JEE *Journal of Ecological Engineering*

Journal of Ecological Engineering 2023, 24(10), 77–85
https://doi.org/10.12911/22998993/170078
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Received: 2023.07.04
Accepted: 2023.07.26
Published: 2023.08.19

Assessment of the Impact of Military Actions on the Soil Cover at the Explosion Site by the Nemerov Method and the Pearson Coefficient Case Study of the City of Lviv

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ABSTRACT

The military actions of the Russian Federation's aggression in Ukraine cause irreparable damage to the soil cover, realizing that its natural restoration will take decades. However, missile attacks on residential areas bring no less damage and trouble to Ukraine. The main goal of the conducted research was to determine the content of potentially toxic elements (PTE) in the soil at the site of the explosion and on its surface. Soil sampling was carried out at the explosion sites of the city of Lviv using the method of concentric circles. The soil research area is 30–50 m^2 (depending on the type of cruise missile), which allows assessing the distribution of PTE relative to the depth of the crater and on its surface. The soil samples were analyzed by X-ray fluorescence analyzer Expert-3L. The main studied elements were Cd, Cr, Cu, Ni, Pb, and Zn. The pollution index (*Pi*) was estimated using the Nemerov method. The degree of soil pollution was assessed by the ecological risk factor (Er), and the potential ecological risk index (Ri). Using the Pearson correlation index (PCI), their number and the possibility of distribution of heavy metals (*HM*) in the soil were determined. Similarity between levels of heavy metal concentrations was determined using cluster analysis (CA). The values of the environmental risk index of each element based on the Nemerov index show a very high level of pollution (Ps=48.64), exceeding the permissible value of Ps>3 by 15 times. The highest environmental risk factor (*Er*) is created by cadmium (Cd). The investigated elements concerning the environmental risk factor can be arranged in the following sequence: Cd>Cu>Pb>Ni>Zn>Cr>Ti. Considering the minimum values of potential environmental risk (*RI*), only two elements have a low coefficient of potential environmental risk ($RI<40$)—titanium and chromium. All other investigated elements have significant and very high environmental risk potential.

Keywords: soil, heavy metals (*HM*), migration, environmental risk, the Nemerov index.

INTRODUCTION

Recent military operations in Ukraine have made our country one of the countries most polluted by ammunition in the world. The aggressor (the Russian Federation) has already caused and continues to cause enormous damage to the population and infrastructure of settlements where hostilities continue. However, war also affects the environment. It is currently impossible to fully assess the impact of military and terrorist actions on the environment because of the lack of accurate information. However, it is well known that explosions of cruise missiles and artillery shells in the ground cause the formation of a number of chemical compounds: carbon monoxide (CO), carbon dioxide (CO_2), water vapor (H_2O), brown gas (NO), nitrous oxide (N_2O), nitrogen dioxide (NO_2), formaldehyde (CH_2O), cyanic acid vapors (HCN), nitrogen (N_2), as well as numerous toxic organic substances that oxidize surrounding soils, wood, peat, and buildings. Metal fragments of projectiles that fall into the environment as a result of an explosion on the surface of the ground and at the epicenter are also dangerous and can interact with the chemical elements of the soil. The main material for the production of ammunition is cast iron with steel impurities, which contains carbon, sulfur and copper. These substances infiltrate the soil and groundwater and, as a result, enter the food chain, affecting both animals and humans. On a smaller scale of anthropogenic impact on the environment, but with a wider spectrum of influence, there is decommissioned military heavy equipment, aircraft and other remnants of hostilities. Besides the fact that explosive devices that did not explode during shelling are dangerous, they enter a chemical reaction with other elements, which causes the contamination of the soil and, therefore, groundwater and the atmosphere.

Environmental pollution by (*HM*) is a global problem since they are persistent, and most of them have toxic effects on living organisms when the limit concentration is exceeded (Chakraborty et al., 2009). The toxicity of a metal is usually determined by the concentration necessary for the reaction to occur (Smith, 1986; Onder et al., 2007; Page et al., 1982). The quality of the urban environment is of vital importance, as most people now live in cities. Because of continuous urbanization and industrialization in many parts of the world, metals are continuously released into the Earth's environment and pose a great threat to human health (Lee et al., 2006; Adriano, 2001). Urbanization of territories leads to the replacement of natural ecosystems with artificial ones, which have a significant chemical, physical and mental impact on people (Al Obaidy and Al Mashhadi, 2013; Davydova, 2005).

With the development of mankind, wars began to be more "developed" in terms of the usage of modern weapons. As a result, the scientific direction "War and Ecology" appears. Any war inflicts a heavy blow on the ecology of the area where hostilities take place. Military actions lead to a number of negative environmental consequences (Al-Adili, 1998; Imevbore and Adeyemi, 1981).

Military conflicts dangerously affect the state of soils and landscapes, surface and underground waters, vegetation and animal life; hostilities significantly increase the risks of emergencies at industrial enterprises and infrastructure facilities. Conflicts occurring in industrialized areas with a large number of environmentally hazardous enterprises and facilities pose a particular danger to the environment (OSCE, 2017).

Many scientific works are focused on the anthropogenic impact of toxic metals on the environment. However, at present, as a result of the terrorist attacks of the Russian Federation on the territory of Ukraine, there has been a need to forecast the consequences of military actions on the environment of Ukraine (Blaga et al., 2017).

MATERIALS AND METHODS

Localization and selection of soil samples

The actual material of soil samples from the site of the explosion of cruise missiles in Lviv in 2022 was used for the research. During the research, 12 soil samples were taken. This method of soil sampling allows obtaining the following information: the concentration of substances in the centre of the explosion, the distribution of soil contamination depending on the depth of the funnel and the form of pollution distribution.

In this case, four samples were taken (at the epicentre of the explosion, at a depth of 1 meter and on the surface – 5 meters from the epicentre) in concentric circles, which were then mixed to obtain averaged results (Fig. 1):

1. The epicentre of the explosion (depth of the eruption – 5 meters) – soil samples – G1, G4, G7, G10;

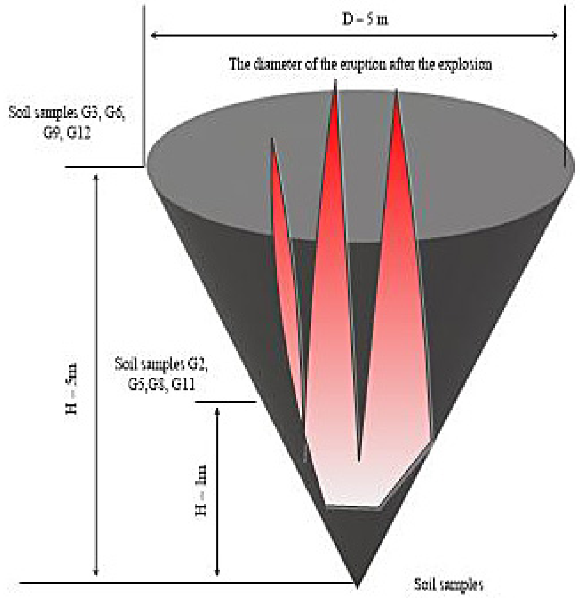

Figure 1. Methodology of soil sampling by concentric circles

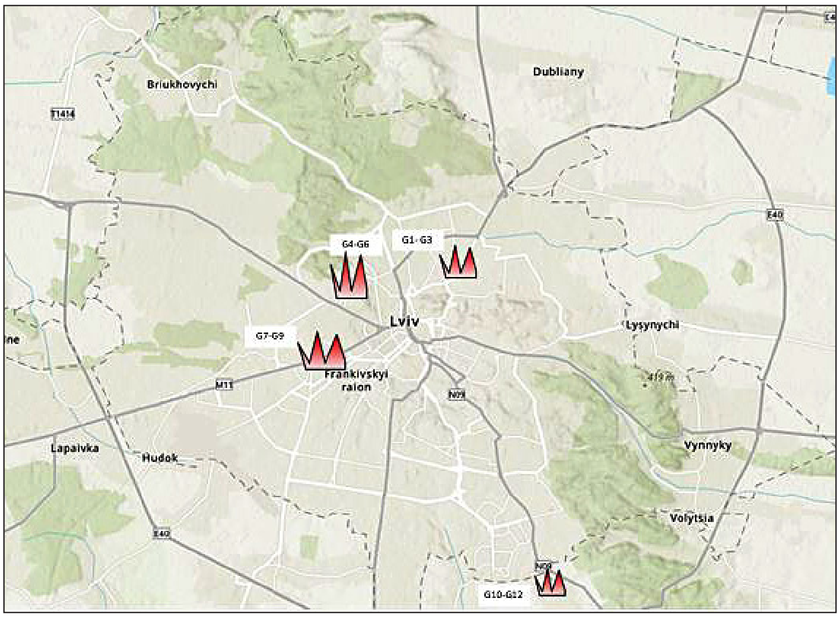

Figure 2. Map of soil sampling in 2022 on the territory of Lviv

2. At the level of the first meter from the epicentre of the explosion (along a conical line) – soil samples – G2, G5, G8, G11;
3. At the level of 5 meters from the epicentre of the explosion (along a conical line on the surface) – soil samples – G3, G6, G9, G12;

Sampling at each of the levels was carried out in concentric circles. Four samples were taken from each level in concentric circles to be able to average experimental data. The map of soil sampling in 2022 on the territory of Lviv is shown in Figure 2.

According to the standards of sampling, to detect heavy metal ions by chemical analysis, samples were taken with a plastic spatula. They were placed in a plastic (opaque) airtight container. The samples were prepared for analysis at the laboratory. The soil was spread evenly on paper and crushed, if necessary. Then, the samples of the studied soil were ground in a porcelain mortar and sieved through a sieve with holes with a diameter of 1 mm.

For further chemical research, each sample was placed in a drying cabinet to remove residual moisture at a temperature of 105 °C. After drying, the soil samples were placed in a sealed opaque plastic container.

Analysis of contaminated soil samples

The study of soil samples after the impact of cruise missiles on the territory of Lviv from April 2022 to October 2022 was carried out on an Expert-3L mobile X-ray fluorescence analyzer. To increase the sensitivity to “light” elements (Na, Mg, Al, Si), the analyzer is equipped with a system for blowing the collimator channels with helium. The thermal printer built into the system allows displaying the received data on the screen. Expert-3L can simultaneously determine the mass percentage of chemical elements in samples from magnesium to uranium and estimate the carbon content in steels and cast irons.

Assessment of soil contamination by (*HM*) according to the Nemerov index

The Nemerov index (Ps) and the ecological risk index (RI) of the levels in the selected soil samples were used to assess soil contamination with (*HM*). Reference values (average values of heavy metal concentrations in the soil) of the studied metals, which were used as background, were taken from Riley and Chester (Table 1) (Riley and Chester, 1971).

Table 1. Reference values of concentrations of heavy metals in the studied soil (average values) of the studied metals, which were used as background (mg/kg)

Elements	Cd	Cr	Cu	Ni	Pb	Zn	Ti
Maximum allowable concentrations (mg/kg)	0.2	100	55	75	12.5	70	5.7

The soil quality assessment of the studied area was carried out using the composite index method (Nemerov index) according to (Liang et al., 2011). In the composite index method, the P_i was used, which best reflects the indicators of environmental pollution:

$$P_i = \frac{C_i}{C_{ref}} \tag{1}$$

where: P_i is a unit pollution index;
C_i is the mean concentration of (*HM*) from at least three sampling sites;
C_{ref} indicates the value of the evaluation criteria (Hakanson, 1980).

The method of complex Nemerov index (Ps) takes into account all individual evaluation factors from (2), and also emphasizes the dominant nature of the negative environmental impact of the elements that are present in the samples.

$$P_S = \sqrt{\frac{(P_{ave}^2 + P_{max}^2)}{2}} \tag{2}$$

where: P_{ave} is the average value of a separate P_i of all metals;
P_{max} is the maximum value of a separate P_i, the pollution index of all metals.

The quality of the soil environment according to the levels of the Nemerov index is classified into five levels (Cheng et al., 2007): (Ps < 0.7, safe area; 0.7 ≤ Ps < 1.0, caution area; 1.0 ≤ Ps < 2.0, lightly polluted area; 2.0 ≤ Ps < 3.0, moderately polluted area; and Ps > 3.0, heavily polluted area).

The *RI* index method proposed by (Hakanson, 1980) for the evaluation of heavy metal pollution from the point of view of sedimentology was applied to estimate the level of heavy metal pollution in soils as a result of military operations, as well as to calculate ecological risks according to their toxic effects on the environment (Qu et al., 2004).

Although the risk factor was originally used as a diagnostic tool for water pollution control, it has been successfully employed to assess the quality of precipitation and soil from the point of view of heavy metal contamination (Qingjie et al., 2008).

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

$$Er = T_r^i \cdot P_i \tag{4}$$

Table 2. Value of environmental risk indicators (Riyad Al-Anbariet al., 2015)

Er	Individual coefficient of potential environmental risk
Er < 40	Low - low coefficient of potential environmental risk
40 ≤ Er < 80	Moderate – moderate coefficient of potential environmental risk
80 ≤ Er < 160	Considerable - significant coefficient of potential environmental risk
160 ≤ Er < 320	High-risk potential
Er ≥ 320	Significantly very high

Table 3. Limit values of integrated (*RI*)

RI	Complex potential environmental risk
RI < 90	Low potential environmental risk
90 ≤ RI < 180	Moderate potential environmental risk
180 ≤ RI < 360	Hight potential environmental risk
360 ≤ RI < 720	Very high environmental risk potential
RI ≥ 720	Significantly high environmental risk potential

where: Er is the individual coefficient of potential environmental risk, and Tr is the reaction coefficient for metal toxicity.

The toxicity coefficients for Cd, Cr, Cu, Ni, Pb, Zn, and Ti were 30, 2, 5, 5, 5, and 1 and 2, respectively, and the indicators of Ri are given in Tables 2 and 3 (Hakanson, 1980).

RESULTS AND DISCUSSION

Results of X-ray fluorescence analysis

The results of X-ray fluorescence analysis of soil samples at the explosion sites are presented in Figures 3 and 4.

The analysis of the obtained data allows asserting that the maximum allowable concentrations of (*HM*) in the studied soil are exceeded. According to the intensity of the impact on the environment, the listed elements can be arranged in the following sequence: Cu > Pb > Cr > Cd > Ni > Ti.

The results of previous studies show that the concentration of Cd in the soil (on average 23 mg/kg) is 10–40 times higher than the permissible value of the world standard (0.30–0.70 mg/kg), the concentration of Ni on average is 43 mg/kg) above the permissible level (34–12 mg/kg), Cu concentration (on average 39.39 mg/kg)

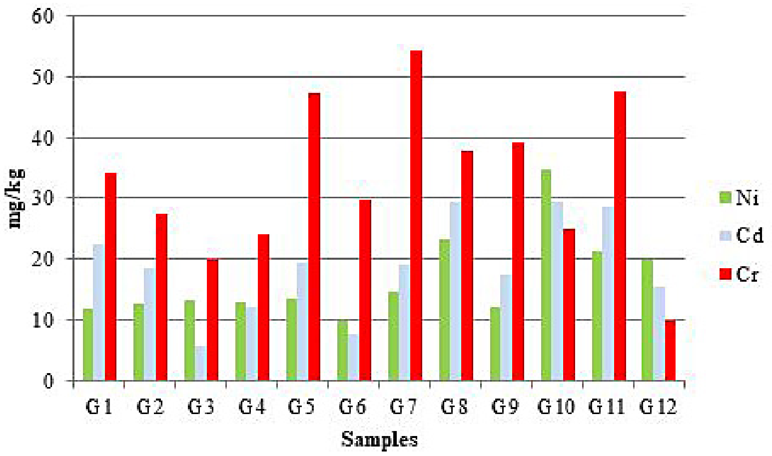

Figure 3. Chromium, cadmium, and nickel concentrations in the studied soil samples

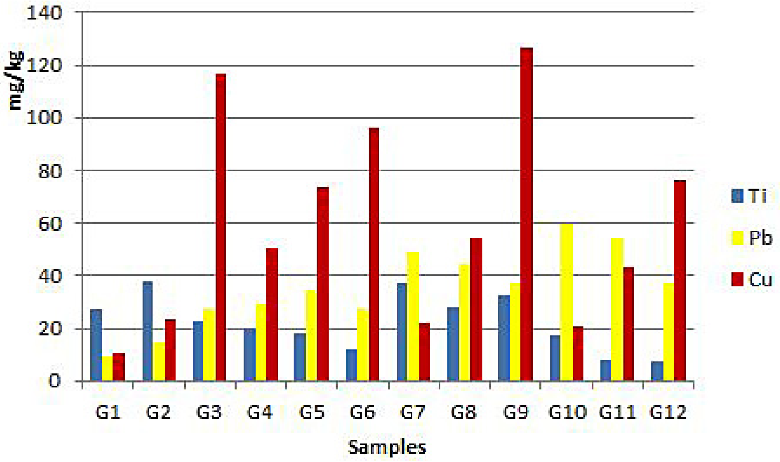

Figure 4. Copper, lead and titanium concentrations in the studied soil samples

above the permissible level (24–13 mg/kg), Zn concentration (on average 55.11 mg/kg) also exceeds the permissible limit. (45–100 mg/kg), and the concentration of Pb (on average 103.78 mg/kg) exceeds the permissible value (44–22 mg/kg) (OSCE, 2017). The soil accumulation index value was used to confirm the presence of contamination and to indicate that the elements in the soil originated from the massive hostilities in Ukraine on its territory.

Assessment of the level of potential ecological risk of environmental pollution

The obtained results of the Nemerov index (*Ps*) (Table 4) of the studied area belong to a highly polluted area with a classification of the quality of the soil environment (*Ps* > 3.0), which indicates a significant impact of the aggression of the Russian Federation as a result of missile attacks on the territory of Lviv. A wide range of heavy metal contamination in soil sampling sites can cause the release of (*HM*). The phenomenon of synergism can be enhanced in the studied sites of missle attacks due to vehicle emissions in highly urbanized areas of Lviv with heavy traffic. This analysis is also described by Hu (Hu et al., 2013).

Table 4 shows the ecological risk index (*Ri*), based on which, according to equation (2), the Nemerov complex index (*Ps*) was calculated, which allows taking into account the total individual evaluation factors and also emphasizes the

Table 4. The value of the Nemerov complex pollution index (*Ps*)

RI							Ps
Cd	Cr	Cu	Ni	Pb	Zn	Ti	
3.353571	3.369388	2.863462	1.697959	3.512245	2.98096	1.28	48.64

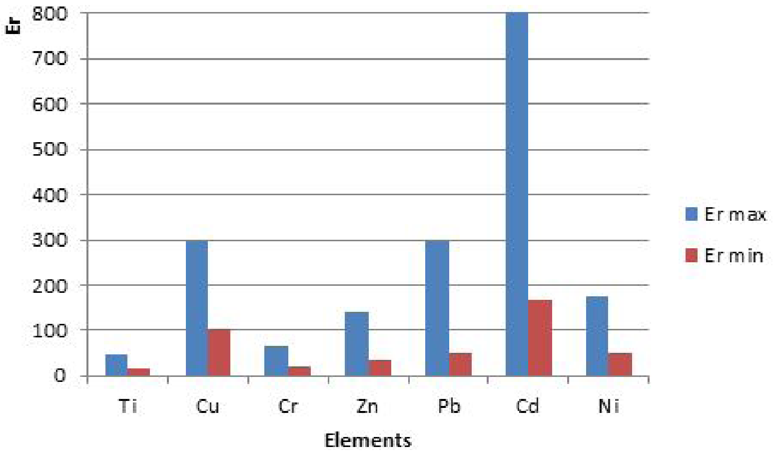

Figure 5. The environmental risk factor (Er) of (*HM*) and their contribution to the complex potential environmental risk of soils at Er_{max} - Ri_{max} = 44.92 and Er_{min} - Ri_{min} = 14.18

importance of the greatest impact of elements on soil pollution at the sites of shelling.

Figure 5 shows the environmental risk (*Er*) factors of heavy metals and their contribution to the integrated potential environmental risk (*RI*) of soils.

The environmental risk factor (Er) for Cd represented the highest level of potential environmental risk, while the other one (*HM*) had a much lower risk level with risk factor values of less than 35. The entry of Cd into soils poses a major threat due to its high toxic response factor. Soil contamination with cadmium has a long history of accumulation and can pose a very serious environmental risk to both ecosystems and human health. The load of cadmium and lead on the human body mainly impacts the central nervous system and kidneys.

The kidney is the main target organ for the cumulative effect of the toxic metal Cd (Jankiewicz and Ptaszyński, 2005; Dolan et al., 2006). Copper (Cu) is an essential trace element, but it can be dangerous when one is exposed to high doses. Chronic exposure to copper dust or soil can cause health problems, such as nausea, headaches, and diarrhea. Cadmium can also travel long distances from the emission source by atmospheric transfer (WHO, 2001). In addition, as one of many other components of explosive materials, cadmium can enter the environment through bombs and cruise missiles, with which Russian aggressors shell the territory of Ukraine.

These results are consistent with the findings of other authors. Liang and Qiu (Liang et al., 2011; Qiu, 2010) reported that their study recorded significant overestimations of *Ri,* which was mainly the product of high Cd loading in soils.

The value of the complex index (*RI*) was 44.92, which indicates the general (low *RI*) of heavy metals. However, the value of the Nemerov index proves a highly polluted area due to missile attacks on the studied soil, which will cause the distribution of these elements in the soil (Table 5).

Statistical analysis of the impact of (*HM*) in the soil on the environment

Statistical values were evaluated using one-way analysis of variance (STATISTICA) to test whether there was a significant difference in heavy metal concentrations between the studied soil samples at the blast sites. The Pearson Correlation Index (PCI) was used to determine the content of (*HM*) in the soil and their distribution potential. The similarity between the concentrations of (*HM*) in the soil was determined using cluster analysis (CA). SPSS 22 software was used to calculate statistical data.

Descriptive statistics of selected heavy metal datasets for soil samples are shown in Table 7.

Table 5. Magnitude (*Er*) and complex (*RI*)

Er							RI
Cd	Cr	Cu	Ni	Pb	Zn	Ti	
870	66.02	trace	175	295	140	44.18	44.92

A high standard deviation reflects the skewed distribution and a high degree of variation of (*HM*) in the soil. As for cadmium, copper and zinc, the concentrations are unevenly distributed, showing skewed distribution. Therefore, medians of migration in the soil were used for the specified elements as they describe the possibility of (*HM*) distribution in the studied soil more accurately.

The concentration of (*HM*) in the studied soils is as follows: Zn > Pb > Ni > Cu > Cr > Cd > Ti. All metals, except Cr, show higher concentrations than the calculated global average value for uncontaminated soils (Kabata-Pendias and Pendias, 2001) (Table 6).

Data on the concentrations of (*HM*) in the studied soil samples (mg/kg) after missile attacks on Lviv from three locations (3 samples from each) are shown in Table 7.

The obtained data from the statistical analysis of the studied soil samples concerning the Pearson coefficient are shown in Figure 6.

The correlation coefficient takes on values from −1 to 1 (Table 8). A value of +1 means that the relationship between X and Y is linear, and all points of the function lie on a line that represents Y increasing as X increases. A value of −1 means that all points lie on a line that represents Y decreasing as X increases. If the Pearson correlation coefficient = 0, then there is no linear correlation between the variables. Different authors (Buda and Jarynowski, 2010; Cohen, 1988) offer varying approaches to interpreting the value of the correlation coefficient. At the same time, all criteria are somewhat conditional and should not be interpreted too meticulously. Interpretation of correlation depends on context and purpose. For example, a correlation coefficient of 0.9 may be very low in the case of studying the laws of physics using high-quality equipment, but it may be interpreted as very high in the humanities, where many other factors are involved.

When analyzing the values of the Pearson coefficient, one can claim a significant anthropogenic

Table 6. Basic statistical data on the concentration of (*HM*) in the soil (mg/kg)

Element	Minimum	Maximum	Average		Error	Average value of uncontaminated soils
Cd	5.6	29.38	18.77	-0.93	±1.23	0.53
Cr	9.8	39.2	33.02	-0.88	±31.23	83
Cu	20.86	126.5	59.57	0.79	±14.33	24
Ni	9.8	34.8	16.65	-0.43	±31.65	34
Pb	9.8	59.7	34.42	0.35	±41.28	44
Zn	37.29	140.45	111.16	0.76	±35.93	100
Ti	7.4	37.3	22.46	0.86	±12.53	5.7

Table 7. Concentrations of (*HM*) in the studied soil samples (mg/kg)

Soil samples	Pb	Cd	Cu	Zn	Cr	Ni	Ti
G1	4	0.4	19.1	21.8	19.1	11.8	27.3
G2	14.7	0.4	116.4	57.9	27.1	12.6	38.2
G3	25.1	0.4	12.3	77.6	34.1	13.1	22.4
G4	20.1	0.508	41.1	74.7	30.7	12.9	20.3
G5	24.1	0.076	30.3	83.5	30.7	13.4	18.2
G6	14.7	0.317	60.2	89.2	35.9	9.8	12.4
G7	35.1	0.048	75.7	124	35.5	14.5	37.3
G8	9.55	0.714	18.2	34.2	30.2	23.4	28.2
G9	4	0.107	8.51	47.9	2.9	12.1	32.4
G10	59.7	59.7	20.8	137.333	24.9	34.8	17.3
G11	54.59	54.59	43.4	120.445	47.5	21.4	8.2
G12	37.1	37.1	76.5	97.213	9.8	19.9	7.4
The average concentration of elements in the soil (mg/kg)	35.415	0.327	59.566	111.6	33.016	16.641	22.466
The average error of the experiment, % device data	2.39	0.385	8.433	6.622	4.345	3.213	5.433

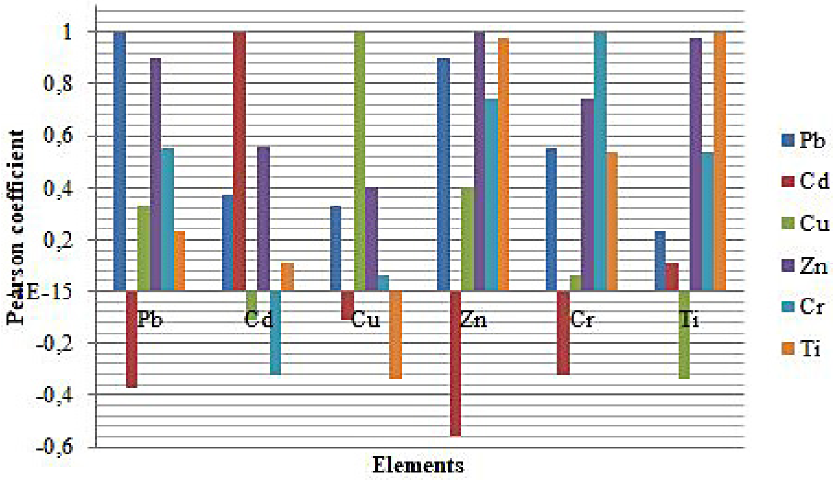

Figure 6. The value of Pearson's coefficients for the averaged concentrations of elements in the soil at the site of the explosion

Table 8. Interpretations of the value of the Pearson correlation coefficient

Correlation	Negative	Positive
Absent	−0.09 to 0.0	0.0 to 0.09
Low	−0.3 to −0.1	0.1 to 0.3
Average	−0.5 to −0.3	0.3 to 0.5
High	−1.0 to −0.5	0.5 to 1.0

impact on the environment of such metals as lead in the presence of all the listed metals except cadmium in relation to lead (Cd = -0.37); cadmium in relation to copper (Cu = -0.11); copper in relation to cadmium (Cd = -0.11); zinc relative to cadmium (Cd = -0.56); chromium in relation to cadmium (Cd = -0.32) and titanium in relation to copper (Cu = -0.34).

Taking into account the phenomenon of synergism of the studied elements, it is possible to predict the strengthening of the toxic effect of (*HM*) on the environment, in particular, this is confirmed by the value of the Pearson coefficient in relation to Pb, Zn, Cr and Ti.

The foci of heavy metal contamination of the soil after the missile attacks on Lviv in 2022 indicate a significant level of danger not only at present, but also impact on future generations, which will significantly affect the restoration of the soil cover, which may last for decades.

CONCLUSIONS

On the basis of the obtained data, taking into account the value of the ecological risk index of each element, the value of the comprehensive assessment of the level of soil contamination based on the Nemerov index ($Ps = 48.64$ – a very high level of pollution) exceeds the value of $Ps > 3$ by 15 times.

The highest environmental risk factor (*Er*) is created by cadmium (Cd). The investigated elements in relation to the environmental risk factor can be arranged in the following sequence: d > Cu > Pb > Ni > Zn > Cr > Ti.

That is, it can be claimed that all the detected elements in the soil create a significant and very high level of soil pollution at the sites of missile attacks. For Cd, very high contamination, which significantly exceeds the values given in the classification, was found at the explosion site on the crater surface.

Using the minimum values of potential environmental risk (*RI*), only two elements have a low coefficient of potential environmental risk ($RI < 40$) – titanium and chromium. All other investigated elements have significant and very high environmental risk potential.

Thus, the conducted studies of the effect of rocket attacks on the soil and the migration of (*HM*) on the example of the city of Lviv enable to assert a high anthropogenic impact on the soil cover of the places of rocket attacks and, accordingly, there is a need for further research on the migration of *PTE* into the soil and groundwater and their impact on the environment.

Acknowledgments

Kateryna Petrushka acknowledges support from the Organization for the Prohibition of Chemical Weapons (OPCW), Fellowship program (Project No. L/ICA/ICB-213/22).

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