth. No visual signs of bombturbation zones (according to Bonchkovskiy et al., 2023) were found on the topsoil.

Heavy metals content. The heavy metal content within the test site does not exceed the background values, and the spatial variability of heavy metal content is almost not related to the location of the craters. However, such variability is still observed (Fig. 3). None of the tested soil samples showed heavy metal content above the maximum permissible

concentrations (except for Cd in one sample). This is due to the lack of industrial soil contamination before and during the war.

Lead content ranges from 15–22 mg/kg according to XRF analysis and from 9.7 to 18.6 mg/kg according to AAS (Table 2). The copper content according to AAS is 32.0–34.9 mg/kg, while XRF analyser detected copper in several samples (20–22 mg/kg). The zinc concentration determined by AAS is two times higher than measured by XRF analyser – 80.0–90.9 ppm versus 31–46 mg/kg. The cadmium content is below the detection limit of the XRF analyser. However, AAS yielded Cd concentration around of 1.1–1.4 mg/kg. Significant enrichment with cadmium is detected only in one sample (2.1 mg/kg), which was not collected near the crater.



Fig. 2. Craters within the study site.

General view of the study site (A). Crater from a 152 mm ordnance (B); Crater from a 120 / 122 mm ordnance (C)

The chromium content (measured by XRF analyser) ranges from 39 to 80 mg/kg and vanadium from 60 to 130 mg/kg and does not correlate with the location of the craters. The screening revealed insignificant concentrations of molybdenum, arsenic and tin in some samples. Only lead showed elevated concentrations near craters from the whole range of measured elements.

Discussion and conclusions

Soil contamination with heavy metals has been reported at many sites affected by military operations worldwide (Broomandi et al., 2020; Certini, Scalenghe, & Woods, 2013; Tešan Tomić et al., 2018; Vidosavljević et al., 2013; Williams, & Rintoul-Hynes, 2022; and others) and in Ukraine (Solokha et al., 2022, 2024; Splodytel et al., 2023; Tonkha

et al., 2025; Zaitsev et al., 2022; and others). Most studies have shown that they are not highly contaminated with heavy metals (Bonchkovskiy et al., 2025; Bondar et al., 2025; Datsko et al., 2024; Smirnova et al., 2024; Solokha et al., 2022), despite initial findings of critical contamination (Shebanina et al., 2024; Splodytel et al., 2023; Zaitsev et al., 2022). The most considerable contamination with cadmium, copper, zinc and lead has been reported by the cited authors (Bonchkovskiy et al., 2025), collecting samples at different distances from craters, showed that the content of heavy metals decreases from crater to background, rarely showing peaks at the crater rim. However, the average content of heavy metals near the craters exceeded that in the background sample by only 1.2–1.5 times.

Table 2

Comparison of trace elements content (ppm) determined by portable XRF analyser and AAS Contra 800 D.

Sample number	Lead (Pb)		Copper (Cu)		Zinc (Zn)		Cadmium (Cd)	
	AAS	XRF	AAS	XRF	AAS	XRF	AAS	XRF
1	12.07	15	32.01	-	82.55	45	1.101	-
3	9.67	18	32.39	22	85.83	42	1.141	-
6	13.63	13	34.85	20	90.91	35	1.208	-
12	16.91	16	32.70	-	79.95	36	1.325	-
15	18.59	22	34.26	-	86.33	46	2.056	-
21	12.22	14	32.61	-	82.7	31	1.354	-

The study site near the Stepova Dolyna did not reveal significant contamination with heavy metals. Only cadmium showed high concentration in one sample, therefore it can be related to the local contamination, which is not associated with the cratering. It is impossible to compare our results with findings of Bulba et al. (2024) and Splodytel (2023), who reported critical contamination with heavy metals. This is due to the fact that Splodytel (2023) did not specify the methodology of soil sampling, whereas Bulba et al. (2024) did not specify the type of damage and soil typology and took background samples far from the damaged areas.

Our study revealed that only lead shows a slight enrichment near craters (Fig. 3). The concentrations of other heavy metals are not associated with craters. On the other hand, this may be a drawback of the incremental sampling protocol since it represents the average elemental content within a plot.

The highest levels of contamination have been independently recorded by researchers at the sites of military equipment explosions (Bonchkovskiy et al., 2025; Solokha et al., 2024; Zaitsev et al., 2022), where soils are contaminated with various substances, including heavy metals, oil products, polycyclic hydrocarbons, and even radioactive elements. Tonkha et al. (2025) also found significant soil pollution at military positions and fortifications. However, there are currently no published results of geochemical analyses at the sites of military equipment explosions in Mykolaiv region.

Datsko et al. (2024) proposed the use of X-ray fluorescence analysis to accelerate of soil chemical survey in the war-affected areas. Vanhoof, Corthouts, & Tirez, (2004); Vanhoof et al. (2013) demonstrated that portable

XRF systems are quite effective for preliminary assessment of contaminated soils. Our results show that the efficiency of a portable XRF analyser depends on the element and its detection limit. Very good agreement between the portable XRF analyser and the AAS was found for lead content. The zinc content measured by the AAS is constantly twice than that determined by the XRF analyser, which may be a result of the analyser settings. Due to the low concentrations of copper, cadmium and arsenic in the soil, the XRF analyser cannot measure them. However, the XRF system can accurately identify areas contaminated with Cu, Cd and As. On the other hand, we believe that the technical parameters and setting of specific portable XRF systems determine the accuracy of the measurement. Thus, portable XRF systems are very useful for screening soil contamination with heavy metals, notably when sample preparation is performed. However, accurate measurements of heavy metal concentrations require precise laboratory methods, such as inductively coupled plasma spectrometry or atomic absorption spectrometry.

Thus, the soil contamination with heavy metals due to explosion of artillery shells, MLRS and mortar is slight. No heavy metal enrichment is observed near craters which can indicate drawbacks of taking incremental samples in the case of high-resolution studies. The portable XRF analyser enables to rapidly test the war-damaged soils for heavy metals and identify areas of heavy metal contamination. However, more precise laboratory methods are required to provide accurate data on heavy metal contamination.

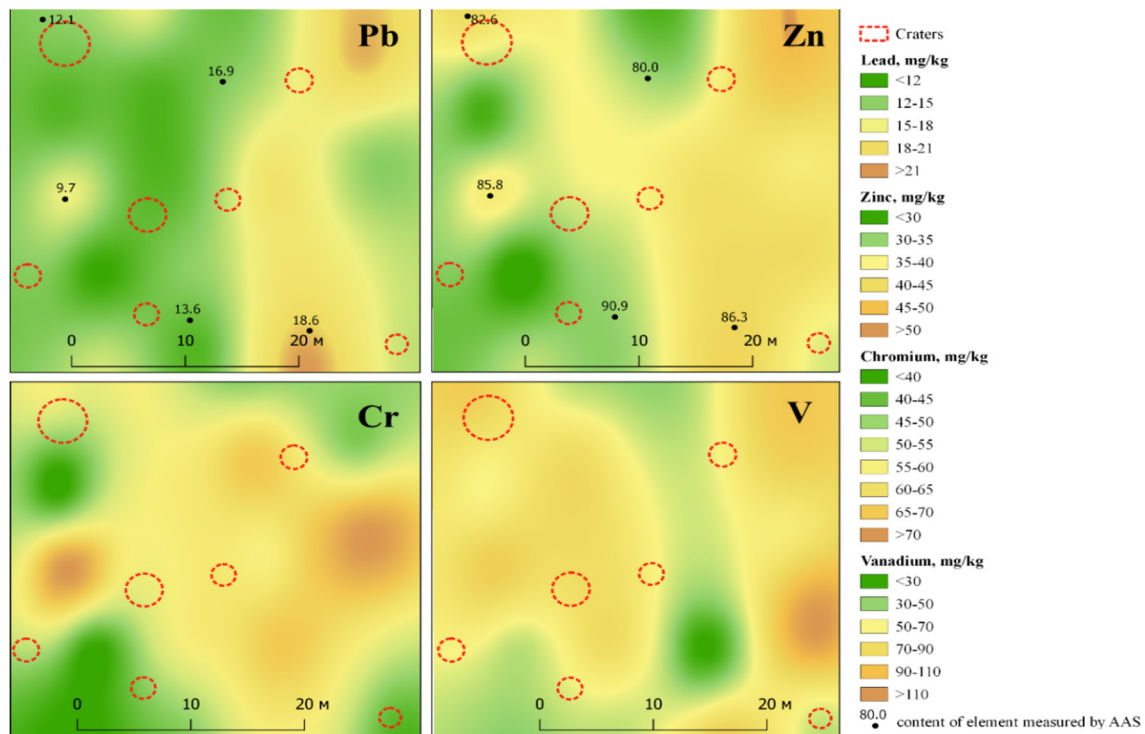


Fig. 3. Spatial variation of heavy metal content in the soil of the test site (according to the portable XRF analyser)

Authors' contribution: Oleksandr Bonchkovskiy – writing, conceptualization, methodology; Pavlo Ostapenko – writing, conceptualization; Yaroslava Zhukova – writing, methodology; Illia Kravchuk – writing, methodology, data validation; Serhii Petryshchenko – methodology; Adelina Lazarets – field works, formal analysis; Oleksandr Halahan – methodology; Nazar Stepanenko – methodology.

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ЗАБРУДНЕННЯ ҐРУНТІВ ВАЖКИМИ МЕТАЛАМИ ВНАСЛІДОК ВЕДЕННЯ БОЙОВИХ ДІЙ: РЕЗУЛЬТАТИ З ТЕСТОВОЇ ДІЛЯНКИ У МИКОЛАЇВСЬКІЙ ОБЛАСТІ

Вступ. Війна в Україні серйозно впливає на фізичні, хімічні та біологічні властивості ґрунтів. Хімічне забруднення ґрунтів у зонах ведення бойових дій є однією з найбільш дискусюваних тем, оскільки в процесі детонації зброї різного типу в ґрунт потрапляє комплекс забруднювачів, серед яких одним із найтоксичніших є важкі метали. Як наслідок – сформувалися протилежні думки стосовно рівня забруднення важкими металами.

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Методи. Вміст важких металів на досліджуваній ділянці площею 2000 м² (с. Степова Долина) було виміряно за допомогою портативного рентгенофлуоресцентного аналізатора. Для визначеності точності рентгенофлуоресцентного аналізу вміст важких металів (Cd, Zn, Pb, Cu, As) додатково визначено за допомогою атомно-абсорбційної спектрометрії (ContrA 800 D).

Результати. Дослідження латеральної мінливості вмісту різних важких металів на тестовій ділянці у Миколаївській області, сильно постраждалій від артилерійських обстрілів у 2022 році, практично не виявили забруднення ґрунтів важкими металами (окрім кадмію в одному зразку). Здебільшого вміст важких металів не пов'язаний із розташуванням кратерів (за винятком свинцю), концентрація якого зростає поблизу кратерів. Для вмісту свинцю виявлено дуже хороше узгодження між портативним рентгенофлуоресцентним аналізатором і атомно-абсорбційною спектрометрією. Через низькі концентрації міді, кадмію та миш'яку в ґрунті рентгенофлуоресцентний аналізатор не має можливості до їх вимірювання.

Висновки. На досліджуваній ділянці забруднення ґрунту важкими металами внаслідок вибухів артилерійських снарядів, РСЗВ та мінометів є незначним. Поблизу кратерів не прослідковується збагачення важкими металами, що може свідчити про недоліки відбору змішаних проб у разі проведення досліджень з високою роздільною здатністю. Використання портативного рентгенофлуоресцентного аналізатора дає змогу швидко перевірити пошкоджені війною ґрунти на вміст важких металів та виявити місця забруднення важкими металами. Однак для отримання точних даних про забруднення важкими металами потрібні більш точні лабораторні методи.

Ключові слова: російсько-українська війна, ґрунти, важкі метали, забруднення, портативний рентгенофлуоресцентний аналізатор, атомно-абсорбційна спектрометрія.

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