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The object of the study is soils in areas with active military operations.

The study is dedicated to assessing the environmental impact of military operations through forecasting.

The paper highlights the impact of military conflict on the distribution of heavy metals in soils. An analysis of the distribution and interaction of heavy metals in soil is carried out, which helps to understand the dynamics of pollution in the context of military conflict, and allows to understand the complex processes of the impact of military operations on the environment and the state of soil resources.

The complex interrelationships between military operations and environmental pollution are revealed, with an emphasis on the importance of studying the distribution and immobilization of iron and heavy metals in the current conditions of the risk of military operations.

It is shown that the most rapidly distributed metals in the soil are: iron (Fe), zinc (Zn), cadmium (Cd), antimony (Sb); the slowest: arsenic (As), lead (Pb), copper (Cu), nickel (Ni), mercury (Hg), manganese (Mn), vanadium (V).

It was found that loams and chernozems are more prone to the accumulation of heavy metals and iron than sandy soils. Compared to sandy soil, the rate of metal release in loam decreases from 16.7 % to 69.7 %. In comparison of chernozem to loam, the release rate slows down from 17.85 % to 32.08 %. It was found that the rate of spreading of barium, cobalt, arsenic, lead, mercury, manganese, strontium and titanium does not depend on the type and mechanical parameters of the soil.

The practical use of the results will help to predict the mechanism of pollution spread and help to identify the highest risk areas. The results of the study indicate the need to develop scientifically sound strategies for environmental protection and promotion of sustainable development in the area affected by military events

Keywords: war, immobilization of metals, soil contamination, heavy metals, impact of military operations

ASSESSMENT OF IRON AND HEAVY METALS ACCUMULATION IN THE SOILS OF THE COMBAT ZONE

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1. Introduction

Against the background of military conflicts, the problem of environmental pollution is particularly acute and

urgent, as such pollution endangers not only environmental stability, but also human well-being.

Fighting often leads to serious damage to the environment. One of the most important environmental problems

that requires scientific understanding is the assessment of the impact of hostilities on the dynamics of pollution and the distribution of heavy metals in soils. During the detonation of military rockets and artillery shells, toxic elements, including sulfur and nitrogen oxides, enter the soil, heavy metals are released, which can lead to oxidation of the surrounding soils. These substances can cause the formation of acid rain, change the pH of the soil and lead to burns in plants, mucous tissues of the respiratory organs of humans, birds and mammals [1].

The problem of the accumulation of heavy metals in the soil where military missiles and artillery shells hit has a direct impact on environmental safety and the health of the population. Military conflicts lead to significant changes in the composition and physical and chemical properties of soils, especially in regions where active hostilities take place. Heavy metals such as cadmium, lead, and mercury can enter the environment through the use of weapons and military equipment, destruction of infrastructure. This leads to serious consequences for ecosystems and human health.

This problem is so complex and acute that it deserves a proper scientific study aimed at evaluating the dynamics of contamination, distribution and immobilization of heavy metals in soils that have entered the battlefield.

The study of the dynamics of pollution and distribution of heavy metals in soils affected by hostilities meets the needs of not only the scientific community. The results of such studies are needed in practical activities. It should be understood that heavy metal contamination can occur over a very large area that may not be accessible for traditional sampling observations due to the hazards to specialists. Therefore, the study of the dynamics of the distribution of these substances is an important component of remote monitoring of the state of the environment in conditions of limited access to the territory.

The extent of soil contamination with iron and heavy metals in the zone of active hostilities in Ukraine is not yet known. However, it is clear that the war will cause long-term damage and prevent the potential of the soil from being used for years to come. The main problem of researching the impact of hostilities on soils is limited access to a significant number of contaminated territories. That is, it will be possible to record the damage only when the territory is freed from occupation. However, the distribution and distribution of harmful substances in the soil is a dynamic process. If the analysis of the samples is carried out years later, it will be difficult to estimate the concentration of harmful substances at the time of their entry into the soil, and therefore the assessment may not correspond to the actual situation. For this, it is important to carry out a preliminary assessment of the impact of soil pollution in the combat zone. Therefore, there is a need for such an assessment of pollution, which should be substantiated taking into account the physical and mechanical parameters of the soil.

It is important to understand the scale of pollution and identify areas of highest risk for natural ecosystems. This will help establish the necessary priorities and develop measures for effective pollution management. Research can clarify the relationship between the nature of hostilities, the types of heavy metals and their distribution in soils, which will help identify sources of contamination and develop effective strategies to reduce their impact. The research results can be used in the development of technologies for the immobilization of heavy metals in soils, which can reduce

their toxicity and prevent their transition into the system of living organisms.

Solving the problem of immobilization of heavy metals in contaminated soils can contribute to the restoration of natural ecosystems and reduce the negative impact on the health of people who live or will live in the regions of the possible course of military operations.

Assessment of the dynamics of heavy metal pollution can serve as a basis for the development of effective strategies for cleaning and rehabilitation of affected areas.

The results of such research can contribute to the development of effective environmental protection measures, restoration of environmental security in conflict areas.

This determines the problem of the research – understanding the scale of soil contamination with heavy metals and its consequences, which will make it possible to formulate appropriate strategies and actions to solve this problem. Solving this problem is of great importance for the restoration of the ecological state of the territories that became victims of the military conflict, as well as for the preservation of the quality of life of the local population.

The relevance of studies of the dynamics of pollution, distribution and immobilization of heavy metals in soils that have fallen into the field of hostilities is extremely important from an ecological and humanitarian point of view.

Considering the current situation, it can be argued that the study of the impact of heavy metals on the soil is relevant for the development of effective strategies for the restoration of affected areas and preventive measures for the future avoidance of similar environmental disasters.

2. Literature review and problem statement

The distribution of heavy metals depending on the physico-mechanical parameters of the soil is most fully investigated in works [2, 3]. The authors of [2] developed a multicomponent model for the kinetic behavior of adsorption/desorption of heavy metals in soil. Special attention is paid to soil adsorbents and dissolved organic matter. According to the research methodology proposed in the works, one should start with a large number of field soil samples, which is not possible in the conditions of hostilities. In addition, the work examines exclusively sandy soils with a pH of less than 5.6 and with inclusions of a fine fraction of clay. Therefore, the developed model is territorially limited and it is not advisable to use it in the regions of Ukraine. It is fundamentally impossible to apply the model proposed in [2], since it is designed for civilian conditions. Research [3] does not take into account the peculiarities of active warfare and the cumulative effect of the spread of iron and heavy metals.

The authors of the studies indicate that land pollution by military activity differs significantly from urban and industrial pollution sources, both in terms of intensity and type [4–6].

The authors of the study [4] indicate that military exercises play a key role in the deterioration of the environment due to the release of heavy metals from bullets and their fragments. The study revealed extremely high concentrations of Zn, Sb, Pb, Cu, Cd, Cr, Ni, Co, etc. in the soils of military training grounds in Canada, South Korea, the USA, Spain, Pakistan and the Czech Republic. A key feature of the contamination of military training grounds is that the continuous dissolution of ammunition fragments due to

oxidation-reduction reactions in the soil increases the labile fractions of heavy metals.

The authors of the study point to a significant influence on the mobility of heavy metals from geochemical processes in the soil [5]. In particular, precipitation, adsorption, complex formation, redox reactions, and the content of organic matter play a key role. Different combinations of metals also have an effect. Accordingly, the increase in speed is caused by the interaction of combinations of Al, Fe and Mn.

The question of changing the chemical composition of the soil in order to reduce the negative impact from the course of military operations is covered in sufficient detail. Thus, the study [6] is devoted to the influence of stabilizers in contaminated soils. According to the authors' conclusions, precipitates reduce the bioavailability of heavy metals by reducing adsorption. There are also studies devoted to environmentally sustainable methods of restoring contaminated soil. For example, the authors [7] emphasize the immobilization of heavy metals in soils by phytoremediation. In the study, heavy metal contamination was stabilized by adding limestone, chalcocite, and activated carbon to the grant. However, the limitations of research [6, 7] are the stabilization of urbanized soils. Therefore, the research results cannot be projected onto soils that fall into the zone of active hostilities.

The work [8] gives the results of the study of two military training grounds in Latvia using X-ray fluorescence spectrometry with total reflection (TXRF). The authors of the study did not find an extremely high level of pollution. Researchers point to increased concentrations of trace elements such as Cr, Pb, Cd and Cu. However, the presence of elements that are usually found only in trace amounts is determined, which in turn indicates the presence of harmful substances that pose a danger. The research is of considerable interest in the methodological aspect in terms of data collection, but its application is possible only in security conditions. In addition, the assessment of heavy metal contamination in the zone of military influence, which is based solely on the total concentrations of the elements, may not always show a clear picture of the contamination. In order to draw convincing conclusions, the most important soil parameters should be characterized. This can significantly increase the reliability of the assessment of the contaminated area. Setting up a laboratory experiment can be an option for overcoming the relevant difficulties.

So, there are available studies on the assessment of the mobility of heavy metals in soils, which were carried out in laboratory conditions. The work [9] is devoted to the mobility of the element antimony (Sb). This is one contaminant that can be present in elevated concentrations in range soil due to mobilization from spent lead/antimony bullets. The research was based on a series of experiments conducted in oxygen conditions. The composition of berm soils with a high content of organic matter was simulated for them. An important finding of the study is that Sb in berm soils has a longer half-life compared to soils with low organic matter content. However, the limitation of the study is its methodology, which does not take into account the influence of external factors. Studies that are based on laboratory experiments are not possible for representative comparisons with models for open soil.

In the field, the release of heavy metals in soil can be a rate-limited process due to uptake by plant roots. Absorption can also be influenced by the aging process and previous history of contamination of this soil. In already polluted

soils, only a part of heavy metals is considered reactive to short-term adsorption and desorption reactions [10]. Therefore, it is extremely important to take into account only representative data when selecting data for the model. Such words include studies where the sampling was carried out in open ground, on which combat operations were constantly or intermittently taking place. In particular, these are the territories of active armed conflicts or training grounds for military exercises using modern military equipment, not older than the 1980s.

The methods proposed in [8, 9] have specific features: the assessment begins with the collection of soil samples. However, under conditions of full-scale invasion, researchers do not have free access to collect soil samples. Therefore, for the purpose of remote pollution forecasting, a literature collection of representative data and the development of an artificial network model are proposed to obtain a large sample of data.

In studies [2, 3] the dynamic behavior of metals in the soil has been worked out, but there are no quantitative models for predicting the release rate of heavy metals in different soils. This indicates the importance of developing a quantitative model to predict the release rate of heavy metals from contaminated different soil types.

It can be concluded that there are no studies that would preliminarily assess the spread of iron and heavy metals in different types of soil in conditions of active hostilities. Many studies are devoted to the release of heavy metals in soils in civilian conditions (from railways, industrial facilities, etc.) or already after the end of the conflict. However, the work does not take into account the variable nature of the impact of emissions of harmful substances (that is, the intensity of shelling). This allows to state that it is expedient to carry out a study of predicting soil contamination from artillery shells and rockets, especially in areas of active hostilities, access to which is difficult.

3. The aim and objectives of the study

The aim of the study is to assess the dynamics of contamination, distribution and immobilization of iron and heavy metals in soils that have entered the battlefield. The research will increase the level of understanding of the mechanisms of interaction between heavy metals and soil components, which in turn may contribute to the development of more accurate and effective methods of soil rehabilitation. This will make it possible to develop effective strategies for the restoration of contaminated areas, including methods of phytostabilization, phytoremediation, and others.

To achieve the aim, the following objectives were set:

- carry out a selection and study of the influence of factors of the dependence of physical and mechanical properties of the soil on the rate of distribution and immobilization of iron and heavy metals;
- carry out numerical modeling of the distribution dynamics of iron and heavy metals in sandy soils, loams and chernozems.

4. Materials and methods of research

The object of the study is soils in the territories with an active course of hostilities. The hypothesis of the study

is the assumption that the speed of movement of iron molecules and heavy metals in the soil depends on the duration of hostilities and on the physical and mechanical properties of the soil.

To solve the problem, the effect of the main geochemical forms of heavy metals, which are formed as a result of artillery and missile strikes, was studied, and the absorption capacity of soil with different physical and mechanical properties was modeled.

The first stage involved obtaining data for modeling. Since the setting of the laboratory experiment does not reflect the influence on the absorption of other factors (due to the existing processes of soil aging, the previous history of pollution, absorption by plants), it was decided to use the data of already known field studies. The search for representative data on heavy metal concentrations in the combat zone involved a literature search covering the period between 2010 and 2022. The search focused on studies conducted in war-affected areas, i.e., war-torn areas, areas of active or abandoned military bases, and detonation sites. Several searches were performed using combinations of keywords, including: “soil pollution during warfare,” “heavy metal contamination in war-affected soils,” “immobilization of heavy metals in soils,” “impact of military conflicts on soil ecosystems.” Data were obtained from training grounds in Canada [11–13], USA [14], Australia [15], Croatia [16], Kuwait [17], Ukraine, Kazakhstan [18]. A fragment of a sample of data from military training grounds is indicated in the Table 1.

Table 1

Concentrations of heavy metals in the soils of military training grounds of different countries

Metal concentration, (mg/kg)												
Fe	As	Pb	Zn	Ba	Cd	Cr	Cu	Ni	Hg	Mn	Sr	Sb
Canada; Soil type: sandy; Porosity: 35; SEC: 6.10; SOC:0.19; pH: 8.10; T=24 hours												
1 205	10	10	53	65	7	3	14	16	0.07	709	170	140
Australia; Soil type: loam; Porosity:37; SEC: 6.10; SOC: 0.19; pH: 6.40; T=24 hours												
1 401	10	11	63	70	8	32	13	27	0.07	648	165	252
USA; Soil type: sandy; Porosity: 40; SEC: 2.20; SOC:1.01; pH: 6.72; T=24 hours												
1 601	n/a	70	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	190	n/a
Croatia; Soil type: loam; Porosity: 52; SEC: 29.00; SOC:0.44; pH: 7.20; T=45 years												
n/a	n/a	17	53	n/a	0	32	13	19	0.07	506	n/a	n/a
Kuwait; Soil type: sandy; Porosity: 33; SEC: 5.87; SOC: 0.40; pH: 8.90; T=5 years												
n/a	n/a	9	17	65	n/a	3	14	16	n/a	n/a	n/a	n/a
Ukraine; Soil type: chernozem; Porosity: 47; SEC: 28; SOC: 0.93; pH: 5.50; T=3 months												
3 104	n/a	13	44	n/a	1	77	8	69	0.53	276	6	
Ukraine; Soil type: chernozem; Porosity: 47; SEC: 22.30; SOC: 0.67; pH: 6.40; T=3 months												
1 151	10	10	215	68	12	39	10	22	0.05	659	173	400
Kazakhstan; Soil type: sandy; Porosity: 30; SEC: 5.90; SOC: 0.05; pH: 8.60; T=24.hours												
n/a	23	230	180	n/a	n/a	44	32	39	n/a	810	81	n/a

The study proposes to carry out a numerical simulation of the absorption capacity of the soil, taking into account its

various physical and mechanical properties. For this purpose, it is advisable to use computer simulation.

The dataset of iron and heavy metal concentrations was extended by artificial neural network (ANN) generation. The areas of the military training grounds under consideration differ greatly in terms of the time of exposure to combat activity and soil properties, so the data obtained from these areas were ideal for additional training of the artificial neural programming model when selecting variation data. The applied neural modeling tools made it possible to expand the input data of the study. This is due to the self-learning nature of the artificial neural network. From a technical point of view, the learning process of the proposed data included optimization of the coefficients of connections between neurons. In general, this means that after successful training, the network adequately processes information that was missing from the training set, and also works with incomplete or “noisy”, partially distorted data.

During this process, the neural network revealed close relationships between the physico-mechanical properties of the soil and the rate of spread of iron and heavy metals, and also allowed to expand the data sample.

ANN for the training sample was implemented using the Neural Network Tool of the Matlab 2014a software package. A learning function based on Levenberg-Marcard back-propagation optimization was used for data generation. The developed ANN is based on 10 neurons in the hidden layer with a sigmoidal activation function for the hidden layer layers and a linear one for the output layer layers.

Data up to 100 positions were synthesized with the help of ANN. It should be noted that the application of ANN was an important step from the point of view that it is possible to study all parameters of pollution in a complex and to evaluate how the presence of one heavy metal affects the rate of spread of another. Such an influence cannot be traced using other mathematical methods of scientific analysis.

The next stage of the research was the selection and study of the influence of the factors of dependence of the physical and mechanical properties of the soil on the rate of distribution of iron and heavy metals. The selection of the most suitable factors representing the behavior of the propagation process is a very important point for the accurate description of the soil system. Therefore, in order to find weighting effects and avoid multicollinearity of parameters, a correlation analysis by the Pearson method was carried out.

Numerical modeling of the dynamics of contamination, distribution, and immobilization of iron and heavy metals in sandy soils, loams, and chernozems was performed to search for analytical regularities.

Numerical modeling of the distribution of heavy metals was carried out based on consideration of the diffusion process of substance distribution in the soil, taking into account the physical and chemical properties of substances and the peculiarities of the soil environment.

The calculation is based on partial differential equations that describe the dynamics of metal concentrations in soils over time.

It is taken into account that the distribution of harmful substances in the soil depends on time and spatial coordinates (x, y, z), which makes it possible to monitor changes in the concentration of iron and heavy metals in the soil at different depths over time.

It is known that the distribution of metals in the depth of the soil is mathematically described by the following diffusion equation:

$$\frac{\partial C_{Fe,j}}{\partial t} = D_j \cdot \left(\frac{\partial^2 C_{Fe,j}}{\partial x^2} + \frac{\partial^2 C_{Fe,j}}{\partial y^2} + \frac{\partial^2 C_{Fe,j}}{\partial z^2} \right) + R_{Fe,j} + Q_{Fe,j}; \quad (1)$$

$$\frac{\partial C_{HM,j}}{\partial t} = D_j \cdot \left(\frac{\partial^2 C_{HM,j}}{\partial x^2} + \frac{\partial^2 C_{HM,j}}{\partial y^2} + \frac{\partial^2 C_{HM,j}}{\partial z^2} \right) + R_{HM,j} + Q_{HM,j}, \quad (2)$$

where $C_{Fe,j}$ and $C_{HM,j}$ – concentrations of iron and heavy metals in soil j (j is chernozem, loam, sandy soil);

D_j – the diffusion coefficient for soil j , which determines the rate of diffusion of a substance in the soil;

$R_{Fe,j}$ and $R_{HM,j}$ – reaction rates of iron and heavy metals in soil j , which depend on the physical and mechanical parameters of the soil, such as cation exchange capacity, pH, and organic carbon content;

$Q_{Fe,j}$ and $Q_{HM,j}$ – additional external influences that contribute to the absorption of iron and heavy metals.

To solve the system of equations by the finite difference method, approximation of partial derivatives using central differences was used.

Numerical modeling was performed using the Matlab 2014a computer tool, and Oasys Safe 19.1 was used to visualize the propagation speed.

The uniqueness of this research lies in the study of the complex dynamics of the formation of iron and heavy metal contamination during artillery and missile strikes, their distribution and the possibility of immobilization in various types of soils.

5. Research results of the assessment of the dynamics of iron and heavy metal contamination in soils

5.1. Selection and study of the influence of dependence factors of the physical and mechanical properties of the soil on the distribution rate of heavy metals

In the soil environment, the dynamic behavior of heavy metals is usually influenced by numerous physical and chemical processes, such as stream transport, diffusion processes, uptake by plant roots, and a number of chemical reactions: adsorption/desorption and precipitation/dissolution. These reactions and processes can affect the behavior of the metal on different time scales and are highly dependent on specific field conditions.

It has been established that the following factors have the most significant influence on the absorption of iron and heavy metals by soils: soil type, soil physical and mechanical parameters: porosity, soil cation exchange capacity (SEC), soil organic carbon (SOC), pH. Also, due to the specifics of pollution, the time that has passed after artillery and missile strikes has a significant impact. Let's consider in more detail:

The type of soil and its physical and chemical properties: the indicator can affect the distribution and movement of substances in the soil. Different types of soils can have different capacity of cation exchange, which determines their ability to retain ions of substances. For each type of soil, it is possible to use specific equations that take into account its features.

Soil porosity: the indicator characterizes the intensity of exchange, is responsible for the actual rate of filtration of the flow of substances.

Cation exchange capacity of soils: the indicator affects the ability of the soil to retain and exchange ions of substances.

Soil organic carbon: Soil organic carbon affects its density and ability to retain heavy metals. It can be connected to the ions of the substance, which affects their distribution in the soil. The higher the carbon content, the greater its ability to bind metals.

pH: the pH level of the soil determines its acidity or alkalinity, which can affect the toxicity and rate of distribution of the substance. A low pH level increases the solubility of metals in the soil, while a high pH level can reduce their availability to plants.

Period since the end of operations: the time that has passed since the end of hostilities also affects the spread of contamination in the soil. This parameter takes into account transient processes and immobilization of metals over time.

Correlation analysis was performed using Excel. The correlation matrix and diagram of solar rays, which demonstrates how the speed of distribution of metals is affected by soil parameters, which are built on the basis of Pearson's correlation coefficients, is presented in Fig. 1.

As can be seen from Fig. 1, the structure of the soil and its physical and mechanical properties play an important role in the mobility and retention of harmful substances. However, each metal reacts differently. In particular, the physical and mechanical parameters of the soil practically do not affect the rate of diffusion of lead, zinc, chromium and copper.

In contrast to these metals, the effect of soil on the diffusion rate of iron and titanium is obvious. Thus, the porosity parameter has a strong influence on the diffusion rate of barium, antimony, titanium, and vanadium. SEC is a key parameter for strontium and titanium. The distribution of iron, cobalt, and titanium depends on the SOC. Soil pH affects the diffusion rate of all metals.

The obtained correlation dependence demonstrated the relevance of the dependence of the physical and mechanical parameters of the soil on the rate of distribution of iron and heavy metals. Correlation matrix data in blue shows positive correlations, while red indicates negative correlations. The level of significance of correlation coefficients is indicated by the intensity of color saturation of the matrix. The deeper the color, the stronger the correlation.

Correlation coefficients can be found in the block diagram in the lower left corner of Fig. 1. Fig. 1 shows that soil pH has a direct correlation with the rate of distribution of all elements of heavy metals in soils, except for barium and vanadium. On the other hand, organic carbon content is inversely correlated with all heavy metals except chromium, nickel, strontium, and vanadium. The content of organic carbon affects the adsorption and mobility of heavy metals in the soil. Because there are important correlations between soil heavy metal contamination and soil nutrient status, a comprehensive soil quality assessment considers both of these assessment categories.

It should be noted that since barium, titanium, vanadium, and mercury showed a negative correlation with other heavy metals during the construction of the correlation matrix, it is advisable to investigate their impact on the soil separately in subsequent works.

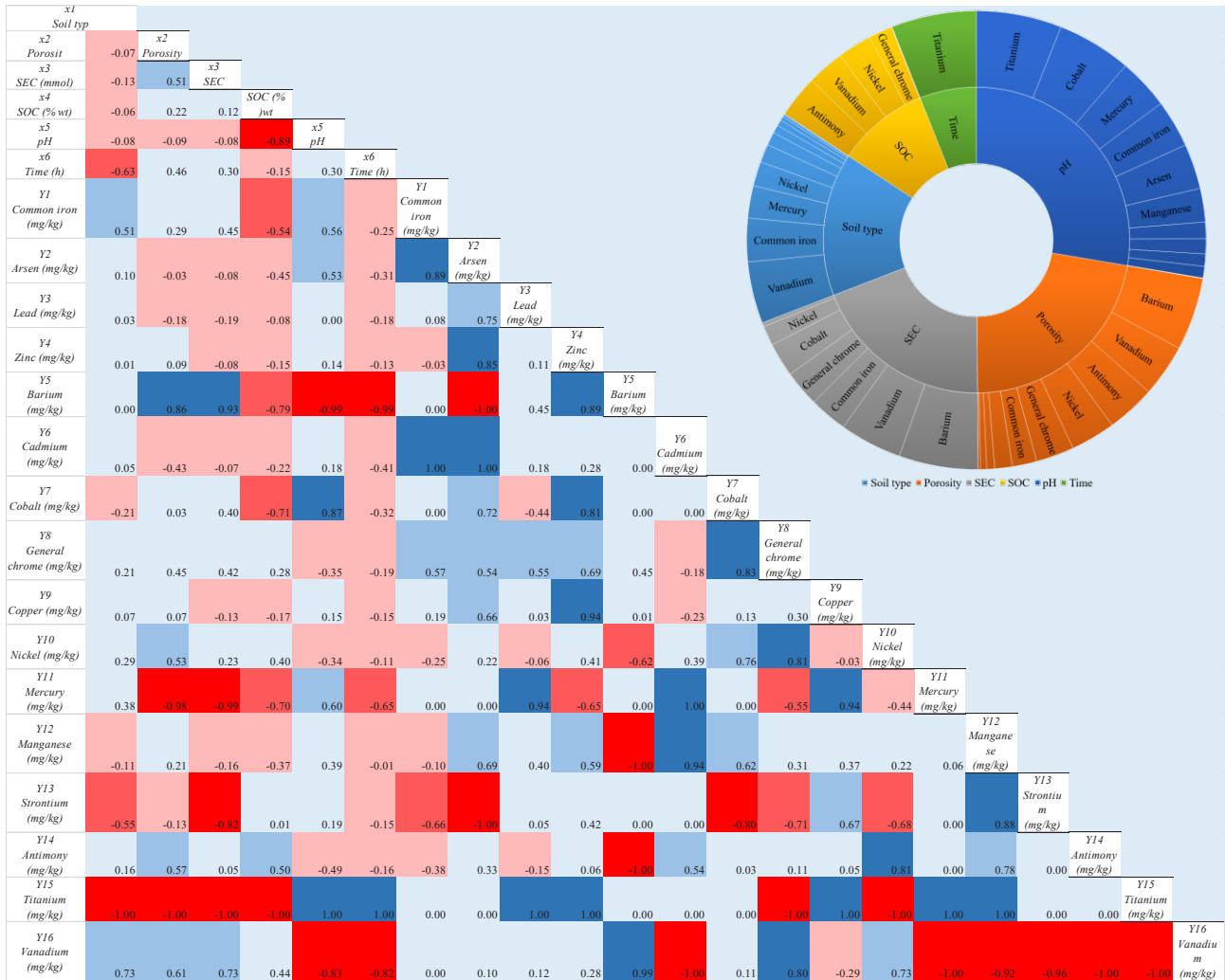


Fig. 1. Correlation matrix and correlation diagram

Barium, titanium, vanadium, and mercury correlate both positively and negatively with other metals. In addition, titanium and mercury were significantly negatively correlated with all physical and mechanical soil parameters. The same situation (except for the pH parameter) is characteristic of arsenic, lead, zinc and cadmium. Chromium, nickel, antimony and vanadium have a direct dependence of the speed of propagation on the dependence of the physical and mechanical parameters of the soil.

5. 2. Results of numerical modeling of the dynamics of distribution of iron and heavy metals in sandy soils, loams and chernozems

Numerical modeling of the diffusion rate of iron and heavy metals is described by the diffusion equation in the soil space. The finite difference method was used for the numerical solution.

Equations (1), (2) were solved by the numerical method. At each time step of the simulation, the total dissolved metal concentration was calculated.

To find the size of the concentration of heavy metals, computer simulation was carried out in software products of the MatLab system.

The process of spreading heavy metals and explosive substances that penetrate the soil during the explosion of an artillery projectile is described. A “zero flux” boundary

condition was applied for iron and heavy metals at the upper boundary. Boundary conditions of the second kind are used on the upper boundary, and boundary conditions of the first kind are used on other parts of the boundary.

Oasys Safe 19.1 was used to visualize the rate of spread of metals.

The data of calculated concentrations of metals depending on time – 1 hour and 8,760 hours are shown in the Table 2.

The conducted numerical modeling demonstrates how the concentration of a harmful substance changes with time and spatial coordinates, taking into account that the movement occurs from an area of higher concentration to an area of lower concentration, causing the spread of contamination in the soil.

Based on the results of the calculations, distribution isolines of heavy metals in the soil profile were constructed. The visualization result is presented in Fig. 2.

Fig. 2 shows the result of numerical modeling of the rate of Zn diffusion in loam and chernozem. The distribution zones that have formed are displayed. The speed is indicated in cm/h.

Comparing the results of the rate of spread of various heavy metals among themselves, it is possible to indicate that one of the most mobile metals is iron, lead, antimony, and zinc, cobalt, chromium. At the same time, strontium,

cobalt, barium, titanium, and nickel behave actively only in the first hours of soil penetration, and then their activity and speed of spread decrease significantly.

However, the metals arsenic, manganese, cadmium, mercury, vanadium, and copper are not very mobile metals, neither during the first day of entering the soil nor during the following months of distribution.

The difference between the experimental data and the obtained calculations is indicated in the Table 3.

As can be seen from the Table 3, the results of the calculation of the rate of heavy metals in the soil profile and the data of actual field data obtained a satisfactory

convergence. However, the actual rate of spread of mercury and vanadium exceeds the value obtained according to the calculated values by 70 % and 30 %, respectively. This discrepancy can be explained by the influence of humidity: the movement of water in the soil can accelerate the transport of metals in the field. On the contrary, the negative deviation can be explained by interaction with other soil components, interaction with the root system of plants, which slow down the mobility of metals.

It should be noted that the conducted numerical modeling made it possible to obtain complete information on the distribution of heavy metals in the soil profile for 10 years.

Table 2

Concentrations of iron and heavy metals in different soil types one hour after their entry into the soil

Parameter,	Chernozem			Loam			Sandy soil		
	min	max	median	min	max	median	min	max	median
SOC, mmol/100 g of soil	15	30	22	10	20	16	5	10	7
SOD, %	2	5	5	1	3	2	0	1	1
pH	6	8	7	7	8	7	6	8	7
Porosity, %	40	50	47	45	55	48	30	40	39
Metal concentration after 1 hour, (mg/kg)									
Iron	2635	11457	9809	1274	5537	4740	1580	6261	4935
Arsen	9	50	45	7	75	69	7	77	72
Lead	6	28	20	7	188	18	31	28	25
Zinc	376	1838	1223	1097	6840	1454	144	9234	1870
Barium	116	169	91	89	130	70	92	134	72
Cadmium	0	6	5	0	4	3	1	4	4
Cobalt	34	52	41	26	40	32	27	41	33
Chrome	40	178	116	31	137	89	32	141	92
Copper	14	294	175	97	347	105	30	1351	140
Nickel	119	346	311	17	346	197	22	99	62
Mercury	0	1	1	0	1	1	0	1	1
Manganese	279	728	606	344	912	689	355	940	711
Strontium	17	25	15	243	568	554	250	585	572
Trumpet	1471	2517	2120	1131	1936	1631	539	4616	935
Titanium	3840	5760	3407	2954	4430	3966	3045	4568	4089
Vanadium	111	140	171	85	108	95	88	111	98
Metal concentration after 8,760 h, (mg/kg)									
Iron	66	262	206	39	154	121	49	192	152
Arsen	5	13	7	4	10	5	4	10	5
Lead	13	67	59	9	51	46	9	53	47
Zinc	17	57	35	12	44	39	12	45	40
Barium	17	29	4	12	22	3	12	23	3
Cadmium	0	19	9	0	15	7	0	15	7
Cobalt	5	16	6	4	13	5	4	13	5
Chrome	3	20	14	2	15	11	2	16	11
Copper	10	194	50	7	149	39	7	154	40
Nickel	15	26	23	10	20	17	11	21	18
Mercury	0	1	1	0	1	0	0	1	1
Manganese	620	1236	631	430	951	485	443	980	500
Strontium	14	29	28	9	22	22	10	23	22
Trumpet	47	72	61	32	55	47	33	57	48
Titanium	182	246	220	126	189	169	130	195	175
Vanadium	32	50	32	22	39	24	23	40	25

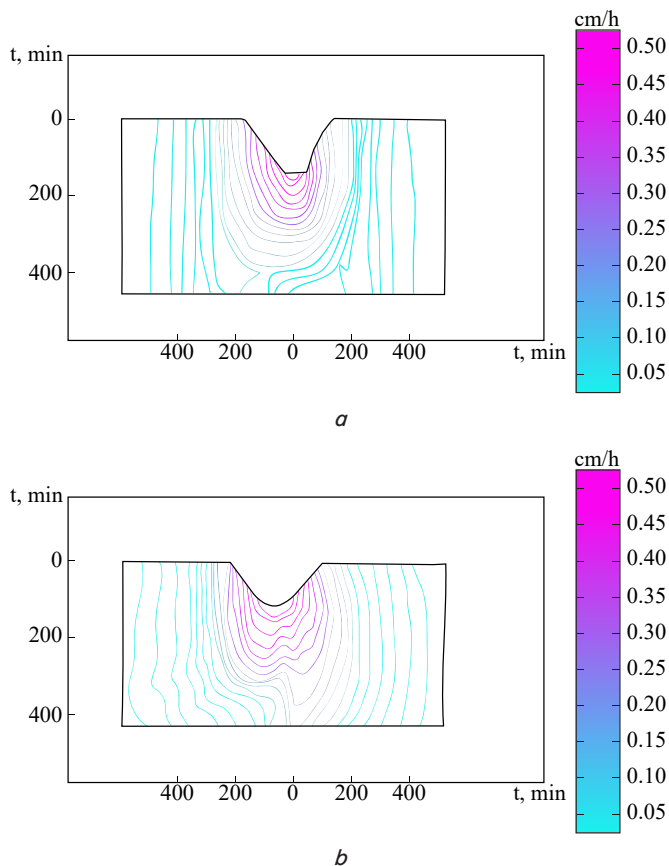


Fig. 2. Zn diffusion rate: *a* – in chernozem; *b* – in loam

It was determined that soils with low porosity have a lower level of sorption, while soils with a higher proportion of small particles have a larger reaction surface. Therefore, soils with a dominant mechanical composition of silty loams can be characterized as favorable from the point of view of immobilization of harmful substances.

From the correlation diagram (Fig. 1), it is determined that soil pH has the strongest influence on the behavior of metals, determining their solubility and availability. Alkaline pH has a positive effect on their immobilization, while in an acidic environment, metal cations are almost always more mobile, that is, a larger amount can be released into the soil solution and thus potentially become toxic. Neutral soils contribute to the highest level of immobilization of metals. This fact can be explained by the formation process of carbonates or hydroxides.

The correlation matrix shows that the organic carbon content is another key indicator of the soil, on which the rate of distribution of heavy metals in the soil strongly depends. Thus, increasing the organic carbon content and cation exchange capacity of soils is one way to improve the properties of metal-contaminated soils by achieving lower overall heavy metal mobility, plant bioavailability, and oral bioavailability.

The study demonstrates that measures to change soil parameters can reduce the mobility of iron, while increasing the mobility of other heavy metals or affecting soil biota.

Summarizing the study of influencing factors, it can be stated that the specific characteristics of acidic soils, sandy structure, low SOC and low SOD (individually or in combination) will enhance leaching/mobilization processes. In turn, this will lead to increased mobility of heavy metals and, thus, to higher concentrations of elements in the soil. In contrast to the previous one, alkaline loam/silty loam/clay type soils, high SOC and high SOD condition the mobility of heavy metals and thus restrain their concentration in the soil solution and its further distribution.

Numerical modeling of the diffusion rate of heavy metals in the various types of soils considered generally demonstrates a typical two-phase behavior. Initially, there is an intense release of metal for several hours, followed by a decrease in the rate of propagation lasting several hours, which was demonstrated in Fig. 2 (on the example of Zn).

It was found that the rate of diffusion of heavy metals strongly depends on the type of soil and the concentration of the reactive metal.

The fastest spreading metals are: Fe, Zn, Cd, Sb; the slowest: As, Pb, Cu, Ni, Hg, Mn, V. At the same time, there is a peak point for Fe, Zn, Cd, Sb, after which the concentration rate decreases. For Fe, Zn, it is 180+5 min (in sandy soils), 220+5 min (in loams), 230+5 min (in chernozems); for Cd, Sb – 310+10 min (in sandy soils), 350+5 min (in loams), 350+5 min (in chernozems) The diffusion rate of As, Pb, Cu, Hg, Mn, V is conditionally linear, without a peak the maximum.

Table 3

Deviation between actual (AD) and calculated (CD) values

Element	Pos	AD	CD	Δ,%	AD	CD	Δ,%	AD	CD	Δ,%
Type	X1	Loam			Sandy soil			Chernozem		
Fe	Y1	1 401	1 359	3	1 205	1 084	10	1 151	1 047	9
As	Y2	10	7	25	10	8	15	10	9	10
Pb	Y3	11	9	15	10	9	15	10	9	17
Zn	Y4	63	58	8	53	47	11	215	187	13
Ba	Y5	70	66	5	65	61	7	68	63	8
Cd	Y6	8	7	7	7	6	13	12	8	28
Co	Y7	13	12	12	14	12	13	15	12	18
Cr	Y8	32	28	12	3	2	8	39	37	5
Cu	Y9	13	11	13	14	13	7	10	9	7
Ni	Y10	27	25	7	16	14	12	22	20	9
Hg	Y11	0.07	0.03	55	0.07	0.02	70	0.05	0.02	63
Mn	Y12	648	609	6	709	659	7	659	580	12
Sr	Y13	165	140	15	170	148	13	173	118	32
Sb	Y14	252	229	9	140	125	11	400	368	8
Ti	Y15	1 070	1 006	6	1 131	1 119	1	1 041	1 041	0
V	Y16	12	8	30	11	8	25	14	12	14

6. Discussion of the results of the assessment of the dynamics of soil contamination with iron and heavy metals

The study of the factors of dependence of the physical and mechanical properties of the soil on the rate of spread of iron and heavy metals was carried out.

The decrease of Sb, Cd, and Zn concentrations in the soil is extremely rapid during the first hour, while the decrease of As, Pb, Cu, Hg, and Mn concentrations was generally slow.

From the results of numerical modeling (Table 2), it can be noted that loams and chernozems are more prone to the accumulation of heavy metals and iron than sandy soils.

Compared to sandy soil, the release rate of iron in loam decreases by 16.7 %, nickel by 69.71 %, antimony by 44.37 %, and zinc by 18.18 %. Compared with chernozem to loam, the release rate of iron slows down by 17.85 %, nickel by 17.67 %, vanadium by 27.58 %, cadmium by 32.08 %, copper by 22 %. At the same time, for barium, cobalt, arsenic, lead, mercury, manganese, strontium and titanium, there is no significant deviation (more than 5 %) of the dependence of the propagation speed on the type and parameters of the soil.

It was also found that the rate of spread of arsenic, mercury, manganese, strontium, titanium and vanadium in sandy soils and loam is the same. The rate of diffusion of antimony in chernozem and loam is the same.

The obtained results in general do not contradict existing studies. However, in the work [9] it is stated that fine-grained silts and soils rich in organic matter can more quickly sorb Pb and Sb, and in the prediction made, the speed of Pb distribution does not depend on the type of soil. Presumably, such a discrepancy indicates its interaction with other metals, which is released in military operations during the bursting of shells when compared to the civilian conditions considered in the above study.

The work [12], which investigates the propagation speeds of 4 heavy metals, also indicates a linear distribution of copper and lead. At the same time, the rate of spread of cadmium and zinc can be characterized by an exponential decline, which is also confirmed by the conducted research. A study [10] indicates the presence of a peak point of the nickel diffusion rate, which also does not contradict the obtained results.

Iron, zinc, and antimony have the highest propagation speed. At the same time, let's note that the speed of zinc diffusion does not depend on the type of soil, and iron spreads in chernozem by 31.58 % more slowly than in sandy soil. For antimony, a similar indicator is as much as 44.37 %.

However, a large deviation was obtained between the known and estimated data (Table 3), which was observed at low metal concentrations in emissions (for example, less than 10 mg) and may be a consequence of analytical errors at such low metal concentrations. The specified significant deviations can be caused by other factors. Discrepancies are likely due to inaccuracies in the raw data and processing. Given the variety of sources and the possibility of involving different experts in data collection, it is possible to assume the presence of errors in experimental conclusions, as well as the possibility of inaccuracies in the process of data collection or in making observations. In particular, large errors in the estimation of concentrations of mercury (up to 70 %) and vanadium (up to 30 %) may arise due to the influence of these factors on the reliability of the input data.

The large deviation between calculated and known data for mercury and vanadium indicates the need for additional work on predicting metal binding in the natural soil environment. Therefore, the content of mercury and vanadium as residual concentrations of heavy metals should be investigated separately as an object of research in future works.

Unlike the methods proposed in [8, 9], the application of the proposed prediction does not require the collection of field samples. This is extremely important, as it will contribute to the safety of observers: in conflict situations, researchers do not have the possibility of free access to collect soil samples. However, the research methodology allows

obtaining preliminary data to calculate risks for areas that will be released over time. In addition, the use of ANN models enables a comprehensive assessment of the behavior of iron and heavy metals, as they affect each other. This demonstrates the most complete picture of pollution, rather than the study of specific elements [2, 3], where mutual influences are not reflected.

A limitation of the study is the assessment of iron and heavy metal concentrations only during the bombardment. That is, the study does not take into account the influence of surface relief violations (for example, from trenching, construction of anti-tank structures), which in global terms can significantly affect the result. The presence of geochemical barriers, the influence of temperature and the annual amount and nature of precipitation, which affect the dissolution of explosive substances in the soil, increasing their bioavailability, are also not taken into account.

The disadvantage of the study is the probability of a rather large error when calculating the rate of spread of metals with small concentrations, such as mercury and vanadium.

A significant drawback of the study is that precipitation and dissolution reactions were not taken into account in the current study, which is typical of highly contaminated field soils or soils with high pH values. The reason for this was the lack of relevant data for consideration.

Thus, further work is needed to understand what other environmental factors (i.e., organic matter, colloids, competing ions, sunlight) besides the redox environment play a role in stabilizing iron and heavy metal diffusion rates. Future studies can be extended to consider the effects of precipitation and dissolution reactions for field-contaminated soils.

The results of numerical modeling demonstrate the dynamics of soil contamination due to shelling, the distribution of metals in the soil, as well as the immobilization of metals over time after the end of hostilities. This allows to understand the scale of contamination in different soils and will provide an opportunity to develop effective strategies for the rehabilitation of contaminated areas after conflict.

The obtained results of numerical modeling of the dynamics of soil pollution can be used to develop effective measures to reduce pollution and restore environmental safety, to forecast the possible consequences of military conflicts in the long term.

7. Conclusions

1. The selection and study of the influence of the factors of the dependence of the physical and mechanical properties of the soil on the rate of distribution and immobilization of iron and heavy metals was carried out. The dynamic behavior of metals in soil depends on a variety of factors, such as stream transport, diffusion, plant root uptake, adsorption/desorption, and precipitation/dissolution, as well as soil parameters such as soil type, porosity, electrical conductivity, soil organic carbon, and pH. An important role is also played by the time that has passed after the mechanical effect of the artillery strike.

It was found that different metals react to these factors in different ways. Soil parameters such as type, porosity, soil organic carbon content, and pH were found to be key to the

rate of metal distribution in the soil environment during metal release from an artillery shell explosion.

The results of the analysis of the correlation matrix constructed in the work indicate the importance of taking into account the physical and mechanical properties of the soil for understanding and predicting the behavior of heavy metals in the soil environment.

In the soil environment, the behavior of heavy metals is determined by physical and chemical processes – flow transfer, diffusion, absorption by plant roots, adsorption/desorption and precipitation/dissolution. They depend on conditions and time scales. The study focused on the physical and mechanical parameters of the soil, such as type, porosity, ECO, HOB, pH.

Soil parameters are important: soil type and GHG affect metal distribution, porosity determines filtration rate, EC affects ion exchange, pH determines toxicity and distribution.

Soil exposure varies for metals such as lead, zinc, chromium, and copper. Porosity affects the diffusion rate of barium, antimony, titanium and vanadium, EKO affects strontium and titanium, GOV affects iron, cobalt and titanium. pH affects all metals.

2. Numerical modeling of the dynamics of pollution, distribution and immobilization of heavy metals in soils during missile or artillery fire was performed. The result is presented using the finite difference method in the MatLab environment.

Numerical modeling of the rate of distribution of iron and heavy metals in different types of soil (chernozems, loams, and sandy soils) is based on the diffusion process of substance distribution, which takes into account the physical and mechanical properties of the soil environment related to the movement and sorption of elements. It is based on partial differential equations that describe the dynamics of metal concentrations in soils over time.

The study is based on changes in dissolved metal concentrations over time and distance.

The results showed that different heavy metals exhibit different degrees of mobility in the soil. Some metals such as Fe, Pb, Sb, Zn, Co, Cr show high mobility, while others such as As, Mn, Cd, Hg, V, Cu show less activity.

The study examined the effect of soil type on the rate of release of metals. Barium, cobalt, arsenic, lead, strontium and titanium showed little dependence of diffusion rate on soil type.

It was found that the rate of diffusion of some heavy metals in different types of soils shows two-phase dynamics: first, the metals are intensively released, then the rate drops sharply. The dependence of the speed on the type of soil and metal is clearly visible. Fe, Zn, Cd, Sb spread the fastest; slower – As, Pb, Cu, Ni, Hg, Mn, V. The peak points for some metals, after which the speed decreases: for Fe, Zn, it is 180+5 min (in sandy soils), 220+5 min (in loams), 230+5 min (in chernozems); for Cd, Sb – 310+10 min (in sandy soils), 350+5 min (in loams), 350+5 min (in chernozems) The diffusion rate of As, Pb, Cu, Hg, Mn, V is conditionally linear, without a peak maximum.

It is estimated that loams and chernozems contribute to a greater accumulation of metals than sandy soils. Compared to sandy soil, the rate of release of metals in loam decreases from 16.7 % to 69.7 %. In relation to chernozem and loam, the rate of release slows down from 17.85 % to 32.08 %.

Numerical modeling helps to understand the mechanisms of the spread of pollution, to determine the areas of highest risk. The conducted research makes it possible to understand the extent of soil pollution and to develop measures for the rehabilitation of polluted areas. The results are useful for restoring environmental security after the war. The obtained results are of practical importance when developing management strategies and minimizing the impact of heavy metals on the environment.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

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Data availability

The manuscript has no associated data.

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