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Ecological Assessment of Heavy Metal Content in Ukrainian Soils

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ABSTRACT

Military actions bring many negative consequences both in the short and long term. In particular, not only people suffer during armed aggression, but also the ecosystem and agrocenoses. This article examined the impact of bombardment of agricultural land with aerial bombs and established whether it was really contaminated with heavy metals. Samples were collected in two regions of Ukraine – Sumy and Chernihiv – from craters formed by bombing. The soil was taken directly from the bottom of the crater, at three points on its slope and 20 meters from the crater, in a conditionally undamaged area. The soil was analyzed in the laboratory using X–ray fluorescence analysis. The study analyzed the content of barium, zirconium, rubidium, zinc, and vanadium soil samples from a crater. The impact of aerial bombings on the concentration of heavy metals in the soils of the farms under investigation is unclear, it may be inferred. The concentration of barium, zirconium, and manganese on the crater slopes is higher in certain farms than in others, but overall trends do not show an obvious increase in these elements when compared to the control sites. However, several farms did not report significant shifts in the heavy metal composition, indicating how challenging it is to monitor whether explosions affect the concentrations of these elements. With a few exceptions, other heavy elements including strontium, rubidium, and zinc did not consistently exhibit excesses in the craters. Therefore, further, more thorough assessment of soil contamination should be carried out and methods for remediation should be developed.

Keywords: heavy metals, anthropogenic influence, soil, crops, pXRF, trace elements, contamination, ecosystem.

INTRODUCTION

The role of soil in humans' life is hard to overestimate, spatially in Ukraine, where are 30% of European Black soil (Chernozem) reserve [Alieksieiev and Vradiy, 2023]. Chornozem soils are the richest in humus [Altermann et al., 2005], which makes it possible to ensure high crop fertility without using excessive amounts of mineral fertilizers. Mostly, military operations are taking place in the "Chernozem Belt" of Ukraine, which stretches from the northeast to the southwest of the country. Accordingly, the hostilities result in soil degradation and accumulation of various pollutants that can accumulate in soils and directly or indirectly affect agroecocoenoses. Moreover, only 40% of the Earth's surface are used for food production [Silver et al., 2021]. Ukraine is a net exporter of food and is responsible for 50% of sunflower oil, 15% of corn and barley, and 10% of wheat of globally traded commodities [FAOSTAT, 2022]. Therefore, the war in Ukraine influences global food trade and it was evidenced by escalating grain prices when war was first declared.

War actions which influence the land used for agricultural purposes can have serious implications on food safety. Many studies have shown that agricultural land becomes contaminated with heavy metals and/or oil [Stadler et al., 2022]. The impacts of soil contamination by heavy metals can lead to bioaccumulation within the food chain, in animal or human organisms, and as an outcome can cause great harm to health [Kolisnyk et al., 2020; Velayatzadeh, 2023]. Oil pollution of the soil may result degradation [Xuezhi, 2020; Karbivska et al., 2020] and changes in the soil microbiome [Huang et al., 2021].

The explosion of a missile or other projectile can produce large quantities of a range of chemical compounds that can be toxic to the environment, including carbon dioxide and carbon monoxide, nitrogen oxides, formaldehyde, cyanide acid, mercury and many others [Chvaliuk and Hrubinko, 2022; Pykhtieieva et al., 2023; Hryhoriv et al., 2024] depending on the construction of the munition. The consequence of military operations is not only the formation of craters, disturbance of the soil profile but also loss of vegetative cover. Bombturbation may also alter the topography of the area where military operations took places well as changes caused by the construction of defense structures. Additionally, soil compaction is caused due to the movement of military machines, which negatively impacts not only the flora of the area, but also the biota [Splodytel et al., 2023; Chernysh et al., 2024; Kolisnyk et al., 2024; Kovalenko et al., 2024a].

Studies conducted in France at the site of shelling during the First World War revealed a general excess of lead and copper in comparison with the region, but the excess was not higher than allowed by the legislation of the European Union [Williams and Hynes, 2022].

Many studies have evaluated the impact of warfare on soil contamination, but less is known about the impact of more recent warfare munitions on soils. Studies from mined land in Croatian Prasnik rainforest revealed that military operations had a major effect since, in comparison to the control region, increased levels of zinc, cadmium, chromium, and other elements were found [Mesić Kiš et al., 2016]. Simultaneously, investigations carried out in another part of Croatia (Slavonia and Baranja) found increased concentrations of arsenic, mercury, lead, and antimony at the combat sites [Vidosavljević et al., 2014]. A further examination conducted in Croatia verified that military operations involving significant combat resulted in higher levels of lead, mercury, and arsenic when compared with the country's ecological agricultural regulations [Vidosavljević et al., 2013; Karbivska et al., 2022]. Tešan Tomić et al. [2018] examined the effects of long–term detonation of explosive devices at the military firing ground Glamoc in Bosnia and Herzegovina and found that concentrations of zinc, copper, nickel, and cadmium are exceeded in such sites. Studies conducted in Lithuania found that the presence of heavy metals rises and organic matter reduces in the areas where military actions had occurred [Greičiūtė et al., 2007; Kovalenko et al., 2024b].

The impact of the military invasion is also felt in many of the territories of Ukraine. For example, there is evidence that after the military contingent was stationed in Chornobyl, chemical contamination of soil and water occurred, which significantly affected the ecosystem of the territory [Patseva et al., 2022]. Also, in the Sumy region, Zaitsev et al. [2022] collected samples from the areas where military machinery was destroyed or where holes were left by aerial bomb blasts. It was found that the levels of zinc, manganese, nickel, iron, and lead at the sample locations were substantially greater compared to those in the background meanings. The study by Solokha et al. [2023] found that the number of heavy metals, in particular, cobalt, copper, chromium, iron, manganese, lead and nickel were elevated in the places of shelling. That is why the aim of the conducted study was to determine the content of heavy metals in the fields that were hit by aerial bombs.

MATERIAL AND METHODS

Sites of soil sampling

Soil samples were taken at seven areas from the fields in Sumy and Chernihiv region (Table 1), where aerial bomb hits were recorded, to protect the personal data of the farms their names were replaced by numbers.

Method of soil sampling

Soil samples were taken in the center of the crater, on the slope of the crater from three sides and in intact area at a distance of 20 m from the crater, each sample was replicated three times from each point (Fig. 1). Undisturbed soil from the same area was sampled at the same depths at which the main samples in the crater were taken and recorded as an "intact" sample. Each soil sample was bagged separately and labelled with location reference (GPS coordinates), then soil samples have been delivered to the lab.

Table 1. The location of the fields that were shelled by aerial bombs

No.	Soil sample	Location	Crater size	Crater depth	Soil type	pHKCl	OM, %	CEC, meq/100 g
Sumy region								
1.	1 crater (a); 1 slope (b); 1 intact (c).	51.133380, 34.761758	Diameter 5 m	2 m	Silty clay loam Chernozem chernic	6.7	4.7	23.0
2.	1 crater (a); 1 slope (b); 1 intact (c).	51.120327, 34.786823	3 · 6 m	1.4 m	Silty clay loam Chernozem Chernic	6.3	4.2	22.8
3.	1 crater (a); 1 slope (b); 1 intact (c).	50.17274, 34.56323	8.0 · 7.5 m	2 m	Silty clay loam Chernozem Chernic	6.8	4.5	23.7
4.	1 crater (a); 1 slope (b); 1 intact (c).	52.2803139, 33.4931999	Diameter 25 m	4 m	Sandy loam soils Soddy–medium podzolic	5.0	2.0	11.0
Chernihiv region								
5.	1 crater (a); 1 slope (b); 1 intact (c).	51.40248871, 31.38254738	Diameter 8 m	2 m	Sandy loam Albic Luvisols	4.66	1.2	13.8
6.	1 crater (a); 1 slope (b); 1 intact (c).	51.49725342, 31.06747246	Diameter 8 m	2 m	Sandy loam Albeluvisols Umbri	6.26	1.4	12.5
7.	1 crater (a); 1 slope (b); 1 intact (c).	51.29894638, 31.2717495	Diameter 13 m	5 m	Sandy loam Albic Luvisols	6.91	3.6	15.5

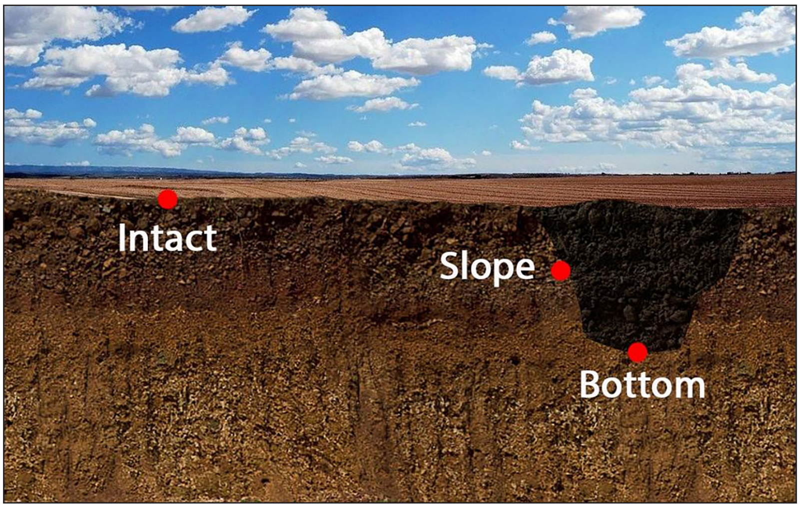

Figure 1. Points of soil sampling

Soil analysis

To prepare samples for the analysis, soil was dried at the temperature 100 °C 6 hours; after drying, all plant residues were ground to 1 mm in diameter using a PM–5M mill. The soil was placed into the weighing bottle and then was analyzed by pXRF (Thermo scientific Niton XL 2) 90 seconds for each range triplicate. Twenty–seven chemical elements were determined, but in this paper only six were shown, because of their potential influence on human health.

Statistical analysis

Descriptive statistics were made using Statistica 10.0 (StatSoft Inc., Tulsa, USA).

RESULTS AND DISCUSSION

First, the heavy metals that do not have high phytotoxicity on crops should be considered. In particular, among those studied in this research are barium, zirconium and manganese. In general, these elements do not participate in physiological processes during plant growth [Shahid et al., 2013; Madejón, 2019; Radchenko et al., 2024]. At the same time, manganese is still one of the leading factors influencing the process of photosynthesis and is actively absorbed by plants from the soil.

As it can be seen from Figure 2, the content of an element depends on the soil, samples of which were taken. However, it is rather difficult to clearly track the effects of the aerial bomb on the content of the studied heavy metals. For example, in farms 1–3, 5 and 7, the barium content in the control area is lower than in the crater or on its slope. However, it is impossible to assert this about farms 4 and 6. The situation is similar with zirconium, where preferably in the area considered to be the control, the amount of the element is higher compared to the affected area, the same situation occurs with the content of manganese in the samples. A more detailed analysis is presented in Table 2. In farm 1 it is seen that there was a significant increase in barium and zirconium on the slope of the crater (1b) in comparison with the control. An increase in the concentration of these elements is also noted in the crater (2a) and on its slope (2b) for farm 2. A significant increase in the content of all three studied elements was recorded on the slope of the crater (3b) of farm 3. However, in farms 4–7 there was no significant increase in the concentration of heavy metals, with the exception of the slope (7b) of farm 7, where a significant increase in barium was recorded.

Strontium, rubidium and zinc were also measured in the samples. Strontium and rubidium are considered dangerous to any living organism [Chowdhury and Blust, 2011]. However, zinc is an important component involved in the formation of proteins in the plant organism [Broadley et al., 2007]. The graph (Figure 3) shows the concentrations of heavy metals in the vents of the studied farms. In general, there is no clear excess of the content of the investigated elements in comparison with the control area. Except for the bottom of the funnel (4a) for farm 4, where the amount of strontium is higher by 48 ppm. Speaking about the significant excess content of heavy metals

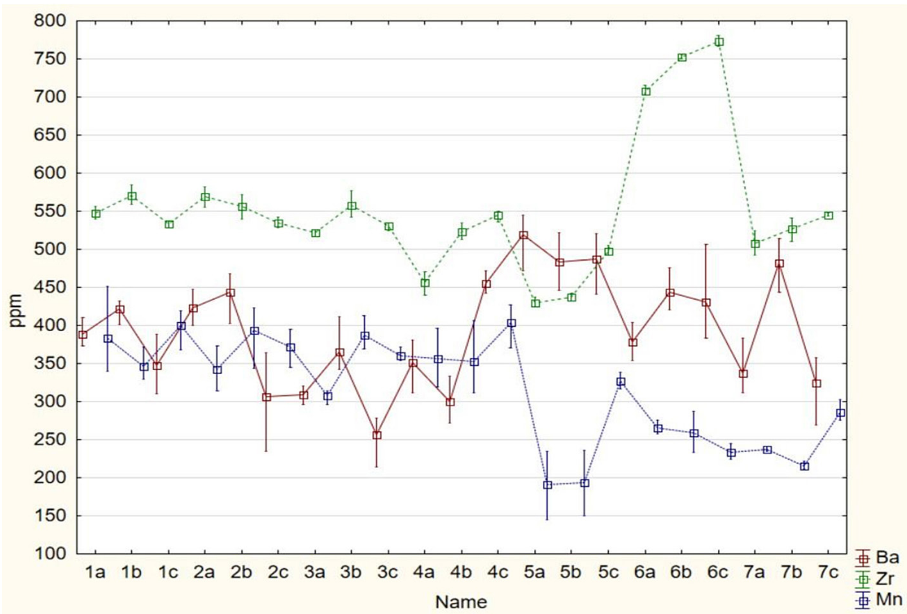

Figure 2. Average barium, zirconium and manganese content in soil samples of the studied farms

Table 2. Least significant difference criterion, grouped according to farm and heavy metal

	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b	6a	6b	7a	7b
Ba	0.114^{a*}	0.015^{b}	0.019^{b}	0.099^{b}	0.087^{a}	0.005^{b}	0.004^{c}	0.001^{c}	0.411^{a}	0.929^{a}	0.200^{a}	0.714^{a}	0.722^{a}	0.003^{b}
Zr	0.123^{a}	0.002^{b}	0.017^{b}	0.081^{b}	0.350^{a}	0.020^{b}	0.001^{c}	0.074^{a}	0.001^{c}	0.001^{c}	0.001^{c}	0.005^{c}	0.012^{c}	0.131^{a}
Mn	0.637^{a}	0.152^{a}	0.333^{a}	0.451^{a}	0.005^{a}	0.074^{b}	0.0195^{a}	0.167^{a}	0.008^{c}	0.014^{c}	0.068^{a}	0.123^{a}	0.001^{c}	0.001^{c}

Note: a – the value does not have a statistically significant difference compared to the control, b – the value is significantly higher than the control option, c – the value is significantly lower than the control option.

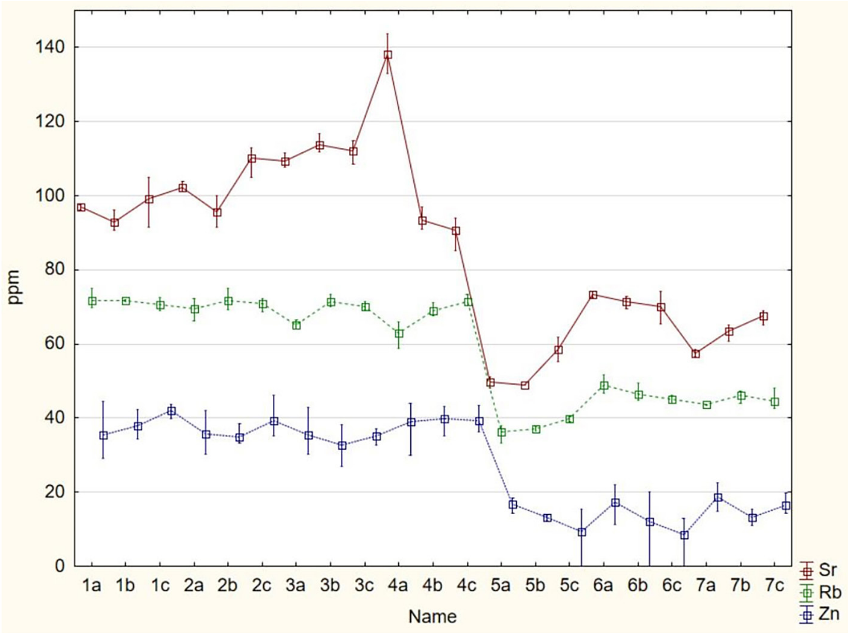

Figure 3. Average strontium, rubidium and zinc content in soil samples of the studied farms

more substantively, it can be seen from Table 3 that for farms 1 and 6, no statistically significant difference was noted between soil samples in the craters and in the control area. For farms 2, 3, 5 and 7, the situation is much more intact area. A significantly higher strontium content was indeed recorded in the crater (4a) of farm 4.

Although in the study of Yakymchuk, et al. [2024] it is said that the content of such heavy metals as lead, cadmium, copper, zinc, etc. has increased significantly in the soils of Ukraine. However, this study did not find unequivocal confirmation of this, at least speaking about the content of these elements in the funnels formed as a result of the explosion of air bombs. Shebanina et al. [2023] also raises the important issue of shelling of chemical enterprises of Kharkiv region by the aggressor country, according to the authors, as a result, the amount of cadmium in the adjacent zones increased by 200 percent. However, military actions definitely have a negative impact on the soil of agricultural land, when talking about a significant number of explosions. This effect can be manifested not only by an increase in the concentration of heavy metals, but also by a significant change in the relief. For example, Bonchkovskyi et al. [2023] reflected in his work the influence of hostilities on the Kyiv community in the Chernihiv region. It was found that the size of the contaminated area can reach more than 380 hectares, and as a result of migration of heavy metals, re–infection of the territories can occur. Unfortunately, so far not many research results have been highlighted about the consequences of military operations in Ukraine. However, results from the study of the impact of various kinds of bombing and the assessment of soil pollution with heavy metals have been published by many scientists around the world. For example, Specht et al. [2024] investigated the soil on the content of heavy metals in Fallujah, Iraq due to bombing by XRF analysis and found that the amount of metals, such as lead and uranium was increased. Al Lami et al. [2021], proved that the increase in the amount of zirconium, rubidium, vanadium and arsenic in the

Table 3. Least significant difference criterion, grouped according to farm and heavy metal

	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b	6a	6b	7a	7b
Sr	0.561[a*]	0.130[a]	0.037[c]	0.002[c]	0.249[a]	0.515[a]	0.001[b]	0.518[a]	0.005[c]	0.005[c]	0.183[a]	0.578[a]	0.001[c]	0.043[c]
Rb	0.482[a]	0.443[a]	0.532[a]	0.725[a]	0.006[c]	0.266[a]	0.006[c]	0.274[a]	0.062[a]	0.149[a]	0.072[a]	0.424[a]	0.628[a]	0.378[a]
Zn	0.189[a]	0.380[a]	0.435[a]	0.358[a]	0.957[a]	0.568[a]	0.958[a]	0.887[a]	0.160[a]	0.483[a]	0.231[a]	0.595[a]	0.427[a]	0.239[a]

Note: a – the value does not have a statistically significant difference compared to the control, b – the value is significantly higher than the control option, c – the value is significantly lower than the control option.

soil is associated with hostilities in the northwestern part of Iraq. The possibility of soil contamination with heavy metals was also confirmed by the scientists who conducted their research in Nigeria. In particular, an increase in the amount of lead in the soils located on the territory of shooting ranges has been confirmed [Etim and Onianwa, 2012].

Determination of heavy metals in soil using XRF analysis is a fairly new technique that allows scientists to obtain data on the chemical composition quickly and accurately. It has already shown its effectiveness in many studies [Jang, 2010; Hu et al., 2017; Xia et al., 2019]. The only condition for a reliable comparison of the data obtained is to bring the soil samples to the same state. Scientists have proven that when performing soil analysis, which differs even in moisture content, inaccuracies in the determination are possible [Qu, et al., 2019; Datsko et al., 2024]. Using this analysis, the study examined the impact of bomb detonation on the distribution of heavy metals directly in the crater, on slopes, and in undamaged areas of agricultural land. For example, Wan et al. [2019] proved that the determination of the content of heavy metals in soil by XRF analysis and conventional methods coincides in terms of performance and the accuracy rate is quite high. The results of the study indicate a variety of relationships between the content of chemical elements in the soils of different areas of the studied farms after the explosion. In particular, the analysis showed differences in the content of barium, zirconium, strontium, rubidium, zinc and vanadium depending on the type of soil and the location of sample collection. This distribution may be due to the phenomenon of antagonism and synergism of ions in the soil. In particular, in all the farms where samples were collected, it is currently impossible to establish a clear correlation between the distribution of heavy metals depending on the impact of the bomb. Each identified element had its own distribution peculiarity depending on the soil at the research site. Scientists have shown that the phenomenon of antagonism is observed between zinc and arsenic [Guzman–Rangel et al., 2018] or zinc and lead [Golubović and Blagojević, 2012]. That is, zinc allows immobilizing both arsenic and lead, which makes their concentration in the soil lower and, accordingly, reduces their absorption [Wang et al., 2016]. At the same time, to establish a clear relationship between the damage and possible potential contamination, it is necessary to collect soil samples in a narrower range (area) and increase the number of replications.

CONCLUSIONS

On the basis of the analysis, it can be concluded that the effect of aerial bombs on the content of heavy metals in the soils of the studied farms is ambiguous. Although in some cases, such as farms 1, 2 and 3, there is an increase in the concentration of barium, zirconium and manganese on the slopes of the funnels, the general trend does not indicate a clear increase in these elements compared to the control sites. At the same time, some farms did not record significant changes in the content of heavy metals, which indicates the difficulty of tracking the consequences of explosions on the concentration of these elements. Other heavy metals, such as strontium, rubidium and zinc, also did not show unambiguous excesses in the funnels, except in some cases. In general, the results of the study indicate the complexity and ambiguity of the impact of hostilities on soil pollution with heavy metals. Consequently, a more comprehensive evaluation of soil contamination is warranted, along with the development of remediation strategies.

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