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Risks of Soil Pollution with Toxic Elements During Military Actions in Lviv

Kateryna Petrushka[1], Myroslav Malovanyy[1*], Dawid Skrzypczak[2], Katarzyna Chojnacka[2], Jolanta Warchoł[2]

[1] Department of Ecology and Sustainable Environmental Management, Viacheslav Chornovil Institute of Sustainable Development, Lviv Polytechnic National University, S. Bandery Str. 12, 79013 Lviv, Ukraine

[2] Department of Advance Materials Technologies, Wroclaw University of Science and Technology, C. K. Norwida Str. 4/6, 50-373 Wroclaw, Poland

* Corresponding author's e-mail: myroslav.mal@gmail.com

ABSTRACT

Considering that approximately 20% of the nation's land remains under the occupation of Russian forces, assessing the impact of the invasion in the midst of ongoing conflict is a formidable challenge. However, even the limited available data offers a distressing glimpse into an ecological catastrophe. The detonation of rockets and artillery shells leads to the generation of a variety of chemical compounds containing elements such as zinc (Zn), copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), and cadmium (Cd). The primary goal of this research was to ascertain the presence of potentially hazardous elements (PTE) within the soil in areas subjected to targeted rocket attacks within the Lviv districts. Soil samples were gathered from four locations in the city of Lviv, which had been impacted by rocket fire, using a concentric circle sampling methodology. Two distinct instrumental techniques, namely X-ray fluorescence spectroscopy (XRF) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), were employed to quantify the concentration of heavy metals within the soil samples. Results revealed that all soil samples exhibited a significant exceedance of the maximum allowable concentrations for titanium (Ti), zinc (Zn), lead (Pb), and nickel (Ni). To assess the leachability and bioavailability of these elements within the soil, various extraction methods were applied in aqueous conditions and in the presence of ammonium citrate. The latter method demonstrated high effectiveness in extracting zinc (Zn), copper (Cu), chromium (Cr), and cadmium (Cd) from the soil. The level of soil contamination was evaluated using diverse criteria, including the contamination factor (Cf), the environmental risk factor (Er), the potential environmental risk index (Ri), the geoaccumulation index (Igeo), and the environmental risk factor (NIPI – National Iron plus Initiative). The computed cumulative environmental impact of all elements (NIPI = 49.001 and NIRI = 54.941, National Investor Relations Institute) underscores the substantial pollution within the surveyed area.

Keywords: military affected area, heavy metals, soil pollution, risk assessment.

INTRODUCTION

Military activities represent one of the most impactful ways in which humans influence soil. This influence encompasses various forms of physical disruption, including the construction of defense structures, excavation of trenches or tunnels, soil compaction resulting from the movement of military equipment and troops, and the creation of craters due to bomb explosions (Certini et al., 2013). Explosions, in particular, can displace large volumes of soil, leaving behind disturbed earth contaminated with metal debris and ash (Rodríguez-Seijo et al., 2016). This type of bombing causes significant disturbances in the landscape as it mixes soil horizons, alters topography, and modifies soil properties. As a consequence, military operations give rise to environmental challenges related to the accumulation of various pollutants within the soil, in plants, and in surface waters. Furthermore, it's essential to recognize that environmental transgressions can constitute war crimes. In accordance with the Geneva Convention, the use of methods or means of warfare that are intended to cause, or are expected to cause, widespread, long-lasting, and severe harm to the environment is strictly prohibited (Ligazakon, 2023).

The chemicals present in ammunition and explosives comprise a wide array of organic and inorganic substances, which can be categorized into Potentially Toxic Elements (PTE), Energetic Compounds (EC), and Chemical Warfare Agents (CWA) (Tomic et al., 2018). PTEs originating from areas affected by warfare primarily encompass lead (Pb) and its associated contaminants, including antimony (Sb), chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), zinc (Zn), and cadmium (Cd). Explosives contain significant quantities of Pb and Hg, with mercury (II) fulminate being particularly prevalent. Zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), and chromium (Cr) are used for coating bullets, missiles, gun barrels, and military vehicles. Barium (Ba), antimony (Sb), and boron (B) serve as weapon charging compounds, while tungsten (W) is employed for kinetic bombardment due to its high density (19.3 g/cm3) (Gebka et al., 2016). Once released into the environment, the majority of PTEs in ammunition undergo oxidation upon contact with air and subsequently condense into fine particles in the atmosphere. These particles are then deposited into various environmental matrices through rainfall (Dinake et al., 2020). Over time, PTEs have the potential to mobilize, and new minerals, primarily oxides, may precipitate, starting from a supersaturated soil solution. Different soil fractions that were initially inert can become reactive due to changes in soil conditions (e.g., pH, moisture) or when their concentration exceeds the soil's sorption capacity (Yi et al., 2017).

It is estimated that the damage caused to the Ukrainian environment since the beginning of the Ukrainian-Russian war, as of March 10, 2023, amounts to about 2 trillion UAH. Specifically, according to resource allocations, they are as follows: UAH 11.8 billion for soil pollution and UAH 844 billion for littering the earth with 'war waste' (State Environmental Inspection of Ukraine, 2023; Neuter et al., 2022; Pereira et al., 2022). The degree of soil degradation is especially important since the Ukraine has one of the most fertile soil in the world, black soil. Although such soils are extremely resistant and self-healing, they can also accumulate heavy metals (Dmytruk et al., 2022). Gozak at al. (2023) determined that soils solution containing compounds of explosive substances penetrates into the roots of the plant without any obstacles or due to a large flow of water during evaporation. Compounds of explosive substances inside the roots move freely between the membranes, and eventually completely settle in the plant. Accumulation of Pb, Cu and Ni was confirmed in forage plants and lichens. As steam from the scientific research, the degree of soil contamination depends not only on the type of military weapons usage (missiles, guns, kamikaze drones, unmanned aerial vehicles, etc.) but also on the type of soils and environmental conditions (Golubtsov et al., 2023). The thought, a research carried out in various regions affected by military actions would enable a predicted assessment of soil destruction and possible ways of its restoration.

The main purpose of the research was to determine the degree of soil contamination from point rocket attacks in the districts of Lviv. The performed analysis was related to the detection of PTE and the characteristics of the magnitude of environmental risks associated with the war-affected area. Since, contaminated areas can exhibit huge variability in the distribution and content of metals, for detailed screening two different instrumental techniques were employed: direct analysis by XRF and indirect method based on microwave-assisted soil digestion followed by the extracts analysis by ICP-OES. The leachability and bioavailability of metal in the soils were analyzed by extraction in water and neutral ammonium citrate solution.

MATERIALS AND METHODS

Contaminated soil localization

For the study, 12 soil samples were collected from actual explosion sites of long-range X-101/X-555 cruise missiles. The cruise missile strikes occurred in industrial and residential areas as well. The sampling was done in three different districts of the city of Lviv (western Ukraine), approximately 60 km from the border with Poland (refer to Figure 1):

- Explosion E1: samples G1-G3 in the Zaliznychnyy district;
- Explosion E2 and E3: samples G4-G6 and G7-G9, respectively, in the Shevchenkiv district;
- Explosion E4: samples G10-G12 in the Stryiskyi district.

On the day of sampling, the prevailing meteorological conditions were characterized by overcast skies, with an average air temperature of 18°C and an air humidity level of 20%. The surveyed area predominantly comprises low-lying vegetation, including common trees, hosta, and gorse, as well as tree plantations featuring species like poplar, linden, alder, oak, and more (Petrushka et al., 2023).

Contaminated soil sampling

Soil samples were collected using a plastic spatula and placed in plastic (opaque) sealed containers. Sampling at each level was performed in concentric circles, with four mixed samples taken from each level in the concentric circles to allow for data averaging (Figure 2). Destructive soil disturbances were observed during the sampling process. As a result of the cruise missile impact, a crater with a diameter of 5 m and a depth of 5 m was formed. The employed soil sampling method provided the following information: concentration of substances at the center of the explosion, distribution of soil contamination that depends on the depth of the crater, and the pattern of contamination distribution (Petrushka K., Petrushka I., 2023).

Figure 1. Localization of contaminated soil sampling

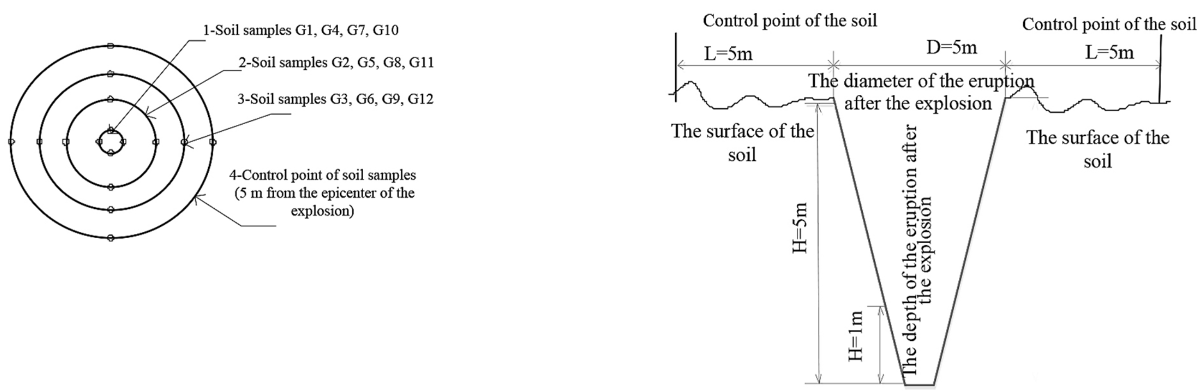

Figure 2. Methodology of soil sampling by concentric circles: Position 1, in the epicenter of the explosion at a depth of 5 m, samples G1, G4, G7, G10; Position 2, from the level of the 1st m from the epicenter of the explosion along a conical line, samples G2, G5, G8, G11; Position 3, from the level of 5 m on the surface of the explosion, samples G3, G6, G9, G12; Position 4, from the level of the soil surface at a distance of 5 m from the explosion, soil control samples

Soil samples analysis

Before undergoing analysis, the soil samples were first evenly spread on filter paper and allowed to air-dry for a period of one day at the surrounding ambient temperature. Following the drying process, the samples were carefully ground in a porcelain mortar and subsequently sieved to isolate the fraction with a diameter exceeding 250 µm. Finally, these prepared soil samples were placed in securely sealed plastic containers for further examination and analysis.

Chemical composition of soil samples

The chemical composition of the soil samples was determined through the use of the wavelength dispersive X-ray fluorescence technique, utilizing the Thermo Scientific ARL QUANT'X analyzer, which from Switzerland. This analyzer was equipped with the WinTrace software for data analysis. To ensure accurate results, the instrument was calibrated prior to the research, using reference samples of various elements. For the analysis, the prepared soil samples were loaded into the instrument's container, and the experimentation process had a duration of approximately 1.5 hours. The multielemental soil samples composition was assessed by ICP-OES technique (Varian Vista-MPX, Australia). Before analysis soil samples (0.5 g) were digested in a microwave digestion system (Start D, Milestone, Italy) using time-temperature programs (180°C, 21 minutes) with a two-acid ultrapure mixture of 7.5 mL HCl and 2.5 mL HNO_3 (Merck, Germany).

Extraction test

To assess the leachability and bioavailability of elements in the soils, extraction tests were conducted based on the current European standards EN 16962:2018 (water-soluble forms) and EN 15957:2011 (forms soluble in neutral ammonium citrate). The study allows predicting the leaching of elements (including heavy metals) into groundwater, and their potential transfer in the soil-plant system (Tuhy et al., 2013).

Water extraction

Soil samples (1 g) were weighed and transferred to an Erlenmeyer flask containing 110 mL of ultrapure water. The flask was then shaken on an orbital shaker (180 rpm) at ambient temperature for 30 min. After that, the sample was filtered and subjected to the ICP-OES multielement analysis.

Neutral ammonium citrate extraction

Soil samples (1 g) were weighed and transferred to an Erlenmeyer flask containing 100 mL of neutral ammonium citrate. The solution was shaken on an orbital shaker (180 rpm) at temperature of 65°C for 60 min. The filtered solution was then diluted to 250 mL and subjected to the ICP-OES multielement analysis.

Assessment of soil contamination

The evaluation of soil contamination was determined based on several key factors, including the contamination factor (E_r), environmental risk factor (C_f), potential environmental risk index (*RI*), and the geoaccumulation index (I_{geo}).

To ascertain the degree of metal enrichment, the ratio between the total metal content in the soil samples (C_s) and the background concentration (C_b) was employed, as suggested by Mugosa et al. (2016):

$$C_f = \frac{C_s}{C_b} \tag{1}$$

The degree of soil metal enrichment (C_f) was divided into four groups (Hakanson, 1980, Pekey et al., 2004): the first ($C_f < 1$) no metal enrichment; the second ($1 \leq C_f \leq 3$) moderate pollution; the third ($3 \leq C_f \leq 6$) significant pollution; the fourth ($C_f > 6$) very high pollution. The environmental risk (E_r) was calculated using the equation proposed by Hakanson (1980):

$$E_r = T_i \cdot C_f \tag{2}$$

$$C_f = \frac{C_i}{B_i} \tag{3}$$

where: T_i is the represents the Hakanson's toxic reaction coefficient for each specific metal (Cd - 30, Cu - 5, Pb - 5, Cr - 2, Zn - 1)); C_f is the pollution coefficient, indicating the level of pollutiont; C_i is the stands for the metal concentration in the analyzed soil sample; B_i is a reference value, which may vary depending on the context and the specific term used, such as background level or baseline level. These coefficients and factors are essential for assessing the contamination and potential environmental risks associated with the presence of specific metals in the soil.

The environmental risk factor (E_r) serves as a valuable indicator to gauge the impact on the environment, with specific thresholds indicating the level of risk. In this classification system: E_r<40 signifies a low environmental risk; 40≤ E_r < 80 suggests a moderate level of risk; 80≤E_r<160 indicates a significant risk to the environment; 160 ≤ E_r < 320 points to a high level of risk; E_r ≥ 320 reflects a very high environmental risk.

This risk factor was originally designed for monitoring water pollution but has also been applied to assess environmental soil contamination, particularly in cases involving heavy metals. It allows for a quick assessment of the potential environmental impact of various pollutants, helping guide appropriate remediation and management actions. The index of potential environmental risk (R_i) is calculated by summing the individual risk factors for different factors or parameters (Equation 4).

$$R_i = \sum E_r \quad (4)$$

where: R_i accounts for the toxicity of heavy metals and the environmental response to all five risk factors (Pb, Cd, Cu, Zn, and Cr) in the studied soils (Dong et al., 2010). The potential risk index (R_i) is typically categorized as follows to provide a clearer understanding of the level of risk: R_i<150 indicates a low level of potential risk; 150 ≤ R_i < 300 suggests a moderate level of potential risk; 300 ≤ R_i < 600 indicates a significant level of potential risk; R_i ≥ 600 reflects a very high level of potential risk. This classification system helps in assessing and communicating the overall potential environmental risk based on the combined influence of various factors or parameters. It offers a useful framework for evaluating the significance of the potential environmental impact in a given area or situation.

The confirmation of the environmental risk factors was done by comparison with the *NIPI* and *NIRI* methods. To do so, the following approach for *NIPI* was developed (Men et al., 2019, Wang et al., 2014, Yang et al., 2011, Fang et al., 2019):

$$NIPI = \sqrt{\frac{(PI_{ave}^2 + PI)_{max}^2}{2}} \quad (5)$$

$$PI = \frac{C_i}{S_i} \quad (6)$$

where: C_i is the concentration of heavy metals in the soil sample; S_i is the maximum allowable concentration of the element in the soil; PI_{ave}, PI_{max} is the average and maximum, respectively, values of the element concentration (mg/kg).

A priori, when calculating the complex environmental risk according to the *NIPI* method, the elements' toxicity factors are not taken into account. Therefore, to confirm the reliability of the obtained experimental results, the complex ecological risk of the influence of the studied elements on the environment was calculated according to the *NIRI* method. The introduction of the toxic influence factor and differentiation of the influence of heavy metals, resulted in the following equation:

$$NIRI = \sqrt{\frac{(E_{rmax}^2 + E_{raverage}^2)}{2}} \quad (7)$$

The impact of each of the sources of pollution on the risk can be assessed by dividing the risk. In risk allocation, the new *NIRI* assessment method and source allocation by *RAp* were combined. Types and contributions to heavy metal concentrations were imported into the *NIRI* equation, giving:

$$RAp = \sqrt{\frac{(RA_{ip\ max}^2 + RA_{ip\ average}^2)}{2}} \quad (8)$$

$$RAip = T_r^i \cdot \frac{C_{ip}}{S_i} \quad (9)$$

where: *PI* – concentrations of the studied elements in a soil sample; *RAp* is the value of the risk factor; $RAp_{ip\ max}^2$ – the maximum value of the risk factor; $RA_{ip\ average}^2$ – the value of the risk factor. The classification of the ecological safety factors is provided in Table 1.

The geoaccumulation index (I_{geo}) is typically calculated using the equation proposed by Müller (1969):

$$I_{geo} = \log_2\left[\frac{C_r}{1{,}5 \cdot C_{ri}}\right] \quad (10)$$

where: C_r is the measured concentration of the metal in the study soil; C_{ri} is the geochemical background concentration, or reference value for that metal.

The coefficient of 1.5 is utilized to account for potential variations in background values for a given metal in the environment and to accommodate very minor anthropogenic influences. The resulting Igeo values are then categorized into seven

Table 1. Classification of ecological safety factors (Men et al., 2019)

Index	Category		Description
NIPI	*NIPI* ≤ 0,7 0.7 < *NIPI* ≤ 1 1 < *NIPI* ≤ 2 2 < *NIPI* ≤ 3 *NIPI* >3	*PI* ≤ 1 - 1< *PI* ≤2 2 < *PI* ≤ 3 *PI* > 3	Unpolluted Warning limit of pollution Low polluted Moderately polluted Strongly polluted
Ri	*Ri* ≤ 150 150 < *Ri* ≤ 300 300 < *Ri* ≤ 600 *Ri* > 600 -	E_r^i ≤ 40 40< E_r^i ≤ 80 80 < E_r^i ≤ 160 160 <E_r^i ≤320 E_r^i> 320	Low risk Moderate risk Significant risk High risk Extreme risk
NIRI	*NIRI* ≤ 4 0 40 < *NIRI* ≤ 80 80 < *NIRI* ≤ 160 160 < *NIRI* ≤ 320 *NIRI* > 320	E_r^i≤ 40 40 < E_r^i ≤ 80 80 < E_r^i ≤ 160 160 < E_r^i ≤ 320 E_r^i > 320	Low risk Moderate risk Significant risk High risk Extreme risk

classes to assess the degree of contamination: class 0: I_{geo} ≤ signifies uncontaminated conditions; class 1: 0 < I_{geo} ≤ 1 suggests uncontaminated to moderately contaminated conditions; class 2: 1< I_{geo} ≤2 indicates moderately contaminated conditions; class 3: 2 <I_{geo} ≤3 represents moderately to heavily contaminated conditions; class 4: 3 <I_{geo} ≤4 reflects heavily polluted conditions; class 5: 4< I_{geo} ≤5 suggests heavily to extremely polluted conditions; class 6: I_{geo} >5 designates extremely polluted conditions. These classes help in characterizing the extent of contamination and provide a useful framework for assessing the environmental impact of metal accumulation in the soil.

RESULTS

Elemental composition of soil

Results of XRF analysis

The content of PTEs (XRF analysis) in the soil samples is presented in Figure 3. For better visualisation the elements were grouped according to their concentration. As steam from the results obtained from the XRF analysis, the elements can be arranged in the following sequence by the magnitude of their concentration in soil samples: Ti > Zr > Zn > Cu > Pb > Sr > Ni > Cr. In the studied areas of rocket fire in the city of Lviv (May - October 2022), an excess of the maximum permissible concentrations (MPC) according to European standards was found (Alengebawy et al., 2021) for Cu up to 2.6 times (sample G12); for Ni up to 1.3 times (sample G12); for Cr up to1.15 times (sample G12); for Pb up to 2.5 times (sample G8); for Sr up to 1.7 times (sample G12). The highest exceedance of MPC was found for Zn up to 4.6 times, and for Zr and Ti up to 5 times (samples G1, G12, respectively).

Results of ICP-OES analysis

The Figure 4 in question presents the total content and descriptive statistics for the six heavy metals that were investigated at the rocket explosion sites. These statistics typically include values such as the minimum and maximum concentration levels, as well as the average or mean values for each of the heavy metals being analyzed. This information helps provide an overview of the metal content in the soil samples taken from the areas affected by rocket explosions. The order of the elements content in the soil samples is as follows: Zn>Cu>Pb>Cr >Cd >Ni. The data obtained revealed the presence of Cd in soil samples up to 4 times excess of the maximum permissible concentration in the Shevchenkiv district (points DII, DIII). The heavy metals distribution maps (Fig. 4) were obtained by using the ArcGIS software and the Inverse Distance Weighted (IDW) interpolation method. The data depicted identified spatial variations of heavy metals distribution in different soil samples. This indicates the natural variability of concentrations of the elements. The color intensity identified that the soil sampled from DII and DIII was the most contaminated with heavy metals. It probably results from the nature of the point shelling infrastructure focused on energy facilities.

Metals extraction from soil

The contamination of agricultural soils represents a significant environmental concern, given

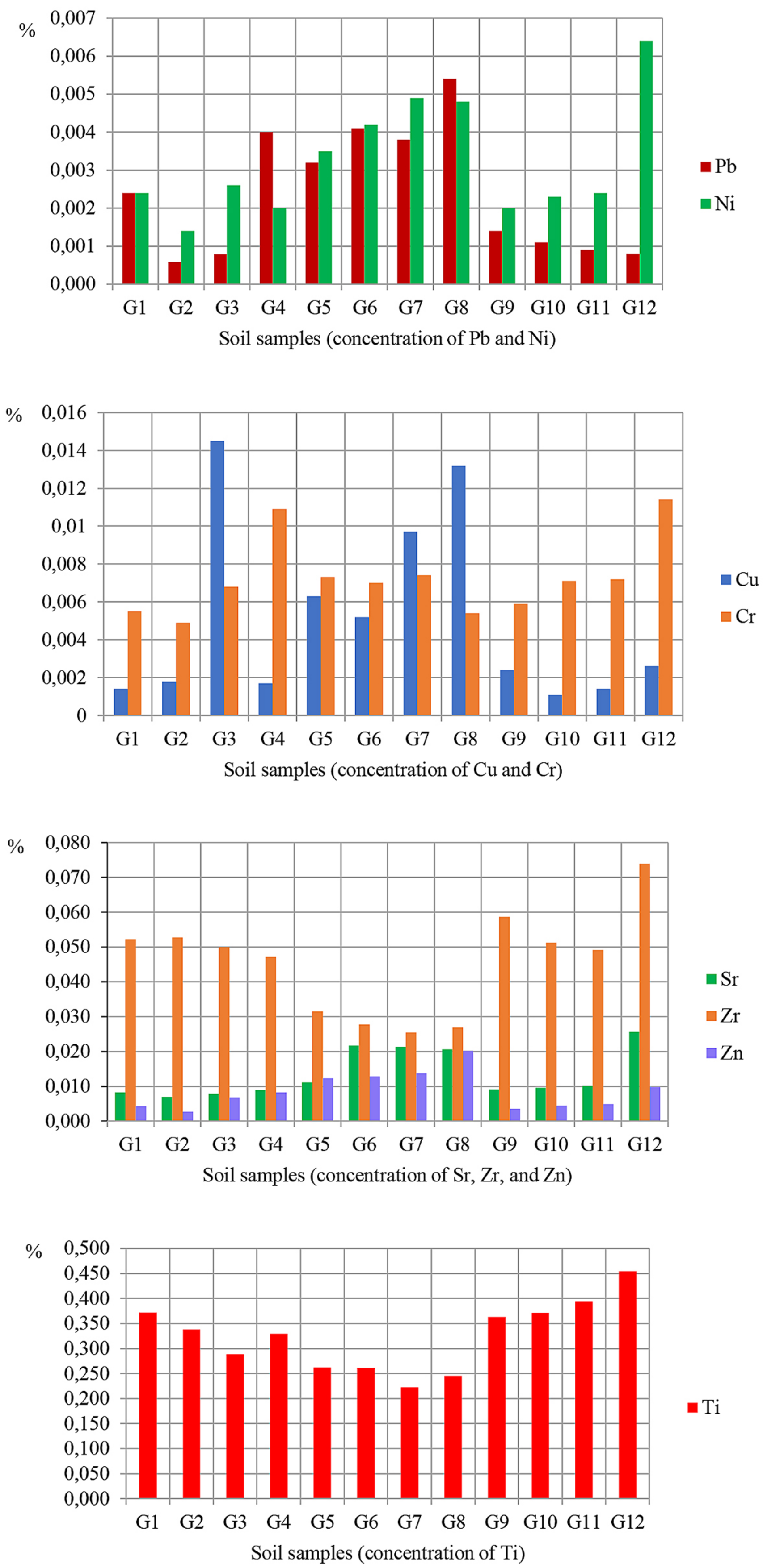

Figure 3. Elemental composition of analyzed soil samples (XRF); contaminated sites: E1 (G1, G4, G7, G10); E2 - (G2, G5, G8, G11); E3 (G3, G6, G9, G12); E4 control point of soil samples

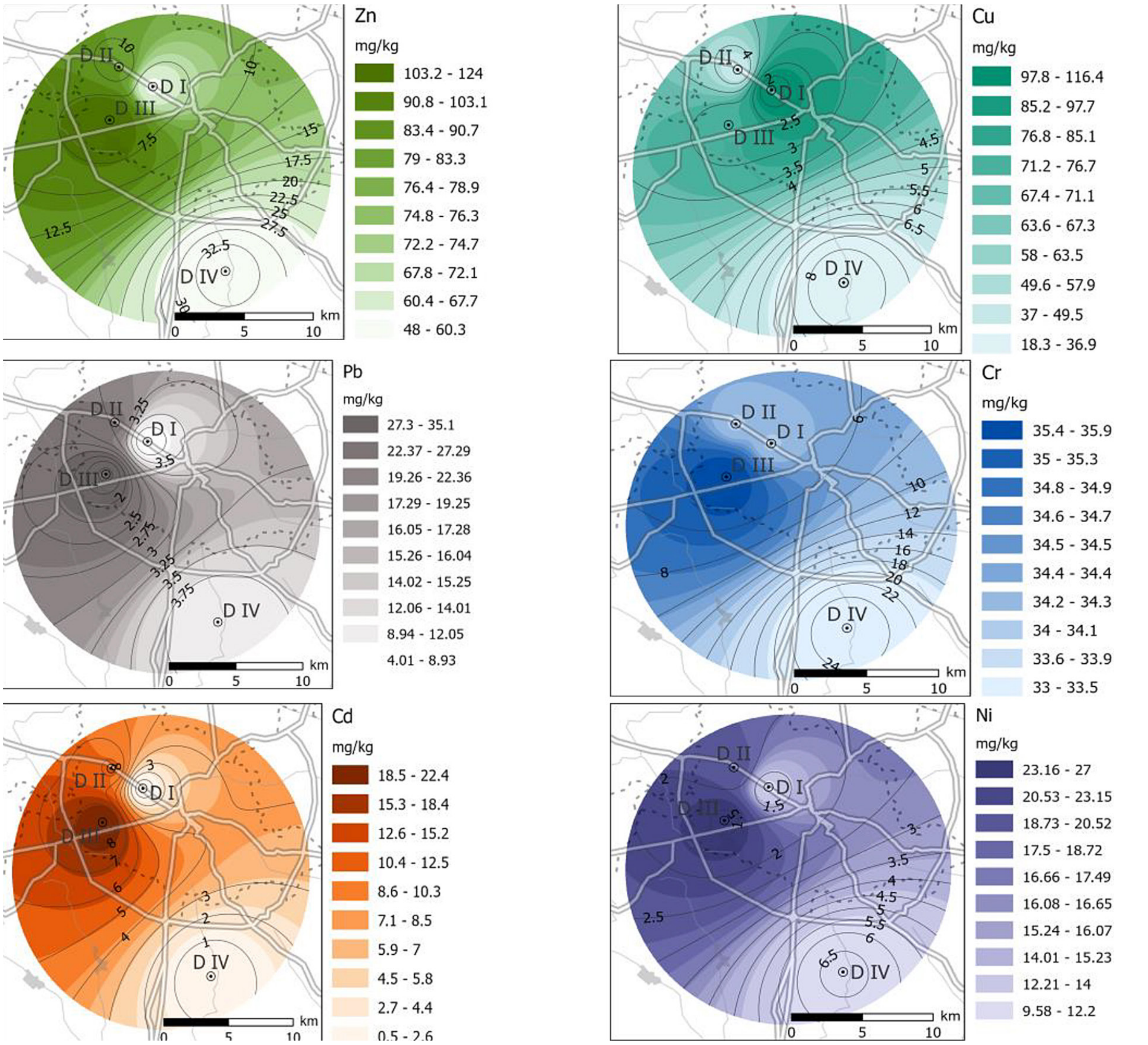

Figure 4. Elemental distribution of PETs in soil samples (ICP-OES analysis)

its impact on crop quality and its potential to affect human health through the accumulation of contaminants in the food chain (Liu et al., 2020). Figure 5 displays the content of contaminants in the soil samples, highlighting the elevated levels of zinc (Zn), lead (Pb), copper (Cu), nickel (Ni), and chromium (Cr). Notably, in the case of lead (Pb) and zinc (Zn), their content exceeds that of the control sample in certain instances. While the total metal content in the soil serves as a crucial parameter for assessing soil quality, it doesn't provide insights into the risks associated with the mobility of these metals (Wieczorek et al., 2023). The mobility of metals depends not only on the chemical forms of the contaminants but also on soil properties such as pH and redox state. Ionic and carbonate forms are among the most mobile, while elements bound to silicates or primary minerals exhibit lower mobility (Wang et al., 2022). Understanding these factors is essential for evaluating the potential impact of soil contamination on both the environment and human health.

To assess the potential mobility of the components under real conditions, extraction tests were performed in water and neutral ammonium citrate. The data obtained from extraction tests are presented in Figure 6. As can be seen, Pb is practically not leached out by water from the soil. The bioavailability of Pb depends strictly on the solubility of Pb solid phases and other site-specific soil chemistry (Hettiarachchi & Pierzynski, 2004). The concentration of all other elements in the water was within the range of 0.0030 – 0.054 mg/L (Fig. 6). The minimum presence of the other elements in water follows the order: Cr>Zn >Cu>Cd. The extraction of elements in neutral ammonium citrate is significantly higher compared to the water one. This means that although the contaminants are not in water-soluble forms, they are still available to plants. The highest concentrations were recorded for Zn, Pb and Cd. This can result in their accumulation in biomass and consequently lead to their long-term toxic effect on the environment.

Ecological risk of the polluted soil

The results of calculations for the soil pollution coefficient (C_f), environmental risk factor (E_r), potential ecological risk index (R_i), and geoaccumulation index (I_{geo}) for each measured element are presented in Table 2. The highest value of the soil contamination factor (C_f) was found for Cu at the surface of the explosion crater. Pb and Zn also showed moderate contamination at the surface of the pit. No metal enrichment was observed for Cr and Cd at any of the measured sites. The sequence of metal enrichment in the studied soil was as follows: Cu>Zn>Pb>Cr>Cd. In terms of the environmental risk factor (E_r), all elements except Cu are in the low-impact zone, indicating a moderate impact of Cu on the environment. The numerical values of the potential environmental risk index (R_i) for the studied elements below 300 correspond to low and moderate risk. Only in one sample case, the environmental Cu risk index reached 58.2. It is worth to mentioning that Cu in concentration above 3.0 mg/kg is highly toxic and can cause tissue damage, changes in root cell elongation, alterations in membrane permeability, and inhibition of electron transfer during photosynthesis. The geoaccumulation index (I_{geo}) suggests moderate soil contamination with copper (Cu) based on a numerical value of 1.78. Zn and Pb also fall within the class of moderate pollution ($1< I_{geo}<2$). Based on the applied *NIPI* method, the calculated environmental risk assessment factor is 49.001 (*NIPI* >3), indicating a highly polluted territory (according to the classification presented in Table 1). On the other hand, when considering the *NIRI* method, the calculated value is 54.94 (*NIRI*< 80), indicating a moderate risk for the environment. Figure 7 provides a graphical representation of the ecological risk (E_r) factor for each element analyzed. The highest risk is observed for Cr. The toxicological properties of Cr (VI) are particularly concerning due to its carcinogenic and mutagenic effects. Based on the magnitude of the environmental risk factor, the elements can be ranked as follows: Cr>Zn>Cd>Cu>Pb.

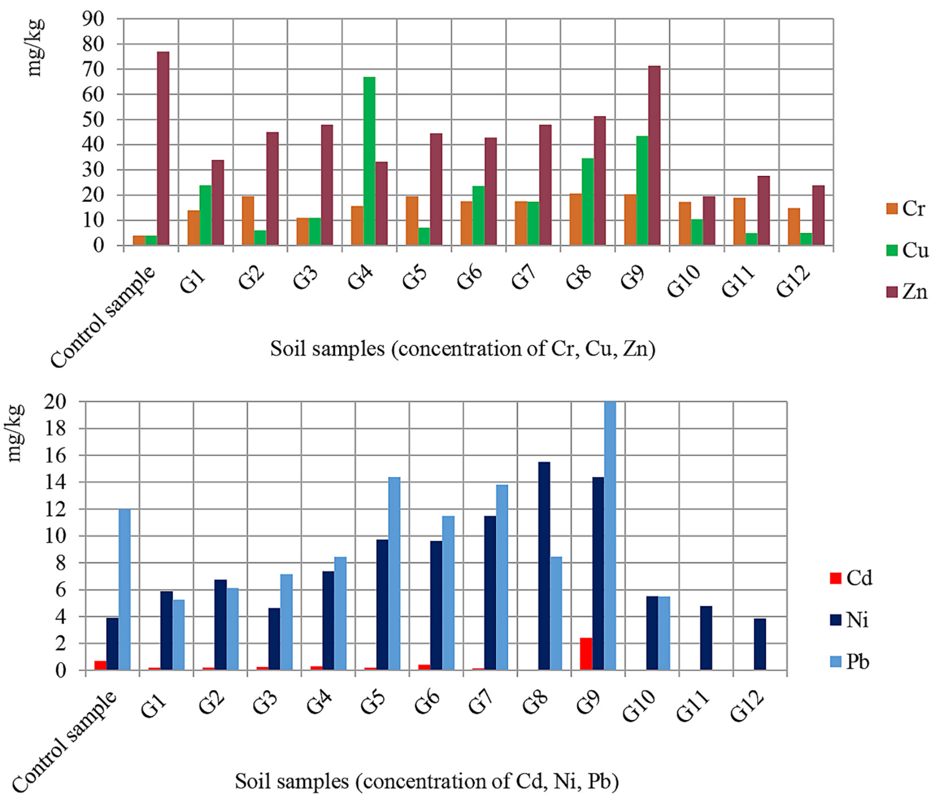

Figure 5. The content of elements in the soil samples; E1 (G1, G4, G7, G10); E2 (G2, G5, G8, G11); E3 (G3, G6, G9, G12); E4 control point of soil samples

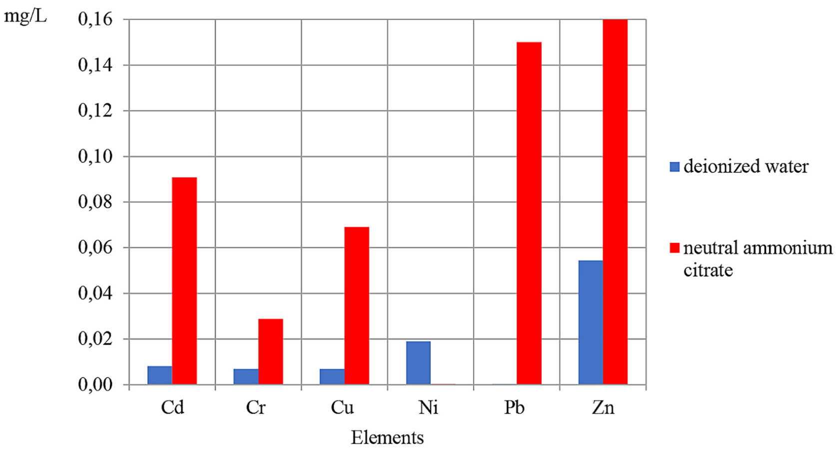

Figure 6. Extraction of heavy metals from soil samples – water and neutral ammonium citrate soluble forms

DISCUSSION

The heavy metals content (mainly Ti, Zn, Zr, Cu, Pb, Cr, Sr, and Ni) in the analyzed soil samples was up to 5 times higher in comparison with the standard of the permissible content (Alengebawy, 2021; Tomic et al., 2018; Bordeleau et al., 2008; Meerschman et al., 2011). The identified heavy metals in the soil sampling after the shelling by missile strikes of the surroundings of the city of Lviv is similar to the samples taken from the sites of hostilities in the Donbas region (Ukraine) struck by of small arms, artillery and rocket bombardments (mainly Cd, Pb, Cu, Zn). They mostly exceeded the background value by 3–6 times, sometimes up to 25 times.

The data presented confirmed the an unpredictable nature of the impact of the studied elements

Table 2. Values of Contamination Factor (C_f), Environmental Risk Factor (E_r), Geoaccumulation Index (I_{geo}), and Environmental Risk Index (*Ri*) for specific heavy metals in soil collected during environmental surveys

Descritiv statistics	Element				
	Pb	Cd	Cu	Zn	Cr
MAC	20	3	10	50	100
Max	35.1	0.714	116.4	124	35.9
Min	4	0.4	8.51	21.8	19.1
Mean	14.48	0.32	36.44	62.94	30.55
$C_f$max	1.755	0.238	11.64	2.48	0.359
$C_f$min	0.08	0.008	0.1702	0.436	0.382
C_f mean	0.2896	0.0064	0.7288	1.258	0.611
E_r max	8.775	7.14	58.2	2.48	0.718
E_r min	0.4	0.24	0,851	0.436	0.764
E_r mean	1.448	0.192	3.644	1.258	1.222
$R_i$max	77.13				
R_i min	2.691				
$R_i$mean	7.765				
I_{geo} max	0.13	< 0	1.78	0.44	< 0
I_{geo} min	< 0	< 0	< 0	< 0	< 0
I_{geo} mean	< 0	< 0	0.78	< 0	< 0
NIPI	49.001				
NIRI	54.941				
R_{ap}	54.815				

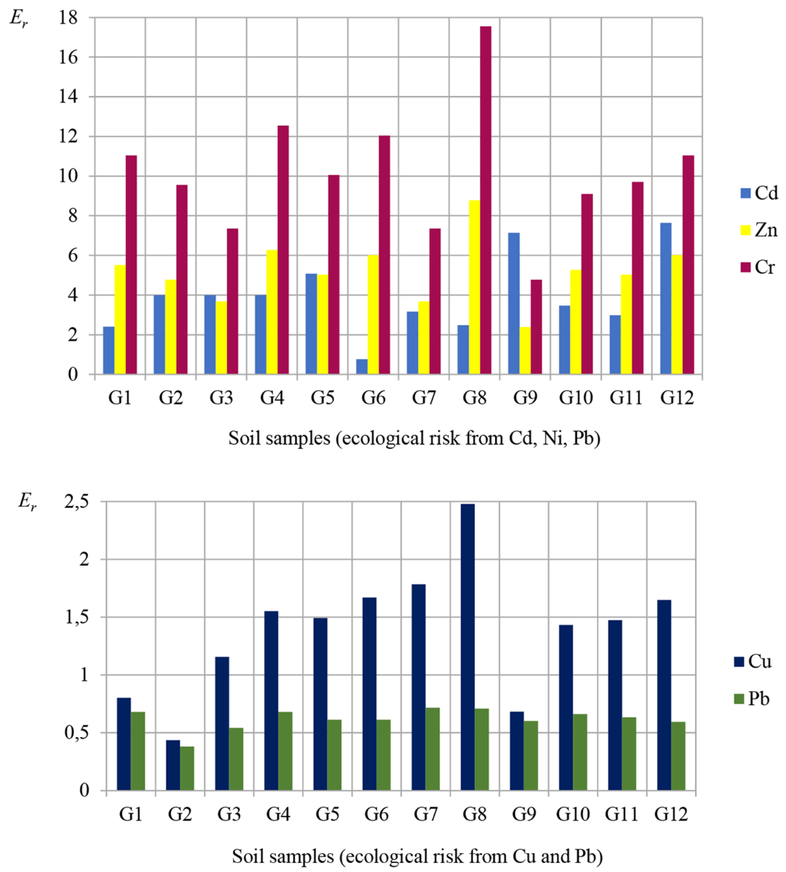

Figure 7. The value of the ecological risk factor (E_r) of heavy metals in soil samples: E (G1, G4, G7, G10); E2 (G2, G5, G8, G11); E3 (G3, G6, G9, G12).

on the environment since heavy metals are characterized by accumulation rather than biodegradation (Broomandi et al., 2020). The performed extraction tests identified the water-soluble and non-water soluble forms of heavy metals, which can be available for plants. The excess of heavy metals, particularly Zn, Pb, Cd, Cr, and Ni, was found in the analyzed biomass as well. The same elements were also identified in a terrestrial biomass sampling from the Milovice-Mlada military base (Czech Republic) (Sladkova et al., 2015).

Numerous research highlighted the significant anthropogenic impact of PTEs on soil in military and war-affected areas (Knechtenhofer et al., 2003; Meerschman et al., 2011; Okkenhaug et al., 2016). Quantitative comparison of the heavy metals content is usually done with the reference soil samples such as agricultural soil, industrial soil, urban and/or recreational soil (Bausinger et al., 2007; Denton et al., 2016; DOG, 2009, Lafond et al., 2012; Lafond et al., 2014; Sladkova et al., 2015; Rajapaksha et al., 2015), or military training ground soil (see tabular summary in Table 3). The comparison of the data depicted identified a much higher content of Zr in the investigated soil samples. This is likely due to the utilization of Zr as an ingredient in numerous alloys used in rocket production and other aerospace applications. Combining zirconium with other metals in alloys enhances technical characteristics, increases fire resistance, and improves the piezoceramic properties of materials. Moreover, Zr addition to an allow enhances the material's ability to withstand various aggressive environments (Pichtel et al., 2016, Broomandi et al., 2020). The presence of Sr can result from the following salts: $Sr(ClO_4)_2$ and $Sr(NO_3)_2$. Both compounds are employed in liquid-injected thrust vector control systems of rockets to facilitate rudder control through a fixed nozzle mechanism and enhance the corrosion resistance of cruise missile hulls. In terms of Cd, this element is present in all of the collected samples, with a maximum concentration 3.5 times higher than that found in the soil data from the hostilities in Bosnia. The concentrations of Cr and Zn in the studied soil fall within the average range of environmental impact. The amount of lead found in the investigated soil is comparable to the data

Table 3. The concentrations of common PTEs in the soil from areas affected by military operations and war are typically measured in milligrams per kilogram (mg/kg)

Site	Activity	Cd	Cr	Cu	Ni	Pb	Ti	Zn	Zr
Croatia 1991-1995 (Broomandi et al., 2020)	War-impacted	0.13	32		19	17	-	53	-
Bosnia (Tomic et al., 2018)	Military base	0.8-6.1	-	23.6-443	40.4-73.6	27.7-40.9		91.7-238	
Switzerland (Knechtenhofer et al., 2003)	Military base			63-66	55–61	500-620	-	100-110	-
Norway (Yang et al., 2011)	Military base	-	-	4-88	-	356-1112	-	-	-
Spain (Okkenhaug et al., 2016)	Military base	-	40-79	19-98	11-33	55-6309	-	34-264	-
Czech republic (Sladkova et al., 2015)	Military base	0.235	18.4	6.91	10.7	15.5	-	34.3	-
Ukraine, Lviv region (Environment of Lviv region, 2018)	War-impacted G1-3, explosion 1	0.508	34.1	116.4	12.8	14.7	824	57.9	52.4
	War-impacted G4-6, explosion 2	0.714	34.1	41.1	16.9	25.1	712	77.6	66.5
	War-impacted G7-9, explosion 3	2.15	35.9	75.7	27.0	24.1	526	124.1	43.2
	War-impacted G10-12, explosion 4	0.451	32.9	18.2	8.31	35.1	816	47.9	76.4
Lviv before the war (Pozniak, 2019)		0.363	0.68	1.62	-	2.1	21	49	-

from military operations in Croatia between 1991 and 1995. Based on the value of the environmental risk factor (E_r) of the investigated heavy metals in the soil samples, they can be arranged in the following toxicity sequence: Cr>Zn>Cd>Pb>Cu. On the other hand, analyzing the geoaccumulation index (I_{geo}) for each studied element, it can be concluded that there is moderate soil contamination with Cu. The calculated index values for Zn and Pb also fall within the range of moderate pollution ($1< I_{geo}<2$). The coefficient of environmental risk assessment according to both the *NIPI* and the *NIRI* methods indicated that the studied area falls into the heavily 3-19 polluted category.

CONCLUSIONS

The military action in Ukraine has grave consequences for the biosphere, particularly the destruction and degradation of soils, which suffer a significant negative impact due to the hostilities. All soil samples collected exceeded the maximum permissible concentrations of heavy metals. The soil samples taken after the explosion in the railroad and Stryiskyi districts (G7-9 and G10-12) were found to be the most contaminated. Experimental data obtained confirm that all soil samples show a few times higher Ti, Zn, Cu, and Ni concentrations than the permissible standards. As it was confirmed, the excess of these elements hampers plant growth by around 5-10%. The extraction of Zn, Cu, Cr, and Cd from the soil by using ammonium citrate solution demonstrated the metals presence in non-water-soluble forms, which allowed their availability to plants and consequently accumulation in biomass. The comprehensive analysis of the various environmental indicators and risk factors allowed to identify the degree of soil contamination and its impact on the environment. The presented case study on the impact of military operations in a specific region of Ukraine highlighted a serious threat to public safety and posed a significant health hazard to the population.

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